UNIVERSIDADE DE SÃO PAULO
INSTITUTO DE GEOCIÊNCIAS

**GEOQUÍMICA E GÊNESE DAS FORMAÇÕES FERRÍFERAS
BANDADAS E DO MINÉRIO DE FERRO DA MINA DE ÁGUAS
CLARAS, QUADRILÁTERO FERRÍFERO, MG**

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TESE DE DOUTORAMENTO

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SÃO PAULO
2005

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INSTITUTO DE GEOCIÊNCIAS

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FERRÍFERAS BANDADAS E DO MINÉRIO DE FERRO
DA MINA DE ÁGUAS CLARAS, QUADRILÁTERO
FERRÍFERO, MG**

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LISTA DE SIGLAS E ABREVIATURAS

ACTLABS	Activation Laboratories
AND	Depósito de Andaime
CDTN	Centro de Desenvolvimento de Tecnologia Nuclear
CMM-UQ	Center for Microscopy and Microanalysis da Universidade de Queensland
CPX	Mina do Capão Xavier
CVRD	Companhia Vale do Rio Doce
MAC	Mina de Águas Claras
MBR	Minerações Brasileiras Reunidas
NEG-LABISE	Laboratório de Isótopos Estáveis da Universidade Federal de Pernambuco
QF	Quadrilátero Ferrífero
SAP	Mina do Sapecado
TAM	Mina de Tamanduá
UFMG	Universidade Federal de Minas Gerais

UFOP	Universidade Federal de Ouro Preto
UQ	Universidade de Queensland
UQ-AGES	University of Queensland Argon Geochronology in Earth Sciences
USP	Universidade de São Paulo

RESUMO

O minério de ferro e os itabiritos da Mina de Águas Claras foram estudados em detalhe do ponto de vista mineralógico, petrológico e geoquímico, com os objetivos de caracterizá-los e de contribuir para o melhor entendimento da gênese dos mesmos. Dois tipos de itabiritos ocorrem em Águas Claras: dolomítico e quartzo itabirito. Os minérios de alto teor (%Fe >64%) foram formados a partir do primeiro. Tanto um como outro tipo de itabirito apresentam meso e microbandamento. No itabirito dolomítico alternam-se bandas ricas em hematita com bandas ricas em dolomita, enquanto que no quartzo itabirito a alternância ocorre entre bandas ricas em quartzo com bandas ricas em hematita. Dolomita, quartzo e hematita são os principais constituintes mineralógicos, ocorrendo clorita, sericita, talco e apatita como minerais acessórios. A composição química dos itabiritos é muito simples. Fe_2O_3 , CaO, MgO e PF são os principais componentes do itabirito dolomítico e Fe_2O_3 e SiO_2 do quartzo itabirito. Os teores de elementos menores são geralmente inferiores a 10 ppm, tanto no itabirito dolomítico como no quartzo itabirito, sem evidenciarem uma maior concentração em um ou outro tipo de BIF. Apenas Zn, Sr e Pb estão mais caracteristicamente associados com o itabirito dolomítico, e Cd, Sb e Ge com o quartzo itabirito. O padrão de fracionamento dos ETR, quando normalizados pelo padrão PAAS, assemelha-se aos de outras BIFs paleoproterozóicas, com anomalias positivas de Eu e Y e aumento gradativo dos ETR leves em direção aos pesados. Os isótopos de C e O do itabirito dolomítico apresentaram valores negativos de $\delta^{13}\text{C}$ variando entre -2,5‰ e -0,8‰, enquanto que os dados isotópicos de O mostraram valores de $\delta^{18}\text{O}$ entre -12,4‰ e -8,5‰, compatíveis com os valores de $\delta^{13}\text{C}$ e $\delta^{18}\text{O}$ encontrados em outras seqüências carbonáticas paleoproterozóicas. As observações de campo e os dados de laboratório sugerem que o itabirito dolomítico e o quartzo itabirito representem variações faciológicas laterais e verticais dos sedimentos originais da Formação Cauê.

Dois tipos principais de minério de alto teor foram reconhecidos: friável e compacto. O minério friável é o principal tipo, ocorrendo na forma de uma lente contínua de cerca de 2,5 km de extensão, no interior da qual ocorrem lentes subordinadas de minério compacto. O minério friável passa lateral e verticalmente para o itabirito dolomítico (protominério). Nesta transição, as bandas ricas em hematita do itabirito passam a ser as bandas maciças do minério, enquanto que as bandas dolomíticas passam a constituir as bandas porosas. A hematita é o mineral minério tanto do minério friável como do minério compacto, ocorrendo sob a forma de hematita granular

e tabular, com tamanho de cristal entre 10 e 30 μm . Os minerais de ganga são raros e consistem de apatita, clorita, sericita, talco e, eventualmente, dolomita, além de feridrita e minerais de manganês, estes últimos originados na dissolução da dolomita. Os minérios friável e compacto consistem quase que totalmente de Fe_2O_3 , com teores médios superiores a 96% no primeiro e a 98% no segundo. As impurezas consistem de Al_2O_3 , SiO_2 , MnO e P_2O_5 , cujos teores são ligeiramente maiores no minério friável do que no minério compacto. Os dois tipos de minério são muito pobres em elementos traços. Uma grande parte destes elementos ficou abaixo do limite de detecção do método analítico, sendo que a quase totalidade dos mesmos apresentou teor médio inferior a 30 ppm, com exceção do Ba, V, Zn e Cr, que apresentaram teores médios entre 30 e 100 ppm. Os teores de elementos traços são significativamente maiores na banda porosa do que na banda maciça, indicando que a maior parte dos mesmos está associado aos minerais de ganga do minério, presentes em maior volume na banda porosa. Tanto um como outro tipo de minério apresentaram baixos totais de ETR. Quando normalizados pelo PAAS, o minério friável mostra padrão de fracionamento dos ETR similar ao do protominério. Já o minério compacto apresenta padrão de fracionamento distinto com relação aos ETR pesados, os quais sofrem discreto empobrecimento em relação aos ETR médios. Os dados de campo, petrológicos, geoquímicos e geocronológicos indicam uma origem hipogênica para o minério compacto e supergênica para o minério friável.

A datação pelo método $^{40}\text{Ar}/^{39}\text{Ar}$ de minerais de manganês presentes no itabirito manganífero das Minas do Sapecado e Andaime trouxe importantes informações sobre a evolução do perfil de intemperismo das BIFs no Quadrilátero Ferrífero e sobre o minério de ferro supergênico nele contido. Os resultados geocronológicos forneceram idades entre 61.5 ± 1.2 Ma a 14.2 ± 0.18 Ma, sugerindo uma prolongada história de intemperismo na região. A maior parte dos óxidos de Mn, entretanto, precipitou no intervalo entre 51 e 41 Ma, com um pico em 46.7 Ma, indicando um período de intenso intemperismo químico, durante o qual formou-se a maior parte do minério friável da mina de Águas Claras.

Os dados apresentados neste trabalho mostraram que, sob idênticas condições estruturais, topográficas e climáticas, o itabirito dolomítico é muito mais favorável à formação de depósitos de ferro de alto teor do que o quartzo itabirito. Forneceram também indicações de que a gênese de depósitos gigantes de minério friável de alto teor a partir do quartzo itabirito requer a atuação de outros controles além do litológico, possivelmente envolvendo processos hipogênicos e supergênicos.

ABSTRACT

Iron ore and itabirites from Águas Claras mine were accurately examined and assessed for their mineralogical, petrological and geochemical features, in order to appropriately characterize and better understand their respective genesis. Two types of itabirite were identified in the Águas Claras mine, to wit: dolomitic itabirite and quartz itabirite. High-grade ores (%Fe >64%) were originally formed from dolomitic itabirite. Both itabirite types feature meso and microbanding. Dolomitic itabirite consists of alternating hematite-rich and dolomite-rich bands, whereas quartz itabirite consists of alternating quartz-rich and hematite-rich bands. Dolomite, quartz and hematite are the major minerals, the accessory minerals being chlorite, sericite, talc and apatite. Itabirites have a quite simple chemical composition. Fe₂O₃, CaO, MgO and PF are the major elements in dolomitic itabirite's composition, whereas Fe₂O₃ and SiO₂ are predominant in quartz itabirite. The contents of minor elements generally equal less than 10 ppm in both dolomitic and quartz itabirites, and no higher concentration is found in any other BIF type. Only Zn, Sr and Pb are more specifically associated with dolomitic itabirite, whereas Cd, Sb and Ge are associated with quartz itabirite. Itabirite's REE (Rare Earth Elements) fractionation pattern, when normalized by PAAS standard, is similar to other Paleoproterozoic BIFs' patterns, displaying Eu and Y positive anomalies and gradual increase of light REE towards the heavy REE. C and O isotopes of dolomitic itabirite have shown negative values for $\delta^{13}\text{C}$, ranging from -2,5‰ to -0,8‰, while O isotopic data has shown values for $\delta^{18}\text{O}$ between -12,4‰ and -8,5‰, which are compatible with the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values identified in other Paleoproterozoic carbonate sequences. Field relationships and laboratory data suggest that both dolomitic and quartz itabirite represent the lateral and vertical facies transitions of the Cauê Formation's original sediments.

Two main high-grade ore types have been identified: soft and hard ores. Soft ore is dominant and occurs as a continuous lens approximately 2,5 km long, comprising subordinate lenses of hard ore. Soft itabirite undergoes a lateral and vertical transition and turns into dolomitic itabirite (protore). During the above-mentioned transition, the hematite-rich bands turn into massive ore bands, whereas the dolomitic bands turn into porous bands. Hematite is the ore mineral of both soft and hard ore and occurs as granular and tabular hematite, its crystal size ranging from 10 to 30 μm . Gangue minerals are scarce and consist of apatite, chlorite, sericite, talc and, occasionally, dolomite, ferrihydrite and Mn-minerals, the latter two resulting from dolomite dissolution. Soft and hard ores consist almost entirely of Fe₂O₃, with average contents exceeding 96% for soft ores and 98% for hard ores. Impurities consist of Al₂O₃, SiO₂, MnO and

P₂O₅. Their contents are slightly higher in soft ore than in hard ore. Trace element content is quite low in both ore types. The level of most trace elements stand below the analytical method detection limit, having almost all of them showing an average content of less than 30 ppm, except for Ba, V, Zn e Cr, whose average contents range between 30 and 100 ppm. The trace element contents are significantly higher within the porous band than within the massive band, thus indicating that most of them are associated with ore gangue minerals, which are concentrated in the porous band. Both types of ore feature low REE totals. When normalized by PAAS, the soft ore presents a REE fractionation pattern similar to the protore pattern. On the other hand, the hard ore displays a different fractionation pattern with regard to heavy REE, which undergoes a slight depletion when compared to middle REE. The petrological, geochemical and geochronological field relationships indicate a hipogene origin for the hard ore and a supergene origin for the soft ore.

⁴⁰Ar/³⁹Ar dating of the Mn-minerals detected in the mangesiferous itabirite from the Sapecado and Andaime Mines has provided significant information on the development of the weathering profile of BIFs in the Quadrilátero Ferrífero and on the supergene iron ore therein contained. According to the geochronological results, ages from 61.5 ± 1.2 Ma to 14.2 ± 0.18 Ma were obtained, therefore suggesting this region underwent a long, lasting weathering period experienced. However, most of Mn oxides precipitated between 51 and 41 Ma, a peak being identified in 46.7 Ma. The data above indicates a period of intense chemical weathering during which most of the soft ore found in Águas Claras Mine was formed.

The data contained in this paper shows that under identical structural, topographic and climatic conditions, dolomitic itabirite is much more liable to forming high-grade iron deposits than quartz itabirite. There are also indications that the genesis of the huge high-grade soft ore deposits originally formed from quartz itabirite requires the action of other controls, besides the lithological one, possibly involving hipogene and supergene processes.

CAPÍTULO 1 - INTRODUÇÃO

1.1 - APRESENTAÇÃO

A indústria da mineração do ferro tem grande importância econômica na economia mineral brasileira. O valor de sua produção representa 15% do valor da produção mineral nacional, sendo superado apenas pelo petróleo. O minério de ferro é um dos principais itens da pauta de exportação do país, representando cerca de 80% das exportações dos bens minerais primários e cerca de 5% das exportações totais (Quaresma, 2001).

Dada a sua importância econômica, inúmeros trabalhos envolvendo a caracterização tecnológica e mineralógica do minério de ferro têm sido realizados nas áreas de geologia, mineração e siderurgia. Particularmente na região do Quadrilátero Ferrífero, diversas dissertações de mestrado e teses de doutorado trataram da geologia dos corpos de minério, do comportamento estrutural dos mesmos, de características químicas e mineralógicas, assim como de aspectos relacionados ao beneficiamento e metalurgia do minério de ferro (Casquet, 1995; Ramos, 1997; Ribeiro, 2003; Silva, 2004; Silva, 1999; Trzaskos-Lipski, 2001; Veríssimo, 1999; Zavaglia, 1995).

A economicidade do aproveitamento dos minérios está também intrinsecamente ligada às condições geológicas e metalogenéticas das jazidas. A mineralogia do minério, os teores de ferro, a estrutura e a textura das rochas que contêm o mineral-minério, a paragenese e toda uma série de parâmetros geológicos influem para que os empreendimentos minerários possam se tornar uma realidade econômica (Pinheiro, 2000). Além disto, as características estruturais, texturais e mineralógicas do minério de ferro têm grande impacto na obtenção de elevados índices de produtividade nos processos siderúrgicos de aglomeração e redução do minério de ferro, sendo ainda insuficientemente conhecidas e pouco exploradas na seleção dos minérios a serem processados na siderurgia (Pimenta *et al.*, 1999). Além de ser extremamente importante nas etapas industriais de lavra, beneficiamento e metalurgia, a caracterização química e mineralógica do minério de ferro contribui para o entendimento da gênese dos jazimentos.

O Quadrilátero Ferrífero responde por cerca de 60% da produção de minério de ferro brasileira, a maior parte da mesma ainda oriunda de minérios de alto teor em ferro (%Fe > 64), denominados de minérios hematíticos, ou simplesmente hematitas. Os minérios hematíticos estão próximos de serem exauridos, e estão sendo substituídos pelos minérios de baixo teor (%Fe

~40%), denominados de minérios itabiríticos ou itabiritos. Os minérios itabiríticos representam mais de 70% dos 29 bilhões de toneladas de recursos geológicos de minério de ferro remanescente no Quadrilátero Ferrífero (MBR e CVRD, relatórios internos) e sua gênese é atribuída ao enriquecimento supergênico das formações ferríferas bandadas (BIFs) metamorfizadas, denominadas de itabiritos, encaixantes do minério de ferro (Dorr II, 1964).

Apesar da importância econômica do minério de ferro na economia nacional, poucos trabalhos foram realizados objetivando a sua gênese. No Quadrilátero Ferrífero, estes trabalhos estão limitados ao estudo do minério de ferro formado a partir de quartzo itabirito (Dorr II, 1964, 1965; Eichler, 1968; Guild, 1953; Veríssimo, 1999).

O presente estudo trata da caracterização e gênese do minério de ferro na Mina de Águas Claras, onde o protominério é o itabirito dolomítico. A Mina de Águas Claras é propriedade da Minerações Brasileiras Reunidas S/A – MBR, e foi explorada por esta empresa no período de 1973 a 2002, quando foram lavradas cerca de 290 Mt de minério de ferro de altíssimo teor (~68% Fe). Esta mina foi selecionada para este trabalho devido às excelentes exposições de itabirito dolomítico presentes na mesma e pelo pouquíssimo volume de informações disponíveis na literatura sobre estas rochas ou sobre o minério formado a partir delas. O autor era o responsável pelas atividades de geologia de Mina da Mina de Águas Claras por ocasião do início deste trabalho, o que também contribuiu para a seleção da mesma como alvo do estudo e facilitou os trabalhos de campo.

Inicialmente serão apresentados dados sobre a geologia, mineralogia e geoquímica das BIFs da Mina de Águas Claras, sugerindo-se um modelo genético para as mesmas. Formações ferríferas bandadas constituem um dos temas que têm gerado enorme acervo de publicações na literatura geológica, dada a sua grande importância na compreensão dos fenômenos que levaram a evolução da vida, dos oceanos e da atmosfera no pré-Cambriano. Entretanto, poucas informações existem publicadas sobre as BIFs do Quadrilátero Ferrífero. A disponibilização destes novos dados será muito útil no entendimento do quadro evolutivo da geologia regional, assim como contribuirá para o conhecimento da formação das BIFs no Paleoproterozóico.

Em seguida, o assunto focalizado será o minério, cujas características mineralógicas, petrológicas e geoquímicas serão detalhadas e comparadas com as do protominério, visando a um melhor entendimento de sua gênese.

Finalmente, serão apresentadas datações pelo método $^{40}\text{Ar}/^{39}\text{Ar}$ de óxidos de manganês formados no decorrer do intemperismo de quartzo itabiritos das Minas de Sapecado e Andaime. Estas minas foram selecionadas por apresentarem corpos de itabiritos manganíferos

intercalados ao minério de ferro, interceptados em furos de sonda em diferentes níveis do perfil de intemperismo, permitindo desta forma a coleta de amostras de óxidos de manganês passíveis de serem datados pelo método $^{40}\text{Ar}/^{39}\text{Ar}$ desde a superfície topográfica até próximo ao contato com o itabirito compacto. Estes dados são relevantes para a compreensão da cronologia dos processos de formação do perfil de alteração intempérica das BIFs e, conseqüentemente, para o melhor entendimento da gênese dos depósitos supergênicos de minério de ferro no Quadrilátero Ferrífero.

1.2 - OBJETIVOS

Os objetivos propostos neste trabalho foram traçados a partir da necessidade de estudos mais detalhados envolvendo a caracterização do minério de ferro e sua gênese. As investigações de campo e de laboratório envolveram diferentes análises e ensaios que tiveram como metas principais estudar:

- a mineralogia e petrologia do minério de ferro e do protominério (BIFs),
- a geoquímica dos elementos maiores, menores e de terras-raras destas rochas,
- a evolução mineralógica e geoquímica do itabirito dolomítico até o minério,
- a gênese dos minérios de ferro friáveis no Quadrilátero Ferrífero; e
- a idade dos perfis de intemperismo das BIFs no Quadrilátero Ferrífero.

1.3 – LOCALIZAÇÃO E ASPECTOS GERAIS

A Mina de Águas Claras situa-se na porção noroeste do Quadrilátero Ferrífero, no Estado de Minas Gerais, a sul da capital Belo Horizonte (Figuras 1 e 2). As Minas de Sapecado e Andaime, onde foram coletadas as amostras de óxidos de manganês para datação do perfil de intemperismo, da mesma forma que a Mina de Águas Claras, são pertencentes a MBR. Estas Minas localizam-se no flanco leste do Sinclinal da Moeda (Figura 1), a cerca de 50 km da cidade de Belo Horizonte. A Mina do Sapecado é atualmente a principal mina em operação pela MBR

no Complexo Pico, integrado pelas Minas do Pico, Galinheiro e Sapecado, com uma produção anual bruta de 12 Mt de minério (Figura 3).

Figura 1: Localização da área de estudo.

Figura 2: Vista geral da Mina de Águas Claras.

Figura 3: Vista geral da Mina do Sapecado. Ao fundo está o Pico do Itabirito, formado por hematita compacta, e a cava da Mina do Pico.

O relevo na região do Quadrilátero Ferrífero é caracterizado por um conjunto de serras e planaltos, com elevações variando entre 700 e 2.000 m, e faz parte da unidade representada pelos “Planaltos Dissecados do Leste de Minas” (Baltazar and Raposo, 1993). A topografia é caracterizada por um controle lito-estrutural. Sustentando o topo das serras encontram-se rochas metassedimentares do Supergrupo Minas (quartzitos e formações ferríferas bandadas). Nas regiões menos elevadas, ocorrem rochas proterozóicas do tipo *greenstone belt* do Supergrupo Rio das Velhas, e rochas granítico-gnáissicas do embasamento arqueano – Complexo Bação (Dorr II, 1969; Schobbenhaus, 1984). Em diferentes locais e altitudes são reconhecidas superfícies “aplainadas” interpretadas como testemunhos residuais de antigas superfícies de aplainamento geradas em diferentes ciclos erosivos (Barbosa, 1965; King, 1956), ou como produto de erosão diferencial das várias unidades geológicas (Varajão, 1991).

1=Serra do Curral, 2=Serra da Moeda, 3=Serra do Itabirito, 4= Serra do Ouro Branco, 5=Serra do Caraça, 6 e 7= vale do rio das Velhas, MAC= Mina de Águas Claras, CPX= Mina do Capão Xavier, TAM= Mina de Tamanduá, AND= Depósito de Andaime, SAP = Mina do Sapecado

Figura 4: Modelo digital do terreno (base de dados: Prodemge, MG; resolução 27 m).

O clima na região do Quadrilátero Ferrífero é quente e úmido, com precipitações médias anuais de 1.900 mm, concentradas no período vai de outubro a março (Nimer, 1989). A temperatura média anual varia em torno de 20-24 °C, com valores menores (18-20 °C) em regiões de elevadas altitudes.

1.4 – ESTRUTURA DA TESE

Esta tese está estruturada na forma de dois capítulos introdutórios, onde são apresentados os objetivos do trabalho e resultados esperados, e os materiais e métodos utilizados. Seguem-se quatro capítulos que contêm os resultados e discussões. Estes capítulos são apresentados na forma de artigos publicados ou submetidos para publicação em revistas especializadas com ampla divulgação no meio científico nacional e internacional. Cada capítulo trata de um dos temas centrais da tese de forma independente, e foi escrito de modo a permitir ao leitor a compreensão do tema tratado sem a necessidade de leitura dos demais artigos. Este procedimento tem o inconveniente de levar a uma certa superposição da parte inicial dos textos de cada artigo, quando os mesmos são lidos conjuntamente.

O primeiro artigo (Capítulo 3, Anexo 1), denominado “*Geology and geochemistry of the Águas Claras and Pico iron mines, Quadrilátero Ferrífero, Minas Gerais, Brazil*” foi publicado em 2003 no volume 38 do periódico “*Mineralium Deposita*”. Ele apresenta a geologia geral da Mina de Águas Claras, recuperando e divulgando o conjunto de dados geológicos e geoquímicos obtidos no decorrer da vida da mina. Para efeito de comparação com o minério formado a partir de quartzo itabiritos, este artigo apresenta também a geologia e geoquímica dos minérios de ferro da Mina do Pico.

O segundo artigo (Capítulo 4, Anexo 2), intitulado “*Geochemistry and genesis of the banded iron formations of the Cauê Formation, Quadrilátero Ferrífero, Minas Gerais, Brazil*” foi submetido para publicação em maio de 2004 ao periódico “*Precambrian Research*”. Este artigo foi devolvido para revisões em janeiro de 2005, as quais estão sendo processadas. O artigo apresenta a geologia e geoquímica das formações ferríferas bandadas da Mina de Águas Claras, e propõe um modelo genético para as mesmas.

O terceiro artigo (Capítulo 5, Anexo 3), trata da geologia e geoquímica do minério de ferro da Mina de Águas Claras, e tece comparações com as Minas de Capão Xavier e Tamadua.

Este artigo, denominado “*The iron ore of the Águas Claras mine, Quadrilátero Ferrífero, Brazil*”, foi submetido para publicação em junho de 2005 ao periódico “*Mineralium Deposita*”.

O último artigo (Capítulo 6, Anexo 4), denominado “ *$^{40}\text{Ar}/^{39}\text{Ar}$ geochronology and the evolution of lateritic iron deposits in the Quadrilátero Ferrífero, Minas Gerais, Brazil*”, foi submetido para publicação em janeiro de 2005 ao periódico “*Chemical Geology*”. Este artigo trata da idade do perfil de intemperismo das formações ferríferas bandadas (e conseqüentemente da idade de formação dos minérios supergênicos) no Quadrilátero Ferrífero, e foi devolvido para pequenas revisões em junho de 2005.

Finalizando a tese, apresenta-se um capítulo que integra o conteúdo dos artigos e enuncia as principais conclusões obtidas.

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CAPÍTULO 2 – AMOSTRAGEM E TÉCNICAS ANALÍTICAS

2.1 - AMOSTRAGEM

2.1.1 – MINA DE ÁGUAS CLARAS

Três grupos distintos de rochas foram amostrados e estudados na Mina de Águas Claras: (1) filito sericítico, dolomito argiloso e quartzo dolomito, (2) BIFs representadas por itabirito dolomítico e quartzo itabirito, (3) minério de ferro. No Anexo 5 encontram-se relacionadas todas as amostras estudadas, com suas respectivas coordenadas e procedimentos analíticos realizados.

A amostragem foi realizada em diferentes oportunidades, entre agosto de 2000 e dezembro de 2002, época em que a mina estava em operação e o autor trabalhava na mesma. Foram coletadas amostras em afloramentos e testemunhos de sondagem, com massa variando, conforme a finalidade da amostragem, entre 200 g e 3 kg. Para estudos petrográficos e análises de isótopos de C e O foram coletadas amostras pequenas, em torno de 200 g, enquanto que para as análises químicas foram coletadas amostras de até 3 kg.

A amostragem do filito sericítico, do dolomito argiloso e do itabirito dolomítico foi realizada ao longo da bancada situada na cota 1.000 m, na parede leste da mina (Figuras 5 e 6). Neste local as rochas encontram-se a mais de 200 m abaixo da superfície topográfica e não apresentam sinais de alteração intempérica. Nesta parede, o itabirito dolomítico foi lavrado quase que perpendicularmente à direção do acamamento, em uma extensão de mais de 300 m. Este afloramento possivelmente representa a melhor exposição desta rocha em todo o Quadrilátero Ferrífero. Foram coletadas amostras de itabirito dolomítico a partir da base da Formação Cauê até o contato com o minério de ferro, seguindo um espaçamento de aproximadamente 30 m entre amostras, as quais foram utilizadas nos estudos petrográficos e análises químicas. Amostras adicionais de itabirito dolomítico foram coletadas no centro da mina e nos furos de sonda PZ55 e FS09. Em uma segunda etapa de amostragem, neste mesmo local e obedecendo a um espaçamento de aproximadamente 10 m entre amostras, foram coletados fragmentos centimétricos da banda carbonática do itabirito dolomítico para análise de isótopos de C e O. Todas estas amostras foram analisadas ao microscópio óptico. A fim de complementar a amostragem realizada ao longo da bancada 1.000, de forma a se ter toda a Formação Cauê estudada desde a sua base até a transição para a Formação Gandarela, foram coletadas amostras

de itabirito dolomítico, quartzo itabirito e quartzo dolomito nos furos de sonda PZ03, PZ54 e PZ55 (Figura 6).

A amostragem do minério friável e compacto foi efetuada em diferentes pontos da mina e também nos furos de sonda FS08, FS09 e FS11, onde foram coletadas amostras para ensaios de densidade e análises químicas. Para algumas amostras de minério friável procedeu-se a coleta em separado das bandas maciça e porosa do mesmo.

2.1.2 – MINA DO SAPECADO E ANDAIME

A amostragem realizada nas Minas do Sapecado e Andaime teve por objetivo a coleta de óxidos de manganês susceptíveis à datação pelo método $^{40}\text{Ar}/^{39}\text{Ar}$ (óxidos de Mn do grupo da hollandita), com o intuito de se obter a idade do perfil de intemperismo das BIFs no Quadrilátero Ferrífero e, por consequência, do minério de ferro supergênico. A escolha do local levou em consideração o objetivo de obter amostras distribuídas o mais regularmente possível no perfil de intemperismo, e foi realizada em conjunto com o Dr. Paulo Marcos de Vasconcelos, da Universidade de Queensland (UQ), Austrália, que treinou o autor na amostragem e orientou-o nas etapas posteriores de preparação das amostras, análises e interpretação dos dados. Planejou-se a coleta de amostras de minerais de manganês presentes no minério de ferro desde a superfície topográfica original até junto ao contato do minério com a BIF hospedeira. Estes minerais são mais comumente encontrados próximos ao contato do minério com as rochas intemperizadas das Formações Batatal e Gandarela. A inexistência de testemunhos de sondagem nas regiões propícias à ocorrência de minerais de manganês na Mina de Águas Claras, aliada à dificuldade de acesso aos locais favoráveis à ocorrência dos mesmos no interior da cava, inviabilizou a utilização desta mina para o estudo geocronológico do perfil de intemperismo das BIFs. Por este motivo, foi necessária a escolha de outro local para este trabalho, sendo selecionada a Mina do Sapecado como alvo prioritário e a Mina de Andaime para amostragem complementar (Figuras 1 e 4). A Mina do Sapecado estava em fase inicial de lavra por ocasião da amostragem, com regiões ricas em minerais de manganês aflorantes, e intensa campanha de sondagem em desenvolvimento. A maior facilidade de acesso aos minerais de manganês nesta mina motivou a sua escolha.

Os minerais de manganês estão presentes no minério de ferro da Mina do Sapecado em uma rocha denominada de itabirito manganesífero. Foram consultadas as seções geológicas da mina, buscando-se identificar aquelas onde o itabirito manganesífero ocorre em maior volume, selecionando-se os furos de sonda das seções mais favoráveis. A maior parte destes furos está

Figura 5: Vista geral da parede leste da Mina de Águas Claras mostrando o Banco 1.100, onde foram coletadas a maioria das amostras dos Grupos 1 e 2.

Figura 6: Mapa geológico simplificado da Mina de Águas Claras mostrando os locais amostrados.

localizada na seção 6.300 (Figura 7), a qual foi escolhida para a amostragem principal. Foram consultados os resultados das análises químicas dos furos de interesse, disponibilizados pela MBR, objetivando a identificação dos intervalos com teores de Mn superiores a 3%. Estes intervalos foram observados com lupa de mão, procurando-se identificar a presença dos minerais de manganês e coletando-se fragmentos centimétricos da rocha, a intervalos de aproximadamente 1 m, sempre que os mesmos eram encontrados (Figura 8). Procedimento idêntico foi adotado na Mina do Andaime, a qual foi selecionada pela ocorrência de itabiritos manganésíferos tanto aflorantes quanto em profundidade, permitindo desta forma a comparação dos dados geocronológicos em dois locais distintos. Foram coletadas 19 amostras de itabirito manganésífero na Mina do Sapecado, estando 15 localizadas na seção 6.300E e as 4 restantes na seção 4.700E. Na Mina do Andaime foram coletadas 4 amostras (Figura 9).

Figura 7: Seção geológica 6.300E da Mina do Sapecado mostrando pontos de coleta das amostras para datação $^{40}\text{Ar}/^{39}\text{Ar}$.

Figura 8: (a) Furo de sonda da Mina do Sapecado mostrando itabirito manganês intercalado no itabirito limonítico. (b) Detalhe dos minerais de manganês formando concreções.

Figura 9: Seção geológica 3.500E da Mina do Andaime mostrando pontos de coleta das amostras para datação $^{40}\text{Ar}/^{39}\text{Ar}$.

2.2 – TÉCNICAS ANALÍTICAS

Diversos tipos de análise foram empregados no estudo das BIFs e do minério de ferro da Mina de Águas Claras, e no estudo geocronológico do itabirito manganêsífero das Minas do Sapecado e Andaime. Nas Figuras 10 a 12 apresenta-se um roteiro simplificado do tipo de análise a que cada grupo litológico amostrado na Mina de Águas Claras foi submetido, assim como o número de amostras analisadas. Detalham-se a seguir as principais técnicas analíticas utilizadas.

Figura 10: Fluxuograma ilustrando os procedimentos analíticos utilizados para as rochas do Grupo 1 e o número de amostras (entre parênteses) analisado em cada procedimento.

Figura 11: Fluxuograma ilustrando os procedimentos analíticos utilizados para as rochas do Grupo 2 e o número de amostras (entre parênteses) analisado em cada procedimento.

Figura 12: Fluxograma ilustrando os procedimentos analíticos utilizados para as rochas do Grupo 3 e o número de amostras (entre parênteses) analisado em cada procedimento.

2.2.1 – ANÁLISE PETROGRÁFICA

A análise petrográfica envolveu a descrição de seções delgadas e polidas ao microscópio óptico (luz natural e refletida), observando-se aspectos texturais, estruturais e composicionais do minério de ferro, das BIFs e dos minerais de manganês.

Grande parte das amostras, tais como as de minério friável e de itabirito dolomítico parcialmente alterado, foram impregnadas com uma mistura de resina polyester cristal e monômero de estireno, antes de seguirem para corte com serra, preparação de seções e polimento. As lâminas delgado-polidas e polidas foram preparadas nos laboratórios de laminação da Universidade de São Paulo (USP), da Universidade Federal de Ouro Preto (UFOP) e da UQ.

2.2.2 – ANÁLISE POR DIFRAÇÃO DE RAIOS-X (DRX)

As análises por DRX foram realizadas em algumas das amostras de minério e BIFs, como complemento às análises petrográficas, e para o cálculo dos parâmetros de rede da hematita. As amostras selecionadas foram preparadas através do método do pó, utilizando almofariz e pilão de ágata, sendo cada amostra colocada em um suporte adequado. As análises foram realizadas nos laboratórios de difração de raios-X do Departamento de Mineralogia e Geotectônica do Instituto de Geociências da USP, e do Instituto de Física da Universidade Federal de Minas Gerais (UFMG).

O equipamento utilizado na USP foi um difratômetro Siemens-Brucker modelo D5000, operando a 40 kV e 40 mA com 2θ entre 3 e 65°, em passos de 0,05° e 1s/ passo, sendo usada a radiação Cu-K α ($\lambda = 1,5118 \text{ \AA}$). Na UFMG as análises de DRX foram realizadas em um difratômetro Rigaku-Geigerflex, na geometria de Bragg-Bretano, sendo também usada a radiação Cu-K α , e monocromador de grafite, com 30 mA de corrente e 40 kV de tensão. Os dados foram coletados no modo 2θ - θ , com 2θ entre 4 e 140°, em passos de 0,05°.

Os parâmetros de rede da hematita foram obtidos em quatro amostras de minério de ferro fazendo-se refinamentos de estrutura, empregando o Método de Rietveld com o programa DBWS-9807 (Young *et al.*, 1998). Para a interpretação dos difratogramas utilizou-se o programa de computador DIFFRAC Plus conjuntamente com o banco de dados PDF2-release 2001 do International Center for Diffraction Data (<http://www.icdd.com>).

2.2.3 – ANÁLISE POR MICROSCOPIA ELETRÔNICA DE VARREDURA (MEV)

Amostras de BIFs e de minério de ferro foram examinadas ao MEV para verificação de aspectos texturais e investigação de fases minerais não detectadas na microscopia óptica, seja por se apresentarem em pequenas quantidades, seja pelo baixo grau de cristalinidade. Os minerais de manganês foram investigados para comprovar a presença de fases minerais portadoras de K, obter uma análise qualitativa da composição dos mesmos, e identificar a presença em potencial de minerais contaminantes nas amostras, tais como micas e argilas, passíveis de prejudicarem os resultados geocronológicos. Foram utilizados microscópios eletrônicos de varredura do Instituto de Geociências da USP e do Centre for Microscopy and Microanalysis da UQ (CMM-UQ).

As amostras estudadas por MEV na USP foram recobertas com carbono, utilizando-se para tanto uma máquina evaporadora Emitech K250. Fitas de carbono dupla face foram utilizadas para fixação da amostra no suporte amostral. Foi utilizado para observação um

microscópio eletrônico de varredura LEO440I, sendo procedidas as microanálises por espectrometria dispersiva de raios-X com espectrômetro Oxford e detector de estado sólido Si-Li.

As amostras estudadas no CMM-UQ foram metalizadas com carbono (*Carbon Coater* JEOL JEE-4X). Para as análises foram utilizados dois microscópios eletrônicos: (i) Philips XL30 equipado com sistema de elétron retro-espalhado (*back-scattered electron* – BSE) e um espectrômetro de energia dispersiva (*energy dispersive spectrometer* – EDS) capaz de detectar elementos entre boro e urânio (condições analíticas: corrente a 20 kV e diâmetro do feixe de elétrons = 6 μm); e (ii) JEOL JSM6400F (a corrente e diâmetro do feixe de elétrons foram variáveis, dependendo das características do material analisado). Todos os equipamentos utilizados no CMM-UQ, incluindo a microsonda eletrônica, foram operados diretamente pelo autor, que passou por treinamento prévio, teórico e prático.

2.2.4 – ANÁLISE POR MICROSSONDA ELETRÔNICA (MSE)

Através da microsonda eletrônica foi determinada a composição química do carbonato do itabirito dolomítico e dos minerais de manganês do itabirito manganífero. Em algumas amostras de itabirito dolomítico e de minério de ferro procedeu-se à determinação da composição química da hematita. Todas as análises deste mineral, entretanto, apresentaram teores de Fe_2O_3 superiores a 99%, motivo pelo qual optou-se por não dar seguimento às análises do mesmo.

As análises por MSE dos carbonatos (e algumas de hematita) do itabirito dolomítico foram realizadas no laboratório de microsonda eletrônica do Departamento de Mineralogia e Geotectônica do Instituto de Geociências da USP. As amostras foram previamente metalizadas com carbono e analisadas em uma microsonda eletrônica JEOL-JXA 8600 operando a 15 kV e corrente de 20 μA , com diâmetro do feixe de elétrons variando entre 1 e 5 μm . Foram analisados 8 elementos (Si, Sr, Fe, Mn, Mg, Ca, Zn, Ba) no carbonato e 7 elementos na hematita (Si, Ti, Al, Cr, Fe, Mn e P). O método de correção para as análises foi o “ZAF”.

As análises de minerais de manganês, assim como de algumas hematitas, foram realizadas no CMM-UQ em uma microsonda eletrônica JEOL JXA8800 dotada de quatro espectrômetros de dispersão de comprimento de onda (*wavelength dispersion spectrometer* – WDS) e utilizando quatro cristais (LDE1, LIFH, PET e TAP), um detector (EDS) Oxford Ge Model-6640, e operada por uma estação de trabalho Hewlett Packard Apollo 9000/425t para

aquisição e redução dos dados, operando a 15 kV e corrente de 15 η A, com diâmetro do feixe de elétrons variando entre 0 e 10 μ m. Foram analisados 13 elementos (O, Mn, Zn, P, Co, Fe, Si, Al, Pb, Ba, Ca, K, e Na), sendo o oxigênio analisado como amostra desconhecida e os demais elementos como metal. A aquisição dos dados e redução dos resultados foi feita através do programa JXA-8800L “Basic Software 1”, e o método de correção para as amostras foi “metal PRZ”.

2.2.5 – ANÁLISE QUÍMICA

As amostras destinadas a análises químicas foram preparadas nos laboratórios de preparação de amostras da MBR. A preparação consistiu de britagem, seguida de pulverização em panela de carbeto de tungstênio. Em algumas amostras de itabirito dolomítico, as bandas dolomítica e hematítica foram analisadas separadamente, para fins de comparação com as bandas correspondentes no minério de ferro friável. Para tanto, procedeu-se à coleta em separado das bandas, mediante britagem da amostra global abaixo de 5 mm, e catação manual, com auxílio de lupa binocular, de fragmentos de cada tipo de material. Quatro amostras das bandas maciça e porosa do minério friável, correspondentes às bandas hematítica e dolomítica do protominério, respectivamente, foram também coletadas e analisadas separadamente, para fins de estudo das alterações ocorridas na composição química e mineralógica.

A maioria das análises químicas foi realizada no Laboratório de Análises Químicas da MBR. As análises para Fe total e FeO foram realizadas por Dicromatometria (Titulação do teor de Fe / FeO por Dicromato de Potássio 0,1N). SiO₂, Al₂O₃, P₂O₅, MnO₂, TiO₂, CaO, MgO, Ba, V, Ni, Cu, Zn e Cr foram determinados por espectrometria de plasma (ICP). Na₂O e K₂O foram analisados por absorção atômica. A perda ao fogo (PF) foi determinada mediante calcinação da amostra em mufla, a uma temperatura de 1.000 °C.

Algumas das amostras previamente analisadas na MBR foram selecionadas para análise de um conjunto maior de elementos no Activation Laboratories, Canadá (ACTLABS/Canadá). Neste laboratório, SiO₂, Al₂O₃, Fe₂O₃, P₂O₅, MnO, TiO₂, CaO, MgO, Na₂O, K₂O, Ba, Sr, Y, Sc, Zr, Be e V foram analisados por ICP, enquanto que Ni, Cu, Zn, Ga, Ge, Rb, Nb, Mo, Ag, In, Sn, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Pb, Bi, Cr, Th e U foram determinados por ICP-MS, após a abertura da amostra com fusão por metaborato/tetraborato de Li, a qual foi rapidamente dissolvida em solução de ácido nítrico fraco. Au, As, Br, Co, Ir, Sb, Sc e Se foram analisados por ativação neutrônica instrumental

(INAA). Na Tabela 1 estão relacionados os limites de detecção das análises realizadas na MBR e no ACTLABS.

%	MBR		ACTLABS		ppm	MBR		ACTLABS		ppm	ACTLABS		
											ppm		ppm
SiO ₂	0,1	0,01	Ba	10	3	Ge	0,5	Sm	0,01	W	0,5		
TiO ₂	0,01	0,001	V	10	5	Rb	1	Eu	0,005	Tl	0,05		
Al ₂ O ₃	0,1	0,01	Ni	10	20	Nb	0,2	Gd	0,01	Pb	5		
Fe ₂ O ₃	0,1	0,01	Cu	10	5	Mo	2	Tb	0,01	Bi	0,1		
FeO	0,1	Na	Zn	10	30	Ag	0,5	Dy	0,01	Th	0,05		
MnO	0,01	0,001	Cr	10	20	In	0,1	Ho	0,01	U	0,01		
MgO	0,01	0,01	Sr	Na	2	Sn	1	Er	0,01				
CaO	0,01	0,01	Y	Na	0,5	Cs	0,1	Tm	0,005				
Na ₂ O	0,001	0,01	Sc	Na	0,1	La	0,05	Yb	0,01				
K ₂ O	0,001	0,01	Zr	Na	1	Ce	0,05	Lu	0,002				
P ₂ O ₅	0,01	0,01	Be	Na	1	Pr	0,01	Hf	0,1				
PF	0,1	0,01	Ga	Na	1	Nd	0,05	Ta	0,01				

Na= não analisado

Tabela 1: Relação dos elementos analisados em cada laboratório químico com seus respectivos limites de detecção.

2.2.6 – DETERMINAÇÃO DE DENSIDADE

A determinação de densidade foi realizada em fragmentos de 20 a 30 cm de comprimento de minério friável e itabirito dolomítico, coletadas em testemunhos de sondagem. Apesar do minério friável ser muito friável, foi possível coletar fragmentos contínuos, medindo cerca de 5 cm de diâmetro por 20 cm de comprimento, os quais foram secos em estufa por 12 h, pesados, e revestidos por um filme de PVC, quando foram novamente pesados ao ar e, posteriormente, imersos em água. As amostras de itabirito dolomítico foram processadas da mesma forma. A densidade aparente foi obtida diretamente, através da relação entre massa e volume. Após a determinação da densidade aparente, todos os fragmentos foram submetidos à análise química.

2.2.7 – ANÁLISE DE ISÓTOPOS DE CARBONO E OXIGÊNIO

Isótopos de C e O foram analisados em amostras da banda dolomítica do itabirito dolomítico e em veios carbonáticos que cortam esta rocha. As análises isotópicas foram realizadas no Laboratório de Isótopos Estáveis da Universidade Federal de Pernambuco (NEG-LABISE). A metodologia consistiu na extração do gás CO₂ de amostras de carbonato pulverizadas, colocadas em solução de ácido fosfórico a 100% durante três dias, o qual foi criogenicamente limpo de acordo com o método descrito por McCrea (1950). Os isótopos de C e

O do CO₂ liberado foram analisados em um espectrômetro de massa SIRA, o qual foi calibrado com os padrões NBS-18, NBS-19 e NBS-20, usando o gás BSC (*Borborema skarn calcite*) como referência ($\delta^{18}\text{O}$ e $\delta^{13}\text{C} = -11.28\text{‰}_{\text{PDB}}$ e $-8.58\text{‰}_{\text{PDB}}$, respectivamente).

2.2.8 – ANÁLISE POR ESPECTROSCOPIA MÖSSBAUER (MS)

As análises por espectroscopia Mössbauer foram realizadas em amostras de minério de ferro compacto e friável. As bandas maciça e porosa do minério friável foram analisadas separadamente, com o intuito de investigar-se a presença de diferentes fases minerais portadoras de ferro nas mesmas. Foram também analisadas duas amostras da banda dolomítica do itabirito dolomítico, para efeito de comparação com a banda porosa do minério de ferro friável, a qual resulta da dissolução da primeira. As análises foram realizadas no Laboratório de Física Aplicada do Centro de Desenvolvimento de Tecnologia Nuclear (CDTN), em Belo Horizonte. Os espectros Mössbauer de transmissão do ^{57}Fe foram obtidos a 300 K em um espectrômetro de aceleração constante usando uma fonte $^{57}\text{Co/Rh}$. Quatro amostras foram também analisadas a 50 K. Um programa de mínimos quadrados (programa NORMOS) foi utilizado para o cálculo dos parâmetros hiperfinos. Todas as amostras estudadas por MS foram também analisadas por DRX no Instituto de Física da UFMG.

2.2.9 – ANÁLISE GEOCRONOLÓGICA PELO MÉTODO $^{40}\text{Ar}/^{39}\text{Ar}$

O método de datação $^{40}\text{Ar}/^{39}\text{Ar}$ é uma variante do método K-Ar e, assim como este, fornece o tempo em função do decaimento radioativo, espontâneo e natural do ^{40}K para o $^{40}\text{Ar}^*$ (argônio radiogênico), a uma taxa conhecida. Uma descrição detalhada da técnica pode ser obtida em McDougall *et al.* (1999). O método $^{40}\text{Ar}/^{39}\text{Ar}$ é um dos métodos geocronológicos mais confiáveis e versáteis atualmente disponíveis, em função de fatores tais como:

- (1) somente razões isotópicas, e não quantidades absolutas de ^{40}Ar , precisam ser determinadas para uma amostra (Renne, 2000);
- (2) várias sub-alíquotas de gases são analisadas em uma mesma amostra, a diferentes temperaturas (aquecimento gradual), o que permite a determinação da história de retenção do Ar (história térmica) em um mineral ou rocha;
- (3) a quantidade de material utilizada na técnica de $^{40}\text{Ar}/^{39}\text{Ar}$ (um grão de 0,2-2 mm de diâmetro) é bem menor que a necessária no K-Ar (0,1-1 g), permitindo que problemas de contaminação sejam evitados;
- (4) a análise por aquecimento gradual permite testar a presença de várias gerações do mineral datável em uma mesma amostra;

(5) a análise por aquecimento gradual permitir testar a presença de argônio herdado ou em excesso, de contaminantes, ou a presença de várias gerações da fase datável em uma mesma amostra;

(6) a análise por aquecimento gradual permite a extração e análise de gases hospedados em diferentes reservatórios em um mineral, facilitando a separação dos gases atmosféricos dos gases radiogênicos na amostras, aumentando a precisão das análises;

(7) o método é passível de completa automação, permitindo a realização de um número estatisticamente válido de análises em um curto período de tempo.

No método de $^{40}\text{Ar}/^{39}\text{Ar}$, o potássio é medido indiretamente através da geração do isótopo nucleogênico de ^{39}Ar pela reação $^{39}\text{K}(n,p)^{39}\text{Ar}$ (Merrihue & Turner, 1966), que implica na absorção de um nêutron rápido e na emissão de um próton. A amostra é irradiada (isto é, bombardeada por nêutrons), juntamente com um padrão, em um reator nuclear, com fluxo de nêutrons apropriado para a geração de ^{39}Ar . O tempo é obtido através da relação:

$$t = (\lambda^{-1}) \cdot \ln [J \cdot (^{40}\text{Ar}^*/^{39}\text{Ar}_k) + 1] \quad (\text{Equação 1})$$

onde,

λ representa a constante de decaimento total do ^{40}K ($5.543 \pm 0.010 \times 10^{-10}$) (soma de λ_β e λ_ϵ) - (Steiger & Jager, 1977);

λ_β representa a constante de decaimento do ^{40}K ao ^{40}Ca ($4.962 \pm 0.009 \times 10^{-10}$);

λ_ϵ a constante de decaimento do ^{40}K ao ^{40}Ar ($5.508 \pm 0.004 \times 10^{-11}$);

$^{40}\text{Ar}^*$ é a quantidade total do ^{40}Ar radiogênico (obtida subtraindo-se a quantidade de ^{40}Ar atmosférico e $^{40}\text{Ar}_k$ da quantidade total de ^{40}Ar obtida em uma alíquota da amostra, e onde $^{40}\text{Ar}_k$ é a quantidade de ^{40}Ar gerada pela reação $^{39}\text{K}(n,p)^{39}\text{Ar}$;

$^{39}\text{Ar}_k$ é a quantidade de ^{39}Ar gerada pela reação $^{39}\text{K}(n,p)^{39}\text{Ar}$ (obtida subtraindo-se o $^{39}\text{Ar}_{\text{Ca}}$ da quantidade total de ^{39}Ar medido em uma alíquota da amostra, onde $^{39}\text{Ar}_{\text{Ca}}$ é a quantidade de ^{39}Ar gerada pela reação $^{42}\text{Ca}(n,\alpha)^{39}\text{Ar}$).

O parâmetro de irradiação J (fator J), adimensional, é determinado irradiando-se um padrão de fluência de nêutrons de idade conhecida colocado próximo à amostra cuja idade quer se determinar. O padrão deve ficar fisicamente o mais próximo possível da amostra para evitar incertezas causadas por heterogeneidades no fluxo de nêutrons (Renne, 1998). A determinação das quantidades de ^{40}K e $^{39}\text{Ar}_k$ produzidos no padrão fornece as informações necessárias para o cálculo do fator J :

$$J = (e^{\lambda t} - 1) / (^{40}\text{Ar}^*/^{39}\text{Ar}_k) \quad (\text{Equação 2})$$

onde,

t é a idade do padrão, determinada independentemente;

λ é definido na Equação 1;

$^{40}\text{Ar}^*$ é a quantidade total de ^{40}Ar presente no padrão;

$^{39}\text{Ar}_k$ é a quantidade de ^{39}Ar nucleogênico gerado pela reação $^{39}\text{K}(\text{n},\text{p})^{39}\text{Ar}$ no padrão.

O método $^{40}\text{Ar}/^{39}\text{Ar}$ pode ser aplicado a uma ampla escala de tempo, abrangendo desde o recente (ca. 2.000 anos) até a idade do sistema solar (Renne, 2000). Em minerais supergênicos, as idades mais nova já obtidas estão em torno de 100.000 anos (Feng & Vasconcelos, 2001).

As amostras de óxidos de Mn das Minas do Sapecado e Andaime foram datadas no Laboratório de Geocronologia de Argônio da Universidade de Queensland (University of Queensland Argon Geochronology in Earth Sciences – UQ-AGES). A aplicação do método $^{40}\text{Ar}/^{39}\text{Ar}$ consiste de uma série de etapas descritas por Vasconcelos (1999) e Vasconcelos *et al.*, (2002), resumidamente ilustradas na Figura 17. As amostras foram quebradas com o auxílio de um martelo em fragmentos milimétricos (0,5-2 mm) e lavadas em ultrassom para retirada de materiais finos (argilominerais, minerais finamente ou pouco cristalizados) por cerca de 1 hora, até a limpeza total do material, sendo utilizados água destilada e álcool etílico absoluto na lavagem. Os fragmentos limpos foram examinados em lupa binocular, e seis a oito grãos visualmente homogêneos de cada amostra foram colocados em um disco de alumínio para irradiação por nêutrons. Aproximadamente a mesma quantidade de grãos de foi colocada em discos plásticos, ao qual foi adicionada resina epóxi. Após polimento, estas amostras foram examinadas ao MEV e MES, permitindo desta forma que as análises mineralógicas e geocronológicas sejam realizadas em praticamente uma mesma alíquota da amostra.

As amostras foram irradiadas por 14 horas, juntamente com o padrão *Fish Canyon Sanidine* (28.02 ± 0.28 Ma) no reator nuclear Triga da Oregon State University (OSU – CLICIT Facility). Após um período de resfriamento de três semanas, três grãos de cada amostra foram colocados em um disco de cobre, secos em estufa a 180°C por 13 horas, e aquecidos gradualmente em um laser contínuo (*Coherent 10W continuous Ar-ion laser*) no UQ-AGES. Os gases liberados durante o aquecimento foram limpos criogenicamente, sendo a fração limpa dos gases analisadas em um espectrômetro de massa MAP-215-50 especialmente construído para a análise de gases raros. O sistema a laser é totalmente automatizado pelo programa *Mass Spec v. 5.11*, escrito especificamente para análises pelo método $^{40}\text{Ar}/^{39}\text{Ar}$. Este mesmo programa faz o cálculo da idade aparente para cada estágio de aquecimento (*step heating*), levando em consideração as correções necessárias (análise de amostras em branco, interferências nucleogênicas, contaminação por ^{36}Ar atmosférico, fator J).

O método $^{40}\text{Ar}/^{39}\text{Ar}$ fornece **idades aparentes**, obtidas para cada estágio de aquecimento, uma **idade integrada**, que é aquela calculada a partir do gás total liberado pela amostra, e uma **idade isocrônica**, obtida a partir da reta de regressão entre as razões $^{39}\text{Ar}/^{40}\text{Ar}$ vs. $^{36}\text{Ar}/^{40}\text{Ar}$. Fornece ainda uma **idade patamar**, que é calculada conforme definição de Fleck *et al.* (1977), a partir de estágios de aquecimento contíguos que juntos representam mais de 50% do total de ^{39}Ar liberado da amostra, para os quais inexista diferença entre as idades ao nível de confiança de 95%. Em condições ideais, as idades integrada, isocrônica e patamar devem apresentar os mesmos resultados. Vasconcelos (1999) discute o significado geológico de cada uma destas idades, apresentando diferentes tipos de espectros obtidos na datação $^{39}\text{Ar}/^{40}\text{Ar}$ de minerais supergênicos e a interpretação dos mesmos.

Figura 13: Diagrama esquemático mostrando as principais etapas da análise pelo método geocronológico por $^{40}\text{Ar}/^{39}\text{Ar}$ (Carmo, 2004).

CAPÍTULO 3 – GEOLOGIA E GEOQUÍMICA DO MINÉRIO DE FERRO DA MINA DE ÁGUAS CLARAS, QUADRILÁTERO FERRÍFERO, MINAS GERAIS, BRASIL

Este tema é apresentado sob a forma do artigo “*Geology and geochemistry of the Águas Claras and Pico iron mines, Quadrilátero Ferrífero, Minas Gerais, Brazil*” (Spier, C.A.; Oliveira, S.M.B.; Rosière, C.A. 2003. *Mineralium Deposita*, **38**:751-774), no Anexo 1. Este artigo sintetiza as informações geológicas e geoquímicas adquiridas ao longo dos 30 anos de existência da Mina de Águas Claras, apresentando-os de forma sistemática, e trazendo-os ao conhecimento público. Apresenta, ainda, o mesmo tipo de informação para a Mina do Pico, de modo a familiarizar o leitor com os diferentes tipos de protominério do minério de ferro existentes no Quadrilátero Ferrífero, e apresentá-lo à complexidade do tema que é a gênese do minério de ferro. Segue-se, abaixo, uma síntese do artigo.

As Minas de Águas Claras e Pico são duas minas de ferro de classe mundial, hospedadas dentro de formações ferríferas bandadas paleoproterozóicas (regionalmente conhecidas como itabiritos) do Supergrupo Minas, localizadas no Quadrilátero Ferrífero, Minas Gerais. O Depósito de Águas Claras consiste de um corpo de minério lenticular, com cerca de 2.500 m de extensão, alojado dentro de itabirito dolomítico da Formação Cauê. O itabirito dolomítico é o protominério do minério de ferro friável de alto teor, o qual foi o principal tipo de minério lavrado, e representou mais de 85% dos 284 Mt de minério minerados entre 1973 e 2002, quando a mina foi fechada. Os restantes 15% são formados por minério compacto de alto teor. A hematita é o principal constituinte mineralógico do minério, ocorrendo como martita, hematita granular, tabular e, localmente, especular. Magnetita ocorre de forma subordinada, como relictos no interior dos cristais de martita e hematita. Minerais de ganga são muito raros, consistindo de dolomita, clorita, talco e apatita, sendo especialmente comuns no contato com o protominério. O baixíssimo conteúdo de minerais de ganga está refletido na composição química dos minérios, caracterizada por teores muito elevados de Fe (média de 68,2%).

O Depósito do Pico é constituído por um corpo de minério lenticular, com aproximadamente 3.000 m de extensão, alojado dentro de quartzo itabirito, o qual foi o protominério dos minérios de alto e baixo teor de ferro da Mina do Pico. O minério friável de alto teor, juntamente com o minério friável de teores de ferro um pouco mais baixos (itabirito

friável rico) são os principais tipos de minério, representando cerca de 51% e 29% das reservas. Os restantes 20% consistem de minério compacto de alto teor. Os minerais de ferro do minério são os mesmos do minério de Águas Claras. Minerais de ganga são raros nos minérios de alto teor, aumentando em quantidade no itabirito rico. O quartzo é o principal mineral de ganga, com clorita ocorrendo subordinada. A composição química dos minérios de alto teor é caracterizada pelos elevados teores de Fe (média de 67%) e baixos de P, Al_2O_3 e SiO_2 , os quais estão concentrados nas frações finas do minério. O itabirito rico apresenta teores médios de Fe e SiO_2 de 58,6% e 13,5%, respectivamente.

A gênese do minério friável de alto teor e do itabirito rico das Minas de Águas Claras e Pico está relacionada a processos supergênicos. Os minerais de ganga dos itabiritos foram lixiviados pela água subterrânea, o que promoveu o enriquecimento residual em ferro na rocha. Este processo foi favorecido pelo clima tropical e topografia favorável. A composição mineralógica original do itabirito e a presença de estruturas controlando a circulação da água subterrânea influenciou o grau de enriquecimento em ferro da rocha. O minério compacto de alto teor é de origem supergênica. Sua gênese é atribuída a soluções hidrotermais que lixivaram os minerais de ganga, preenchendo os poros formados com hematita. Este processo ainda não está completamente entendido e permanece uma fonte de debates na literatura.

CAPÍTULO 4 – GEOQUÍMICA E GÊNESE DAS FORMAÇÕES FERRÍFERAS BANDADAS DA FORMAÇÃO CAUÊ, QUADRILÁTERO FERRÍFERO, MINAS GERAIS, BRASIL

Este tema é apresentado sob a forma do artigo “Geochemistry and genesis of the banded iron formations of the Cauê Formation, Quadrilátero Ferrífero, Minas Gerais, Brazil” (Spier, C.A; Oliveira, S.M.B.; Sial, A.N.; Rios, F.J. 2005. *Precambrian Research* - submetido), no Anexo 2. O artigo descreve a geologia, mineralogia e petrologia dos itabiritos da Formação Cauê na Mina de Águas Claras, dando especial atenção ao itabirito dolomítico (protominério do minério friável). Apresenta, ainda, dados sobre a geoquímica dos itabiritos e resultados de análises de isótopos de C e O do itabirito dolomítico, sugerindo um modelo genético para estas rochas. Apresenta-se, a seguir, um resumo do artigo.

A Formação Cauê, do Supergrupo Minas, é composta por formações ferríferas bandadas (BIFs) paleoproterozóicas do tipo “Lago Superior”, denominadas regionalmente de itabiritos. Dois tipos composicionais de itabiritos ocorrem na região noroeste do Quadrilátero Ferrífero: itabirito dolomítico e quartzo itabirito. O primeiro consiste de bandas ricas em dolomita, alternadas com bandas ricas em hematita, enquanto que o segundo é formado por bandas ricas em quartzo alternadas com bandas ricas em hematita. Dolomita, quartzo e hematita são os principais constituintes mineralógicos destes itabiritos, com clorita, sericita e apatita ocorrendo como minerais acessórios.

A composição química dos itabiritos da Formação Cauê é tão simples quanto a de outras BIFs mundiais. No itabirito dolomítico Fe_2O_3 mais CaO , MgO e PF variam entre 95.8% e 97.8%, enquanto que no quartzo itabirito Fe_2O_3 mais SiO_2 variam entre 94.4% e 99.6%. Os dois tipos de itabiritos estão intensamente oxidados, apresentando razões $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ maiores do 0.98, muito superiores as razões médias de outras BIFs paleoproterozóicas. Os teores de elementos traços são muito baixos, variando entre < 10 ppm (Y, Sc, Be, Cu, Ga, Ge, Rb, Nb, Mo, Ag, In, Sn, Cs, Hf, Tl, Pb, Bi, As, Cd, Th, U, Sb) até concentrações entre 10 e 55 ppm (Ba, Sr, Zr, V, Ni, Zn, Co, Cr e ΣETR).

A dolomita do itabirito dolomítico apresenta valores negativos de $\delta^{13}\text{C}$ variando entre -2.5‰ a -0.8‰, enquanto que os dados de isótopos de oxigênio exibem valores de $\delta^{18}\text{O}$ variando entre -12.4‰ to -8.5‰. Os valores do $\delta^{13}\text{C}$ mostram um enriquecimento em ^{13}C da

base para o topo da Formação Cauê, o qual possivelmente continua para cima na estratigrafia, nos dolomitos estromatolíticos da Formação Gandarela. Os dados isotópicos de C e O, as assinaturas de ETR e as razões Y/Ho indicam uma origem marinha para os sedimentos do itabirito dolomítico.

O padrão de enriquecimento em ETRP apresentado pelos itabiritos é característico do padrão de fracionamento dos ETR da água do mar moderna, superimposto pelo padrão de ETR dos fluidos hidrotermais exalados nas *vents* das dorsais meso-oceânicas, os quais estão refletidos nas anomalias positivas de Eu. A forte correlação positiva entre Al_2O_3 e TiO_2 ($r > 0.9$) indica uma pequena participação de componentes terrígenos nos sedimentos predominantemente químicos e marinhos da Formação Cauê. As diferenças no padrão de fracionamento dos ETRP dos itabiritos sugerem que seus sedimentos foram precipitados a partir de diferentes profundidades do mar, com os sedimentos do itabirito dolomítico sendo precipitados em águas marinhas mais rasas, carregando maior quantidade de sedimentos continentais, e os sedimentos do quartzo itabirito sendo precipitados a partir de águas mais profundas. Variações do nível do mar, causadas por transgressões e regressões, seriam responsáveis por mudanças na composição da água durante a deposição da Formação Cauê. Estas mudanças estariam refletidas pelo itabirito dolomítico, quartzo itabirito e itabirito anfibolítico, os quais representariam variações faciológicas laterais e verticais de BIFs carbonática, quartzosa (*cherty*) e argilosa (*shaly*).

CAPÍTULO 5 – OS MINÉRIOS DE FERRO DE ALTO TEOR DA MINA DE ÁGUAS CLARAS, QUADRILÁTERO FERRÍFERO, BRASIL

Este tópico é apresentado sob a forma do artigo “The high-grade iron ores of the Águas Claras mine, Quadrilátero Ferrífero, Brazil” (Spier, C.A; Oliveira, S.M.B.; Rosière, C.A; Ardisson, J.D. 2005. *Mineralium Deposita* - submetido), no Anexo 3. O artigo trata do tema central da tese, que é a caracterização e a gênese do minério de ferro da Mina de Águas Claras. São apresentados dados mineralógicos, petrológicos e geoquímicos para os minérios friável e compacto, e discutidos os processos envolvidos nas suas gêneses. Na discussão da gênese dos minérios, é feita uma rápida apresentação da geologia dos Depósitos de Capão Xavier e Tamanduá, de modo a melhor ilustrar a complexidade dos processos que levaram a formação dos vários tipos de minério de ferro no Quadrilátero Ferrífero. Apresenta-se, a seguir, uma síntese do artigo.

Muitos depósitos de ferro de classe mundial ocorrem no Quadrilátero Ferrífero, na região sudeste do Brasil, onde formações ferríferas bandadas metamorfas e heterogeneamente deformadas, regionalmente denominadas de itabiritos, foram convertidas em minérios hematíticos de alto ($\text{Fe} > 64\%$) e baixo ($30\% < \text{Fe} < 64\%$) teor de ferro. Com base em sua composição mineralógica, são descritos três tipos principais de itabiritos no Quadrilátero Ferrífero: quartzo itabirito, itabirito dolomítico e itabirito anfíbolítico. Diferentemente de outras minas no Quadrilátero Ferrífero, onde os minérios de alto teor ocorrem associados a minérios de baixo teor, na Mina de Águas Claras os minérios de alto teor são largamente predominantes, tendo sido formados a partir do itabirito dolomítico. Dois tipos principais de minério de alto teor ocorrem em Águas Claras: friável e compacto. O minério friável é o principal tipo, e representou cerca de 85% do minério lavrado entre 1973 e 2002, quando a mina foi fechada. O minério friável tem porosidade muito elevada e preserva parcialmente a estrutura original do itabirito dolomítico (protominério), particularmente o meso e microbandamento, característica esta refletida nas bandas maciças e porosas do minério. O minério compacto é muito denso e duro. Ele ocorre como lentes métricas a decimétricas, isoladas, tanto no meio do minério friável como no interior do itabirito dolomítico inalterado. Os minérios friável e compacto são formados essencialmente por hematita, a qual ocorre na forma de martita, hematita anédrica, granular e

tabular e, localmente, especular. Os minerais de ganga são muito raros, consistindo de dolomita, sericita, clorita e apatita nos minérios compacto e friável, e minerais de manganês e ferrihidrita no minério friável, onde estes últimos minerais ocorrem em maior quantidade na banda porosa. As análises químicas mostraram que os minérios friável e compacto consistem quase que totalmente de Fe_2O_3 , com maiores quantidades de impurezas, especialmente MnO , no minério friável. Tanto o minério friável como o minério compacto são extremamente pobres em elementos traços.

Os minérios de alto teor da Mina de Águas Claras tem origens distintas, envolvendo processos hipogênicos e supergênicos. A ocorrência do minério compacto no interior do itabirito dolomítico inalterado é uma boa indicação de sua origem hipogênica. Apesar dos questionamentos em relação à gênese do itabirito dolomítico (se esta rocha representa uma fácies carbonática da Formação Cauê ou se resulta da substituição hidrotermal do chert/quartzo por dolomita), diversas características observadas no minério friável indicam a sua origem supergênica, como, por exemplo: (1) a transição lateral e vertical para o itabirito dolomítico, (2) o gradual desaparecimento em profundidade, formando interdigitações com esta rocha, (3) a presença em meio ao minério de blocos isolados do protominério, em tudo similares ao itabirito dolomítico que ocorre fora da área mineralizada, (4) a presença de dobras do tipo *kink* e *slump*, ausentes no protominério, as quais em conjunto com a ocorrência de depressões preenchidas por sedimentos terciários recobrimdo parcialmente o corpo de minério, indicam o colapso do mesmo após a lixiviação da dolomita, (5) a presença de ferrihidrita e de minerais de manganês formados a partir da dissolução da dolomita, (6) padrões de fracionamento dos ETR idênticos aos do itabirito dolomítico.

A composição mineralógica dos itabiritos teve um papel importante na gênese dos minérios de alto e baixo teor no Quadrilátero Ferrífero. A comparação entre a geologia da Mina de Águas Claras com a de Capão Xavier e Tamanduá, mostrou que, sob idênticas condições estruturais, topográficas e climáticas, o itabirito dolomítico é muito mais favorável à formação de depósitos de ferro de alto teor do que o quartzo itabirito. Forneceu também indicações de que a gênese de depósitos friáveis de alto teor a partir do quartzo itabirito requer a atuação de outros controles além do litológico, possivelmente envolvendo processos hipogênicos e supergênicos, com predominância de um ou outro processo em cada depósito em particular.

CAPÍTULO 6 – GEOCRONOLOGIA $^{40}\text{Ar}/^{39}\text{Ar}$ E EVOLUÇÃO DOS DEPÓSITOS DE FERRO LATERÍTICOS DO QUADRILÁTERO FERRÍFERO, MINAS GERAIS, BRASIL

Este tema é tratado sob a forma do artigo “ $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology and the evolution of lateritic iron deposits in the Quadrilátero Ferrífero, Minas Gerais, Brazil” (Spier, C.A; Vasconcelos, P.M.; Oliveira, S.M.B. 2005. *Chemical Geology* - submetido), no Anexo 4. O artigo trata da datação do perfil de intemperismo dos itabiritos no Quadrilátero Ferrífero, e por extensão da idade do minério de ferro supergênico nele contido, apresentando idades obtidas através da técnica de datação $^{40}\text{Ar}/^{39}\text{Ar}$, aplicada em minerais de manganês supergênicos presentes no minério de ferro friável. A dificuldade de acesso aos locais mais favoráveis para a ocorrência destes minerais na Mina de Águas Claras, e a indisponibilidade de testemunhos de sondagem contendo minerais de manganês passíveis de serem datados pela técnica $^{40}\text{Ar}/^{39}\text{Ar}$, fez com que fossem escolhidas as Minas de Sapecado e Andaime para este estudo. Apresenta-se, a seguir, um resumo do artigo.

Os perfis de intemperismo recobrimo os depósitos de minério de ferro de Sapecado, Pico e Andaime, localizados no Quadrilátero Ferrífero, em Minas Gerais, atingem profundidades de 140-400 m, e hospedam depósitos de minério de ferro supergênicos de classe mundial. Além de hematita, goethita e algum quartzo remanescente, o minério de ferro friável e os itabiritos profundamente intemperizados contêm criptomelano, hollandita e pirolusita supergênicos. Estes minerais de manganês ocorrem preferencialmente na região de contato entre os itabiritos e dolomitos intemperizados das Formações Cauê e Gandarela, respectivamente. A sua distribuição no perfil de intemperismo dos itabiritos fornece informações sobre a propagação da frente de alteração intempérica e sobre a formação do minério de ferro supergênico.

Os resultados de datação $^{40}\text{Ar}/^{39}\text{Ar}$ por aquecimento gradual a laser de 69 grãos de minerais de manganês, obtidos em 23 amostras coletadas em profundidades entre 5 e 150 m, revelam idades entre 70 e 12 Ma. Os óxidos de manganês mais antigos ocorrem próximos da superfície, enquanto que os mais jovens ocorrem em profundidade. Entretanto, a maioria das amostras coletadas na interface rocha alterada-rocha sã apresentaram idades entre 51 e 41 Ma, sugerindo que os perfis de intemperismo no Quadrilátero Ferrífero já tivessem atingido as profundidades atuais no Paleógeno. A partir daí o avanço da frente de alteração foi limitado.

CAPÍTULO 7 – CONSIDERAÇÕES FINAIS E CONCLUSÕES

Os estudos mineralógicos e geoquímicos das BIFs e do minério de ferro da Mina de Águas Claras permitiram a caracterização destas rochas, em especial do itabirito dolomítico e do minério de ferro friável, contribuindo para o seu melhor conhecimento, o qual poderá ser útil no planejamento da lavra e beneficiamento do minério de ferro de outros depósitos da região com características geológicas similares, como, por exemplo, Capão Xavier. Permitiram, ainda, a elaboração de algumas considerações sobre suas gêneses.

A gênese do minério de ferro vem sendo explicada, recentemente, através de modelos híbridos, hipogênico-supergênicos (Beukes *et al.*, 2002; Dalstra & Guedes, 2004; Taylor *et al.*, 2001). De acordo com estes modelos, no estágio hipogênico haveria a substituição metassomática do chert/quartzo da BIF por carbonatos (dolomita ou ankerita), os quais seriam lixiviados por fluidos meteóricos no estágio posterior. A substituição do quartzo por carbonato parece ter sido uma etapa importante na gênese dos depósitos gigantes de ferro de Carajás (Guedes *et al.*, 2002; Lobato *et al.*, 2004; Silva *et al.*, 2005; Silva *et al.*, 2004; Zuccheti & Lobato, 2005) e da Província de Hamersley (Taylor *et al.*, 2001; Thorne *et al.*, 2004; Webb *et al.*, 2004), embora existam diversos depósitos em Hamersley onde esta associação é inexistente, como, por exemplo, Paraburdoo e Mt. Walleback (Morris, 2002; Webb *et al.*, 2003; Webb *et al.*, 2004). O mesmo acontece no Quadrilátero Ferrífero, onde existem muitos depósitos, como por exemplo os de Tamanduá, Capitão do Mato, Abóboras, Galinheiro, Pico e Sapecado, onde o quartzo itabirito foi claramente o protominério, inexistindo evidências de metassomatismo do quartzo por carbonato.

Por outro lado, a ocorrência de grandes corpos de itabirito dolomítico no Quadrilátero Ferrífero, associados a depósitos gigantes de minério de ferro de alto teor, poderia ser um indicativo de que estes depósitos também teriam sido resultantes do enriquecimento de BIFs quartzosas, através da atuação conjunta de processos hipogênicos-supergênicos. De acordo com esta hipótese, o itabirito dolomítico da Mina

de Águas Claras representaria a primeira etapa da gênese do minério de ferro, e teria sido formado por substituição metassomática do quartzo do quartzito itabirito por dolomita, conforme sugerido por Beukes *et al.* (2002). Entretanto, neste trabalho não pode ser constatada uma relação direta desta substituição metassomática.

Concluimos que a formação de depósitos gigantes de minério de alto teor nem sempre envolve uma fase de substituição metassomática do quartzo por carbonato, e que o itabirito dolomítico é produto de dolomitização, metamorfismo e oxidação de BIFs originalmente carbonáticas, que representariam tão somente uma variação faciológica dos sedimentos da Formação Cauê.

Uma forte indicação da origem sedimentar do itabirito dolomítico é dada pelos resultados das análises dos isótopos de C e O, que apresentaram valores negativos de $\delta^{13}\text{C}$ variando entre -2,5‰ a -0,8‰, enquanto que os dados isotópicos de O mostraram valores de $\delta^{18}\text{O}$ entre -12,4‰ a -8,5‰, similares aos encontrados por Bekker *et al.* (2003) e Sial *et al.* (2000) em dolomitos estromatolíticos da Formação Gandarela, e compatíveis com os valores de $\delta^{13}\text{C}$ e $\delta^{18}\text{O}$ encontrados em outras seqüências carbonáticas paleoproterozóicas bem preservadas (Bekker *et al.*, 2003; Veizer *et al.*, 1992; Veizer *et al.*, 1990; Veizer *et al.*, 1989).

A composição química global tanto do itabirito dolomítico como do quartzito itabirito indica uma origem a partir de sedimentos químicos muito puros. Por outro lado, a presença em pequena quantidade de Al, Ti, Zr e Th e a elevada correlação linear positiva entre eles nestas rochas, indica que houve pelo menos uma limitada participação de componentes detríticos nos sedimentos das BIFs na região da Mina de Águas Claras. Os teores ligeiramente maiores de Al_2O_3 , TiO_2 , Zr e Th no itabirito dolomítico indicam que os sedimentos originais desta rocha receberam uma contribuição ligeiramente maior de componentes detríticos do que os sedimentos do quartzito itabirito. Estes componentes detríticos estão representados nos itabiritos pelos minerais micáceos, como clorita e sericita.

As análises petrográficas e químicas do quartzito itabirito inalterado das Minas de Águas Claras e Pico apresentaram resultados muito similares, sugerindo que este tipo de BIF formou-se nas mesmas condições deposicionais, em diferentes locais do Quadrilátero Ferrífero. Por outro lado, as associações litológicas reconhecidas nas duas minas são

distintas: itabirito dolomítico e quartzo itabirito em Águas Claras e quartzo itabirito e itabirito anfíbolítico na Mina do Pico. Na base da Formação Cauê em Águas Claras ocorre itabirito dolomítico, enquanto que na mesma posição estratigráfica na Mina do Pico ocorre quartzo itabirito. Estas relações sugerem variações laterais e verticais no ambiente de sedimentação da Formação Cauê, que propiciaram a formação de diferentes tipos de BIFs — carbonática, *cherty* e argilosa — as quais, no decorrer da evolução geológica da região, originaram os itabiritos dolomítico, quartzo itabirito e anfíbolítico, respectivamente.

A participação de processos hipogênicos na gênese dos itabiritos do Quadrilátero Ferrífero ainda não está inteiramente compreendida. Entretanto, é inquestionável o envolvimento dos mesmos na gênese do minério compacto, conforme evidenciado, na Mina de Águas Claras, pela ocorrência em grandes profundidades deste tipo de minério intercalado ao itabirito dolomítico inalterado. Os dados microtermométricos obtidos por Rosière & Rios (2004) em hematitas de minérios compactos da Mina de Conceição sustentam esta conclusão. Os resultados obtidos neste trabalho não permitiram avanços significativos no conhecimento da gênese dos minérios compactos, indicando apenas que os mesmos foram formados por processos hipogênicos, em fase(s) anterior(es) à formação do minério friável.

Por outro lado, diversas características apresentadas pelo minério friável, tais como: (1) a transição lateral e vertical para o itabirito dolomítico, (2) o gradual desaparecimento em profundidade, formando interdigitações com rocha fresca, (3) a presença em meio ao minério de blocos isolados do protominério, em tudo similares ao itabirito dolomítico que ocorre fora da área mineralizada, (4) a presença de dobras do tipo *kink* e *slump*, ausentes no protominério, as quais em conjunto com a ocorrência de depressões preenchidas por sedimentos terciários recobrindo parcialmente o corpo de minério, indicam o colapso do mesmo após a lixiviação da dolomita, (5) a presença de ferrihidrita e de minerais de manganês formados a partir da dissolução da dolomita, indicam uma origem supergênica para este tipo de minério. O resultado das análises químicas para ETR sustenta esta conclusão, na medida em que tanto o minério friável como o itabirito dolomítico apresentam padrão de fracionamento muito similares, com forte enriquecimento do lantânio em direção ao lutécio e anomalias positivas de Eu e Y.

Por outro lado, este padrão é distinto do padrão de fracionamento do minério compacto, onde se verifica uma diferença nos ETR pesados, os quais sofrem discreto empobrecimento em relação aos ETR médios.

Os estudos petrográficos, combinados com as análises por DRX e MEV mostraram que a dissolução da dolomita pelos fluidos supergênicos produz um resíduo, cuja caracterização por espectrometria Mössbauer e microscopia de transmissão eletrônica revelou ser formado por ferrihidrita e minerais de manganês. A ocorrência destes novos minerais, preferencialmente na banda porosa do minério friável, é uma indicação de que o Fe^{2+} e o Mn^{2+} , originalmente presentes na composição da dolomita, foram rapidamente oxidados pelas soluções que lixiviaram este mineral e promoveram a concentração residual de hematita na rocha. A identificação da ferrihidrita, mineral típico do intemperismo, no resíduo da dissolução da dolomita, é uma forte evidência de que a dissolução ocorreu pela ação da água subterrânea. Este mineral é meta-estável e transforma-se em hematita em temperaturas a partir de 4 °C (Schwertmann *et al.*, 1985), a menos que esteja associado a minerais de manganês (Cornell, 1988), como é o caso em Águas Claras. A ocorrência de múltiplas gerações de minerais de manganês no itabirito manganífero das Minas de Sapecado e Andaime, exibindo texturas botrioidal e radial, típicas de minerais precipitados a partir de soluções intempéricas, corroboram a conclusão anterior sobre a origem supergênica do minério friável da Mina de Águas Claras. As análises por DRX, MEV e MES mostraram que estes minerais consistem de pirolusita, criptomelano e hollandita, e que estão frequentemente associados a goethita e gibbsita.

A ocorrência de depósitos de bauxita formados a partir de sedimentos caoliníticos depositados nas bacias terciárias que recobrem os corpos de minério friável em algumas minas do Quadrilátero Ferrífero (Boulangé *et al.*, 1997; Pomerene, 1964), como, por exemplo, Capão Xavier, reflete a alta intensidade do intemperismo químico que atuou na região. Esse processo permitiu a completa dissolução da dolomita e a formação de minerais de manganês a partir das BIFs. A datação pelo método $^{40}\text{Ar}/^{39}\text{Ar}$ de minerais de manganês do grupo da hollandita, presentes no itabirito manganífero das Minas do Sapecado e Andaime, trouxe importantes informações sobre a evolução do perfil de intemperismo das BIFs no Quadrilátero Ferrífero e, conseqüentemente, sobre o minério

de ferro supergênico nele contido. Os resultados geocronológicos obtidos em 69 grãos de óxido de Mn forneceram idades patamar entre 61.5 ± 1.2 Ma a 14.2 ± 0.18 Ma, sugerindo uma prolongada história de intemperismo na região. A ausência de idades mais antigas do que 61.5 ± 1.2 Ma na Minas de Sapecado e Andaime não elimina a possibilidade de ocorrência de perfis de intemperismo ainda mais antigos na região, uma vez os minerais de manganês mais antigos podem não ter sido amostrados, terem sido erodidos, ou dissolvidos por soluções intempéricas mais jovens.

A maior parte dos óxidos de Mn, entretanto, precipitou no intervalo entre 51 e 41 Ma, com um pico em 46.7 Ma. Este intervalo coincide com a deposição das bacias que recobrem o minério de ferro e os dolomitos da Formação Gandarela, conforme indicado por estudos palinológicos dos sedimentos de algumas delas (Lima & Salard-Cheboldaëff, 1981; Maizatto, 2001). Essa é, portanto, a idade de formação do minério friável em Águas Claras e Capão Xavier.

Os resultados geocronológicos mostraram também uma distribuição de idades muito similares no interior do perfil de intemperismo da Mina do Sapecado. Embora tenham sido obtidas algumas idades mais antigas próximo à superfície topográfica, e outras mais jovens em partes profundas do perfil, a maior parte dos óxidos de Mn que ocorrem próximo à interface entre a BIF alterada e a BIF não alterada apresentou idades de ~46 Ma. Estes dados confirmam a conclusão de que o perfil de intemperismo das BIFs no Quadrilátero Ferrífero já havia atingindo o atual estágio de desenvolvimento há cerca de 50 Ma, sugerindo que a frente de alteração intempérica tenha avançado muito pouco durante o Neógeno. A partir dessa época as soluções intempéricas devem ter se tornado ineficientes na promoção do avanço da alteração.

A comparação entre a geologia da Mina de Águas Claras e Capão Xavier de um lado, e Tamanduá de outro, mostrou que, sob idênticas condições estruturais, topográficas e climáticas, o itabirito dolomítico é muito mais favorável à formação de depósitos de ferro de alto teor do que o quartzo itabirito, dando origem a corpos de maior volume. Forneceu também indicações de que a gênese de depósitos friáveis de alto teor a partir do quartzo itabirito requer a atuação de outros controles além do litológico, possivelmente envolvendo processos hipogênicos e supergênicos, com predominância de um ou outro processo em cada depósito em particular.

ANEXO 1 – GEOLOGY AND GEOCHEMISTRY OF THE ÁGUAS CLARAS AND PICO IRON MINES, QUADRILÁTERO FERRÍFERO, MINAS GERAIS, BRAZIL

Abstract

The Águas Claras and Pico mines are two world-class iron-ore mines hosted within the Lower- Proterozoic banded iron-formations (locally known as itabirites) of the Minas Supergroup located in the Quadrilátero Ferrífero District, Minas Gerais, Brazil. The Águas Claras orebody consists of a 2,500 m long roughly tabular-shaped lens hosted within the dolomitic itabirite of the Cauê Formation. Dolomitic itabirite is the protore of the soft high-grade iron ore, which is the main ore type of the Águas Claras orebody, representing about 85% of the 284 Mt mined since 1973, with the remaining 15% comprising hard high-grade ore. Hematite is the main constituent of the iron ores. It occurs as martite, granular hematite and locally as specularite. Magnetite appears subordinately as relicts within martite and hematite crystals. Gangue minerals are very rare. These consist of dolomite, chlorite, talc and apatite, and are especially common in contact with the protore. This virtual absence of gangue minerals is reflected in the chemistry of ores which are characterized by very high Fe contents (an average of 68.2% Fe).

The Pico orebody is a continuous ~3,000 m long body of a lenticular shape hosted within quartz itabirite, which is the protore of the soft high- and low-grade ores at the Pico mine. The soft high-grade ores, together with the low-grade ores, called iron-rich itabirite, are the main types of ore and respectively represent approximately 51 % and 29 % of the reserves. The remaining 20% consists of hard high-grade ore. The iron oxide mineralogy is the same as that of the Águas Claras mine, but in different proportions. Gangue minerals are very rare in the high-grade ores, but are slightly more common in the iron-rich itabirite. Quartz is the dominant gangue mineral, and is found with minor quantities of chlorite. The chemistry of the high-grade ores is characterized by high Fe contents (an average of 67.0 %) and low P, Al₂O₃, and SiO₂ which are concentrated in the fines. Iron-rich itabirites average 58.6% Fe and 13.5% SiO₂.

The genesis of the soft high-grade ores and iron-rich itabirites is related to supergene processes. Leaching of the gangue minerals by ground-water promoted the residual iron enrichment of the itabirites. This process was favored by the tropical climate and topographic

situation. The original composition of the itabirites and the presence of structures controlling the circulation of the ground-water have influenced the degree of iron enrichment. The hard high-grade ores are of a hypogene origin. Their genesis is attributed to hydrothermal solutions that leached the gangue minerals and filled the spaces with hematite. This process remains a source of debate and is not yet fully understood.

Keywords: banded iron-formation itabirite iron ore Quadrilátero Ferrífero Águas Claras Pico

INTRODUCTION

The Quadrilátero Ferrífero is one of the most important iron-ore mining districts in the world. It is located on the southeastern border of the São Francisco Craton, in the State of Minas Gerais, Brazil (Fig. 1). The Águas Claras and Pico mines of Minerações Brasileiras Reunidas – MBR are both located at the western low-strain domain of the Quadrilátero Ferrífero but display different characteristics. The quality of the products of these mines, especially those of the Águas Claras mine (probably the world's richest iron mine in terms of ore grade) has turned MBR into the most important supplier of high-quality iron ore in the world.

The Águas Claras mine is located near the Serra do Curral Range, on the northern border of the Quadrilátero Ferrífero (Figs. 1 and 2a). It contains high-grade soft ores ($\text{Fe} > 64\%$) and subordinate hard ores hosted mainly within dolomitic iron formation, locally called itabirite. The Pico mine is located in the Itabirito Range, close to its eponymous settlement (Figs. 1 and 2b). In this mine high-grade, hard, massive, banded ores and soft ores occur interbedded with weathered and fresh quartz itabirite.

Although a significant volume of data has been gathered since mining began in 1973, very little geological information concerning the deposits is available in the literature (e.g. Pomerene 1964; Wallace 1965; Gomes 1986; Viel et al. 1987; Klein and Ladeira 2000). Hackspacher (1979) studied the structure of the Águas Claras mine and Rosière (1981) developed a structural analysis of the Pico mine. The purpose of this paper is to present a description of the geology of these world-class iron ore mines, thus improving the limited geological information available, and offering new geochemical and petrographic data which may provide a background for further studies.

Figure 1 Location and geological sketch map of the Quadrilátero Ferrífero region (After Alkmim and Marshak 1998).

Figure 2 **a** Birds-eye view of the Águas Claras mine, looking west. **b** Birds-eye view of the Pico mine, looking northwest. Rv = Rio das Velhas Supergroup, Mo= Moeda Formation, Ba=Batatal Formation, Ca=Cauê Formation, Ga=Gandarela Formation.

GEOLOGICAL SETTING

The Quadrilátero Ferrífero District

The geology and lithostratigraphy of the Quadrilátero Ferrífero were described in detail by the USGS-DNPM team between 1946 and 1963, and summarized by Dorr (1969). Since then, the subject has been reviewed by several authors (Ladeira and Viveiros 1984, Marshak and Alkmim 1989, Chemale Jr. et al. 1994, Renger et al. 1994, Alkmim and Marshak 1998). The most important lithostratigraphic units of the Quadrilátero Ferrífero (Figs. 1 and 3) are the Archean to Paleoproterozoic granite-gneiss terrains, the Archean greenstone belt sequences (Rio das Velhas Supergroup), the Minas Supergroup and the post-Minas intrusive rocks.

The giant iron ore deposits of the Quadrilátero Ferrífero are hosted in the metamorphosed sedimentary rocks of the Minas Supergroup, which consists of three Paleoproterozoic sequences (Renger et al. 1994; Noce 1995; Babinsky et al. 1995). The lowest unit is the Caraça Group, which consists of alluvial conglomerate and sandstone grading upwards into shallow-water marine pelites. The middle Itabira Group consists mainly of chemical sedimentary rocks. An extensive iron formation layer with variable composition occurs at the base of the Itabira Group and, together with hematitic and dolomitic phyllites, marbles and dolomites, comprises the Cauê Formation. The sequence grades upward to dolomites and dolomitic/manganiferous itabirites of the 2.4 Ga Gandarela Formation (Babinsky et al. 1995). Clastic sediments (with subordinate dolomites) of the Piracicaba Group occur over the Itabira Group. The uppermost sequence of the Minas Supergroup is the Sabará Group, a sequence of metamorphosed volcanoclastics, turbidites, banded iron- formations (BIFs) and conglomerates, considered to belong to the Transamazonian orogenic period (2.1 – 1.7 Ga., Renger et al. 1994).

Post-Minas intrusives, namely granite, pegmatite, metamorphosed mafic dykes and diabase, cut the Rio das Velhas and Minas Supergroups. Granite and pegmatite cutting basement rocks yield monazite and zircon U-Pb ages of 2.06 and 2.08 Ga respectively (Noce 1995). Foliated and metamorphosed mafic dykes occur throughout the Quadrilátero Ferrífero. One of them yielded a 1.714 Ga age (Alkmim and Marshak 1998). Diabase and gabbros, not affected by metamorphism, are also encountered locally (Pomenere 1964, Wallace 1965).

A supergene cap locally called canga covers the iron ores and other rocks in the Quadrilátero Ferrífero. It consists of a lithified superficial or near-surface iron-rich rock formed with various quantities of detrital fragments, commonly iron ores or itabirites, cemented by limonite into a blanketing body (Dorr 1964).

Figure 3 Stratigraphic column of the Quadrilátero Ferrífero region. The right-hand portion of the column represents the relationships in the eastern part of the Quadrilátero Ferrífero, while the left-hand side of the chart represents the relationships in the western part of the Quadrilátero Ferrífero (After Alkmim and Marshak 1998).

Structurally, the Quadrilátero Ferrífero District consists of two distinct domains: an eastern high-strain domain and a western low-strain domain (Rosière et al. 2001). The former is dominated by thrusts and transcurrent shear zones which generate tight to isoclinal folds and thick mylonitic zones. The main regional structures of the latter are well-preserved megasynclines with discontinuous shear zones and thrust faults that intersect with the megascopic structures (Almeida 1977; Chemale et al. 1994; Rosière et al. 2001). Iron deposits occur in both domains and present structural particularities due to local deformation. Table 1 presents a synthesis of the tectonic events in the Quadrilátero Ferrífero region.

Table 1 Synthesis of the tectonic events at the Quadrilátero Ferrífero Region

Age (Ga)	Event	Lithological groups of rock formation and other characteristics
> 2.6	Amalgamation of an Archean Granite-Greenstone terrain	
< 2.6 to >2.4	Extensional event. Development of an ensialic or passive-margin basin (Minas Basin)	Deposition of the Caraça and Itabira Groups
< 2.12 to > 2.09	Transamazonian northwest-verging thrusting and folding (D1)	Development of thrust-sense shear zones and regional-scale folds
< 2.09 to > ?	Extensional Event. Transamazonian orogenic collapse	Development of a dome-and-keel terrain. Deposition of the Itacolomi Group
~ 1.75	Extensional Event	Intrusion of mafic dikes
~1.0 to 0.9	Extensional Event	Intrusion of mafic dikes
0.7 to 0.45	Brasiliano west-verging thrusting (D2)	Regional folds. Reactivation and overprinting of older structures
~ 0.13	Extensional Event	Intrusion of mafic dikes
After Alkim and Marshak (1998)		

The rocks of the Rio das Velhas Supergroup were deformed prior to the deposition of the Minas Supergroup and, together with granite-gneiss complexes, acted as the basement of the Proterozoic Minas Basin (Marshak et al. 1992). After 2.6 Ga and prior to 2.4 Ga, the region evolved into a passive-margin basin where sediments of the Minas Supergroup were deposited.

During the Transamazonian Cycle (2.1 – 1.7 Ga) the supracrustal units of the Rio das Velhas and Minas Supergroups were folded into large-scale synclines and anticlines, and the underlying crystalline basement was uplifted. Shear zones were developed at the contact between supracrustal and basement rocks. The origin of these structures remains a source of controversy. Chemale et al. (1994) attribute the development of the megasynclines and the uplift of the basement to an extensional event during the Paleoproterozoic. Chauvet et al. (1994) postulate a model in which a tectonomagmatic event was responsible for both the uplift of the basement

domes and the generation of regional folding. On the other hand, Alkmim and Marshak (1998) interpret these structures as a consequence of a fold-thrust belt developed after 2.125 Ga during the closure of a passive-margin basin. This, they conclude, was followed by the emplacement of basement domes against supracrustal rocks at 2.095 Ga, as the consequence of an orogenic collapse.

During the Brasiliano Cycle (650 – 500 Ma), west-vergent thrusts overprinted the earlier structures, causing inversion, amplification, translation and rotation of the synclines and developing thrust and fold structures represented by shear zones, tear faults, transcurrent zones and various types of folds (Chauvet et al. 1994, Chemale et al. 1994, Alkmim and Marshak 1998, Rosière et al. 2001).

The metamorphic grade increases progressively from greenschist facies in the west and central parts of the Quadrilátero Ferrífero to almandine-amphibolite facies in the east. This is demonstrated by the increase in quartz grain size and the presence of diagnostic metamorphic minerals (Dorr 1964). Herz (1978) identified the isograds of biotite and staurolite separating three metamorphic zones (chlorite, biotite and staurolite). He also noted the change from hematite to specularite under medium and higher grades of metamorphism. Pires (1995) redefined these isograds in carbonatic metapelites, which resulted in the definition of three metamorphic zones: grunerite, cummingtonite-actinolite, and tremolite-antophyllite. Moving east one may observe that the equilibration temperatures of mineral assemblages in these zones increase from about 300 °C to 600 °C for estimated pressures at 3 to 5 kbar.

The Itabirites of the Itabira Group

Itabirites are oxidized, metamorphosed and heterogeneously deformed banded iron formations (BIFs) containing discontinuously distributed orebodies, which vary in scale from just a few centimeters to hundreds of meters. Multiple processes have obliterated partially or totally the mineralogy, texture and structure of the original sediments, making it difficult to identify primary characteristics, especially in the high-strain domain. In the low strain domain, the itabirites have preserved several sedimentary and diagenetic features such as meso and microbanding pods formed by differential compaction and pisolites (Rosière et al. 2001). Banding is the main internal feature of the itabirites. Tight and isoclinal folds commonly showing a crenulation cleavage and pinch-and-swell structures are locally observed. Shear zones are restricted to a few places and found parallel to banding or truncating it. Kink-bands are very

common in the weathered itabirites and have been interpreted by Ribeiro and Zavaglia (1998) as collapse structures.

Quartz itabirite is the major type of itabirite in the Quadrilátero Ferrífero. In this rock type the original chert or jasper bands have been recrystallized into granular quartz, and iron is present as hematite, magnetite or martite. Dolomitic itabirite is a dolomitized BIF consisting of alternating red carbonate and black iron oxide bands, each being between 1 mm and 50 cm thick. Amphibolitic itabirite consists of bands of many types of amphiboles (grunerite, tremolite, actinolite, cummingtonite and/or anthophyllite) alternating with bands of iron oxides (Rosière et al. 1993).

Hematite is the major iron oxide in the itabirites, occurring in different forms: martite (pseudomorphs of hematite after magnetite), granular hematite and specularite (Dorr 1964, 1965; Rosière 1981, 1983, 2000). Magnetite appears subordinately as the Fe^{2+} deficient variety kenomagnetite (metastable magnetic phases which are somewhere between magnetite and maghemite in composition), and as relicts in martite and hematite aggregates. Both iron oxides were developed at various stages during the complex evolution of the Quadrilátero Ferrífero, as shown by Rosière (1981, 1983) and Rosière et al. (2001). Magnetite is the oldest recognizable iron oxide. Mostly it appears to have been totally or partially martitized. Granular hematite results from the progressive martitization, inversion and recrystallization of magnetite. Specularite results from recrystallization of kenomagnetite, martite or hematite in high-strain domains or shear zones (Rosière et al. 2001). Otherwise it occurs in extensional sites associated with quartz or carbonates (Lagoeiro 1998). Goethite occurs close to the surface, or along fracture planes, locally associated with gibbsite and kaolinite.

Quartz is the main gangue mineral of itabirites. The next most common are dolomite and amphiboles, which are present either as intercalated bands or disseminations. Chlorite, talc, apatite and various silicate minerals occur in very small quantities except in the high metamorphic-grade zones, where they can be common (Dorr 1973). Wavelite ($\text{Al}_3(\text{PO}_4)_2(\text{OH})_{3.5}\text{H}_2\text{O}$) is restricted to a few deposits in the Quadrilátero Ferrífero.

The Iron Ores of the Itabira Group

Iron ores have been formed throughout the Quadrilátero Ferrífero by the enrichment of itabirites. They are generally classified, according to the iron content, into high-grade and low-grade ores. High-grade ores have Fe contents higher than 64%, with very low contents of the

contaminants SiO_2 , Al_2O_3 , CaO , MgO etc. The Fe contents of the low-grade ores vary from 32% to 64%, with different amounts of contaminants.

The iron oxide mineralogy of ores is the same as that of the itabirites. Gangue minerals are rarely present in the high-grade ore but, where found, consist of relicts of quartz, dolomite, chlorite, amphibole and talc. Low-grade ores contain the same gangue minerals found in the protore. These vary in quantity according to the degree of iron enrichment.

The iron ores can be subdivided into hard and soft types. Hard ores can be banded, massive, lineated, schistose and secondarily brecciated. Soft ores can be foliated, lineated or free of any structure (blue dust ore) (Rosière et al. 1993; Rosière 2000).

Genetic Models For The Iron Ores

Although largely discussed in the international literature, the genesis of the high-grade iron ore deposits hosted within BIFs remains unclear. Different genetic models have been proposed worldwide to explain the iron enrichment of the BIFs. Morris (2002) identified eleven iron ore genetic models and grouped them in three classes: syngenetic, supergene and hypogene. Based on field investigations and literature surveys, Beukes et al. (2002) recognized three genetic models of high-grade iron ore deposits: ancient supergene, hydrothermal and supergene-modified hydrothermal deposits.

The supergene models explain the iron enrichment as a result of leaching of the gangue minerals by supergene fluids. (e.g. Dorr 1964, Morris 1985). These models are generally accepted as an explanation for the high-grade iron ores associated with present or past erosion surfaces. Hypogene models are more complex. They propose the action of hydrothermal fluids substituting the gangue minerals for iron oxides or iron carbonates (e.g. Dorr 1965, Gruner 1937, Powell et al. 1999, Morey 1999). Taylor et al. (2001) recently proposed a composite model to explain the genesis of the high-grade iron ore of the Hamersley Province. For a general understanding concerning the high-grade iron ores genesis see Beukes et al. (2002) and Morris (2002). For additional information see Lascelles (2002), Morey (1999), Morris (1987), Powell et al. (1999), Taylor et al. (2001), Van Schalkwyk and Beukes (1986), and references therein.

The genesis of the iron ores within the Cauê Formation in the Quadrilátero Ferrífero has been the subject of debate since the beginning of the 20th century, and continues to be the focus of studies by several researchers (e.g. Harder and Chamberlin 1915; Guild 1953; Park 1959; Dorr 1964, 1965; Ramanaidou 1989; Ramanaidou et al. 1996; Rosière and Rios 2003). Soft ores have been explained as residual concentrations of iron oxides due to leaching of contaminants

during supergene processes (Dorr 1964; Eichler 1968; Melfi et al. 1976; Viel et al. 1987; Ramanaidou 1989; Ramanaidou et al. 1996). They have also been viewed as a consequence of incomplete metasomatism of the BIF followed by weathering, as suggested by Dorr (1965). Hard ores have been generally considered to result from the replacement or leaching of gangue minerals (Dorr 1965). The precise timing of ore formation is also a source of controversy. Dorr (1965), for instance, postulated both syn-metamorphic and syn-deformational mineralization. But there remains debate over the importance of these events (Rosière 1981, Rosière and Rios 2003).

THE ÁGUAS CLARAS OREBODY

General Description

Mining at Águas Claras commenced in 1973 and by 2002 ca. 288 Mt of high-grade iron ore had been mined. The highest annual output was in 1992 when 14 Mt of iron ore were mined. The Águas Claras mine was closed in 2002 with an annual production of 1.2 Mt. About 88 Mt of high-grade iron ore remains, but economic and environmental restrictions indicate that mining cannot continue. The ore was mined by open-pit methods and treated at a local ore-dressing plant. This resulted in three products: lump ore (13%: 31.5- 6.30 mm), sinter feed (43%: 6.30 – 0.15 mm) and pellet feed (32%: 0.15 mm – 0.038 mm), with 12% of tailings. Table 2 presents the size distribution of the particles and the chemical composition of these products over recent years.

Structure and Stratigraphy of the Mine Area

The Águas Claras iron mine is located on the northern edge of the Serra do Curral, in a northeast-southwest trending homocline with bedding dipping steeply to the southeast (Fig. 2a). The Caraça, Itabira and Piracicaba Groups of the Minas Supergroup crop out along most of the extension of the Serra do Curral in an inverted sequence without repetition (Chemale et al. 1994). The inverted stratigraphic sequence, as well as locally preserved sedimentary structures, led Pomerene (1964), Dorr (1969), Pires (1979) and Alkmim and Marshak (1998) to propose that the homocline represents a remnant of the overturned limb of a northwest-vergent anticline. At its northern segment, the Serra do Curral is highly strained and left-laterally rotated from its original position. Wide shear zones occur at the contact of the Minas Supergroup with the Rio das Velhas Supergroup (Chemale et al. 1994). In the vicinity of the mine bedding is transposed

by axial plane schistosity and locally developed mylonitic foliations, generally striking N45°E, with dips ranging from 30° to 70° to the southeast.

Table 2 Chemical composition (wt%) of the products of the Águas Claras and Pico mines

Product	Variable	1995		1996		1997		1998		1999		2000		2001	
		MAC	PIC	MAC	PIC	MAC	PIC	MAC	PIC	MAC	PIC	MAC	PIC	MAC	PIC
Lump 31.5 – 12.0 mm	%	17.50	13.50	11.19	13.00	11.77	16.90	14.18	16.10	14.59	13.90	17.33	16.50	33.43	15.80
	Fe _T	68.46	66.68	68.17	67.79	67.71	67.64	65.61	67.41	66.79	67.85	67.43	67.36	68.32	68.01
	P	0.026	0.042	0.025	0.033	0.031	0.040	0.034	0.047	0.037	0.035	0.033	0.031	0.055	0.031
	Al ₂ O ₃	0.36	1.35	0.33	0.84	0.32	0.79	0.34	0.83	0.38	0.73	0.39	0.87	0.45	0.85
	SiO ₂	0.57	1.66	0.59	1.06	0.63	1.28	0.87	1.40	0.93	1.24	0.89	1.00	0.65	0.81
	Mn	0.19	0.03	0.14	0.04	0.23	0.09	0.09	0.13	0.08	0.06	0.09	0.11	0.05	0.09
Hematitinha 12.0 – 6.30 mm	%		11.80		9.60		5.50		3.10		4.30		6.30		6.90
	Fe _T		66.96		67.34		67.28		67.36		67.81		67.94		67.99
	P		0.044		0.038		0.045		0.050		0.035		0.030		0.030
	Al ₂ O ₃		1.25		1.05		0.93		0.88		0.77		0.82		0.88
	SiO ₂		1.29		1.22		1.39		1.47		1.27		0.97		0.79
	Mn		0.039		0.05		0.10		0.08		0.05		0.04		0.05
Sinter Feed 6.30 – 0.15 mm	%	41.76	36.50	47.58	36.20	44.55	32.20	43.30	31.60	44.90	35.10	45.11	32.30	45.31	32.70
	Fe _T	68.89	66.46	68.93	66.97	68.67	66.92	68.48	67.19	68.57	67.64	68.55	67.61	67.93	67.66
	P	0.021	0.054	0.024	0.043	0.037	0.050	0.031	0.048	0.032	0.033	0.027	0.029	0.052	0.032
	Al ₂ O ₃	0.30	1.25	0.26	0.95	0.25	0.89	0.23	0.82	0.26	0.66	0.29	0.72	0.42	0.78
	SiO ₂	0.52	1.93	0.46	1.80	0.54	1.95	0.59	1.82	0.66	1.69	0.81	1.54	0.69	1.40
	Mn	0.17	0.06	0.16	0.07	0.15	0.07	0.12	0.08	0.13	0.06	0.13	0.09	0.06	0.055
Pellet Feed 0.15 – 0.045 mm	%	32.26	16.40	32.99	23.90	34.02	26.30	30.48	28.00	29.37	29.00	26.38	28.10	14.12	25.70
	Fe _T	68.08	67.16	68.24	67.80	67.76	67.89	67.71	68.09	67.68	68.32	67.99	68.21	68.21	67.80
	P	0.038	0.036	0.040	0.032	0.056	0.030	0.050	0.026	0.048	0.025	0.044	0.022	0.067	0.028
	Al ₂ O ₃	0.48	0.74	0.39	0.59	0.43	0.55	0.40	0.50	0.42	0.39	0.40	0.38	0.55	0.57
	SiO ₂	0.84	2.06	0.76	1.71	1.10	1.67	1.21	1.47	1.25	1.36	1.12	1.54	0.87	1.48
	Mn	0.46	0.04	0.41	0.05	0.42	0.05	0.39	0.05	0.42	0.04	0.35	0.06	0.13	0.07

MAC=Águas Claras mine, PIC=Pico mine. % = percentage of each product in comparison with the feed of the beneficiation plant, differences to 100% represent tailings.

The stratigraphy of the mine (Fig. 4) area consists of clastic metasedimentary rocks of the Moeda and Batatal Formations (Caraça Group), and the predominant chemical metasedimentary rocks of the Cauê Formation (Itabira group). The Moeda Formation outcrops to the south of the mine, forming the hanging wall of the deposit. This unit comprises fine quartzites with interlayered quartz–phyllites, and is generally intensely deformed. However, large lens of undeformed quartzite surrounded by anastomosing mylonitic quartzite are common. The quartzite grades to strongly foliated sericite-phyllite of the Batatal Formation. The contact between quartzite and phyllite is transitional and interfingering is common.

Figure 4 Águas Claras mine. a Cross section 2200E. b Geological sketch map.

A ~60 m thick layer of dolomitic phyllite occurs at the lowermost part of the Cauê iron-formation. This is interpreted by Renger et al. (1994) as the beginning of the chemical sedimentation of the Cauê Formation. Interlayered centimeter to meter thick lens of meta-chert

occur in the middle of the dolomitic phyllite sequence. Towards the top, these lens change into ~50 cm layers of quartz itabirite within the dolomitic phyllite.

The contact between the dolomitic phyllite and the overlying dolomite is gradational over a few meters. In the contact region, centimeter thick lens of dolomitic phyllite are interlayered with red dolomite. Irregular fragments and pisoids of iron formation cemented by dolomite (Fig. 5a) are observed within a dolomite lens of ~50 cm (Fig. 5a) at this zone. Those fragments and pisoids are largely made up of iron oxides, with subordinate quartz. A ~8 m thick dolomite layer overlies this contact region forming the base of the dolomitic itabirite sequence.

The beginning of the dolomitic itabirite sequence is marked by the appearance of centimeter bands of iron oxides. These first iron-oxide bands are thinner than the predominant carbonate bands. A ~400 m thick unweathered dolomitic itabirite layer outcrops at the east wall of the pit. This layer was cut approximately perpendicular to the strike, resulting in an excellent exposure of this otherwise easily altered rock. The absence of an easily recognizable marker layer makes it extremely difficult to define the stratigraphy of the itabirite sequence. The contact between the dolomitic itabirite and the high-grade soft ore is sharp. Unweathered pinnacles of dolomitic itabirite can be found at several levels throughout the mine (Fig. 5d).

At the Águas Claras mine, dolomitic itabirite is much more common than quartz itabirite. The latter is only found in the north wall of the mine, interlayered with the dolomitic rock. The contact between these rocks is gradational. It is characterized by the gradual appearance of quartz within the dolomite bands and by the appearance of quartz bands. A banded itabirite formed by alternate bands of quartz, dolomite and iron oxide can be locally observed at the contact region (Fig. 5e). Beyond the limits of the mine, to the north, the gradational contact between the Cauê and the Gandarela Formation can also be observed.

The dolomitic itabirite: mesoscopic features, petrography and chemistry

Banding is the most striking structure of the dolomitic itabirite. It occurs as mesobanding and microbanding of Trendall (1973). The characteristic centimeter-scale mesobanding of carbonate/oxide layers produces the reddish/dark rock banding (Fig. 5b). Mesobands range in thickness from 0.1 cm to 50 cm, with an average thickness of approximately 1 cm. At the lowermost part of the dolomitic layer, in the contact with the phyllite, the carbonate mesobands are thicker (10-50 cm) than the oxide mesobands (0.5 -3 cm). The thickness of the carbonate mesobands decreases upwards, so that in the mid section of the sequence both mesobands display approximately the same thickness varying from less than 1 mm to 0.6 cm. At the top of

the sequence, the thickness of the carbonate mesobands increases again in relation to the oxide mesobands, reaching 15-50 cm.

Fig. 5 Águas Claras mine. **a** Pisoids within the dolomitic layer of the Cauê Formation. **b** Hand specimen of dolomitic itabirite. Mesobanding is preserved as dolomite-rich and iron oxide-rich layers. **c** Hand specimen of folded dolomitic itabirite. Secondary dolomite lens are parallel to the mesobanding. **d**. Detail of the contact between soft high-grade ore and dolomitic itabirite **e**. Idiomorphic crystals of hematite and dolomite filling cavities in the dolomitic itabirite, forming geodes. **f**. Drill core sample of banded itabirite showing alternated bands of quartz (q), dolomite (d) and iron oxides (i)

Fig. 5 Águas Claras mine. **g.** Banded soft high-grade ore **h.** Hand specimens of hard high grade ores: 1-massive, 2-banded, 3-schistose, 4-banded porous and 5-coated by goethite.

Dolomite lens and veins of variable thickness - from a few millimeters to ~ 20 cm - are irregularly distributed in the dolomitic itabirite, crosscutting or parallel to the bedding. Some of these dolomite lens and veins have been deformed together with the dolomitic itabirite (Fig. 5c). Especially at the base of the sequence, but also in some narrow centimeter thick zones towards the top, the dolomitic itabirite is brecciated, with the bands of carbonate and iron oxides cemented by dolomite.

The red carbonate mesobands of dolomitic itabirite consist of very fine grained sparry dolomite and hematite with grain size varying from $5 - 30 \mu\text{m}$ (at an average of $12 \mu\text{m}$, Fig. 6a-b). The volume of hematite within the carbonate mesobands is highly variable (5% to 50% from band to band). Locally, the dolomite occurs together with hematite in extensional sites, forming geodes (Fig. 5f). Hematite occurs mainly as martite, forming euhedral crystals in masses of elongated and lobate shapes (Fig. 6b). It also occurs as euhedral to subhedral crystals in the martite aggregates, and as isolated crystals occupying the interstices or included in grains of dolomite. Platy hematite (specularite) occurs in shear planes, surrounding crystals of martite or granular hematite (Fig. 6c).

Randomly oriented red-brown microcrystals of hematite ($< 1 \mu\text{m}$) are found in dolomite crystals in the carbonate mesobands (Figs. 6d and 7a), resulting in the characteristic deep red color of these mesobands. Small fluid inclusions ($< 8 \mu\text{m}$) are abundant in dolomite. These are currently

under investigation. Preliminary data reveal two phase fluid inclusions made up of gas and liquid, without salt crystals.

The iron oxide mesobands contain hematite (>90%), interstitial carbonates and pores. The average hematite grain size is similar to that of the dolomite mesobands (~ 12 μm) varying from 5 - 20 μm . Hematite occurs mainly in the form of martite, and locally as specularite. Relicts of kenomagnetite are observed in the nuclei of some martite crystals, especially in the coarser mesobands of iron oxides. Martite and granular hematite crystals can be found fused together forming a dense network.

Accessory minerals are also present in the mesobands. Talc occurs intergrown with dolomite and in thin veins with chlorite. Apatite can be found in layers (< 1 mm) as isolated euhedral crystals (4 - 10 μm) and intergrown with or included in hematite and dolomite crystals (Fig. 6e). Chlorite occurs along veins and shear planes. An iron and nickel oxide (possibly trevorite) was identified in one sample forming fine crystals intergrown with hematite in the iron oxide band (Fig. 6f). Isolated crystals of titanite were also identified in one sample of dolomitic itabirite.

In order to assess the bulk composition of the dolomitic itabirite, 33 samples were taken from the bottom to the top of the stratigraphic sequence and analyzed for major elements in the MBR laboratory. Because of the extreme bimodal composition of the dolomitic itabirite, each sample (~100 kg) consisted of several band couplets of alternating iron- and carbonate-rich layers. The results are shown in Table 3. These reveal that the bulk composition is dominated by Fe_2O_3 , CaO and MgO which, together with LOI, make up more than 97% of the rock.

Fig. 6 Photomicrographs of the dolomitic itabirite of the Águas Claras mine. **a** Microbanding of dolomite-rich and iron oxide-rich laminae - transmitted light. **b** Detail of the dolomite-rich micro-band. Euhedral crystals of martite/granular hematite (h) between the dolomite crystals (d) - transmitted light. **c** Specularite crystals (s) grown along a shear plane surrounding a porphyroblast of idiomorphic tabular hematite (h), SEM-image. **d** Inclusions of hematite microcrystals within a dolomite grain, SEM backscattered image **e** Dolomite rich micro-band. Dolomite (d) crystals are intergrown with apatite (a) and martite/granular hematite (h), SEM-image. **f** Fine crystals of trevorite (tr) intergrown with the martite/hematite (h), SEM-image.

Table 3 Averages and ranges of major components of dolomitic itabirite (bulk analyses)

Variable	Avg	Std	Max	Min
Fe _T	31.92	5.06	42.50	22.00
Fe ₂ O ₃	45.65	7.24	60.78	31.46
P	0.044	0.017	0.089	0.004
Al ₂ O ₃	0.24	0.11	0.67	0.10
SiO ₂	0.89	0.32	1.84	0.46
Mn	0.24	0.05	0.36	0.04
CaO	16.22	2.42	20.67	11.41
MgO	11.47	1.78	14.87	8.47
TiO ₂	0.011	0.002	0.017	0.008
S	0.003	0.001	0.004	0.002
LOI	25.29	3.18	31.56	18.53

Data from MBR, number of samples = 33, LOI = loss on ignition

Figure 7 Photomicrographs of the dolomitic itabirite of the Águas Claras mine – transmitted light. **a** Detail of a dolomite-rich micro-band. Note the multitude of reddish hematite microcrystals (h) included within the dolomite grains (d) giving the crystals a dusty aspect. **b** Detail of a deeply weathered dolomite micro-band showing martite/granular hematite crystals (h) between pores (p) and relicts of the dolomite dissolution (brownish).

The high-grade Fe ore at the Águas Claras Mine

Unlike other mines in the Quadrilátero Ferrífero, the Águas Claras mine contains only high-grade ores. These consist of two distinct, main types: soft and hard ore. The soft ore represents 85% of the overall resource, whereas the hard ore represents only 15%. The orebody was a concordant, 2,500 m long, roughly tabular-shaped lens with a maximum thickness of 300 m, formed essentially by soft ores (Fig. 4b). The depth of the ore is variable, extending to over 400 m below the surface at the center of the pit bottom and then grading into the parental fresh dolomitic itabirite deeper down (Fig. 4a). The hard ores generally occur within the soft ores as minor lens. These are concordant to the bedding, although locally they may be discordant and associated with shear zones. The main hard ore occurrences are concentrated to the west of the mine, close to the top of the sequence. Here they are in contact with quartz itabirite forming lens of up to 200 m length along the strike, with thicknesses varying from 5 - 60 m (Fig. 4b). Small concordant lens of hard ore measuring from a few centimeters to nearly a meter thick occur within the dolomitic itabirite at the east side of the pit. These lens consist of massive hard ore formed by almost pure hematite.

The soft ore is characteristically porous and very friable. It disaggregates during the mining operations and generates a low lump yield. It usually preserves the structure of the itabirite, particularly the meso and microbanding (Fig. 5g), and sometimes exhibits kink-bands not present in the protore.

The hard ore is dense, compact and generates a high lump yield. Three main subtypes of hard ore are found at the Águas Claras mine: massive, banded and schistose (Fig. 5h). Massive hard ore has a very low porosity, does not exhibit any kind of structure and commonly shows signs of conchoidal fracture. Banded hard ore varies in porosity and is characterized by conspicuous banding. This is the typical hard ore found as small lens within the soft ore. Schistose hard ore generally has low porosity, does not preserve the original structures and exhibits a conspicuous cataclastic foliation. This type of hard ore is associated with shear zones which are mainly found on the north wall of the pit. The larger bodies of hard ore are usually intensely fractured, with thin films of goethite and kaolinite along the fracture planes (Fig. 5h5). The iron oxides which form the soft and hard ores are the same as those observed in the dolomitic itabirite: hematite as martite, granular hematite and specularite with subordinated remnant kenomagnetite cores preserved in some martite grains. These minerals typically preserve the original size and shapes present in the protore. Gangue minerals are rarely found in the masses of soft ore, and consist of dolomite, chlorite, talc and apatite. They occur mainly at

the contact zone with the protore. In this zone, the soft ore contains remnants of dolomite and a brownish residue generated from the dissolution of dolomite (Fig. 7b). Microcrystals of hematite are present, as well as apatite, chlorite and talc. The latter is observed as isolated platelets or as millimeter-sized aggregates. A few meters away from the contact zone, most of the gangue minerals disappear. In the hard ores interbedded with fresh dolomitic itabirite, the dolomite occurs as an accessory mineral. Manganese-oxides (mainly lithioforite) occur in narrow zones at the contact with the protore. Goethite occurs filling pores, voids and fractures in soft and hard ores close to the land surface.

The soft ore consists of alternate microbands of lower and higher porosity, containing martite and hematite (Fig. 8a), with intergranular porosity visually estimated at 35-45 percent (Fig. 8b). Thin bands of specularite occur parallel to or cross-cutting the banding. The hard ores have a similar mineralogical composition regardless of their physical characteristics. They consist of a dense network of martite and hematite with a varying proportion of pores (Fig. 8c-d). Kenomagnetite is regularly observed in the nuclei of martite crystals especially in the larger lens of hard ores.

Figure 8 Photomicrographs of the high-grade ores at the Águas Claras mine, SEM backscattered images. **a** Soft high-grade ore. **b** Detail of the soft high-grade ore. Note the high volume of pores (p). **c** Unweathered hard high-grade ore with dolomite crystals (d) in the interstices within the dense network of martite/granular hematite (h). **d** Detail of the hard high-grade ore.

The massive hard ore consists of weakly oriented aggregates of martite (with relicts of kenomagnetite) and hematite with a granoblastic texture and an average grain size ranging from 5-15 μm . A visual estimation suggests that intergranular porosity is around 5-10 percent. Banded hard ores exhibit a primary banding formed by the alternation of microbands where hematite is predominant (low porosity) with microbands where martite is predominant (high porosity). The global intergranular porosity of the banded hard ores is extremely variable (from 10% to 30%). Samples collected from thin lens of the banded ore present within the soft ores are more porous than those collected from larger lens on the west side of the mine. Schistose hard ores are essentially formed of specularite, which is strongly oriented, and exhibits a low intergranular porosity.

Table 4 shows statistics regarding the major element composition of about 5,300 samples of run-of-mine iron ore collected by MBR since 1971. This geochemistry database was used by the company to estimate the quality of the products. It illustrates the size distribution of the particles, and the chemical composition of the 288 Mt of iron ore which has been mined. The samples were screened into 3 size fractions (50.00 - 6.30 mm, 6.30 - 0.15 mm and < 0.15 mm), and analyzed together with the bulk samples. No bulk sample contained less than 64% Fe_T , which was the arbitrary limit set between the high-grade iron ore and the itabirite. Lower grades of Fe occur in the < 0.15 mm size fraction, where impurities are concentrated. SiO_2 , Al_2O_3 , Mn and P contents are higher than those observed in the coarser sized fractions. The chemistry of the hard and soft ores is very similar. The hard ore has higher P and Al_2O_3 contents while the soft ore is higher in Mn, CaO, MgO and TiO_2 .

A representative drill core (DH-17/85), which cuts all the soft ore from the bottom of the Cauê Formation going through the fresh dolomitic itabirite, is shown in Figure 9. The coarse fraction is scarce in the soft ore especially when close to the contact with the canga and the fresh dolomitic itabirite. The contaminants are concentrated in the fines (< 0.15 mm), due to their small size crystals. Their SiO_2 and Al_2O_3 contents are due to talc and chlorite, P to apatite and Mn to Mn oxides.

Table 4 Chemical composition (wt%) of the in situ high-grade iron ores — Águas Claras mine

	Variable	Hard high-grade ore					Soft high-grade ore				
		Avg	Std	Max	Min	η	Avg	Std	Max	Min	η
Bulk sample	Fe _T	68.35	0.81	69.64	64.85	343	68.23	0.78	69.84	64.17	4,009
	P	0.052	0.042	0.302	0.012	343	0.038	0.040	0.556	0.009	4,009
	Al ₂ O ₃	0.63	0.43	3.08	0.11	343	0.54	0.35	3.09	0.07	4,009
	SiO ₂	0.53	0.30	2.17	0.11	343	0.63	0.38	3.15	0.03	4,009
	Mn	0.178	0.226	1.380	0.010	343	0.365	0.163	1.278	0.004	2,766
	CaO	0.05	0.05	0.26	0.01	80	0.13	0.18	0.91	0.01	224
	MgO	0.03	0.04	0.31	0.01	80	0.12	0.14	1.01	0.01	224
	TiO ₂	0.06	0.07	0.40	0.01	80	0.04	0.02	0.16	0.01	224
Size range of fraction 50.00 – 6.30 mm	% Weight	66.84	12.73	95.94	50	343	12.33	6.00	24.97	0.00	4,009
	Fe _T	68.67	0.86	69.77	64.70	343	68.56	1.31	69.90	53.90	4,009
	P	0.046	0.041	0.291	0.001	343	0.030	0.053	0.847	0.001	4,009
	Al ₂ O ₃	0.53	0.49	3.99	0.01	343	0.53	0.64	7.98	0.01	4,009
	SiO ₂	0.42	0.27	2.72	0.01	343	0.54	0.38	7.73	0.01	4,009
	Mn	0.102	0.172	1.273	0.001	343	0.114	0.122	2.120	0.001	2,766
	CaO	0.06	0.05	0.28	0.01	80	0.22	0.50	4.78	0.01	224
	MgO	0.03	0.03	0.16	0.01	80	0.18	0.43	4.29	0.01	224
Size range of fraction 6.30 – 0.15 mm	TiO ₂	0.04	0.04	0.25	0.01	80	0.03	0.02	0.15	0.01	224
	% Weight	19.46	7.53	37.81	2.84	343	42.28	6.67	84.37	4.00	4,009
	Fe _T	68.21	1.17	69.60	59.67	343	68.91	0.67	69.98	61.60	4,009
	P	0.058	0.061	0.315	0.008	343	0.024	0.033	0.480	0.001	4,009
	Al ₂ O ₃	0.68	0.52	3.60	0.04	343	0.36	0.30	3.98	0.01	4,009
	SiO ₂	0.55	0.37	3.41	0.02	343	0.49	0.34	4.90	0.02	4,009
	Mn	0.195	0.354	2.660	0.001	343	0.140	0.084	1.120	0.001	2,766
	CaO	0.05	0.04	0.27	0.01	80	0.08	0.12	0.98	0.01	224
Size range of fraction 0.15 – 0.00 mm	MgO	0.03	0.02	0.13	0.01	80	0.07	0.09	0.86	0.01	224
	TiO ₂	0.06	0.07	0.33	0.01	80	0.03	0.02	0.15	0.01	224
	% Weight	13.70	8.08	38.30	0.10	343	45.39	8.71	79.90	2.27	4,009
	Fe _T	66.63	1.70	69.70	51.63	343	67.48	1.24	69.90	59.20	4,009
	P	0.084	0.066	0.399	0.010	343	0.053	0.052	0.800	0.001	4,009
	Al ₂ O ₃	1.22	0.65	4.32	0.18	343	0.71	0.47	4.55	0.01	4,009
	SiO ₂	1.18	0.84	5.57	0.05	343	0.91	0.50	5.04	0.01	4,009
	Mn	0.527	0.503	2.55	0.011	343	0.648	0.300	1.871	0.002	3,698
Size range of fraction 0.15 – 0.00 mm	CaO	0.04	0.03	0.19	0.01	80	0.15	0.26	1.56	0.01	224
	MgO	0.07	0.10	0.77	0.01	80	0.16	0.20	1.55	0.01	224
	TiO ₂	0.16	0.15	0.67	0.01	80	0.16	0.20	1.55	0.01	224

Data from MBR, η = number of samples

Figure 9 Particle size distribution, expressed in weight percent (W%) with correspondent chemical composition at three selected size fraction of the samples of the drill hole DH 17/85 of the Águas Claras mine. Contents of the fresh dolomitic itabirite in the size fraction 50.0 – 6.30 mm, which corresponds to more than 90% of the weight of the samples.

THE PICO OREBODY

General Description

Production of iron ore at Pico has been carried out from 1968. During this period, 120 Mt of iron ore were mined. The Pico mine, together with the Galinheiro and Sapecado mines, form the Pico Complex and are currently responsible for 50% of MBR's production. About 193 Mt of high-grade ores remains at the Pico mine. The ore is mined through open-pit methods and is treated at local ore dressing plants which have an annual capacity of 12 Mt. Four products are found in the major plant: the lump ore (31.5 - 12.0 mm), the "hematitinha" (12.0 - 6.30 mm), the sinter feed (< 6.30 - 0.15 mm) and the pellet feed (< 0.15 - 38 μ m). Historically these have represented 16%, 7%, 32% and 26% of the production respectively, with 19% tailings. Table 2 shows the percentage and chemical composition of each of these products in recent years.

Structure and stratigraphy of the mine area

The Pico iron mine is located on the eastern inverted limb of the Moeda Syncline, which is one of the major structures of the Quadrilátero Ferrífero (Fig. 1). In contrast with the Serra do Curral, where the Águas Claras mine is located, the Moeda Syncline is a relatively less strained domain. Bedding and other sedimentary structures are well preserved. Ductile shear zones occur locally truncating or parallel to the bedding of the Minas Supergroup strata (Chemale et al. 1994).

The major geological units present at the mine are itabirites and iron ores of the Cauê Formation, clastic metasedimentary rocks of the Moeda and Batatal Formations and predominantly chemical metasedimentary rocks of the Gandarela Formation (Fig. 10). The rocks of these units are oriented along a general strike N30°-35°E, dipping 45°-90° to SE or NW. The BIFs have been folded and dips vary from 20° to 85°, either to the SE or to the NW. Nevertheless, the quartzites of the Moeda Formation that crop out continuously along the eastern part of the mine (Fig. 2b) show a very consistent sub-vertical dip and, in general, weakly developed foliation.

The quartzites exhibit abrupt contacts with the phyllites of the Batatal Formation. There are clearly two types of phyllites. The first, in contact with the quartzite, is grey, laminated and rich in sericite. The second, at the top of the sequence, close to the quartz itabirite, is brown, weakly laminated and highly porous. Lens of meta-chert, from several meters to 70 meters long and from 5 to 20 meters wide, occur within this second type of phyllite. The field relations suggest a transition similar to that observed at Águas Claras, from quartzite to sericitic phyllite

and dolomitic phyllite, but no fresh samples are available to confirm this interpretation. The contact between the Batatal and Cauê Formations is abrupt and defined by a thin layer of hematitic phyllite which varies in thickness from 2 - 5 m and occurs between the phyllite and iron formations.

Figure 10 Pico mine. a Cross section 8400N. b Geological sketch map of the current pit wall.

The main iron formation at the Pico mine is the quartz itabirite, which is the protore of the soft high- and low-grade ores. Amphibolitic itabirite occurs locally in the northern part of the mine.

The Gandarela Formation outcrops at the west wall of the pit. It consists of dolomitic phyllite and deeply weathered dolomite with a gradual contact with the itabirites. It is marked by manganese-rich layers interlayered within the itabirites. Fresh samples of the dolomites from drill cores consist essentially of sparry dolomite crystals varying from 7 - 40 μm (average of 15 μm) with accessory talc and hematite.

A dyke of metamafic rock dated at 861 Ma (U-Pb concordia age in baddeleyite, Teixeira 2002, personal communication) with an average thickness of 40 m cuts all lithologies of the Minas Supergroup in the mine area.

Gravels and boulders of itabirite and hard ore cemented by clay, quartz and hematite occur at the base of small basins irregularly distributed along the strike of the itabirite sequence at the Pico Mine. These basins are similar to those described in the region by Wallace (1965) and dated by Lima and Cheboldaev (1981) as Paleocene to Eocene.

Itabirites at the Pico Mine

As elsewhere in the Quadrilátero Ferrífero, banding is the most typical mesoscopic structure of itabirites at the Pico mine. The thickness of the mesobands varies from a few millimeters to 2 cm (0.7 cm in average). The dark oxide bands of the quartz itabirite consist of martite and granular hematite with varying amounts of quartz (Figs. 11a, 12a). Euhedral martite crystals are typically porous and form irregularly shaped aggregates. They generally contain relicts of kenomagnetite in the nuclei (Fig. 12b), especially in the coarser dark bands. Subhedral to euhedral hematite crystals surround the crystals and aggregates of martite.

The light bands consist of quartz with variable amounts of interstitial granular hematite and/or martite (Fig. 12c). Locally, the fresh quartz itabirite may show a higher content of iron oxides within the quartz bands. Quartz grain size ranges from 10 to 120 μm (50 μm in average) while hematite grain size varies from 6 to 80 μm (35 μm in average). Quartz grains are commonly equidimensional and granoblastic-polygonal with equiangular triple points that suggest static recrystallisation. Most grains are slightly strained, showing wavy extinction. Tiny crystals of red hematite (3 - 10 μm) occur commonly as inclusions in the quartz crystals.

Figure 11 Photographs of the quartz-itabirite and iron ores at the Pico mine. **a** Hand specimen of quartz itabirite. Note the preservation of mesobanding and the variable content of iron oxides. **b** Mine exposure of hard high-grade ore (between drums). **c** Contact between hard (h) and soft (s) high-grade ores.

Fig. 12 Photomicrographs of the quartz itabirite of the Pico mine. **a** Microbanding of quartz-rich (white) and iron oxide-rich (black) laminae - polarized light. **d** Mine exposure of the iron-rich itabirite. **b** Detail of an iron oxide micro-band. Note the relicts of kenomanetite (k, dark gray) surrounding the martite crystals (m, light gray) - reflected light. **c** Detail of a quartz rich-micro-band. Note the abundant granular hematite (h) and martite crystals (m) between quartz grains (q). Reflected light.

Table 5 Chemical composition (wt%) of the fresh quartz itabirite (protore) and of the iron-rich itabirite — Pico mine

	Variable	Fresh quartz itabirite					Iron-rich itabirite ore				
		Avg	Std	Max	Min	η	Avg	Std	Max	Min	η
Bulk sample	Fe _T	41.34	4.68	51.72	30.49	183	58.57	3.61	63.99	52.02	963
	P	0.026	0.024	0.212	0.006	183	0.039	0.034	0.403	0.006	963
	Al ₂ O ₃	0.31	0.25	1.51	0.04	183	0.93	0.47	1.99	0.06	963
	SiO ₂	39.80	7.17	55.91	20.14	183	13.45	5.74	25.36	0.18	963
	Mn	0.045	0.092	1.025	0.001	183	0.083	0.232	2.664	0.003	963
	CaO	0.043	0.022	0.090	0.022	152	0.018	0.008	0.052	0.010	298
	MgO	0.021	0.007	0.035	0.015	152	0.025	0.010	0.060	0.011	298
	TiO ₂	0.017	0.005	0.024	0.011	152	0.040	0.035	0.190	0.010	298
	LOI	0.60	1.10	6.86	0.03	152	1.45	1.68	9.31	0.10	298
Size range of fraction 50.00 – 6.30 mm	% Weight	71.53	12.98	95.69	50.03	183	20.40	15.95	94.54	0.00	963
	Fe _T	44.63	6.16	60.80	33.60	183	65.09	3.30	69.40	37.70	960
	P	0.025	0.026	0.240	0.004	183	0.037	0.034	0.371	0.005	960
	Al ₂ O ₃	0.25	0.22	1.55	0.04	183	0.92	1.21	15.41	0.10	960
	SiO ₂	35.25	9.11	51.62	11.12	183	4.24	4.29	44.78	0.04	960
	Mn	0.039	0.078	0.867	0.001	183	0.070	0.265	4.804	0.001	960
	CaO	0.045	0.027	0.103	0.023	152	0.019	0.009	0.072	0.010	118
	MgO	0.020	0.009	0.039	0.012	152	0.020	0.011	0.106	0.010	118
	TiO ₂	0.019	0.008	0.030	0.001	152	0.045	0.102	1.082	0.010	118
LOI	0.56	1.14	6.96	0.01	152	1.55	2.09	10.50	0.00	298	
Size range of fraction 6.30 – 0.15 mm	% Weight	12.63	5.66	27.63	2.66	183	32	10.29	82.96	0.00	963
	Fe _T	44.81	7.36	61.29	22.90	183	62.56	4.22	69.10	26.40	963
	P	0.032	0.030	0.250	0.005	183	0.037	0.044	0.670	0.004	963
	Al ₂ O ₃	0.35	0.35	2.66	0.04	183	0.59	0.42	3.41	0.01	963
	SiO ₂	34.60	11.03	66.14	10.09	183	8.37	5.92	56.34	0.42	963
	Mn	0.072	0.203	2.285	0.01	183	0.083	0.317	4.206	0.001	963
	CaO	0.039	0.015	0.065	0.022	152	0.016	0.008	0.059	0.010	118
	MgO	0.020	0.005	0.027	0.014	152	0.019	0.007	0.063	0.010	118
	TiO ₂	0.017	0.002	0.020	0.014	152	0.038	0.048	0.429	0.010	118
LOI	0.68	1.25	8.22	0.004	152	1.32	1.90	8.83	0.030	298	
Size range of fraction 0.15 – 0.00 mm	% Weight	15.83	8.86	39.48	1.06	183	47.60	17.01	100.00	19.09	963
	Fe _T	25.52	8.40	52.00	8.70	183	51.67	7.98	67.10	21.20	962
	P	0.025	0.017	0.093	0.002	183	0.043	0.042	0.733	0.003	962
	Al ₂ O ₃	0.57	0.50	3.64	0.10	183	1.29	0.78	7.75	0.05	962
	SiO ₂	61.82	12.90	86.88	24.09	183	22.57	12.07	68.60	0.03	962
	Mn	0.056	0.110	0.880	0.012	183	0.091	0.224	2.400	0.001	962
	CaO	0.037	0.013	0.049	0.019	152	0.018	0.008	0.053	0.010	118
	MgO	0.021	0.006	0.029	0.015	152	0.030	0.014	0.091	0.011	118
	TiO ₂	0.013	0.003	0.018	0.010	152	0.043	0.039	0.207	0.010	118
LOI	0.77	0.95	5.70	0.05	152	1.64	1.50	8.31	0.10	298	

Data from MBR, η = number of samples, LOI = loss on ignition

The Iron Ores

The Pico orebody, which encompasses high- and low-grade ores, is a continuous ~ 3,000 m long body of lenticular shape. It extends from the south side of the metamafic dyke to the southern limit of the Sapecado mine. There it grades into soft limonitic BIF. This lens exhibits great variation in width due to internal folding and faulting. Its average width is 300 m and it reaches up to 450 m at the contact with the metamafic dyke. The orebody extends to over 300 m depth (Fig. 10a). It is generally concordant with the country rock, but discordant bodies are also present.

The ores typically preserve the original structures of the itabirite, but schistosity is not well developed. Small folds superimposed on the major folds, tight folds, local shear zones and

normal faults complete the complex structural scenario, which was developed during at least three deformational phases (Rosière 1981).

There are two distinct types of iron ore at the Pico mine: high-grade ores and iron-rich itabirite, both hosted within the quartz itabirite. The iron-rich itabirites are soft itabirites with iron contents between 52% and 64%, and alumina contents under 2%.

The high-grade ores occur as hard and soft ores. Pico de Itabira is the most striking example of a hard ore lens (Fig. 2b). It is 150 m long, 80 m thick, sub-vertical, and surrounded by soft ore and itabirite. Other lenticular hard bodies are up to 350 m long, with thickness varying from few centimeters to 150 meters. These lens occur interlayered with soft ore or itabirite and show variable lateral and vertical continuity (Fig. 11b). The contact with the itabirite is abrupt and grade over a few centimeters or a few meters into the host rock. In some places quartz-rich bands extend into the ore giving the serrated effect mentioned by Dorr (1965) (Fig. 11c). In some areas, especially close to the contact with the phyllite, hard orebodies are highly fractured. The physical aspect of the hard orebodies is essentially similar to that of Águas Claras. Some show conspicuous relicts of primary banding, but others are massive. Porosity is highly variable in some bodies, especially those that are smaller and more thinly interlayered with soft ore or weathered itabirite.

Two distinct subtypes of high-grade soft ores are found at the Pico mine. The first one occurs immediately below the surface of the soil/canga as a 40 m thick blanket grading downward into iron rich itabirite. The second type of high-grade soft ore is concentrated close to the south side of the mafic dyke and reaches to a depth of 300 meters or more from the land surface. It forms a continuous lenticular body roughly parallel to the strike of the dyke. The banding of the protore is typically preserved in both types of soft high-grade ores thus resulting in banded ores of high porosity. Locally, the soft ore close to the mafic dyke does not exhibit any structure and forms a massive soft ore (blue dust ore).

Iron-rich itabirite is widespread throughout the mine, typically grading to soft ore or quartz itabirite. It consists of friable itabirite where quartz was, in great part, leached and iron oxides were concentrated (Fig. 11d).

Gangue minerals in the high-grade ores - quartz and very small amounts of sericite and chlorite - are scarce. The transition to iron-rich itabirite is marked by an increased amount of quartz. Hard ores consist of dense agglomerates of hematite and martite crystals (with relicts of kenomagnetite in the nuclei). These have an average grain size of 25 μm . Quartz is absent in hard ores situated below the weathering surface, but occurs as an accessory mineral in hard ores

interlayered with fresh quartz itabirite. The hard ores generally exhibit a porous granoblastic fabric where the volume of pores is highly variable. The banded hard ore is generally more porous than the massive hard ore. It is formed by the alteration of massive bands made up of hematite with some martite and with porous bands composed of porous martite grains and hematite.

Soft ores are generally well laminated and highly porous. A visual estimation suggests intergranular porosity in the soft ore of 30-45 percent. The soft ores consist of microbands formed by aggregates of martite and hematite which alternate with highly porous microbands where martite and hematite are dispersed between the pores. Canga is present close to the land surface.

Statistics with regard to approximately 2,300 samples of hard and soft high-grade ores obtained during production at the Pico mine until the present day are shown in Table 6. This geochemistry database is used by MBR to estimate the quality of the products of this mine. Hard ores have an average of 67.3% of Fe (ranging from 64.0 - 69.9%), 1.0% Al_2O_3 and 1.1% SiO_2 . The soft ores average 67.0% Fe (ranging from 64.0 - 69.9%). The SiO_2 content is higher (average of 1.6%) and the Al_2O_3 (average of 1.0%) similar to those of hard ores. A total of 963 samples of iron-rich itabirite have been sampled and analyzed by MBR (Table 5). The bulk samples have an average of 58.6 % Fe (ranging from 52.0 - 58.01%) and 13.4% SiO_2 (ranging from 0.2% - 25.4%).

Table 6 Chemical composition (wt%) of the in situ high-grade iron ores — Pico Mine

	Variable	Hard high-grade ore					Soft high-grade ore				
		Avg	Std	Max	Min	η	Avg	Std	Max	Min	η
Bulk sample	Fe _T	67.36	1.36	69.86	64.00	695	66.98	1.39	69.86	64.00	1,617
	P	0.056	0.056	0.670	0.008	695	0.039	0.028	0.354	0.007	1,617
	Al ₂ O ₃	1.02	0.70	3.84	0.02	695	0.96	0.63	3.74	0.10	1,617
	SiO ₂	1.14	1.07	7.17	0.11	695	1.64	1.39	8.70	0.10	1,617
	Mn	0.040	0.060	0.950	0.003	695	0.127	0.206	2.275	0.002	1,617
	CaO	0.026	0.013	0.064	0.012	255	0.019	0.006	0.047	0.010	433
	MgO	0.030	0.020	0.124	0.016	255	0.029	0.013	0.098	0.010	433
	TiO ₂	0.046	0.031	0.146	0.011	255	0.053	0.045	0.377	0.010	433
	LOI	0.80	0.86	4.88	0.05	255	0.99	0.59	4.24	0.17	433
Size range of fraction 50.00 – 6.30 mm	% Weight	68.61	13.64	96.66	50.00	695	12.15	6.47	24.96	0.00	1,607
	Fe _T	68.09	1.13	69.90	63.80	695	67.11	2.48	69.90	51.60	1,607
	P	0.047	0.054	0.691	0.002	695	0.035	0.040	0.953	0.003	1,607
	Al ₂ O ₃	0.80	0.67	4.42	0.02	695	1.35	1.90	16.52	0.04	1,607
	SiO ₂	0.62	0.50	6.25	0.08	695	0.89	0.88	11.07	0.01	1,607
	Mn	0.029	0.039	0.526	0.001	695	0.074	0.160	2.648	0.002	1,607
	CaO	0.026	0.013	0.066	0.012	255	0.018	0.008	0.098	0.010	432
	MgO	0.024	0.009	0.049	0.014	255	0.024	0.013	0.139	0.010	432
	TiO ₂	0.033	0.016	0.089	0.010	255	0.040	0.037	0.327	0.010	432
Size range of fraction 6.30 – 0.15 mm	LOI	0.65	0.79	4.78	0.04	255	1.03	1.27	6.65	0.05	432
	% Weight	18.68	8.06	40.70	1.80	695	34.93	9.92	67.41	8.57	1,617
	Fe _T	67.16	1.88	69.70	55.00	695	67.89	1.36	69.90	56.02	1,617
	P	0.068	0.072	0.581	0.005	695	0.028	0.029	0.335	0.003	1,617
	Al ₂ O ₃	1.07	0.89	6.39	0.08	695	0.63	0.64	6.44	0.02	1,617
	SiO ₂	1.16	1.52	18.79	0.02	695	1.10	1.19	18.02	0.09	1,617
	Mn	0.043	0.093	1.502	0.002	695	0.062	0.124	2.065	0.002	1,617
	CaO	0.027	0.030	0.180	0.012	255	0.016	0.005	0.043	0.010	433
	MgO	0.027	0.017	0.107	0.014	255	0.024	0.012	0.102	0.010	433
Size range of fraction 0.15 – 0.00 mm	TiO ₂	0.047	0.031	0.136	0.010	255	0.044	0.039	0.267	0.007	433
	LOI	1.00	1.28	8.01	0.08	255	0.56	0.60	4.37	0.01	433
	% Weight	12.71	7.50	34.90	0.37	695	52.99	12.80	80.00	17.87	1,617
	Fe _T	63.03	4.62	69.60	39.30	695	66.17	2.14	69.90	55.00	1,617
	P	0.105	0.097	0.835	0.007	695	0.049	0.035	0.420	0.006	1,617
	Al ₂ O ₃	2.36	1.86	14.52	0.10	695	1.15	0.83	5.57	0.10	1,617
	SiO ₂	4.13	4.99	35.29	0.03	695	2.27	2.24	20.23	0.02	1,617
	Mn	0.089	0.191	2.992	0.003	695	0.183	0.316	3.030	0.002	1,617
	CaO	0.030	0.016	0.068	0.012	255	0.021	0.008	0.061	0.010	433
Size range of fraction 0.15 – 0.00 mm	MgO	0.056	0.057	0.332	0.018	255	0.034	0.016	0.109	0.010	433
	TiO ₂	0.105	0.140	0.633	0.011	255	0.063	0.054	0.505	0.010	433
	LOI	2.23	1.78	10.17	0.16	255	1.30	0.68	4.38	0.18	433

Data from MBR, η =number of samples, LOI = loss on ignition

DISCUSSION

Major differences between the Águas Claras and Pico mines

Both the Águas Claras and Pico mines are hosted within the Paleoproterozoic itabirites of the Cauê Formation. Although located in the western and less deformed side of the Quadrilátero Ferrífero, the two mines exhibit different patterns of deformation. At the Águas Claras mine a penetrative schistosity and a crenulation have developed as a consequence of events that folded and thrust the rocks of the Minas Supergroup. In the Pico mine the deformation was less

intense. The structures observed reflect shallow depths and low temperatures. Pervasive schistosity and crenulation were not developed.

The main lithological difference between the deposits is the presence of dolomitic itabirite in Águas Claras and amphibolitic itabirite in Pico. The genesis of the dolomitic and amphibolitic itabirites remains a source of controversy and discussion (Dorr 1965, Veríssimo et al. 2002, Rosière and Rios 2003). For some authors (Veríssimo 1999, Veríssimo et al. 2002), they represent a sedimentary facies variation of the Minas sediments. For others (Beukes et al. 2002), the dolomitic itabirite results from the diagenetic replacement of chert by carbonate.

The gradual appearance of quartz within the dolomite bands, the absence of evidence indicating replacement of one mineral by the other and the alternating banding of quartz bands, dolomite bands and iron oxide bands (Fig. 5e) characterize a gradual contact between dolomitic and quartz itabirites at the Águas Claras mine and could represent a sedimentary facies variation. The same mineral assemblage of quartz-dolomite-iron oxides found in a very low-grade metamorphic iron-formation of the Sokoman Iron Formation in Canadá was described by Klein and Fink (1976) as a sedimentary hematite-carbonate facies of the BIF. This could also be the case in Águas Claras.

At the Pico mine, lens of amphibolitic itabirite occur interlayered with quartz itabirite. The same occurs at the Alegria mine, in the eastern region of the Quadrilátero Ferrífero (Veríssimo 1999, Veríssimo et al. 2002). Based on field relations, petrology and geochemistry data, they have interpreted the amphibolitic itabirite and the quartz itabirite as representatives of the silicate facies and chert facies respectively. The difficulty in applying the concept of sedimentary facies to iron formations (James 1974) of the Quadrilátero Ferrífero is due to the fact that the mineral assemblage presently observed may not reflect the original mineralogical composition of the sediments of the Minas basin, which have undergone a complex evolution. No primary minerals are preserved, the textures of the rocks are typically metamorphic and the new mineral assemblage is strongly oxidized.

Otherwise there is no field evidence of a regional desilicification and carbonatization of the quartz itabirite as suggested by Beukes et al. (2002). Dolomitic itabirite and dolomite of the Cauê Formation occur along tens of kilometers of the Serra do Curral presenting gradual contacts. The gradual contact between the Cauê and Gandarela Formations brings an additional and important difficulty for the idea of carbonatization of the quartz itabirite. The rocks of the Gandarela Formation are typically shallow-water carbonate sediments which comprise dolomites and marbles with stromatolitic structures (Dorr 1965, Babinsky et al. 1995). At the base, the

Gandarela Formation is composed of dolomitic itabirite and the marble facies is subordinate or absent. Quartz itabirite occurs interlayered with dolomitic itabirite, dolomite and marbles (Dorr 1965). These relations suggest again sedimentary facies variation. At the Águas Claras mine the transition from the Cauê Formation to the Gandarela Formation is marked by the gradual disappearance of iron oxides in the itabirite. If the dolomitic itabirite were a product of desilicification and carbonatization of the quartz itabirite, why would it be in gradual contact with typical marine carbonate of the Gandarela Formation? And what would be the origin of carbonates, if there is no carbonate rocks underlying the Cauê Formation?

Recent exploration works conducted by MBR along the eastern limb of the Moeda Syncline have shown that the interlayering of amphibolitic itabirite and quartz itabirite and, on a small scale, dolomitic itabirite and dolomite, is very frequent. The absence of additional data on fluid inclusions, trace and isotope geochemistry etc. precludes a final conclusion on this subject. The protore of the iron ores in the Águas Claras mine was dolomitic itabirite, whereas in the Pico mine it is the quartz itabirite. This significant difference plays an important role with regard to the type of ore in each mine. In the Águas Claras mine there are only high-grade iron ores. Soft ores predominate and exhibit sharp contacts with the protore. They consist of almost pure hematite with no relicts of carbonate. The weathering of the quartz itabirite generated only small bodies of iron-rich itabirite and left the main part of it unaltered. At the Pico mine the soft high-grade iron ore is associated with iron-rich and quartz itabirites of various degrees of alteration. The transition from the soft high-grade ore to the iron-rich itabirite, and from this to the quartz itabirite, is typically gradational especially in the soft ore close to the land surface. In this ore, relicts of quartz are common.

The iron oxide mineralogy of the ores in the Águas Claras and Pico mines is similar in grain size, crystal shape and the types of minerals found - basically martite and granular/tabular hematite. Specularite is a minor component and is restricted to shear zones in the Pico mine. It occurs more extensively in the Águas Claras mine due to a higher degree of deformation. Although the high-grade ores in both mines have very low contents of gangue minerals, they are quite different from each other. In the Águas Claras mine, dolomite is the main gangue mineral, which is found as relict in contact regions with the protore, or as an accessory mineral in the unweathered hard ores. In the Pico mine, quartz is the main gangue mineral, present as a relict in soft and hard high-grade ores, as an accessory mineral in unweathered hard high-grade ores and as an important constituent of the iron-rich itabirite.

The different protores in the Águas Claras and Pico mines imply that the chemistry of the ores is a little different. In general, the high-grade ores of the Águas Claras mine have higher Fe, Mn, CaO and MgO contents than those of the Pico mines (Tables 5 and 6). High-grade ores from the Pico mine exhibit higher contents of SiO_2 and especially Al_2O_3 , both of which are particularly scarce in Águas Claras. The chemical differences between Águas Claras and Pico high-grade ores are well illustrated in the size fraction < 0.15 mm of the soft hematite ores. The Mn, Ca and Mg contents of the Águas Claras mine are respectively 3.6, 7.1 and 4.7 times higher than those of the Pico mine. In addition, the SiO_2 and Al_2O_3 contents of the same size interval in the Pico mine are respectively 2.5 and 1.6 higher than those of the Águas Claras mine. Table 7 summarizes the major differences between the mines.

Table 7 Summary of the major differences between the Águas Claras and Pico mines

	Águas Claras	Pico
Tectonism	Moderate	Weak
Protore	Dolomitic itabirite	Quartz itabirite
Ore Types	Only high-grade ore. Predominates soft-ore.	High- and low-grade ores. Predominate soft ores but hard ores are significant.
Gangue minerals	Very rare. Dolomite, talc, chlorite and apatite in contact regions.	Rare in high-grade ores. Quartz in iron-rich itabirites.
Ore mineralogy	Martite and hematite with varied specularite	Martite and hematite
Chemistry of the ores	Higher Fe, Mn, CaO and MgO.	Higher SiO_2 and Al_2O_3

Considerations about the iron ore genesis

Hypotheses on the genesis of the Quadrilátero Ferrífero iron ores have long been discussed in the literature, but reseachers are still far from reaching a consensus on this matter (Harder and Chamberlin 1915, Guild 1953, Park 1959, Dorr 1964 and 1965, Rosière 1983, Pires 2002, Rosière and Rios 2003). The complex scenario where by the Minas Supergroup rocks evolved, with a multitude of processes generating several sub-types of hard and soft-ores, and the lack of information concerning those processes make it difficult to build a genetic model.

The two major types of iron ores at the Águas Claras and Pico mines – hard and soft ores – have clearly different genesis: hard ore is hypogene whereas soft ore is supergene. In both mines, hard high-grade ore is found interbedded or cutting unweathered itabirites, which indicates its hypogene origin. The timing of its origin is unknown. However, a general indication

can be given. In the Pico mine a 861 Ma metamafic dyke cuts thin lens of the hard ore. On the other hand, there is no evidence of contact metamorphism in the soft ores. This indicates that the hard ore is older than 861 Ma and that the soft ore is younger.

Recent papers concerning the genesis of the hard ores in the Quadrilátero Ferrífero (Pires et al. 2002, Rosière and Rios 2003) review old genetic models based on the metamorphic-metasomatic replacement of the gangue minerals by hematite during metamorphism and deformation (Dorr and Barbosa 1963, Dorr 1965). Hydrothermal processes, generally accepted by Brazilian geologists, are probably responsible for the genesis of the hard ores, but many questions remain regarding the timing of those processes, frequency, origin, composition and temperature of the fluids. Several sub-types of hard high-grade ores occur at the Águas Claras and Pico mines (and throughout the Quadrilátero Ferrífero). Rosière and Rios (2003) interpret the massive hard ore as the first generation of the high-grade ore, which occurred during a first hydrothermal event (low-salinity fluids) at temperatures lower than 150 °C. This event would be related to the late diagenesis of the Minas sequence. Pires (2002) argues that this same massive ore and the brecciated hard ore were formed later during metamorphism and deformation of the sequence under brittle regime. Thin bedded, banded, micaceous and schistose hard ores were created during the same metamorphic event in a previous synkinematic, acid and oxidant metasomatism, under ductile regime.

The genesis of the soft high-grade ores and iron-rich itabirites was studied by several authors (Dorr 1964; Eichler 1968; Melfi et al. 1976; Viel et al. 1987; Ramanaidou 1989; Ramanaidou et al. 1996). According to them, field relations and petrographic observations clearly demonstrate that these ores are the result of the residual concentration of the iron oxides due to the leaching of associated gangue minerals by supergene fluids. The weathering process was enhanced by the well-defined bedding at high angles in the itabirites at the Águas Claras and Pico mines. This allowed deep penetration of weathering fluids, which are abundant in humid, tropical climates. This process was also favored by the appropriate physiographic environment where the itabirites occur along high ridges with adjacent steep slopes, enhancing the circulation of ground water (Dorr 1964).

A supergene origin seems very clear, especially for the soft ore and the iron-rich itabirite that occur close to the land surface, where it is possible to document the gradual transition from the fresh itabirite to the iron-rich itabirite and then to the soft ore. It is not so clear in the lower benches of the mine where the soft high-grade ore is in sharp contact with the soft itabirite of

low iron content. In this case one could suppose a previous iron enrichment of the itabiritic protore, but there is no evidence of this.

Soft high-grade ores cropping out close to the land surface at the Pico mine have the same physical and chemical characteristics as those present at deeper depths, except where they are in contact with the canga. In this case, they show higher Al_2O_3 and P contents and higher LOI.

The soft ores of the Pico mine present Fe contents similar to those of the Águas Claras mine. This fact led to interesting discussions on why two different protores generate similar soft ores. For Viel et al. (1987) the composition of the primitive itabirite would control the type of soft ore generated. For instance, dolomitic itabirite would generate soft high-grade ore whereas quartz itabirite would generate iron-rich itabirite. This idea could explain the soft ores of the Águas Claras mine, but not those of the Pico mine. Unweathered quartz itabirite cropping out close to the soft ores at the Pico mine do not contain carbonate. Therefore, though the original composition of the itabirite represents a very important factor in the genesis of the soft ore, it is not the only factor. The presence of favorable structures must also be considered.

Faults and fractures, for instance, facilitate the access of weathering fluids to the unweathered rock. A very good example of structural control can be found at the Pico mine, where the soft ore occurs only on the south side of the metamafic dyke (Fig. 10). The dyke acted as a barrier for the fluids coming from the south and favored an intensive leaching of the gangue minerals close to its contact.

At the Águas Claras mine it is reasonable to consider that, though both dolomitic and quartz itabirite are present as protores, the majority of soft ores are derived from the carbonatic rock due to its higher susceptibility to be leached. The absence of favorable structural control preserved the quartz itabirite. This was not the case at the Pico mine, where favorable structural controls facilitated the weathering of the quartz itabirite and the formation of high-grade soft ores.

Chemically, the weathering process is characterized by a high concentration of Al_2O_3 and P in the canga and in the iron ores that are in contact with it. The contents of these contaminants decrease quickly at greater depths (Fig. 9), where the soft ores consist of almost pure hematite with more than 97 % Fe_2O_3 .

The high concentration of goethite close to the surface, marked by a high loss on ignition, also decreases quickly at depth, suggesting that a majority of contaminants are incorporated in the goethite structure (Ainsworth et al. 1985). Close to the contact with the dolomitic itabirite, at

the lower levels of the Águas Claras mine, the contents of P and Mn increase greatly (Fig. 9). This fact is explained by the decreasing permeability observed in these zones. This favors the residual concentration of the Mn oxides produced during the dissolution of the carbonates, together with apatite, which is less soluble than dolomite.

Preliminary studies on the weathering of the Águas Claras and Pico protorees indicate that the first steps of the process are iso-volumetric. No substitution of quartz by goethite septa, as described by Ramanaidou (1989) and Ramanaidou et al. (1996) in the Capanema mine have yet been identified. The continuity of the leaching process leads to the collapse of the rock, with a volume reduction of about 40% and the generation of a significant porosity in the soft ore and rich itabirite (Ribeiro et al. 1998; Ribeiro et al. 2002). The pores created during weathering close at the land surface, filled by goethite.

The weathering processes may also have had an important role on the genesis of the porosity of the hard ores, dissolving the accessory gangue mineral and oxidizing the residual magnetite not oxidized by previous processes, as suggested by Varajão et al. (2002).

High-grade soft ores and iron-rich itabirites represent more than 80% of the iron ore reserves in the Águas Claras and Pico mines. This proves the importance of the weathering processes in the genesis of these orebodies.

CONCLUSION

The Águas Claras and Pico iron mines are two world-class mines hosted within Lower-Proterozoic metamorphosed banded iron formations of the Lake Superior type. The Águas Claras orebody consists of a roughly tabular-shaped lens formed by high-grade iron ores hosted within dolomitic itabirite. The high-grade ores comprise more than 85% of soft ore, with the remainder 15% formed by hard ore. Hematite is the main constituent of the iron ores. Gangue minerals are very rare and consist of dolomite, chlorite, talc and apatite, especially common close to the contact with the protore. Chemically the ores are characterized by a very high Fe content (an average of 68.2% Fe) and low contents of the contaminants P, Al_2O_3 and SiO_2 .

The Pico orebody consists of a lenticular shape body hosted within a quartz itabirite, which is the protore of the high- and low-grade ores. The high-grade ores comprise hard and soft ores respectively representing 20% and 51% of the reserves. These ores present the same iron oxide mineralogical composition as that found in the Águas Claras mine. Low-grade ores have a higher content of gangue minerals and account for 29% of the reserves. Quartz is the dominant

gangue mineral and is found with minor quantities of chlorite. The chemistry of the high-grade ores is characterized by high Fe contents (an average of 67.0%) and low P, Al_2O_3 and SiO_2 which are concentrated in the fines. Low-grade ores average 58.6% Fe and 13.5% SiO_2 .

The genesis of the hard high-grade ores is not yet well understood. It is probably related to hydrothermal processes acting during diagenesis or metamorphism of the BIF. Soft high-grade ores and iron-rich itabirites appear to be formed by supergene processes. The leaching of gangue minerals by weathering fluids leads to the residual iron enrichment. This process is favored by the presence of carbonate protores and structures which control the circulation of the ground water.

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ANEXO 2 – GEOCHEMISTRY AND GENESIS OF THE BANDED IRON FORMATIONS OF THE CAUÊ FORMATION, QUADRILÁTERO FERRÍFERO, MINAS GERAIS, BRAZIL

Abstract

The Cauê Formation of the paleoproterozoic Minas Supergroup hosts banded iron formations (BIFs) of the Lake Superior type, locally called itabirites. Two major compositional types of itabirite occur at the northwest of the Quadrilátero Ferrífero (QF): dolomitic itabirite and quartz itabirite. The former consists of alternating dolomite-rich and hematite-rich bands while the latter is formed with alternating quartz-rich and hematite-rich bands. Dolomite, quartz and hematite are the major mineralogical constituents, with accessories chlorite, sericite and apatite.

The chemical composition of the itabirites is as simple as that of the BIFs which occurs worldwide. At the dolomitic itabirite Fe_2O_3 plus CaO, MgO and LOI range from 95.8% to 97.8% while at the quartz itabirite Fe_2O_3 plus SiO_2 range from 94.4% to 99.6%. Both itabirites are highly oxidized and present $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratios higher than 0.98, much greater than the average ratio of other paleoproterozoic BIFs. Trace elements concentrations in itabirites are very low and range from < 10 ppm (Y, Sc, Be, Cu, Ga, Ge, Rb, Nb, Mo, Ag, In, Sn, Cs, Hf, Tl, Pb, Bi, As, Cd, Th, U, Sb) to concentrations between 10 and 55 ppm (Ba, Sr, Zr, V, Ni, Zn, Co, Cr and ΣREE).

Dolomite of the dolomitic itabirite shows negative $\delta^{13}\text{C}$ values varying from -2.5‰ to -0.8‰ while the oxygen isotope data displays $\delta^{18}\text{O}$ values varying from -12.4‰ to -8.5‰ . The $\delta^{13}\text{C}$ values show an enrichment trend in ^{13}C from the base to the top of the Cauê Formation, probably continuing upsection through the overlying stromatolitic dolomites of the Gandarela Formation. C and O isotopes, REE signatures and Y/Ho ratios indicate a marine origin for the sediments of the dolomitic itabirite.

The HREE enrichment pattern exhibited by the itabirites shows a modern seawater REE signature overprinted by a hydrothermal pattern marked by positive Eu anomalies. A strong correlation between Al_2O_3 and TiO_2 ($r > 0.9$) indicates a minor terrigenous component for the chemically precipitated, marine sediments of the Cauê Formation. Differences on the HREE signatures of itabirites suggest that they precipitated from different seawater depths, with the

dolomitic itabirite precipitating in shallower waters receiving continental sediment laden waters while the quartz itabirite was precipitating in deeper waters. Sea-level fluctuations caused by marine transgression–regressions are responsible for changes on the composition of seawater during the deposition of the Cauê Formation. These changes are expressed by dolomitic-, quartz- and amphibolitic itabirites, which represent lateral and vertical facies transitions of carbonatic, cherty and shaly BIFs, respectively.

INTRODUCTION

Banded iron formations have long been an object of interest to research not only due to their economic aspects, as they are the major source of iron ore, but also due to their importance for the understanding of atmosphere evolution, the chemical composition of the oceans and the appearance of life on Earth. Trendall (2002) presents an interesting and updated summary of the meaning of those rocks on the Precambrian stratigraphic record, and his references introduce the readers to this vast and complex theme.

The Cauê Formation of the Minas Supergroup is worldly known for hosting giant iron ore deposits at the Quadrilátero Ferrífero of the Minas Gerais State in the southern region of Brazil (Fig. 1). It is a classical proterozoic BIF deposited on the continental shelf (Dorr II, 1969), classified as of the Superior type, according to the scheme of Gross (1980). The Cauê Formation integrates the group of the great Gondwana BIFs together with the Carajás Formation of the Grão Pará Group at the Amazonic craton, the Kuruman and Penge Formations of the Transvaal Supergroup in South Africa, the Mulaingiri Formation of the Bababundan Basin in India and the BIFs of the Hamersley Basin in Australia.

Several geological processes have obliterated many of the primary characteristics of the original sediments of the Cauê Formation therefore originating the itabirites, a common name adopted in Brazil for the metamorphosed and oxidized BIF. Three major compositional types of itabirite occur at the QF: quartz, dolomitic and amphibolitic (Dorr II, 1969; Rosière et al., 1993). Great doubts persist in the literature about the origin of this compositional variation and, therefore, about the genesis of itabirites. Does it represent an original sedimentary facies variation within the Minas Basin or are itabirites products of a later process after sedimentation? Dorr II (1969) correlates the quartz and dolomitic itabirites with BIFs of the oxide facies of James (1954). He considered the amphibolitic itabirite as a product of the contact metamorphism of dolomitic itabirite by nearby granitic rocks. Beukes et al. (2002) attribute the genesis of the dolomitic itabirite to be the result of hydrothermal metasomatism of the original cherty BIF

during a hypogene enrichment stage of the iron ore. Veríssimo (1999) and Veríssimo et al. (2002), however, interpreted the variations on the compositional type of the itabirite as representative of the original sedimentary facies variation. These authors describe the quartz and amphibolitic itabirites at the Alegria Mine, East of the QF (Fig. 1), and correlate them to the oxide and silicate BIFs of James (1954).

The international literature of itabirites of the Cauê Formation is very scarce and most work was conducted during the 1960's and 1970's (e.g. Dorr II, 1969; Dorr II 1973). Recently, Klein and Ladeira (2000) studied the petrology and geochemistry of sixteen itabirite samples collected at four different sites of the western QF. These authors interpreted minor element and REE geochemistry of the itabirite to indicate precipitation and deposition from mixed Precambrian seawater and sub-oceanic hydrothermal fluids, but with no detailed explanation for the origin of the dolomitic and quartz itabirite. They also suggest that the presence of hematite and absence of magnetite or martite in the samples examined indicates that the hematite was formed after sedimentary ferric oxide/hydroxides during diagenesis or low-grade metamorphism. The presence of martite and relicts of magnetite, as well as formations of hematite after martite, however, have long been described in itabirite samples of the QF (Dorr II, 1969; Rosière et al., 1993). Their genesis of itabirites is therefore far from a satisfactory explanation.

The Águas Claras Mine is located on the northeast segment of the Serra do Curral, North of the QF (Fig.1), where the dolomitic and quartz itabirite crop out. Mining of iron ore during thirty years has exposed a complete unweathered sequence of dolomitic itabirite. Several drill holes intersect quartz itabirite in the north side of the mine. The quality of itabirite exposed on mining benches and thousands of meters of drill core provide ideal sites to sample all the sequence of the Cauê Formation in this part of the QF. This paper presents petrological and geochemical data of 46 samples of rocks collected throughout the Cauê Formation, from its base to the transition zone to dolomite of the overlying Gandarela Formation. Our aims are to combine petrographic and geochemical analyses to contribute for discussions about the genesis of the itabirites in the QF. This study represent the first comprehensive chemostratigraphic analysis of the Cauê Formation to date. C and O isotopic analysis of dolomitic itabirite further constrain the geochemistry of the fluid at the time of deposition. Special attention is given to dolomitic itabirite because this rock is the protore of the iron ore within this world class iron mine (Spier et al., 2003; Viel et al., 1987).

Figure 1 – Location and geological sketch map of the Quadrilátero Ferrífero region (After Dorr, 1969).

GEOLOGICAL SETTING

The Cauê Formation and Gandarela Formation are the lower and upper rock units, respectively, of the Itabira Group, which are the predominant chemical sediments of the Paleoproterozoic Minas Supergroup (Fig. 2). The Minas basin represented by sediments of the Minas Supergroup is interpreted as either an intracratonic basin (Chemale Jr. et al., 1994) or a platform supracrustal sequence with a sialic substrate (Cordani et al., 1980; Marshak and Alkmim, 1989; Teixeira and Figueiredo, 1991). It rests unconformably on Archean greenstones of the Rio das Velhas Supergroup and basement granite-gneiss terrains (Chemale Jr. et al., 1994).

Figure 2 - Stratigraphic column of the Quadrilátero Ferrífero region. The right-hand portion of the column represents relationships in the eastern part of the Quadrilátero Ferrífero, while the left-hand side of the chart represents relationships in the western part of the Quadrilátero Ferrífero (After Alkmim et al., 1998, based on Dorr II, 1969; Schorscher et al., 1982 and Silva, 1992).

The Minas Supergroup comprises clastic sediments of the Caraça Group at its base, which consist of an extensive quartzose (Moeda Formation) and argillaceous (Batatal Formation) formations. The Moeda Formation occurs in three facies: two alluvial coarse grained quartzite and conglomerate sediments, and a fine-grained marine quartzite and phyllite (Villafa, 1981). It is conformably overlain by the Batatal Formation, which consists of sericitic phyllite with minor graphitic phyllite. The Caraça Group is interpreted to be a transgressive sequence deposited over an old peneplaned surface (Villafa, 1981). The Moeda Formation was deposited under paralic to stable shelf environments while the Batatal Formation is an offshore sediment deposited on a slowly subsiding passive margin continental shelf or platform (Dorr II, 1969). The transition from clastic sediments of the Caraça Group to chemical sediments of the Itabira Group in the northern segment of the Serra do Curral is characterized by an argillaceous dolomite with lenses of metachert.

The Itabira Group comprises itabirites (BIFs) with minor dolomite and phyllite of the Cauê Formation and carbonate rocks of the Gandarela Formation. Both units are intergradational. Itabirites of the Cauê Formation are generally lithologically similar to most major oxide-facies BIFs known worldwide (Dorr II, 1969). Carbonate rocks of the Gandarela Formation include dolomites, limestones, dolomitic phyllite, dolomitic iron formation and phyllite. They were deposited in shallow water, and are locally rich in stromatolitic structures (Souza and Müller, 1984). Pb-Pb dating of this stromatolitic dolomite yielded an age of 2420 ± 19 Ma, which is considered by Babinski et al. (1995) as a depositional age. Based on this upper limit, and considering the Pb-Pb ages on detrital zircons of the Moeda Formation which vary between 3.0 and 2.6 Ga, Babinski et al. (1995a) suggest that the deposition of the itabirites of the Itabira Group occurred between 2.6 and 2.4 Ga.

The upper unit of the Minas Supergroup is the Piracicaba Group, which consists of predominantly clastic sediments with minor chemical sediments deposited in marine shallow water and deltaic environments. The Piracicaba Group overlies the Itabira Group generally with structural conformity, but erosional disconformity has been locally found (Dorr II, 1969).

Although the tectonic history of the QF remains controversial (e.g. Alkmim and Marshak, 1998; Chemale Jr. et al., 1994; Davis and Hippert, 2000), there is a general consensus that the rocks of the Minas Supergroup were subjected to at least two main tectonic events during the Proterozoic. According to Chemale Jr. et al. (1994) the first event in the Transamazonian (~ 2.1 Ma) was extensional and resulted in the formation of Archean granite-gneiss domes and nucleation of regional synclines in the overlying Rio das Velhas and Minas supergroups strata.

The second event was compressional and of Brasiliano age (~0.6 Ga). The Brasiliano event resulted in a west-verging fold-and-thrust belt causing inversion, amplification, translation and rotation of the basinal synclines, affecting mainly the eastern portion of the QF, and obliterating many of the tectonic features of the extensional event.

Two main structural domains are recognized at the QF: an eastern high strain domain with thick shear zones and important thrust systems, and a western low strain domain with well preserved synclines discontinuously cut by discrete shear zones and thrust faults (Rosière et al., 2001). The deformational gradient comes along with a metamorphic zoning which increases from west to east, and is defined by Herz (1978) as chlorite, biotite and staurolite zones. Pires (1995) redefined these metamorphic grade zones as grunerite, cummingtonite, actinolite and tremolite-antophyllite zones based on the compositional variation of the amphiboles of itabirite and phyllite of the Itabira Group. Equilibrium temperatures range from 300 °C on the western side to 600 °C on the eastern side of the QF, with pressures ranging from 3 to 5 kbar respectively (Pires, 1995).

LOCAL GEOLOGY

The Águas Claras mine is located at the northern segment of the Serra do Curral, a northeast-southwest trending ~100 km-long ridge that defines the northwest edge of the QF (Fig. 1). The Serra do Curral is a homocline, where bedding dips steeply to the southeast (Alkmim and Marshak, 1998; Chemale Jr. et al., 1994; Pires, 1979). Units of the Minas Supergroup crop out along most of its extension as an inverted sequence without repetition. At the northern segment of the Serra do Curral the rocks are very strained, sinistrally rotated from their original position, and beds are overturned (Chemale Jr. et al., 1994). Extensive shear zones occur at the contact between rocks of the Minas Supergroup and the Rio das Velhas Supergroup. In spite of being highly strained, the rocks of the Minas Supergroup were submitted only to green schist facies metamorphism (Pires, 1995).

At the Águas Claras mine, quartzite and phyllite of the Moeda and Batatal formations, and dolomite, itabirite and iron ore of the Cauê Formation crop out (Fig. 3a-b). The contact between these stratigraphic units is gradational. Quartzite and phyllite occur on the south wall of the pit, and cap the iron orebody (Fig. 3a). The gradational contact between the Moeda and the Batatal Formations is initially marked by interfingering lenses of coarse and fine quartzite. Upper on the sequence, lenses of fine quartzite occur interlayered with sericitic phyllite, which becomes

predominant. Lenses of graphitic pyhillite with porphyroblasts of pyrite occur locally, interlayered within the sericitic phyllite.

Figure 3 - Águas Claras mine. A Cross section 2550E. B Geological sketch map.

The contact between clastic sediments of the Batatal Formation and chemical sediments of the Cauê Formation is gradational over a few centimeters. It is marked by the appearance of dolomite in the Batatal Formation. Dolomite content increases markedly upwards in the Cauê Formation to form an argillaceous dolomite. Argillaceous dolomite is considered to be the base of the Cauê Formation at the Águas Claras mine. A black color and fine grained and anisotropic fabric characterize argillaceous dolomite. Lenses of metachert ranging in thickness from tens of centimeters to meters occur within the argillaceous dolomite. Within the argillaceous dolomite these lenses of metachert gradate to quartz itabirite. This is the first appearance of BIF within the Cauê Formation. It is distinguished from other BIFs in the QF by its high magnetism. Figure 4 shows detail of the transition from the Batatal to the Cauê Formation, including the main lithotypes.

The contact between argillaceous dolomite and dolomitic itabirite is characterized by a complex transition zone of approximately 10 m wide, where argillaceous dolomite, ferruginous dolomite and minor metachert/quartz itabirite occur interlayered. Within this transition zone a 50 cm to 1.2 m layer of ferruginous dolomite with peloids and sub-angular fragments of quartz itabirite cemented by dolomite is observed (Fig. 5). This rock, a typical Granular Iron Formation (GIF) in accordance with Trendall's (2002) description, is described at the QF for the first time. The quartz itabirite from which the fragments observed at the GIF were originated crops out within a few meters, and it is possible to accompany the lateral transition from BIF to GIF. Transitions between BIFs and GIFs are uncommon in the global stratigraphic record (Beukes and Klein, 1990). They are only described at the transition zone between the microbanded Kuruman Iron Formation and the granular Griquatown Iron Formation, both of the Lower Proterozoic of the Transvaal basin (Beukes, 1980; Beukes, 1984) and at iron formations of the Frere Formation of the Lower Proterozoic of the Naberru basin, Western Australia (Goode et al., 1983).

A ~6 m-thick layer of ferruginous dolomite, characterized by a strong red color, within the uppermost part of the transition zone is overlain by dolomitic itabirite. The high proportion of microcrystalline hematite (see petrography below) is responsible for the strong red color of the ferruginous dolomite. Microcrystalline hematite producing these striking red colours is also observed in the dolomitic bands of the itabirite.

The appearance of iron mineral bands, typical of itabirite and other BIF's marks the transition from ferruginous dolomite to the dolomitic itabirite. This banding corresponds to the mesobanding of the BIF of the Hamersley basin defined by Trendall and Blockley (1970). Initially, dolomitic bands are thicker than the iron-rich mesobands (Fig. 6a). The former are one

Figure 4 – Detail of the transition zone from the Batatal to Cauê Formation and photographs of the major rock types observed at the profile studied. **A** Sericitic phyllite. **B** Argillaceous dolomite. **C** Granular iron formation (GIF). **D** Quartz itabirite within argillaceous dolomite. **E** Ferruginous dolomite. **F** Dolomitic itabirite. **G** Quartz itabirite.

centimeter to tens of centimeters thick and vary from deep red to pink, while iron-rich bands are generally one millimeter to three centimetres thick and grey. Approximately 50 m from the base of the dolomitic itabirite, dolomitic bands become thinner forming a more typical dolomitic itabirite. Typical dolomitic itabirite exhibits alternating millimeter thick dolomite and hematite bands (Fig. 6b). After ~ 250m of typical dolomitic itabirite, hematitic bands gradually disappear forming a ferruginous dolomite, which is similar to that present at the base of the Itabira Group.

Within the mining pit dolomitic itabirite is much more common than quartz itabirite, which occurs only on the north wall on the top of the sequence (Fig. 3a). The contact between both rocks is gradational and marked by small lenses of quartz itabirite within the dolomitic itabirite. Drill core indicates this contact zone contains a triply layered rock with alternating bands of quartz, iron minerals and dolomite (Fig. 6c). Outside this contact zone the quartz itabirite exhibits the typical mesobanding of quartz and iron minerals (Fig. 6d).

The transition from the quartz itabirite to the carbonate rocks of the Gandarela Formation, which was observed in drill cores, is also gradational. The gradual appearance of dolomite and the disappearance of hematite and inherent loss of the typical mesoband texture of itabirite characterize the transition zone from quartz itabirite to carbonates. Although the dolomitic itabirite and the iron ore occur throughout the whole length of the mine along the contact with the Batatal Formation, some exploratory drills completed outside of the pit found only quartz itabirite at this equivalent stratigraphic position. This indicates that the transition from dolomitic itabirite to quartz itabirite occurs not only vertically, but also laterally along the Cauê Formation.

The dolomitic itabirite is locally brecciated, with clasts formed either by the hematitic bands or by the dolomitic bands cemented by white carbonate. Some of these breccias suggest a syn-sedimentary origin, others, however, are typically associated with tensional gash veins (Fig. 6e). Several generations of carbonate veins varying from millimeter to tens of centimeters in width crosscut or parallel banding. Some of these veins were affected by the same deformational events which affected the itabirites (Fig. 6f).

The orebody is a concordant, 2.500 m long, roughly tabular-shaped lens which occurs within the dolomitic itabirite with a maximum thickness of 300 m. The depth of the ore is variable and extends to over 400 m below the surface, then grading into the parental dolomitic itabirite deeper down (Fig. 3a). The iron ore is typically soft (friable) and consists of almost pure hematite, with very low levels of contaminants ($\text{Fe}_2\text{O}_3 > 98\%$). The soft ore was formed by leaching of the dolomite from the parental rock by supergene processes fluids and the consequent residual

enrichment of the rock (Spier et al., 2003; Viel et al., 1987). For additional information concerning the genesis of this type of ore refer to Spier et al. (2003).

Figure 5 – Photographs of Granular Iron Formation (GIF). **A** Outcrop showing peloids and intraclasts cemented by dolomite and sericite/chlorite. **B** Detail of the GIF. **C** Thin section showing peloids and intraclasts cemented by dolomite and sericite/chlorite and cut by secondary dolomite and quartz veins.

Figure 6 – Photographs of itabirites of the Cauê Formation. **A** Hand specimen of dolomitic itabirite showing thick dolomite mesobands. **B** Hand specimen of typical dolomitic itabirite. **C** Drill core sample of triply layered itabirite showing mesobands of dolomite (*d*), hematite (*h*) and quartz (*q*). **D** Drill core sample of typical quartz itabirite. **E** Brecciated dolomitic itabirite with clasts of hematite and dolomite cemented by secondary dolomite. **F** Hand specimen of folded dolomitic itabirite. Secondary dolomite lens are parallel to the mesobanding.

SAMPLING AND ANALYTICAL PROCEDURES

Thirty four samples of dolomite and itabirite of the Cauê Formation, the locations of which are shown in Figure 4, were analyzed for major, traces and rare earth elements (REE). Six samples of dolomitic itabirite had the hematitic and dolomitic bands analyzed separately. Two samples of sericitic phyllite of the Batatal Formation were also analyzed to assess the chemistry of a potentially clastic contaminant of the chemical sediments. Some samples were also analyzed for total graphitic and organic carbon. The majority of the sampling was performed at Section 2.550 E (Fig. 3), along a ~300 m section of the 1010 m bench. Bench 1010 is located more than 200 m from the current land surface. Itabirite at bench 1010 is not altered by weathering processes and therefore provides the best samples for chemical analysis. A representative suite of rocks from the base to the top of the Cauê Formation was collected. Samples of quartz itabirite and dolomite from the transition zone to the Gandarela Formation were collected in drill cores of the drill hole P3 in this same section. Additional samples of dolomitic and quartz itabirite were collected in drill cores P55 and P54 in the neighboring area of Section 2550E.

To avoid bias sampling (i.e., extreme bimodal compositional variation of the itabirite, typical of BIFs everywhere) larger samples of three to five kilograms comprising several couplets of mesobands of iron minerals and dolomite/quartz were selected for bulk analysis. We avoided samples with carbonate or quartz veins to reduce the possibility of contamination. Six samples of dolomitic itabirite were crushed in a tungsten carbide ringmill and <0.15mm fraction of the hematite-rich bands was collected by sieving. The grains were visually inspected under a binocular microscope and handpicked. We preferred to analyze six different samples of visually pure dolomitic bands to ensure pure separates for chemical analysis, and to accentuate the chemical differences between mesobands.

All samples were prepared for analysis by grinding in a tungsten carbide vessel, and because this method causes contamination by W, Co and Ta, these elements are not reported. Chemical analyses were carried out at the Activation Laboratories – ACTLABS in Canada. Major and trace elements were determined by ICP/ICP-MS after the opening of the sample with a lithium tetraborate/metaborate fusion. Base metals were determined by ICP-MS/INAA after total digestion by acid attack. Ferrous iron was determined at the laboratories of MBR by titration potassium dichromate.

Forty two samples of dolomitic bands of dolomitic itabirite were analyzed for carbon and oxygen isotopes. Fragments from thicker mesobands (>1cm) weighing ~200g were collected

approximately 10 m from the base to the top of the sequence along Section 2550E. Dolomite samples (~200g) were also collected along a vertical section of Section 2550E, while avoiding potentially contaminating hematitic bands. Isotopic analyses were carried out at the Stable Isotope Laboratory of the Federal University of Pernambuco – NEG-LABISE. CO₂ gas was extracted from powdered carbonates in a high vacuum line after reaction with 100% phosphoric acid at 25 °C for three days, and then cryogenically cleaned according to the method described by McCrea (1950). The CO₂ gas released was analyzed for O and C isotopes in a double inlet, triple collector SIRA mass spectrometer, using the BSC reference gas (Borborema skarn calcite) that was calibrated against NBS-18, NBS-19 and NBS-20 standards, and has $\delta^{18}\text{O}$ value of -11.28 ‰_{PDB} and $\delta^{13}\text{C}$ of - 8.58 ‰_{PDB}. The precision of the method has been assessed by repeated analyses of the BSC reference gas, and the accuracy by comparison of NBS standard measurements. The results are expressed in the notation ‰ (per mil) in relation to PeeDee belemnite (PDB).

Detailed petrographic examination using transmitted and reflected light, scanning electron microscopy (SEM) and electron microscopy analyses (EMP) were carried out to determine the mineralogy and paragenesis of all samples. SEM and EMP analyses were performed at the laboratories of the Geoscience Institute of the University of São Paulo and at the Center for Microscopy and Microanalyses of the University of Queensland, Australia. EMP analyses of dolomite were performed using a JEOL JXA-8600 electron microprobe operating at 15 kv and 20 nA current with a focussed 5 µm electron beam.

For purposes of data presentation and discussion, the samples analyzed have been divided into five groups on the basis of their chemical compositions and mineral assemblages, as shown in Figure 7. These include: (I) sericitic phyllite; (II) argillaceous dolomite; (III) dolomitic itabirite; (IV) quartz itabirite, and (V) quartz-carbonate rocks (transition from Cauê to Gandarela Formations). The argillaceous dolomite was chosen as the representative lithotype of the transition zone to the dolomitic itabirite for comparison with other rocks of the Cauê Formation as it is the major lithotype of this zone and hosts both the subordinated metachert and the quartz itabirite. A limit of 2% SiO₂ is defined to separate dolomitic from quartz itabirite. We avoided sampling mixed dolomitic and quartz itabirite types to facilitate this separation. A limit of 2% CaO separates quartz itabirite from quartz-carbonate rocks of the transition to the Gandarela Formation. This suite of samples, described above, is the most complete chemical database of the Cauê Formation published to this date.

Figure 7 – Triangular diagram showing major element composition of the samples studied, grouped into five major groups.

MINERALOGY AND PETROGRAPHY

Sericitic Phyllite

Sericitic phyllite is a uniformly dark-grey very fine-grained phyllite (Fig. 4a). It is laminated on a fine scale (1-3 mm thick) and consists of quartz and sericite with minor biotite, and shows a lepidoblastic texture with foliation defined by sericite and biotite. Large porphyroclasts of quartz surrounded by sericite and quartz exhibiting wavy extinction indicate strong deformation that this rock was submitted.

Argillaceous Dolomite

Argillaceous dolomite is a black, very fine-grained impure dolomite (Fig. 4b). Local geologists name this rock dolomitic phyllite because when weathered, argillaceous dolomite resembles a phyllite. However, the high dolomite content and absence of any well-defined lamination do not allow for the use of the term phyllite. Mineralogically, the argillaceous dolomite comprises dolomite (> 85 %), chlorite with minor quartz and rare pyrite (Fig. 8a-c). Quartz occurs as aggregates showing strong wavy extinction. The absence of hematite and

magnetite in argillaceous dolomite distinguishes this rock from the overlying ferruginous dolomite. Argillaceous dolomite is strongly deformed and poorly foliated.

Granular Iron Formation

Granular iron formation is restricted to a one meter long lens which persists laterally for tens of meters along the top of the argillaceous dolomite. Generally, it is not internally banded, but coarsening reducing clasts size is locally observed. The granular texture comprises hematite clasts set in a cement or matrix of dolomite, sericite and chlorite (Fig. 5a-c). The clastic fraction is usually peloidal, but may contain angular intraclasts of hematite-rich bands of itabirite. The peloids are rounded, subspherical grains of either itabirite or dolomite ranging from 0.2 to 5 mm in diameter. Some peloids contain concentric layers of hematite (Fig. 8f). Angular fragments are lithologically similar to itabirite and form tabular fragments up to two centimeters long although smaller ones may be rounded and graded into peloids. Although the GIF is not weathered, indicated by the preservation of carbonate cement, the clasts are strongly goethitized, which poses a very intriguing question.

Ferruginous Dolomite

Ferruginous dolomite occurs at the base and top of the dolomitic itabirite, and as meter thick layers randomly distributed within the dolomitic itabirite. Macroscopically and microscopically the ferruginous dolomite resembles the dolomite bands of the dolomitic itabirite, but lacks larger crystals of tabular hematite and martite common to dolomitic itabirite. Ferruginous dolomite is deep red to pink, very fine-grained, and poorly banded (Fig. 4e). It consists of small crystals of dolomite (average grain size of 15 μm) with micrometer size inclusions of hematite, which appear dust-like within the dolomite crystals (Fig. 9a). These hematite inclusions are responsible for the strong red color of the rock. They are generally concentrated on the nuclei of the dolomite crystals (Fig. 9b). Talc, chlorite and apatite occur as accessory phases.

Figure 8 – Photomicrographs of various rock types of the base of the Cauê Formation. **A** Argillaceous dolomite; plane polarized light, (*d*=dolomite). **B** and **C** Pyrite (*py*) crystals in argillaceous dolomite; transmitted light - **B**, reflected light - **C**. **D** Dolomite crystals in metachert; plane polarized light. **E** Quartz itabirite; transmitted light, (*q*=quartz). Note the shapes of martitized magnetite (*m*) and the associated chlorite (*c*). **F** Peloids within GIF.

Figure 9 – Photomicrographs of the dolomitic itabirite; transmitted light. **A** Inclusions of hematite microcrystals within dolomite crystals forming a dust. **B** Inclusions of hematite microcrystals concentrated within the nuclei of the dolomite crystals which show clean rims. **C** Microbanding of dolomite-rich and hematite rich laminae; transmitted light. **D** Detail of the dolomite-rich microband. Euhedral crystals of martite (*m*) between the dolomite crystals (*d*); transmitted light.

Dolomitic and Quartz itabirites

Mesobanding is the most striking macroscopic characteristic of itabirites at the QF. Mesobanding is defined by alternating millimeter to decimeter hematite rich bands and dolomite/quartz bands (Fig. 6b-d). Microbanding defined by alternating sub-millimeter hematite and dolomite/quartz laminae are commonly observed within mesobands of itabirites (Fig. 9c). In dolomitic itabirite, the dolomitic bands consist largely of dolomite and up to 40% hematite (Fig. 9d). Talc, chlorite and apatite occur as accessory minerals. Thin laminae of apatite parallel to banding are locally observed (Fig. 10a). Dolomite occurs as euhedral crystals varying from 2 µm to 15 µm intergrown with hematite and accessory minerals (Fig. 10b). Like the ferruginous dolomite, micrometer hematite inclusions form an iron dust within dolomite crystals (Fig. 9a). Hematite in itabirites occurs as martite (pseudomorphs of magnetite after oxidation), tabular

hematite and, locally, specularite. Specularite occurs along shear planes, parallel to or truncating the banding. The hematitic bands are largely comprised of hematite with up to 20% dolomite and traces of talc, chlorite and apatite (Fig. 10 c-d). Hematite occurs as dense aggregates of martite and tabular hematite with individual grains varying from 5 μm to 10 μm . Thicker hematite bands preserve relict magnetite within martite crystals.

Quartz itabirite is macroscopically and texturally similar to dolomitic itabirite, but mesobands rich of quartz replace dolomite (Figs. 10e, 11a-b). Quartz is generally clean, without hematite inclusions, and exhibits wavy extinction. Relicts of magnetite are locally observed within martite crystals (Fig. 11c-d). When present, dolomite occurs intergrown with quartz (Fig. 10f). Apatite, chlorite and sericite occur as accessory phases intergrown with quartz and hematite (Fig. 10 g-h) and, locally, as fine inclusions within quartz (Fig. 11 e-f). The grain size of all minerals is very fine (5 μm to 25 μm). Quartz bands of the quartz itabirite consist of quartz with varying proportions of hematite (up to 25%) and accessory minerals (i.e., apatite, chlorite and sericite). Hematite-rich mesobands consist of dense aggregates of hematite with up to 15% of quartz.

Quartz-Carbonate Rocks of the Transition Zone to the Gandarela Formation

This group of rocks comprises quartz itabirite bearing dolomite, cherty dolomite and dolomite that occurs overlying quartz itabirite at the transition zone to the Gandarela Formation. The gradual appearance of dolomite and the disappearance of quartz and hematite in the quartz itabirite characterize this group. Micro and mesobanding typical of itabirites is replaced by a poor banding defined by micaceous minerals. The typical dolomite of this zone consists of very fine dolomite (average size of 15 μm) with accessory sericite, chlorite and hematite (Fig. 11g). Locally the dolomite is enriched with chlorite, which comprises up to 30% of the rock. Chlorite occurs as thin, millimeter laminas, which define conspicuous microbands (Fig. 11h). Talc with minor chlorite and hematite form thin veins that crosscut these chlorite-rich bands.

Figure 10 – SEM images of dolomitic and quartz itabirite. **A** and **B** Dolomite-rich microband of dolomitic itabirite. In **A** dolomite crystals (*d*) are intergrown with apatite (*a*) and martite/granular hematite (*h*). In **B** dolomite crystals (*d*) are intergrown with talc (*t*). **C** Hematite rich microband of dolomitic itabirite. **D** Detail of the hematite-rich microbanding showing intergrown of martite and granular/tabular hematite (*h*) with dolomite (*d*). **E** Microbanding of quartz-rich and hematite-rich laminae in quartz itabirite. **F** - **H** Detail of a quartz-rich microband of quartz itabirite showing in **F** intergrown of quartz (*q*), hematite (*h*) and dolomite (*d*), in **G** intergrown of quartz (*q*), martite/tabular hematite (*h*) and apatite (*a*), in **H** intergrown of quartz (*q*), hematite (*h*), sericite (*s*), chlorite (*c*) and dolomite (*d*).

Figure 11 – Photomicrographs of quartz itabirite and dolomite of the transition zone to the Gandarela Formation. **A** Microbanding of quartz-rich and hematite-rich laminae; transmitted light. **B** Detail of a quartz-rich laminae of quartz itabirite showing intergrown of quartz (*q*) and hematite (*h*); transmitted light. **C** Relicts of magnetite (*mg*) within martite; reflected light. **D** Detail of a martite crystal showing oxidation of magnetite; reflected light. **E** – **F** Detail of a quartz-rich laminae of quartz itabirite showing in **E** intergrown of quartz (*q*), apatite (*a*) and hematite (*h*); in **F** intergrown of quartz (*q*), hematite (*h*) and sericite (*s*). **G** – **H** Dolomite of the transition zone to the Gandarela Formation, showing in **G** intergrown of dolomite (*d*), quartz (*q*) and hematite (*h*), plane polarized light; in **F** laminae of chlorite (*c*) and hematite (black minerals within laminae), transmitted light.

Mineral Chemistry

Electron microprobe analyses of twenty six carbonate samples of the argillaceous dolomite, ferruginous dolomite, itabiritic dolomite and dolomite of the transition zone to the Gandarela Formation indicates the dolomite has approximately 1 Ca : 1 Mg ratio and average CaO and MgO contents ranging from 29.6% to 30.5%, and from 18.4% to 20.6%, respectively. FeO and MnO contents are low, averaging 3.7% to 1.0% FeO and 0.5% to 0.9% MnO, respectively. Table 1 summarizes the EMP analyses. The complete dataset is available from the authors as electronic data.

The dolomite composition changes at the transition from argillaceous dolomite to dolomitic itabirite (Fig. 12). Dolomite of the argillaceous dolomite is richer in FeO and poorer in MgO contents than dolomite of the overlying rocks. Dolomite of the dolomitic itabirite has very uniform composition through the 300 m of the sampled profile. Ca:Mg and Ca/(Fe+Mn) ratios remain almost constant around 1:1 and 20:1 respectively, from the base to the top of the sequence. A little difference in composition is observed only on the dolomite of the transition zone to the Gandarela Formation, which has a higher FeO and MnO contents, of up to 5.1% and 1.8%, respectively.

Table 1 – Average Electron Microprobe Analyses of Dolomite

	Argillaceous Dolomite	Dolomitic Itabirite	Dolomite (Transition to Gandarela Fm.)	Veins
	(n = 28)	(n = 331)	(n = 38)	(n = 115)
Wt%				
CaO	29.63	30.51	30.00	30.82
MgO	18.37	20.60	19.00	20.81
FeO	3.66	1.01	2.61	0.74
MnO	0.47	0.60	0.90	0.32
Recalculated on the basis of 2 (Ca, Mg, Fe, Mn)				
Ca	1.003	1.008	1.013	1.016
Mg	0.864	0.947	0.892	0.955
Fe	0.098	0.026	0.069	0.014
Mn	0.013	0.016	0.024	0.014

EMP analyses of carbonate veins that crosscut the dolomitic itabirite indicate that dolomite contains an average 30.8% CaO and 20.8% MgO, which are similar contents of the host rocks. Carbonates veins exhibit lower average contents of FeO and MnO (0.5%). Petrographic and EMP analyses indicate that dolomite is the only carbonate mineral in veins but other carbonates may be present within other generations of carbonate veins observed along mining exposures. EMP analyses performed on tabular hematite and martite indicate relatively high and invariant iron contents (>99% Fe₂O₃).

Figure 12 – **A - B** Plots of Ca/Mg and Ca/(Fe+Mn) ratios of dolomite of the dolomitic itabirite as a function of stratigraphic location. **C - D** Plots of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of dolomitic bands of the dolomitic itabirite and stromatolitic dolomites of the Gandarela Formation as a function of stratigraphic location. Data from Gandarela Formation are from (Bekker et al., 2003), obtained from samples collected at the Hargraves quarry.

Geochemistry

The geochemical data of thirty six samples of rocks grouped into five major lithological groups and 12 separate analyses of dolomitic and hematitic bands of the dolomitic itabirite are presented in Appendixes 1 and 2. The triangular diagram of Figure 7 shows that dolomitic and quartz itabirite have simple compositions, while sericitic phyllite, argillaceous dolomite and carbonate rocks of the transition zone to the Gandarela exhibit higher compositional variation. Averages of major, trace and REE are present in Tables 2 and 3 according to their lithotype groups. We did not calculate the statistics for those variables with results always below or very close to the detection limit. In cases where the results of just a few samples were below this limit the statistics were calculated using half the detection limit for those samples. This procedure was chosen to allow for attaching some distinction to those values which stood slightly above the detection limit. It was used in all graphs presented in this paper.

Major, trace and REE data of the Post Archean Australian Shale (PAAS) obtained by McLennan (1989) are used as normalization values in this paper. Occasionally, data of the C1-chondrite of Taylor and McLennan (1985) is also used. We present REE patterns with Y inserted between Dy and Ho according to its ionic radius. We included Y to the lanthanides for comparison with REE and Y studies of other iron formations. The Eu anomaly is defined quantitatively as:

$$Eu/Eu^* = ((Eu/Eu_{PAAS}) / (Sm/Sm_{PAAS}) \times (Gd/Gd_{PAAS}))^{1/2}$$

where Eu^* is the hypothetical concentration that Eu would have. The anomalies of Ce, Pr and Y were similarly calculated. The degree of light REE enrichment relative to heavy REE is presented as the ratios of PAAS-normalized La and Yb (La/Yb), La and Sm (La/Sm), and Sm and Yb (Sm/Yb).

Table 2 – Average major and trace element composition

	Sericitic Phyllite				Argillaceous Dolomite				Dolomitic Itabirite			
Wt%	Avg	Std	Min	Max	Avg	Std	Min	Max	Avg	Std	Min	Max
SiO ₂	63.33	4.31	60.28	66.38	13.01	4.84	7.37	19.19	1.01	0.46	0.53	1.97
Al ₂ O ₃	18.61	1.53	17.52	19.69	1.34	0.55	0.61	1.81	0.32	0.25	0.07	0.77
Fe ₂ O ₃	1.67	0.52	1.31	2.04	1.17	0.92	0.42	2.44	48.90	8.49	39.65	67.61
Fetot	3.53	2.55	1.73	5.33	5.99	1.83	4.21	8.54	49.64	8.48	40.26	68.11
FeO	1.67	1.82	0.38	2.96	4.34	1.01	3.27	5.49	0.66	0.19	0.44	0.93
MnO	0.03	0.03	< 0.01	0.05	0.49	0.16	0.40	0.72	0.28	0.07	0.18	0.43
MgO	3.06	2.60	1.22	4.90	15.59	0.81	14.81	16.72	10.33	1.80	6.49	12.30
CaO	0.11	0.02	0.09	0.12	24.39	1.23	22.63	25.38	14.36	2.42	9.47	17.26
Na ₂ O	0.07	0.04	0.04	0.09	< 0.01				< 0.01			
K ₂ O	5.88	1.20	5.03	6.73	0.30	0.26	0.06	0.59	0.03	0.04	0.01	0.11
TiO ₂	0.77	0.03	0.74	0.79	0.06	0.02	0.03	0.08	0.02	0.02	< 0.01	0.06
P ₂ O ₅	0.08	0.02	0.06	0.09	0.03	0.01	0.02	0.03	0.12	0.04	0.05	0.19
Ctot					10.80	0.61	10.10	11.20	6.45	0.70	5.50	7.05
Cgrap					0.30	0.06	0.25	0.36	0.03	0.01	0.03	0.05
Corg					0.11	0.02	0.10	0.13	0.04	0.01	0.03	0.05
CO ₂					38.07	2.25	35.50	39.70	23.60	2.55	20.20	25.80
S	0.008	0.002	0.006	0.009	0.07	0.04	0.03	0.12	< 0.001			
LOI	3.99	0.94	3.32	4.65	38.35	1.82	35.67	39.78	22.77	4.15	13.49	27.27
ppm												
Ba	328.0	45.3	296.0	360.0	17.0	8.2	8.0	24.0	12.9	4.3	5.0	19.0
Sr	14.0	4.2	11.0	17.0	21.0	5.1	16.0	28.0	29.8	12.4	17.0	56.0
Y	26.0	1.4	25.0	27.0	8.5	1.7	7.0	11.0	7.7	2.3	4.0	12.0
Sc	16.5	0.7	16.0	17.0	2.3	0.5	2.0	3.0	< 1.0			
Zr	178.5	7.8	173.0	184.0	18.3	6.6	11.0	27.0	14.0	5.7	5.0	21.0
Be	2.5	0.7	2.0	3.0	< 1.0				< 1.0			
V	122.0				13.0	3.2	10.0	17.0	25.6	22.2	5.0	84.3
Ni	66.5	31.0	44.5	88.4	7.9	2.3	5.3	10.2	10.0	8.3	2.8	33.0
Cu	38.2	14.4	28.0	48.3	13.0	5.5	5.7	18.9	7.0	4.0	0.5	10.9
Zn	25.8	25.7	7.6	44.0	< 1.0				13.5	12.3	0.5	47.4
Ga	25.5	2.8	23.6	27.5	2.0	0.7	1.0	2.6	< 1.0			
Ge	2.7	0.2	2.6	2.9	< 0.5				1.8	0.7	< 0.5	3.2
Rb	201.1	37.5	174.6	227.6	10.0	7.1	4.4	19.4	< 1.0			
Nb	11.1	0.7	10.6	11.6	0.8	0.3	0.4	1.0	0.8	0.5	0.1	1.6
Mo	< 2.0				< 2.0				< 2.0			
Ag	< 0.3				< 0.3				< 0.3			
In	< 0.1				< 0.1				< 0.1			
Sn	3.3	0.4	3.0	3.6	< 1.0				< 1.0			
Cs	6.8	2.7	4.9	8.7	0.42	0.26	0.14	0.77	< 0.1			
ΣREE	226.6	8.9	220.3	232.8	34.6	8.3	28.6	46.8	14.53	9.2	7.3	39.8
Hf	5.3	0.1	5.2	5.3	0.5	0.2	0.2	0.8	0.12	0.1	< 0.1	0.2
Tl	1.0	0.6	0.6	1.5	0.1	0.1	< 0.1	0.3	< 0.1			
Pb	14.8	10.7	7.3	22.4	2.3	1.6	1.5	4.8				
Bi	1.5	0.8	1.0	2.1	1.3	0.6	1.0	2.3	1.2	2.2	0.1	6.0
Th	20.4	1.9	19.1	21.7	1.8	0.9	0.7	2.6	0.5	0.4	0.1	1.4
U	5.5	1.6	4.4	6.7	0.8	0.3	0.5	1.2	2.1	1.0	1.0	4.5
As	9.3	9.7	2.5	16.2	< 5.0				9.3	9.7	2.5	16.2
Cr	222.1	16.6	210.3	233.8	< 20.0				52.9	47.9	< 20.0	148.0
Sb	2.8	1.7	1.5	4.0	0.5	0.3	0.3	0.8	1.6	1.0	0.2	3.4
Cd	0.7	0.1	0.6	0.8	1.2	0.8	0.2	2.1	2.0	2.2	0.4	6.2
Fe#	0.57	0.26	0.38	0.76	0.18	0.10	0.07	0.29	0.98	0.01	0.98	0.99

Fe_{TOT} expressed as Fe₂O₃. Fe# = (Fe³⁺)/(Fe³⁺ + Fe²⁺)

Table 2 (Continued)

	Quartz Itabirite				Quartz-Carbonate Rocks			
Wt%	Avg	Std	Min	Max	Avg	Std	Min	Max
SiO ₂	41.74	14.49	19.71	61.95	26.61	17.31	6.56	53.28
Al ₂ O ₃	0.18	0.15	0.06	0.52	0.70	0.98	0.08	3.07
Fe ₂ O ₃	55.71	13.54	37.18	76.75	19.74	12.85	5.20	37.08
Fetot	56.50	13.95	37.37	79.34	21.70	11.56	8.32	37.40
FeO	0.71	0.79	0.12	2.33	1.77	1.44	0.29	4.32
MnO	< 0.01				0.38	0.18	0.09	0.66
MgO	0.14	0.25	0.01	0.80	10.64	6.09	1.79	18.44
CaO	0.46	0.58	0.06	1.69	15.08	8.26	2.98	25.87
Na ₂ O	< 0.01				0.05	0.04	0.01	0.10
K ₂ O	< 0.01				0.03	0.04	0.01	0.10
TiO ₂	< 0.01				0.05	0.08	0.00	0.26
P ₂ O ₅	0.13	0.09	0.03	0.32	0.06	0.05	0.02	0.17
Ctot					7.58	2.54	4.80	9.80
Cgrap					< 0.05			
Corg					< 0.05			
CO ₂					27.78	9.29	17.60	35.90
S	< 0.001				< 0.001			
LOI	0.59	0.78	< 0.02	2.23	23.79	13.05	4.51	39.83
ppm								
Ba	15.4	6.4	5.0	21.0	7.3	3.9	4.0	16.0
Sr	5.0	2.8	1.0	8.0	24.8	12.9	8.0	41.0
Y	3.9	1.4	1.0	6.0	4.6	2.3	3.0	9.0
Sc	< 1.0				< 1.0			
Zr	12.0	4.6	7.0	20.0	13.4	9.3	4.0	35.0
Be	< 1.0				< 1.0			
V	22.6	16.2	2.5	52.0	8.9	9.9	2.5	32.4
Ni	10.5	4.6	4.7	20.0	13.6	10.6	2.8	36.8
Cu	< 1.0				2.8	3.1	< 1.0	9.1
Zn	2.4	1.8	0.5	5.2	7.5	8.1	0.5	21.0
Ga	< 1.0				< 1.0			
Ge	3.6	1.2	2.4	6.3	1.9	1.7	0.3	5.2
Rb	< 1.0				< 1.0			
Nb	0.8	0.8	0.3	2.9	0.7	0.5	0.1	1.8
Mo	< 2.0				< 2.0			
Ag	< 0.3				< 0.3			
In	< 0.1				< 0.1			
Sn	< 1.0				< 0.1			
Cs	< 0.1				< 0.1			
ΣREE	8.2	3.3	4.1	13.9	9.1	3.1	4.7	15.2
Hf	< 0.1				0.2	0.1	< 0.1	0.5
Tl	< 0.1				< 0.1			
Pb	< 3.0				4.1	4.2	1.5	13.7
Bi	< 0.1				< 0.1			
Th	0.1	0.1	0.03	0.4	0.6	0.5	< 0.1	1.8
U	1.6	0.7	0.9	3.0	1.1	0.5	0.4	2.1
As	9.7	4.3	2.5	15.6	5.8	6.0	< 5.0	19.7
Cr	< 20.0				< 20.0			
Sb	2.8	0.5	1.6	3.3	1.1	0.8	0.3	2.5
Cd	3.0	1.8	0.8	5.5	1.5	1.1	0.4	2.8
Fe#	0.99	0.01	0.97	1.00	0.84	0.17	0.57	0.99

Fe_{TOT} expressed as Fe₂O₃. Fe# = (Fe³⁺)/(Fe³⁺ + Fe²⁺)

Table 2 – (Continued)

	Dolomite-Rich Band				Iron-Rich Band			
Wt%	Avg	Std	Min	Max	Avg	Std	Min	Max
SiO ₂	0.73	0.80	0.14	2.31	0.91	0.25	0.62	1.27
Al ₂ O ₃	0.33	0.37	0.07	1.02	0.28	0.13	0.10	0.47
Fe ₂ O ₃	10.93	7.42	4.49	23.92	77.88	8.32	65.04	84.77
Fetot	11.74	7.46	6.15	25.00	78.23	8.24	65.57	85.13
FeO	0.73	0.45	0.19	1.49	0.32	0.09	0.21	0.48
MnO	0.50	0.10	0.32	0.62	0.12	0.06	0.06	0.20
MgO	18.50	1.51	15.99	19.73	4.11	1.60	2.92	6.51
CaO	26.19	2.09	22.62	28.40	5.45	2.52	3.08	9.18
Na ₂ O	0.05	0.09	0.01	0.23	< 0.01			
K ₂ O	0.06	0.06	0.01	0.13	0.02	0.02	0.01	0.06
TiO ₂	< 0.01				< 0.01			
P ₂ O ₅	0.06	0.08	0.02	0.22	0.12	0.07	0.04	0.20
S	< 0.01				< 0.01			
LOI	40.98	3.64	34.51	43.91	9.91	4.25	6.07	16.30
ppm								
Ba	20.7	11.8	7.0	37.0	11.2	2.1	8.0	14.0
Sr	46.2	16.2	29.0	74.0	12.8	3.9	8.0	19.0
Y	9.5	2.6	5.0	13.0	4.7	1.4	3.0	6.0
Sc	< 1.0				< 1.0			
Zr	8.0	4.6	1.0	15.0	14.7	0.5	14.0	15.0
Be	< 1.0				< 1.0			
V	10.2	6.4	< 5.0	20.2	36.3	42.1	13.0	121.0
Ni	7.3	3.1	2.6	10.9	15.1	5.5	9.8	25.2
Cu	5.2	3.7	1.8	11.6	< 1.0			
Zn	7.4	5.2	< 1.0	15.0	12.9	1.2	11.6	14.3
Ga	< 1.0				0.8	0.5	< 1.0	1.5
Ge	< 0.5				3.6	0.7	2.6	4.5
Rb	< 1.0				1.2	1.3	< 1.0	3.8
Nb	0.9	0.3	0.6	1.4	0.4	0.2	< 0.2	0.7
Mo	< 2.0				1.5	1.2	< 2.0	3.9
Ag	< 0.3				0.4	0.2	< 0.3	0.6
In	< 0.1				< 0.1			
Sn	< 1.0				< 1.0			
Cs	< 0.1				0.2	0.3	< 0.1	0.8
ΣREE	18.8	8.4	11.8	33.9	9.6	1.1	8.2	10.8
Hf	< 0.1				< 0.1			
Tl	< 0.1				< 0.1			
Pb	7.0	2.4	< 3.0	9.4	< 3.0			
Bi	< 0.1				< 0.1			
Th	0.8	0.8	0.2	2.4	0.2	0.1	0.1	0.4
U	1.7	0.6	0.9	2.4	2.1	0.7	1.4	3.0
As	4.8	2.0	< 5.0	7.1	6.5	4.2	< 5.0	13.8
Cr	23.5	19.4	< 20.0	60.0	< 20.0			
Sb	1.5	1.7	0.3	4.9	1.3	0.5	0.5	1.8
Cd	0.4	0.2	0.01	0.7	4.6	1.1	2.8	6.0
Fe#	0.91	0.09	0.73	0.97	1.00	0.00	0.99	1.00

Fe_{TOT} expressed as Fe₂O₃. Fe# = (Fe³⁺)/(Fe³⁺ + Fe²⁺)

Table 3 – Average Rare Earth Element Composition

Litho	Seric.Phyl. (n = 2)	Argil. Dol. ⁽¹⁾ (n = 4)	Dolom. Itab. ⁽²⁾ (n = 9)	Quartz Itab. (n = 8)	Dolomite (Transition to Gandarela Fm (n = 9)	Iron-Rich Band (n = 6)	Dolomite- Rich Band (n = 6)
ppm							
La	49.09	6.24	2.65	1.40	1.35	1.85	3.13
Ce	101.36	13.34	4.21	2.30	2.96	3.00	6.24
Pr	11.00	1.56	0.53	0.33	0.34	0.39	0.76
Nd	38.42	6.23	2.40	1.64	1.57	1.71	3.41
Sm	7.23	1.47	0.57	0.44	0.39	0.39	0.77
Eu	1.65	0.58	0.22	0.15	0.13	0.14	0.32
Gd	5.46	1.31	0.74	0.56	0.52	0.48	0.99
Tb	0.82	0.24	0.13	0.10	0.10	0.08	0.17
Dy	4.54	1.40	0.86	0.58	0.60	0.54	1.11
Y	26.00	8.50	7.44	4.00	4.44	4.67	9.50
Ho	0.97	0.30	0.20	0.12	0.13	0.13	0.25
Er	2.96	0.96	0.63	0.36	0.41	0.43	0.78
Tm	0.41	0.14	0.10	0.05	0.06	0.07	0.11
Yb	2.63	0.89	0.62	0.31	0.36	0.42	0.71
Lu	0.44	0.14	0.10	0.05	0.06	0.07	0.12
ΣREE	226.55	34.61	13.86	8.35	8.91	9.63	18.76
La/Yb _{PAA}	1.38	0.51	0.27	0.35	0.31	0.32	0.34
La/Nd _{PAA}	1.15	0.88	0.85	0.88	0.79	0.98	0.82
Ce/Ce* _{PAA}	1.01	0.99	0.86	0.80	1.01	0.82	0.89
Eu/Eu* _{PAA}	1.24	1.91	1.60	1.49	1.35	1.57	1.74
Y/Y* _{PAA}	0.99	1.07	1.63	1.33	1.35	1.40	1.52
Pr/Pr* _{PAA}	1.04	1.01	1.00	1.00	0.93	1.01	1.00
La/Sm _{PAA}	1.01	0.62	0.61	0.54	0.54	0.69	0.60
Sm/Yb _{PAA}	1.39	0.83	0.45	0.70	0.57	0.47	0.58
Sm/Yb	2.74	1.62	0.89	1.38	1.11	0.93	1.15
Y/Ho	26.78	28.83	42.66	36.23	35.81	36.04	38.89

(1) Excluded samples M138 and M139 (metachert). (2) Excluded samples M4 and M7 (see text for explanation)

Ranges and stratigraphic variation of major elements

The major element composition of the rocks examined is clearly related to the lithological group that they belong to (Fig. 7). This is best observed by plotting the chemical analyses as function of stratigraphy (Fig. 13a). The compositional variation along the stratigraphy within each individual group is less obvious. FeO and TiO₂ contents are higher in the argillaceous dolomite, but significantly reduced towards the contact with the dolomitic itabirite where they remain approximately constant. The CaO and MgO contents are reduced towards the contact with the quartz itabirite, while the Fe₂O₃ content is increased. P₂O₅ contents increase from the base towards the middle of the quartz itabirite, but this trend can be obliterated by the high P₂O₅ content of sample P3-23.

SiO₂, Al₂O₃ and K₂O are the major constituents of the sericitic phyllite with average contents of 63.3%, 18.6% and 5.9% respectively. This rock is also characterized by high TiO₂ (average of 0.8%) and low CaO contents (average of 0.1%).

The argillaceous dolomite group exhibits the greatest compositional variation of major elements when compared with other lithological groups. This major element variation is attributed to the presence of lenses of metachert and quartz itabirite analyzed with the dolomite. CaO (average of 24.4% ranging from 22.6% to 25.4%) and MgO (average of 15.6% ranging from 14.8% to 16.7%) are the main constituents together with SiO₂, which ranges from 4.8% to 19.2% (average of 13%). Loss on ignition (LOI) is high (average of 38.4%) ranging from 35.7% to 39.8%. This sample group has higher contents of Al₂O₃ than the itabirite and carbonate-rocks groups (average of 1.3%), but an order of magnitude less Al₂O₃ than the sericitic phyllite. It is also characterized by the highest weight percent FeO of all sample groups, with an average 4.3 % FeO and ranging from 3.3 % to 5.5% FeO. The organic carbon content of this group, although very low (average of 0.1%), was the highest of all studied groups.

Bulk analysis indicates dolomitic itabirite has the highest iron contents among all chemically classified groups. Iron contents range from 39.7% to 67.6% Fe₂O₃ and average 48.9% Fe₂O₃. CaO and MgO contents average 14.4% and 10.3%, respectively. LOI produced by loss of CO₂ from dolomite is highly variable and may be as high as 27 % of the rock weight. SiO₂ contents are very low because samples containing quartz itabirite were not analyzed. Al₂O₃ contents range from < 0.1 and 0.8% (average of 0.3%), and Na₂O, K₂O and TiO₂ contents are very low (average of 0.02%). P₂O₅ contents range from 0.05% to 0.19% and average 0.12%. FeO contents in dolomitic itabirite of the QF are very low (0.4% - 0.9% FeO) when compared to FeO contents of other BIF's world wide. The Fe₂O₃/(Fe₂O₃ + FeO) ratio for the dolomitic itabirite ranges from 0.98 to 0.99, which indicates a very high degree of oxidation.

Chemical analyses of dolomitic and hematitic bands confirm petrographical analyses and show that, although there is a predominance of dolomite or hematite in their respective bands, both minerals are always present. Therein the dolomitic bands exhibit higher contents of CaO, MgO and LOI than the hematitic bands, but with the Fe₂O₃ content reaching up to 24%. Hematitic bands have a Fe₂O₃ content of up to 85% with CaO and MgO contents reaching 9% and 6% respectively. The FeO content of the dolomitic bands range from 0.2% to 1.5% (average of 0.7%), with the Fe₂O₃/(Fe₂O₃ + FeO) ratio ranging between 0.73 and 0.97 (average of 0.91). In the hematitic bands the FeO content ranges from 0.2% to 0.5% (average of 0.3%), with much higher Fe₂O₃/(Fe₂O₃ + FeO) ratios ranging from 0.99 to 1.00. Lower Fe₂O₃/(Fe₂O₃+FeO) ratios

observed in the dolomitic bands indicate the presence of Fe^{++} in the dolomite composition, which is confirmed by EMP analyses. Otherwise the high $\text{Fe}_2\text{O}_3/(\text{Fe}_2\text{O}_3 + \text{FeO})$ ratio observed in hematitic bands confirms the high degree of oxidation of the dolomitic itabirite as indicated petrographically by the significant martitization of magnetite.

Quartz itabirite consists essentially of Fe_2O_3 (average of 55.7 %) and SiO_2 (average of 41.7 %). CaO, MgO and LOI are very low, generally lower than 0.5%. $\text{Fe}_2\text{O}_3/(\text{Fe}_2\text{O}_3 + \text{FeO})$ ratios range from 0.97 to 1.00, which is also an indication of advanced oxidation of this itabirite.

The lithological variation observed at the transition zone from the Cauê to the Batatal Formations is reflected by the major element data. SiO_2 (average of 26.6 %) and Fe_2O_3 (average of 19.7 %) are the main components followed by CaO (average of 15.1 %), MgO (average of 10.6 %) and LOI (average of 23.8 %). Al_2O_3 (average of 0.7 %) and TiO_2 (average of 0.05%) contents are greater than itabirites and comparable to those of argillaceous dolomite.

Ranges and stratigraphic variation of trace elements

The concentration of trace elements in all samples is generally very low < 10 ppm (Fig. 14a, Table 2). When compared to the PAAS contents only the sericitic phyllite shows similar concentrations, except for Sr and As contents, which are much lower (Fig. 14b). The other lithologies are very poor chemical sediments.

The argillaceous dolomite from the base of the Cauê Formation and the dolomite from the transition zone to the Gandarela Formation have very similar trace elements concentrations while the concentrations of the minor elements are much lower than those of the PAAS. The main difference between the PAAS and the argillaceous dolomite are the higher Cu, Rb, Cs, ΣREE and Th (average of 13, 10, 0.4, 35 and 2 ppm, respectively), and lower Zn (< 1 ppm, much lower than that of PAAS) contents of the argillaceous dolomite.

Quartz and dolomitic itabirite contain low concentrations of trace elements when compared with the PAAS, except for Sb (average of 3 ppm) contents, which are higher in the quartz itabirite (Fig. 14b). The Rb, Cs, Hf and Th contents are particularly low in both itabirites. Figure 14c shows the average trace elements contents of quartz itabirite normalized to dolomitic itabirite. The latter is richer in Sr, Y, Cu, Zn, Pb, Th and Cr while the former has higher contents of Sb and Cd.

Figure 13 – Chemostratigraphic variation along the Section 2550E. **A** Major oxide components. **B – C** Trace elements. **D** Selected ratios.

Figure 13 – Chemostratigraphic variation along the Section 2550E. **A** Major oxide components. **B – C** Trace elements. **D** Selected ratios.

Figure 13 – Chemostratigraphic variation along the Section 2550E. A Major oxide components. B – C Trace elements. D Selected ratios.

Figure 13 – Chemostratigraphic variation along the Section 2550E. **A** Major oxide components. **B – C** Trace elements. **D** Selected ratios.

Figure 14d shows the average trace elements contents of the hematitic bands of the dolomitic itabirite normalized to the average contents of the dolomitic bands highlighting any differences between them. The dolomitic bands have higher Ba (2x), Sr (4x), Y (2x), Cu (10x), Nb (2x), Σ REE (2x), Pb (5x) and Th (3x) contents than the hematitic bands. Hematitic bands, otherwise, have higher Zr (2x), V (4x), Ni (2x), Zn (2x), Rb (2x), Cs (4x) and Cd (13x) contents than those of the dolomitic bands.

Unlike the major element chemistry which clearly distinguishes each lithotype, the trace element concentrations are not as clearly indicative of a particular rock type (Fig. 13b-c). However, four major groups of elements show some trend within and between each of the lithotypes. Ni, Nb and Cr concentration are very low throughout the sequence. Cu, Y, Zr, Ba, Σ REE and Th exhibit higher average contents in the argillaceous dolomite; Zn, Sr, and Pb are characteristically associated with dolomitic itabirite, and Cd, Sb, Ge and to a lesser extent As, V and Zr have a strong relation with quartz itabirite.

The distribution of minor elements along the sequence shows a remarkable feature at the passage from dolomitic to quartz itabirite, when contents of the last group mentioned above increase abruptly. After this point the contents of those elements reduce gradually and remain constant along the transition zone to the Gandarela Formation. Another important feature observed in Figure 13d is the abrupt change observed in the $\text{Fe}_2\text{O}_3/(\text{Fe}_2\text{O}_3 + \text{FeO})$ ratio at the transition from argillaceous dolomite to dolomitic itabirite. Less clear, but still remarkable, is the gradual reduction found in the Σ REE, Y and U contents from the base of the dolomitic itabirite towards the top of the transition zone to the Gandarela Formation.

Figure 14 – **A** Average trace element composition of each group studied. **B** Average trace element composition normalized to PAAS. **C** Average trace element composition of quartz itabirite normalized to average composition of dolomitic itabirite. **D** Average trace element composition of dolomite-rich mesoband of dolomitic itabirite normalized to hematite-rich mesoband. La# means Σ REE.

Some linear interelement correlations

The results of some linear interelement correlations of major and trace elements are displayed in Table 4. These element-element correlations include the total dataset for samples of the Cauê Formation (disregarding samples of dolomitic and hematitic bands, Table 4a) and only itabirite samples (Table 4b). We have not included results below or close to detection limit. Some significant interelement correlations are showed in Figure 15.

For the entire set of samples of the Cauê Formation, very positive correlation exists for CaO and MgO ($r=0.99$), LOI ($r=1.00$), MnO ($r=0.91$) and Sr ($r=0.72$), which represent the group of elements present in the dolomite composition. Al_2O_3 correlates very well with TiO_2 ($r=0.93$), Zr ($r=0.76$) and Th ($r=0.89$) and somewhat less well with ΣREE ($r=0.61$). Significant concentrations of Al, Ti, Zr and Th are considered by several authors (e.g. Arora et al., 1995; Beukes et al., 1990; Gnaneshwar Rao and Naqvi, 1995; Horstmann and Hälbig, 1995; Manikyamba, 1998) to indicate a detrital contribution during formation of primary BIF. ΣREE correlates well with Th ($r=0.83$) and Y ($r=0.75$). Fe_{TOT} does not correlate with any element except a weak correlation exists for Fe_{TOT} with Sb ($r=0.66$) and P_2O_5 ($r=0.59$). Considering the great variety of rocks within the set of samples studied, the absence of good linear interelement correlations was expected and only the most significant were outlined. When each group of rocks is studied separately, the differences on the interelement correlations between them (if existent) turn more evident, as is observed in Figure 15.

We used identical interelement correlation tests as above for major and trace elements of itabirites. Dolomitic itabirite shows two complementary compositional poles organized between CaO and Fe_{TOT} . There are very strong positive correlations of CaO with MgO ($r=0.98$) and LOI ($r=0.98$), which reflects the dolomitic signature of the itabirite. Fe_{TOT} shows an antipathetic behavior with this group ($r_{CaO-Fe_{TOT}} = -0.98$) and does not exhibit any correlation with other elements. Al_2O_3 correlates very well with SiO_2 ($r=0.90$), TiO_2 ($r=0.90$), Th ($r=0.96$) and Nb ($r=0.85$), and well with ΣREE ($r=0.72$), and As ($r=0.77$). SiO_2 has good correlations with these same elements and also with Sr ($r=0.77$). Once the content of quartz of the samples of dolomitic itabirite is not relevant, the SiO_2 present in that rock is related with sericite and chlorite and certainly reflects the detritic fraction of the BIF sediments.

In the composition of quartz itabirite there are also two complementary poles organized around SiO_2 and Fe_{TOT} with very strong negative correlation between them ($r=-0.99$). SiO_2 correlates with Sb ($r=0.59$) while Fe_{TOT} correlates well only with Zn ($r=0.80$). CaO correlates

very well with MgO ($r=0.98$), LOI ($r=0.96$), TiO_2 ($r=0.99$) and Th ($r=0.97$), and well with MnO ($r=0.78$), Cu ($r=0.68$), REE ($r=0.80$), Y ($r=0.66$), Zr ($r=0.84$), U ($r=0.81$) and Cr ($r=0.85$). Al_2O_3 reveals a fair correlation with CaO ($r=0.95$), MgO ($r=0.92$), LOI ($r=0.90$), TiO_2 ($r=0.91$), U ($r=0.93$) and Cr ($r=0.95$) and good correlations with MnO ($r=0.66$), Y ($r=0.62$), Zr ($r=0.73$), Cu ($r=0.66$), $\sum\text{REE}$ ($r=0.85$) and Th ($r=0.89$).

High correlations showed by elements that usually correlate well with CaO with those elements usually correlated with Al_2O_3 suggest the presence of two different groups of impurities in the composition of quartz itabirite. The first group consists of chemical impurities characterized by good correlations between CaO, MgO, LOI and MnO and related to dolomite. The second group consists of terrigenous impurities represented by micaceous minerals and characterized by fair correlations between Al, Ti, Y, REE, Cr, U and Th.

Table 4a – Linear interelement correlations for all samples of the Cauê and Gandarela Fms.
(n = 34)

	SiO ₂	Al ₂ O ₃	Fe _{TOT}	MnO	MgO	CaO	TiO ₂	P ₂ O ₅	LOI	Ba	Sr	Y	Sc	Zr	V
Al ₂ O ₃	-0.19														
Fe _{TOT}	-0.06	-0.56													
MnO	-0.59	0.47	-0.66												
MgO	-0.67	0.58	-0.70	0.89											
CaO	-0.64	0.53	-0.73	0.91	0.99										
TiO ₂	-0.23	0.93	-0.45	0.42	0.54	0.46									
P ₂ O ₅	0.10	-0.31	0.59	-0.49	-0.50	-0.53	-0.25								
LOI	-0.64	0.55	-0.73	0.91	0.99	1.00	0.48	-0.53							
Ba	-0.02	0.14	0.16	-0.11	-0.13	-0.12	0.01	0.06	-0.11						
Sr	-0.71	0.33	-0.25	0.68	0.72	0.67	0.39	-0.09	0.67	-0.02					
Y	-0.67	0.49	-0.10	0.49	0.56	0.52	0.44	0.11	0.53	0.32	0.63				
Sc	-0.22	0.91	-0.61	0.54	0.62	0.58	0.86	-0.34	0.60	0.05	0.40	0.49			
Zr	-0.36	0.76	-0.10	0.26	0.36	0.29	0.73	-0.05	0.30	0.21	0.35	0.50	0.63		
V	-0.21	0.12	0.37	-0.18	-0.11	-0.16	0.17	0.15	-0.14	0.13	-0.01	0.21	-0.03	0.32	
Ni	-0.08	0.43	0.05	-0.03	0.06	-0.02	0.58	-0.08	0.00	-0.17	0.02	0.09	0.28	0.42	0.45
Cu	-0.07	0.36	-0.31	0.21	0.26	0.29	0.13	-0.30	0.29	0.32	0.12	0.32	0.32	0.30	-0.07
Zn	-0.41	0.15	0.27	0.04	0.13	0.05	0.31	0.11	0.07	-0.20	0.31	0.21	0.09	0.29	0.63
Rb	-0.10	0.73	-0.53	0.38	0.44	0.46	0.48	-0.34	0.47	0.42	0.12	0.39	0.63	0.54	-0.04
Nb	-0.05	0.38	-0.08	0.08	0.13	0.07	0.37	0.00	0.09	0.26	0.28	0.31	0.32	0.48	0.31
Cs	-0.21	0.62	-0.31	0.27	0.39	0.36	0.46	-0.17	0.37	0.29	0.30	0.50	0.59	0.53	0.03
ΣREE	-0.35	0.61	-0.43	0.56	0.54	0.57	0.41	-0.13	0.58	0.33	0.43	0.75	0.67	0.47	0.02
Hf	-0.19	0.85	-0.63	0.51	0.60	0.60	0.68	-0.45	0.61	0.22	0.25	0.40	0.76	0.63	0.03
Pb	-0.26	-0.11	0.16	0.08	0.08	0.06	-0.06	-0.02	0.05	0.01	0.47	0.06	-0.06	0.08	-0.22
Th	-0.34	0.87	-0.57	0.62	0.65	0.64	0.69	-0.34	0.65	0.27	0.45	0.61	0.84	0.68	0.05
U	-0.22	-0.10	0.48	-0.19	-0.19	-0.24	-0.03	0.36	-0.22	0.02	0.09	0.33	-0.16	0.16	0.65
As	0.35	-0.21	0.41	-0.44	-0.56	-0.56	-0.21	0.45	-0.56	-0.05	-0.21	-0.08	-0.23	-0.05	0.15
Cr	-0.30	-0.05	0.15	0.05	0.12	0.08	0.04	0.15	0.08	-0.04	0.42	0.22	0.05	-0.01	0.00
Sb	0.36	-0.39	0.66	-0.71	-0.74	-0.76	-0.34	0.44	-0.75	0.14	-0.52	-0.21	-0.50	-0.21	0.42

	Ni	Cu	Zn	Rb	Nb	Cs	ΣREE	Hf	Pb	Th	U	As	Cr
Cu	-0.19												
Zn	0.63	-0.15											
Rb	0.03	0.53	-0.18										
Nb	0.31	0.13	0.27	0.24									
Cs	-0.01	0.36	-0.04	0.76	0.42								
ΣREE	-0.12	0.50	-0.06	0.66	0.26	0.57							
Hf	0.26	0.43	0.07	0.84	0.24	0.59	0.67						
Pb	-0.07	0.16	0.16	-0.16	0.20	0.07	-0.07	-0.17					
Th	0.11	0.49	0.06	0.85	0.36	0.76	0.83	0.88	-0.03				
U	0.33	-0.15	0.60	-0.22	0.34	-0.01	0.03	-0.14	0.00	-0.09			
As	0.19	-0.14	0.13	-0.16	0.06	-0.05	-0.02	-0.23	0.06	-0.17	0.43		
Cr	-0.07	-0.02	0.46	-0.19	0.02	-0.05	0.08	-0.02	0.29	0.02	0.30	0.00	
Sb	0.30	-0.34	0.13	-0.35	0.03	-0.29	-0.38	-0.43	-0.16	-0.50	0.58	0.68	-0.15

Table 4b – Linear interelement correlations for all samples of itabirites
(n = 19)

	SiO ₂	Al ₂ O ₃	Fe _{TOT}	MnO	MgO	CaO	TiO ₂	P ₂ O ₅	LOI	Ba	Sr	Y	Sc	Zr	V
Al ₂ O ₃	-0.26														
Fe _{TOT}	-0.08	-0.19													
MnO	-0.87	0.42	-0.31												
MgO	-0.89	0.33	-0.38	0.95											
CaO	-0.90	0.30	-0.37	0.95	1.00										
TiO ₂	-0.43	0.90	-0.05	0.55	0.43	0.40									
P ₂ O ₅	0.17	0.01	0.09	-0.12	-0.20	-0.19	-0.09								
LOI	-0.89	0.32	-0.38	0.95	1.00	1.00	0.42	-0.21							
Ba	0.35	-0.27	-0.04	-0.26	-0.31	-0.31	-0.20	-0.20	-0.31						
Sr	-0.76	0.52	-0.35	0.87	0.86	0.85	0.59	0.01	0.85	-0.20					
Y	-0.67	0.56	-0.14	0.75	0.68	0.67	0.64	0.20	0.68	-0.19	0.76				
Sc	-0.26	0.76	-0.19	0.42	0.34	0.30	0.74	0.10	0.32	-0.10	0.62	0.63			
Zr	-0.32	0.70	0.10	0.39	0.26	0.24	0.65	0.02	0.24	-0.15	0.37	0.41	0.42		
V	-0.09	0.37	0.25	0.02	-0.04	-0.04	0.39	-0.17	-0.03	-0.29	-0.09	0.00	-0.01	0.34	
Ni	0.00	0.05	0.26	-0.07	-0.13	-0.13	0.17	-0.24	-0.11	-0.39	-0.30	-0.15	-0.19	-0.07	0.60
Cu	-0.35	0.57	-0.34	0.53	0.48	0.47	0.52	-0.31	0.46	0.02	0.53	0.30	0.36	0.67	-0.07
Zn	-0.50	0.43	0.18	0.44	0.38	0.38	0.61	-0.16	0.39	-0.48	0.34	0.25	0.14	0.32	0.61
Rb	-0.08	0.55	-0.19	0.12	0.17	0.14	0.39	-0.14	0.15	0.06	0.20	0.33	0.58	0.32	-0.04
Nb	0.10	0.45	-0.44	0.13	0.11	0.09	0.35	-0.08	0.10	0.03	0.21	0.16	0.35	0.36	0.20
Cs	-0.17	0.61	-0.22	0.22	0.27	0.24	0.44	-0.08	0.25	-0.05	0.36	0.41	0.71	0.28	-0.08
ΣREE	-0.35	0.75	-0.29	0.60	0.46	0.43	0.77	0.24	0.45	-0.08	0.74	0.80	0.84	0.50	0.01
Hf	-0.24	0.67	-0.07	0.34	0.25	0.23	0.84	-0.27	0.25	-0.04	0.35	0.29	0.47	0.40	0.33
Pb	-0.47	0.38	-0.35	0.51	0.61	0.59	0.39	-0.16	0.59	-0.12	0.70	0.28	0.42	0.24	-0.32
Th	-0.47	0.90	-0.24	0.62	0.56	0.52	0.86	-0.03	0.54	-0.19	0.78	0.69	0.87	0.63	0.14
U	-0.15	0.64	-0.09	0.23	0.17	0.16	0.63	0.04	0.18	-0.43	0.13	0.44	0.27	0.33	0.59
As	0.41	0.44	-0.13	-0.20	-0.32	-0.34	0.34	0.19	-0.32	-0.27	-0.10	0.04	0.40	0.00	0.22
Cr	-0.45	0.31	-0.08	0.44	0.46	0.46	0.44	0.07	0.44	-0.10	0.68	0.48	0.33	0.12	-0.14
Sb	0.59	-0.18	0.09	-0.58	-0.60	-0.59	-0.23	-0.04	-0.57	-0.05	-0.68	-0.34	-0.29	-0.42	0.36

	Ni	Cu	Zn	Rb	Nb	Cs	ΣREE	Hf	Pb	Th	U	As	Cr
Cu	-0.34												
Zn	0.67	0.15											
Rb	-0.23	0.33	-0.10										
Nb	0.15	0.19	0.19	0.43									
Cs	-0.26	0.33	-0.02	0.96	0.38								
ΣREE	-0.23	0.41	0.17	0.30	0.35	0.40							
Hf	0.28	0.43	0.60	0.14	0.23	0.16	0.50						
Pb	-0.32	0.64	0.23	0.28	0.12	0.43	0.32	0.38					
Th	-0.14	0.62	0.38	0.58	0.43	0.70	0.82	0.57	0.61				
U	0.54	0.07	0.57	0.16	0.36	0.14	0.41	0.55	-0.15	0.38			
As	0.37	-0.09	0.14	0.02	0.20	0.08	0.37	0.33	-0.18	0.24	0.54		
Cr	-0.20	0.39	0.36	-0.06	0.01	0.09	0.46	0.39	0.63	0.48	0.09	0.05	
Sb	0.55	-0.60	-0.05	-0.20	-0.05	-0.27	-0.31	-0.07	-0.76	-0.47	0.43	0.57	-0.46

Figure 15 – Inter-element correlations. Note a good correlation between Al_2O_3 with TiO_2 , ΣREE and Th for all samples of the Itabira Group, which suggests participation of terrigenous components during its deposition.

REE Results

REE and Y abundances (REEY) of all samples are listed in Appendix 1 and averages of each major lithological group are presented in Table 3. PAAS normalized REEY patterns of all samples are also divided into the five groups shown in Figure 16a-h. With the exception of sericitic phyllite, all lithologies are characterized by depleted Σ REE (ranging from 8-35 ppm).

The sericitic phyllite shows an average Σ REE of 227 ppm which is slightly higher than that of the PAAS (185 ppm; McLennan, 1989). Although they show a LREE enrichment ($\text{La/Yb}=1.38$), the contents of heavy rare earth elements (HREE) are fairly close to those of the PAAS, plotting as a flat pattern (Fig. 16e). The REEY pattern of the sericitic phyllite is identical to that of the Post-Archean shale as demonstrated when these rocks are plotted against C-1 chondrite (Fig. 16f), except for a slightly more positive Eu anomaly for the PAAS (average $\text{Eu/Eu}^*=1.24$), possibly related to the presence of feldspar in the phyllite.

The argillaceous dolomite samples show depleted Σ REE (average of 35 ppm), but less depleted than that of the overlying itabirite and dolomite. All samples display a similar REEY pattern (Fig. 16c) with HREE enrichment ($\text{La/Yb}=0.52$), middle rare earth element (MREE) enrichment ($\text{La/Sm}=0.76$) and no fractionation of HREE ($\text{Sm/Yb}=1.03$). They show strongly positive Eu anomalies ($\text{Eu/Eu}^*=1.84$), but do not exhibit Ce or Y anomalies, except for sample M139 which displays $\text{Ce/Ce}^*=0.90$.

Samples of dolomitic itabirite show an average Σ REE of 14 ppm with concentration ranging between 7 ppm to 40 ppm. REEY patterns of all samples are very similar (Fig. 16d) and show HREE enrichment ($\text{La/Yb}=0.27$). La/Sm ($=0.62$) and Sm/Yb ($=0.45$) ratios for dolomitic itabirite indicate enrichment of heavier REE elements in both the light and heavy REE categories. Sample MAC06 shows a strong La anomaly. Significantly higher concentrations of REE and Al_2O_3 and TiO_2 suggest that this La anomaly is a result of contamination by terrigenous material. All samples display strong positive Eu ($\text{Eu/Eu}^*=1.65$) and Y ($\text{Y/Y}^*=1.59$) anomalies and negative Ce anomalies, which range from 0.74 to 0.97 (Ce/Ce^*).

Dolomite-rich bands of dolomitic itabirite are less depleted (average Σ REE of 19 ppm) than iron-rich bands (average Σ REE of 10 ppm). The REEY patterns of both bands are similar (Fig. 16g-h) and exhibit the same HREE enrichment of the bulk samples. The major differences between the bands are the more pronounced negative Ce anomaly in the iron-rich bands ($\text{Ce/Ce}^*=0.82$) and the less pronounced HREE enrichment in the dolomite-rich bands ($\text{Sm/Yb}=0.58$) when compared to the iron-rich bands ($\text{Sm/Yb}=0.47$).

The samples of quartz itabirite are the most depleted of the whole set of samples studied (average ΣREE of 8 ppm). They exhibit strong heavy element enrichment within the group of LREE ($\text{La}/\text{Sm}=0.54$) similar to that shown by the dolomitic itabirite, but with a depletion of the heavy elements within the group of the HREE (Fig. 16a). This is the major distinguishing feature of the REEY patterns for both compositional types of itabirites. Positive Eu (average $\text{Eu}/\text{Eu}^*=1.49$) and Y ($\text{Y}/\text{Y}^*=1.33$) anomalies, and negative Ce anomalies (ranging between 0.60 to 0.93) occur in all samples.

Quartz-carbonate rocks of the transition zone to the Gandarela Formation are also, like the quartz itabirite, very depleted in REE. (average ΣREE of 9 ppm). All but one sample (P3_170) show similar REEY pattern (Fig. 16b). There is an enrichment of heavier elements within the group of the LREE ($\text{La}/\text{Sm}=0.54$), while HREE shows a relatively flat pattern. All the samples exhibit positive Eu and Y anomalies, but they are not as pronounced as those of the quartz itabirite. Ce does not display an anomaly; Ce/Ce^* ranges from 0.93 to 1.16.

$\text{Eu}/\text{Eu}^*_{\text{PAAS}}$ ratios decrease continuously up the sequence, ranging from 2.21 in sample M132 of the argillaceous dolomite to 1.35 in sample P196 of the dolomite of the transition zone (Fig. 13d), with a small shift at the transition from quartz itabirite to quartz-carbonate rocks. The $\text{Y}/\text{Y}^*_{\text{PAAS}}$ ratios increase from the argillaceous dolomite up to the transition zone from the dolomitic to the quartz itabirite, then keeping a lower and almost constant value from the quartz itabirite. $\text{Ce}/\text{Ce}^*_{\text{PAAS}}$ ratios show a decreasing trend up to the contact between quartz itabirite and quartz-carbonate rocks, and then increase from this point on.

Figure 16 – PAAS-normalized REE data. **A** Quartz itabirite. **B** Quartz-dolomite rocks of the transition zone to the Gandarela Formation.

Figure 16 – PAAS-normalized REE data. **C** Argillaceous dolomite. **D** Dolomitic itabirite. **E** Sericitic phyllite. **F** Chondrite C2-normalized REE data. **G-H** PAAS-normalized REE data of dolomitic itabirite: (**G**) hematitic band; (**H**) dolomitic band.

C and O Isotopes

The forty five analysed dolomite samples of the dolomitic itabirite of the Cauê Formation show negative $\delta^{13}\text{C}$ values varying from -2.5‰ to -0.8‰ while the oxygen isotope data displays $\delta^{18}\text{O}$ values varying from -12.4‰ to -8.5‰ (Table 5). In a stratigraphic sense, there is a depletion in the ^{13}C content of dolomitic itabirite at the base of the sequence, with ferruginous dolomite exhibiting lower contents (Fig. 12). Dolomitic itabirite becomes less depleted in ^{13}C up to the middle of the sequence, where there is another depletion trend. $\delta^{13}\text{C}$ keeps a lower and relatively constant carbon-13 isotopic composition from approximately the middle to the top of the dolomitic itabirite. In contrast to ^{13}C , ^{18}O contents show a different trend. ^{18}O increases from the base of dolomitic itabirite up to the middle of the sequence, and then continuously decrease up sequence. Close to the top of the dolomitic itabirite, dolomite becomes more enriched in the heavier isotope, again. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ exhibit similar trends along the sequence, with $\delta^{18}\text{O}$ showing small shifts, maybe due to its three order of magnitude higher sensitivity to alteration in diagenetic environment than $\delta^{13}\text{C}$ (Banner and Hanson, 1990).

Figure 12 displays the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data obtained by Bekker et al. (2003) in stromatolitic dolomites in the upper part of the Gandarela Formation. $\delta^{18}\text{O}$ values of the dolomitic itabirite and those of the stromatolitic itabirite are similar and exhibit similar orders of variation. Most samples of the Cauê Formation and Gandarela Formation have $\delta^{18}\text{O}$ values above -10.5 per mil consistent with those found in well-preserved Paleoproterozoic carbonate successions (Bekker et al., 2003; Veizer et al., 1992; Veizer et al., 1990; Veizer et al., 1989). ^{13}C contents of the dolomitic itabirite are lower than those of dolomite of the Gandarela Formation. The most negative $\delta^{13}\text{C}$ values occur at the base of the sequence (-2.4 per mil), grading up-section into values around -1.7 per mil. Red dolomite sampled by Bekker et al. (2003) at the base of the Gandarela Formation in the Gandarela Farm (Fig. 1) displays $\delta^{13}\text{C}$ values ranging from -1.3 to -1.0 per mil. These authors found positive $\delta^{13}\text{C}$ values (around $+0.4$ per mil) for dolomite at the top of the Gandarela Formation. Carbon isotopic data of the Cauê Formation obtained in this study combined with data for dolomite rocks of the Gandarela Formation indicates a positive trend (with slight variations) in $\delta^{13}\text{C}$ values within the rocks of the Minas Supergroup. Positive carbon isotope excursions in seawater composition are generally interpreted as indicating high relative burial rates of organic matter and accompanying increase in the oxygen production (Derry et al., 1992; Karhu and Holland, 1996; Kaufman et al., 1997). The record of a positive trend in the $\delta^{13}\text{C}$ values during the interval of deposition of the Itabira

Group between 2.6 and 2.4 Ga is relevant to our current understanding of global climates during the Paleoproterozoic.

Table 5 – C and O Isotope Composition of Dolomite in Dolomitic Itabirite

Sample	North Coordinate (m)	$\delta^{18}\text{O}$ (‰) PDB	$\delta^{13}\text{C}$ (‰) PDB
MAC-1	-810	-10.33	-0.97
MAC-2	-808	-10.42	-0.75
MAC-3	-807	-12.05	-2.17
MAC-4	-804	-11.06	-2.28
MAC-6	-797	-10.53	-2.30
MAC-8	-793	-9.12	-2.31
MAC-9	-791	-10.05	-1.67
MAC-11	-783	-9.75	-1.76
MAC-12	-775	-10.59	-2.34
MAC-14	-770	-8.50	-2.45
MAC-15	-768	-10.36	-1.95
MAC-16	-765	-9.17	-2.14
MAC-18	-752	-10.44	-1.83
MAC-19	-745	-9.23	-1.79
MAC-20	-742	-11.18	-1.58
MAC-21	-734	-9.34	-1.14
MAC-23	-722	-9.65	-1.21
MAC-24	-717	-9.61	-1.30
MAC-25	-709	-8.86	-0.79
MAC-26	-696	-10.60	-1.46
MAC-27	-692	-10.32	-1.25
MAC-28	-680	-11.57	-1.64
MAC-29	-669	-10.90	-1.71
MAC-30	-660	-12.05	-1.55
MAC-32	-647	-10.85	-1.51
MAC-34	-640	-11.61	-1.56
MAC-36	-629	-12.21	-1.71
MAC-37	-619	-12.34	-1.68
MAC-38	-600	-12.32	-1.71
MAC-39	-587	-11.07	-1.71
MAC-40	-577	-11.49	-1.92
MAC-42	-567	-12.39	-1.79
MAC-43	-562	-10.49	-1.77
MAC-45	-547	-10.74	-2.20
MAC-46	-541	-9.73	-1.75
MAC-47	-535	-9.87	-1.65
MAC-48	-527	-8.76	-1.56
MAC-49	-524	-10.01	-1.84
MAC-50	-519	-9.41	-1.67
MAC-51	-512	-8.63	-1.52
MAC-52	-507	-10.91	-1.74
MAC-53	-505	-11.33	-1.76

Comparison with other iron-formations

The average major and trace elements contents of the dolomitic and quartz itabirite of QF are compared with BIFs of the Carajás Formation (Lindenmayer et al., 2001; Macambira and Schrank, 2002), the Kaapvall Supergroup (Klein and Beukes, 1992) and the Hamersley Group (Klein and Beukes, 1992) in Figure 17. The averages were recalculated without the LOI, according to Klein and Beukes (1992), to allow for comparisons between metamorphic and unmetamorphic BIFs. These authors assume that metamorphic reactions are essentially isochemicals for major elements except for H₂O and CO₂.

A very remarkable feature of dolomitic and quartz itabirites that is observed only in the QF and Carajás BIFs, which distinguishes them from the others BIFs, is their high Fe₂O₃ and low FeO contents (Fig. 17a). The Fe₂O₃/FeO ratio in BIFs from Issua, Transvaal and Hamersley is lower than or close to 1, while in Brazilian BIFs this ratio is much higher reaching an average of 39 in Carajás and values around 70 in itabirites of the QF.

The dolomitic itabirite shows a chemical composition that is very different from the others BIFs as a result of its different mineralogical composition. The SiO₂ content of this rock is very low due to the almost complete absence of quartz. CaO and MgO, however, showed the highest contents of all BIFs considered, which reflects the presence of dolomite. The other major elements are similar to those observed in other BIFs. The quartz itabirite shows a very simple major element composition that consists basically of SiO₂ and Fe₂O₃, with TiO₂, CaO, MgO, MnO, Na₂O, K₂O and P₂O₅ contents being lower than those of the other BIFs found worldwide. The only difference observed is in the Al₂O₃ content, which, although very low, is higher in QF BIF than BIFs of the Transvaal but similar to Carajás BIFs.

A comparison of trace element composition in BIF is problematic because there is no data available in the literature of BIFs for a number of elements presented here. Figure 17b shows that the trace elements composition of itabirites is similar to that of other BIFs found worldwide. All of them contain very low trace element concentrations when compared with PAAS (Fig. 17c). The Ni, Cu, Zn and Rb contents of the dolomitic and quartz itabirite are lower and U contents are higher than other BIF's.

Figure 18 shows the C and O isotopic composition of dolomitic itabirite is distinct when compared to other BIFs considered above. The values of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are quite similar to those obtained by Rivers (1998) for carbonates of the Wittenoom Formation of the Hamersley Basin, and by Sial et al. (2000) and Bekker et al. (2003) to stromatolitic dolomites of the Gandarela Formation of the Minas Basin. These similarities and the gradual ^{13}C enrichment up-

section from the base of the Cauê Formation to the top of the Gandarela Formation suggest that dolomites of the Cauê Formation preserve the depositional carbon isotope composition, likely reflecting the composition of seawater solutions.

The values of $\delta^{13}\text{C}$ of dolomitic itabirite are slightly lower than those of normal marine carbonates, which are typically characterized by $\delta^{13}\text{C}$ values of c. -1 , but higher than those found for BIFs of the Hamersley and Transvaal basin. The higher depletion of ^{13}C in BIFs of these basins is attributed to their formation in an isotopically depleted water mass (Beukes et al., 1990; Kaufman et al., 1990). According to the models of Beukes et al. (1990) and Becker and Clayton (1972), early Proterozoic oceans were stratified with respect to the isotopic signature of dissolved CO_2 , with a lower ocean water mass depleted in ^{13}C . Upwelling would bring deep, anoxic waters to shelves where siderite with isotopic composition near -5 per mil formed below the chemocline, while limestones with isotopic composition near -1 per mil formed in shallow, near-shore environment. The ^{13}C enrichment from BIFs of the Transvaal basin to BIFs of the Cauê Formation, with intermediate ^{13}C contents in BIFs of the Hamersley basin, suggests variation in the seawater carbon isotopic composition within each of the basins or shelf environments where BIF's were precipitated. BIFs of the Transvaal basin have a higher contribution of light carbon in CO_2 from deep, anoxic seawater, whereas BIF of the Cauê Formation which are enriched in isotopically heavy carbon would have a higher contribution of shallow, oxygenated waters. REE data of the dolomitic itabirite support deposition of BIF in near-shore environments (see discussion below).

Figure 17 - Average major (A) and trace element (B) composition of BIFs of Quadrilátero Ferrífero, Isua, Hamersley, Transvaal and Carajás. C - Trace element composition normalized against PAAS of McLennan (1989), with the exception of Ta, Sb and As contents that were normalized against NASC of Gromet et al. (1984). Data from Isua, Hamersley and Transvaal are from Klein and Beukes (1992). Data from Carajás are from Lindenmayer et al. (2001), with the exception of Pb, Zn, Cu, Sc, and Sb contents that are from Macambira and Schrank (2003).

Figure 18 – Carbon and oxygen isotopes from carbonates of dolomitic itabirite of the Cauê Formation and stromatolitic dolomite of the Gandarela Formation at the Quadrilátero Ferrífero; dolomite and BIFs of the Hamersley basin; and BIFs of the Transvaal basin. Note the close association of dolomitic itabirite carbonates with carbonates of the Gandarela and Wittenoom Formations. Data from the Gandarela Formation are from Sial et al. (2000) and Bekker et al. (2003); from the Hamersley basin are from Rivers (1988) in Taylor et al. (2001); and from the Transvaal basin of Beukes and Klein (1990).

DISCUSSION

Most authors agree that BIFs are chemical sediments formed by the precipitation of iron and silica from solutions consisting of a mixture of seawater with hydrothermal fluids, with various degrees of contamination by terrigenous sediments carried by rivers or winds, or emanated from volcanic activities (e.g. Arora et al., 1995; Kato et al., 1998; Kimberley, 1989; Klein and Beukes, 1989). Hydrothermal fluids would be produced in the convection cells along mid-ocean ridges and back-arc spreading centers, where a fluid rock-interaction takes place in a reducing environment with temperatures reaching $> 300\text{ }^{\circ}\text{C}$ and pH staying between 2 and 4

(Bau and Möller, 1993). Convection currents would transport the hydrothermal fluids mixed with deep seawater up to the continental shelf where they would be precipitated. This model is based on comparisons of the REE signature of BIFs with that of deep hydrothermal deposits. The patterns are essentially the same which show pronounced positive Eu anomalies and depletion in the light REE (Danielson et al., 1992; Derry and Jacobsen, 1990).

The geochemical signature of BIFs helps to understand their depositional paleoenvironment. However, the signature can be masked by a high degree of terrigenous contamination, or obliterated by later diagenetic and metamorphic processes, which would lead to wrongful interpretations. The itabirites of the Cauê Formation are the product of at least two tectonic events and metamorphism to green schist facies. The interpretation of the geochemical data for reconstructing a palaeoenvironmental and depositional model requires analysis to determine how preserved are the primary geochemical signatures. To justify our genetic model below, we discuss how our mineralogical, petrological and geochemical data of the Cauê Formation reflects that of primary BIF.

The question of terrigenous contamination

Bau and Möller (1993) showed the REE in the chemically precipitated component of BIFs is a proxy for the composition of contemporaneous seawater, bringing useful insights into the chemistry of ancient sea water, and the secular variations of the atmosphere-hydrosphere-lithosphere system. These REE patterns, however, are significantly modified by terrigenous contaminants, largely because REE abundances may be more than two orders of magnitude higher in clastic detritus than in seawater precipitates (Arora et al., 1995; Bau, 1993). The interpretation of REE patterns needs, therefore, a very careful monitoring of terrigenous contamination.

In BIFs of the Hamersley and Transvaal shales and lutites are considered clastic contaminants with a primary volcanogenic origin (Beukes et al., 1990; Ewers and Morris, 1981; Morris, 1993). These rocks consist essentially of stilpnomelane, and are chemically distinct from stilpnomelane in their host BIFs by higher contents of Al_2O_3 , TiO_2 , K_2O and Zr (Horstmann and Hälbig, 1995). A positive correlation between the TiO_2 and Al_2O_3 in BIF of the Hamersley Province was interpreted by Ewers and Morris (1981) as indicative of clastic contamination. However, this same relationship was not established by Horstmann and Hälbig (1995) in the Transvaal BIFs.

Itabirites of the Cauê Formation at the Águas Claras mine do not contain interlayered shales or lutite as mentioned above. However, volcanic contribution to the chemical sediments of the Cauê Formation in the QF has very recently been suggested by Suckau et al. (oral information). The aluminous micaceous minerals found both in the argillaceous dolomite and in the dolomite of the transition zone to the Gandarela Formation, sometimes forming thin laminae (Fig. 11h), may be terrigenous. The very strong positive correlation between Al_2O_3 and TiO_2 on the whole set of the samples studied (Fig. 15) suggest contribution of a terrigenous component during deposition of the Cauê Formation, and we suggest the aluminous micaceous minerals observed in all lithologies are the major contaminants. Very low K_2O contents suggest a minimal amount of terrigenous contamination, which is comparable to contamination levels in BIF's of Transvaal basin but lower than that of the Hamersley basin (Fig. 17a).

Bau (1993) suggested that the abundance of elements regarded as immobile in aqueous solution, such as Ti, Zr, Hf, Y, Nb, Ta or Sc should be used to examine for potentially contaminated samples. High concentrations of these elements are unlikely to be derived from seawater and most likely reflect input from terrigenous sources. Bau (1993) found linear relationships between Hf, Th and Sc in variably contaminated BIFs and proposed that a Sc abundance of 2 ppm is a practical limiting value above which a chemical precipitate should be excluded from interpretations using the REE's as a proxy for the chemistry of ancient seawater. This limit corresponds to c. 1 ppm of Th according to his Figure 2b. Figure 19 shows a plot of Sc versus Th abundance of the studied samples. The two phyllite samples are clearly above these critical limits specified by Bau (1993), while the argillaceous dolomite and dolomite of the transition zone to the Gandarela Formation are close or above the critical limits. Two samples of dolomitic itabirite (M4 and M7) are disregarded from our interpretation because they are above critical limits. We conclude from this diagram that clastic contamination of itabirites is negligible for our interpretations using the REE's as a proxy for the chemistry of ancient seawater.

Bau (1996) also shows that in contrast to silicate melt systems, the geochemical twin pairs Zr-Hf and Y-Ho are highly fractionated in aqueous solutions, and do not exhibit a charge-and-radius-controlled (CHARAC) behavior. The geochemical behavior of these elements in aqueous solutions is constrained by their electron configuration, which affects the nature of chemical bonding in its various compounds, hence the stability of its various chemical complexes. In Precambrian and Phanerozoic shales the geochemical behavior of the Zr-Hf and Y-Ho pairs is charge-and-radius-controlled, and therefore permits discrimination of clastic and

chemical sediments and the degree of contamination. Figure 20 shows a plot of Zr/Hf versus Y/Ho commonly used to identify such relationships. Samples of sericitic phyllite plot in the CHARAC field. However, argillaceous dolomite and dolomite of the transition zone to the Gandarela Formation plot in or close to this field, which indicates that these samples are contaminated by clastic material. Samples of dolomitic and quartz itabirites plot in intermediate positions between Fe-Mn crust and modern seawater sediments, therefore, corroborating our conclusions stated above of a very low level of terrigenous contamination.

The conclusion we draw from these tests is that the trace elements in itabirite samples truly reflects the chemistry of the seawater from which they were precipitated.

Figure 19 – Plot of Sc versus Th composition for all samples of the Itabira Group. Note that all samples of dolomitic and quartz itabirite (with exception of M4 and M7) have Sc contents lower than 2 ppm and Th contents lower than 1 ppm, indicating small participation of terrigenous components in their sediments. Many samples have Sc content below the detection limit (1 ppm) and were plotted using the half of this value (see text for explanation).

Figure 20 – Plot of the Y/Ho versus Zr/Hf ratio with typical fields after Bau (1996). Note that samples of dolomitic and quartz itabirite plot between Fe-Mn and modern sea-water fields, which indicate a small amount of terrigenous components on their sediments (that plot within CHARAC field) and suggest that the source of their components was the seawater mixed with hydrothermal fluids.

Effects of Post-Depositional Processes

Bau (1991;1996) states that the effects of the diagenesis and metamorphism on the REE distribution in IFs is only of minor importance in most cases, because in common metamorphic environments water/rock ratios are too low to have a significant effect on REE distribution. He also states that, regardless of their metamorphic grade, coeval detritus-free IFs display similar REE patterns. Banner et al. (1988) did an extensive study on the effect of diagenesis on cathodoluminescent behavior, Sr and O isotopic ratios, Fe and Ca content, and REE patterns of ancient carbonates from North America. They determined the relative REE abundance was not significantly altered during the extensive diagenetic alteration of marine limestones through two different phases of dolomitization, which represented two completely different diagenetic fluids and environments. When discussing the geochemistry of BIFs worldwide, Klein and Beukes (1992) considered that the metamorphism of these rocks is isochemical except for the loss of H₂O and CO₂. The chemical similarity between unmetamorphosed and highly metamorphosed Labrador Trough iron-formations is a good example. Pires and Frost (2004) state that during the metamorphism of the Cauê Formation the original bulk composition of the BIFs controlled the composition of the metamorphic fluid phase rather than the opposite. In contrast, a study of the

effects of contact metamorphism associated with intrusion of a diabase sill on BIF from the Kuruman Formation of the Transvaal Basin showed that metamorphism altered the isotopic composition of the carbonates by depleting both ^{13}C and ^{18}O (Kaufman, 1996).

BIFs in the QF are completely metamorphosed; therefore it is not possible to compare the chemical composition of metamorphosed and unmetamorphosed rocks to estimate the degree of chemical changes which may have occurred during metamorphism. However, the chemical composition of (green schist facies) itabirites in QF is very similar to other unmetamorphosed BIFs (Fig. 17). We assume that metamorphic events did not alter the chemical composition of the original sediments of the Cauê Formation significantly, and that our geochemical data can be used for paleoenvironmental reconstructions of BIF deposition.

Dolomitization and the Genesis of the Dolomitic Itabirite

The distribution of dolomite in the dolomitic itabirite of the Cauê Formation and in the dolomite and marbles of the Gandarela Formation suggest that the original sediments of these rocks were largely dolomitized. Although in specific environments, where the seawater is hotter and has higher PCO_2 , higher Mg/Ca ratio, lower SO_4^{2-} and organic acid effects, the direct precipitation of dolomite is possible (Tucker and Wright, 1990), it is more probable that the dolomite found in QF results from the dolomitization of earlier carbonates, a common process in the Proterozoic. According to Tucker and Wright (1990) dolomitization generally appears to be an early near-surface phenomenon, where CaCO_3 minerals precipitated on the seafloor can be dolomitized by seawater with a high dolomitizing potential. Dolomite is a common mineral component in BIFs, where it is usually associated with ankerite and calcite (e.g. Arora et al., 1995; Dymek and Klein, 1988; Ewers and Morris, 1981; Floran and Papike, 1978; Klein and Beukes, 1989). In the Lake Superior region there are unmetamorphosed BIFs composed only of dolomite and iron minerals (e.g. Klein and Fink, 1976; Perry Jr. et al., 1973). The same occurs at the Nabberu basin, western Australia (Hall and Goode, 1978).

It seems likely that the dolomitic rocks of the Cauê and Gandarela Formation result from dolomitization of earlier carbonates during the diagenesis. Beukes et al. (2002), however, consider the dolomitic itabirite as the result of the desilification and carbonatization of quartz itabirite through a hydrothermal process, without presenting any evidence for this process. There is no field evidence to support this paragenetic sequence. On the contrary, the coexistence of quartz and dolomitic itabirite is locally observed in drill cores and outcrops of the Águas Claras Mine sometimes forming a triply banded rock (Fig. 6c). Quartz and dolomite are commonly

intergrown in metachert, dolomite and itabirite without displaying any evidence of metamorphic reaction or hydrothermal substitution (Fig. 8d).

Dolomitic itabirite and dolomite of the Cauê Formation occur throughout the Serra do Curral, along c. 110 Km of extension, indicating a regional distribution for these rocks. It is likely that a regional hydrothermal process of dolomitization of the quartz itabirite, as suggested by Beukes et al. (2002), would leave some indication of its occurrence, which was not observed to this day. Based on the field relations, petrographical and mineralogical observations, geochemical and isotopic data, we consider that dolomitic itabirite of the Cauê Formation are carbonate sediments modified by a dolomitization process which occurred during diagenesis, instead of a product of hydrothermal metasomatism of the quartz itabirite. We also consider that these carbonate sediments represent a lateral and vertical facies variation of the cherty sediments from which the quartz itabirite originated.

Y/Ho ratios of the dolomitic itabirite provide further constraints to their origin. Modern seawater has an Y/Ho ratio (>44) that is substantially higher than chondrite (26-28). The vast majority of geologic materials, including all volcanic rocks and clastic sediments, however, have chondritic ratios (Nozaki et al., 1997). Sampled dolomitic itabirite have Y/Ho ratios ranging from 34 to 52 with an average of 42 (Fig. 20 and Table 3), suggesting the dolomite precipitated from seawater.

A marine origin for the dolomitic itabirite is also indicated by the C and O isotopes, which present $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ correlated with that of the stromatolitic carbonates of the Gandarela Formation of the Minas basin, and with the Wittenoom Formation of the Hamersley basin (Fig. 18). Carbon isotope data of the Cauê Formation are similar to those found in all studied marine carbonates older than ca. 2.32 Ga supporting the interpretation that they are seawater precipitates slightly modified by diagenetic and metamorphic alteration.

The High Degree of Oxidation

The dolomitic itabirite of the Cauê Formation has $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratios ranging from 0.977 to 0.993 (average of 0.984), while in quartz itabirite this ratio ranges from 0.967 to 0.997 (average of 0.985), as observed in Table 2. Discussing the average chemical composition of the major BIFs found worldwide, Klein and Beukes (1992) presented $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratios ranging from 0.05 (siderite BIF in the Kuruman Iron Formation) to 0.58 (metamorphosed iron formation in Montana), except for one value of 0.97 (Rapitan Group).

Comparison of $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratios of magnetite (0.67) and hematite (1.0) with those of itabirites in the QF shows that iron is in an average oxidation state very close to that of hematite, which reflects the high oxidation process these rocks were submitted to, and which distinguishes them from other BIFs found worldwide. This high oxidation degree is petrographically evidenced by the total predominance of hematite over magnetite; magnetite occurs only as small relicts within martite crystals (Fig. 11c-d).

The hematite present in itabirites, however, results from several geological processes that modified the original sediments of the Cauê Formation. It cannot be considered as the primary iron oxide precipitated in these sediments and therefore used to reconstruct itabirite paleoenvironmental conditions. Even in unmetamorphosed and unweathered BIFs, most of the minerals observed do not represent primary precipitates, but secondary phases crystallized during early diagenesis, when the precipitated iron hydroxide and silica gels recrystallized to hematite/magnetite and quartz, respectively (Ewers and Morris, 1981; Morris, 1993; Trendall, 2002).

Several authors (Dorr II, 1969; Pires, 1995; Pires and Frost, 2004; Rosière et al., 1993; Rosière et al., 2001) who investigated the various generations of iron oxides in itabirites and iron ore in QF consider that magnetite crystallization dominated early stages of itabirite formation. The occurrence of graphitic phyllite yielding pyrite within the sericitic phyllite of the Batatal Formation, as well as the local presence of pyrite in the argillaceous dolomite (Fig. 8b-c) at the base of the Cauê Formation, suggest that the paleoenvironmental conditions were reducing during the beginning of sedimentation, thus favoring the crystallization of magnetite during the diagenesis.

In the quartz itabirite with metachert lenses at the transition zone from argillaceous dolomite to ferruginous dolomite (Fig. 4d) there is no tabular hematite, and martite (with many relicts of magnetite) is the only iron oxide observed (Fig. 8e). Martite is also the major iron oxide found in hematitic bands of itabirite, where it occurs intergrown with tabular hematite. According to Rosière and Rios (2004), tabular hematite is formed after martite during metamorphism and deformation, and therefore originates these intergrowths. A progressive deformation led to the disappearance of martite and the predominance of aggregates of tabular hematite, with specularite forming in higher deformed areas.

The origin of the fluids responsible for the pervasive martitization of magnetite in itabirite, as well as the absolute timing of this oxidation event, is not well defined. If the formation of hematite after martite occurred during the Transamazonian metamorphism event

(~2.1 Ga), oxidation processes occurred at least during the Paleoproterozoic. The regional distribution effects of this oxidation event and its great intensity produced a highly oxidized itabirite in the QF, which distinguishes them from other BIF's found worldwide.

The Source of the Sediments and Depositional Environment

Although controversies remain regarding the origin of Fe and SiO₂ in BIFs, with some authors attributing their origin to the weathering of continental rocks (e.g. Isley, 1995; Manikyamba et al., 1993) most workers consider that these components together with Mn and a very low amount of trace elements are derived from the leaching of basalt and komatiites of the ocean floor by hydrothermal fluids (e.g. Bau and Möller, 1993; Beukes and Klein, 1990; Dymek and Klein, 1988; Kato et al., 1998; Klein and Beukes, 1992; Shimizu et al., 1990). Itabirites of the Cauê Formation display geochemical signatures similar to that of other BIFs with very low trace element contents, high HREE fractionation and positive Eu, Y and La anomalies (Tables 2 and 3). These geochemical signatures are consistent with the latter interpretation. Further support for a hydrothermal origin is illustrated by the diagram in Figure 21. All the samples of itabirites (as well as of other BIFs) fall in or near the field of the “*Hydrothermal Deposits*” which consist in large part of the Fe-rich layer silicate nontronite with a bulk composition similar to those of the BIFs.

Figure 21 - Plot of (Co+Ni+Cu) abundances versus total REE content for dolomitic and quartz itabirite and others BIFs (data from Klein and Beukes, 1992). Data points for all the BIFs are contained within or very close to the “hydrothermal field”, suggesting a common origin.

A small participation of terrigenous sediments in the composition of the water solutions from where itabirites precipitated, however, is suggested by the strong correlation between Al_2O_3 with TiO_2 , Zr and Th (Fig. 15, Table 4b) as demonstrated above, suggested minor contamination of itabirite by a terrigenous component. Al_2O_3 also shows a good correlation with ΣREE ($r=0.75$), which suggests part of the REE budget in seawater is of terrigenous origin (and not only hydrothermal fluids). This is also suggested by the higher amount of ΣREE of the dolomitic band of dolomitic itabirite when compared with the hematitic band (Table 2). The former is two-fold richer in ΣREE than the latter. Several papers have mentioned that REE concentrations in seawater increase with increased fluxes of clastic material mixing with hydrothermal waters (e.g. Beukes and Klein, 1990; Gnaneshwar Rao and Naqvi, 1995; Khan and Naqvi, 1996). The nature and origin of the terrigenous sediments in BIFs of the QF is still unclear. The terrigenous component maybe suspended clastic material or a dissolved component of river waters, or possibly volcanic ash carried by winds to the ocean. The mineralogical composition of itabirites provides little information to answer this question. However, major and trace elements of itabirite provide some insights to the palaeoenvironment of deposition of the itabirite. Dolomitic itabirite at the Águas Claras mine has higher average Al_2O_3 and ΣREE contents than quartz itabirite, suggesting a greater contribution of terrigenous material to dolomitic itabirite. Al_2O_3 and REE contents are higher at the base of the dolomitic-quartz itabirite sequence and decrease towards the top (Fig. 13). This trend of the REE and Al_2O_3 data suggests a gradual transition from shallow to deeper waters. Beside to suggest that sedimentation of dolomitic itabirite occurred in a shallower platform than that of quartz itabirite, higher amount of terrigenous components in dolomitic itabirite also suggest a higher proximity with the continent.

Better constraints of the source of sediments and the palaeodepositional environment of itabirite comes from the $\text{REEY}_{\text{PAAS}}$ patterns of these rocks. The $\text{REEY}_{\text{PAAS}}$ patterns of the dolomitic and quartz itabirites show that both rocks precipitated from seawater mixed with hydrothermal fluids, (i.e., indicated by a positive Eu and Y anomalies and $\text{La/Yb}_{\text{PAAS}} < 1$, see Table 3). Different REE fractionation patterns of dolomitic and quartz indicate variation in the composition of this hydrothermal-seawater aqueous solution (Fig. 16a and d). This variation most likely reflects the location of BIFs relative to hydrothermal vents and continent, and variations in the intensity of the hydrothermal fluxes. According to the studies by Derry and Jacobsen (1990) and Danielson et al. (1992), slightly higher values of the Eu anomaly in the dolomitic itabirite indicate precipitation from higher temperature fluids ($>300^\circ\text{C}$), which suggests either a more proximal source of hydrothermal fluids or a greater contribution of higher

temperature hydrothermal fluids. Higher temperature fluids leach more Eu from ocean-floor basalts (Bau, 1993). This enhances higher Eu anomalies in precipitates closer to the source of the hydrothermal fluids, or with the contribution of fluids with high temperatures, because the capacity of absorption of REE by hydrothermal precipitates is proportional to their concentrations in the fluids (Olivarez and Owen, 1991).

Kato et al. (1998) studying the REE fractionation pattern in BIFs and associated ferruginous/siliceous mudstone in mid-Archean rocks of the Pilbara craton, Western Australia, identified two different types of Eu anomalies. The first type occurs in BIFs and is derived from the hydrothermal solutions emanating from the mid-ocean ridge. The second type occurs in mudstone and is inferred to be caused by detrital feldspar and feldspar derived clay minerals from the exposed continental crust or island arcs. Once sericitic phyllite and all rocks of the Cauê Formation shows positive Eu anomaly (Fig. 16), one could associate these anomalies in argillaceous dolomite and itabirites to clastic contamination. This is not the case, due to the small positive Eu anomaly showed by the sericitic phyllite (~ 1.2) and the great difference to the following argillaceous dolomite (~ 2.2 , with much lower amount of pelitic sediments). Therefore, it is reasonable to infer that the gradual decreasing of the Eu_{PAAS} anomaly observed in the Cauê Formation from the base of the sequence towards the contact with the quartz itabirite (Fig. 13), where it becomes almost constant, is related to a gradual reduction of hydrothermal fluid temperature, or to a higher mixture of it with the seawater.

Elderfield et al. (1990) showed that the $(\text{Sm}/\text{Yb})_{\text{PAAS}}$ ratio and pH are negatively correlated in seawater. The higher $(\text{Sm}/\text{Yb})_{\text{PAAS}}$ ratio of the quartz itabirite (and consequently its flatter REEY pattern) is therefore consistent with a lower pH solution from which silica precipitated. $(\text{Sm}/\text{Yb})_{\text{PAAS}}$ ratio in BIFs is controlled by marine surface water component (Bau and Möller 1993). Differences on the REEY pattern of dolomitic and quartz itabirites shown in Figure 16 probably reflect variation of the pH of seawater, with dolomitic itabirite having a higher participation of marine (alkaline) surface water and quartz itabirite of marine (slightly acidic) bottom water.

The precipitation of chert in the seawater is independent of the Eh conditions (Kato and Nakamura, 2003), and is dependent only on the concentration of silica in solution and the pH of the solution. Local variation on the pH and concentration of silica in solution of the seawater would favor the presence of carbonate or chert components, and together with varied degree of clastic input would control the three major compositional types of BIFs observed in the QF. The co-precipitation of chert and carbonate petrographically observed in samples of metachert and

dolomite suggests that the sedimentation of the itabirites occurred very close to the limit of stability of both minerals. Small variations on the pH conditions would therefore favor the presence of one or another mineral. The occurrence of triply layered itabirite (Fig. 6c) indicates seasonal variation on the pH condition of the environment. It gives additional support to our suggestion that pH was one of the major control on the type of BIF precipitating.

An additional feature of the REEY pattern of the itabirites is the negative Ce_{PAAS} anomaly. Ce behavior in aqueous solutions is strongly dependent on the redox conditions and it is removed from seawater by oxidation (De Baar et al., 1985; Elderfield et al., 1990). Both the dolomitic and the quartz itabirite exhibit negative Ce_{PAAS} anomalies. These anomalies become slightly more negative from the bottom of the dolomitic itabirite towards the top of the quartz itabirite, where Ce/Ce^* has values around unity (Fig. 13d). The presence of a negative Ce_{PAAS} anomaly in many samples of itabirites indicates that the waters from which these sediments precipitated from were sufficiently oxidizing to promote formation of less soluble or more reactive Ce(IV) species.

Variation of the magnitude of the Ce_{PAAS} anomalies in both the dolomitic and quartz itabirite suggests fluctuation in the degree of oxidation of the seawater. These variations may be a function of water depth. Heterogeneous REEY distribution in the seawater where the sediments of the dolomitic and quartz itabirite precipitated from, expressed by differences in the $(Sm/Yb)_{PAAS}$ ratio, and Eu_{PAAS} and Y_{PAAS} anomalies, may reflect variation of the water depth, once the REEY distribution in seawater is depth-dependent (Elderfield, 1988). Considering that both quartz and dolomitic itabirite are contemporaneous (see text below), and were precipitated in different pH conditions of the basin (due to its significant differences at $(Sm/Yb)_{PAAS}$ ratios), we suggest that the sedimentation of the BIFs of the Minas basin occurred in a restricted basin rather than in an open shelf. A restricted basin would be more propitious to local variation in the depositional environment, and would enhance the regional lithological variation observed in BIFs of the QF. This basin, otherwise, should be opened to the ocean due to the typical and very homogeneous marine signature of the C and O isotopes of the dolomitic itabirite. Considering these points, we suggest that sedimentation of the carbonatic BIF occurred in a slightly shallower (and maybe narrow) site, maybe closer to the continent, with higher participation of marine surface water. We also suggest that the sedimentation of the cherty BIF occurred in a slightly deeper site of the basin, with a higher participation of more acidic marine bottom water. The dolomitic and quartz itabirite would then represent two distinct sedimentary facies of the Cauê basin: one carbonatic and another cherty. Both characterized by oxic conditions.

The Depositional Model

Gross (1983) suggested that iron formations interbedded with dolomite, quartzite, shales and volcanic rocks were deposited on continental shelves close to craton margins. The upward lithological gradation from conglomeratic quartzite to phyllite to BIFs to stromatolitic dolomite led Renger et al. (1994) to suggest that sediments of the Minas basin were deposited in a continental shelf environment. Changes in water depth evidenced by lithological variations in the Minas Supergroup indicate that marine transgression-regression cycles acted during the deposition of the Minas basin.

Deposition of BIFs during marine transgressions is suggested for BIFs of the Hamersley basin and the Transvaal basin (Klein and Beukes, 1989; Simonson, 1996; Simonson et al., 1993), both contemporaneous with the Minas basin (Babinski et al., 1995a). Klein and Beukes (1989) associated the deposition of the Kuruman BIF to a major transgressive event that extensively submerged the Kaapvaal craton. Renger et al. (1994) emphasized the close similarities between the Kapvaal basin and the Minas basin, and suggested that the Cauê Formation is the counterpart of the Kuruman Formation. The lithological variation in the Minas Supergroup indicate that there were progressive deeper water conditions from the Moeda Formation to the Cauê Formation associated with transgression, and indicates that BIFs in the Cauê Formation were also deposited during a marine transgression that blanketed the São Francisco craton.

Differently from the Kaapvaal craton, which was completely submerged, the continuous contribution of terrigenous sediments to BIF's during the sedimentation in QF, as previously discussed, suggest the existence of emerged areas of the São Francisco craton that could act as source for these sediments. Higher terrigenous contribution occurs in the argillaceous dolomite at the base of the Cauê Formation and in the dolomite of the transition to the Gandarela Formation. Geochemical data suggests that itabirites have a very low terrigenous component, which indicates sedimentation probably occurred during the climax of the marine transgression.

Additional support of marine transgression-regression cycles during the deposition of the Cauê Formation comes from the occurrence of GIF in the transition from argillaceous dolomite to ferruginous dolomite. GIF is considered to have formed by submarine erosion and the deposition of earlier formed BIFs. Regression-transgression cycles representing sea level changes are generally responsible for such erosion, which result in the deposition of eroded

material close to BIF (Klein and Beukes, 1989; Morris, 1993; Simonson, 1985). When the quieter conditions prevailed again, the deposition of BIFs took over and produced short scale lateral and vertical transitions. The GIF interbedded with argillaceous dolomite exhibits fining upwards graded bedding, which indicates increasing sea levels. It was formed from the erosion of older quartz itabirite, but its peloids are cemented by carbonate, which indicates the existence of not only variations in the sea level, but also changes in the seawater composition.

Regression-transgression cycles would strongly affect the bulk composition of seawater in a more restricted BIF depositional basin. We suggest these bulk compositional changes in seawater are represented in the QF by a lithological variation in the itabirites, with dolomitic-, quartz- and amphibolitic-itabirites representing carbonatic, cherty and shaly facies of the Cauê basin, respectively. Lateral and vertical transitions between different lithotypes would mean sedimentologic facies changes in response to the local variation in the aqueous solution composition, maybe related to changes in water depth, pH and input of clastic components.

The lack of regional maps showing facies changes within the itabirites of the Cauê Formation makes paleoenvironmental studies and the elaboration of depositional models extremely difficult. Recent exploratory works carried out by MBR in the eastern limb of the Moeda Syncline (Fig. 1) show major differences in the stratigraphy of the Cauê Formation (Fig. 22). In the Águas Claras mine dolomitic itabirite is found at the base of the sequence and is overlain by quartz itabirite, while in the Pico mine quartz itabirite occurs from the base to the top. Layers of amphibolitic itabirite occur interlayered with quartz itabirite toward to the top of the sequence at the Pico mine. This context allows us to suggest the presence of a lateral and vertical facies variation within the Cauê Formation, going from dolomitic to quartz to amphibolitic itabirite as a result of variation in the seawater composition. We suggest that during the beginning of a transgressive cycle, while carbonatic sediments of dolomitic itabirite were deposited in a slightly shallower site of the basin (with a higher contribution of the marine surface waters richer in terrigenous components and alkaline pH), cherty sediments of quartz itabirite were deposited in a deeper site (with very low content of terrigenous components and acid pH). Gradual increasing water depths led to deposition of quartz itabirite in the Águas Claras region. This occurred during the climax of the transgression. During the regression cycle, the depositional conditions changed in the Águas Claras region from those favouring quartz itabirite to dolomite and marbles. In the Pico region, however, conditions favouring deposition of quartz itabirite alternated to those favouring formation of an itabirite containing layers rich in terrigenous material now preserved as amphibolitic itabirite. This would represent shaly

sediments, with a much higher participation of terrigenous sediments carried by river waters. Figure 23 displays this depositional model.

Figure 22 – Geological cross section 2550E of the Águas Claras mine (A) and 8550E of the Pico mine (B). Note the variation of lithotypes of the Itabira Group from the northwest to west of the Quadrilátero Ferrífero.

Figure 23 – Schematic depositional model for the Cauê Formation.

CONCLUSIONS

Dolomitic and quartz itabirite are metamorphosed oxide facies BIFs of the Lake Superior type of Paleoproterozoic age, contemporaneous to the giant BIFs of the Hamersley and Transvaal basins. They consist of alternated millimetric to decimetric bands of dolomite-rich and hematite-rich, and quartz-rich and hematite-rich, respectively. Both rocks have a very simple chemical composition, with Fe_2O_3 , CaO , MgO and LOI representing more than 98% of the average composition of dolomitic itabirite and Fe_2O_3 and SiO_2 constituting more than 98% of the average composition of quartz itabirite. Itabirites were highly oxidized and present $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratios higher than 0.98, much greater than the average ratio of other Paleoproterozoic BIFs.

Trace elements concentrations in itabirites are very low and range from < 10 ppm (Y, Sc, Be, Cu, Ga, Ge, Rb, Nb, Mo, Ag, In, Sn, Cs, Hf, Tl, Pb, Bi, As, Cd, Th, U, Sb) to concentrations between 10 and 55 ppm (Ba, Sr, Zr, V, Ni, Zn, Co, Cr and ΣREE). Dolomitic and quartz itabirite do not present major differences in trace element contents.

The HREE enrichment pattern exhibited by both itabirites shows a modern seawater REE signature overprinted by a hydrothermal pattern represented by positive $\text{Eu}_{\text{PAA}}\text{S}$ anomalies. A marine sedimentary origin of the sediments of the dolomitic itabirite is reinforced by its REE signature, by the C and O isotopic composition, typical of marine carbonates, and by its Y/Ho ratios very similar to that of seawater. A strong correlation between Al_2O_3 and TiO_2 ($r>0.9$) indicates a minor terrigenous component for the chemically precipitated, marine sediments of the Cauê Formation.

The differences on the REE signatures of the itabirites suggest that they precipitated from aqueous solutions of different compositions, with the dolomitic itabirite receiving higher contribution of marine surface waters laid on continental sediments and quartz itabirite of marine bottom waters. Sea-level fluctuations caused by marine transgression–regressions are responsible for changes in the aqueous solution composition. These changes are expressed by dolomitic-, quartz- and amphibolitic itabirites, which represent lateral and vertical facies transitions of carbonatic, cherty and shaly BIFs respectively.

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Appendix 1 – Major and trace element composition

Sample	M140	M141	M132	M134	M135	M137	M138	M139	M4	M5	M6	M7
	Seric.	Seric.	Argil.	Argil.	Argil.	Argil.	Argil.	Argil.	Dol.	Dol.	Dol.	Dol.
Wt%	Phyl.	Phyl.	Dol.	Dol.	Dol.	Dol.	Dol.	Dol.	Itabir.	Itabir.	Itabir.	Itabir.
SiO ₂	66.38	60.28	7.37	19.19	12.48	13.01	40.27	51.57	1.97	1.27	1.73	0.80
Al ₂ O ₃	19.69	17.52	1.81	1.72	1.23	0.61	1.42	0.05	0.77	0.33	0.72	0.26
Fe ₂ O ₃	1.31	2.04	2.44	0.58	1.26	0.42	0.23	0.33	45.30	39.65	44.62	45.86
Fetot	1.73	5.33	8.54	4.21	5.43	5.79	3.71	2.67	46.30	40.26	45.65	46.46
FeO	0.38	2.96	5.49	3.27	3.75	4.83	3.13	2.11	0.90	0.55	0.93	0.54
MnO	<0.01	0.05	0.72	0.40	0.43	0.40	0.20	0.22	0.25	0.27	0.43	0.37
MgO	1.22	4.90	15.27	14.81	16.72	15.55	11.44	8.97	11.19	12.30	11.04	11.13
CaO	0.09	0.12	25.08	22.63	24.45	25.38	16.54	14.36	14.48	17.26	14.83	15.51
Na ₂ O	0.09	0.04	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.05	< 0.01	< 0.01
K ₂ O	6.73	5.03	0.45	0.59	0.06	0.10	0.20	< 0.01	0.11	0.06	0.05	< 0.01
TiO ₂	0.79	0.74	0.08	0.07	0.06	0.03	0.05	< 0.01	0.04	0.01	0.06	0.01
P ₂ O ₅	0.09	0.06	0.02	0.03	0.03	0.02	0.03	0.01	0.10	0.11	0.19	0.13
Ctot		0.25		10.10	11.10	11.20					6.35	
Cgrap		0.18		0.30	0.36	0.25					< 0.05	
Corg		0.04		0.10	0.13	0.10					0.05	
CO ₂		0.11		35.50	39.00	39.70					23.10	
S	0.009	0.006	0.029	0.089	0.027	0.116	0.153	0.010	< 0.001	< 0.001	< 0.001	< 0.001
LOI	3.32	4.65	39.78	35.67	38.92	39.01	26.21	22.61	23.79	27.27	23.95	24.05
Total	100.14	98.72	99.12	99.28	99.80	99.88	100.07	100.42	99.00	99.20	98.62	96.68
ppm												
Ba	360.0	296.0	24.0	24.0	8.0	12.0	16.0	< 1.0	11.0	15.0	15.0	19.0
Sr	17.0	11.0	28.0	21.0	16.0	19.0	13.0	12.0	38.0	48.0	56.0	28.0
Y	27.0	25.0	11.0	7.0	8.0	8.0	7.0	< 1.0	10.0	7.0	12.0	8.0
Sc	16.0	17.0	3.0	2.0	2.0	2.0	2.0	< 1.0	2.0	< 1.0	2.0	< 1.0
Zr	184.0	173.0	18.0	27.0	17.0	11.0	16.0	< 1.0	17.0	11.0	21.0	18.0
Be	3.0	2.0	1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	2.0	< 1.0	2.0	1.0
V	122.0	122.0	17.0	14.0	11.0	10.0	13.0	< 5.0	23.5	14.3	25.8	11.9
Ni	44.5	88.4	5.3	9.4	10.2	6.6	12.3	1.4	5.6	3.5	6.9	2.8
Cu	48.3	28.0	18.9	13.0	5.7	14.5	37.5	3.9	9.5	9.4	10.7	10.9
Zn	7.6	44.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	9.9	13.6	16.5	3.7
Ga	27.5	23.6	2.6	2.5	1.9	1.0	2.2	< 1.0	1.6	< 1.0	1.4	< 1.0
Ge	2.6	2.9	< 0.5	< 0.5	< 0.5	< 0.5	0.9	0.6	2.1	1.8	1.8	2.1
Rb	227.6	174.6	11.5	19.4	4.4	4.5	8.7	< 1.0	5.5	< 1.0	< 1.0	2.2
Nb	10.6	11.6	0.9	1.0	0.8	0.4	0.9	< 0.2	1.6	1.1	1.5	0.9
	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0
Ag	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
In	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Sn	3.6	3.0	< 1.0	1.1	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Cs	8.7	4.9	0.4	0.8	0.3	0.1	0.3	< 0.1	1.0	0.2	0.2	0.3
ΣREE	233.3	220.7	47.0	30.6	32.7	28.7	21.8	4.9	21.7	14.6	40.0	13.6
Hf	5.3	5.2	0.4	0.8	0.5	0.2	0.5	< 0.1	0.1	0.1	0.3	< 0.1
Tl	1.5	0.6	0.1	0.3	0.1	< 0.1	0.2	< 0.1	0.1	< 0.1	0.2	0.1
Pb	22.4	7.3	< 3.0	< 3.0	< 3.0	4.8	< 3.0	< 3.0	8.7	10.1	5.7	3.2
Bi	2.1	2.0	2.3	2.5	3.0	< 0.1	4.0	3.0	0.4	0.1	0.2	< 0.1
Th	21.7	19.1	2.6	2.4	1.5	0.7	1.3	< 0.1	1.4	0.7	1.3	0.5
U	6.7	4.4	1.2	0.8	0.7	0.5	0.6	0.2	2.5	1.6	2.8	1.3
As	16.2	< 5.0	5.9	6.5	< 5.0	< 5.0	< 5.0	< 5.0	9.6	5.9	15.5	< 5.0
Cr	210.3	233.8	< 20.0	< 20.0	< 20.0	< 20.0	< 20.0	< 20.0	44.0	148.0	104.0	< 20.0
Sb	4.0	1.5	0.4	0.7	0.8	0.3	0.8	< 0.2	1.3	0.7	1.2	0.9
Cd	0.80	0.64	2.06	1.26	< 0.30	1.24	1.67	0.75	0.73	0.84	0.55	1.15
Fe#	0.76	0.38	0.29	0.14	0.23	0.07	0.06	0.12	0.98	0.98	0.98	0.99

Fe_{TOT} expressed as Fe₂O₃. Fe# = (Fe³⁺/(Fe³⁺ + Fe²⁺))

Appendix 1 – Major and trace element composition (Continued)

Sample	M8	M9	M10	M11	M96	P55_27	P55_61	P3_18	P3_23	P3_36	P3_50	P54_80
	Dol.	Dol.	Dol.	Dol.	Dol.	Dol.	Dol.	Sil.	Sil.	Sil.	Sil.	Sil.
Wt%	Itabir.	Itabir.	Itabir.	Itabir.	Itabir.	Itabir.	Itabir.	Itabir.	Itabir.	Itabir.	Itabir.	Itabir.
SiO ₂	0.83	0.53	0.84	0.63	1.00	0.65	0.86	61.95	49.19	39.87	30.89	19.71
Al ₂ O ₃	0.20	0.09	0.26	0.10	0.57	0.17	0.07	0.14	0.32	0.52	0.06	0.12
Fe ₂ O ₃	42.14	52.43	54.03	67.61	59.05	44.36	42.84	37.18	49.10	54.27	68.44	76.75
Fetot	42.92	53.00	54.92	68.11	60.03	45.02	43.33	37.37	49.37	54.51	68.66	79.34
FeO	0.70	0.51	0.80	0.45	0.88	0.59	0.44	0.17	0.24	0.22	0.20	2.33
MnO	0.28	0.23	0.27	0.18	0.25	0.32	0.25	<0.01	0.01	0.04	0.03	<0.01
MgO	12.02	9.69	9.24	6.49	7.98	11.00	11.50	0.06	0.12	0.80	0.02	0.03
CaO	16.79	13.74	12.91	9.47	11.07	15.68	16.27	0.09	0.38	1.21	0.06	0.22
Na ₂ O	< 0.01	< 0.01	< 0.01	< 0.01	0.27	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01
K ₂ O	< 0.01	< 0.01	< 0.01	0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.03	< 0.01	0.01
TiO ₂	0.01	0.02	0.01	0.01	0.04	0.01	<0.01	<0.01	0.01	0.03	<0.01	<0.01
P ₂ O ₅	0.05	0.08	0.17	0.17	0.07	0.12	0.10	0.07	0.32	0.04	0.03	0.19
Ctot	7.05		5.50			6.90						
Cgrap	0.05		< 0.05			< 0.05						
Corg	< 0.05		0.05			< 0.05						
CO ₂	25.80		20.20			25.30						
S	< 0.001		< 0.001			0.007	0.016	0.003	0.007	< 0.001	< 0.001	0.003
LOI	25.97	21.33	20.10	13.49	18.33	25.68	26.49	0.21	0.46	2.23	0.40	< 0.02
Total	99.03	98.71	98.72	98.70	99.55	98.60	98.92	99.85	100.21	99.27	100.08	99.61
ppm												
Ba	7.0	17.0	11.0	13.0	5.0	17.0	12.0	21.0	5.0	21.0	13.0	18.0
Sr	29.0	22.0	24.0	19.0	17.0	24.0	23.0	1.0	4.0	3.0	2.0	8.0
Y	4.0	5.0	7.0	9.0	6.0	8.0	9.0	1.0	5.0	6.0	3.0	4.0
Sc	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Zr	15.0	7.0	21.0	11.0	19.0	5.0	9.0	8.0	10.0	20.0	7.0	14.0
Be	< 1.0	< 1.0	< 1.0	< 1.0	1.0	< 1.0	1.0	< 1.0	1.0	1.0	2.0	1.0
V	36.4	5.0	9.6	20.0	84.3	38.0	13.0	7.2	27.0	42.8	21.0	22.0
Ni	4.7	10.0	10.2	10.0	33.0	13.1	10.6	8.8	9.4	7.5	20.0	4.7
Cu	10.6	5.0	10.2	5.0	5.0	< 1.0	< 1.0	9.0	< 1.0	11.8	< 1.0	< 1.0
Zn	8.4	5.0	9.3	5.0	47.5	9.4	< 1.0	< 1.0	2.0	< 1.0	5.2	4.4
Ga	< 1.0	< 1.0	< 1.0	< 1.0	1.0	< 1.0	< 1.0	1.2	< 1.0	1.2	< 1.0	< 1.0
Ge	1.9	2.1	< 0.5	0.8	3.2	2.1	2.0	3.6	3.8	2.4	6.3	3.2
Rb	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	1.9	< 1.0	< 1.0
Nb	0.8	< 0.2	0.8	< 0.2	1.6	0.3	0.9	0.8	0.4	0.9	0.3	0.4
Mo	< 2.0	< 2.0	< 2.0	< 2.0	< 1.0	53.7	< 2.0	< 2.0	< 2.0	< 2.0	4.7	< 2.0
Ag	< 0.3	1.6	< 0.3	1.5	< 0.5	0.4	0.5	< 0.3	0.4	< 0.3	0.3	0.4
In	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Sn	< 1.0	< 1.0	< 1.0	4.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Cs	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1
ΣREE	8.3	7.4	10.4	9.6	9.7	12.7	12.9	4.1	12.1	14.0	4.8	7.7
Hf	< 0.1	0.2	< 0.1	< 0.1	0.2	< 0.1	< 0.1	0.1	< 0.1	0.2	< 0.1	< 0.1
Tl	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Pb	5.1	8.0	7.3	< 3.0	< 3.0	< 3.0	< 3.0	4.6	< 3.0	< 3.0	< 3.0	< 3.0
Bi	0.1	0.2	< 0.1	0.5	0.1	5.1	6.0	0.2	4.1	< 0.1	< 0.1	6.5
Th	0.3	0.2	0.4	0.2	0.6	0.2	0.1	0.1	0.1	0.4	< 0.1	0.1
U	1.0	1.1	1.2	2.0	4.5	2.1	2.8	1.4	2.7	3.0	1.0	1.0
As	< 5.0	< 5.0	< 5.0	6.1	12.0	5.0	7.0	12.3	15.6	8.4	12.5	< 5.0
Cr	26.0	68.0	23.0	110.0	29.0	< 20.0	< 20.0	< 20.0	20.3	22.0	< 20.0	< 20.0
Sb	1.1	1.1	0.2	2.1	3.4	2.6	3.2	3.0	3.3	3.0	3.2	1.6
Cd	0.37		1.25			6.19	4.80	0.91	3.99	0.81	3.35	4.97
Fe#	0.98	0.99	0.98	0.99	0.98	0.99	0.99	0.99	0.99	1.00	1.00	0.97

Fe_{TOT} expressed as Fe₂O₃, Fe# = (Fe³⁺)/(Fe³⁺ + Fe²⁺)

Appendix 1 – Major and trace element composition (Continued)

Sample	P54_85	P54_120	P54_124	P3_69	P3_83	P3_103	P3_122	P3_138	P3_152	P3_170	P3_185	P3_196
Wt%	Sil.	Sil.	Sil.	Sil.	Mixed	Sil.	Mixed	Cherty	Cherty	Cherty	Cherty	Cherty
SiO ₂	Itabir.	Itabir.	Itabir.	Itabir.	Itab.	Itabir.	Itab.	Dol.	Dol.	Dol.	Dol.	Dol.
Al ₂ O ₃	38.18	58.82	50.43	26.62	27.74	53.28	50.34	28.21	11.08	6.56	21.06	14.58
Fe ₂ O ₃	0.10	0.13	0.13	0.09	0.44	0.12	0.08	0.73	3.07	0.27	0.55	0.33
Fetot	58.92	40.43	47.74	68.58	31.99	37.08	31.88	21.29	5.20	6.64	16.85	6.96
FeO	60.63	40.86	49.07	68.71	33.10	37.40	32.34	22.95	9.17	8.32	18.56	11.76
MnO	1.54	0.39	1.20	0.12	1.00	0.29	0.41	1.49	3.57	1.51	1.54	4.32
MgO	< 0.01	< 0.01	< 0.01	0.08	0.33	0.09	0.26	0.30	0.41	0.66	0.39	0.58
CaO	0.01	< 0.01	0.02	0.17	8.05	1.79	3.18	10.08	18.44	17.25	12.37	13.95
Na ₂ O	0.13	0.16	0.18	1.69	11.24	2.98	5.20	13.84	21.42	25.87	17.63	22.45
K ₂ O	0.02	0.02	< 0.01	< 0.01	0.04	0.01	0.10	0.02	0.07	0.02	< 0.01	0.10
TiO ₂	< 0.01	< 0.01	0.02	0.04	0.04	< 0.01	0.08	< 0.01	0.10	< 0.01	< 0.01	< 0.01
P ₂ O ₅	< 0.01	< 0.01	< 0.01	< 0.01	0.03	0.01	< 0.01	0.06	0.26	0.03	0.04	0.02
Ctot	0.14	0.15	0.17	0.08	0.06	0.17	0.06	0.05	0.06	0.02	0.03	0.02
Cgrap					4.80			6.05	9.65			9.80
Corg					< 0.05			< 0.05	< 0.05			< 0.05
CO ₂					< 0.05			< 0.05	0.05			< 0.05
S					17.60			22.20	35.40			35.90
LOI	0.005	0.013	0.007	< 0.001	< 0.001	< 0.001	< 0.001	0.004	< 0.001	0.038	0.014	< 0.001
Total	0.04	0.20	0.18	1.58	17.79	4.51	7.76	22.44	35.14	39.83	28.10	34.78
ppm	99.25	100.34	100.17	99.05	98.86	100.33	99.40	98.62	99.21	98.81	98.71	98.56
Ba	21.0	20.0	14.0	6.0	16.0	4.0	7.0	6.0	9.0	7.0	4.0	5.0
Sr	8.0	4.0	7.0	8.0	37.0	9.0	8.0	19.0	38.0	41.0	23.0	23.0
Y	4.0	4.0	5.0	3.0	5.0	3.0	3.0	4.0	9.0	7.0	3.0	3.0
Sc	< 1.0	< 1.0	< 1.0	< 1.0	1.0	< 1.0	< 1.0	2.0	4.0	< 1.0	2.0	1.0
Zr	13.0	10.0	8.0	18.0	14.0	9.0	4.0	12.0	35.0	9.0	14.0	10.0
Be	1.0	< 1.0	1.0	2.0	1.0	2.0	< 1.0	2.0	1.0	1.0	1.0	< 1.0
V	52.0	18.0	11.0	< 5.0	6.5	< 5.0	< 5.0	10.0	32.4	6.0	9.0	< 5.0
Ni	7.9	12.5	9.1	14.8	16.4	12.7	3.4	13.9	36.8	13.5	9.0	2.8
Cu	< 1.0	< 1.0	< 1.0	9.6	5.8	< 1.0	9.1	1.2	1.8	1.6	< 1.0	1.9
Zn	3.6	1.9	2.8	< 1.0	8.2	7.1	< 1.0	18.4	20.9	< 1.0	3.8	< 1.0
Ga	< 1.0	< 1.0	< 1.0	< 1.0	1.2	< 1.0	< 1.0	1.1	5.2	< 1.0	< 1.0	< 1.0
Ge	4.3	2.7	3.0	3.2	2.4	5.2	3.2	1.6	1.2	< 0.5	0.9	< 0.5
Rb	< 1.0	1.7	< 1.0	< 1.0	1.1	< 1.0	< 1.0	< 1.0	6.3	1.1	1.3	< 1.0
Nb	0.6	2.9	0.3	0.5	1.3	< 0.2	0.7	0.6	1.8	0.3	0.5	0.7
Mo	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0
Ag	0.3	0.4	0.3	< 0.3	< 0.3	< 0.3	< 0.3	0.3	< 0.3	< 0.3	< 0.3	< 0.3
In	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Sn	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Cs	< 0.1	0.2	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.4	< 0.1	< 0.1	< 0.1
ΣREE	5.8	9.8	8.8	7.1	7.7	7.5	4.8	10.5	15.3	10.6	9.6	7.5
Hf	< 0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	0.2	0.5	0.2	0.2	0.1
Tl	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Pb	< 3.0	< 3.0	< 3.0	8.2	13.7	< 3.0	5.6	< 3.0	3.3	< 3.0	< 3.0	4.2
Bi	< 0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1	2.1	< 0.1
Th	0.1	0.1	0.1	0.1	0.4	0.1	0.1	0.6	1.8	0.4	0.7	0.6
U	0.9	1.7	1.6	1.5	1.3	0.7	0.9	2.1	1.1	1.0	1.1	0.4
As	5.7	7.4	9.1	14.3	7.9	19.6	6.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Cr	< 20.0	< 20.0	< 20.0	< 20.0	28.0	< 20.0	< 20.0	164.9	< 20.0	< 20.0	< 20.0	< 20.0
Sb	2.5	2.5	3.2	2.6	2.0	2.5	1.3	0.8	0.7	0.3	0.7	0.3
Cd	5.46	2.74	3.68	0.99	0.37	2.30	0.80	2.14	0.38	2.78	2.74	0.41
Fe#	0.97	0.99	0.97	1.00	0.97	0.99	0.99	0.93	0.57	0.80	0.91	0.59

Fe_{TOT} expressed as Fe₂O₃. Fe# = (Fe³⁺)/(Fe³⁺ + Fe²⁺)

Appendix 1 - Major and trace element composition (Continued)

Sample	M5A	M6A	M7A	M8A	M10A	M11A	M1	M16	M81	M100	M102	M103
	Iron-Rich Band of Dolomitic Itabirite						Dolomite-Rich Band of Dolomitic Itabirite					
Wt%												
SiO ₂	1.10	1.27	0.98	0.79	0.71	0.62	0.34	0.77	0.33	0.14	2.31	0.49
Al ₂ O ₃	0.37	0.47	0.26	0.22	0.28	0.10	0.10	0.46	0.12	0.07	1.02	0.21
Fe ₂ O ₃	83.43	84.77	82.38	69.75	65.04	81.92	15.42	23.92	8.74	7.00	4.49	5.99
Fetot	83.74	85.13	82.61	70.11	65.57	82.23	16.06	25.00	9.48	7.21	6.15	6.55
FeO	0.28	0.32	0.21	0.32	0.48	0.28	0.58	0.97	0.67	0.19	1.49	0.50
MnO	0.07	0.06	0.11	0.18	0.20	0.10	0.48	0.55	0.62	0.54	0.32	0.48
MgO	3.00	2.92	3.36	5.76	6.51	3.09	17.35	15.99	18.86	19.73	19.72	19.34
CaO	3.59	3.08	4.28	8.03	9.18	4.56	25.12	22.62	26.82	28.40	26.40	27.80
Na ₂ O	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	0.23	0.02	0.03
K ₂ O	< 0.01	0.06	0.02	< 0.01	< 0.01	< 0.01	0.11	< 0.01	0.01	< 0.01	0.10	0.13
TiO ₂	0.02	0.02	0.02	0.01	0.02	0.01	< 0.01	0.03	0.02	0.01	0.05	< 0.01
P ₂ O ₅	0.12	0.04	0.04	0.11	0.18	0.20	0.22	0.06	0.02	0.04	0.02	0.02
S	<	< 0.001	< 0.001	< 0.001	0.012	0.005	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
LOI	6.83	6.07	8.13	14.17	16.30	7.93	36.88	34.51	42.63	43.91	42.39	43.55
Total	98.78	99.12	99.80	99.35	98.89	98.77	98.69	99.99	98.81	100.28	98.50	98.60
ppm												
Ba	10.0	8.0	14.0	11.0	11.0	13.0	30.0	21.0	37.0	7.0	8.0	21.0
Sr	12.0	8.0	10.0	15.0	19.0	13.0	41.0	38.0	56.0	74.0	29.0	39.0
Y	3.0	3.0	6.0	5.0	6.0	5.0	10.0	9.0	10.0	13.0	10.0	5.0
Sc	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	1.0	< 1.0
Zr	15.0	15.0	15.0	14.0	14.0	15.0	7.0	15.0	9.0	1.0	10.0	6.0
Be	2.0	2.0	1.0	1.0	1.0	1.0	< 1.0	1.0	< 1.0	< 1.0	1.0	< 1.0
V	14.0	28.0	29.0	121.0	13.0	13.0	15.6	20.2	< 5.0	6.9	8.8	7.5
Ni	11.2	16.7	14.5	13.4	25.2	9.8	6.4	10.9	8.4	10.0	5.5	2.6
Cu	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	7.4	4.8	2.6	11.6	1.8	2.9
Zn	13.8	13.9	14.3	11.7	11.6	12.4	9.2	4.7	10.5	5.0	4.4	< 1.0
Ga	1.2	1.5	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	1.7	< 1.0
Ge	2.6	4.0	4.5	3.1	3.2	4.2	0.6	0.7	< 0.5	< 0.5	< 0.5	< 0.5
Rb	1.6	3.8	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	1.2
Nb	0.3	0.4	0.7	0.3	0.3	< 0.2	1.4	0.9	0.8	0.6	1.0	0.6
Mo	< 2.0	< 2.0	3.9	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 1.0	< 2.0	< 2.0
Ag	0.5	0.4	0.3	< 0.3	0.6	0.5	< 0.3	< 0.3	< 0.3	< 0.5	< 0.3	< 0.3
In	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Sn	< 1.0	< 1.0	< 1.0	< 1.0	1.4	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Cs	0.3	0.8	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
ΣREE	10.2	10.0	10.8	8.4	10.5	8.2	12.7	19.5	11.9	21.7	34.0	13.5
Hf	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	0.2	< 0.1
Tl	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1
Pb	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	7.0	9.4	8.2	< 3.0	8.1	6.9
Bi	5.0	< 0.1	< 0.1	2.2	3.0	< 0.1	< 0.1	0.1	0.1	< 0.1	0.3	< 0.1
Th	0.3	0.3	0.3	0.2	0.3	0.1	2.4	0.6	0.5	0.2	1.1	0.2
U	2.9	3.0	1.5	1.7	1.4	1.9	1.3	2.3	2.1	0.9	2.4	1.1
As	< 5.0	13.8	7.3	< 5.0	7.6	5.6	5.8	7.1	< 5.0	4.4	< 5.0	6.5
Cr	81.1	< 20.0	< 20.0	< 20.0	< 20.0	< 20.0	27.0	24.0	< 20.0	60.0	< 20.0	< 20.0
Sb	0.5	1.8	1.4	1.1	1.4	1.8	0.7	0.9	1.1	0.3	1.2	4.9
Cd	2.87	4.75	6.00	4.99	4.07	5.14	0.55	0.33	0.67		0.31	0.32
Fe#	1.00	1.00	1.00	0.99	0.99	1.00	0.96	0.96	0.92	0.97	0.73	0.92

Fe_{TOT} expressed as Fe₂O₃. Fe# = (Fe³⁺)/(Fe³⁺ + Fe²⁺)

Appendix 2 – Rare Earth Element Composition

	M140	M141	M132	M134	M135	M137	M138	M139	M4	M5	M6	M7	M8	M9	M10	M11
SAMPLE	Ser.Phyl.	Ser.Phyl.	Arg. Dol.	Arg. Dol.	Arg. Dol.	Arg. Dol.	Arg. Dol.	Arg. Dol.	Dol. Itab.	Dol. Itab.	Dol. Itab.	Dol. Itab.	Dol. Itab.	Dol. Itab.	Dol. Itab.	Dol. Itab.
Litho ppm	47.32	50.86	8.93	5.18	5.93	4.92	3.38	1.01	3.89	2.46	10.92	2.29	1.52	1.08	1.71	1.43
La																
Ce	101.83	100.90	17.57	12.29	13.08	10.40	7.66	1.86	7.17	4.92	12.88	4.21	2.42	2.21	3.00	2.75
Pr	11.68	10.33	1.95	1.52	1.46	1.32	1.00	0.22	0.82	0.56	1.44	0.49	0.32	0.28	0.39	0.38
Nd	42.65	34.19	8.08	5.70	5.70	5.45	4.21	0.91	3.64	2.49	5.97	2.25	1.48	1.25	1.90	1.69
Sm	8.32	6.15	2.23	1.16	1.32	1.17	0.96	0.19	0.81	0.55	1.16	0.51	0.29	0.33	0.40	0.44
Eu	1.87	1.44	0.96	0.46	0.43	0.45	0.31	0.07	0.34	0.24	0.56	0.25	0.14	0.11	0.17	0.18
Gd	6.32	4.59	1.88	1.09	1.07	1.20	0.93	0.18	1.06	0.73	1.59	0.71	0.45	0.45	0.62	0.60
Tb	0.90	0.75	0.34	0.19	0.20	0.22	0.18	0.03	0.20	0.14	0.28	0.13	0.08	0.08	0.11	0.11
Dy	4.75	4.33	2.04	1.03	1.27	1.26	1.04	0.16	1.32	0.90	1.91	0.92	0.54	0.51	0.73	0.69
Y	27.00	25.0	11.0	7.0	8.0	8.0	7.0	1.0	10.5	8.0	14.1	8.7	5.4	6.1	7.5	7.6
Ho	1.01	0.93	0.39	0.24	0.28	0.28	0.24	0.04	0.31	0.21	0.41	0.22	0.13	0.12	0.18	0.16
Er	3.11	2.81	1.10	0.80	0.84	0.93	0.84	0.12	0.98	0.66	1.31	0.69	0.41	0.40	0.54	0.51
Tm	0.42	0.40	0.16	0.11	0.13	0.14	0.13	0.02	0.14	0.09	0.19	0.10	0.06	0.06	0.08	0.08
Yb	2.69	2.57	1.17	0.71	0.87	0.82	0.79	0.10	0.92	0.60	1.21	0.69	0.38	0.46	0.48	0.51
Lu	0.44	0.43	0.17	0.13	0.14	0.14	0.14	0.02	0.16	0.09	0.20	0.11	0.07	0.08	0.08	0.08
ΣREE	260.29	245.69	57.96	37.61	40.71	36.71	28.82	5.93	32.27	22.63	54.11	22.28	13.74	13.53	17.93	17.22
La/Yb _{PAAS}	1.30	1.46	0.57	0.54	0.51	0.44	0.31	0.78	0.31	0.30	0.67	0.25	0.29	0.17	0.26	0.21
La/Nd _{PAAS}	0.98	1.32	0.98	0.81	0.92	0.80	0.71	0.98	0.95	0.88	1.62	0.90	0.92	0.77	0.80	0.75
Ce/Ce* _{PAAS}	1.00	1.02	0.97	1.01	1.03	0.94	0.96	0.90	0.93	0.97	0.75	0.91	0.80	0.92	0.85	0.86
Eu/Eu* _{PAAS}	1.21	1.27	2.21	1.95	1.69	1.79	1.57	1.84	1.73	1.79	1.95	1.97	1.88	1.42	1.62	1.61
Y/Y* _{PAAS}	0.99	0.99	0.98	1.13	1.08	1.07	1.12	1.02	1.31	1.46	1.27	1.54	1.67	2.00	1.67	1.84
Pr/Pr* _{PAAS}	1.04	1.03	0.96	1.07	0.99	1.03	1.03	1.01	0.94	0.94	0.97	0.94	0.99	1.01	0.96	1.03
La/Sm _{PAAS}	0.83	1.20	0.58	0.65	0.65	0.61	0.51	0.76	0.70	0.65	1.37	0.65	0.75	0.48	0.62	0.47
Sm/Yb _{PAAS}	1.57	1.22	0.97	0.83	0.78	0.73	0.62	1.03	0.45	0.47	0.49	0.38	0.39	0.36	0.42	0.44
Sm/Yb	3.09	2.39	1.91	1.63	1.53	1.43	1.21	2.02	0.88	0.92	0.96	0.74	0.77	0.71	0.83	0.87
Y/Ho	26.83	26.74	28.03	29.73	29.03	28.54	29.59	26.48	33.81	37.79	34.11	39.22	43.49	52.03	42.41	48.69

Y content is not included in ΣREE. $(Eu/Eu^*)_{PAAS} = ((Eu/Eu_{PAAS}) / (Sm/Sm_{PAAS}) * (Gd/Gd_{PAAS}))^{1/2}$, Ce/Ce^*_{PAAS} and Y/Y^*_{PAAS} calculated by similar way.

Appendix 2 – Rare Earth Element Composition (Continued)

SAMPLE	M96	P55_27	P55_61	P3_18	P3_23	P3_36	P3_50	P54_80	P54_85	P54_120	P54_124	P3_69	P3_83	P3_103	P3_122	P3_138
Litho ppm	Dol. Itab.	Dol. Itab.	Dol. Itab.	Sil. Itab.	Sil. Itab.	Sil. Itab.	Sil. Itab.	Sil. Itab.	Sil. Itab.	Sil. Itab.	Sil. Itab.	Qz Dol.	Qz Dol.	Qz Dol.	Qz Dol.	Qz Dol.
La	1.32	2.17	1.27	0.68	1.81	2.15	1.37	1.22	1.00	1.53	1.41	1.41	1.25	1.14	0.61	1.79
Ce	2.95	3.40	3.32	1.22	3.61	3.11	1.38	2.05	1.53	2.81	2.68	2.51	2.39	2.51	1.46	3.70
Pr	0.40	0.51	0.52	0.14	0.52	0.57	0.21	0.28	0.20	0.39	0.31	0.24	0.26	0.32	0.15	0.47
Nd	1.83	2.39	2.60	0.73	2.42	3.36	0.67	1.46	0.97	2.06	1.49	1.12	1.27	1.48	0.78	1.90
Sm	0.49	0.63	0.82	0.20	0.66	0.87	0.16	0.41	0.28	0.54	0.43	0.26	0.30	0.33	0.21	0.40
Eu	0.16	0.20	0.25	0.08	0.21	0.28	0.05	0.16	0.11	0.17	0.18	0.10	0.13	0.10	0.08	0.14
Gd	0.60	0.73	0.90	0.29	0.85	1.14	0.22	0.48	0.34	0.65	0.50	0.40	0.47	0.43	0.35	0.47
Tb	0.10	0.13	0.17	0.05	0.14	0.18	0.04	0.09	0.07	0.11	0.09	0.07	0.09	0.07	0.07	0.08
Dy	0.62	0.86	1.03	0.32	0.75	1.01	0.26	0.58	0.45	0.63	0.63	0.42	0.58	0.42	0.42	0.51
Y	6.4	8.0	9.0	2.0	5.0	7.3	3.0	4.0	4.0	4.0	5.0	3.8	5.1	3.0	3.8	4.0
Ho	0.15	0.19	0.23	0.06	0.17	0.20	0.06	0.13	0.10	0.13	0.13	0.09	0.13	0.10	0.09	0.12
Er	0.47	0.63	0.71	0.18	0.46	0.56	0.17	0.38	0.32	0.40	0.41	0.26	0.40	0.30	0.26	0.39
Tm	0.07	0.10	0.12	0.03	0.06	0.08	0.03	0.06	0.05	0.06	0.06	0.04	0.06	0.04	0.03	0.06
Yb	0.49	0.66	0.79	0.14	0.33	0.44	0.17	0.35	0.32	0.32	0.40	0.21	0.36	0.27	0.21	0.36
Lu	0.08	0.10	0.13	0.02	0.05	0.07	0.02	0.05	0.05	0.05	0.06	0.04	0.06	0.04	0.04	0.06
ΣREE	16.11	20.71	21.87	6.13	17.05	21.27	7.80	11.70	9.78	13.85	13.81	10.91	12.81	10.54	8.56	14.47
La/Yb _{PAAS}	0.20	0.24	0.12	0.35	0.40	0.36	0.60	0.26	0.23	0.35	0.26	0.50	0.26	0.31	0.22	0.36
La/Nd _{PAAS}	0.64	0.81	0.43	0.83	0.66	0.57	1.83	0.74	0.92	0.66	0.84	1.12	0.87	0.69	0.70	0.84
Ce/Ce _{PAAS}	0.94	0.74	0.94	0.92	0.86	0.65	0.60	0.81	0.79	0.84	0.93	1.00	0.96	0.96	1.09	0.93
Eu/Eu _{PAAS}	1.40	1.37	1.38	1.50	1.33	1.33	1.18	1.72	1.67	1.36	1.80	1.42	1.58	1.30	1.43	1.49
Y/Y _{PAAS}	1.70	1.58	1.49	1.13	1.11	1.30	1.94	1.18	1.51	1.13	1.37	1.56	1.50	1.19	1.53	1.29
Pr/Pr _{PAAS}	1.01	1.06	1.04	0.87	1.04	1.03	1.27	0.94	0.96	0.96	0.92	0.83	0.89	0.97	0.85	1.04
La/Sm _{PAAS}	0.39	0.50	0.22	0.50	0.40	0.36	1.26	0.43	0.53	0.41	0.48	0.79	0.60	0.50	0.42	0.65
Sm/Yb _{PAAS}	0.51	0.48	0.52	0.70	1.01	0.99	0.48	0.60	0.44	0.85	0.54	0.63	0.43	0.62	0.52	0.56
Sm/Yb	1.00	0.95	1.03	1.37	1.98	1.96	0.94	1.18	0.87	1.68	1.07	1.25	0.85	1.23	1.03	1.10
Y/Ho	43.80	41.74	39.88	32.04	29.25	36.82	51.30	31.62	40.14	31.47	37.23	42.33	40.28	31.00	40.46	32.99

Y content is not included in ΣREE. $(Eu/Eu^*)_{PAAS} = ((Eu/Eu_{PAAS}) / (Sm/Sm_{PAAS}) * (Gd/Gd_{PAAS}))^{1/2}$, Ce/Ce^*_{PAAS} and Y/Y^*_{PAAS} calculated by similar way.

Appendix 2 – Rare Earth Element Composition (Continued)

SAMPLE	P3_152	P3_170	P3_185	P3_196	M5A	M6A	M7A	M8A	M10A	M11A	M1	M16	M81	M100	M102	M103
Litho ppm	Qz Dol.	Qz Dol.	Qz Dol.	Qz Dol.	Hem.Bd	Hem.Bd	Hem.Bd	Hem.Bd	Hem.Bd	Hem.Bd	Dol.Bd	Dol.Bd	Dol.Bd	Dol.Bd	Dol.Bd	Dol.Bd
	1.63	1.37	1.65	1.26	1.90	1.88	2.56	1.61	1.89	1.28	1.88	2.87	2.37	3.60	5.67	2.40
La																
Ce	4.64	3.24	3.46	2.74	3.42	3.41	3.49	2.44	2.94	2.30	3.34	6.41	3.10	6.85	13.02	4.70
Pr	0.52	0.41	0.42	0.29	0.41	0.39	0.43	0.33	0.41	0.33	0.52	0.86	0.46	0.84	1.31	0.55
Nd	2.65	1.84	1.82	1.26	1.77	1.60	1.66	1.58	2.02	1.50	2.52	4.04	2.06	3.55	5.83	2.48
Sm	0.78	0.55	0.38	0.29	0.41	0.39	0.37	0.32	0.48	0.38	0.60	0.91	0.45	0.79	1.33	0.53
Eu	0.21	0.17	0.10	0.10	0.15	0.15	0.14	0.13	0.14	0.15	0.24	0.31	0.18	0.39	0.57	0.25
Gd	1.04	0.76	0.41	0.37	0.49	0.42	0.38	0.44	0.57	0.55	0.90	1.14	0.64	1.06	1.51	0.67
Tb	0.21	0.15	0.08	0.07	0.08	0.07	0.07	0.08	0.10	0.09	0.14	0.18	0.12	0.20	0.27	0.11
Dy	1.35	0.81	0.43	0.43	0.51	0.53	0.55	0.46	0.66	0.57	0.92	1.12	0.81	1.36	1.73	0.71
Y	8.8	7.0	3.0	3.4	3.0	3.0	6.0	5.0	6.0	5.0	10.5	9.3	9.5	13.5	10.7	5.3
Ho	0.29	0.18	0.10	0.10	0.13	0.12	0.12	0.11	0.15	0.14	0.21	0.23	0.20	0.33	0.38	0.16
Er	0.87	0.56	0.32	0.28	0.41	0.40	0.41	0.38	0.50	0.45	0.67	0.65	0.65	1.15	1.12	0.43
Tm	0.13	0.08	0.05	0.04	0.06	0.06	0.07	0.06	0.08	0.06	0.09	0.09	0.10	0.19	0.15	0.06
Yb	0.86	0.45	0.31	0.25	0.40	0.41	0.48	0.38	0.50	0.38	0.56	0.57	0.60	1.20	0.99	0.36
Lu	0.15	0.07	0.05	0.04	0.07	0.07	0.08	0.06	0.08	0.06	0.10	0.10	0.11	0.19	0.17	0.06
ΣREE	24.10	17.65	12.57	10.91	13.21	12.91	16.83	13.38	16.53	13.24	23.19	28.80	21.35	35.18	44.77	18.76
La/Yb _{PAAS}	0.14	0.22	0.40	0.38	0.35	0.34	0.39	0.32	0.28	0.25	0.25	0.37	0.29	0.22	0.42	0.49
La/Nd _{PAAS}	0.55	0.66	0.81	0.89	0.96	1.04	1.37	0.91	0.83	0.75	0.66	0.63	1.02	0.90	0.86	0.86
Ce/Ce _{PAAS}	1.16	1.00	0.96	1.05	0.89	0.91	0.76	0.77	0.77	0.82	0.78	0.94	0.68	0.91	1.10	0.94
Eu/Eu _{PAAS}	1.09	1.26	1.24	1.35	1.60	1.70	1.70	1.59	1.30	1.53	1.54	1.42	1.60	1.98	1.90	2.01
Y/Y _{PAAS}	1.13	1.48	1.16	1.31	0.94	0.94	1.84	1.74	1.50	1.41	1.89	1.48	1.86	1.60	1.06	1.24
Pr/Pr _{PAAS}	0.88	0.99	0.99	0.91	0.99	0.99	1.06	0.99	0.99	1.03	1.06	0.99	1.08	1.01	0.89	0.95
La/Sm _{PAAS}	0.30	0.36	0.63	0.62	0.67	0.70	0.99	0.72	0.57	0.49	0.45	0.46	0.76	0.66	0.62	0.66
Sm/Yb _{PAAS}	0.46	0.62	0.63	0.61	0.52	0.49	0.39	0.44	0.49	0.51	0.54	0.81	0.38	0.34	0.68	0.74
Sm/Yb	0.91	1.22	1.24	1.20	1.03	0.96	0.77	0.86	0.96	1.01	1.07	1.60	0.75	0.66	1.34	1.46
Y/Ho	30.78	39.73	30.66	34.07	23.98	24.66	48.27	44.36	38.88	36.07	49.50	41.16	46.63	40.85	28.39	32.83

Y content is not included in ΣREE. (Eu/Eu_{PAAS})^{*}=(Eu/Eu_{PAAS})/(Sm/Sm_{PAAS})*(Gd/Gd_{PAAS})^{1/2}, Ce/Ce_{PAAS} and Y/Y_{PAAS} calculated by similar way. Hem.Bd=Iron-rich band of dolomitic itabirite; Dol.Bd=dolomite-rich band of dolomitic itabirite.

ANEXO 3 – THE HIGH-GRADE IRON ORES OF THE ÁGUAS CLARAS MINE, QUADRILÁTERO FERRÍFERO, BRAZIL

Abstract

Several major iron deposits occur in Quadrilátero Ferrífero (QF), Southeastern Region of Brazil, where metamorphosed and heterogeneously deformed banded iron formation (BIF) of the Cauê Formation, regionally called itabirites, were converted to high- ($\text{Fe} > 64\%$) and low-grade ($30\% < \text{Fe} < 64\%$) hematite ores. Based on their mineralogical composition, three major types of itabirites are described as occurring in the QF: quartz, dolomitic and amphibolitic. Unlike other mines in the QF, the Águas Claras mine contained mainly high-grade ores, which occur within dolomitic itabirite. Two distinct types of high-grade ore occurred at the mine: soft and hard. The soft ore was the most abundant and represented more than 85% of the total ore mined until the mine was depleted in 2002. The soft ore is highly porous, friable and partially preserves the original structure of the dolomitic itabirite protore, particularly meso- and microbanding, which is characterized by the presence of massive and porous bands within the ore. The hard ore is dense, tough and compact. It occurs as small concordant lenses within the soft ore and within the fresh dolomitic itabirite. Soft and hard ores consist essentially of hematite, occurring as martite, anhedral to granular/tabular hematite and, locally specularite. Gangue minerals are very rare, consisting of dolomite, sericite, chlorite and apatite in the hard and soft ores, and Mn-oxides and ferrihydrite in the soft ore, where they are concentrated within the porous bands. Chemical analyses showed that hard and soft ores consist almost entirely of Fe_2O_3 , with higher amount of detrimental impurities, especially MnO, in the soft ore. Both hard and soft ores are very depleted in trace elements.

The high-grade ores have at least a dual origin, involving hypogene and supergene processes. The occurrence of the hard massive high-grade ore within fresh dolomitic itabirite is a good evidence of its hypogene origin. Despite the contention about the origin of the dolomitic itabirite (if this rock is a carbonatic facies of the Cauê Formation or a hematite-carbonate precursor of the soft high-grade ore formed by hydrothermal alteration that removed all the chert from the BIF and replaced it with dolomite), many features observed in the soft ore, such as: (1) clear transition from the dolomitic itabirite into the soft ore; (2) disappearance of the soft ore

down dip, forming pinnacles; (3) pockets of dolomitic itabirite within the soft ore; (4) occurrence of slump folds in the soft ore, and Tertiary basins locally blanketing the orebody; (5) petrographic evidences of dolomite dissolution forming Mn-oxides and ferrihydrite (a metastable iron hydroxide that transforms into hematite at temperatures as low as 4 °C, and (6) a similar REEY pattern for the dolomitic itabirite and the soft ore, indicate that the soft high-grade ore in the Águas Claras mine was formed by leaching of dolomite from the dolomitic itabirite by meteoric water.

The original composition of the itabiritic protore has a major role in the genesis of high- and low-grade soft ores in the QF. Under the same weathering and structural conditions, the dolomitic itabirite is more likely to form high-grade deposits than quartz itabirite, due to the higher solubility of dolomite in relation to quartz. Field relationships at the Águas Claras and Capão Xavier deposits suggest that it is not possible to form huge soft high-grade supergene deposits from quartz itabirite, unless another control, such as impermeable barriers, had played an important role.

INTRODUCTION

The Águas Claras iron-ore mine is located in the Quadrilátero Ferrífero (QF), Southeastern Region of Brazil, state of Minas Gerais (Fig. 1). Open-pit mining at Águas Claras commenced in 1973 and, by 2002, when the mine was closed, approximately 288 Mt of high-grade iron ore (average Fe>68%) had been mined on the crest and along the slopes of a segment of the Serra do Curral. About 88 Mt of high-grade iron ore remained, but economic and environmental restrictions prevented mining from continuing. The high quality of its products and the large tonnage obtained placed the Águas Claras mine among the most important iron mines during that time.

Despite its world-class category and the significant amount of data gathered on the mine since mining began in 1973, very little geological information on the mine is available in published literature (Gomes 1986; Viel et al. 1987; Hackspacher 1979). Recently, Spier et al. (2003) described the geology of the Águas Claras and Pico iron mines and presented data for the main chemical constituents of the iron ore at those mines. This study complements that previous work, presenting a detailed study on the mineralogy and geochemistry of the iron ores of the Águas Claras mine and aims at contributing to the discussion on their genesis.

The majority of the iron orebodies at the QF are hosted in itabirites (oxidized, metamorphosed and heterogeneously deformed BIFs) of the Cauê Formation, Itabira Group. Itabirites of the Cauê Formation are very similar in lithology to most major oxide-facies BIFs known worldwide (Dorr II 1969). Based on their mineralogical composition, three major types of itabirites are described as occurring in the QF: quartz, dolomitic and amphibolitic.

Unlike other mines of the QF, the Águas Claras mine contained mainly high-grade ore (Fe >64%) hosted within dolomitic itabirite. Although quartz and dolomitic itabirite crop out at the mine, the high-grade ore was developed mainly within the latter. Two distinct types of high-grade ore occur at the mine: soft and hard. The soft ore was the most abundant and represented more than 85% of the total ore mined. It was considered by Spier et al. (2003) as of supergene origin, whereas the hard ore was considered by the same authors as of hypogene origin, because it occurs within fresh dolomitic itabirite. Some features of the soft ore such as the great depth of mineralization and the lack of goethite, otherwise, could suggest that this type of ore is also of hypogene origin.

The genesis of the high-grade (Fe > 64%) and low-grade (30% < Fe < 64%) iron ores within the Cauê Formation has been the object of debate since the beginning of the 20th century and continues to be the focus of studies by several researchers (e.g. Cabral et al. 2003; Dorr II 1964; Dorr II 1965; Guild 1953; Harder and Chamberlain 1915; Park 1959; Ramanaidou 1989; Ramanaidou et al. 1996; Rosière and Rios 2004). Most studies are concentrated in ores originating from quartz itabirite, the most common type of itabirite in the region, probably because dolomitic itabirite is more restricted to and concentrated along the Serra do Curral (Fig. 1). The genesis of the iron ore originating from dolomitic itabirite in the QF has never been studied in detail, and several questions remain open. Why were the high-grade ores at the Águas Claras mine formed mainly from dolomitic itabirite and not from quartz itabirite? Why were the high-grade ores formed from quartz itabirite limited to few meters below the topographic surface? Were the hard and soft ores formed during the same event? Could the soft ore be produced only by weathering? Are new minerals formed during leaching of the carbonates? This paper address those questions, in order to contribute for discussions about the genesis of the iron ore in the QF and worldwide.

Figure 1 – Location and geological sketch map of the Quadrilátero Ferrífero region (After Alkmim and Marshak 1998).

GEOLOGICAL SETTING

Paleoproterozoic Minas Supergroup metasedimentary rocks form the mountain ranges of the QF, whereas the lowlands are occupied by Archean granite-gneiss basement rocks and the Rio das Velhas Greenstone Belt sequence (Fig. 1). The giant iron ore deposits of the QF are hosted in the platformal sediments of the Minas Supergroup and consist of three metamorphic sequences (Dorr 1969). The lowest unit is the Caraça Group, which contains clastic sediments. The middle Itabira Group comprises itabirites with minor dolomite and phyllite of the Cauê Formation and carbonate rocks of the Gandarela Formation. Itabirites grade upward to dolomites and dolomitic/manganiferous itabirites of the 2.4 Ga Gandarela Formation (Babinski et al. 1995).

The Piracicaba Group comprises clastic sediments (with subordinate dolomites), separated by an unconformity from the underlying Itabira Group.

The Águas Claras mine is located in the northern segment of the Serra do Curral, a northeast-southwest trending ~100 km-long ridge that limits the northwest edge of the QF (Fig. 1). Units of the Minas Supergroup crop out along most of its extension as an inverted sequence without repetition. In the northern segment of the Serra do Curral, the rocks are strained, sinistrally rotated from their original position, and beds are overturned (Chemale Jr. et al. 1994). Extensive shear zones occur at the contact between the Minas Supergroup and the underlying Archean Rio das Velhas Supergroup. At this region of the QF, the rocks of the Minas Supergroup were submitted to a low-grade metamorphism of the greenschist-facies (Pires 1995).

At the Águas Claras mine, quartzite and phyllite of the Moeda and Batatal Formations, as well as dolomite, itabirite and iron ore of the Cauê Formation, crop out (Fig. 2a-b). Within the pit, the dolomitic itabirite is much more common than the quartz itabirite, which occurs only in the north wall on the top of the sequence (Fig. 2a).

The Dolomitic Itabirite (Protore)

The dolomitic itabirite occurs as a continuous 150 to 400 m thick layer and represents the protore of the soft iron ore. Its petrography and geochemistry were described in detail by Spier et al. (2005a) and will be briefly addressed herein. Banding of cm-sized iron-rich and dolomite-rich bands is the most conspicuous macroscopic features of the dolomitic itabirite, characterizing the mesobanding defined by Trendall and Blockley (1970) for BIFs of the Hamersley basin. At the base of the sequence, the dolomitic bands are thicker and predominate over the iron-rich bands. The former display color shades ranging from deep red to pink and have a cm- to dm-sized thickness, while the latter are gray and range from less than one millimeter to 3 cm thick. At about 50 m up on the sequence, the thickness of the dolomitic band is reduced thus giving origin to the typical dolomitic itabirite, where ~1cm bands of dolomite alternate with hematitic bands (Fig. 3a) throughout ~250 meters of itabirite. To the top, hematitic bands gradually disappear, and a ferruginous dolomite predominates. A mm-sized banding of iron-rich and dolomite-rich laminae (microbanding) also occurs, especially within dolomite-rich mesobands (Fig. 4a).

The carbonate bands of dolomitic itabirite consist of very fine grained sparry dolomite and hematite with grain size ranging from 5-30 μm (the average being 20 μm , Fig. 4b). The volume of hematite within the carbonate bands is highly variable (5% to 50% from band to band). Hematite occurs mainly as individual crystals of tabular shape intergrown with dolomite, or else

forming aggregates of granular and tabular crystals of irregular shapes (Fig. 4c). Platy hematite (specularite) occurs in shear planes, surrounding crystals of tabular/granular hematite (Fig. 4d). Randomly oriented red-brown microcrystals of hematite ($<1\ \mu\text{m}$) within dolomite crystals in the carbonate bands account for the characteristic deep red color of these bands.

Figure 2 - Águas Claras mine. A Cross section 2200E. B Geological sketch map.

Figure 3 – **A** Hand specimen of dolomitic itabirite. Mesobanding is preserved as dolomite-rich (d) and iron oxide-rich (h) layers. **B-C** Mine exposures of the soft (SO) and hard (HO) ores. **D** Deeper contact zone of the soft ore and dolomitic itabirite (DI). Note the pinnacles of dolomitic itabirite surrounded by the soft ore. **E** Detail of the contact between soft ore and dolomitic itabirite. **F** Detail of the soft ore showing massive bands (MB) and porous bands (PB). **G** Hand specimens of hard ore: 1 massive, 2 banded, 3 schistose, 4 coated by goethite.

Figure 4 – Photomicrographs and SEM images of dolomitic itabirite. **A** Microbanding of dolomite-rich (white) and iron oxide-rich (black) laminae; transmitted light. **B** Detail of the dolomite-rich microband. Aggregates of euhedral crystals of tabular hematite (h) between the dolomite crystals (d); transmitted light. **C** SEM image of the dolomite-rich band showing aggregates of hematite (h) between dolomite (d); backscattered image. **D** Specularite crystals (s) grown along a shear plane surrounding a porphyroblast of idiomorphic tabular hematite (th). **E** SEM image of an iron oxide-rich laminae; backscattered image. **F** Detail of the iron oxide-rich laminae showing dolomite crystals (d) between hematite (h). **G-H** Detail of a dolomite-rich microband showing talc crystal (t) intergrown with dolomite (d) and hematite (h) in **G** and apatite between dolomite and hematite in **H**.

The iron-rich bands contain hematite (>80%), interstitial carbonates and pores (Fig. 4e-f). The average hematite grain size is similar to that of the dolomitic bands (~ 20 μm) ranging from 5-30 μm . Hematite occurs mainly as tabular and granular crystals growing over martite (hematite pseudomorphous after magnetite), forming a dense network. Hematite also occurs locally as specularite. Traces of magnetite are observed in the nuclei of some hematite crystals, especially in the coarser iron-rich bands.

Accessory minerals are also present in the dolomitic itabirite. Talc occurs intergrown with dolomite (Fig. 4g) and associated with chlorite in thin veins. Apatite can be found forming monomineral layers (<1 mm) or as isolated euhedral crystals (4-10 μm) intergrown with or included in hematite and dolomite crystals (Fig. 4h). Chlorite occurs along veins and shear planes.

The Iron Ore

The Águas Claras orebody comprises soft and hard high-grade ores (Fig. 3b-c). The orebody is a bedding-concordant, 2,500 m long, roughly tabular-shaped lens with a maximum thickness of 300 m and formed essentially by soft ores (Fig. 2b). The hard ores generally occur within the soft ores as minor lenses concordant to the bedding. The depth of the orebody is variable, extending to over 400 m below the surface at the center of the pit bottom and then grading into the parental fresh dolomitic itabirite deeper down (Fig. 2a). In this contact region, it is very common to find the presence of pinnacles of fresh dolomitic itabirite surrounded by the soft ore (Fig. 3d). Higher levels of contaminants in the iron ore, especially apatite, occur in this zone. Dip and strike of the orebody are conformable with regional trends, i.e., strike is northeast-southwest, dip is 65° to 80° SE.

The soft ore is gray, friable and has a laminated appearance. It preserves partially the original structure of the protore, particularly meso- and microbanding, which is characterized by the presence of massive and porous bands within the ore, parallel to the banding of the itabirite (Figs. 3b, 5a-f). Adjacent bands are rarely of similar thickness. Field relationships show that iron-rich bands of dolomitic itabirite grade into the massive bands in the iron ore, while dolomite-rich bands grade into the porous bands. Even massive bands are porous, but they have less than 30 percent of pore space, and individual pores are isolated in massive hematite. Generally massive bands are broken and disrupted while porous bands show free aggregates of hematite between pores (Fig. 5f-g). Kink-bands (not present in the protore) are locally observed.

Figure 5 – SEM backscattered images of the soft ore. A-B Typical image of soft ore showing massive bands (mb, white) broken and disrupted, with aggregates and individual crystals of hematite (h) between pores (black) in the porous bands (pb). C Microbanding of massive and porous bands. Note the preservation of microbanding of the protore. D-E Massive bands showing the dense packing of hematite (h). F Massive and porous bands showing the beginning of breaking and disrupting of the former. G Detail of a massive band highly broken and disrupted. H Coarse crystals of tabular hematite (th) in the massive and porous bands, surrounding a porphyroblast of martite (m) in the former. Note the small crystals of specularite (s) in the lower part of the picture.

The main hard ore occurrences are concentrated on the west side of the mine, close to the top of the sequence. Here, they are in contact with quartz itabirite forming lenses up to 200 m in length along the strike, ranging from 5 to 60 m in thickness (Fig. 2b). Small concordant lenses of hard ore from a few centimeters to nearly a meter thick also occur within the soft ore and within the fresh dolomitic itabirite on the east side of the pit.

The hard ore is dense, tough, compact, dark bluish gray and has a dull to metallic luster (Fig. 3c). Three main subtypes of hard ore are found at Águas Claras mine: massive, banded and schistose (Fig. 3f). Massive hard ore has visually low porosity, does not exhibit any kind of structure and usually shows signs of conchoidal fracture. Banded hard ore is the major type of hard ore, being characterized by conspicuous banding and varied porosity. Schistose hard ore generally has low porosity, does not preserve the original structures and exhibits a conspicuous foliation. This type of hard ore is associated with the shear zones which are mainly found on the northern wall of the pit.

SAMPLING AND ANALYTICAL PROCEDURES

Eighty-six samples representing the hard and soft ores were collected from diamond drill cores and outcrops along the benches of the mine. Appendix 1 presents the local coordinate of each sample and the respective analytical procedure followed. Detailed sampling was carried out in the zone of contact with the protore, in order to access the transition from the dolomitic itabirite to the iron ore. All samples were impregnated with epoxy resin and polished for petrographic analyses purposes. Samples of each type of ore were submitted to scanning electron microscopy (SEM). The porous band of the soft ore was examined by transmission electron microscopy (TEM). SEM analyses were carried out at the laboratories of the Geoscience Institute of the University of São Paulo, Brazil, and at the Center for Microscopy and Microanalyses of the University of Queensland, Australia, where TEM analyses were also carried out.

Eight ore samples were selected for Mössbauer spectroscopy (MS), consisting of four soft ore and four hard ore. For each sample of soft ore, the massive band (samples MAC-126A to MAC-129A) was carefully separated from the porous band (samples MAC-126B to MAC-129B). For the hard ore, samples of sub-types massive (MAC-97), banded (MAC-67 and MAC-105), and schistose (MAC-68) ores were selected. Besides the iron ore samples, two samples (MAC-96 and MAC-100) of the fresh dolomitic band of the dolomitic itabirite were examined

by MS. Transmission ^{57}Fe Mössbauer spectra at 300 K were obtained on a constant acceleration spectrometer using a $^{57}\text{Co/Rh}$ source at the Laboratory of Applied Physics of the Nuclear Technology Development Center (CDTN) in Belo Horizonte. Mössbauer spectra of four samples (MAC97, MAC127A, MAC127B and MAC100) were also recorded at 50 K. A least-square fit-program was employed to calculate the spectral hyperfine parameters. All samples studied by MS were characterized by X-ray diffraction (XRD) at the Institute of Physics of the Federal University of Minas Gerais (UFMG). Unit cell parameters of hematite were determined using the Rietveld refinement for samples MAC67, MAC 97 and MAC 127A and B.

Eighty-six samples of the iron ore were analyzed by ICP for major and some trace elements (Ba, V, Ni, Cu and Zn) at the chemical laboratory of MBR. From the total number of samples, 48 were selected for analyses of major, trace and rare earth elements (REE) at the Activation Laboratories – ACTLABS in Canada. All samples were prepared for analysis by grinding in a tungsten carbide vessel. Since this method causes contamination by W, Co and Ta, concentrations of these elements are not reported. In ACTLABS, major and trace elements were determined by ICP/ICP-MS after the opening of the sample with a lithium tetraborate/metaborate fusion. Base metals were determined by ICP-MS/INAA after total digestion by acid attack. Ferrous iron was determined at the laboratories of MBR by potassium dichromate titration. REE data on the Post Archean Australian Shale (PAAS) obtained by McLennan (1989) were used as normalization values. We present REE patterns with Y inserted between Dy and Ho according to its ionic radius. The reason why we included Y in the lanthanides lies in the value of comparative studies of the behavior of Y and REE in aqueous solutions and their precipitates (Bau and Dulski 1996). In our case, the precipitates were the original sediments of the dolomitic itabirite. The Eu anomaly is defined quantitatively as:

$$\text{Eu/Eu}^* = ((\text{Eu}/\text{Eu}_{\text{PAAS}})/(\text{Sm}/\text{Sm}_{\text{PAAS}}) \times (\text{Gd}/\text{Gd}_{\text{PAAS}}))^{1/2}$$

where Eu^* is the hypothetical concentration of Eu. The anomalies of Ce and Y were similarly calculated. The degree of light REE enrichment relative to heavy REE is presented as the ratios of PAAS-normalized La and Yb (La/Yb), La and Sm (La/Sm), and Sm and Yb (Sm/Yb).

MINERALOGICAL AND GEOCHEMICAL CHARACTERISTICS

The Dolomitic Itabirite (Protore)

In order to allow comparisons between the protore and the iron ore, we present a brief summary of the dolomitic itabirite chemical data. For additional information, readers should refer to Spier et al. (2005a). The average major, trace and REE composition of the dolomitic itabirite is presented together with statistics of the iron ore. Dolomite within dolomitic bands has a very uniform composition, with Ca:Mg ratio around 1:1 and average contents of CaO and MgO ranging from 29.6% to 30.5% and from 18.4% to 20.6%, respectively. The average contents of FeO and MnO are low, ranging from 3.7% to 1.0% and from 0.5% to 0.9%, respectively. Electron microprobe analyses (EMP) were also carried out on many grains of hematite and martite. The results, however, did not show any variation of the chemical composition, giving the Fe_2O_3 content always higher than 99%.

XRD analyses of the two samples of the dolomite-rich bands (MAC-96 and MAC-100) showed only the presence of hematite and dolomite (Fig. 6a). MS identified hematite and siderite in the samples (Fig. 6b, Table 1), represented by a typical sextet and a less defined doublet, respectively. The values of the hyperfine field of hematite at 300 K (51.9 T) and at 50 K (54.8 T) are typical of well-crystallized pure hematite (Murad and Schwertmann 1986). The isomer shifts of the doublet at 300 K (1.2 mm/s) and at 50 K (1.4 mm/s) match well with those of siderite and represent the FeCO_3 content of the dolomite. The low iron content of dolomite is responsible for the ill-defined doublet shown by the samples. As the iron content of the dolomite is relatively constant through the dolomitic itabirite sequence, the better defined doublet shown in sample MAC-100, as compared to the doublet in sample MAC-96, can be interpreted as a higher amount of dolomite in sample MAC-100. The relative abundance of these minerals is expressed by the subspectral areas of hematite and siderite in the MS of the samples MAC-100 and MAC-96 (Table 1).

Figure 6 – **A** Powder XRD patterns of dolomite-rich bands of the dolomitic itabirite showing hematite (Hm) and dolomite (Dol). **B** Mössbauer spectra at 300 K of the same samples.

Table 1 – Mössbauer hyperfine parameters of iron ore and dolomitic itabirite samples

Sample Code	Sample Description	Temperature (K)	Subspectrum	Isomer shift (± 0.05) (mm·s ⁻¹)	Quadrupole Splitting (± 0.05) (mm·s ⁻¹)	Hyperfine Field (± 0.6) (T)	Line Width (± 0.5) (mm·s ⁻¹)	Relative Abundance (%)
Mac67	HO	300	Hematite	0.37	-0.16	51.9	0.34	100
Mac68	HO	300	Hematite	0.37	-0.15	51.9	0.34	100
Mac97	HO	300	Hematite	0.37	-0.16	51.9	0.34	100
Mac97	HO	50	Hematite	0.48	0.38	55.8	0.37	100
Mac105	HO	300	Hematite	0.37	-0.15	51.9	0.35	100
Mac126A	SO - Massive	300	Hematite	0.36	-0.16	51.9	0.34	100
Mac127A	SO - Massive	300	Hematite	0.37	-0.16	51.9	0.34	100
		50	Hematite	0.48	0.37	54.9	0.37	100
Mac128A	SO - Massive	300	Hematite	0.37	-0.17	51.9	0.34	100
Mac129A	SO - Massive	300	Hematite	0.37	-0.15	51.9	0.35	100
Mac126B	SO-Porous	300	Hematite	0.37	-0.13	51.9	0.34	98
			Ferrihydrite	0.34	0.68	-		2
Mac127B	SO-Porous	300	Hematite	0.37	-0.13	51.9	0.34	98
			Ferrihydrite	0.34	0.68	-		2
		50	Hematite	0.48	0.32	54.9	0.39	97
			Ferrihydrite	0.42	0.76	-	0.48	3
Mac128B	SO-Porous	300	Hematite	0.37	-0.13	51.9	0.34	98
			Ferrihydrite	0.34	0.68	-		2
Mac129B	SO-Porous	300	Hematite	0.36	-0.13	51.9	0.34	98
			Ferrihydrite	0.35	0.68	-		2
Mac96	Dol. Itabirite	300	Hematite	0.37	-0.14	51.9	0.34	98
			Siderite	1.20	1.60	-		2
Mac100	Dol. Itabirite	300	Hematite	0.37	-0.13	51.9	0.34	90
			Siderite	1.20	1.55	-		10
		50	Hematite	0.48	0.39	54.8	0.34	90
			Siderite	1.37	2.03	-	0.51	10

HO means hard ore; SO-Massive means massive band of soft ore; SO-Porous means porous band of the soft ore; Dol. Itabirite means dolomitic itabirite

Soft Iron Ores

Mineralogy and Petrology

The soft ore consists of alternated mm- to cm-sized massive and highly porous bands, both rich in iron oxides (Figs. 5 and 7). The former corresponds to the iron-rich bands of the dolomitic itabirite while the latter corresponds to the dolomite-rich bands. The soft ore as a whole is highly porous, with intergranular porosity visually estimated in thin sections at 35 – 45% (Fig. 5b). Hematite is the major iron oxide in both bands, occurring as martite, anhedral to granular/tabular hematite and, locally, specularite. Magnetite is locally observed as remnants within martite and granular hematite crystals, especially within thicker massive bands. Ferrihydrite (identified by Mössbauer analyses; see text below) is more frequent within the porous bands, where it occurs as an accessory mineral (Figs. 7a-d). Gangue minerals are rare, increasing in amount in samples

Figure 7 – Photomicrographs of the soft ore. **A** Microbanding of massive and porous bands, transmitted light. **B-C** Detail of a porous band, transmitted light (**B**), reflected light, PPL (**C**). **D** Detail of the previous picture showing ferrihydrite (f) surrounding aggregates and individual crystals of hematite **E** Massive band (mb) between porous bands (pb), reflected light, PPL. **F** Detail of the massive band showing granoblastic fabric of granular/tabular hematite, reflected light, partially XPL. **G** Massive band showing granoblastic fabric of granular/tabular hematite growing over martite (m), reflected light, PPL. **H** Detail of a porous band showing aggregates and individual crystals of tabular hematite.

obtained close to contacts with both the protore and the phyllite. They are also more frequent within the porous bands and consist of apatite, talc, chlorite and Mn-oxides (Figs. 8a-f). Apatite is more frequent in samples from the lower levels of the mine, especially from the bottom pit, where the pinnacles occur.

The massive bands of the soft ore generally show a granoblastic fabric and consist of fine granular and tabular hematite (5-20 μm), forming a dense package (Figs. 7e-g). The porous bands have variable porosity, visually estimated at 30 – 60%. They consist of aggregates ranging from 50 μm to 10 mm of granular and tabular hematite crystals (up to 60%) and/or of individual crystals of tabular hematite ranging from 10 to 30 μm (Figs. 7e and h). Locally, it is possible to observe the development of tabular and granular hematite growing over coarser martite crystals ($\sim 50 \mu\text{m}$) and the desaggregation of these crystals, causing the release of the finer tabular hematite (Fig. 7 g-h). Hematite crystals are surrounded by a brownish residue of poorly crystalline ferrihydrite (Figs. 7 a-d). Ferrihydrite is produced during the dissolution of dolomite, a process which is clearly represented in thin sections of partially weathered dolomitic itabirite, where it forms a brownish residue.

SEM observations of the <0.15 mm size fraction of some samples of the soft ore have also shown a few small particles of Mn oxides besides hematite (Fig. 8d). TEM analyses confirm the presence of these Mn oxides within the porous bands (Figs. 9a-c). They occur as very small particles ($\sim 100 \text{ nm}$) mixed with the iron oxides.

In samples collected from the zone of contact with the protore, it is possible to observe remnants of dolomite intergrown with hematite and gangue minerals. Apatite is very well preserved in this zone, forming thin laminae parallel to the banding or occurring as isolated euhedral crystals (Figs. 8a-c). Talc and chlorite are also observed as isolated crystals or forming mm-sized aggregates (Figs. 8 e-f).

Figure 8 – SEM backscattered images of gangue minerals in the iron ore. **A** Microbanding of apatite-rich laminae (a) between massive bands (mb) of hematite. **B** Detail of the apatite-rich laminae. **C** Porous band of the soft ore showing apatite (a) and aggregates of hematite (h) between pores (p). **D** Detail of the size fraction < 0.15 mm of the soft ore showing small crystals of Mn-oxides on the surface of hematite aggregates, SEM image, secondary electrons. **E** Porous band of the soft ore showing aggregates of talc (t) and hematite (h) between pores. **F** Detail of the previous picture.

Figure 9 – **A** TEM image of the porous band of the soft ore. Large white particles are hematite (h). **B** Detail of the small particles between hematite. EDS spectra (**C**) indicate that some of them have high contents of Mn and Ni.

XRD and Mössbauer Analyses

XRD analyses of the massive bands of the soft ore (Samples MAC-126A to MAC-129A) revealed only the presence of hematite (Fig.10). The sharp XRD peaks suggest high crystallinity. The 300 K Mössbauer spectra fitted perfectly with hematite, with a hyperfine field of about 52 T, isomer shift of about 0.37 mm/s, and a quadrupole shift of about -0.15 mm/s (Table 1). All the spectra are very similar, consisting of 100% of hematite and are represented by the spectrum recorded at 300 and 50 K of sample MAC127A in Fig. 11a and b. The MS of the massive bands

Figure 10 – Powder XRD patterns of the massive bands (mb) and porous bands (pb) of the soft ore samples showing hematite (Hm).

Figure 11 – Mössbauer spectra at 300 K and at 50 K of the massive (A-B) and porous bands (C-D) of the sample MAC127 (Soft ore). E Detail of the central part of the spectra of the porous band at 300 K showing the doublet of ferrihydrite.

have also revealed the presence of the Morin transition (a transition from an antiferromagnetic to a weakly ferromagnetic state, at about 265 K). This transition is very sensitive to microcrystalline effects, lattice imperfections and impurities. Its observation in the studied samples indicates a very pure composition of hematite and crystallites larger than 20 nm. The nearly absent variation of the Mössbauer parameters (Table 1) shows that the ore is made up of pure hematite, with a rather uniform composition, which was also indicated by XRD and by the unit cell parameters obtained for the hematite in the sample MAC127A (Table 2), which are very similar to those of the reference cell of hematite.

Table 2 – Unit cell parameters of hematite in the iron ores of the Águas Claras mine

Sample	Ore Type	aÅ	cÅ
MAC67	Hard Ore	5.0347(1)	13.7474(2)
MAC97	Hard Ore	5.0355(1)	13.7485(2)
MAC127A	Massive band of the soft ore	5.0338(1)	13.7470(2)
MAC127B	Porous band of the soft ore	5.0339(1)	13.7468(2)
Reference cell of hematite		5.0340	13.7520

Data for the reference cell of hematite are from Cornell and Schwertmann (1996, pg. 5)

XRD analyses of the porous bands of the soft ore (Samples MAC-126B to MAC-129B) showed the presence of only hematite (Fig. 10). Thus, the observed diffused, limonitic, brownish material in the porous bands must be amorphous.

The Mössbauer spectra at 300 K of the porous bands are represented by sample MAC127B in Fig. 11c. There is a major sextet corresponding to a hyperfine field of about 52 T and a quadrupole shift of about -0.13 mm/s, parameters that fit perfectly with those of hematite. MS at 50 K of this sample confirms the presence of hematite, characterized by an isomer shift of 0.48 mm/s and a hyperfine field of 54.9 T (Table 1, Fig. 11d). The hyperfine parameters of hematite in the porous bands are quite similar to those observed for this mineral in the dolomitic itabirite and massive bands of the soft ore (Table 1). The unit cell parameters of hematite in sample MAC127B are also very similar not only to those of hematite in the massive bands of the soft and hard ores but also to the reference cell parameters of hematite (Table 2).

An ill defined doublet superimposed to the hematite sextet is present in all spectra of the porous band (Fig. 11e). This doublet can be ascribed to the limonitic, brownish material which is the residue of the dissolution of dolomite. The isomer shift ($0.34 - 0.35$ mm/s) and the quadrupole splitting (0.68 mm/s) at 300 K of these samples match well with those of ferrihydrite

(Cornell and Schwertmann 1996, p. 149). In the MS at 50 K of sample MAC127B (which presents the best defined doublet at 300 K), the doublet is still present, with an isomer shift of 0.42 mm/s and a quadrupole splitting of 0.76 mm/s. These values are compatible with those found by Childs and Baker-Sherman (1984) for synthetic ferrihydrite at 77 K. The absence of a sextet at 50 K indicates the poor crystallinity of this mineral, given that magnetic ordering is strongly dependent on crystallinity (Cornell and Schwertmann 1996). The low crystallinity of ferrihydrite, on the other hand, explains its absence from the XRD patterns. Mössbauer spectroscopy confirms, therefore, that the brownish material observed by optical petrography in the residue of the dolomite dissolution is ferrihydrite. Based on the values of the relative subspectral areas, the abundances of hematite and ferrihydrite were estimated. It is seen from Table 1 that ferrihydrite is a subordinate component in the soft ore.

Although remnants of magnetite were locally recognized within hematite crystals by petrographic observation, this mineral was not detected in the MS. The same occurred with siderite (present in dolomite) in sample MAC-67. The appearance of six lines in the MS and the hyperfine parameters of the hard ore samples are due to the presence of the single iron-bearing phase, i.e., hematite. The absence of magnetite lines is related to the very high degree of martitization (oxidation).

Geochemistry

Analytical results for the 48 samples analyzed for major, trace and rare earth elements (REE) of the soft and hard ores are presented in Appendixes 2 and 3. The results of the remaining 38 samples analyzed for major and some trace elements can be obtained from the authors. Average compositions and standard deviations of populations for the soft and hard iron ores are given in Tables 3 and 4. Statistics for variables below or very close to the detection limit were not calculated. When the results of just a few samples were below this limit, statistics were calculated using half the detection limit. This procedure was chosen in order to establish a distinction for those values which stood slightly above the detection limit. The following variables (with their respective detection limit) presented analytical results below or very close to the detection limit: Na₂O (0.01%), K₂O (0.01%), Sc (3 ppm), Be (3 ppm), Zn (30 ppm), Ga (1 ppm), Rb (1 ppm), Nb (0.2 ppm), Mo (2 ppm), In (0.1 ppm), Sn (1 ppm), Cs (0.1 ppm), Hf (0.1 ppm), Tl (0.1 ppm), Pb (5 ppm), Bi (0.1 ppm), Au (2 ppb), Br (0.5 ppm), Ir (5 ppm) and Se (3 ppm).

Table 3 Average major and trace element composition

Wt%	Hard Ore					Soft Ore					Dolomitic Itabirite (n=11)
	Avg	Std	Min	Max	n	Avg	Std	Min	Max	n	
SiO ₂	0.66	0.33	0.24	1.32	12	1.06	0.63	0.18	3.57	62	1.01
Al ₂ O ₃	0.24	0.23	0.02	0.91	12	0.46	0.44	0.08	2.10	62	0.32
Fe ₂ O ₃	97.66	1.16	95.11	99.13	10	95.65	2.29	87.66	98.79	62	48.90
Fetot	97.93	1.77	94.44	99.54	12	95.74	2.31	87.72	98.90	62	49.64
FeO	0.82	0.80	0.22	2.70	10	0.08	0.07	0.05	0.50	62	0.66
MnO	0.025	0.025	0.005	0.093	12	0.818	0.379	0.221	2.139	62	0.28
MgO	0.22	0.35	<0.03	1.20	12	0.36	0.32	0.03	2.04	62	10.33
CaO	0.33	0.42	0.02	1.41	12	0.19	0.22	<0.03	1.13	62	14.36
Na ₂ O	<0.01				12	<0.01				36	<0.01
K ₂ O	0.044	0.041	<0.01	0.140	12	<0.01				36	0.03
TiO ₂	0.018	0.009	0.006	0.033	12	0.031	0.035	0.005	0.156	62	0.021
P ₂ O ₅	0.13	0.07	0.03	0.22	12	0.18	0.27	<0.03	1.58	62	0.12
LOI	0.52	0.41	0.13	1.39	12	0.85	0.44	0.29	2.31	62	23.60
ppm(*)											
Ba	13.1	10.6	<3.0	37.2	12	32.7	35.1	6.7	211.0	62	12.9
Sr	6.2	3.2	<2.0	9.3	10	18.2	10.9	4.0	35.5	24	29.8
Y	5.0	1.5	2.2	7.6	10	18.8	9.5	5.5	33.7	24	7.7
Sc	<3.0				10	<3.0				24	<3.0
Zr	5.8	3.8	2.4	15.1	10	13.6	9.9	3.5	40.1	24	14.0
Be	<3.0				10	<3.0				24	<3.0
V	35.6	35.6	10.0	132.0	10	59.9	36.0	9.1	138.4	62	25.6
Ni	<20.0				10	23.9	21.1	<20.0	96.0	62	10.0
Cu	10.0	6.0	<5.0	22.0	10	10.2	7.3	<5.0	45.3	62	7.0
Zn	<30.0				10	<30.0				62	13.5
Ga	<1.0				10	<1.0				24	<1.0
Ge	4.3	1.1	2.8	6.0	10	3.0	1.1	0.7	5.0	24	1.8
Rb	<1.0				10	<1.0				24	<1.0
Nb	0.4	0.4	<0.2	1.0	10	<0.2				24	0.9
Mo	<2.0				10	<2.0				24	<2.0
Ag	<0.5				10	0.3	0.4	<0.5	1.3	24	<0.5
In	<0.1				10	<0.1				24	<0.1
Sn	<1.0				10	<1.0				24	<1.0
Cs	<0.1				10	<0.1				24	<0.1
ΣREE	7.0	1.9	3.2	10.0	10	22.7	10.1	9.3	46.0	24	14.5
Hf	<0.1				10	<0.1				24	0.1
Tl	<0.1				10	<0.1				24	<0.1
Pb	<5.0				10	<5.0				24	5.1
Bi	<0.1				10	<0.1				24	1.2
Th	0.2	0.1	0.1	0.5	10	0.4	0.4	0.1	1.5	24	0.5
U	4.5	3.4	0.6	12.3	10	3.9	1.8	1.0	7.2	24	2.9
Au	<2.0				8	<2.0				24	na
As	12.4	6.7	<5.0	23.1	10	13.6	6.6	3.9	28.4	24	9.3
Br	<0.5				8	<0.5				24	na
Cr	65.3	59.5	<20.0	202.0	12	78.8	73.0	16.0	429.0	62	52.9
Ir	<5.0				8	<5.0				24	na
Sb	4.0	1.7	2.0	6.9	10	3.2	1.3	1.4	6.1	24	1.6
Sc	0.5	0.3	0.1	1.0	8	1.1	0.9	0.4	3.5	24	na
Se	<3.0				8	<3.0				24	na
Fe#	0.988	0.009	0.970	0.997	9	0.999	0.001	0.994	0.999	61	0.980

Fe_{TOT} expressed as Fe₂O₃, Fe# = (Fe³⁺)/(Fe³⁺ + Fe²⁺); (*) Au in ppb; na means not analyzed. Data of the dolomitic itabirite are from Spier et al. (submitted)

Table 3 Average major and trace element composition (Continued)

Wt%	Soft ore								Dolomitic itabirite	
	Massive band (n=6)				Porous band (n=8)				Iron-rich band (n=6)	Dolomite-rich band (n=6)
	Avg	Std	Min	Max	Avg	Std	Min	Max	Avg	Avg
SiO ₂	0.35	0.13	0.15	0.51	1.69	1.48	0.38	4.74	0.91	0.73
Al ₂ O ₃	0.08	0.05	0.03	0.16	0.84	1.13	0.14	3.25	0.28	0.33
Fe ₂ O ₃	98.24	0.85	96.84	99.15	92.80	3.84	86.96	97.07	77.88	10.93
Fetot	98.58	0.53	97.90	99.27	92.98	3.76	87.22	97.07	78.23	11.74
FeO	0.36	0.55	0.11	1.35	0.19	0.10	0.10	0.37	0.32	0.73
MnO	0.10	0.10	0.02	0.29	1.69	0.63	0.77	2.55	0.12	0.50
MgO	0.08	0.03	0.02	0.11	0.54	0.73	0.07	2.29	4.11	18.50
CaO	0.10	0.14	0.03	0.38	0.12	0.11	<0.03	0.31	5.45	26.19
Na ₂ O	<0.01				<0.01				<0.01	0.05
K ₂ O	<0.01				<0.01				0.02	0.06
TiO ₂	0.006	0.003	<0.001	0.010	0.054	0.076	0.011	0.223	<0.001	<0.001
P ₂ O ₅	0.06	0.10	<0.03	0.27	0.10	0.07	0.03	0.25	0.12	0.06
LOI	0.32	0.10	0.19	0.45	1.86	0.81	0.78	2.97	9.91	40.98
ppm(*)										
Ba	11.5	9.8	<3.0	29.4	116.2	127.2	20.7	405.2	11.17	20.67
Sr	3.8	4.5	<2.0	12.4	17.4	12.9	2.3	42.8	12.83	46.17
Y	3.1	1.6	2.0	6.1	32.6	13.6	13.9	56.0	4.67	9.50
Sc	<3.0				<3.0				<3.0	<3.0
Zr	3.2	1.1	2.2	4.8	9.4	11.9	2.3	38.6	14.67	8.00
Be	<3.0				<3.0				<3.0	<3.0
V	27.2	25.1	9.2	77.0	44.5	21.0	23.0	75.0	36.33	10.25
Ni	<20.0				30.5	18.6	<20.0	63.6	15.13	7.31
Cu	<5.0				31.9	42.0	<5.0	115.3	0.50	5.19
Zn	<30.0				101.2	128.1	<30.0	407.1	12.95	7.38
Ga	<1.0				2.1	1.7	<1.0	5.9	0.79	<1.0
Ge	3.8	0.8	3.1	5.3	4.0	1.3	2.1	6.0	3.6	<0.5
Rb	<1.0				<1.0				1.24	<1.0
Nb	0.3	0.3	<0.2	0.5	0.8	0.80	<0.2	2.4	0.36	0.88
Mo	<2.0				<2.0				1.49	<2.0
Ag	<0.5				<0.5				0.41	<0.3
In	<0.1				<0.1				0.05	<0.1
Sn	<1.0				<1.0				0.64	<1.0
Cs	<0.1				<0.1				0.21	<0.1
ΣREE	5.0	1.5	3.6	7.6	42.9	31.8	14.4	116.9	9.63	18.76
Hf	<0.1				<0.1				<0.1	<0.1
Tl	<0.1				<0.1				<0.1	<0.1
Pb	<5.0				13.7	23.2	2.5	70.5	1.5	7.01
Bi	<0.1				<0.1				2.2	<0.1
Th	0.1	0.1	<0.05	0.2	0.8	1.3	0.1	3.8	0.25	0.84
U	1.7	1.2	0.7	4.1	4.7	2.5	1.5	8.4	2.07	1.67
Au	<2.0				9.4	12.5	<2.0	35.0	na	na
As	7.4	1.6	5.5	9.6	16.0	6.4	9.2	26.3	6.55	4.80
Br	<0.5				<0.5				na	na
Cr	54.5	62.1	23.0	181.0	68.7	59.8	26.0	206.0	21.84	23.50
Ir	<5.0				<5.0				na	na
Sb	5.5	4.2	2.9	14.0	4.9	3.8	1.8	14.0	1.35	1.52
Se	0.2	0.1	<0.1	0.3	1.7	2.7	0.3	7.7	na	na
Fe	<3.0	0.0	1.5	1.5	<3.0				na	na
Fe#	0.996	0.006	0.985	0.999	0.998	0.001	0.996	0.999	1.000	0.910

Fe_{TOT} expressed as Fe₂O₃. Fe# = (Fe³⁺)/(Fe³⁺ + Fe²⁺); (*) Au in ppb; na means not analyzed. Data of the dolomitic itabirite are from Spier et al. (submitted)

Table 4 – Average rare earth element composition

	Hard ore			Soft ore			Dolomitic itabirite		
	(n = 10)	Bulk	Massive band	Porous band	Bulk	Iron-rich band	Dolomite-rich band		
		(n = 24)	(n = 6)	(n = 8)	(n = 11)	(n = 6)	(n = 6)		
ppm									
La	1.06	3.50	0.85	6.65	2.65	1.85	3.13		
Ce	1.88	6.42	1.58	11.95	4.21	3.00	6.24		
Pr	0.28	0.98	0.20	1.70	0.53	0.39	0.76		
Nd	1.34	4.36	0.90	7.35	2.40	1.71	3.41		
Sm	0.36	0.98	0.20	1.72	0.57	0.39	0.77		
Eu	0.14	0.40	0.07	0.74	0.22	0.14	0.32		
Gd	0.53	1.27	0.28	2.56	0.74	0.48	0.99		
Tb	0.09	0.23	0.04	0.46	0.13	0.08	0.17		
Dy	0.55	1.51	0.30	3.10	0.86	0.54	1.11		
Y	4.99	18.76	3.11	32.59	7.44	4.67	9.50		
Ho	0.12	0.35	0.07	0.77	0.20	0.13	0.25		
Er	0.34	1.12	0.24	2.53	0.63	0.43	0.78		
Tm	0.05	0.18	0.04	0.41	0.10	0.07	0.11		
Yb	0.28	1.17	0.24	2.59	0.62	0.42	0.71		
Lu	0.04	0.19	0.04	0.43	0.10	0.07	0.12		
ΣREE	6.96	22.66	5.04	42.94	13.86	9.63	18.76		
La/Yb _{PAA}	0.28	0.22	0.26	0.17	0.27	0.32	0.34		
La/Sm _{PAA}	0.46	0.52	0.61	0.53	0.61	0.69	0.60		
Dy/Yb _{PAA}	1.17	0.78	0.75	0.71	0.82	0.78	0.94		
Ce/Ce* _{PAA}	0.82	0.80	1.04	0.76	0.86	0.82	0.89		
Eu/Eu* _{PAA}	1.48	1.67	1.67	1.63	1.60	1.57	1.74		
Y/Y* _{PAA}	1.68	2.09	2.09	1.85	1.63	1.40	1.52		

$Eu/Eu^*_{PAA} = ((Eu/Eu_{PAA}) / (Sm/Sm_{PAA}) * (Gd/Gd_{PAA}))^{1/2}$, Ce/Ce^*_{PAA} and Y/Y^*_{PAA} calculated by similar way. Data of the dolomitic itabirite are from Spier et al. (submitted).

The soft iron ore consists almost entirely of Fe_2O_3 (average of 95.6%), with FeO representing less than 0.5% (average 0.1%). LOI (average of 0.9%), SiO_2 (average of 1.1%), MnO (average of 0.8%) and Al_2O_3 (average of 0.5%) complete the list of significant major elements (Table 3, Fig. 12a). Na_2O and K_2O contents are below the detection limit of 0.01%. A comparison of the major element composition of the dolomitic itabirite (protore) with that of the soft ore (Table 3, Fig. 12b) shows that the mineralizing process is chemically characterized by the enrichment in Fe_2O_3 , Al_2O_3 , MnO , P_2O_5 and TiO_2 , with depletion in FeO , MgO , CaO and LOI .

The average values of major elements in the massive and porous band of the soft ore analyzed separately confirm the results of petrological analyses and show that impurities are concentrated within the porous bands (Table 3, Fig. 12c). These impurities consist almost entirely of SiO_2 (average of 1.7%), MnO (average of 1.7%) and Al_2O_3 (average of 0.8%), and are in the form of chlorite, talc and Mn-oxides. The Fe_2O_3 content of the porous band is still very high (average of 92.8%), but lower than that of the massive bands (average of 98.2%), which

have very low concentrations of SiO_2 (average 0.3%), Al_2O_3 (average of 0.1%) and MnO (average of 0.1%).

Figure 12 - **A** Average major element composition of the soft ore (SO), hard ore (HO) and dolomitic itabirite (Dol. Itab.). **B** Average major element composition of the iron ores normalized to the dolomitic itabirite. **C** Average major element composition of the massive and porous bands of the soft ore.

No significant enrichments in trace elements were encountered in the soft ore (Table 3, Fig. 13a). Most show concentrations of less than 10 ppm, except for Ba (33 ppm), V (60ppm), Cr (79 ppm), Y (19 ppm), Ni (24 ppm), Cu (79 ppm) and Σ REE (23 ppm). When compared to the average composition of dolomitic itabirite (Fig. 13b), the soft ore is enriched in all trace elements, except for Sr and Nb. With a behavior similar to that of major elements, trace elements are concentrated in the porous bands of the soft ore (Table 3, Fig. 13c). Only Ge, Cr, Sb, V and Ni have similar values in the porous and massive bands. Some elements, such as Ba (10x), Y (10x), REE (9x) and Th (7x) are highly enriched in the porous bands if compared to the massive bands.

The average REE composition of the soft ore is presented in Table 4. The REEY patterns are shown in Figs. 14a-b. These patterns show similar trends, characterized by a pronounced depletion in the light REE relative to heavy REE (average La/Yb=0.2). This depletion occurs either in the LREE group (average La/Sm=0.5) as in the HREE group (average Dy/Yb=0.8). Most samples display strong positive anomalies of Eu (Eu/Eu*=1.7) and Y (Y/Y*=2.1), as well as negative anomalies of Ce ranging from 0.7 to 1.0.

The average REEY pattern of the soft ore clearly illustrates the enrichment of REEY by a factor of about 1.6 relative to dolomitic itabirite (Fig. 14c). This figure also illustrates the remarkably similar REEY pattern between the ore and the protore and suggests that weathering promoted a residual enrichment in REE in the soft ore, preserving the original pattern, without fractionation. This is also observed by comparing the average REEY pattern of the iron-rich and dolomite-rich bands of the dolomitic itabirite with that of the massive and porous bands of the soft ore (Fig. 14d). Such patterns are conspicuously similar, the only difference being a depletion in REEY of the iron-rich band compared with its correspondent massive band and, conversely, a REEY enrichment of the porous band compared with its correspondent dolomite-rich band.

Figure 13 - **A** Average trace element composition of the soft ore (SO), hard ore (HO) and dolomitic itabirite (Dol. Itab.). **B** Average trace element composition of the soft ore normalized to the dolomitic itabirite. **C** Average trace element composition of the massive and porous bands of the soft ore. La# means Σ REE.

Figure 14 – PAAS-normalized REEY data. **A** Soft ore. **B** Massive and porous bands of the soft ore. **C** Averaged iron ores and dolomitic itabirite. **D** Averaged massive and porous bands of the soft ore, and iron-rich and dolomite-rich bands of the dolomitic itabirite (protore of the soft ore). Data for the itabirites are from (Spier et al. 2005a). **E** Hard ore.

Some Linear Interelement Correlations

Table 5 reveals a strong negative correlation of Fe_{TOT} with LOI, Al_2O_3 and SiO_2 , and a significant negative correlation of Fe_{TOT} with MnO, MgO, TiO_2 , and Ni. Table 5 and Figure 15 show that LOI correlates positively with SiO_2 , Al_2O_3 , TiO_2 and MnO, confirming that the higher amount of impurities in the iron ores is associated with dolomite or its product of dissolution.

Al_2O_3 correlates very well with SiO_2 and TiO_2 (Table 5, Fig.15). These correlations are also observed in the dolomitic itabirite reflecting a slight contribution of detritic contaminants in the original sediments (Spier et al. 2005a). These detritic contaminants are concentrated in the porous band of the soft ore during the leaching process (Fig. 12c). SiO_2 correlates well with MgO, confirming the presence of talc in the group of contaminants. CaO has a strong correlation with P, reflecting the occurrence of apatite in the ores.

Table 5 – Linear interelement correlations for all samples of the sof ore (n=62)

	SiO_2	Al_2O_3	Fe_{TOT}	MnO	MgO	CaO	TiO_2	P_2O_5	LOI	Ba	V	Ni	Cu
Al_2O_3	0.88												
Fe_{TOT}	-0.95	-0.91											
MnO	0.64	0.74	-0.79										
MgO	0.67	0.37	-0.60	0.23									
CaO	0.09	-0.10	-0.16	-0.17	0.24								
TiO_2	0.80	0.88	-0.84	0.66	0.40	-0.03							
P_2O_5	0.13	0.00	-0.21	-0.14	0.17	0.96	0.08						
LOI	0.82	0.90	-0.92	0.91	0.39	-0.10	0.81	-0.04					
Ba	-0.10	0.08	-0.06	0.09	-0.26	-0.23	0.06	-0.14	0.04				
V	0.28	0.35	-0.41	0.46	0.22	-0.10	0.28	-0.08	0.50	-0.05			
Ni	0.70	0.79	-0.71	0.57	0.24	-0.09	0.65	0.02	0.70	0.16	0.33		
Cu	-0.06	0.01	-0.06	0.19	-0.14	-0.13	-0.04	-0.07	0.13	0.22	0.30	0.13	
Cr	0.13	0.15	-0.12	0.06	0.01	-0.07	0.13	-0.04	0.06	-0.03	0.05	0.18	0.16

Figure 15 – Interelement correlations for the soft ore samples.

Hard Iron Ores

Mineralogy and Petrology

Petrographic and SEM observations of the massive, banded and schistose hard iron ores have shown a very simple mineralogical composition. The iron oxide mineralogy is the same of the soft ore. Gangue minerals are very rare, consisting of dolomite and, locally, apatite and talc. In weathered hard ores gangue minerals are generally absent, creating a macroporosity. In highly fractured orebodies, goethite and kaolinite occur as thin films on the surface of the ore, even at deeper depths (Fig. 3f). There is no difference in the mineralogical composition of the three major sub-types of hard ore, except in fabric and porosity.

Massive hard ore consists of tabular and granular hematite (up to 80%) ranging in size from 5 to 30 μm (average of 20 μm), forming a granoblastic fabric (Figs. 16a-d). Martite (up to 50 μm) with remnants of magnetite occur between hematite crystals (Fig. 16e). Locally, it is possible to observe the growth of hematite over martite crystals. Porosity in hard massive ores may vary from approximately 5 to 20%, and pore size from < 1 to 50 μm . Fresh ores exhibit the lowest porosity of all hard ores, around 3%, increasing up to 20% in weathered samples.

Banded hard ore consists of alternated massive and porous layers (Fig. 16f). Tabular and granular hematite are the main iron oxides (up to 70%) with grain size ranging from 5 - 20 μm (Fig. 16g). They grow over martite or occur as isolated crystals. Martite with remnants of magnetite may occur as individual crystals ranging from 30 - 50 μm or forming dense aggregates, representing up to 5% of the volume. Specularite (up to 5%) occurs locally, along shear planes parallel to or cutting the banding and defining a discontinuously developed foliation. Porosity is highly variable in banded iron ores, reaching up to 30% of the volume.

Schistose hard ore presents a lepidoblastic fabric which is composed mainly of tabular hematite and specularite (up to 70%) wrapping around porphyroclastic aggregates of tabular and granular hematite (up to 50%, Fig. 16h). Porosity in the schistose ore ranges from 5 to 20%.

Figure 16 – Photomicrographs and SEM backscattered images of the hard ores. **A** Massive hard ore, reflected light, PPL. **B** Granoblastic fabric of massive hard ore, reflected light, partially XPL. **C-D** SEM image of massive hard ore. **E** Detail of a martite crystal in massive hard ore with relict of magnetite (m), reflected light, PPL. **F** Banded hard ore, reflected light, PPL. Note alternation of highly porous (pb) with less porous bands (mb). **G** Detail of the banded ore showing intergrown of tabular hematite (th), reflected light, PPL. **H** Schistose hard ore showing porphyroclastic aggregates of martite wrapped around by porous and platy (specularite) hematite, reflected light, XPL.

XRD and Mössbauer Analyses

Hematite was the only iron oxide identified by XRD, with very sharp peaks (Fig. 17). Gangue minerals are almost absent, as shown by their small peaks, consisting of dolomite in sample MAC-67 and kaolinite in sample MAC-97. These results are confirmed by the 300 K MS (Fig. 18), with a hyperfine field of about 52 T and a quadrupole shift of about -0.15 mm/s assigned to hematite (Table 1). They are also corroborated by the Mössbauer spectra of sample MAC97 at 50 K, which also presents only a sextet ascribed to hematite (hyperfine field of 56 T, isomer shift of 0.48 mm/s and quadrupole splitting of 0.38 mm/s). Sharp XRD peaks and Mössbauer parameters of hematite indicate a high degree of crystallinity, with little heterogeneity. The unit cell parameters of hematite in samples MAC67 and MAC97, very similar to those of the reference cell of hematite (Table 2), corroborate this indication.

Figure 17 – Powder XRD patterns of the hard ore samples showing hematite (Hm), dolomite (Dol) and kaolinite (Ka).

Figure 18 – Mössbauer spectra at room temperature of the hard ore samples.

Geochemistry

The bulk geochemical composition of the hard ore is very simple, consisting almost entirely of Fe_2O_3 (avg. 97.6%), ranging from 95.0% to 99.1% (Table 3, Fig. 12a). The average FeO content is 0.8% (ranging from 0.2% to 2.7%), whereas SiO_2 ranges from 0.2% to 1.3% (avg. of 0.7%). CaO (avg. of 0.3%) and MgO (avg. of 0.2%) contents present a similar distribution, ranging from 0.01% to 1.2%. Al_2O_3 is the next most abundant component, ranging from 0.02% to 0.9% (avg. of 0.2%). Na_2O , K_2O and P_2O_5 contents are always below 0.5%, whereas TiO_2 averages 0.02%.

The trace element composition of the hard ore is also remarkably simple, with only Cr (avg. of 65 ppm) and V (avg. of 35 ppm) showing average values higher than 30 ppm (Table 3, Fig. 13a). The Zn and Ni contents of most of the samples were below the detection limits of 30 ppm and 20 ppm, respectively. As (avg. of 12 ppm) and Ba (avg. of 14 ppm) have average contents higher than 10 ppm, whereas all other trace elements present average values below 10 ppm and, in most cases, below the detection limits of 5 ppm (Pb and Ir), 3 ppm (Sc, Be and Se), 2 ppm (Mo), 1 ppm (Ga, Rb, Sn) and 0.1 ppm (In, Cs, Hf, Tl and Bi).

The hard ore is depleted in REE, with an average content of 7 ppm, ranging from 3 ppm to 10 ppm (Table 3). The REEY patterns are all similar (Fig. 14e), being characterized by a strong depletion in light REE relative to heavy REE, negative Ce anomalies (with the exception of sample MAC68), marked positive Eu and Y anomalies, and depletion of the heavy REE relative to the middle REE ($Dy/Yb > 1$).

DISCUSSION

Comparison between hard and soft ores

The major difference between hard and soft ores, besides the mechanical strength, is their mode of occurrence. The soft ore forms a large, km-sized lens, which grades laterally and vertically to the parent dolomitic itabirite. Field relationships show the transition from the dolomite-rich bands of the dolomitic itabirite into the porous band of the soft ore. This transition is marked by dissolution of the dolomite-rich bands, thereby producing a highly porous residue which is very rich in the hematite originally present within the dolomite-rich bands. The iron-rich bands of the dolomitic itabirite are little affected by this dissolution process and form the massive band of the soft ore. The hard ore occurs as discontinuous lenses within the fresh dolomitic itabirite and soft ore. These field relationships indicate that the hard iron ore was formed earlier than the soft iron ore. It also suggests that the hard iron ore, like the iron-rich bands of the dolomitic itabirite, was little affected by the dissolution process, remaining as lenses within the soft ore.

The next important difference between hard and soft ores is porosity, which control their mechanical strength. Two types of porosity are observed in the iron ores: macro and microporosity. The former is related to the spaces between the iron oxides crystals and constitutes the major factor affecting the hardness of the ore. It is formed by leaching of the gangue minerals, probably by weathering solutions (see text below). The latter is related to the presence of pores within the iron oxide crystals which are formed during the oxidation of

magnetite into martite. The hard iron ore is much less porous than the soft ore, which accounts for its hardness. The soft ores are highly porous and, consequently, soft. A more frequent presence of carbonate in the rock prior to dissolution results in higher porosity and higher friability. Variations in the porosity and fabric of the hard ore are responsible for the different sub-types observed.

The major difference in the mineralogy of the hard and soft ores is the slightly higher amount of gangue minerals in the latter. The gangue minerals are also different in each type of ore. Although both ores have a very low amount of detrimental impurities, these are concentrated in the soft ore. Dolomite, sericite, chlorite and apatite are the most common gangue minerals, both in the hard and in the soft ore. Mn-oxides and ferrihydrite are concentrated within the porous bands of the soft ore and are absent from the hard ore. Higher amounts of gangue minerals, especially apatite and Mn-oxides, occur in deeper depths close to the contact of the soft ore with the protore. This zone has lower permeability, thus favoring the residual concentration of apatite (which is less soluble than dolomite) together with Mn-oxides produced during dolomite dissolution (see discussion below).

The iron oxide mineralogy of the hard and soft ores is exactly the same, as demonstrated by optical microscopy, SEM, XRD and MS, and consists essentially of granular and tabular hematite. This mineral occurs growing over martite crystals or as individual crystals forming the dense aggregates of a granoblastic fabric both in hard ores and in massive bands of soft ore. Hematite has the same Mössbauer hyperfine parameters both in fresh dolomitic bands and in hard and soft ores (Table 1). The Mössbauer spectra of all samples can be well fitted with only one sextet. The value of the hyperfine field (51.9 T) corresponds to that of pure, well-crystallized hematite, indicating that it does not contain detectable amounts of Al (Fysh and Clark 1982; Murad and Schwertmann 1986). This conclusion is also supported by the hematite unit cell parameters obtained from the Rietveld analyses, which point to the purity of this mineral. The isomer shift of all the sextets shows that iron is exclusively present in the Fe^{3+} state. Although remnants of magnetite are locally observed either in hard or in soft ores, this mineral was submitted to a very high degree of martitization. This phenomenon occurred prior to the genesis of the soft ore, considering the identical hyperfine parameters of the iron oxides observed in the dolomitic itabirite (protore) and in the soft ore. This is further supported by chemical analyses of the dolomitic itabirite, which reveal $\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Fe}^{2+})$ ratios close to one (Spier et al. 2005a).

The geochemistry of the hard and soft ores reflects a higher amount of detrimental impurities in the soft ore (Table 3, Fig. 12a), especially MnO, whose average content in the soft

ore is 33 times higher than in the hard ore. Other major constituents like Al_2O_3 (2.0x), SiO_2 (1.6x), TiO_2 (1.7x) and P_2O_5 (1.4x), together with LOI (1.6x), also show the increase of impurities in the soft ore. Both hard and soft ores are very depleted in trace elements (Table 3, Fig. 13a), excepted for Ba (2.5x), Sr (3.0x), Y (3.7x), V (1.7x), Th (1.8x) and ΣREE (3.2x), which show higher concentrations in the soft ore than in the hard ore. Another important difference between hard and soft ores is their respective REEY contents and fractionation patterns. While the soft ore preserves the REEY pattern of the dolomitic itabirite (Fig. 14c), even when the correspondent iron-rich/massive bands and dolomite-rich/porous bands are considered separately (Fig. 14d), the hard ore presents a distinct REEY pattern, characterized by depletion in heavy REE relative to middle REE.

Formation of Tabular and Granular Hematite Within Martite Crystals

Even though the question of which primary iron minerals precipitated on the sea floor during the growth of the BIFs remains a source of debate in literature, there is a general consensus that they were mostly ferric (hydr)oxides (goethite and/or hematite) (Ohmoto 2003; Trendall 2002). A later process during diagenesis and/or metamorphism transformed the ferric (hydr)oxides into magnetite (Morris 1993; Perry Jr. et al. 1973; Walker 1984; Walker 1987). Magnetite is found ubiquitously in BIFs throughout the world. In the QF region, it is interpreted to be the oldest iron oxide of the iron mineral assemblage (Rosière 1981; Rosière and Chemale Jr. 2000; Rosière et al. 1993; Rosière and Rios 2004). The coarse crystals of magnetite in BIFs of the QF suggest that they were formed during diagenesis and/or metamorphism, considering that primary iron precipitates must have been colloidal.

Magnetite was almost totally oxidized and recrystallized during the metamorphic and tectonic evolution of the BIFs of the Cauê Formation (Rosière 1981). The transition from magnetite to martite is less well preserved in the Águas Claras rocks, but it is well documented in other sites in the QF. The most impressive feature observed in this study is the development of hematite within martite crystals. The petrographical analyses indicate that recrystallization of martite during metamorphism and deformation (probably during the Transamazonian Orogenesis) was responsible for the generation of the hematite crystals within martite, according to the mechanisms proposed by Hackspacher et al. (2001), Lagoeiro (1998), Rosière (1981) and Rosière et al. (2001). The degree of recrystallization, however, was not uniform, making it possible to observe the several steps of transformation from martite to tabular hematite, passing through anhedral and granular hematite (Fig. 19). These hematite crystals correspond to the

Hematite II of Rosière and Rios (2004) and are conspicuously observed in our samples. The passage from martite to tabular hematite in Águas Claras is an intermediate step in the development of specularite, which occurs in high strained zones of the QF, according to Rosière and Rios (2004). Its register in our samples offers further support to the model of those authors.

Figure 19 – SEM backscattered images and microphotographs showing several stages of development of hematite crystals after martite. **A** Euhedral magnetite crystal, partially oxidized, showing small pores, SEM image. **B** Ex-magnetite grains, now completely oxidized to martite, along octahedral planes. **C-D** Anhedral and tabular hematite forming after martite. **E** Small crystals of tabular hematite within ex-martite grain. **F** Partially deformed martite crystal with several tabular hematite within it.

Comparisons with other iron mines on the western side of the Quadrilátero Ferrífero

In order to contribute to the discussion on the genesis of iron ores at the Águas Claras mine, we will give a brief presentation of another two, giant, world-class iron mines on the western side of the QF: Capão Xavier and Tamanduá. Capão Xavier is located on the western side and Tamanduá on the eastern side of the Moeda Syncline (Fig 1). Geological sections of each mine are presented in Figure 20.

Capão Xavier Mine

The Capão Xavier orebody is quite similar to the Águas Claras orebody. It consists of a large, concordant lense of high-grade ore hosted within dolomitic itabirite. Soft high-grade ore is largely predominant and represent 82% of the 233 Mt of geological resources. Hard high-grade ore occurs as local, metric lenses within the soft ore. Low-grade ores ($30\% < \text{Fe} < 64\%$), formed from quartz itabirite, are subordinated within the pit of the mine, but widespread outside of this limit, having not been considered in the geological resources mentioned above. Differently from the Águas Claras and Tamanduá, the Capão Xavier's whole structure, and particularly the BIFs, dips gently, with a maximum angle of 45 degrees to the northeast. The weathering front varies in depth from a few meters in the quartz itabirite to more than 300 m in the dolomitic itabirite. Soft high-grade ore reaches a maximum depth of 280 m. A thick (5 – 50 m) transition zone, characterized by high contents of Al_2O_3 and Mn, is usually observed in the contact of the soft ore with the dolomitic itabirite. The greater thickness of the transition zone can be attributed to the gentle dip of the dolomitic itabirite in the Capão Xavier orebody, which would have hampered the action of the downward weathering solutions through the banding.

Weathering of the quartz itabirite at the Capão Xavier deposit produced a goethitic rock, called limonitic itabirite. This rock consists essentially of hematite and goethite with subordinated quartz. The iron content of limonitic itabirite decreases in depth into the iron-rich quartz itabirite, according to the gradual reduction of the goethite content and increase of quartz (Fig. 20a). The iron-rich quartz itabirite is a low-grade iron ore ($52\% < \text{Fe} < 64\%$) and consists of a soft, powdered, quartz itabirite made up of hematite, with subordinated quartz. The goethite content is variable. With the gradual increase of quartz in the iron-rich itabirite, the iron content reduces, and the rock is called soft itabirite. Soft itabirite is also considered a low-grade ore ($30\% < \text{Fe} < 52\%$), with an average Fe content of 46% at the Capão Xavier deposit. Soft itabirite has a very low goethite content and grades to hard quartz itabirite, with an intermediate stage of weathering alteration called medium itabirite, which is not represented in the section. Figure 20a

Figure 20 – Cross sections of the Capão Xavier (A) and Tamanduá (B) mines.

shows that, though weathering reached a similar depth in the dolomitic and quartz itabirites, its final result is quite different. While high-grade iron ore was produced from the dolomitic itabirite, from the quartz itabirite only low-grade ore was formed. Otherwise, both protorees show a transition zone from the BIF to the iron ore, with an iron-enrichment from the bottom to the top of the weathering profile, more gradual in the quartz itabirite profile than in the dolomitic itabirite profile.

Tertiary basins of up to 200 m long and 80 m depth occur locally at the Capão Xavier deposit, blanketing the soft ore and the iron-rich and soft itabirites. These basins were originally filled with kaolinitic sediments that were almost totally transformed into bauxite through weathering processes (Pomeroy 1964; Maizatto 2001). The occurrence of Tertiary bauxite deposits covering the high- and low-grade ores at the Capão Xavier deposit illustrates the strong action of weathering in the QF region during the Tertiary.

Thus, the soft high-grade ore of this mine must have been formed by weathering of the dolomitic itabirite protore. The field relationships indicate that, under the same weathering and structural conditions, dolomitic itabirite is much more favorable to the formation of high-grade iron ore deposits than quartz itabirite.

Tamanduá Mine

The Tamanduá deposit is located in the Tamanduá Syncline, which is a second-order fold of the Moeda Syncline (Fig. 1). The orebody, hosted within quartz itabirite, strikes NW/SE, sub-parallel to the eastern limb of the Moeda Syncline (Fig. 1). In this area, the Cauê Formation is 2,000 m thick, due to folding. The orebody is transversally cut by two strike-slip faults hosting important dykes mostly of basic composition, which limits the orebody and divides it in three domains. The richest and thickest high-grade bodies are located in the central domain, within a syncline, in contact with phyllite (Fig. 20b).

The Tamanduá orebody is composed of soft, high-grade ore, with lenses of hard ore, and low-grade ore. Soft and hard ores represent 80% and 20%, respectively, of the 297 Mt of high-grade resources. Low-grade ore comprises 480 Mt of iron-rich itabirite, soft-itabirite and limonitic itabirite. The orebody is approximately 2,800 m long and 400 m thick.

High-grade ores occur mainly within the syncline, in contact with the phyllite, where lenses of hard ore, strongly fractured, occur involved by medium and soft high-grade ores and by iron-rich/soft itabirites, forming a complex arrangement (Fig. 20b). The soft ore reaches more than 500 m depth in this site. The hard orebodies may be massive or porous, and their shapes

are controlled by mesoscopic, acilindric, SE-plunging folds. Hard, schistose ore occurs in the central domain of the Tamanduá deposit and is related to oblique shear zones. Subordinated high-grade orebodies occur on the western side of the deposit, immediately below the canga surface. The contact between hard ore and fresh itabirite observed in drill cores are sharp or gradual for the protore into a few decimeters (Fig. 21a-b). Generally this contact is highly fractured, which would favor the circulation of ground water. The contact between the soft ore and the low-grade ore is gradual when it occurs close to the topographic surface and sharp when it occurs in greater depths (Fig. 21c).

Figure 21 – Drilling cores and mine exposure and of the Pico mine showing contacts between iron ore and quartz itabirite. **A-B** Contact between high-grade hard ore (HO) and hard quartz itabirite (HIB). **C** Straight contact between high-grade soft ore (SO) and low-grade soft itabirite (SIB).

Low-grade ores consist of limonitic, iron-rich, and soft itabirites, and are predominate on the western side of the deposit, where the same transition limonitic itabirite → iron-rich itabirite → soft and medium itabirite → hard quartz itabirite observed at the Capão Xavier deposit occurs. The weathering front in the quartz itabirite in this area varies from few meters below the topographic surface down to 250 m depth (Fig. 20b). Iron-rich and soft itabirites have a high

content of goethite close to limonitic itabirite, which gradually decreases (and locally disappears) toward the hard quartz itabirite.

The complex interfingering of hard, medium and soft ores within the Tamanduá Syncline (Fig. 20b), the great depths of the soft ore within the syncline and small depths outside it, associated with the gradation from massive hard ore to porous hard ore suggest suggest that mineralization of the quartz itabirite to form the soft high-grade ore in Tamanduá involved at least two different processes: hypogene and supergene. The former was responsible for the development of the hard and probably part of the soft high-grade ores. The latter was responsible for the development of the low-grade ores. This is a good indication that hypogene-supergene modified models were involved in the genesis of the soft high-grade ores of the QF.

Ore Genesis

Most of the iron ore produced in the world results from the enrichment of precambrian BIFs, but the processes responsible for this enrichment are still unclear and constitute a source of debates in the literature (Dalstra et al. 2002; Kneeshaw and Kepert 2002; Morris 2002a-c). Two end-member genetic models have been proposed: supergene versus hydrothermal enrichment of a BIF protore. Supergene iron ores are the most abundant type of iron ores either in the QF, where they represent more than 70% of the 27 Gt of geological resources (Gomes, 1986; MBR and CVRD, internal reports), or in the Western Australian Hamersley basin, where the martite-goethite ores account for some 90% or more of the BIF-derived enrichment ores (Harmsworth et al., 1990; Morris, 2002c). Supergene ore arises by the selective leaching of gangue minerals from the BIF by ground water and the residual accumulation of the iron oxides. Hypogene ores form the richest iron orebodies. Their genesis is ascribed to the interaction of the BIFs with a hydrothermal fluid, which dissolved chert (quartz), leaving pores spaces, that were or not filled by a new generation of iron oxides.

The occurrence of the hard, massive high-grade ores within fresh itabirite at the Águas Claras and Tamanduá mines is a strong evidence of their hypogene origin. This type of ore is similar to those described, for instance, by Taylor et al. (2001), Beukes et al. (2002) and Guedes et al. (2002), which are interpreted as formed by hydrothermal fluids. However, at Águas Claras, petrographic and mineralogic data provide little information regarding the hypogene solutions and their precipitates. Hematite has a very simple chemical composition and a wide stability field, thereby restricting its use in metallogenetic studies. Additional difficulties, such as superimposition of tectonic events and weathering, turn the understanding of the genesis of this

hard ore into a difficult puzzle. Nevertheless, there are some new insights into this subject. They arose from the infrared microscopic analysis and fluid inclusion studies in hematite carried out by Rosière and Rios (2004). These authors suggest that the formation of the hard massive high-grade orebodies occurred during the Transamazonian event (ca. 2.1-2.0 Ga; Alkmim and Marshak, 1998) and developed in two stages. In the first, contractional stage of the Transamazonian orogeny a pervasive magnetite mineralization occurred in the BIF by reduced metamorphic fluids. Hematite mineralization occurred during the collapse stage of the orogeny, coincident with the uplift of the basement, intrusion of granitic plutons and extension of the crust, and involved low-temperature meteoric fluids moving downwards from the surface along normal faults and fractures. These fluids were also responsible for the oxidation of magnetite (martitization), and were concentrated only at sites of great permeability such as fold hinges, forming the hard, massive high-grade orebodies.

Harder to explain is the origin of the giant, soft high-grade orebodies, such as the Águas Claras orebody. The general lack of typical secondary minerals as goethite in the ore could indicate leaching of gangue minerals from BIFs by hypogene solutions, but in some cases, other arguments point to a supergene origin.

The soft ore at the QF orebodies is generally interlayered with or surrounding the hard, massive, hypogene ores. This relation led many authors (Beukes et al. 2002; Dorr 1965; Guild 1953; Rosière and Rios 2004) to propose its hypogene-supergene modified origin. Hypogene-supergene modified models comprise an initial, hypogene stage, with either leaching of all the chert from the BIF protore leaving pore spaces (Dorr 1965; Guild 1953) or with metasomatic replacement of those minerals by carbonates, followed by a supergene stage that leached the hydrothermal minerals formed in the previous stage (Beukes et al. 2002). Águas Claras mine was mentioned by Beukes et al. (2002) as the best example, one where the dolomitic itabirite “obviously developed from the replacement of chert bands in iron-formation”. Hypogene-supergene modified genetic models were also proposed for the genesis of the high-grade hematite ores at the Hamersley and Carajás Provinces (Beukes et al. 2002; Guedes et al. 2002; Taylor et al. 2001; Thorne et al. 2004; Webb et al. 2004). Recently, Dalstra and Guedes (2004) suggested that magnetite-carbonate-amphibole, magnetite-carbonate or hematite-carbonate precursors were essential in the formation of high-grade hematite ores worldwide. Their proposed genetic model involves early hydrothermal depletion of silica in the host iron formation and introduction of Ca-Fe-Mg-carbonates, followed by supergene leaching of the carbonates, long after they are formed, to create the high-grade hematite ores.

The use of hypogene- supergene models proposed by Beukes et al. (2002), Dalstra and Guedes (2004) and Rosière and Rios (2004) to explain the genesis of the soft high-grade ore at the Águas Claras and Capão Xavier mines presents some issues that need to be addressed. One of them concerns the origin of the dolomitic itabirite. Beukes et al. (2002) considered the dolomitic itabirite of the Águas Claras mine as a product of dolomitisation of a chert BIF by hydrothermal solutions. However, they did not take into account the regional geological setting. The Cauê Formation (including quartz and dolomitic itabirite) grades upward into the dolomite of the Gandarela Formation, a typical marine sequence hosting stromatolites. The contacts of the Cauê and the Gandarela Formations are laterally and vertically intergradational, and dolomitic itabirite occurs also within the dolomites of the Gandarela Formation (Dorr II, 1969). So, it seems more probable that the dolomitic itabirite represents a carbonatic facies of the Cauê Formation modified by a dolomitization process which occurred during diagenesis, instead of a product of carbonate-rich mineralization of the quartz itabirite. The marine origin of the dolomitic itabirite is also indicated by the C and O isotopes of dolomite, which present $\delta^{13}\text{C}$ varying from $-2.5\text{‰}_{\text{PDB}}$ to $-0.8\text{‰}_{\text{PDB}}$ (average of -1.7‰), while the oxygen isotope data displays $\delta^{18}\text{O}$ values varying from $-12.4\text{‰}_{\text{PDB}}$ to $-8.5\text{‰}_{\text{PDB}}$ (average of -10.5‰). These values correlate well with those of the stromatolitic carbonates of the Gandarela Formation of the Minas basin (Sial et al. 2000) and also with carbonates of the Wittenoom Formation of the Hamersley basin (Veizer et al. 1990). Isotope data of the dolomitic itabirite are quite different from those found in carbonates of the dolomitised jaspilite of the N4 mine in Carajás and in hypogene carbonates of the North Deposit in Tom Price (Table 6). Depleted $\delta^{13}\text{C}$ values of hypogene carbonates from these mines compared with the values of dolomite of the dolomitic itabirite are additional evidence that this rock was not formed by hydrothermalism of the quartz itabirite.

Table 6 – The C and O isotopic composition of carbonate samples from Águas Claras, and Carajás

Mine	Alteration Zone	$\delta^{18}\text{O}$ (‰PDB)		$\delta^{13}\text{C}$ (‰PDB)	
		Range	Average	Range	Average
Águas Claras ⁽¹⁾		-12.4 to -8.5	-10.5	-2.5 to -0.8	-1.7
North Deposit (Tom Price) ⁽²⁾	Magnetite-siderite-iron silicate	-17.3 to -11.8	-14.2	-10.3 to -6.3	-8.8
	Hematite-ankerite-magnetite	-16.1 to -13.5	-16.0	-7.5 to -0.9	-4.9
Carajás ⁽³⁾		-24.0 to -10.0	NA	-6.0 to -3.0	-5.0

(1) Spier et al. (2005a) (2) Thorne et al. (2004) (3) Sial et al. (2000) NA = not available

Another issue in the hypogene-supergene models of Beukes et al. (2002) and Dalstra and Guedes (2004) regards the protore of the soft high-grade ores. According to the authors, the soft high-grade ore could not have been formed only from quartz itabirite. Still, thousands of meters of drill cores from the Tamanduá mine and other mines of the region, such as the Capitão do Mato, Pico and Sapecado (Fig. 1), many of them in fresh itabirites, intercept only quartz itabirite. Carbonate-rich altered itabirites have never been found in deepest levels below the water table in these mines. Then, it is highly reasonable to assume that the soft high-grade ores at those mines originated from the quartz itabirite.

Despite the contentions about the origin of the dolomitic itabirite, it is unquestionable that the original composition of the itabiritic protore had a major role in the genesis of high- and low-grade soft ores in the QF, the dolomitic itabirite being the more favorable to form high-grade deposits due to the higher solubility of dolomite in relation to quartz. In fact, although the majority of the iron ore reserves in the QF come from quartz itabirite protore, the richest orebodies come from dolomitic itabirite. This is clearly verified in the Águas Claras and Capão Xavier mines, where the high-grade ores were formed only from the dolomitic itabirite. As to the nature of the mineralizing fluid, Viel et al. (1987) suggested that it was meteoric water enriched in CO₂ originated from the decomposition of the superficial vegetation that would have leached dolomite. Hematite was not affected by meteoric solutions (Dorr II 1965; Eichler 1968), remaining residually enriched. Viel et al. (1987) also suggest that, depending on the Eh and pH of the solution, any ferrous iron present in dolomite would be oxidized and precipitated. The weathering process was highly enhanced by the marked bedding at high angle to the ground surface shown by the BIFs in the Águas Claras mine, thus allowing a deep penetration of weathering fluids, abundant in humid tropical climates, especially along fault and fracture planes.

Our petrographic and geochemical data fit well with the model proposed by Viel et al. (1997). They show that the dissolution of the the dolomitic bands of the itabirite generates a highly porous material made of hematite and a brownish residue. Petrographic and Mössbauer analyses indicate that hematite was not affected by the meteoric solutions. Thus, this brownish residue comes from the dolomite dissolution. The dolomite composition is quite constant throughout the whole sequence of dolomitic itabirite at the Águas Claras mine, with average Fe and Mn contents around 1.5%. SEM and TEM analyses revealed the presence of iron and manganese oxides within the brownish residue, while MS indicate ferrihydrite in its mineralogical composition. These observations led to the conclusion that the dissolution of

dolomite during weathering produced solutions carrying Mn^{2+} and Fe^{2+} , according to the following reaction:

Calcium and magnesium were leached out from the weathering profile, while iron and manganese precipitated along pores and fracture planes forming Mn-oxides and ferrihydrite.

The supergene alteration begins along fractures close to the surface and spreads laterally and downward from these zones. At the bottom contact zone of the soft ore with the dolomitic itabirite, the weathering solutions are more saturated in Ca and Mg and are, consequently, less reactive, favoring the concentration of less soluble minerals, such as apatite. The interfingering contact observed in this zone reflects the development of the weathering front downwards, along the most favorable, fractured zones, forming the pinnacles and preserving remnants of the dolomitic itabirite.

Kink-bands and slang folds in the soft ore associated with a Tertiary basin situated in the central and deeper part of the Águas Claras orebody also suggest that the soft ore resulted from the leaching of dolomite by supergene solutions. The removal of large quantities of dolomite created large pore space volumes in the soft ore, which collapsed, forming kink-bands and slang folds, according to the model described by Ribeiro (2003) and Ribeiro and Carvalho (2002) for the soft itabirite of the Pico mine. This process produced depressions in the central part of the orebody, which were filled by sediments of Tertiary age, according to palynological studies of Lima and Salard-Chebouldaeff (1981) and Maizatto (2001). $^{40}\text{Ar}/^{39}\text{Ar}$ dating of supergene Mn-oxides hosted within the soft iron ore of the Sapecado mine carried out by Spier et al. (2005b) suggests that most of the soft ore in the QF was formed during a major, intense, chemical weathering period, around 51-41 Ma.

An additional evidence to support our hypothesis comes from the presence of poorly crystalline ferrihydrite within the porous bands of the soft ore. This mineral is widespread in surface environments and, unless stabilized in some way, is transformed into more stable goethite or hematite. Ferrihydrite can be produced from Fe^{II} solutions by fast oxidation followed by hydrolysis in $\text{pH} < 5$. The rate of oxidation governs the formation of goethite (slow oxidation) or ferrihydrite (fast oxidation). Due to its metastable nature, ferrihydrite can only be expected to be found in environments where its transformation into more stable oxides is inhibited or retarded (Cornell and Schwertmann 1996). According to Cornell (1988), the presence of transition elements such as Mn can stabilize ferrihydrite. The close association of Mn-oxides with ferrihydrite in the residue of the dolomite dissolution could, therefore, have been

responsible for inhibiting the transformation of ferrihydrite into hematite or goethite. Ferrihydrite transforms into hematite at temperatures as low as 4°C, and the higher the temperature, the higher the formation of hematite (Schwertmann et al. 1985). Thus, if the soft ore had been produced by the leaching of dolomite by hypogene solutions, ferrihydrite would not be expected to be found.

Another important feature shown by the soft ore is the REEY distribution pattern, very similar to that of the dolomitic itabirite (Fig. 14c). Even when the massive and porous bands of the soft ore are considered separately, the REEY pattern is the same, as shown in Figs. 14b and d. Figure 14d and Table 3 show that REEY are concentrated in the dolomitic bands of the protore. The leaching of dolomite promoted the REEY enrichment in the porous bands of the soft ore and depletion in the massive bands, but the original trend was preserved. This can be explained by taking into account that REEY in the dolomitic bands of the dolomitic itabirite are associated mainly with the clastic contamination of these predominantly chemical sediments (Spier et al. 2005a). Depletion in REEY in the massive bands of the soft ore in relation to the iron-rich bands of the protore (Fig. 14d) indicates that the REEY were mostly in dolomite which was leached away during weathering.

In summary, many features observed in the soft high-grade ore of the Águas Claras mine, such as: (1) gradual transition from the dolomitic itabirite into the soft ore; (2) disappearance of the soft ore down dip, leaving pinnacles formed by dolomitic itabirite; (3) pockets of dolomitic itabirite within the soft ore; (4) occurrence of slump folds in the soft ore, and Tertiary basins locally blanketing the orebody; (6) petrographic evidences of dolomite dissolution forming Mn-oxides and ferrihydrite, and (7) a similar REEY pattern for the dolomitic itabirite and the soft ore indicate that soft high-grade ore in the Águas Claras mine was formed by leaching of dolomite from the dolomitic itabirite by meteoric water.

The occurrence of bauxite deposits formed from Tertiary kaolinitic sediments locally blanketing the high- and low-grade ores of the Capão Xavier mine is a strong evidence that the chemical weathering in the region was intense. It was enough to leach dolomite from the dolomitic itabirite of the Águas Claras and Capão Xavier mines, but was not able to form large volumes of soft high-grade ores from quartz itabirite in either mine. On the other hand, at the Tamanduá mine, quartz itabirite was the protore of the huge soft high-grade orebody. It is unlikely that the soft ore could have been formed by meteoric leaching from quartz itabirite in this mine, unless another structural control, such as metavolcanic or mafic dykes, acting as impermeable barriers, had played an important role. This hypothesis needs to be considered, but

there are many field relationships previously mentioned in the text which favor the genesis of soft ores in the Tamanduá mine by hypogene solutions.

CONCLUSIONS

The detailed mineralogical and geochemical study of the soft and hard high-grade ores in the Águas Claras mine showed a very simple mineralogical and chemical composition. Both ores consist essentially of hematite, occurring as martite, anhedral to granular/tabular hematite and, locally specularite. Hematite is very pure and well crystallized. It occurs growing over martite crystals or as individual crystals. Gangue minerals are very rare, consisting of dolomite, sericite, chlorite and apatite in the hard and soft ores, and Mn-oxides and ferrihydrite in the soft ore, where they are concentrated within the porous bands. Hard and soft ores consist almost entirely of Fe_2O_3 , with higher amount of detrimental impurities, especially MnO, in the soft ore. Both hard and soft ores are very low in trace elements. The soft ore preserves the REEY pattern of the dolomitic itabirite, suggesting that weathering promoted a residual enrichment in REEY, without fractionation.

Field relationships, petrological and geochemical data indicate that the high-grade ores at the Águas Claras mine have a dual origin, involving hypogene and supergene processes. The occurrence of the hard massive high-grade ore within fresh dolomitic itabirite is a good evidence of its hypogene origin. Microstructures and granoblastic fabric of the hard ore indicate that its genesis occurred prior to or concomitant with the main deformational event that affected the rocks at the western side of the QF, during the Transamazonian orogeny (2.1-2.0 Ga). Mineralogical and geochemical data provided little information regarding the hypogene solutions and their precipitates at the Águas Claras mine. Further investigations on the detailed structural control of the hard high-grade orebodies, combined with microthermometric investigations, are necessary to determine the role of hydrothermal fluids in the formation of the hard high-grade ores at the QF.

Otherwise, despite the arguments about the origin of the dolomitic itabirite, the field relationships, mineralogical and geochemical data strongly indicate the supergene origin of the soft high-grade ore of the Águas Claras mine. Weathering of the dolomitic itabirite leached dolomite, leaving a highly porous, saprolitic ore, consisting almost entirely of hematite with very subordinated gangue minerals. Among these are Mn-oxides and ferrihydrite, precipitated along

pores and fractures planes of the ore from solutions carrying Mn^{2+} and Fe^{2+} liberated during dolomite dissolution. The occurrence of ferridydrate in the soft ore is a good evidence of its supergene origin. Data from palynological studies carried out in sediments of basins that blanket some high-grade deposits in the QF, associated with $^{40}\text{Ar}/^{39}\text{Ar}$ dating of supergene Mn-oxides hosted within the soft iron ore of the Sapecado mine, suggest that most of the soft ore in the QF was formed during a major, intense, chemical weathering period, around 51-41 Ma.

The original composition of the itabiritic protore has a major role in the genesis of high- and low-grade soft ores in the QF. Under the same weathering and structural conditions, the dolomitic itabirite is more favorable to form high-grade deposits than quartz itabirite, due to the higher solubility of dolomite in relation to quartz. Field relationships at the Águas Claras and Capão Xavier deposits suggest that it is not possible to form huge soft high-grade deposits from quartz itabirite, unless another control, such as impermeable barriers, had played an important role.

The occurrence of huge tonnage of soft ore hosted in quartz itabirite in the Tamaduaí deposit, and the close association between hard, medium and soft ores, suggest that all those ores were mostly formed during the hypogene process that generated the hard ore, representing different stages of the hypogene alteration. If this hypothesis is correct, the presence of a carbonate-rich protore is not a necessary condition to the genesis of large high-grade orebodies, as suggested by Beukes et al. (2002) and by Dalstra and Guedes (2004).

Though many issues remain to be clarified, we believe that the hypogene-supergene modified genetic model is the best one to explain the origin of the high-grade ores at the QF. The diversity of geological and structural contexts where the ore occurs suggests the local preponderancy of hypogene or supergene processes in each particular orebody.

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Appendix 1 – List of the samples, location and analytical procedures

Hand specimens samples											
Sample	Coordinates (m)			Type	Petrography	MEV	XRD	Rietveld	Mössbauer	Chemical analyses	Chemical analyses
	East	North	Altitude							MBR	ACTLAB
MAC2	1589	-511	1050	HO	X		X			X	X
MAC3A	2272	-753	939	PB	X		X			X	X
MAC12	2300	-720	920	SO	X		X			X	
MAC14	2464	-610	920	SO	X		X			X	
MAC14A	2464	-610	969	MB						X	X
MAC14B	2464	-610	969	PB						X	X
MAC15	1965	-529	917	PB	X		X				
MAC17A	2270	-735	931	SO	X		X			X	X
MAC18A	2308	-717	928	SO	X		X			X	
MAC19A	2483	-655	978	SO	X	X	X			X	
MAC20A	1943	-500	929	SO	X		X			X	X
MAC44	1930	-530	899	HO	X					X	X
MAC54A	1859	-623	908	SO	X	X	X			X	
MAC55A	1847	-572	914	SO	X					X	
MAC56A	1883	-578	908	SO	X					X	
MAC57A	2181	-543	925	SO	X	X				X	
MAC58A	2235	-560	925	SO	X					X	
MAC59A	2413	-636	954	SO	X	X	X			X	
MAC59H	2413	-636	954	MB						X	X
MAC59I	2413	-636	954	PB						X	X
MAC60A	2930	-450	1210	SO	X		X			X	X
MAC62	1230	-410	1229	HO	X	X	X			X	
MAC67	2289	-579	918	HO	X		X	X	X	X	X
MAC68	1862	-499	965	HO	X		X		X	X	X
MAC69A	2320	-568	918	SO	X					X	
MAC77A	2356	-642	920	SO	X					X	
MAC84	2380	-670	922	HO	X					X	X
MAC97	1980	-500	932	HO	X	X	X	X	X	X	X
MAC105A	1400	-425	1167	HO	X		X		X	X	X
MAC105B	1400	-425	1167	HO	X					X	X
MAC107	2350	-650	928	PB	X					X	X
MAC112	1300	-410	1210	HO	X					X	
MAC115	1350	-420	1208	HO	X					X	X
MAC126A	2425	-603	957	MB			X		X	X	X
MAC126B	2425	-603	957	PB			X		X	X	X
MAC127A	2423	-625	956	MB			X	X	X	X	X
MAC127B	2423	-625	956	PB			X	X	X	X	X
MAC128A	2418	-649	951	MB			X		X	X	X
MAC128B	2418	-649	951	PB			X		X	X	X
MAC129A	2459	-594	966	MB			X		X	X	X
MAC129B	2459	-594	966	PB			X		X	X	X

HO= hard ore; SO=soft ore; PB=porous band of the soft ore; MB=massive band of the soft ore

Appendix 1 (Continued)

Appendix 1 (Continued)

Sample	Depth along the drill hole (m)	Type	Drill core samples						Chemical analyses MBR	Chemical analyses ACTLAB
			Petrography	MEV	XRD	Rietveld	Mössbauer			
FSD08-99	2.20	SO							X	
FSD08-99	4.80	SO							X	
FSD08-99	7.30	SO							X	
FSD08-99	12.50	SO							X	
FSD08-99	13.20	SO							X	
FSD08-99	14.70	SO							X	
FSD08-99	14.80	SO							X	
FSD08-99	16.80	SO							X	
FSD08-99	17.00	SO							X	
FSD08-99	19.00	SO							X	
FSD09-99	3.50	SO							X	
FSD09-99	4.10	SO							X	
FSD09-99	8.60	SO							X	
FSD09-99	10.50	SO							X	
FSD09-99	12.50	SO							X	
FSD09-99	13.50	SO							X	
FSD09-99	19.70	SO							X	
FSD09-99	20.90	SO							X	
FSD09-99	24.70	SO							X	
FSD09-99	27.70	SO							X	
FSD09-99	28.70	SO							X	
FSD11-99	2.50	SO	X	X					X	
FSD11-99	4.80	SO							X	X
FSD11-99	5.50	SO							X	
FSD11-99	5.70	SO							X	
FSD11-99	5.80	SO							X	
FSD11-99	6.50	SO							X	
FSD11-99	6.80	SO							X	
FSD11-99	7.00	SO							X	
FSD11-99	7.10	SO							X	
FSD11-99	8.30	SO							X	
FSD11-99	8.50	SO							X	
FSD11-99	8.60	SO							X	
FSD11-99	8.90	SO							X	
FSD11-99	9.20	SO							X	
FSD11-99	12.40	SO							X	X
FSD11-99	13.40	SO							X	
FSD11-99	20.40	SO							X	
FSD11-99	22.80	SO							X	
FSD11-99	25.50	SO							X	
FSD11-99	25.70	SO							X	X
FSD11-99	26.30	SO							X	
FSD11-99	26.50	SO							X	
FSD11-99	26.70	SO							X	
FSD11-99	28.30	SO							X	

HO= hard ore; SO=soft ore; PB=porous band of the soft ore; MB=massive band of the soft ore

Appendix 2 – Major and trace element composition of the hard and soft ores

Sample	MAC2	MAC44	MAC67	MAC68	MAC84	MAC97	MAC105A	MAC105B	MAC115	PZ55AM7	MAC17A
Ore Type	HO	HO	HO	HO	HO	HO	HO	HO	HO	HO	SO
Wt%											
SiO ₂	0.48	0.24	0.93	0.71	0.36	1.32	0.57	0.77	0.89	0.99	0.42
Al ₂ O ₃	0.12	0.14	0.20	0.25	0.02	0.91	0.16	0.13	0.41	0.21	0.24
Fe ₂ O ₃	97.46	96.40	95.11	98.19	98.58	95.00	97.86	97.94	97.51	94.44	98.38
Fetot	99.46	99.40	96.00	98.96	98.84	95.00	98.40	98.50	98.00	94.44	98.49
FeO	1.80	2.70	0.80	0.69	0.23	na	0.49	0.50	0.44	na	0.10
MnO	0.021	0.034	0.019	0.010	0.049	0.005	0.008	0.005	0.018	0.093	0.492
MgO	<0.03	0.08	0.59	0.05	0.05	1.20	0.04	0.14	0.23	0.27	0.06
CaO	0.03	0.16	0.89	0.04	0.29	0.26	0.16	0.35	0.34	1.41	<0.03
Na ₂ O	<0.01	<0.01	0.01	0.37	<0.01	0.22	<0.01	<0.01	<0.01	<0.01	<0.01
K ₂ O	<0.01	0.06	0.06	0.06	0.08	<0.01	0.05	0.05	0.14	<0.01	<0.01
TiO ₂	0.009	0.018	0.017	0.006	0.017	0.033	0.012	0.007	0.030	0.024	0.009
P ₂ O ₅	0.06	0.12	0.18	0.03	0.22	0.17	0.14	0.18	0.017	0.18	<0.03
LOI	0.27	0.24	1.39	0.13	0.43	0.89	0.28	0.32	0.21	1.17	0.54
Total	100.34	100.21	100.20	100.54	100.34	100.02	99.78	100.41	100.40	98.80	100.26
ppm											
Ba	15.3	4.4	10.9	37.2	9.9	3.7	8.2	6.0	24.0	<3.0	21.7
Sr	7.8	<2.0	7.6	2.3	8.4	2.1	8.8	8.7	9.3	5.6	9.3
Y	7.6	6.2	4.6	2.2	4.6	3.5	6.1	5.8	5.2	4.1	12.7
Sc	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
Zr	3.3	2.4	4.0	4.5	7.8	7.9	6.7	2.5	4.1	15.1	4.3
Be	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
V	132.0	32.0	10.0	24.0	17.0	29.7	17.2	13.1	36.3	45.0	30.0
Ni	<20.0	20.3	<20.0	<20.0	<20.0	45.0	<20.0	<20.0	<20.0	<20.0	31.6
Cu	15.1	<5.0	<5.0	22.0	<5.0	<5.0	<5.0	13.6	13.6	10.2	<5.0
Zn	31.1	<30.0	<30.0	<30.0	<30.0	<30.0	<30.0	<30.0	<30.0	<30.0	40.6
Ga	<1.0	<1.0	<1.0	<1.0	<1.0	1.2	<1.0	<1.0	<1.0	<1.0	1.1
Ge	4.7	5.9	6.0	4.1	3.4	4.8	3.7	3.2	2.8	4.9	3.8
Rb	1.2	<1.0	<1.0	1.9	<1.0	<1.0	<1.0	<1.0	1.1	<1.0	<1.0
Nb	<0.2	<0.2	<0.2	0.7	<0.2	1.0	0.6	0.7	0.8	<0.2	<0.2
Mo	3.4	3.2	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	2.4
Ag	3.8	1.3	1.0	<0.5	0.8	<0.5	<0.5	<0.5	<0.5	<0.5	1.3
In	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sn	<1.0	<1.0	3.6	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Cs	<0.1	<0.1	0.2	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
ΣREE	10.0	7.5	6.6	3.2	6.1	6.9	8.7	8.1	8.3	5.2	18.2
Hf	<0.1	<0.1	<0.1	<0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Tl	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pb	29.0	13.2	<5.0	<5.0	21.8	<5.0	<5.0	<5.0	<5.0	<5.0	10.6
Bi	<0.1	<0.1	<0.1	0.1	<0.1	0.1	<0.1	0.1	<0.1	<0.1	<0.1
Th	0.15	0.11	0.16	0.05	0.15	0.44	0.22	0.30	0.45	0.1	0.3
U	12.3	3.8	0.6	2.6	4.8	8.4	2.6	2.3	3.7	3.6	3.2
Au	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	10.0	na	na	<2.0	18.0
As	12.6	23.1	6.3	15.8	12.6	19.8	8.8	<5.0	5.1	17.3	9.8
Br	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	na	na	<0.5	<0.5
Cr	71.0	202.0	170.0	36.0	52.0	23.0	29.0	<20.0	25.0	65.0	192.0
Ir	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	na	na	<5.0	<5.0
Sb	6.2	4.6	2.1	4.1	6.9	4.4	3.7	2.0	2.2	4.1	2.2
Sc	1.0	0.6	0.4	0.1	0.5	0.7	0.5	na	na	0.3	1.0
Se	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	na	na	<3.0	<3.0
Fe#	0.980	0.970	0.991	0.992	0.997	na	0.994	0.994	0.995	na	0.999

HO = hard ore; SO = Soft ore; MB = Massive band of the soft ore; PB = Porous band. Fe_{TOT} expressed as Fe₂O₃.Fe# = (Fe³⁺/(Fe³⁺ + Fe²⁺)), na = not analyzed

Appendix 2 (Continued)

Sample	M20A	M60A	FSD8/ 4.8m	FSD8/ 7.30m	FSD8/ 12.50m	FSD8/ 14.70m	FSD8/ 16.8m	FSD8/ 19.0m	FSD9/ 3.50m	FSD9/ 8.60m	FSD9/ 24.70m
Ore Type	SO	SO	SO	SO	SO	SO	SO	SO	SO	SO	SO
Wt%											
SiO ₂	0.24	0.18	2.05	1.14	1.95	0.93	1.62	1.08	1.41	1.02	2.85
Al ₂ O ₃	0.18	0.33	1.26	0.33	0.63	0.33	0.57	0.33	0.69	0.45	2.1
Fe ₂ O ₃	97.43	97.90	90.49	95.31	93.21	95.52	93.09	94.68	93.48	95.46	89.19
Fetot	97.59	98.07	90.55	95.37	93.27	95.58	93.15	94.74	93.54	95.52	89.25
FeO	0.14	0.15	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
MnO	0.525	0.73	1.378	0.705	1.2	0.726	1.587	1.242	1.092	0.846	2.139
MgO	0.06	0.06	0.75	0.3	0.69	0.24	0.39	0.27	0.36	0.36	0.36
CaO	0.06	<0.03	0.39	0.15	0.21	0.12	0.18	0.15	0.15	0.12	0.18
Na ₂ O	<0.01	<0.01	0.39	0.36	0.45	0.33	0.45	0.39	0.39	0.42	0.36
K ₂ O	<0.01	<0.01	0.03	0.24	0.3	0.005	0.21	0.09	0.09	0.005	0.005
TiO ₂	0.009	0.009	0.155	0.024	0.048	0.021	0.045	0.021	0.045	0.045	0.156
P ₂ O ₅	0.06	0.06	0.28	0.03	0.06	0.03	0.06	0.03	0.03	0.005	0.09
LOI	0.60	0.78	1.82	0.6	1.26	0.72	1.44	0.99	1.08	0.84	2.31
Total	99.33	100.25	98.55	99.27	100.08	98.97	99.75	99.36	98.91	99.45	99.72
ppm											
Ba	79.3	161.0	53.8	78.9	11.4	30.6	43.7	28.9	28.2	6.7	49.8
Sr	4.0	4.4	34.1	10.9	33.7	15.0	35.5	29.5	26.6	24.5	34.8
Y	33.7	5.5	32.2	26.3	14.6	20.7	37.7	30.8	13.3	9.1	31.7
Sc	<3.0	<3.0	4.0	0.5	3.0	0.5	0.5	0.5	0.5	0.5	0.5
Zr	4.2	3.5	26.1	15.2	14.9	11.2	28.6	11.3	15.0	18.4	33.2
Be	<3.0	<3.0	4.0	0.5	3.0	3.0	6.0	6.0	3.0	0.5	3.0
V	94.0	34.0	69.9	72.2	138.4	87.5	93.3	74.7	99.4	84.1	56.1
Ni	<20.0	<20.0	59.8	12.5	20.1	18.3	30.5	27.5	35.0	9.1	65.0
Cu	45.3	<5.0	22.0	14.5	7.7	14.7	34.1	24.8	10.0	6.8	8.8
Zn	<30.0	<30.0	6.0	0.5	0.5	0.5	45.1	29.5	0.5	0.5	109.8
Ga	<1.0	<1.0	1.7	0.5	1.1	0.5	1.2	0.5	1.8	1.1	2.4
Ge	3.8	3.5	2.4	0.7	4.1	3.0	3.0	0.7	2.2	3.4	2.7
Rb	4.2	<1.0	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Nb	<0.2	<0.2	1.2	0.4	0.5	0.4	0.5	0.3	0.4	0.4	1.6
Mo	2.9	<2.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ag	1.3	1.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
In	<0.1	<0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sn	<1.0	6.3	1.6	0.5	1.1	0.5	1.1	0.5	0.5	0.5	1.2
Cs	0.4	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
ΣREE	29.3	24.1	46.0	29.4	21.8	24.9	39.3	28.7	14.3	14.7	41.1
Hf	<0.1	<0.1	0.5	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.6
Tl	<0.1	<0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pb	7.8	12.6	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Bi	<0.1	<0.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Th	0.1	0.2	1.2	0.2	0.4	0.1	0.6	0.2	0.4	0.4	1.5
U	4.2	6.9	6.2	7.2	3.5	4.5	3.6	2.9	3.7	3.0	5.9
Au	<2.0	<2.0	1.0	5.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0
As	19.5	11.5	28.4	16.6	18.7	11.7	15.8	14.8	22.0	18.5	22.9
Br	<0.5	<0.5	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Cr	148.0	29.0	50.0	18.0	32.0	29.0	40.0	38.0	74.0	42.0	80.0
Ir	<5.0	<5.0	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Sb	3.7	5.6	5.0	6.1	3.4	3.5	3.9	3.6	4.4	3.5	3.4
Se	0.5	2.3	3.5	0.8	1.1	0.5	1.1	0.7	1.2	1.1	3.3
Fe#	0.998	0.998	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

HO = hard ore; SO = Soft ore; MB = Massive band of the soft ore; PB = Porous band. Fe_{TOT} expressed as Fe₂O₃.Fe# = (Fe³⁺)/(Fe³⁺ + Fe²⁺), na = not analyzed

Appendix 2 (Continued)

Sample	FSD9/ 27.70m	FSD9/ 28.70m	FSD11/ 4.8m	FSD11/ 5.70m	FSD11/ 7.10m	FSD11/ 10.50m	FSD11/ 12.4m	FSD11/ 13.4m	FSD11/ 20.4m	FSD11/ 25.7m	FSD11/ 26.7m
Ore Type	SO	SO	SO	SO	SO	SO	SO	SO	SO	SO	SO
Wt%											
SiO ₂	3.57	1.26	1.16	1.53	1.08	1.86	0.55	1.05	2.31	0.68	1.23
Al ₂ O ₃	1.89	0.39	0.38	0.3	0.21	0.81	0.14	0.18	1.5	0.10	0.12
Fe ₂ O ₃	87.66	94.62	95.90	93.18	96.15	92.22	98.11	96.48	91.35	97.63	95.52
Fetot	87.72	94.68	95.96	93.24	96.21	92.28	98.22	96.54	91.47	97.69	0.05
FeO	0.05	0.05	0.05	0.05	0.05	0.05	0.10	0.05	0.11	0.05	0.05
MnO	1.479	0.561	0.49	0.666	0.756	1.014	0.39	0.618	0.996	0.59	0.552
MgO	2.04	0.75	0.75	0.78	0.33	0.96	0.12	0.21	0.27	0.33	0.48
CaO	0.24	0.48	0.54	0.6	0.15	0.15	0.05	0.12	0.12	0.12	0.39
Na ₂ O	0.33	0.39	<0.01	0.27	0.42	0.45	0.15	0.3	0.45	0.11	0.42
K ₂ O	0.005	0.12	<0.01	0.12	0.15	0.06	<0.01	0.12	0.09	<0.01	0.09
TiO ₂	0.153	0.021	0.005	0.21	0.021	0.024	0.010	0.024	0.069	0.011	0.021
P ₂ O ₅	0.06	0.21	0.37	0.33	0.03	0.005	0.02	0.06	0.06	0.06	0.21
LOI	2.1	0.51	0.70	0.72	0.63	1.26	0.44	0.54	1.41	0.67	0.51
Total	99.54	99.36	100.37	98.58	99.96	98.91	100.08	99.81	98.73	100.37	99.63
ppm											
Ba	32.2	24.3	11.0	22.6	24.5	13.6	16.1	24.5	21.7	14.4	16.4
Sr	29.3	12.7	14.2	15.5	8.1	29.5	4.0	4.2	10.6	19.2	12.1
Y	26.3	17.7	10.3	15.9	11.0	12.4	6.7	9.8	26.1	18.0	12.8
Sc	6.0	1.5	<3.0	0.5	0.5	0.5	<3.0	0.5	0.5	<3.0	0.5
Zr	40.1	5.2	5.4	10.4	14.3	13.7	4.1	3.8	19.0	5.4	12.3
Be	3.0	0.5	<3.0	0.5	0.5	3.0	<3.0	0.5	0.5	<3.0	0.5
V	63.6	91.2	65.5	131.6	34.1	96.4	9.1	23.5	40.4	39.3	9.9
Ni	89.9	10.1	25.4	15.6	13.1	20.2	<20.0	11.8	85.3	<20.0	0.5
Cu	9.0	10.1	<5.0	8.1	7.4	7.2	<5.0	7.2	10.5	<5.0	7.2
Zn	17.8	0.5	<30.0	0.5	0.5	0.5	<30.0	0.5	39.9	31.3	0.5
Ga	1.8	0.5	1.1	0.5	0.5	1.3	<1.0	0.5	3.0	<1.0	0.5
Ge	3.2	1.1	3.6	3.6	2.9	5.0	3.0	3.8	3.4	4.0	2.3
Rb	0.5	1.1	<1.0	0.5	0.5	0.5	<1.0	0.5	0.5	<1.0	0.5
Nb	1.5	0.3	0.3	0.2	0.4	0.5	0.3	0.1	0.6	0.3	0.1
Mo	1.0	1.0	<2.0	1.0	1.0	1.0	<2.0	1.0	1.0	<2.0	1.0
Ag	0.4	0.2	<0.5	0.2	0.2	0.2	<0.5	0.2	0.2	<0.5	0.2
In	0.1	0.1	<0.1	0.1	0.1	0.1	<0.1	0.1	0.1	<0.1	0.1
Sn	1.2	0.5	<1.0	0.5	0.5	0.5	<1.0	0.5	0.5	<1.0	0.5
Cs	0.1	0.1	<0.1	0.1	0.1	0.1	<0.1	0.1	0.1	<0.1	0.1
ΣREE	33.5	21.0	13.5	16.1	17.6	17.6	9.3	13.2	28.4	15.2	10.6
Hf	0.6	0.1	<0.1	0.1	0.1	0.1	<0.1	0.1	0.3	<0.1	0.1
Tl	0.0	0.0	<0.1	0.0	0.0	0.0	<0.1	0.0	0.0	1.8	0.0
Pb	1.5	1.5	<5.0	1.5	1.5	1.5	<5.0	1.5	1.5	<5.0	1.5
Bi	1.0	1.0	<0.1	1.0	1.0	1.0	<0.1	1.0	1.0	<0.1	1.0
Th	1.0	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.7	0.20	0.1
U	7.0	6.1	2.6	3.1	1.7	1.7	1.2	1.9	2.8	4.0	1.0
Au	1.0	1.0	<2.0	1.0	1.0	1.0	<2.0	1.0	1.0	<2.0	1.0
As	16.6	16.2	9.0	8.8	6.5	6.5	<5.0	5.8	7.2	6.0	7.5
Br	0.3	0.3	<0.5	0.3	0.3	0.3	<0.5	0.3	0.3	<0.5	0.3
Cr	56.0	16.0	89.0	61.0	25.0	25.0	25.0	24.0	28.0	64.0	17.0
Ir	2.5	2.5	<5.0	2.5	2.5	2.5	<5.0	2.5	2.5	<5.0	2.5
Sb	3.4	3.9	2.3	2.6	2.2	2.2	1.6	2.0	2.1	1.7	1.6
Se	2.7	0.4	0.5	0.6	0.8	0.8	0.5	0.5	1.7	0.5	0.4
Fe#	1.5	1.5	<3.0	1.5	1.5	1.5	<3.0	1.5	1.5	<3.0	1.5
Fe#	1.0	1.0	0.998	1.0	1.0	1.0	0.999	1.0	1.0	0.999	1.0

HO = hard ore; SO = Soft ore; MB = Massive band of the soft ore; PB = Porous band. Fe_{TOT} expressed as Fe₂O₃.

Fe# = (Fe³⁺/(Fe³⁺ + Fe²⁺)), na = not analyzed

Appendix 2 (Continued)

Sample	FSD11/ 28.3m	MAC14A	MAC59H	MAC126A	MAC127A	MAC128A	MAC129A	MAC3A	MAC14B
Ore Type	SO	MB	MB	MB	MB	MB	MB	PB	PB
Wt%									
SiO ₂	1.2	0.51	0.30	0.43	0.15	0.26	0.44	3.17	4.74
Al ₂ O ₃	0.12	0.09	0.12	0.06	0.04	0.03	0.16	3.25	0.39
Fe ₂ O ₃	94.32	96.84	97.90	99.15	98.68	97.99	98.89	86.96	87.69
Fetot	0.05	98.34	97.90	99.27	98.80	98.15	99.01	87.22	86.95
FeO	0.05	1.35	na	0.11	0.11	0.14	0.11	0.23	0.23
MnO	0.525	0.29	0.03	0.05	0.07	0.11	0.020	2.551	1.929
MgO	0.45	0.09	0.10	0.08	0.09	0.02	0.11	0.30	2.29
CaO	0.84	0.06	0.06	0.03	0.38	0.03	0.05	0.08	0.11
Na ₂ O	0.42	<0.01	<0.01	<0.01	<0.01	0.15	<0.01	0.01	<0.01
K ₂ O	0.005	<0.01	0.04	<0.01	<0.01	<0.01	0.03	0.07	<0.01
TiO ₂	0.024	0.009	0.010	0.005	<0.001	0.005	0.005	0.223	0.022
P ₂ O ₅	0.45	<0.03	0.04	0.01	0.27	0.01	0.04	0.25	0.05
LOI	0.54	0.45	0.38	0.23	0.27	0.39	0.19	2.97	2.54
Total	98.88	99.72	99.01	100.21	100.12	99.17	100.09	100.07	100.02
ppm									
Ba	9.6	9.9	10.3	13.4	<3.0	29.5	4.2	138.4	20.7
Sr	14.9	5.1	2.2	<2.0	12.4	<2.0	<2.0	42.8	20.2
Y	15.0	6.0	2.0	2.6	2.0	2.2	3.8	56.0	27.1
Sc	0.5	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	8.0	<3.0
Zr	7.7	2.3	2.2	4.2	4.8	2.6	3.2	38.6	4.7
Be	0.5	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	4.0	4.0
V	19.2	77.0	14.0	18.8	9.2	17.2	26.8	75.0	59.0
Ni	2.7	<20.0	<20.0	<20.0	<20.0	23.0	<20.0	63.6	39.0
Cu	6.7	<5.0	<5.0	<5.0	19.7	<5.0	<5.0	115.3	14.6
Zn	0.5	<30.0	<30.0	<30.0	<30.0	<30.0	<30.0	407.1	87.3
Ga	0.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	5.9	2.2
Ge	2.3	3.4	5.3	4.3	3.3	3.6	3.1	3.5	6.0
Rb	0.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Nb	<0.2	<0.2	<0.2	0.4	0.5	0.3	0.3	2.4	<0.2
Mo	1.0	3.3	2.2	<2.0	<2.0	<2.0	<2.0	<2.0	2.8
Ag	0.2	1.5	1.2	<0.5	<0.5	<0.5	<0.5	1.7	1.5
In	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sn	0.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	2.3	<1.0
Cs	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
ΣREE	12.4	7.6	4.5	4.8	3.6	3.9	5.9	116.9	29.0
Hf	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.0	0.1
Tl	0.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.06	<0.1
Pb	1.5	8.4	5.5	<5.0	<5.0	<5.0	<5.0	70.5	12.6
Bi	1.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1
Th	0.1	0.20	0.13	0.15	<0.05	0.07	0.1	3.8	0.2
U	3.3	4.1	1.1	1.8	0.7	1.6	1.1	8.4	4.5
Au	1.0	<2.0	<2.0	<2.0	<2.0	<2.0	4.0	15.0	10.0
As	7.5	9.6	5.5	6.3	7.7	6.2	8.9	22.8	26.3
Br	0.3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cr	17.0	181.0	33.0	23.0	33.0	26.0	31.0	83.0	206.0
Ir	2.5	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Sb	1.4	4.9	3.5	4.0	2.9	14.0	3.7	3.0	4.8
Sc	0.4	0.3	0.3	0.3	<0.1	0.2	0.2	7.7	1.2
Se	1.5	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
Fe#	1.0	0.985	na	0.999	0.999	0.998	0.999	0.997	0.997

HO = hard ore; SO = Soft ore; MB = Massive band of the soft ore; PB = Porous band. Fe_{TOT} expressed as Fe₂O₃.

Fe# = (Fe³⁺/(Fe³⁺ + Fe²⁺)), na = not analyzed

Appendix 2 (Continued)

	MAC59I	MAC107	MAC126B	MAC127B	MAC128B	MAC129B
Sample						
Ore Type	PB	PB	PB	PB	PB	PB
Wt%						
SiO ₂	0.99	1.26	0.94	1.05	0.38	0.97
Al ₂ O ₃	0.14	1.88	0.27	0.25	0.20	0.35
Fe ₂ O ₃	97.07	92.17	95.39	92.03	96.63	94.44
Fetot	97.07	92.58	95.51	92.20	96.74	94.56
FeO	na	0.37	0.11	0.15	0.10	0.11
MnO	0.767	1.612	0.954	2.452	1.499	1.716
MgO	0.33	0.07	0.29	0.64	0.08	0.30
CaO	0.26	0.01	0.04	0.31	0.10	0.07
Na ₂ O	0.01	<0.01	0.20	0.19	<0.01	0.14
K ₂ O	0.01	<0.01	<0.01	0.01	<0.01	0.03
TiO ₂	0.017	0.111	0.024	0.013	0.011	0.013
P ₂ O ₅	0.13	0.14	0.06	0.08	0.03	0.09
LOI	0.78	2.20	1.13	2.55	1.09	1.62
Total	100.50	99.84	99.42	99.73	100.14	99.85
ppm						
Ba	156.8	24.0	84.4	40.2	405.2	60.1
Sr	13.6	20.6	2.3	24.5	5.0	9.7
Y	13.9	22.7	27.2	40.6	28.1	45.2
Sc	<3.0	3.0	<3.0	<3.0	<3.0	<3.0
Zr	2.3	8.4	7.9	5.2	3.9	4.3
Be	<3.0	3.0	3.0	<3.0	<3.0	6.0
V	23.0	57.0	25.1	62.9	24.5	29.6
Ni	<20.0	16.9	23.9	39.3	41.3	<20.0
Cu	<5.0	80.3	<5.0	18.3	11.7	<5.0
Zn	<30.0	51.1	<30.0	91.1	101.8	40.9
Ga	<1.0	2.8	1.1	1.8	1.2	1.7
Ge	5.1	2.1	3.6	5.0	3.1	3.4
Rb	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Nb	<0.2	1.5	0.6	0.5	0.4	0.3
Mo	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Ag	1.3	<0.5	<0.5	<0.5	<0.5	<0.5
In	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sn	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Cs	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
ΣREE	14.4	52.5	31.5	35.4	25.6	38.3
Hf	<0.1	0.3	0.1	<0.1	<0.1	<0.1
Tl	<0.1	0.106	<0.1	<0.1	<0.1	<0.1
Pb	<5	7.1	<5	<5	5.9	6.1
Bi	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Th	0.1	1.4	0.4	0.2	0.2	0.3
U	1.1	6.2	3.4	7.6	2.1	3.7
Au	<2.0	na	35.0	3.0	<2.0	<2.0
As	9.2	10.0	13.7	13.6	12.0	20.8
Br	<0.5	na	<0.5	<0.5	<0.5	<0.5
Cr	26.0	50.0	41.0	32.0	30.0	82.0
Ir	<5.0	na	<5.0	<5.0	<5.0	<5.0
Sb	3.5	1.8	4.1	4.6	14.0	3.7
Sc	0.3	na	1.0	0.7	0.6	0.5
Se	<3.0	na	<3.0	<3.0	<3.0	<3.0
Fe	na	0.996	0.999	0.998	0.999	0.999

HO = hard ore; SO = Soft ore; MB = Massive band of the soft ore; PB = Porous band. Fe_{TOT} expressed as Fe₂O₃. Fe# = (Fe³⁺/(Fe³⁺ + Fe²⁺)), na = not analyzed

Appendix 3 – Rare earth element composition of the hard and soft ores

SAMPLE	MAC2	MAC44	MAC67	MAC68	MAC84	MAC97	MAC105A	MAC105B	MAC115	PZ55AM7	MAC17A	MAC20A	MAC60A	FSD8/ 4.8m	FSD8/ 7.3m	FSD8/ 12.5m
Ore Type ppm	HO	HO	HO	HO	HO	HO	HO	HO	HO	HO	SO	SO	SO	SO	SO	SO
La	1.42	1.05	1.15	0.49	1.07	1.06	0.97	1.08	1.36	0.91	3.10	3.08	3.5	8.74	3.95	3.92
Ce	2.65	2.02	1.85	1.09	1.77	2.09	1.92	2.07	1.88	1.45	5.04	6.10	9.34	13.88	7.55	7.41
Pr	0.41	0.29	0.26	0.10	0.22	0.30	0.30	0.36	0.33	0.20	0.69	1.47	1.26	1.98	1.19	0.93
Nd	1.85	1.38	1.19	0.47	1.01	1.34	1.71	1.82	1.74	0.91	2.96	6.98	5.10	8.40	5.76	3.89
Sm	0.56	0.39	0.29	0.12	0.27	0.34	0.46	0.49	0.42	0.25	0.67	1.97	1.16	1.81	1.42	0.85
Eu	0.18	0.13	0.11	0.05	0.11	0.10	0.19	0.19	0.18	0.11	0.34	0.66	0.36	0.69	0.58	0.31
Gd	0.77	0.61	0.44	0.18	0.43	0.42	0.71	0.75	0.62	0.32	1.12	2.95	1.00	2.19	1.80	1.00
Tb	0.13	0.11	0.07	0.04	0.07	0.07	0.12	0.12	0.11	0.06	0.20	0.42	0.14	0.39	0.33	0.18
Dy	0.82	0.62	0.45	0.22	0.44	0.42	0.74	0.74	0.66	0.40	1.34	2.30	0.79	2.62	2.25	1.14
Y	7.60	6.21	4.59	2.18	4.64	3.52	6.08	5.75	5.22	4.14	12.70	33.70	5.50	32.16	26.30	14.60
Ho	0.17	0.12	0.11	0.05	0.10	0.09	0.16	0.16	0.15	0.08	0.31	0.49	0.15	0.60	0.52	0.25
Er	0.46	0.37	0.33	0.15	0.28	0.30	0.44	0.46	0.41	0.23	1.01	1.40	0.47	1.97	1.69	0.81
Tm	0.06	0.05	0.05	0.02	0.04	0.04	0.05	0.06	0.05	0.03	0.15	0.19	0.08	0.31	0.26	0.13
Yb	0.39	0.30	0.30	0.16	0.25	0.27	0.031	0.34	0.031	0.18	1.07	1.16	0.64	2.03	1.81	0.85
Lu	0.06	0.05	0.05	0.02	0.04	0.04	0.04	0.05	0.05	0.02	0.18	0.18	0.10	0.34	0.29	0.14
ΣREE	9.96	7.47	6.65	3.16	6.09	6.88	8.72	8.13	8.27	4.24	18.17	29.35	24.08	45.96	29.40	21.79
La/Yb _{PAAS}	0.27	0.26	0.29	0.23	0.32	0.29	0.23	0.23	0.32	0.37	0.21	0.20	0.41	0.32	0.16	0.34
La/Sm _{PAAS}	0.37	0.39	0.57	0.61	0.58	0.45	0.32	0.31	0.47	0.52	0.68	0.23	0.44	0.70	0.41	0.67
Dy/Yb _{PAAS}	1.26	1.24	0.93	0.86	1.06	0.95	1.30	1.45	1.28	1.33	1.18	1.45	0.86	0.78	0.75	0.81
Ce/Ce* _{PAAS}	0.80	0.85	0.77	1.11	0.84	0.85	0.76	0.81	0.65	0.80	0.80	0.66	1.02	0.77	0.80	0.90
Eu/Eu* _{PAAS}	1.32	1.27	1.38	1.48	1.55	1.26	1.47	1.58	1.66	1.84	1.85	1.29	1.57	1.64	1.71	1.59
Y/Y* _{PAAS}	1.63	1.79	1.66	1.64	1.81	1.42	1.4	1.34	1.34	2.77	1.58	2.54	1.27	2.04	1.94	2.17

HO = hard ore; SO = Soft ore; MB = Massive band of the soft ore; PB = Porous band. Y content is not included in ΣREE. $Eu/Eu^*_{PAAS} = ((Eu/Eu_{PAAS}) / (Sm/Sm_{PAAS}) * (Gd/Gd_{PAAS}))^{1/2}$,
 Ce/Ce*_{PAAS} and Y/Y*_{PAAS} calculated by similar way.

Appendix 3 (Continued)

SAMPLE	FSD8/ 14.7m	FSD8/ 16.8m	FSD8/ 19.0m	FSD9/ 3.5m	FSD9/ 8.6m	FSD9/ 24.7m	FSD9/ 27.7m	FSD9/ 28.7m	FSD11/ 4.8m	FSD11/ 5.7m	FSD11/ 7.1m	FSD11/ 10.5m	FSD11/ 12.4m	FSD11/ 13.4m	FSD11/ 20.4m	FSD11/ 25.7m	FSD11/ 26.7m	FSD11/ 28.3m
Ore Type ppm	SO	SO	SO	SO	SO	SO	SO	SO	SO	SO	SO	SO	SO	SO	SO	SO	SO	SO
La	3.20	5.14	3.57	2.62	2.75	6.49	5.13	3.18	2.02	2.59	3.23	4.18	1.34	2.25	4.64	2.02	1.64	1.81
Ce	6.89	9.46	6.88	4.50	5.12	12.89	9.66	5.88	3.17	3.89	5.37	7.17	2.54	3.66	7.80	3.67	3.07	3.21
Pr	1.10	1.68	1.16	0.59	0.63	1.84	1.51	1.00	0.56	0.70	0.74	0.88	0.36	0.53	1.19	0.57	0.44	0.45
Nd	5.10	7.96	5.58	2.54	2.54	7.85	6.66	4.56	2.65	3.12	3.31	3.72	1.65	2.43	5.33	2.65	1.82	2.12
Sm	1.19	1.90	1.35	0.49	0.53	1.76	1.50	0.99	0.61	0.65	0.64	0.73	0.38	0.50	1.02	0.64	0.43	0.46
Eu	0.50	0.82	0.59	0.20	0.21	0.65	0.55	0.38	0.25	0.30	0.28	0.29	0.16	0.22	0.50	0.26	0.20	0.23
Gd	1.54	2.56	1.85	0.62	0.63	2.13	1.74	1.19	0.95	0.87	0.79	0.84	0.55	0.61	1.35	1.00	0.53	0.67
Tb	0.27	0.48	0.36	0.12	0.12	0.40	0.33	0.21	0.16	0.17	0.15	0.15	0.10	0.12	0.27	0.17	0.11	0.13
Dy	1.75	3.24	2.43	0.83	0.76	2.60	2.18	1.37	1.04	1.23	1.02	1.03	0.64	0.90	1.92	1.21	0.73	0.98
Y	20.66	37.65	30.79	13.33	9.13	31.67	26.35	17.72	10.30	15.90	11.01	12.41	6.70	9.78	26.11	18.00	12.80	15.02
Ho	0.39	0.73	0.57	0.20	0.17	0.56	0.49	0.30	0.25	0.29	0.23	0.24	0.16	0.21	0.47	0.32	0.17	0.24
Er	1.27	2.27	1.84	0.66	0.54	1.72	1.56	0.89	0.81	0.94	0.76	0.77	0.55	0.72	1.59	1.14	0.60	0.84
Tm	0.20	0.36	0.30	0.11	0.09	0.27	0.25	0.13	0.12	0.15	0.12	0.12	0.10	0.12	0.26	0.19	0.10	0.14
Yb	1.32	2.36	1.95	0.71	0.58	1.71	1.63	0.83	0.80	1.07	0.82	0.83	0.62	0.82	1.79	1.18	0.64	0.94
Lu	0.20	0.37	0.31	0.11	0.10	0.28	0.26	0.13	0.13	0.18	0.13	0.13	0.09	0.14	0.29	0.19	0.10	0.16
ΣREE	24.94	39.33	28.74	14.30	14.74	41.14	33.46	21.03	13.52	16.15	17.59	21.08	9.26	13.25	28.41	15.21	10.60	12.38
La/Yb _{PAAS}	0.18	0.16	0.14	0.27	0.35	0.28	0.23	0.28	0.19	0.18	0.29	0.37	0.16	0.20	0.19	0.13	0.19	0.14
La/Sm _{PAAS}	0.39	0.39	0.39	0.78	0.76	0.53	0.50	0.46	0.48	0.58	0.73	0.83	0.51	0.65	0.66	0.46	0.55	0.58
Dy/Yb _{PAAS}	0.80	0.83	0.75	0.71	0.79	0.91	0.81	1.00	0.20	0.69	0.75	0.74	0.76	0.66	0.65	0.62	0.69	0.63
Ce/Ce* _{PAAS}	0.85	0.74	0.78	0.83	0.90	0.86	0.80	0.76	0.68	0.67	0.80	0.86	0.84	0.77	0.77	0.79	0.84	0.82
Eu/Eu* _{PAAS}	1.74	1.76	1.77	1.73	1.70	1.59	1.61	1.65	1.53	1.91	1.85	1.72	1.61	1.87	2.00	1.54	1.96	1.98
Y/Y* _{PAAS}	1.99	1.95	2.09	2.62	2.05	2.09	2.03	2.22	1.60	2.14	1.80	2.00	1.64	1.78	2.20	2.30	2.85	2.45

HO = hard ore; SO = Soft ore; MB = Massive band of the soft ore; PB = Porous band. Y content is not included in ΣREE. $Eu/Eu^*_{PAAS} = ((Eu/Eu_{PAAS}) / (Sm/Sm_{PAAS}) * (Gd/Gd_{PAAS}))^{1/2}$,
 Ce/Ce*_{PAAS} and Y/Y*_{PAAS} calculated by similar way.

Appendix 3 (Continued)

	MAC14A	MAC59H	MAC126A	MAC127A	MAC128A	MAC129A	MAC3A	MAC14B	MAC59I	MAC107	MAC126B	MAC127B	MAC128B	MAC129B
SAMPLE														
Ore Type	MB	MB	MB	MB	MB	MB	PB	PB	PB	PB	PB	PB	PB	PB
ppm														
La	1.16	0.86	0.79	0.55	0.73	1.02	20.23	4.54	2.02	6.66	4.31	5.35	4.29	5.79
Ce	2.18	1.44	1.60	1.04	1.42	1.79	42.46	7.35	3.95	13.00	7.43	8.19	5.35	7.89
Pr	0.34	0.19	0.18	0.15	0.13	0.23	4.49	1.23	0.55	2.09	1.25	1.42	1.06	1.49
Nd	1.39	0.75	0.81	0.76	0.58	1.05	18.06	5.31	2.41	9.15	5.98	6.30	4.59	6.99
Sm	0.33	0.20	0.17	0.17	0.11	0.25	3.97	1.19	0.59	2.33	1.55	1.44	1.00	1.68
Eu	0.13	0.06	0.07	0.06	0.05	0.08	1.90	0.53	0.26	0.79	0.60	0.61	0.45	0.77
Gd	0.48	0.23	0.23	0.24	0.15	0.32	5.13	1.82	0.94	3.46	2.33	2.23	1.65	2.90
Tb	0.07	0.04	0.04	0.04	0.03	0.06	0.96	0.30	0.16	0.69	0.39	0.39	0.29	0.48
Dy	0.47	0.25	0.28	0.22	0.19	0.37	6.45	2.02	1.06	4.85	2.43	2.67	2.07	3.28
Y	6.00	2.00	2.60	2.00	2.20	3.80	56.00	27.10	13.90	22.70	27.20	40.60	28.10	45.20
Ho	0.11	0.05	0.07	0.05	0.05	0.10	1.46	0.50	0.27	1.14	0.61	0.73	0.56	0.86
Er	0.38	0.17	0.24	0.15	0.18	0.30	4.80	1.69	0.89	3.69	1.98	2.55	1.87	2.80
Tm	0.06	0.03	0.04	0.02	0.03	0.04	0.79	0.28	0.15	0.57	0.32	0.42	0.30	0.43
Yb	0.40	0.18	0.27	0.13	0.19	0.27	5.31	1.92	0.99	3.46	1.97	2.66	1.87	2.54
Lu	0.07	0.03	0.04	0.02	0.03	0.04	0.89	0.33	0.17	0.61	0.31	0.43	0.29	0.40
ΣREE	7.57	4.47	4.82	3.59	3.87	5.91	116.88	29.01	14.41	53.48	31.46	35.39	25.64	38.28
La/Yb _{PAAS}	0.21	0.36	0.21	0.32	0.29	0.28	0.28	0.17	0.15	0.14	0.16	0.15	0.17	0.17
La/Sm _{PAAS}	0.52	0.63	0.67	0.48	0.94	0.60	0.74	0.55	0.49	0.41	0.40	0.54	0.62	0.50
Dy/Yb _{PAAS}	0.71	0.84	0.63	1.05	0.62	0.84	0.73	0.63	0.64	0.84	0.74	0.61	0.67	0.78
Ce/Ce* _{PAAS}	0.80	0.83	0.98	0.84	1.04	0.85	1.03	0.72	0.86	0.80	0.74	0.69	0.58	0.62
Eu/Eu* _{PAAS}	1.53	1.41	1.58	1.45	1.67	1.35	1.98	1.70	1.65	1.31	1.49	1.61	1.64	1.65
Y/Y* _{PAAS}	2.09	1.41	1.50	1.50	1.73	1.59	1.46	2.15	2.08	0.77	1.79	2.32	2.09	2.15

HO = hard ore; SO = Soft ore; MB = Massive band of the soft ore; PB = Porous band. Y content is not included in ΣREE. $Eu/Eu^*_{PAAS} = ((Eu/Eu_{PAAS}) / (Sm/Sm_{PAAS}) * (Gd/Gd_{PAAS}))^{1/2}$,
 Ce/Ce*_{PAAS} and Y/Y*_{PAAS} calculated by similar way.

ANEXO 4 – $^{40}\text{Ar}/^{39}\text{Ar}$ GEOCHRONOLOGY AND THE EVOLUTION OF LATERITIC IRON DEPOSITS IN THE QUADRILÁTERO FERRÍFERO, MINAS GERAIS, BRAZIL

Abstract

Weathering profiles overlying the Sapecado, Pico and Andaime iron ore deposits, Quadrilátero Ferrífero (QF), Minas Gerais, Brazil, reach depths of 150-400 m and host world-class supergene iron orebodies. In addition to hematite, goethite, and some relic quartz, the deeply weathered itabirites (metamorphosed banded iron formation) contain supergene cryptomelane, hollandite, and pyrolusite. These manganese oxides are preferentially concentrated at the contact between weathered Cauê Formation itabirites and adjacent dolomites of the Gandarela Formation, and their distribution provides information on the propagation of the weathering front as the supergene ore bodies formed.

Laser incremental-heating $^{40}\text{Ar}/^{39}\text{Ar}$ results for 69 grains extracted from 23 samples collected at depths ranging from 5 to 150 m reveal ages ranging from ca. 62 to 14 Ma. Older Mn-oxides occur near the surface, while younger Mn-oxides occur at depth. However, many samples collected at the weathering-bedrock interface yield ages in the 51-41 Ma range, suggesting that the weathering profiles in the Quadrilátero Ferrífero had already reached their present depth in the Paleogene. The age versus depth distribution obtained in this study suggests that little further advance of the weathering front has occurred in the Quadrilátero Ferrífero lateritic profiles during the Neogene.

INTRODUCTION

The Quadrilátero Ferrífero (literally, the Iron Quadrangle), Minas Gerais (Fig. 1), hosts one of the largest concentrations of lateritic iron ore deposits on Earth. It also hosts the most complete and well-developed weathering profiles in southeastern Brazil, reaching depths of 400 – 500 m, and averaging 150 m. These weathering profiles are developed on Paleoproterozoic Minas Supergroup rocks which outcrop along plateaus and ridges with heights ranging from 1.100 to 2.100 m elevation, surrounded by dissected areas, where Archean granite-gneiss basement units and the Rio das Velhas Greenstone Belt are exposed (Fig. 2).

Figure 1. Location and geological sketch map of the Quadrilátero Ferrífero region (After Alkmim and Marshak, 1998).

The QF weathering profiles have great economic significance because they host world-class supergene iron ore deposits as well as economically important manganese, bauxite, and industrial clay deposits. They also have significant geomorphologic and paleoclimatic implications because of the extreme depths and antiquity of weathering processes recorded in these profiles (Carmo and Vasconcelos, 2004; Carmo and Vasconcelos, 2003; Dorr II, 1969; King, 1956). Despite their importance, several questions regarding the genesis of QF weathering profiles remain unanswered: How did they form? How long did it take? When did it start? Under what climatic conditions did these weathering profiles evolve? Why are they preserved? Are they still forming today? Answers to these questions have many implications to our understanding of surficial processes in general and in quantifying the genesis of supergene ore deposits in particular.

1=Serra da Moeda, 2=Serra das Serrinhas, 3=Serra do Ouro Branco, 4=Serra do Caraça, 5 e 6= vale do rio das Velhas

Figure 2. Digital elevation model for the Quadrilátero Ferrífero region (a) illustrating location of weathering profiles investigated in this study (b). (c) SW-NE topographic profile from the Serra da Moeda (MO) to the Sapecado mine (SAP) at the Serra das Serrinhas.

Active mining operations in the Quadrilátero Ferrífero provide a unique opportunity to answer some of these questions. Open pits and drill cores permit sampling complete weathering profiles. Extensive mining exposures and several thousands of meters of drill-cores maximize the chances of obtaining suitable samples for geochemical and geochronological studies. Abundant Mn-oxides in some of these profiles, particularly the supergene ore bodies formed on

manganiferous itabirites at the Sapecado and Andaime MBR mines (Figs. 1-2), provide suitable samples for $^{40}\text{Ar}/^{39}\text{Ar}$ dating. $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology permits dating of K-bearing manganese oxides formed at different depths in the weathering profiles and therein allows to measure the rate of propagation of the weathering front and the timing of formation of the profiles (Vasconcelos, 1999a; Vasconcelos et al., 1994b).

The laser incremental-heating $^{40}\text{Ar}/^{39}\text{Ar}$ method has been used to date supergene hollandite-group minerals from weathering profiles across the world (Dammer et al., 1996; Dammer et al., 1999; Hénocque et al., 1998b; Li and Vasconcelos, 2002; Ruffet et al., 1996b; Vasconcelos, 1992; Vasconcelos et al., 1992; Vasconcelos et al., 1994a) providing a useful tool in the study of weathering processes. Hollandite-group Mn-oxides are suitable to $^{40}\text{Ar}/^{39}\text{Ar}$ dating due to their relatively high K contents (1-5 wt%) and their K and ^{40}Ar retentivity. These hollandite-group minerals generally form clusters of oriented crystallites (10-20 μm long and 1-2 μm wide) (Vasconcelos et al., 1994c). These clusters have a large volume of intercrystalline space that may absorb and adsorb large quantities of atmospheric ^{40}Ar (Vasconcelos et al., 1995). On the other hand, hollandite-type crystallites form tunnel structures that favors the imprisonment of large cations like K, Ba, and Pb. These tunnel sites quantitatively retain ^{40}Ar produced by ^{40}K decay (Vasconcelos et al., 1995). Incremental-heating analyses of Mn-oxide clusters liberate atmospheric argon adsorbed or trapped in intercrystalline or damaged intracrystalline sites at low temperature heating steps; radiogenic $^{40}\text{Ar}^*$ and nucleogenic ^{39}Ar hosted in the intracrystalline tunnel sites are only liberated at higher temperatures steps. The ability to tap each argon reservoir separately permits determining accurate and precise ages for these minerals, in addition to retrieving useful information on a sample's Ar and K retentivity, the physical properties of the sites where these elements occur, the possible presence of contaminants, and any significant ^{39}Ar recoil losses the mineral may undergo during irradiation (Vasconcelos, 1999b).

We will present below the results of $^{40}\text{Ar}/^{39}\text{Ar}$ dating of 69 grains extracted from 23 samples of Mn-oxides distributed from ~5 m to ~150 m below the present surface in two distinct QF weathering profiles. We will discuss the reliability of the results obtained in light of informations obtained by petrographic observations and scanning electron microscopy (SEM), x-ray diffractometry (XRD), and electron microprobe (EMP) analyses. We will finally discuss the significance of the geochronological results to the formation of the weathering profiles in the QF region, in particular, and the genesis of the supergene iron ore bodies, in general.

GEOLOGICAL SETTING

Regional Geology

The geology and the lithostratigraphy of the QF were described in detail by the USGS-DNPM team between 1946 and 1963, and summarized by Dorr II (1969). Since then, the subject has been reviewed by several authors (Alkmim and Marshak, 1998; Chemale Jr. et al., 1994; Ladeira and Viveiros, 1984; Marshak and Alkmim, 1989; Renger et al., 1994). The most important lithostratigraphic units of the Quadrilátero Ferrífero (Fig. 1) are Archean to Paleoproterozoic granitic-gneissic basement, Archean greenstone belt sequences (Rio das Velhas Supergroup), the Paleoproterozoic Minas Supergroup and post-Minas intrusive rocks.

The giant iron ore deposits of the Quadrilátero Ferrífero are hosted in itabirites of the Minas Supergroup, which consist of three Paleoproterozoic sequences (Babinski et al., 1995; Noce, 1995; Renger et al., 1994). The lowest unit is the Caraça Group, which consists of alluvial conglomerates and sandstones grading upwards into shallow-water marine siltstones and mudstones. The intermediate Itabira Group consists mainly of chemical sedimentary rocks. A metamorphosed banded iron formation (itabirite) unit of variable composition occurs at the base of the Itabira Group and, together with hematitic and dolomitic phyllites, marbles and dolomites, constitutes the Cauê Formation. The original stratigraphic thickness of the iron formation may have been in the order of 250-300 m, but it now ranges in apparent thickness from a few meters to more than 1,400 m, owing to tectonic rock flowage (Dorr II, 1964). The Cauê Formation grades upward into dolomites and dolomitic/manganiferous itabirites of the 2.4 Ga Gandarela Formation (Babinski et al., 1995). Clastic sediments (with subordinate dolomites) of the Piracicaba Group overlie the Itabira Group. The uppermost sequence of the Minas Supergroup is the Sabará Group, a sequence of metamorphosed volcanoclastic sediments, turbidites, BIFs (banded iron formations), and conglomerates (Renger et al., 1994) dated as Transamazonian (2.1 – 1.7 Ga.).

Deep weathering of the Itabira Group BIFs, postulated to have occurred during the Mesocenozoic, produced the large supergene iron orebodies spread throughout the QF (Dorr, 1969). A total of 29 Gtons of iron ore, mined continuously since the beginning of the 40's and having produced more than 3 Gtons of high-grade iron ore, are estimated to occur in the region (TEX Report, 2002; Walde, 1986; Wallace, 1965). Total production in 2000 in the QF region was 115 Mtons and is estimated for 2004 at 160 Mtons (TEX Report, 2002). Most of the deep weathering profiles in the region are complete stratified weathering profiles, exhibiting an

indurated cap (canga) overlying absolute and relative enriched supergene iron ores, which immediately overlie saprolitic horizons.

Geomorphologically, the Quadrilátero Ferrífero (literally the iron quadrangle) consists of a roughly square 7000 km² region (Fig. 2a) characterized by various plateaus, ranging in height from 1100 to 2100 m elevation, surrounded by dissected plains at ca. 500-600 m elevation. The quadrangle is delimited by steeply dipping BIFs and quartzites that constitute elevated and highly resistant barriers to erosion and scarp retreat driven by the creeks and streams draining into the plateau. The western limit of the QF is the Serra da Moeda, its northern limit the Serra do Curral, the eastern limit the Serra do Caraça, and the southern limit the Serra do Ouro Branco (Figs. 1 and 2). The core of the Quadrangle is drained by the north-flowing Rio das Velhas, creating a dissected window into the Archean Bação Complex (Fig. 2a). This inner depression is surrounded by several deeply weathered plateaus developed on BIFs and quartzites. The eastern section of the QF hosts a 700 km² plateau, the Moeda Syncline, delimited by the Serras da Moeda (W), Serra do Curral (N), Serra das Serrinhas (E), and Serra do Ouro Branco (S) (Fig. 2a). This plateau hosts several important supergene ore bodies, included the Sapecado and Andaime deposits, located in the Serra das Serrinhas, investigated in this study (Fig. 2b). Weathering profiles along the Serra da Moeda were investigated in an associated study (Carmo and Vasconcelos, 2003).

The QF plateaus have been interpreted as remnants of an ancient erosion surface developed before the Africa-South America break-up (the Gondwana Surface of King (1956)). Weathering profiles on the plateaus are consistently deeper (up to 400 m) and more developed than weathering profiles on surrounding plains and dissected valleys (< 100 m). Landsurfaces on the plateaus are also distinct from the surrounding plains because they are blanketed by strongly iron-hydroxide cemented covers (cangas), which impart a smooth character to the plateau landsurfaces. When the cangas are breached by recent erosion, they form sharp scarps (Fig. 2c), another distinctive characteristic of this landscape. Finally, internal basins on the plateaus (e.g., Bacias do Fonseca and Gandarela), filled with argillite, lignite, sandstone, diamictite, and kaolinitic sediments now partially weathered to bauxite, are associated with collapse structures (karstic lakes) formed during weathering of underlying banded iron formations (Ribeiro, 2003) or with extensional tectonic activity during the Paleogene (Maizatto, 2001; Sant'Anna et al., 1997). We chose to study the weathering history of two supergene iron ore deposits in the Moeda Syncline because of the likelihood that these supergene systems host the most complete information about the weathering history of the Quadrilátero Ferrífero and of the hypothesized

Gondwana landsurface of King (1956). We also chose to study these profiles because the intimate relationship between supergene iron ore and datable supergene Mn-oxides permits relating the timing of Mn-oxide precipitation with the evolution of the chemical reactions leading to the formation of supergene enriched iron orebodies in the region.

Local Geology

Three adjacent iron mines (Sapecado, Pico, and Andaime), located along the Serra das Serrinhas on the eastern margin of the Moeda Syncline (Figs. 1-2), provide access to deeply weathered and supergene enriched BIFs. Weathering profiles at these mines vary from a few meters to ca. 200 m below the present surface (Fig. 3a-c). This large variation in weathering profile depth results on an interlayering of unweathered itabirites with deeply weathered itabirites and soft-hematite ores. Spier et al. (2003) provides detailed characterizations of the iron ores and their hosts rocks in these deposits. In this study, we dated samples from the Sapecado and Andaime weathering profiles, briefly described below.

The Sapecado orebody represents the southern extension of the Pico orebody. It is composed of lenses of unindurated and indurated iron ores interlayered with relatively weathered quartz itabirite. The geological resources of the Sapecado orebody are of 400 Mtons (MBR, internal report). The major geological units present at the Sapecado mine are itabirites and iron ores of the Cauê Formation, clastic metasedimentary rocks of the Moeda and Batatal Formations, and predominantly chemical metasedimentary rocks of the Gandarela Formation (Fig. 3b-c). The rocks are oriented along a general strike N30°-35°E, dipping 45°-90° to SE or NW. The quartzites of the Moeda Formation crop out continuously along the eastern edge of the mine and show a very consistent sub-vertical dip and, in general, weakly developed foliation. The quartzites exhibit abrupt contacts with the overlying phyllites of the Batatal Formation. The uppermost Gandarela Formation crops out at the pit's western wall. It consists of dolomitic phyllite and deeply weathered dolomite with a gradual contact with the itabirites. The main banded iron formation at the Sapecado mine is the quartz itabirite, the protore of the iron ore bodies. This quartz itabirite is a typical metamorphosed BIF and consists of alternate microbands of quartz with martite and hematite. Total or partial leaching of quartz during weathering promoted the residual enrichment of iron, generating the soft iron ores (Spier et al., 2003). Soft ores are highly porous and consist of microbands of aggregates of martite and hematite still cemented together with highly porous bands where martite and hematite grains fill

Figure 3. Studied geological sections showing distribution of weathering profile. (a) Andaime Deposit. (b-c) Sapecado Mine.

cavities generated by the removal of large quantities of primary quartz and carbonate. Some remnant quartz, highly etched and corroded, may occur in varied proportions.

The Andaime orebody is located 10 km North of the Pico mine (Fig. 1), representing the northern continuity of the iron mineralization. The rocks of the Minas Supergroup at this region are oriented along strike N10°-30°W, dipping 40°-80° to NE. The exploration of the Andaime orebody started in 2004 and its geological resources, still under evaluation, are ca. 100 Mtons (MBR, internal report). The orebody consists of soft quartz itabirite which occurs within the weathering profile, along the strike of the siliceous banded iron formation. Lenses of manganiferous itabirite are interlayered with the iron ore.

Manganiferous itabirite is a particular type of soft iron ore that generally occurs at the top of the Cauê Formation, at the contact with the Gandarela Formation (Fig. 3a-b) in all three – Pico, Sapecado, and Andaime – mines. It consists of irregularly distributed lenses varying from decimeters to 20 m width, 5 – 100 m length, with depths varying from a few meters to 150 m. The lenses occur parallel to the itabirite units, interbedded with them (Figs. 3a-b and 4a). The manganiferous itabirite contains on average 48 wt% (11 wt% -63 wt%) Fe and 6 wt% (3 wt% - 14 wt%) Mn. Rarely the Mn content exceeds 15 wt%. In this case, the ore is called Fe-Mn ore. Manganese oxides in the manganiferous itabirite are irregularly distributed. They generally cement the walls of pores in the soft iron ores or form cm-size botryoidal bands precipitated in cavities and cracks (Fig. 4b).

Figure 4. (a) Drill hole of the Andaime Deposit showing manganiferous itabirite between limomitic itabirite. (b) Detail of the manganiferous itabirite showing concretion formed by cryptomelane (c) and pyrolusite (p).

The Pico, Andaime, and Sapecado orebodies are capped by small basins filled with argillites and siltstones. These type of basins, associated with karstic depressions created by the collapse of the BIF after leaching of silica and carbonate minerals during weathering (Ribeiro, 2003; Ribeiro and Carvalho, 2002), were dated as Paleocene to Eocene based on pollen assemblages (Lima and Salard-Chebouldaef, 1981; Maizatto, 2001).

SAMPLING AND ANALYTICAL PROCEDURE

The visual identification of black Mn-oxides dispersed throughout dark hematite ores is a major challenge. To overcome this sampling difficulty, we focused our search for datable supergene Mn-oxides on drill cores previously analyzed for Mn. Sections with high Mn contents, where manganiferous itabirite and Fe-Mn ore occur, were carefully examined with a hand lens and any suitable occurrence of datable Mn-oxide sampled. Datable Mn-oxides, hollandite-group minerals, are easily recognizable based on their superior hardness (> 6), a steel-blue metallic luster, and a botryoidal texture. Section 6300E of the Sapecado mine was chosen for detailed sampling due to the presence of a prominent manganiferous itabirite unit, which forms a continuous lens from the surface down to ~ 150 m (Fig. 3b). We sampled each meter of manganiferous itabirite that contained suitable Mn-oxide minerals. The samples selected are supposed to represent a time-stratigraphic sequence from the oldest samples at the near surface environment to the youngest sample at the base of the weathering profile (fresh rock-weathering interface).

Complementary sampling at Sections 4700E and 3500E, at the Sapecado and Andaime mines, respectively (Figs. 2-3), provide information on weathering age variation along strike. At Section 4700E (Sapecado), we sampled Mn-minerals that occur along fracture planes of deeply weathered dolomites of the Gandarela Formation (Fig. 3c); at Section 3500E (Andaime), we sampled manganiferous itabirite (Fig. 3a).

Sample preparation followed the method detailed by Vasconcelos (1999b) and Vasconcelos et al. (2002). Samples were crushed to 0.5 - 2 mm, ultrasonically cleaned in distilled water and absolute ethanol, and dried under a heat lamp. The clean sample fragments were examined under a binocular microscope, and six to eight visually homogeneous grains were hand-picked and loaded into aluminum disks for neutron irradiation. The samples were irradiated for 14 hours, along with the Fish Canyon Sanidine standard (28.02 ± 0.28 Ma), in the Triga reactor at the B-1 CLICIT Facility, Radiation Centre, Oregon State University Reactor, Oregon,

USA. After a cooling-off period of three weeks, three grains from each sample were loaded into a 145-pit copper disk, baked at 180 °C for 13 hours, and incrementally heated by a continuous 10 W Ar-ion laser with a defocused beam at the UQ-AGES laboratory, Australia. Gases released during incremental-heating were cleaned by a cryocooled trap ($T = -130$ °C) and two C-50 SAES Zr-V-Fe getter pumps, and the clean gas fraction expanded into a MAP-215-50 mass spectrometer. Air pipettes and blanks were run before and after each sample to correct for background and mass discrimination. Air pipettes, blanks, and unknowns were analyzed by the peak hopping method, 8-10 cycles were measured for each isotope, and 7 measurements of ^{40}Ar , ^{39}Ar , ^{38}Ar and ^{37}Ar and 25 measurements of ^{36}Ar were made at each peak top. Isotope evolution was fitted with either parabolic or linear fits. Typical blank values and air pipette $^{40}\text{Ar}/^{36}\text{Ar}$ ratios are reported in Appendix 1. The neutron flux for each sample was estimated from J-factors (Appendix 1) calculated for each disk from the analyses of a minimum of 15 grains of FC sanidine standard placed in the disk following the geometry illustrated in Vasconcelos et al. (2002). All ages are reported using the constants of Steiger and Jäger (1977). Corrections for interfering isotopes generated during irradiation are as follows: $(2.64 \pm 0.62) \times 10^{-4}$ for $(^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$, $(7.04 \pm 0.06) \times 10^{-4}$ for $(^{39}\text{Ar}/^{37}\text{Ar})_{\text{Ca}}$, and $(8 \pm 3) \times 10^{-4}$ for $(^{40}\text{Ar}/^{39}\text{Ar})_{\text{K}}$. Data corrected for blanks, mass discrimination, nucleogenic interferences, and atmospheric contamination were used to calculate apparent ages for each degassing step and are reported on Appendix 1.

From the same batch of grains used for isotope analyses, additional aliquots of 3-5 grains were mounted in an epoxy container and polished for petrographic, SEM and EMP analyses. The SEM and EMP analyses were carried out at the Centre for Microscopy and Microanalyses at the University of Queensland, Australia. A JEOL JXA 8800L Superprobe, operating at 15 kV and 15 nA current and with 0.5 μm probe diameter, was used for EMP analyses. Oxygen was analyzed as unknown and the following standards were used: MnO (Mn and O), Cl-apatite (P), CoO (Co), TiO_2 (Ti), PbS (Pb), Al_2O_3 (Al), Fe_2SiO_4 (Fe, Si), ZnO (Zn), CaSO_4 (Ca), BaSO_4 (Ba), $\text{NaAlSi}_3\text{O}_8$ (Na) and KAlSi_3O_8 (K). Approximately 450 spots were analyzed on ~ 60 samples. Whenever possible, microprobe analyses were pre-programmed perpendicularly to the growth bands to investigate possible variations in Mn-oxide compositions during mineral precipitation.

RESULTS AND DISCUSSION

Mineralogy and Petrography

Reflected-light microscopy and SEM investigation show that cryptomelane, pyrolusite and hollandite are the main Mn-oxides present. These minerals occur cementing pore spaces in the iron ore or form mm-size growth bands (Fig. 5a-d). Minor Al-enrichment generally occurs at the contact between Mn-oxides and the hosting iron ore. Pure lithiophorite was not detected in any of the grains analyzed. Most Mn-oxides are mineralogically complex (Fig. 5d-g). Hematite (either as martite or tabular hematite) inclusions are common within Mn-oxide grains, particularly at the contact of void-filling concretions with the iron ore (Fig. 5a). Goethite and gibbsite bands alternate with Mn-oxides in some botryoidal samples (Fig. 5h).

Manganese oxide textures are also variable. When cementing pores in the iron ore, hollandite-group Mn-oxides are generally very pure, cryptocrystalline, and characterized by botryoidal textures composed of micrometric growth bands (Fig. 5b-d). Individual microbands display uniform grain size and mineralogical composition. Cryptomelane crystals in microbands occur as 10-20 micron needle-like crystals, with 10:1 aspect ratio, and oriented perpendicularly to the growth bands (Fig. 5e). When pyrolusite is present, coarse aggregates of 0.01 – 0.20 mm grains occur. Pyrolusite may also occur as radiating prismatic crystals aligned perpendicularly to the growth bands, and it is often partially replaced by hollandite-group phases (Fig. 5f-g). Desiccation cracks are often observed in pyrolusite crystals (Fig. 5f-g).

Textural relationships and mineralogy of the samples indicate that Mn-oxides were directly precipitated from weathering solutions. Paragenetic relations among Mn minerals were difficult to assess. Generally, cryptomelane and hollandite are older than pyrolusite (Fig. 5c), but this is not always the case. Multiple generations of Mn-oxides, indicated by banded and colloform textures, systems of intersecting veinlets, and mutual replacements, are observed (Fig. 6a-h). The small size of the Mn-oxide growth bands (less than 20 μm in average) does not allow for the selection of fragments from a single generation. In addition, many grains selected for geochronology may contain minor supergene pyrolusite, goethite, or gibbsite inclusions. Some grains also contain martite-hematite inclusions, which may cause further complications during dating (see discussion below). Petrographic and SEM examinations, however, clearly show the absence of any hypogene K silicate in the samples submitted to $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology.

Figure 5. Reflected-light photomicrographs of Mn-oxides from the Sapecado and Andaime profiles showing textural relationships and mineralogy of the Mn-oxides investigated. (a) Cryptomelane (c) filling voids between hematite crystals (h), and forming a thin layer. (b) Botryoidal texture formed by alternated layers of cryptomelane and voids (v). Pyrolusite (p) occurs in the center of the concretion. (c) Mn-concretion formed by layers of cryptomelane and pyrolusite. Hematite and goethite (g) occur in the center of the concretion. (d) Several layers of cryptomelane showing variation on the size of the crystals with crystallization. (e) Detail of a coarse layer showing needle shape crystals between voids. (f-g) Several generations of pyrolusite. (h) Botryoidal texture showing alternation between pyrolusite and goethite.

Figure 6. Backscattered electron micrograph showing several generations of Mn-oxides. (a) Layering of cryptomelane (c), hollandite (ho), cryptomelane and pyrolusite (p). Hematite (h) occurs in the external layer. Note the thin vein of cryptomelane cutting the layering. (b) Thin veins of hollandite and pyrolusite cutting two generations of pyrolusite. (c) Veins of pyrolusite cutting cryptomelane. (d-f) Several generations of cryptomelane, hollandite and pyrolusite. Goethite (g) occurs subordinately. (g) Two generations of pyrolusite. (h) Concentric layers of pyrolusite forming a botryoidal texture.

Electron microprobe analysis

Electron microprobe analyses for 448 spots in 60 grains of Mn-oxides show that weathering solutions from which they precipitated were rich in Mn, Al, Fe, K and Ba (Fig. 7), consistent with cryptomelane, hollandite, and pyrolusite stoichiometries (Table 1). Total Mn contents vary from 48 – 63 wt% (Fig. 8a). Variation on Mn concentrations reflects distinct mineralogy and variation in tunnel cation occupancy (Ba, K, etc.). When the contents of K and Ba were under 0.5% the mineral was called pyrolusite. Figure 8b shows that the potassium concentrations reach 3.9 wt% in cryptomelane (average of 2 wt%).

Figure 7. Ternary plots showing the major chemical composition of the Mn-oxides from the Sapecado and Andaime deposits. Note the complete exchanges between Al, Fe, K and Ba.

Table 1. Average composition of the Mn-oxides

	Cryptomelane (n=253)	Hollandite (n=131)	Pyrolusite (n=64)
O	34.75	33.66	34.45
Mn	58.37	53.65	61.08
K	1.99	1.22	0.08
Ca	0.12	0.10	0.05
Pb	0.02	-	0.02
P	0.07	0.15	0.11
Ba	0.47	5.11	0.12
Fe	0.27	0.70	0.32
Co	0.08	0.05	0.02
Zn	0.05	0.01	0.03
Ti	0.01	-	-
Na	0.10	0.04	0.01
Al	0.51	1.37	0.22
Si	0.04	0.10	0.08

Elements with (-) were not detected

Figure 8. Histograms of the Mn and K contents of 60 Mn-oxide grains by ca. 448 spot EMP analyses.

Manganese Oxide Paragenesis

Field and petrographic observations indicate that Mn-oxides sampled in this study formed during chemical weathering of the dolomite-bearing itabirite of the Cauê Formation and the dolomite of the Gandarela Formation. Manganese and iron are present as minor elements in the dolomite. Manganese and iron are also common in carbonate cements associated with the diagenetic or hydrothermal alteration of the BIFs. Mn^{+2} and Fe^{+2} are released into the weathering solutions during the dissolution of the Mn-bearing carbonates. As long as the weathering solutions remain relatively reducing and neutral to acidic, Mn^{+2} stays in solution. If the Mn^{+2} -bearing solutions encounter descending oxygenated meteoric solutions along permeable horizons and fault planes, Mn^{+2} readily oxidizes and precipitates as Mn^{+4} -oxides and -hydroxides (pyrolusite, ramsdellite, manganite). Alternatively, when Mn^{+2} -bearing weathering solutions encounter strongly alkaline conditions, which often occurs at the contact between the BIF and the host carbonates of the Gandarela Formation, Mn^{+2} may also readily oxidize and precipitate as Mn^{+4} oxides/hydroxides. If, in addition to Mn^{+2} , the weathering solutions also contain dissolved K^{+1} , Ba^{+2} , or other cations, complex tunnel structure manganese oxides (romanéchite, hollandite, cryptomelane, todorokite) may form. The processes above account for the common occurrence of Mn-oxides along faults and along the contact between the BIF and the adjacent carbonate rocks. Manganese oxide paragenesis in the supergene iron orebodies suggests an intimate association of the oxides with the weathering of the banded iron formations. This, in turn, assures that geochronological analyses of the Mn-oxides provide information on the weathering history of the BIFs.

$^{40}\text{Ar}/^{39}\text{Ar}$ Geochronological Analysis

Laser-heating $^{40}\text{Ar}/^{39}\text{Ar}$ dating of 69 grains extracted from 23 samples of Mn-oxides yields the results summarized in Table 2 and illustrated in Fig. 9. Complete results, corrected for interfering isotopes and mass discrimination, are listed in Appendix 1.

The incremental heating spectra in Fig. 9 reveals that 31 grains yield plateau ages, where plateaus are defined by 2 or more contiguous steps yielding $\geq 50\%$ of the total ^{39}Ar gas released for the sample whose apparent age values are within 2σ from the mean value. Plateau ages are interpreted to represent the age of precipitation of the grains analyzed (Vasconcelos, 1999a). Twenty-one grains do not yield plateaus according to the definition above, but these grains yield flat segments, containing $\geq 50\%$ of total ^{39}Ar released, that define “plateau-like” ages. Ages for

Table 2. Summary of the $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology data of the 23 samples analyzed in this study. The uncertainties are given at the 2σ level

Sample	Location		Elevation (m)	Grain ID	Age (Ma)
	Drill Hole	Depth (m)			
S1	SAP 25/01	45.00	1399.31	2665-1	61.3 ± 1.7
				2665-2	$61.5 \pm 1.2^*$
				2665-3	$61.0 \pm 5.0^*$
S2	SAP 17/01	22.60	1380.93	2649-1	48.6 ± 0.9
				2649-2	$52.0 \pm 0.8^*$
				2649-3	48.8 ± 0.8
S3	SAP 17/02	24.60	1379.20	2650-1	$56.4 \pm 1.7^*$
				2650-2	58.0 ± 0.3
S4	SAP 17/01	25.60	1378.33	2652-1	$50.7 \pm 0.5^*$
				2652-2	$51.6 \pm 0.5^*$
				2652-3	$48.9 \pm 1.6^*$
S5	SAP 17/01	26.60	1377.46	2653-1	$52.9 \pm 0.7^*$
				2653-2	54.1 ± 0.4
				2653-3	53.0 ± 0.5
S6	SAP 17/01	28.50	1375.82	2655-1	46.2 ± 0.2
				2655-2	$55.6 \pm 0.5^{\#}$
				2655-3	45.2 ± 0.5
S7	SAP 19/01	41.00	1357.71	2661-1	$49.6 \pm 0.6^*$
				2661-2	46.9 ± 0.2
				2661-3	$49.3 \pm 0.4^*$
S8	SAP 19/01	45.00	1354.25	2662-1	$47.4 \pm 0.5^*$
				2662-2	$48.3 \pm 0.5^*$
				2662-3	47.6 ± 0.5
S9	SAP 19/01	46.00	1353.38	2663-1	55.9 ± 0.4
				2663-2	56.1 ± 0.3
				2663-3	56.5 ± 0.2
S10	SAP 19/01	49.00	1350.79	2664-1	$45.1 \pm 0.8^*$
				2664-2	45.5 ± 0.3
				2664-3	43.6 ± 0.5
S11	SAP 16/01	67.00	1358.74	2658-1	45.3 ± 0.2
				2658-2	44.1 ± 0.2
				2658-3	44.4 ± 0.3
S12	SAP 16/01	68.00	1357.87	2659-1	$42.7 \pm 0.5^*$
				2659-2	42.6 ± 0.1
				2659-3	43.0 ± 0.2
S13	SAP 16/01	69.00	1357.01	2660-1	$41.6 \pm 0.3^*$
S14	SAP 24/99	83.10	1340.16	2656-1	$47.1 \pm 0.4^*$
				2656-2	46.9 ± 0.2
				2656-3	$46.5 \pm 0.2^*$
S15	SAP 09/99	75.70	1318.4	2666-1	48.0 ± 3.0
				2666-2	53.6 ± 0.6
				2666-3	46.4 ± 1.0

Table 2 (Continued)

Sample	Location		Elevation (m)	Grain ID	Age (Ma)
	Drill Hole	Depth (m)			
S16	SAP 37/02	60.55	1277.95	2667-1	$37.0 \pm 4.0^{\#}$
				2667-3a	$33.0 \pm 5.0^{\#}$
				2667-3b	$30.0 \pm 5.0^{\#}$
S17	SAP 37/02	62.00B	1276.70	2673-1	$18.0 \pm 0.5^*$
				2673-2	19.2 ± 1.5
				2673-3	16.8 ± 0.9
S18	SAP 37/02	62.50	1276.27	2674-1	14.2 ± 0.2
				2674-3	$47.9 \pm 1.5^{\#}$
S19	SAP 51/02	120.60	1351.07	2676-1	$49.0 \pm 4.0^{\#}$
				2676-2	$39.0 \pm 2.0^{\#}$
				2676-3	$50.0 \pm 2.0^{\#}$
S20	AND 15/02	53.30	1310.76	2681-1	$33.2 \pm 0.5^{\#}$
				2681-2	$39.4 \pm 0.3^{\#}$
				2681-3	$31.8 \pm 0.4^{\#}$
S21	AND 15/02	87.65	1281.01	2682-1	32.0 ± 0.1
				2682-2	$32.3 \pm 0.4^*$
				2682-3	$32.5 \pm 0.4^*$
S22	AND 08/02	33.20	1310.60	2679-1	$46.2 \pm 1.4^*$
				2679-2	48.2 ± 1.5
				2679-3	45.4 ± 1.3
S23	AND 08/02	84.15	1266.48	2680-1	$49.1 \pm 1.3^*$
				2680-2	$36.0 \pm 3.0^{\#}$
				2680-3	$46.0 \pm 3.0^{\#}$

Ages with (*) are "plateau-like" ages. Ages with (#) are poor "plateau-like" ages (see text for explanation)

Figure 9. Incremental-heating spectra for the 3 grains of the 23 samples from the Sapecado and Andaime deposits. Ages with (*) are “plateau-like” ages. Ages with (#) are poor “plateau-like” ages (see text for explanation).

Figure 9 (Continued)

Figure 9 (Continued)

Figure 9 (Continued).

these “plateau-like” segments, identified on Fig. 9 by an asterisk next to the age, are consistent with “true” plateau ages yielded by other grains from the same sample (e.g., grains 2665-01/02/03 or grains 2659-01/02/03). Therefore, these “plateau-like” segments are interpreted to also represent the approximate age of precipitation of the Mn-oxide grains. Five of the 69 grains, identified on Fig. 9 by a cross, yield very little ^{39}Ar to permit calculating an age. In addition, these spectra are inconsistent with spectra displayed by other grains from the same sample. The low K-contents suggest that the grain(s) analyzed may contain Mn-minerals other than hollandite, and are not suitable for reliable geochronology. Analytical results from these 5 grains are ignored from any further consideration. The remaining 12 grains (identified on Fig. 9 by an # next to the age) yield poor but geochronologically valid results that cannot be ignored. These grains either suggest the presence of minor contaminants and partial recrystallization (Grain 2655-02), significant recoil (Grains 2680-02, 2680-03, and 2681-03), some recoil with the presence of contaminants (Grains 2660-02 and 2660-03), or yield relative well-defined “plateau-like” age, but the ages are significantly different among the 3 grains from the same sample (Grains 2681-01, 2681-02, and 2681-03).

Petrographic and SEM examination indicates that samples whose various grains yield distinct plateau or plateau-like ages correspond to samples that contain visually distinct generations of Mn-oxides (Fig. 6d – Sample S15). These distinct generations are identified by cross-cutting relationships and may suggest the following sequence: Mn-oxide precipitation, a hiatus, partial dissolution of first generation Mn-oxide, and reprecipitation of cross-cutting veins of a younger generation (or generations) of Mn-oxides.

Despite some of the complicating factors above, a very encouraging aspect of the results is the fact that grains from samples collected in closed proximity to each other (e.g. samples S11 - grains 2658-01/02/03, and S12 - grains 2659-01/02/03) yield similar plateau or “plateau-like” ages, again suggesting that the $^{40}\text{Ar}/^{39}\text{Ar}$ results represent true mineral precipitation ages (Figs. 9-10 and Table 2).

Plateau and plateau-like ages for the QF samples range from 61.3 ± 1.7 to 14.2 ± 0.2 Ma, but are particularly concentrated at 51 - 41 Ma interval. All the analytical results, with the exception of the five samples that were eliminated for the reasons above, are plotted in the ideograms in Fig. 11. These ideograms are useful to visualize the distribution of ages of the supergene minerals formed at different times in a weathering profile (Vasconcelos, 1999a). They are also useful in evaluating whether the results obtained for a single weathering profile

Figure 10. Geological sections of the Andaime and Sapecado deposits showing distribution of the samples and age plateau for each grain of each sample (S20 33.2/39.4/56.3 means Sample 20 and age plateau for grains 1, 2 and 3). Legend as in Fig. 3.

reveal a continuum of ages, or whether the profile contains age clusters. The ideograms in Figure 11 reveal a discontinuous distribution of ages.

A few surface samples from the Sapecado profile had been previously dated in another study (Carmo and Vasconcelos, 2003). In order to compare results obtained from that study with our results, we plotted ideograms for Sapecado samples dated in each of these studies (Fig. 11a). The large differences in the number of grains analyzed, combined with the fact that in one of the studies (Carmo and Vasconcelos, 2003) only surface samples were dated, prevents a in-depth comparison between the two studies. However, both studies suggest that weathering at the Sapecado profile was already on going at the beginning of the Paleogene.

Another ideogram, showing $^{40}\text{Ar}/^{39}\text{Ar}$ ages from the Sapecado and Andaime (this study) and Serra da Moeda (Carmo and Vasconcelos, 2003) profiles separately (Fig. 11b), confirms that the weathering histories preserved in the Moeda Syncline profiles initiated near the K-T boundary. Unfortunately, the large variation in sample sizes, the lack of a systematic sampling strategy (some studies focused primarily on surface samples while other studies sampled deeper horizons in the weathering profiles), and the relatively small number of samples analyzed for this large region (when compared with results from Vasconcelos and Conroy, 2003) prevents an in-depth interpretation of the weathering history of the three sites. Despite these limitations, the geochronological results permit answering some relevant questions regarding the weathering history of the Quadrilátero Ferrífero profiles.

Figure 11 Probability density plot (ideogram) for all the significant steps (steps yielding negative ages, steps in which the analytical uncertainty was too great, and steps from samples showing evidence of major recoil or contamination were eliminated) analyzed for samples from the Moeda Syncline region. (a) Data for the Sapecado mine from this study compared with those of (Carmo and Vasconcelos, 2003). (b) Data for the eastern limb of the Moeda Syncline (Sapecado and Andaime Deposits, this study) compared with those of the western limb (Serra da Moeda, from Carmo and Vasconcelos, 2003).

How old are the Quadrilátero Ferrífero Weathering Profiles?

Well-defined and reproducible plateau and plateau-like ages, ranging from 61.5 ± 1.2 Ma to 14.2 ± 0.2 Ma (2σ), indicate a protracted history of chemical weathering for the Quadrilátero Ferrífero, which was already ongoing in the Paleogene and continued until the Neogene. The ages obtained are compatible with ages obtained from another study of QF weathering profiles (Carmo, 2004; Carmo and Vasconcelos, 2005). They are also in agreement with the palynologic studies of the Gandarela and Fonseca basins carried out by Lima and Salard-Chebouldaeff (1981) and by Maizatto (2001), which indicate that the sedimentation of these basins occurred during the Middle to Late Eocene. Considering that the genesis of the basins can be related to the collapse structures formed during weathering of the underlying BIFs and dolomites (Ribeiro and Carvalho, 2002), the geochronology results of the Sapecado and Andaime mines, corroborated by the palynologic data, indicate a prolonged weathering history for the Quadrilátero Ferrífero, already ongoing in the early Paleocene.

The absence of older geochronological results does not preclude a much older weathering history for the region. Older manganese oxides could exist and have not been sampled; older manganese oxides could have been dissolved by more recent weathering events; or older weathering assemblages could have been eroded from the upper parts of the profile during the past 60 Ma. At this stage, based on the results presented in this study, we can only affirm that the weathering profiles in the Quadrilátero Ferrífero are older than 61.5 ± 1.2 Ma.

One noticeable feature of the distribution of ages in the three weathering profiles illustrated in Figure 10 is the similarity in age vs. depth obtained. Although older results are obtained from samples closer to the present surface, while younger results occur in deeper horizons in the profile (Fig. 10a-b), several Mn-oxides sampled near the bedrock-weathering interface yield ages at ca. 40 Ma (Fig. 10b-c). Younger results (<30 Ma) occur in some deep horizons, but the occurrence of old manganese oxides at the present weathering-bedrock interface suggest that the Moeda Syncline weathering profiles had already reached their present depth ca. 40 Ma, indicating that very little advance of the weathering front has occurred in the Neogene. Neogene ages found deeper in the profile may record recrystallization of older Mn-oxides during more recent events, but they do not require much advance of the weathering front since ca. 40 Ma. Figure 12 illustrates the relationship between ages and elevations for the the Moeda Syncline Mn-oxides.

Figure 12. Correlation of age plateau and elevation for grains of Mn-oxides analyzed at the Moeda Syncline region. Data for the Andaime and Sapecado weathering profiles are from this study and for the Serra da Moeda are from (Carmo and Vasconcelos, 2003). Note the poor correlation ($r = 0.3$).

Continuous or Episodic Weathering Record?

The presence of Paleogene sediments in karstic lakes overlying the Cauê and Gandarela Formations, and the absence of other thick sedimentary units in the area, suggest that the QF lithologies have been continuously exposed to surficial conditions since the beginning of the Tertiary. Ideograms for the weathering profiles at the Sapecado and Andaime mines, however, do not yield a continuous distribution of ages. In reality, the geochronological results strongly cluster in the 50-40 Ma interval, with other prominent peaks at ca. 56 (Sapecado) and 32 (Andaime) Ma. The lack of surface samples from the Andaime profile may explain the absence of older results for that profile. Although it is not our intention to compare the ideograms, peak by peak, it is important to notice that some of the significant intervals (e.g., 50-40 Ma) of manganese oxide precipitation in the Sapecado profiles are also represented in the Serra da Moeda profiles studied by Carmo and Vasconcelos (2005) (Fig. 11b). All of the profiles do show clustering of ages at specific time periods, independently of where in the profiles the samples were collected, suggesting an episodic history of mineral precipitation. Given the longevity and the depth of the profiles, the complex history of mineral dissolution and reprecipitation, and the large area covered by this study, further studies, at different sites and

including the analysis of a much larger number of samples, are necessary if a complete weathering history for the Quadrilátero Ferrífero is to be obtained.

Paleoclimatic Implications

The distribution of lateritic weathering profiles has been used as a paleoclimatic indicator (Crowley and North, 1991; Frakes, 1979; Nahon, 1986). The authors consider the presence of those profiles as indicative of warm temperatures with seasonal rains, favoring intense chemical weathering and consequently the development of deep weathering profiles.

A major limitation in using weathering profiles as paleoclimatic indicator is the absence of reliable numerical ages. In addition, the few studies where ages of profiles are reported (Dammer et al., 1996; Dammer et al., 1999; Ruffet et al., 1996a; Vasconcelos et al., 1994b) suggest that lateritic profiles do not form instantly but record a protracted history of mineral dissolution and reprecipitation lasting tens of millions of years. The present study confirms that lateritic profiles reflect a protracted history of exposure. The ages of the minerals in the profiles record times in the past more propitious to chemical weathering.

The majority of the supergene Mn-oxides samples analyzed precipitated between 51 and 41 Ma, suggesting hot and wet climatic conditions at that time interval. Palynologic data for the Gandarela and Fonseca basins reveals the presence of an exuberant and diversified paleoflora in the Eocene, indicative of hot and wet environmental conditions (Maizatto, 2001). This period is coincident with the major periods of chemical weathering registered at the Carajás, Amazon region, Brazil (Ruffet et al., 1996a; Vasconcelos et al., 1994b), in Australia (Dammer et al., 1996; Dammer et al., 1999) and in Burkina Faso, Africa (Hénocque et al., 1998b). This might indicate that the climatic conditions that favored intense chemical weathering in the Eocene had a more global character.

Landscape Evolution Implications

The deeply stratified weathering profiles in the Quadrilátero Ferrífero record weathering processes already ongoing at the Paleogene, and may suggest even more ancient weathering in the region. The absence of deeply stratified weathering profiles in the adjacent dissected valleys (Fig. 2a), and evidence suggesting that weathering profiles in these dissected parts of the landscape are much younger than the profiles on the plateaus (Carmo and Vasconcelos, 2004) corroborate previous suggestions that the landsurfaces blanketing the QF plateaus are much older than the adjacent dissected landsurfaces. The landsurface characterized by the QF plateaus have

been named “Gondwana Surface” (King, 1956). A subsequent cycle of erosion (the “South America cycle”, King, 1956) would have partially eroded the Gondwana Surface, creating the more dissected landscape surrounding it. Our study does not have the regional character needed to address the existence or not of these postulated landsurfaces and erosional cycles. However, the geochronological results obtained for the QF profiles suggest that profiles in the elevated landscape associated with deeply weathered banded iron formations, quartzites, and karstic paleolake sediments are distinctly older than weathering profiles in the surrounded dissected plains and valleys, consistent with the existence of a more ancient landsurface blanketing the QF plateaus.

Implications for the Supergene Enrichment of Banded Iron Formations

The geochronological results in this study permit drawing three major conclusions:

- that the supergene enrichment blankets that make the Quadrilátero Ferrífero such a prolific iron-producing region were already forming at more than 60 Ma;
- that most of the supergene processes had already reached their present extent at ca. 40 Ma;
- and that weathering processes in the Neogene have contributed little to the further advance of the weathering fronts in the supergene orebodies.

In addition, we may safely conclude that giant supergene iron orebodies are likely to be found only in the high elevation plateaus (Gondwana Surface) that were exposed to the more intense and prolonged weathering history. Dissected plains and valleys surrounding the QF plateaus are likely to host only incipient supergene blankets.

The fact that the supergene enrichment blankets likely reached their present depths at ca. 40 Ma suggest that weathering solutions percolating through the profile were ineffective at promoting further advances of the weathering front once the profile reached a certain depth. This diminished weathering capacity may be related to diminishing reactivity of the weathering solutions at depth (e.g., depletion in dissolved oxygen or saturation with dissolved species), or it may reflect the horizontal, as opposed to the vertical, migration of the weathering solutions once they reach certain depths. The horizontally migrating weathering solutions dewater at the sides of the cliffs (Serra da Serrinha, Figs. 1 and 2) at the headwaters of local springs.

CONCLUSIONS

Deep weathering profiles developed within Paleoproterozoic BIFs of the Cauê Formation at the Quadrilátero Ferrífero host Mn-oxides suitable for $^{40}\text{Ar}/^{39}\text{Ar}$ dating. These Mn-oxides are concentrated in supergene Fe-Mn ore and manganiferous itabirite at the contact with the Gandarela Formation. They consist of minerals of the hollandite group (cryptomelane and hollandite) and pyrolusite formed by precipitation from complex (Mn-, Fe-, K-, and Ba-rich) weathering solutions. Petrographic and SEM investigations reveal the presence of several generations of Mn-oxides.

Laser-heating $^{40}\text{Ar}/^{39}\text{Ar}$ data reveal ages ranging from 62 to 14 Ma, indicating a prolonged history of weathering at the Quadrilátero Ferrífero, already ongoing at least in Paleogene and continued until Neogene. The majority of Mn-oxides, however, precipitated from 51 – 41 Ma with a peak at 47 Ma. This period is coincident with the development of small basins formed by the collapse of the underlying BIFs during intense chemical weathering, as indicated by palynologic data obtained in the sediments.

Samples collected near the present surface or near the contact with the weathering-bedrock interface present similar ages, indicating that the main weathering process was developed around 46 Ma ago. Further chemical weathering had limited effect on the weathering of the BIFs, which means that giant supergene iron ore deposits were completely formed at the Paleogene.

The coincidence of the major period of precipitation of the Mn-oxides (and therefore of intense chemical weathering) at the QF with major periods of precipitation in the Brazilian Amazon (Ruffet et al., 1996a; Vasconcelos et al., 1994b), Australia (Dammer et al., 1996; Dammer et al., 1999) and western Africa (Hénocque et al., 1998a; Hénocque et al., 1998b) suggests that climatic conditions which favored intense chemical weathering in the Eocene had a more global character.

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Appendix I. Analytical results, factors, system blank, and $^{40}\text{Ar}/^{36}\text{Ar}$ discrimination for the ABS. T he uncertainties are given at the 1 σ level

Sample	Gain ID#	Drill Hole - Depth	$^{40}\text{Ar}/^{39}\text{Ar}$	$^{38}\text{Ar}/^{39}\text{Ar}$	$^{37}\text{Ar}/^{39}\text{Ar}$	$^{36}\text{Ar}/^{39}\text{Ar}$	$^{40}\text{Ar}/^{39}\text{Ar}$	% ^{40}Ar	Age (Ma)	$\pm$ (Ma)	J	% ^{40}Ar	^{40}Ar (Moles)	Laser Power (W)	$^{40}\text{Ar}/^{36}\text{Ar}$ Discr.	$\pm$
Sapecado Deposit																
S1	2665-01A	SAP 2501-45.00	45.673	0.055	0.000	0.173	-5.348	-11.70	36.01	76.32	0.003696	± 0.000004	0.008	7.69E-17	0.10	1.0006 0.0018
S1	2665-01B	SAP 2501-45.00	63.670	0.049	0.000	0.206	2.763	4.30	18.33	11.02	0.003696	± 0.000004	0.142	1.25E-15	0.20	1.0006 0.0018
S1	2665-01C	SAP 2501-45.00	21.405	0.020	0.296	0.048	7.298	34.10	48.01	14.74	0.003696	± 0.000004	0.017	1.64E-16	0.22	1.0006 0.0018
S1	2665-01D	SAP 2501-45.00	66.440	0.050	0.243	0.162	18.615	28.00	120.04	34.52	0.003696	± 0.000004	0.028	2.65E-16	0.25	1.0006 0.0018
S1	2665-01E	SAP 2501-45.00	121.607	0.062	0.643	0.378	9.939	8.20	65.09	49.89	0.003696	± 0.000004	0.055	5.02E-16	0.27	1.0006 0.0018
S1	2665-01F	SAP 2501-45.00	16.981	0.015	0.114	0.024	9.907	58.30	64.88	2.66	0.003696	± 0.000004	0.115	1.04E-15	0.30	1.0006 0.0018
S1	2665-01G	SAP 2501-45.00	10.351	0.012	0.057	0.004	9.255	89.40	60.88	1.51	0.003696	± 0.000004	0.083	7.63E-16	0.35	1.0006 0.0018
S1	2665-01H	SAP 2501-45.00	12.768	0.012	0.354	0.012	9.107	71.30	59.73	2.48	0.003696	± 0.000004	0.072	6.75E-16	0.45	1.0006 0.0018
S1	2665-01I	SAP 2501-45.00	15.327	0.017	0.357	0.027	7.363	48.00	48.44	1.65	0.003696	± 0.000004	0.194	1.74E-15	0.99	1.0006 0.0018
S1	2665-01J	SAP 2501-45.00	311.294	0.199	1.903	0.963	26.773	8.60	170.23	178.92	0.003696	± 0.000004	0.064	6.11E-16	2.47	1.0006 0.0018
S1	2665-02A	SAP 2501-45.00	6.057	0.010	0.232	0.002	5.490	90.60	36.24	5.25	0.003696	± 0.000004	0.015	1.29E-16	0.10	1.0006 0.0018
S1	2665-02B	SAP 2501-45.00	7.004	0.013	0.167	0.008	4.595	65.60	30.38	2.85	0.003696	± 0.000004	0.031	2.78E-16	0.20	1.0006 0.0018
S1	2665-02C	SAP 2501-45.00	18.705	0.013	0.060	0.024	11.549	61.70	75.41	7.40	0.003696	± 0.000004	0.034	3.07E-16	0.22	1.0006 0.0018
S1	2665-02D	SAP 2501-45.00	15.591	0.010	0.373	0.020	9.730	62.40	63.74	4.29	0.003696	± 0.000004	0.048	4.28E-16	0.25	1.0006 0.0018
S1	2665-02E	SAP 2501-45.00	10.218	0.009	0.145	0.002	9.709	95.00	63.60	1.64	0.003696	± 0.000004	0.074	6.52E-16	0.27	1.0006 0.0018
S1	2665-02F	SAP 2501-45.00	9.759	0.011	0.201	0.000	9.749	99.90	63.86	1.87	0.003696	± 0.000004	0.065	5.81E-16	0.30	1.0006 0.0018
S1	2665-02G	SAP 2501-45.00	9.835	0.012	0.142	0.002	9.183	93.40	60.21	1.66	0.003696	± 0.000004	0.079	6.99E-16	0.35	1.0006 0.0018
S1	2665-02H	SAP 2501-45.00	9.882	0.013	0.180	0.004	8.793	89.00	57.70	1.16	0.003696	± 0.000004	0.128	1.13E-15	0.45	1.0012 0.0017
S1	2665-02I	SAP 2501-45.00	11.568	0.013	0.235	0.007	9.572	82.70	62.72	0.92	0.003696	± 0.000004	0.223	1.96E-15	0.99	1.0012 0.0017
S1	2665-02J	SAP 2501-45.00	55.531	0.022	0.472	0.070	34.817	62.70	218.39	8.24	0.003696	± 0.000004	0.116	1.03E-15	2.47	1.0012 0.0017
S1	2665-03A	SAP 2501-45.00	8.519	0.017	0.220	-0.015	12.971	152.20	84.48	9.16	0.003696	± 0.000004	0.012	1.02E-16	0.10	1.0012 0.0017
S1	2665-03B	SAP 2501-45.00	6.825	0.015	0.174	-0.006	8.683	127.20	56.99	3.41	0.003696	± 0.000004	0.024	2.12E-16	0.20	1.0012 0.0017
S1	2665-03C	SAP 2501-45.00	21.020	0.007	0.115	0.017	15.874	75.50	102.86	14.32	0.003696	± 0.000004	0.019	1.67E-16	0.22	1.0012 0.0017
S1	2665-03D	SAP 2501-45.00	35.380	0.027	0.491	0.042	23.144	65.40	148.07	14.81	0.003696	± 0.000004	0.031	2.77E-16	0.25	1.0012 0.0017
S1	2665-03E	SAP 2501-45.00	17.778	0.013	0.094	0.016	13.137	73.90	85.54	5.15	0.003696	± 0.000004	0.044	3.90E-16	0.27	1.0012 0.0017
S1	2665-03F	SAP 2501-45.00	11.012	0.013	0.198	-0.003	11.815	107.30	77.11	2.74	0.003696	± 0.000004	0.054	4.75E-16	0.30	1.0012 0.0017
S1	2665-03G	SAP 2501-45.00	10.546	0.010	0.252	0.000	10.590	100.40	69.26	2.19	0.003696	± 0.000004	0.059	5.18E-16	0.35	1.0012 0.0017
S1	2665-03H	SAP 2501-45.00	10.668	0.010	0.169	0.002	10.142	95.10	66.39	1.63	0.003696	± 0.000004	0.097	8.56E-16	0.45	1.0012 0.0017
S1	2665-03I	SAP 2501-45.00	12.135	0.014	0.278	0.014	8.094	66.70	53.18	1.11	0.003696	± 0.000004	0.204	1.78E-15	0.99	1.0012 0.0017
S1	2665-03J	SAP 2501-45.00	94.516	0.034	0.422	0.082	70.335	74.40	416.88	14.56	0.003696	± 0.000004	0.121	1.07E-15	2.47	1.0012 0.0017
S2	2649-01A	SAP 1701-22.60	20.714	0.021	0.027	0.048	6.513	31.40	42.91	2.97	0.003696	± 0.000004	0.181	1.57E-15	0.10	0.9993 0.0017
S2	2649-01B	SAP 1701-22.60	7.635	0.013	0.038	0.001	7.466	97.80	49.11	0.57	0.003696	± 0.000004	0.235	2.05E-15	0.20	0.9993 0.0017
S2	2649-01C	SAP 1701-22.60	7.649	0.014	0.039	0.001	7.233	94.60	47.60	0.78	0.003696	± 0.000004	0.163	1.42E-15	0.30	0.9993 0.0017
S2	2649-01D	SAP 1701-22.60	7.166	0.012	0.018	-0.005	8.675	121.10	56.94	4.31	0.003696	± 0.000004	0.022	1.95E-16	0.40	1.0039 0.0018
S2	2649-01E	SAP 1701-22.60	6.945	0.018	0.143	0.003	6.093	87.70	40.18	24.92	0.003696	± 0.000004	0.004	3.24E-17	0.45	1.0039 0.0018
S2	2649-01F	SAP 1701-22.60	6.593	0.010	0.000	-0.003	7.382	112.00	48.57	24.20	0.003696	± 0.000004	0.003	2.79E-17	0.50	1.0039 0.0018
S2	2649-01G	SAP 1701-22.60	7.190	0.013	0.000	0.015	2.737	38.10	18.16	22.61	0.003696	± 0.000004	0.004	3.12E-17	0.54	1.0039 0.0018
S2	2649-01H	SAP 1701-22.60	6.739	0.010	0.015	0.003	5.934	88.10	39.14	24.65	0.003696	± 0.000004	0.003	2.67E-17	0.59	1.0039 0.0018
S2	2649-01I	SAP 1701-22.60	7.216	0.020	0.000	-0.011	10.598	146.90	69.32	18.61	0.003696	± 0.000004	0.005	4.08E-17	0.69	1.0039 0.0018
S2	2649-01J	SAP 1701-22.60	8.159	0.005	0.000	-0.007	10.326	126.60	67.57	8.20	0.003696	± 0.000004	0.013	1.10E-16	0.99	1.0039 0.0018
S2	2649-01K	SAP 1701-22.60	11.618	0.012	0.000	-0.001	11.873	102.20	77.48	23.75	0.003696	± 0.000004	0.006	5.04E-17	1.49	1.0039 0.0018
S2	2649-01L	SAP 1701-22.60	11.142	-0.052	0.000	0.018	5.944	53.40	39.21	61.60	0.003696	± 0.000004	0.002	1.75E-17	2.47	1.0039 0.0018
S2	2649-02A	SAP 1701-22.60	14.814	0.019	0.000	0.034	4.890	33.00	32.31	2.35	0.003696	± 0.000004	0.133	1.16E-15	0.10	1.0039 0.0018
S2	2649-02B	SAP 1701-22.60	8.056	0.011	0.008	0.000	7.911	98.20	52.00	0.62	0.003696	± 0.000004	0.195	1.69E-15	0.20	1.0039 0.0018
S2	2649-02C	SAP 1701-22.60	8.174	0.016	0.078	0.003	7.324	89.60	48.19	3.50	0.003696	± 0.000004	0.029	2.49E-16	0.30	1.0039 0.0018
S2	2649-02D	SAP 1701-22.60	7.240	0.021	0.000	0.000	7.384	102.00	48.58	9.78	0.003696	± 0.000004	0.010	8.01E-17	0.40	1.0039 0.0018
S2	2649-02E	SAP 1701-22.60	7.084	0.011	0.498	-0.002	7.679	108.40	50.49	14.91	0.003696	± 0.000004	0.006	4.94E-17	0.45	1.0039 0.0018

Appendix (Continued)

Sample	Gain ID#	Drill Hole - Depth	⁴⁰ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar	Age (Ma)	± (Ma)	J	% ⁴⁰ Ar	⁴⁰ Ar (Moles)	Laser Power (W)	⁴⁰ Ar/ ³⁶ Ar Discr.	±	
S2	2649-02F	SAP 1701-22.60	6.976	-0.013	0.000	-0.011	10.109	144.90	66.18	17.19	0.003696	± 0.000004	0.005	4.03E-17	0.50	1.0039	0.0018
S2	2649-02G	SAP 1701-22.60	6.859	0.003	0.917	-0.017	12.036	175.40	78.52	20.04	0.003696	± 0.000004	0.004	2.82E-17	0.54	1.0039	0.0018
S2	2649-02H	SAP 1701-22.60	7.404	0.016	0.443	-0.009	10.005	135.10	65.51	10.76	0.003696	± 0.000004	0.009	7.10E-17	0.99	1.0039	0.0018
S2	2649-02I	SAP 1701-22.60	14.111	0.051	0.755	0.014	9.898	70.10	64.82	126.29	0.003696	± 0.000004	0.001	2.46E-18	2.47	1.0039	0.0018
S2	2649-03A	SAP 1701-22.60	21.521	0.022	0.044	0.045	8.225	38.20	54.03	3.52	0.003696	± 0.000004	0.128	1.12E-15	0.10	1.0039	0.0018
S2	2649-03B	SAP 1701-22.60	7.822	0.012	0.025	0.001	7.405	94.70	48.71	0.46	0.003696	± 0.000004	0.266	2.33E-15	0.20	1.0039	0.0018
S2	2649-03C	SAP 1701-22.60	7.789	0.013	0.037	0.000	7.708	99.00	50.68	0.74	0.003696	± 0.000004	0.154	1.34E-15	0.30	1.0039	0.0018
S2	2649-03D	SAP 1701-22.60	7.240	0.017	0.103	0.006	5.576	77.00	36.80	5.08	0.003696	± 0.000004	0.019	1.68E-16	0.40	1.0039	0.0018
S2	2649-03E	SAP 1701-22.60	7.324	0.012	0.336	-0.003	8.228	112.30	54.04	8.59	0.003696	± 0.000004	0.011	9.58E-17	0.59	1.0039	0.0018
S2	2649-03F	SAP 1701-22.60	10.264	0.017	0.583	0.037	-0.491	-4.80	-3.28	12.15	0.003696	± 0.000004	0.010	9.34E-17	1.49	1.0039	0.0018
S2	2649-03G	SAP 1701-22.60	17.237	0.200	0.026	-0.002	17.906	103.90	115.61	137.32	0.003696	± 0.000004	0.001	1.46E-17	2.47	1.0039	0.0018
S3	2650-01A	SAP 1701-24.60	5.057	0.011	0.000	-0.002	5.567	110.10	36.74	2.28	0.003696	± 0.000004	0.028	2.42E-16	0.10	1.0039	0.0018
S3	2650-01B	SAP 1701-24.60	7.880	0.013	0.029	0.004	6.641	84.30	43.75	1.21	0.003696	± 0.000004	0.086	7.58E-16	0.20	1.0039	0.0018
S3	2650-01C	SAP 1701-24.60	8.761	0.011	0.029	0.001	8.483	96.80	55.70	0.59	0.003696	± 0.000004	0.218	1.90E-15	0.25	1.0039	0.0018
S3	2650-01D	SAP 1701-24.60	9.150	0.012	0.058	0.000	9.071	99.10	59.49	0.59	0.003696	± 0.000004	0.231	2.03E-15	0.30	1.0039	0.0018
S3	2650-01E	SAP 1701-24.60	8.845	0.011	0.026	0.002	8.130	91.90	53.41	0.94	0.003696	± 0.000004	0.142	1.24E-15	0.35	1.0039	0.0018
S3	2650-01F	SAP 1701-24.60	7.146	0.011	0.045	0.000	7.037	98.50	46.32	1.88	0.003696	± 0.000004	0.048	4.25E-16	0.40	1.0039	0.0018
S3	2650-01G	SAP 1701-24.60	6.985	0.014	0.000	0.000	7.092	101.50	46.68	3.31	0.003696	± 0.000004	0.025	2.26E-16	0.50	1.0039	0.0018
S3	2650-01H	SAP 1701-24.60	8.547	0.010	0.000	-0.008	10.854	127.00	70.96	6.93	0.003696	± 0.000004	0.015	1.45E-16	0.59	1.0039	0.0018
S3	2650-01I	SAP 1701-24.60	8.916	0.013	0.016	0.003	8.010	89.80	52.63	3.61	0.003696	± 0.000004	0.033	3.06E-16	0.79	1.0039	0.0018
S3	2650-01J	SAP 1701-24.60	8.587	0.010	0.162	0.001	8.277	96.40	54.36	4.19	0.003696	± 0.000004	0.028	2.56E-16	0.99	1.0039	0.0018
S3	2650-01K	SAP 1701-24.60	8.793	0.018	0.002	0.022	2.155	24.50	14.31	12.26	0.003696	± 0.000004	0.010	1.06E-16	1.49	1.0039	0.0018
S3	2650-01L	SAP 1701-24.60	36.986	0.047	0.000	0.080	13.306	36.00	86.61	77.88	0.003696	± 0.000004	0.007	7.71E-17	2.47	1.0005	0.0017
S3	2650-02A	SAP 1701-24.60	4.697	0.013	0.024	-0.001	5.076	108.10	33.53	1.38	0.003696	± 0.000004	0.044	3.83E-16	0.10	1.0005	0.0017
S3	2650-02B	SAP 1701-24.60	7.532	0.012	0.040	0.000	7.398	98.20	48.66	0.45	0.003696	± 0.000004	0.254	2.21E-15	0.20	1.0005	0.0017
S3	2650-02C	SAP 1701-24.60	8.936	0.012	0.027	0.000	8.877	99.30	58.24	0.29	0.003696	± 0.000004	0.527	4.59E-15	0.25	1.0005	0.0017
S3	2650-02D	SAP 1701-24.60	8.706	0.013	0.033	0.000	8.688	99.80	57.02	0.57	0.003696	± 0.000004	0.244	2.13E-15	0.30	1.0005	0.0017
S3	2650-02E	SAP 1701-24.60	9.468	0.013	0.050	0.002	8.755	92.50	57.45	1.21	0.003696	± 0.000004	0.118	1.02E-15	0.35	1.0005	0.0017
S3	2650-02F	SAP 1701-24.60	9.018	0.016	0.119	0.000	9.060	100.50	59.42	2.88	0.003696	± 0.000004	0.043	3.70E-16	0.40	1.0005	0.0017
S3	2650-02G	SAP 1701-24.60	9.146	0.011	0.165	0.001	8.929	97.60	58.58	2.63	0.003696	± 0.000004	0.048	4.14E-16	0.50	1.0005	0.0017
S3	2650-02H	SAP 1701-24.60	8.816	0.011	0.169	0.000	8.940	101.40	58.64	3.20	0.003696	± 0.000004	0.034	2.95E-16	0.59	1.0005	0.0017
S3	2650-02I	SAP 1701-24.60	8.536	0.013	0.116	0.000	8.524	99.90	55.96	2.60	0.003696	± 0.000004	0.044	3.77E-16	0.79	1.0005	0.0017
S3	2650-02J	SAP 1701-24.60	7.871	0.013	0.278	-0.001	8.207	104.30	53.91	5.81	0.003696	± 0.000004	0.019	1.65E-16	0.99	1.0005	0.0017
S3	2650-02K	SAP 1701-24.60	7.953	0.006	0.401	-0.006	9.890	124.30	64.77	13.28	0.003696	± 0.000004	0.008	6.33E-17	1.49	1.0005	0.0017
S3	2650-02L	SAP 1701-24.60	12.483	0.039	1.173	-0.003	13.344	106.80	86.85	50.22	0.003696	± 0.000004	0.003	2.37E-17	2.47	1.0005	0.0017
S3	2650-03A	SAP 1701-24.60	7.740	0.010	0.254	0.003	6.895	89.10	45.40	6.34	0.003696	± 0.000004	0.016	1.40E-16	0.10	1.0005	0.0017
S3	2650-03B	SAP 1701-24.60	13.324	0.016	0.241	0.010	10.304	77.30	67.43	3.25	0.003696	± 0.000004	0.052	4.57E-16	0.20	1.0005	0.0017
S3	2650-03C	SAP 1701-24.60	13.897	0.012	0.352	0.009	11.299	81.30	73.81	6.09	0.003696	± 0.000004	0.030	2.57E-16	0.22	1.0005	0.0017
S3	2650-03D	SAP 1701-24.60	10.328	0.016	0.280	0.001	10.117	97.90	66.23	10.94	0.003696	± 0.000004	0.012	1.09E-16	0.25	1.0005	0.0017
S3	2650-03E	SAP 1701-24.60	7.479	0.009	0.758	0.015	2.980	39.80	19.76	11.56	0.003696	± 0.000004	0.008	7.33E-17	0.27	1.0005	0.0017
S3	2650-03F	SAP 1701-24.60	5.895	0.017	0.497	0.010	3.049	51.70	20.22	11.93	0.003696	± 0.000004	0.007	5.79E-17	0.30	1.0005	0.0017
S3	2650-03G	SAP 1701-24.60	5.480	0.021	0.438	0.010	2.651	48.40	17.59	7.84	0.003696	± 0.000004	0.009	8.26E-17	0.35	1.0005	0.0017
S3	2650-03H	SAP 1701-24.60	4.643	0.018	0.304	0.013	0.879	18.90	5.85	6.36	0.003696	± 0.000004	0.009	8.53E-17	0.40	1.0005	0.0017
S3	2650-03I	SAP 1701-24.60	7.018	0.011	0.329	0.006	5.200	74.10	34.35	6.25	0.003696	± 0.000004	0.014	1.28E-16	0.59	1.0005	0.0017
S3	2650-03J	SAP 1701-24.60	12.139	0.001	0.116	0.020	6.304	51.90	41.55	19.14	0.003696	± 0.000004	0.008	6.72E-17	0.99	1.0005	0.0017
S3	2650-03K	SAP 1701-24.60	113.302	-0.116	7.435	0.665	-83.068	-72.90	-661.65	706.01	0.003696	± 0.000004	0.005	4.53E-17	1.49	1.0005	0.0017
S3	2650-03L	SAP 1701-24.60	357.865	0.081	15.045	0.573	191.613	53.00	965.98	798.38	0.003696	± 0.000004	0.008	7.39E-17	2.47	1.0005	0.0017

Appendix (Continued)

Sample	Gain ID#	Drill Hole - Depth	⁴⁰ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar	Age (Ma)	± (Ma)	J	% ⁴⁰ Ar	⁴⁰ Ar (Moles)	Laser Power (W)	⁴⁰ Ar/ ³⁶ Ar Discr.	±	
S4	2652-01A	SAP 1701-25.60	4.150	0.013	0.009	0.002	3.542	85.40	23.46	1.19	0.003696	± 0.000004	0.042	3.66E-16	0.10	1.0005	0.0017
S4	2652-01B	SAP 1701-25.60	5.959	0.012	0.022	0.001	5.641	94.70	37.23	0.39	0.003696	± 0.000004	0.215	1.87E-15	0.20	1.0005	0.0017
S4	2652-01C	SAP 1701-25.60	7.014	0.011	0.020	0.001	6.847	97.60	45.09	0.35	0.003696	± 0.000004	0.334	2.89E-15	0.22	1.0005	0.0017
S4	2652-01D	SAP 1701-25.60	7.461	0.012	0.017	0.001	7.307	98.00	48.08	0.29	0.003696	± 0.000004	0.407	3.55E-15	0.25	1.0005	0.0017
S4	2652-01E	SAP 1701-25.60	7.742	0.012	0.013	0.000	7.700	99.50	50.62	0.32	0.003696	± 0.000004	0.379	3.29E-15	0.27	1.0005	0.0017
S4	2652-01F	SAP 1701-25.60	7.922	0.012	0.016	0.001	7.608	96.00	50.03	0.39	0.003696	± 0.000004	0.335	2.92E-15	0.30	1.0005	0.0017
S4	2652-01G	SAP 1701-25.60	7.979	0.012	0.010	0.000	7.862	98.50	51.68	0.43	0.003696	± 0.000004	0.299	2.60E-15	0.35	1.0005	0.0017
S4	2652-01H	SAP 1701-25.60	8.013	0.011	0.054	0.000	7.995	99.80	52.54	1.02	0.003696	± 0.000004	0.106	9.33E-16	0.40	1.0005	0.0017
S4	2652-01I	SAP 1701-25.60	7.416	0.011	0.074	0.002	6.928	93.40	45.62	1.87	0.003696	± 0.000004	0.048	4.23E-16	0.59	1.0005	0.0017
S4	2652-01J	SAP 1701-25.60	7.517	0.014	0.039	-0.001	7.667	102.00	50.41	1.62	0.003696	± 0.000004	0.055	4.81E-16	0.99	1.0005	0.0017
S4	2652-01K	SAP 1701-25.60	7.857	0.010	0.120	0.018	2.579	32.80	17.11	12.99	0.003696	± 0.000004	0.008	7.03E-17	1.49	1.0005	0.0017
S4	2652-01L	SAP 1701-25.60	12.505	0.020	0.121	0.018	7.313	58.50	48.11	16.93	0.003696	± 0.000004	0.010	8.76E-17	2.47	1.0005	0.0017
S4	2652-02A	SAP 1701-25.60	4.449	0.012	0.000	0.000	4.466	100.40	29.54	0.66	0.003696	± 0.000004	0.081	7.13E-16	0.10	1.0005	0.0017
S4	2652-02B	SAP 1701-25.60	6.756	0.013	0.000	0.000	6.719	99.50	44.25	0.31	0.003696	± 0.000004	0.361	3.15E-15	0.20	1.0005	0.0017
S4	2652-02C	SAP 1701-25.60	7.543	0.013	0.006	0.000	7.581	100.50	49.85	0.27	0.003696	± 0.000004	0.521	4.55E-15	0.22	1.0005	0.0017
S4	2652-02D	SAP 1701-25.60	7.760	0.012	0.015	0.000	7.777	100.20	51.13	0.23	0.003696	± 0.000004	0.719	6.27E-15	0.25	1.0005	0.0017
S4	2652-02E	SAP 1701-25.60	7.894	0.012	0.009	0.000	7.899	100.10	51.92	0.25	0.003696	± 0.000004	0.654	5.70E-15	0.27	1.0005	0.0017
S4	2652-02F	SAP 1701-25.60	8.053	0.012	0.009	0.000	8.000	99.40	52.57	0.29	0.003696	± 0.000004	0.438	3.81E-15	0.30	1.0005	0.0017
S4	2652-02G	SAP 1701-25.60	8.183	0.012	0.000	0.000	8.265	101.00	54.28	0.47	0.003696	± 0.000004	0.251	2.19E-15	0.35	1.0005	0.0017
S4	2652-02H	SAP 1701-25.60	8.302	0.012	0.000	-0.001	8.475	102.10	55.64	1.11	0.003696	± 0.000004	0.091	7.92E-16	0.40	1.0005	0.0017
S4	2652-02I	SAP 1701-25.60	7.964	0.011	0.000	-0.001	8.142	102.20	53.49	1.31	0.003696	± 0.000004	0.066	5.74E-16	0.59	1.0005	0.0017
S4	2652-02J	SAP 1701-25.60	7.852	0.010	0.000	-0.001	8.191	104.30	53.81	2.90	0.003696	± 0.000004	0.031	2.62E-16	0.99	1.0005	0.0017
S4	2652-02K	SAP 1701-25.60	11.621	0.016	0.000	0.012	8.045	69.20	52.86	10.57	0.003696	± 0.000004	0.014	1.19E-16	1.49	1.0005	0.0017
S4	2652-02L	SAP 1701-25.60	13.026	0.011	0.000	-0.019	18.684	143.40	120.47	25.26	0.003696	± 0.000004	0.006	5.03E-17	2.47	1.0005	0.0017
S4	2652-03A	SAP 1701-25.60	5.119	0.012	0.014	0.001	4.926	96.20	32.55	0.97	0.003696	± 0.000004	0.070	6.09E-16	0.10	1.0005	0.0017
S4	2652-03B	SAP 1701-25.60	6.844	0.012	0.057	0.001	6.680	97.60	44.00	0.33	0.003696	± 0.000004	0.330	2.87E-15	0.20	1.0005	0.0017
S4	2652-03C	SAP 1701-25.60	8.493	0.011	0.046	0.000	8.452	99.50	55.49	0.45	0.003696	± 0.000004	0.297	2.59E-15	0.22	1.0005	0.0017
S4	2652-03D	SAP 1701-25.60	8.137	0.011	0.032	0.000	8.039	98.80	52.82	0.36	0.003696	± 0.000004	0.375	3.27E-15	0.25	1.0005	0.0017
S4	2652-03E	SAP 1701-25.60	7.739	0.012	0.031	0.000	7.677	99.20	50.48	0.35	0.003696	± 0.000004	0.365	3.17E-15	0.27	1.0005	0.0017
S4	2652-03F	SAP 1701-25.60	7.409	0.012	0.032	0.000	7.364	99.40	48.44	0.35	0.003696	± 0.000004	0.329	2.87E-15	0.30	1.0005	0.0017
S4	2652-03G	SAP 1701-25.60	7.142	0.011	0.037	0.000	7.176	100.50	47.23	0.36	0.003696	± 0.000004	0.311	2.72E-15	0.35	1.0005	0.0017
S4	2652-03H	SAP 1701-25.60	6.861	0.013	0.033	-0.001	7.064	103.00	46.50	0.55	0.003696	± 0.000004	0.195	1.71E-15	0.40	1.0005	0.0017
S4	2652-03I	SAP 1701-25.60	6.562	0.012	0.057	0.001	6.403	97.60	42.20	0.36	0.003696	± 0.000004	0.304	2.65E-15	0.99	1.0005	0.0017
S4	2652-03J	SAP 1701-25.60	19.961	0.022	0.031	0.051	4.779	23.90	31.58	7.41	0.003696	± 0.000004	0.039	3.55E-16	2.47	1.0005	0.0017
S4	2653-01A	SAP 1701-26.60	15.654	0.019	0.000	0.036	5.083	32.50	33.58	2.17	0.003696	± 0.000004	0.174	1.51E-15	0.10	1.0005	0.0017
S5	2653-01B	SAP 1701-26.60	7.494	0.012	0.011	0.002	7.049	94.10	46.40	0.59	0.003696	± 0.000004	0.214	1.88E-15	0.20	1.0005	0.0017
S5	2653-01C	SAP 1701-26.60	7.887	0.011	0.033	0.000	7.771	98.50	51.08	0.50	0.003696	± 0.000004	0.240	2.08E-15	0.22	1.0005	0.0017
S5	2653-01D	SAP 1701-26.60	8.158	0.009	0.055	0.000	8.212	100.70	53.94	0.61	0.003696	± 0.000004	0.203	1.79E-15	0.25	1.0005	0.0017
S5	2653-01E	SAP 1701-26.60	8.251	0.011	0.028	0.000	8.136	98.60	53.45	0.67	0.003696	± 0.000004	0.190	1.66E-15	0.27	1.0005	0.0017
S5	2653-01F	SAP 1701-26.60	8.108	0.011	0.015	0.000	7.993	98.60	52.52	0.87	0.003696	± 0.000004	0.147	1.29E-15	0.30	1.0005	0.0017
S5	2653-01G	SAP 1701-26.60	8.014	0.013	0.011	0.000	7.957	99.30	52.29	0.99	0.003696	± 0.000004	0.112	9.73E-16	0.35	1.0005	0.0017
S5	2653-01H	SAP 1701-26.60	7.113	0.014	0.132	0.000	7.247	101.90	47.69	1.67	0.003696	± 0.000004	0.052	4.60E-16	0.40	1.0005	0.0017
S5	2653-01I	SAP 1701-26.60	8.087	0.013	0.010	0.001	7.834	96.90	51.50	1.07	0.003696	± 0.000004	0.108	9.46E-16	0.99	1.0005	0.0017
S5	2653-01J	SAP 1701-26.60	11.992	0.013	0.034	0.007	9.906	82.60	64.87	3.85	0.003696	± 0.000004	0.043	3.85E-16	2.47	1.0005	0.0017
S5	2653-02A	SAP 1701-26.60	12.438	0.017	0.016	0.022	6.084	48.90	40.12	1.37	0.003696	± 0.000004	0.182	1.58E-15	0.10	1.0005	0.0017
S5	2653-02B	SAP 1701-26.60	7.619	0.013	0.022	0.001	7.279	95.50	47.89	0.35	0.003696	± 0.000004	0.324	2.84E-15	0.20	1.0005	0.0017
S5	2653-02C	SAP 1701-26.60	8.071	0.012	0.013	0.000	8.158	101.10	53.60	0.33	0.003696	± 0.000004	0.374	3.26E-15	0.22	1.0005	0.0017
S5	2653-02D	SAP 1701-26.60	8.224	0.011	0.014	0.000	8.278	100.70	54.37	0.39	0.003696	± 0.000004	0.308	2.69E-15	0.25	0.9995	0.0017

Appendix (Continued)

Sample	Gain ID#	Drill Hole - Depth	⁴⁰ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar	Age (Ma)	± (Ma)	J	% ⁴⁰ Ar	⁴⁰ Ar (Moles)	Laser Power (W)	⁴⁰ Ar/ ³⁶ Ar Discr.	±	
S5	2653-02E	SAP 1701-26.60	8.336	0.012	0.008	0.000	8.343	100.10	54.79	0.55	0.003696	± 0.000004	0.205	1.79E-15	0.27	0.9995	0.0017
S5	2653-02F	SAP 1701-26.60	8.313	0.010	0.007	0.000	8.435	101.50	55.38	0.90	0.003696	± 0.000004	0.123	1.07E-15	0.30	0.9995	0.0017
S5	2653-02G	SAP 1701-26.60	8.530	0.011	0.063	-0.001	8.682	101.80	56.98	1.11	0.003696	± 0.000004	0.089	7.71E-16	0.35	0.9995	0.0017
S5	2653-02H	SAP 1701-26.60	8.836	0.014	0.036	-0.002	9.327	105.60	61.15	1.72	0.003696	± 0.000004	0.060	5.21E-16	0.40	0.9995	0.0017
S5	2653-02I	SAP 1701-26.60	22.570	0.013	0.008	0.010	19.638	87.00	126.41	1.33	0.003696	± 0.000004	0.378	3.30E-15	0.99	0.9995	0.0017
S5	2653-02J	SAP 1701-26.60	24.534	0.017	0.000	0.017	19.578	79.80	126.04	4.46	0.003696	± 0.000004	0.070	6.05E-16	2.47	0.9995	0.0017
S5	2653-03A	SAP 1701-26.60	12.806	0.016	0.000	0.030	3.877	30.30	25.67	4.10	0.003696	± 0.000004	0.041	3.54E-16	0.10	0.9995	0.0017
S5	2653-03B	SAP 1701-26.60	9.896	0.012	0.033	0.010	6.876	69.50	45.27	1.25	0.003696	± 0.000004	0.148	1.28E-15	0.20	0.9995	0.0017
S5	2653-03C	SAP 1701-26.60	7.860	0.011	0.037	0.001	7.443	94.70	48.96	0.86	0.003696	± 0.000004	0.138	1.20E-15	0.22	0.9995	0.0017
S5	2653-03D	SAP 1701-26.60	8.129	0.011	0.006	0.000	8.140	100.10	53.48	0.63	0.003696	± 0.000004	0.185	1.61E-15	0.25	0.9995	0.0017
S5	2653-03E	SAP 1701-26.60	8.069	0.011	0.036	0.000	8.069	100.00	53.02	0.90	0.003696	± 0.000004	0.133	1.15E-15	0.27	0.9995	0.0017
S5	2653-03F	SAP 1701-26.60	8.047	0.011	0.054	0.000	7.973	99.10	52.40	0.88	0.003696	± 0.000004	0.126	1.10E-15	0.30	0.9995	0.0017
S5	2653-03G	SAP 1701-26.60	7.897	0.011	0.000	0.000	7.984	101.10	52.46	1.08	0.003696	± 0.000004	0.099	8.58E-16	0.35	0.9995	0.0017
S5	2653-03H	SAP 1701-26.60	7.838	0.012	0.032	-0.003	8.824	112.60	57.90	2.01	0.003696	± 0.000004	0.049	4.22E-16	0.40	0.9995	0.0017
S5	2653-03I	SAP 1701-26.60	8.741	0.014	0.029	0.001	8.306	95.00	54.55	1.06	0.003696	± 0.000004	0.137	1.19E-15	0.99	0.9995	0.0017
S5	2653-03J	SAP 1701-26.60	14.866	0.012	0.000	0.013	11.064	74.40	72.31	4.21	0.003696	± 0.000004	0.049	4.15E-16	2.47	0.9995	0.0017
S6	2655-01A	SAP 1701-28.50	29.727	0.025	0.052	0.078	6.592	22.20	43.42	3.74	0.003696	± 0.000004	0.261	2.26E-15	0.10	0.9995	0.0017
S6	2655-01B	SAP 1701-28.50	7.883	0.013	0.027	0.006	6.115	77.60	40.32	0.66	0.003696	± 0.000004	0.262	2.27E-15	0.20	0.9995	0.0017
S6	2655-01C	SAP 1701-28.50	6.850	0.012	0.034	0.001	6.515	95.10	42.92	0.67	0.003696	± 0.000004	0.164	1.44E-15	0.22	0.9995	0.0017
S6	2655-01D	SAP 1701-28.50	7.120	0.011	0.024	0.000	7.012	98.50	46.16	0.54	0.003696	± 0.000004	0.214	1.88E-15	0.25	0.9995	0.0017
S6	2655-01E	SAP 1701-28.50	7.109	0.012	0.032	0.000	7.053	99.20	46.42	0.35	0.003696	± 0.000004	0.344	2.99E-15	0.27	0.9995	0.0017
S6	2655-01F	SAP 1701-28.50	7.097	0.011	0.040	0.000	7.060	99.50	46.47	0.32	0.003696	± 0.000004	0.375	3.28E-15	0.30	0.9995	0.0017
S6	2655-01G	SAP 1701-28.50	7.012	0.012	0.026	0.000	6.965	99.30	45.85	0.25	0.003696	± 0.000004	0.546	4.78E-15	0.35	0.9995	0.0017
S6	2655-01H	SAP 1701-28.50	6.980	0.011	0.033	0.000	6.915	99.10	45.53	0.33	0.003696	± 0.000004	0.378	3.31E-15	0.40	0.9995	0.0017
S6	2655-01I	SAP 1701-28.50	6.917	0.012	0.032	0.001	6.522	94.30	42.97	0.31	0.003696	± 0.000004	0.420	3.67E-15	0.99	0.9995	0.0017
S6	2655-01J	SAP 1701-28.50	9.116	0.013	0.057	0.008	6.787	74.40	44.69	1.40	0.003696	± 0.000004	0.093	8.31E-16	2.47	0.9995	0.0017
S6	2655-02A	SAP 1701-28.50	4.451	0.013	0.015	0.007	2.517	56.60	16.70	1.04	0.003696	± 0.000004	0.066	5.67E-16	0.10	0.9995	0.0017
S6	2655-02B	SAP 1701-28.50	5.099	0.014	0.018	0.001	4.929	96.70	32.57	0.54	0.003696	± 0.000004	0.183	1.59E-15	0.20	0.9995	0.0017
S6	2655-02C	SAP 1701-28.50	6.859	0.013	0.004	0.000	6.915	100.80	45.53	0.57	0.003696	± 0.000004	0.198	1.73E-15	0.22	0.9995	0.0017
S6	2655-02D	SAP 1701-28.50	8.424	0.011	0.015	0.000	8.357	99.20	54.88	0.44	0.003696	± 0.000004	0.284	2.46E-15	0.25	0.9995	0.0017
S6	2655-02E	SAP 1701-28.50	8.516	0.011	0.001	0.000	8.599	101.00	56.45	0.44	0.003696	± 0.000004	0.302	2.65E-15	0.27	0.9995	0.0017
S6	2655-02F	SAP 1701-28.50	8.515	0.012	0.003	0.000	8.541	100.30	56.07	0.47	0.003696	± 0.000004	0.270	2.35E-15	0.30	0.9995	0.0017
S6	2655-02G	SAP 1701-28.50	8.380	0.011	0.007	0.000	8.252	98.50	54.20	0.59	0.003696	± 0.000004	0.215	1.86E-15	0.35	0.9995	0.0017
S6	2655-02H	SAP 1701-28.50	8.228	0.012	0.043	0.000	8.113	98.60	53.30	1.19	0.003696	± 0.000004	0.088	7.60E-16	0.45	0.9995	0.0017
S6	2655-02I	SAP 1701-28.50	9.842	0.013	0.029	0.004	8.716	88.60	57.20	0.72	0.003696	± 0.000004	0.198	1.73E-15	0.99	0.9995	0.0017
S6	2655-02J	SAP 1701-28.50	17.029	0.014	0.000	0.009	14.391	84.50	93.49	2.54	0.003696	± 0.000004	0.107	9.31E-16	2.47	0.9995	0.0017
S6	2655-03A	SAP 1701-28.50	11.638	0.016	0.003	0.019	6.080	52.30	40.09	1.56	0.003696	± 0.000004	0.154	1.34E-15	0.10	1.0025	0.0018
S6	2655-03B	SAP 1701-28.50	6.948	0.012	0.035	0.000	6.823	98.20	44.93	0.34	0.003696	± 0.000004	0.392	3.43E-15	0.20	1.0025	0.0018
S6	2655-03C	SAP 1701-28.50	7.183	0.012	0.027	0.000	7.059	98.30	46.46	0.94	0.003696	± 0.000004	0.101	8.83E-16	0.22	1.0025	0.0018
S6	2655-03D	SAP 1701-28.50	7.242	0.011	0.071	0.000	7.230	99.90	47.58	1.90	0.003696	± 0.000004	0.048	4.21E-16	0.25	1.0025	0.0018
S6	2655-03E	SAP 1701-28.50	6.748	0.009	0.034	0.004	5.556	82.40	36.67	4.76	0.003696	± 0.000004	0.018	1.59E-16	0.27	1.0025	0.0018
S6	2655-03F	SAP 1701-28.50	4.633	0.012	0.000	-0.012	8.192	176.80	53.81	8.86	0.003696	± 0.000004	0.006	6.12E-17	0.30	1.0025	0.0018
S6	2655-03G	SAP 1701-28.50	14.139	0.013	0.000	-0.022	20.513	145.10	131.84	23.17	0.003696	± 0.000004	0.007	7.24E-17	0.35	1.0025	0.0018
S6	2655-03H	SAP 1701-28.50	29.653	0.006	0.000	0.012	26.112	88.10	166.21	17.27	0.003696	± 0.000004	0.021	1.87E-16	0.45	1.0025	0.0018
S6	2655-03I	SAP 1701-28.50	21.731	0.013	0.014	0.023	14.980	68.90	97.22	7.83	0.003696	± 0.000004	0.036	3.24E-16	0.99	1.0025	0.0018
S6	2655-03J	SAP 1701-28.50	3.331	0.013	0.064	0.036	-7.191	-215.9	-48.60	49.68	0.003696	± 0.000004	0.001	1.92E-17	2.47	1.0025	0.0018

Appendix I (Continued)

Appendix (Continued)																	
Sample	Gain ID#	Drill Hole - Depth	⁴⁰ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar	Age (Ma)	± (Ma)	J	% ⁴⁰ Ar	⁴⁰ Ar (Moles)	Laser Power (W)	⁴⁰ Ar/ ³⁶ Ar Discr.	±	
S7	2661-01A	SAP 1901-41.00	8.952	0.014	0.081	0.009	6.376	71.20	42.02	1.53	0.003696	± 0.000004	0.116	1.01E-15	0.10	1.0016	0.0018
S7	2661-01B	SAP 1901-41.00	7.885	0.012	0.028	0.003	7.138	90.50	46.98	0.39	0.003696	± 0.000004	0.371	3.24E-15	0.20	1.0016	0.0018
S7	2661-01C	SAP 1901-41.00	7.875	0.012	0.022	0.001	7.597	96.50	49.96	0.23	0.003696	± 0.000004	0.635	5.51E-15	0.22	1.0017	0.0017
S7	2661-01D	SAP 1901-41.00	7.569	0.012	0.018	0.000	7.528	99.50	49.51	0.33	0.003696	± 0.000004	0.360	3.14E-15	0.25	1.0017	0.0017
S7	2661-01E	SAP 1901-41.00	7.410	0.011	0.028	0.000	7.374	99.50	48.51	0.48	0.003696	± 0.000004	0.229	2.00E-15	0.27	1.0017	0.0017
S7	2661-01F	SAP 1901-41.00	7.407	0.012	0.031	0.001	7.209	97.30	47.44	0.69	0.003696	± 0.000004	0.155	1.35E-15	0.30	1.0017	0.0017
S7	2661-01G	SAP 1901-41.00	7.093	0.012	0.015	0.000	6.978	98.40	45.94	0.60	0.003696	± 0.000004	0.164	1.43E-15	0.35	1.0017	0.0017
S7	2661-01H	SAP 1901-41.00	6.108	0.012	0.015	0.002	5.598	91.70	36.95	0.63	0.003696	± 0.000004	0.143	1.24E-15	0.45	1.0017	0.0017
S7	2661-01I	SAP 1901-41.00	5.593	0.013	0.000	0.000	5.453	97.50	36.00	1.50	0.003696	± 0.000004	0.049	4.29E-16	0.54	1.0017	0.0017
S7	2661-01J	SAP 1901-41.00	5.335	0.013	0.000	0.005	3.831	71.80	25.36	7.57	0.003696	± 0.000004	0.008	7.25E-17	0.69	1.0017	0.0017
S7	2661-01K	SAP 1901-41.00	5.390	0.013	0.012	-0.003	6.304	117.00	41.55	3.42	0.003696	± 0.000004	0.019	1.65E-16	0.99	1.0017	0.0017
S7	2661-01L	SAP 1901-41.00	9.219	0.018	0.020	0.015	4.883	53.00	32.27	3.74	0.003696	± 0.000004	0.034	2.97E-16	2.47	1.0017	0.0017
S7	2661-02A	SAP 1901-41.00	7.588	0.014	0.011	0.006	5.880	77.50	38.79	1.23	0.003696	± 0.000004	0.080	6.97E-16	0.10	1.0017	0.0017
S7	2661-02B	SAP 1901-41.00	6.710	0.013	0.025	0.002	6.240	93.00	41.13	0.31	0.003696	± 0.000004	0.347	3.03E-15	0.20	1.0017	0.0017
S7	2661-02C	SAP 1901-41.00	6.926	0.012	0.018	0.001	6.555	94.60	43.18	0.34	0.003696	± 0.000004	0.319	2.80E-15	0.22	1.0017	0.0017
S7	2661-02D	SAP 1901-41.00	7.262	0.012	0.013	0.000	7.116	98.00	46.83	0.19	0.003696	± 0.000004	0.968	8.43E-15	0.25	1.0017	0.0017
S7	2661-02E	SAP 1901-41.00	7.216	0.012	0.014	0.000	7.096	98.30	46.71	0.14	0.003696	± 0.000004	1.302	1.14E-14	0.27	1.0017	0.0017
S7	2661-02F	SAP 1901-41.00	7.314	0.012	0.017	0.000	7.181	98.20	47.26	0.18	0.003696	± 0.000004	0.977	8.55E-15	0.30	1.0017	0.0017
S7	2661-02G	SAP 1901-41.00	7.399	0.012	0.020	0.001	7.227	97.70	47.56	0.19	0.003696	± 0.000004	0.914	8.02E-15	0.35	1.0017	0.0017
S7	2661-02H	SAP 1901-41.00	7.447	0.012	0.015	0.001	7.257	97.50	47.75	0.23	0.003696	± 0.000004	0.782	6.80E-15	0.45	1.0017	0.0017
S7	2661-02I	SAP 1901-41.00	6.626	0.013	0.022	0.001	6.286	94.90	41.43	0.57	0.003696	± 0.000004	0.187	1.66E-15	0.54	1.0017	0.0017
S7	2661-02J	SAP 1901-41.00	5.797	0.014	0.067	0.001	5.637	97.30	37.20	1.71	0.003696	± 0.000004	0.040	3.79E-16	0.69	1.0017	0.0017
S7	2661-02K	SAP 1901-41.00	5.666	0.013	0.145	0.001	5.252	92.70	34.68	3.17	0.003696	± 0.000004	0.022	2.16E-16	0.99	1.0017	0.0017
S7	2661-02L	SAP 1901-41.00	14.519	0.017	0.072	0.028	6.129	42.20	40.41	2.80	0.003696	± 0.000004	0.095	8.60E-16	2.47	1.0017	0.0017
S7	2661-03A	SAP 1901-41.00	5.835	0.014	0.000	-0.001	6.242	107.00	41.15	8.57	0.003696	± 0.000004	0.008	6.74E-17	0.10	1.0017	0.0017
S7	2661-03B	SAP 1901-41.00	5.687	0.012	0.020	0.001	5.445	95.80	35.95	0.86	0.003696	± 0.000004	0.102	8.87E-16	0.20	1.0017	0.0017
S7	2661-03C	SAP 1901-41.00	5.437	0.012	0.095	0.001	5.170	95.10	34.15	0.96	0.003696	± 0.000004	0.068	5.80E-16	0.22	1.0017	0.0017
S7	2661-03D	SAP 1901-41.00	6.120	0.014	0.030	0.001	5.959	97.40	39.30	0.84	0.003696	± 0.000004	0.091	7.86E-16	0.25	1.0017	0.0017
S7	2661-03E	SAP 1901-41.00	6.956	0.012	0.033	0.000	6.953	100.00	45.77	0.56	0.003696	± 0.000004	0.159	1.38E-15	0.27	1.0017	0.0017
S7	2661-03F	SAP 1901-41.00	7.264	0.012	0.002	0.000	7.168	98.70	47.17	0.38	0.003696	± 0.000004	0.295	2.57E-15	0.30	1.0017	0.0017
S7	2661-03G	SAP 1901-41.00	7.619	0.012	0.011	0.000	7.493	98.40	49.28	0.21	0.003696	± 0.000004	0.694	6.04E-15	0.35	1.0017	0.0017
S7	2661-03H	SAP 1901-41.00	7.655	0.012	0.004	0.000	7.582	99.10	49.86	0.17	0.003696	± 0.000004	1.084	9.48E-15	0.45	1.0017	0.0017
S7	2661-03I	SAP 1901-41.00	7.353	0.012	0.007	0.000	7.292	99.20	47.98	0.28	0.003696	± 0.000004	0.464	4.05E-15	0.54	1.0017	0.0017
S7	2661-03J	SAP 1901-41.00	7.503	0.012	0.007	0.001	7.350	98.00	48.35	0.44	0.003696	± 0.000004	0.289	2.52E-15	0.69	1.0017	0.0017
S7	2661-03K	SAP 1901-41.00	5.234	0.015	0.000	0.000	5.139	98.20	33.94	1.17	0.003696	± 0.000004	0.060	5.23E-16	0.99	1.0017	0.0017
S7	2661-03L	SAP 1901-41.00	6.661	0.015	0.016	0.010	3.813	57.20	25.25	2.55	0.003696	± 0.000004	0.032	2.73E-16	2.47	1.0017	0.0017
S8	2662-01A	SAP 1901-45.00	7.222	0.011	0.000	0.001	6.976	96.60	45.93	1.75	0.003696	± 0.000004	0.051	4.51E-16	0.10	1.0017	0.0017
S8	2662-01B	SAP 1901-45.00	7.666	0.010	0.039	0.000	7.534	98.30	49.55	0.63	0.003696	± 0.000004	0.177	1.54E-15	0.20	1.0017	0.0017
S8	2662-01C	SAP 1901-45.00	7.656	0.012	0.036	0.000	7.547	98.60	49.63	0.44	0.003696	± 0.000004	0.266	2.32E-15	0.22	1.0017	0.0017
S8	2662-01D	SAP 1901-45.00	7.490	0.011	0.034	0.000	7.374	98.50	48.51	0.32	0.003696	± 0.000004	0.370	3.24E-15	0.25	1.0017	0.0017
S8	2662-01E	SAP 1901-45.00	7.260	0.012	0.041	0.000	7.289	100.40	47.96	0.30	0.003696	± 0.000004	0.391	3.42E-15	0.27	1.0017	0.0017
S8	2662-01F	SAP 1901-45.00	7.212	0.013	0.031	0.000	7.168	99.40	47.17	0.30	0.003696	± 0.000004	0.396	3.47E-15	0.30	1.0017	0.0017
S8	2662-01G	SAP 1901-45.00	7.128	0.011	0.033	0.000	7.026	98.60	46.25	0.30	0.003696	± 0.000004	0.375	3.27E-15	0.35	1.0017	0.0017
S8	2662-01H	SAP 1901-45.00	7.017	0.011	0.049	0.001	6.758	96.30	44.51	0.45	0.003696	± 0.000004	0.231	2.02E-15	0.45	1.0017	0.0017
S8	2662-01I	SAP 1901-45.00	7.357	0.011	0.044	0.001	7.014	95.30	46.17	0.78	0.003696	± 0.000004	0.134	1.18E-15	0.99	1.0017	0.0017
S8	2662-01J	SAP 1901-45.00	35.920	0.025	0.248	0.105	4.946	13.80	32.68	12.59	0.003696	± 0.000004	0.041	3.77E-16	2.47	1.0017	0.0017
S8	2662-02A	SAP 1901-45.00	7.268	0.011	0.045	0.000	7.291	100.30	47.97	1.30	0.003696	± 0.000004	0.069	5.94E-16	0.10	1.0017	0.0017
S8	2662-02B	SAP 1901-45.00	7.430	0.012	0.056	0.000	7.408	99.70	48.73	0.32	0.003696	± 0.000004	0.350	3.07E-15	0.20	1.0017	0.0017
S8	2662-02C	SAP 1901-45.00	7.023	0.012	0.054	-0.001	7.183	102.30	47.27	0.49	0.003696	± 0.000004	0.206	1.79E-15	0.22	1.0017	0.0017

AppendixI (Continued)

Sample	Gain ID#	Drill Hole - Depth	⁴⁰ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar	Age (Ma)	± (Ma)	J	% ⁴⁰ Ar	⁴⁰ Ar (Moles)	Laser Power (W)	⁴⁰ Ar/ ³⁶ Ar Discr.	±	
S8	2662-02D	SAP 1901-45.00	7.095	0.012	0.074	-0.001	7.513	105.90	49.41	0.89	0.003696	± 0.000004	0.103	8.95E-16	0.25	1.0017	0.0017
S8	2662-02E	SAP 1901-45.00	7.160	0.010	0.096	0.002	6.698	93.60	44.12	1.55	0.003696	± 0.000004	0.056	4.82E-16	0.27	1.0017	0.0017
S8	2662-02F	SAP 1901-45.00	7.172	0.014	0.084	0.000	7.208	100.50	47.43	2.19	0.003696	± 0.000004	0.036	3.06E-16	0.30	1.0017	0.0017
S8	2662-02G	SAP 1901-45.00	7.206	0.012	0.096	-0.004	8.389	116.40	55.09	2.83	0.003696	± 0.000004	0.031	2.58E-16	0.35	1.0017	0.0017
S8	2662-02H	SAP 1901-45.00	7.533	0.011	0.030	0.005	6.126	81.30	40.39	4.76	0.003696	± 0.000004	0.019	1.51E-16	0.45	1.0017	0.0017
S8	2662-02I	SAP 1901-45.00	7.572	0.013	0.019	-0.001	7.861	103.80	51.67	3.71	0.003696	± 0.000004	0.024	1.93E-16	0.99	1.0017	0.0017
S8	2662-02J	SAP 1901-45.00	12.601	0.029	0.286	0.004	11.564	91.80	75.50	31.35	0.003696	± 0.000004	0.005	2.79E-17	2.47	1.0017	0.0017
S8	2662-03A	SAP 1901-45.00	7.291	0.013	0.000	-0.002	7.783	106.80	51.17	1.67	0.003696	± 0.000004	0.048	4.18E-16	0.10	1.0017	0.0017
S8	2662-03B	SAP 1901-45.00	7.575	0.012	0.048	0.000	7.544	99.60	49.61	0.49	0.003696	± 0.000004	0.218	1.90E-15	0.20	1.0017	0.0017
S8	2662-03C	SAP 1901-45.00	7.210	0.013	0.016	0.000	7.165	99.40	47.15	0.50	0.003696	± 0.000004	0.192	1.67E-15	0.22	1.0017	0.0017
S8	2662-03D	SAP 1901-45.00	7.169	0.011	0.096	0.000	7.294	101.70	47.99	0.62	0.003696	± 0.000004	0.152	1.32E-15	0.25	1.0017	0.0017
S8	2662-03E	SAP 1901-45.00	6.991	0.013	0.071	-0.001	7.355	105.20	48.39	1.06	0.003696	± 0.000004	0.074	6.42E-16	0.27	1.0017	0.0017
S8	2662-03F	SAP 1901-45.00	6.839	0.012	0.072	0.002	6.361	93.00	41.93	1.86	0.003696	± 0.000004	0.041	3.59E-16	0.30	1.0017	0.0017
S8	2662-03G	SAP 1901-45.00	6.942	0.012	0.172	0.005	5.492	79.10	36.25	2.31	0.003696	± 0.000004	0.036	3.09E-16	0.35	1.0017	0.0017
S8	2662-03H	SAP 1901-45.00	7.297	0.011	0.164	0.002	6.588	90.30	43.40	3.82	0.003696	± 0.000004	0.021	1.84E-16	0.45	1.0017	0.0017
S8	2662-03I	SAP 1901-45.00	7.336	0.013	0.312	0.005	5.807	79.20	38.31	3.83	0.003696	± 0.000004	0.023	1.98E-16	0.99	1.0017	0.0017
S8	2662-03J	SAP 1901-45.00	17.020	0.022	0.352	0.028	8.843	51.90	58.02	31.77	0.003696	± 0.000004	0.006	5.39E-17	2.47	1.0017	0.0017
S9	2663-01A	SAP 1901-46.00	4.025	0.012	0.075	0.000	4.165	103.50	27.56	0.86	0.003696	± 0.000004	0.055	4.81E-16	0.10	1.0017	0.0017
S9	2663-01B	SAP 1901-46.00	7.468	0.012	0.000	0.000	7.593	101.70	49.93	0.43	0.003696	± 0.000004	0.285	2.49E-15	0.20	1.0017	0.0017
S9	2663-01C	SAP 1901-46.00	8.464	0.012	0.012	0.000	8.461	100.00	55.55	0.29	0.003696	± 0.000004	0.466	4.07E-15	0.22	1.0017	0.0017
S9	2663-01D	SAP 1901-46.00	8.528	0.012	0.013	0.000	8.522	99.90	55.95	0.33	0.003696	± 0.000004	0.469	4.06E-15	0.25	1.0017	0.0017
S9	2663-01E	SAP 1901-46.00	8.620	0.012	0.005	0.000	8.671	100.60	56.91	0.49	0.003696	± 0.000004	0.294	2.55E-15	0.27	1.0017	0.0017
S9	2663-01F	SAP 1901-46.00	8.697	0.010	0.098	-0.001	9.067	104.30	59.47	1.18	0.003696	± 0.000004	0.110	9.52E-16	0.30	1.0017	0.0017
S9	2663-01G	SAP 1901-46.00	8.850	0.011	0.000	-0.003	9.753	110.20	63.89	1.67	0.003696	± 0.000004	0.065	5.66E-16	0.35	1.0017	0.0017
S9	2663-01H	SAP 1901-46.00	8.632	0.008	0.021	0.001	8.401	97.30	55.17	2.99	0.003696	± 0.000004	0.037	3.18E-16	0.45	1.0017	0.0017
S9	2663-01I	SAP 1901-46.00	9.157	0.006	0.105	-0.006	11.020	120.30	72.02	4.37	0.003696	± 0.000004	0.025	2.10E-16	0.54	1.0017	0.0017
S9	2663-01J	SAP 1901-46.00	9.111	0.011	0.000	-0.004	10.267	112.70	67.19	3.49	0.003696	± 0.000004	0.033	2.79E-16	0.69	1.0017	0.0017
S9	2663-01K	SAP 1901-46.00	8.898	0.014	0.000	0.009	6.266	70.40	41.30	5.44	0.003696	± 0.000004	0.021	1.74E-16	0.99	1.0017	0.0017
S9	2663-01L	SAP 1901-46.00	12.692	0.008	0.000	0.003	11.938	94.10	77.89	11.95	0.003696	± 0.000004	0.014	1.11E-16	2.47	1.0003	0.0018
S9	2663-02A	SAP 1901-46.00	4.175	0.011	0.000	0.001	3.735	89.50	24.74	0.82	0.003696	± 0.000004	0.060	5.19E-16	0.10	1.0003	0.0018
S9	2663-02B	SAP 1901-46.00	7.207	0.012	0.009	0.000	7.067	98.10	46.52	0.48	0.003696	± 0.000004	0.239	2.09E-15	0.20	1.0003	0.0018
S9	2663-02C	SAP 1901-46.00	8.501	0.011	0.011	0.000	8.499	100.00	55.80	0.47	0.003696	± 0.000004	0.278	2.42E-15	0.22	1.0003	0.0018
S9	2663-02D	SAP 1901-46.00	8.704	0.012	0.000	0.000	8.676	99.70	56.94	0.41	0.003696	± 0.000004	0.364	3.18E-15	0.25	1.0003	0.0018
S9	2663-02E	SAP 1901-46.00	8.584	0.012	0.015	0.000	8.488	98.90	55.72	0.32	0.003696	± 0.000004	0.413	3.59E-15	0.27	1.0003	0.0018
S9	2663-02F	SAP 1901-46.00	8.581	0.013	0.013	0.000	8.498	99.00	55.79	0.37	0.003696	± 0.000004	0.384	3.35E-15	0.30	1.0003	0.0018
S9	2663-02G	SAP 1901-46.00	8.684	0.012	0.000	0.000	8.598	99.00	56.44	0.61	0.003696	± 0.000004	0.226	1.97E-15	0.35	1.0003	0.0018
S9	2663-02H	SAP 1901-46.00	8.743	0.012	0.040	0.000	8.624	98.60	56.60	1.16	0.003696	± 0.000004	0.103	8.96E-16	0.45	1.0003	0.0018
S9	2663-02I	SAP 1901-46.00	8.798	0.011	0.000	0.005	7.372	83.80	48.50	3.62	0.003696	± 0.000004	0.032	2.79E-16	0.54	1.0003	0.0018
S9	2663-02J	SAP 1901-46.00	8.692	0.013	0.000	0.001	8.403	96.70	55.18	2.21	0.003696	± 0.000004	0.048	4.24E-16	0.69	1.0003	0.0018
S9	2663-02K	SAP 1901-46.00	8.657	0.011	0.000	0.002	8.033	92.80	52.79	2.37	0.003696	± 0.000004	0.046	3.99E-16	0.99	1.0003	0.0018
S9	2663-02L	SAP 1901-46.00	13.648	0.029	0.000	0.039	2.239	16.40	14.87	10.83	0.003696	± 0.000004	0.017	1.46E-16	2.47	1.0003	0.0018
S9	2663-03A	SAP 1901-46.00	4.047	0.013	0.032	0.000	3.974	98.20	26.31	0.72	0.003696	± 0.000004	0.066	5.73E-16	0.10	1.0003	0.0018
S9	2663-03B	SAP 1901-46.00	7.079	0.012	0.030	0.000	6.977	98.60	45.93	0.46	0.003696	± 0.000004	0.255	2.23E-15	0.20	1.0003	0.0018
S9	2663-03C	SAP 1901-46.00	8.463	0.012	0.029	0.001	8.262	97.60	54.27	0.35	0.003696	± 0.000004	0.364	3.17E-15	0.22	1.0003	0.0018
S9	2663-03D	SAP 1901-46.00	8.707	0.011	0.009	0.000	8.622	99.00	56.59	0.31	0.003696	± 0.000004	0.513	4.47E-15	0.25	1.0003	0.0018
S9	2663-03E	SAP 1901-46.00	8.682	0.012	0.021	0.000	8.601	99.10	56.46	0.29	0.003696	± 0.000004	0.561	4.89E-15	0.27	1.0003	0.0018
S9	2663-03F	SAP 1901-46.00	8.673	0.012	0.024	0.000	8.610	99.30	56.52	0.30	0.003696	± 0.000004	0.499	4.34E-15	0.30	1.0003	0.0018

Appendix I (Continued)

Sample	Gain ID#	Drill Hole - Depth	⁴⁰ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar	Age (Ma)	± (Ma)	J	% ⁴⁰ Ar	⁴⁰ Ar (Moles)	Laser Power (W)	⁴⁰ Ar/ ³⁶ Ar Discr.	±	
S9	2663-03G	SAP 1901-46.00	8.700	0.012	0.012	0.000	8.628	99.20	56.63	0.36	0.003696	± 0.000004	0.375	3.27E-15	0.35	1.0003	0.0018
S9	2663-03H	SAP 1901-46.00	8.905	0.011	0.006	-0.001	9.093	102.10	59.63	0.82	0.003696	± 0.000004	0.150	1.31E-15	0.45	1.0003	0.0018
S9	2663-03I	SAP 1901-46.00	8.971	0.010	0.078	0.001	8.804	95.90	56.48	2.83	0.003696	± 0.000004	0.038	3.35E-16	0.54	1.0003	0.0018
S9	2663-03J	SAP 1901-46.00	8.775	0.009	0.045	-0.003	9.625	109.70	63.06	2.32	0.003696	± 0.000004	0.045	3.96E-16	0.69	1.0003	0.0018
S9	2663-03K	SAP 1901-46.00	8.686	0.008	0.070	0.002	8.209	94.50	53.92	1.80	0.003696	± 0.000004	0.057	5.00E-16	0.99	1.0003	0.0018
S9	2663-03L	SAP 1901-46.00	12.932	-0.003	0.197	0.010	9.862	76.20	64.59	7.91	0.003696	± 0.000004	0.021	1.86E-16	2.47	1.0003	0.0018
S10	2664-01A	SAP 1901-49.00	33.796	0.028	0.032	0.096	5.540	16.40	36.57	2.91	0.003696	± 0.000004	0.559	4.88E-15	0.10	1.0003	0.0018
S10	2664-01B	SAP 1901-49.00	7.443	0.013	0.046	0.001	7.142	96.00	47.01	0.33	0.003696	± 0.000004	0.423	3.71E-15	0.20	1.0003	0.0018
S10	2664-01C	SAP 1901-49.00	6.834	0.012	0.037	0.001	6.548	95.80	43.14	0.36	0.003696	± 0.000004	0.291	2.53E-15	0.22	1.0003	0.0018
S10	2664-01D	SAP 1901-49.00	6.751	0.012	0.016	0.000	6.651	98.50	43.81	0.66	0.003696	± 0.000004	0.147	1.28E-15	0.25	1.0003	0.0018
S10	2664-01E	SAP 1901-49.00	6.759	0.011	0.034	0.000	6.865	101.60	45.20	1.00	0.003696	± 0.000004	0.084	7.34E-16	0.27	1.0003	0.0018
S10	2664-01F	SAP 1901-49.00	6.613	0.012	0.019	-0.001	6.843	103.50	45.06	1.42	0.003696	± 0.000004	0.060	5.25E-16	0.30	1.0003	0.0018
S10	2664-01G	SAP 1901-49.00	6.731	0.011	0.011	-0.002	7.200	107.00	47.38	1.53	0.003696	± 0.000004	0.053	4.66E-16	0.35	1.0003	0.0018
S10	2664-01H	SAP 1901-49.00	6.882	0.013	0.043	-0.003	7.671	111.50	50.44	2.48	0.003696	± 0.000004	0.034	2.96E-16	0.45	1.0003	0.0018
S10	2664-01I	SAP 1901-49.00	8.937	0.010	0.038	-0.004	10.165	113.70	66.53	2.36	0.003696	± 0.000004	0.043	3.77E-16	0.99	1.0003	0.0018
S10	2664-01J	SAP 1901-49.00	10.499	0.018	0.098	-0.003	11.410	108.70	74.52	8.64	0.003696	± 0.000004	0.015	1.32E-16	2.47	1.0003	0.0018
S10	2664-02A	SAP 1901-49.00	40.047	0.032	0.007	0.108	8.042	20.10	52.84	3.23	0.003696	± 0.000004	0.576	5.00E-15	0.10	1.0006	0.0018
S10	2664-02B	SAP 1901-49.00	7.214	0.013	0.030	0.001	6.926	96.00	45.60	0.32	0.003696	± 0.000004	0.469	4.08E-15	0.20	1.0006	0.0018
S10	2664-02C	SAP 1901-49.00	6.814	0.011	0.001	0.000	6.842	100.40	45.05	0.74	0.003696	± 0.000004	0.127	1.11E-15	0.22	1.0006	0.0018
S10	2664-02D	SAP 1901-49.00	6.727	0.011	0.098	-0.001	7.038	104.60	46.33	1.42	0.003696	± 0.000004	0.060	5.19E-16	0.25	1.0006	0.0018
S10	2664-02E	SAP 1901-49.00	7.042	0.009	0.041	0.001	6.683	94.90	44.02	2.24	0.003696	± 0.000004	0.036	3.14E-16	0.27	1.0006	0.0018
S10	2664-02F	SAP 1901-49.00	6.706	0.008	0.000	0.001	6.501	97.00	42.84	3.35	0.003696	± 0.000004	0.023	1.97E-16	0.30	1.0006	0.0018
S10	2664-02G	SAP 1901-49.00	6.965	0.005	0.000	-0.001	7.177	103.10	47.23	4.23	0.003696	± 0.000004	0.019	1.62E-16	0.35	1.0006	0.0018
S10	2664-02H	SAP 1901-49.00	7.663	0.008	0.000	-0.008	9.889	129.10	64.76	6.56	0.003696	± 0.000004	0.013	1.10E-16	0.45	1.0006	0.0018
S10	2664-02I	SAP 1901-49.00	9.626	0.007	0.000	-0.006	11.277	117.20	73.67	4.51	0.003696	± 0.000004	0.023	1.97E-16	0.99	1.0006	0.0018
S10	2664-02J	SAP 1901-49.00	10.889	0.001	0.000	0.006	9.201	84.50	60.33	17.16	0.003696	± 0.000004	0.008	6.13E-17	2.47	1.0006	0.0018
S10	2664-03A	SAP 1901-49.00	22.173	0.020	0.030	0.054	6.097	27.50	40.20	2.40	0.003696	± 0.000004	0.251	2.19E-15	0.10	1.0006	0.0018
S10	2664-03B	SAP 1901-49.00	7.529	0.012	0.052	0.001	7.212	95.80	47.46	0.43	0.003696	± 0.000004	0.284	2.48E-15	0.20	1.0006	0.0018
S10	2664-03C	SAP 1901-49.00	6.737	0.011	0.040	0.000	6.631	98.40	43.68	0.47	0.003696	± 0.000004	0.228	1.99E-15	0.22	1.0006	0.0018
S10	2664-03D	SAP 1901-49.00	6.456	0.012	0.044	0.000	6.564	101.70	43.24	0.59	0.003696	± 0.000004	0.136	1.19E-15	0.25	1.0006	0.0018
S10	2664-03E	SAP 1901-49.00	6.479	0.011	0.134	0.000	6.367	98.30	41.96	1.01	0.003696	± 0.000004	0.079	6.81E-16	0.27	1.0006	0.0018
S10	2664-03F	SAP 1901-49.00	6.520	0.011	0.030	-0.002	7.029	107.80	46.27	1.42	0.003696	± 0.000004	0.057	4.92E-16	0.30	1.0006	0.0018
S10	2664-03G	SAP 1901-49.00	6.562	0.011	0.029	-0.001	6.858	104.50	45.16	1.38	0.003696	± 0.000004	0.058	4.98E-16	0.35	1.0006	0.0018
S10	2664-03H	SAP 1901-49.00	6.585	0.013	0.000	0.000	6.729	102.20	44.32	1.87	0.003696	± 0.000004	0.039	3.33E-16	0.45	1.0006	0.0018
S10	2664-03I	SAP 1901-49.00	19.646	0.009	0.029	-0.004	20.805	105.90	133.65	3.50	0.003696	± 0.000004	0.063	5.38E-16	0.99	1.0006	0.0018
S10	2664-03J	SAP 1901-49.00	45.669	0.007	0.007	0.013	41.738	91.40	258.82	10.10	0.003696	± 0.000004	0.057	4.85E-16	2.47	1.0006	0.0018
S11	2658-01A	SAP 1601-67.00	11.757	0.014	0.022	0.021	5.590	47.50	36.89	1.61	0.003696	± 0.000004	0.153	1.33E-15	0.10	1.0013	0.0018
S11	2658-01B	SAP 1601-67.00	6.842	0.013	0.019	0.000	6.753	98.70	44.47	0.51	0.003696	± 0.000004	0.221	1.92E-15	0.20	1.0013	0.0018
S11	2658-01C	SAP 1601-67.00	6.772	0.013	0.017	0.000	6.825	100.80	44.94	0.39	0.003696	± 0.000004	0.282	2.45E-15	0.22	1.0013	0.0018
S11	2658-01D	SAP 1601-67.00	6.705	0.011	0.018	0.000	6.661	99.40	43.88	0.32	0.003696	± 0.000004	0.324	2.82E-15	0.25	1.0013	0.0018
S11	2658-01E	SAP 1601-67.00	6.763	0.012	0.014	0.000	6.844	101.20	45.06	0.34	0.003696	± 0.000004	0.326	2.84E-15	0.27	1.0013	0.0018
S11	2658-01F	SAP 1601-67.00	6.823	0.012	0.018	0.000	6.838	100.20	45.03	0.34	0.003696	± 0.000004	0.325	2.83E-15	0.30	1.0013	0.0018
S11	2658-01G	SAP 1601-67.00	6.877	0.012	0.017	0.000	6.942	101.00	45.70	0.32	0.003696	± 0.000004	0.382	3.33E-15	0.35	1.0013	0.0018
S11	2658-01H	SAP 1601-67.00	6.896	0.012	0.017	0.000	6.913	100.30	45.52	0.35	0.003696	± 0.000004	0.338	2.94E-15	0.45	1.0013	0.0018
S11	2658-01I	SAP 1601-67.00	12.496	0.012	0.025	0.003	11.544	92.40	75.37	0.93	0.003696	± 0.000004	0.240	2.09E-15	0.99	1.0013	0.0018
S11	2658-01J	SAP 1601-67.00	11.047	0.010	0.002	0.001	10.897	98.60	71.23	2.93	0.003696	± 0.000004	0.048	4.09E-16	2.47	1.0013	0.0018

Appendix (Continued)

Sample	Gain ID#	Drill Hole - Depth	⁴⁰ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar	Age (Ma)	± (Ma)	J	% ⁴⁰ Ar	⁴⁰ Ar (Moles)	Laser Power (W)	⁴⁰ Ar/ ³⁶ Ar Discr.	±	
S11	2658-02A	SAP 1601-67.00	23.742	0.022	0.029	0.060	5.958	25.10	39.29	2.16	0.003696	± 0.000004	0.371	3.23E-15	0.10	1.0013	0.0018
S11	2658-02B	SAP 1601-67.00	7.024	0.012	0.064	0.001	6.632	94.40	43.69	0.55	0.003696	± 0.000004	0.208	1.81E-15	0.20	1.0013	0.0018
S11	2658-02C	SAP 1601-67.00	6.867	0.012	0.033	0.000	6.879	100.20	45.30	0.38	0.003696	± 0.000004	0.295	2.58E-15	0.22	1.0013	0.0018
S11	2658-02D	SAP 1601-67.00	6.762	0.012	0.040	0.000	6.637	98.20	43.72	0.31	0.003696	± 0.000004	0.367	3.21E-15	0.25	1.0013	0.0018
S11	2658-02E	SAP 1601-67.00	6.701	0.012	0.043	0.000	6.738	100.60	44.38	0.39	0.003696	± 0.000004	0.277	2.40E-15	0.27	1.0013	0.0018
S11	2658-02F	SAP 1601-67.00	6.744	0.011	0.039	0.000	6.690	99.20	44.06	0.26	0.003696	± 0.000004	0.435	3.79E-15	0.30	1.0013	0.0018
S11	2658-02G	SAP 1601-67.00	6.775	0.012	0.045	0.000	6.713	99.10	44.22	0.23	0.003696	± 0.000004	0.532	4.62E-15	0.35	1.0013	0.0018
S11	2658-02H	SAP 1601-67.00	6.726	0.012	0.089	0.000	6.667	99.10	43.91	0.54	0.003696	± 0.000004	0.191	1.67E-15	0.45	1.0013	0.0018
S11	2658-02I	SAP 1601-67.00	11.496	0.014	0.047	0.003	10.474	91.10	68.52	1.00	0.003696	± 0.000004	0.165	1.43E-15	0.99	1.0013	0.0018
S11	2658-02J	SAP 1601-67.00	15.991	0.018	0.000	0.026	8.392	52.50	55.11	6.46	0.003696	± 0.000004	0.033	2.86E-16	2.47	1.0013	0.0018
S11	2658-03A	SAP 1601-67.00	11.779	0.016	0.037	0.019	6.177	52.40	40.72	1.56	0.003696	± 0.000004	0.159	1.38E-15	0.10	1.0013	0.0018
S11	2658-03B	SAP 1601-67.00	7.047	0.013	0.024	0.001	6.818	96.80	44.90	0.43	0.003696	± 0.000004	0.254	2.22E-15	0.20	1.0013	0.0018
S11	2658-03C	SAP 1601-67.00	6.766	0.012	0.009	0.000	6.697	99.00	44.11	0.36	0.003696	± 0.000004	0.307	2.68E-15	0.22	1.0013	0.0018
S11	2658-03D	SAP 1601-67.00	6.745	0.012	0.016	0.000	6.767	100.30	44.57	0.38	0.003696	± 0.000004	0.280	2.43E-15	0.25	1.0013	0.0018
S11	2658-03E	SAP 1601-67.00	6.686	0.011	0.026	0.000	6.667	99.70	43.92	0.46	0.003696	± 0.000004	0.210	1.83E-15	0.27	1.0013	0.0018
S11	2658-03F	SAP 1601-67.00	6.736	0.011	0.000	-0.001	7.010	104.10	46.15	0.79	0.003696	± 0.000004	0.121	1.05E-15	0.30	1.0013	0.0018
S11	2658-03G	SAP 1601-67.00	6.731	0.012	0.000	-0.001	6.998	104.00	46.07	0.74	0.003696	± 0.000004	0.122	1.07E-15	0.35	1.0013	0.0018
S11	2658-03H	SAP 1601-67.00	6.809	0.011	0.000	0.001	6.636	97.50	43.72	1.04	0.003696	± 0.000004	0.089	7.74E-16	0.45	1.0013	0.0018
S11	2658-03I	SAP 1601-67.00	17.183	0.012	0.000	0.005	15.827	92.10	102.56	2.19	0.003696	± 0.000004	0.112	9.76E-16	0.99	1.0013	0.0018
S11	2658-03J	SAP 1601-67.00	13.720	0.011	0.000	0.023	7.058	51.40	46.46	11.90	0.003696	± 0.000004	0.014	1.23E-16	2.47	1.0013	0.0018
S12	2659-01A	SAP 1601-68.00	17.810	0.018	0.000	0.045	4.648	26.10	30.73	2.45	0.003696	± 0.000004	0.163	1.42E-15	0.10	1.0013	0.0018
S12	2659-01B	SAP 1601-68.00	7.447	0.012	0.006	0.004	6.377	85.60	42.03	0.51	0.003696	± 0.000004	0.286	2.50E-15	0.20	1.0013	0.0018
S12	2659-01C	SAP 1601-68.00	6.670	0.010	0.000	0.000	6.558	98.30	43.21	0.64	0.003696	± 0.000004	0.164	1.44E-15	0.22	1.0013	0.0018
S12	2659-01D	SAP 1601-68.00	6.942	0.012	0.009	0.001	6.786	97.80	44.69	0.70	0.003696	± 0.000004	0.160	1.43E-15	0.25	1.0013	0.0018
S12	2659-01E	SAP 1601-68.00	7.242	0.012	0.000	0.001	6.891	95.20	45.38	0.62	0.003696	± 0.000004	0.201	1.79E-15	0.27	1.0013	0.0018
S12	2659-01F	SAP 1601-68.00	7.060	0.012	0.002	0.001	6.866	97.30	45.21	0.30	0.003696	± 0.000004	0.462	4.06E-15	0.30	1.0013	0.0018
S12	2659-01G	SAP 1601-68.00	6.646	0.012	0.015	0.000	6.579	99.00	43.34	0.14	0.003696	± 0.000004	1.284	1.12E-14	0.35	1.0013	0.0018
S12	2659-01H	SAP 1601-68.00	6.472	0.012	0.017	0.000	6.426	99.30	42.34	0.12	0.003696	± 0.000004	2.570	2.24E-14	0.45	1.0013	0.0018
S12	2659-01I	SAP 1601-68.00	6.551	0.012	0.019	0.001	6.303	96.20	41.55	0.16	0.003696	± 0.000004	2.399	2.10E-14	0.99	1.0013	0.0018
S12	2659-01J	SAP 1601-68.00	8.284	0.012	0.000	0.003	7.250	87.50	47.71	0.71	0.003696	± 0.000004	0.229	2.05E-15	2.47	1.0013	0.0018
S12	2659-02A	SAP 1601-68.00	20.555	0.022	0.000	0.047	6.626	32.20	43.65	3.43	0.003696	± 0.000004	0.116	1.01E-15	0.10	1.0013	0.0018
S12	2659-02B	SAP 1601-68.00	7.990	0.013	0.015	0.006	6.198	77.60	40.86	0.58	0.003696	± 0.000004	0.266	2.33E-15	0.20	1.0013	0.0018
S12	2659-02C	SAP 1601-68.00	6.321	0.011	0.011	-0.002	6.900	109.20	45.43	0.81	0.003696	± 0.000004	0.116	1.02E-15	0.22	1.0013	0.0018
S12	2659-02D	SAP 1601-68.00	6.428	0.013	0.023	-0.001	6.798	105.80	44.77	0.81	0.003696	± 0.000004	0.110	9.68E-16	0.25	1.0013	0.0018
S12	2659-02E	SAP 1601-68.00	6.392	0.012	0.000	-0.001	6.705	104.90	44.16	0.82	0.003696	± 0.000004	0.110	9.77E-16	0.27	1.0013	0.0018
S12	2659-02F	SAP 1601-68.00	6.523	0.012	0.009	-0.001	6.835	104.80	45.01	0.79	0.003696	± 0.000004	0.122	1.07E-15	0.30	1.0013	0.0018
S12	2659-02G	SAP 1601-68.00	6.695	0.012	0.000	0.000	6.796	101.50	44.76	0.46	0.003696	± 0.000004	0.235	2.09E-15	0.35	1.0013	0.0018
S12	2659-02H	SAP 1601-68.00	6.731	0.012	0.009	0.000	6.695	99.50	44.10	0.29	0.003696	± 0.000004	0.443	3.87E-15	0.40	1.0013	0.0018
S12	2659-02I	SAP 1601-68.00	6.588	0.012	0.008	0.000	6.581	99.90	43.36	0.16	0.003696	± 0.000004	1.066	9.32E-15	0.45	1.0013	0.0018
S12	2659-02J	SAP 1601-68.00	6.497	0.012	0.019	0.000	6.453	99.30	42.53	0.13	0.003696	± 0.000004	3.194	2.78E-14	0.59	1.0013	0.0018
S12	2659-02K	SAP 1601-68.00	6.561	0.012	0.022	0.000	6.476	98.70	42.67	0.15	0.003696	± 0.000004	1.382	1.21E-14	0.79	1.0013	0.0018
S12	2659-02L	SAP 1601-68.00	6.718	0.012	0.000	0.001	6.530	97.20	43.02	0.36	0.003696	± 0.000004	0.338	2.98E-15	0.99	1.0013	0.0018
S12	2659-02M	SAP 1601-68.00	7.873	0.012	0.000	0.005	6.341	80.60	41.79	0.65	0.003696	± 0.000004	0.232	2.05E-15	2.47	1.0013	0.0018
S12	2659-03A	SAP 1601-68.00	8.998	0.014	0.028	0.010	6.037	67.10	39.81	1.01	0.003696	± 0.000004	0.170	1.47E-15	0.10	1.0013	0.0018
S12	2659-03B	SAP 1601-68.00	6.560	0.012	0.010	0.001	6.400	97.60	42.18	0.34	0.003696	± 0.000004	0.301	2.63E-15	0.20	1.0013	0.0018
S12	2659-03C	SAP 1601-68.00	6.578	0.012	0.020	0.000	6.533	99.30	43.04	0.13	0.003696	± 0.000004	1.915	1.67E-14	0.30	1.0013	0.0018
S12	2659-03D	SAP 1601-68.00	6.592	0.012	0.024	0.000	6.545	99.30	43.12	0.18	0.003696	± 0.000004	0.869	7.58E-15	0.35	1.0013	0.0018

Appendix I (Continued)

Appendix (Continued)																	
Sample	Gain ID#	Drill Hole - Depth	⁴⁰ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar	Age (Ma)	± (Ma)	J	% ⁴⁰ Ar	⁴⁰ Ar (Moles)	Laser Power (W)	⁴⁰ Ar/ ³⁶ Ar Discr.	±	
S12	2659-03E	SAP 1601-68.00	6.488	0.012	0.028	0.000	6.429	99.10	42.36	0.41	0.003696	± 0.000004	0.299	2.62E-15	0.40	1.0013	0.0018
S12	2659-03F	SAP 1601-68.00	6.317	0.012	0.050	0.001	6.024	95.40	39.73	0.81	0.003696	± 0.000004	0.115	9.99E-16	0.45	1.0013	0.0018
S12	2659-03G	SAP 1601-68.00	6.312	0.015	0.104	0.001	5.914	93.70	39.01	1.83	0.003696	± 0.000004	0.047	4.11E-16	0.50	1.0013	0.0018
S12	2659-03H	SAP 1601-68.00	6.876	0.017	0.066	0.005	5.549	80.70	36.63	4.59	0.003696	± 0.000004	0.019	1.66E-16	0.54	1.0013	0.0018
S12	2659-03I	SAP 1601-68.00	9.220	0.011	0.073	0.004	8.151	88.40	53.55	4.82	0.003696	± 0.000004	0.024	2.03E-16	0.64	1.0013	0.0018
S12	2659-03J	SAP 1601-68.00	9.055	0.012	0.033	-0.003	10.078	111.30	65.98	4.67	0.003696	± 0.000004	0.023	1.99E-16	0.79	1.0013	0.0018
S12	2659-03K	SAP 1601-68.00	8.097	0.020	0.046	0.006	6.369	78.70	41.97	7.82	0.003696	± 0.000004	0.012	1.04E-16	0.99	1.0013	0.0018
S12	2659-03L	SAP 1601-68.00	11.124	0.013	0.057	0.023	4.236	38.10	28.03	4.06	0.003696	± 0.000004	0.039	3.36E-16	1.99	1.0013	0.0018
S12	2659-03M	SAP 1601-68.00	13.960	0.039	0.888	0.058	-2.988	-21.40	-20.04	29.17	0.003696	± 0.000004	0.006	4.98E-17	2.97	1.0013	0.0018
S13	2660-01A	SAP 1601-69.00	13.009	0.016	0.000	0.027	5.083	39.10	33.58	3.06	0.003696	± 0.000004	0.063	5.58E-16	0.10	1.0016	0.0018
S13	2660-01B	SAP 1601-69.00	10.342	0.015	0.038	0.016	5.469	52.90	36.10	1.00	0.003696	± 0.000004	0.243	2.12E-15	0.20	1.0016	0.0018
S13	2660-01C	SAP 1601-69.00	11.158	0.016	0.059	0.020	5.216	46.80	34.45	1.89	0.003696	± 0.000004	0.106	9.42E-16	0.22	1.0016	0.0018
S13	2660-01D	SAP 1601-69.00	12.947	0.018	0.027	0.029	4.475	34.60	29.59	2.96	0.003696	± 0.000004	0.062	5.54E-16	0.25	1.0016	0.0018
S13	2660-01E	SAP 1601-69.00	14.562	0.019	0.057	0.032	5.133	35.20	33.90	4.01	0.003696	± 0.000004	0.051	4.69E-16	0.27	1.0016	0.0018
S13	2660-01F	SAP 1601-69.00	13.314	0.018	0.043	0.023	6.509	48.90	42.88	3.72	0.003696	± 0.000004	0.052	4.78E-16	0.30	1.0016	0.0018
S13	2660-01G	SAP 1601-69.00	9.172	0.013	0.011	0.009	6.510	71.00	42.90	1.24	0.003696	± 0.000004	0.127	1.14E-15	0.35	1.0016	0.0018
S13	2660-01H	SAP 1601-69.00	7.737	0.013	0.029	0.003	6.836	88.40	45.02	0.24	0.003696	± 0.000004	0.880	7.68E-15	0.45	1.0016	0.0018
S13	2660-01I	SAP 1601-69.00	7.293	0.012	0.063	0.003	6.307	86.50	41.57	0.18	0.003696	± 0.000004	1.357	1.18E-14	0.99	1.0016	0.0018
S13	2660-01J	SAP 1601-69.00	13.350	0.016	0.105	0.023	6.661	49.90	43.88	1.99	0.003696	± 0.000004	0.146	1.32E-15	2.47	1.0016	0.0018
S13	2660-02A	SAP 1601-69.00	29.093	0.014	0.000	0.051	14.125	48.60	91.81	11.70	0.003696	± 0.000004	0.035	3.08E-16	0.10	1.0016	0.0018
S13	2660-02B	SAP 1601-69.00	12.607	0.015	0.000	0.016	7.864	62.40	51.69	3.35	0.003696	± 0.000004	0.053	4.60E-16	0.20	1.0016	0.0018
S13	2660-02C	SAP 1601-69.00	16.588	0.014	0.000	0.024	9.402	56.70	61.63	7.67	0.003696	± 0.000004	0.032	2.77E-16	0.22	1.0016	0.0018
S13	2660-02D	SAP 1601-69.00	21.198	0.014	0.000	0.048	6.907	32.60	45.48	7.33	0.003696	± 0.000004	0.041	3.57E-16	0.25	1.0016	0.0018
S13	2660-02E	SAP 1601-69.00	14.032	0.014	0.000	0.015	9.484	67.60	62.16	2.95	0.003696	± 0.000004	0.062	5.34E-16	0.27	1.0016	0.0018
S13	2660-02F	SAP 1601-69.00	11.294	0.011	0.000	0.003	10.391	92.00	67.99	2.20	0.003696	± 0.000004	0.070	6.00E-16	0.30	1.0016	0.0018
S13	2660-02G	SAP 1601-69.00	9.756	0.012	0.000	0.004	8.680	89.00	56.97	1.50	0.003696	± 0.000004	0.087	7.45E-16	0.35	1.0016	0.0018
S13	2660-02H	SAP 1601-69.00	8.302	0.013	0.000	0.002	7.653	92.20	50.32	1.00	0.003696	± 0.000004	0.120	1.04E-15	0.45	1.0016	0.0018
S13	2660-02I	SAP 1601-69.00	8.129	0.013	0.046	0.007	6.059	74.50	39.96	1.71	0.003696	± 0.000004	0.067	5.82E-16	0.54	1.0016	0.0018
S13	2660-02J	SAP 1601-69.00	9.990	0.015	0.153	0.017	4.848	48.50	32.04	1.62	0.003696	± 0.000004	0.104	8.95E-16	0.69	1.0016	0.0018
S13	2660-02K	SAP 1601-69.00	18.424	0.017	0.081	0.020	12.450	67.60	81.16	2.78	0.003696	± 0.000004	0.130	1.13E-15	0.99	1.0016	0.0018
S13	2660-02L	SAP 1601-69.00	96.636	0.025	0.000	0.090	70.099	72.50	415.63	8.86	0.003696	± 0.000004	0.240	2.09E-15	2.47	1.0016	0.0018
S13	2660-03A	SAP 1601-69.00	20.976	0.019	0.202	0.040	9.061	43.20	59.43	10.59	0.003696	± 0.000004	0.026	2.29E-16	0.10	1.0016	0.0018
S13	2660-03B	SAP 1601-69.00	8.661	0.007	0.183	-0.006	10.414	120.20	68.14	10.72	0.003696	± 0.000004	0.010	8.36E-17	0.20	1.0016	0.0018
S13	2660-03C	SAP 1601-69.00	13.121	0.020	0.000	0.008	10.669	81.30	69.78	15.67	0.003696	± 0.000004	0.011	9.38E-17	0.22	1.0016	0.0018
S13	2660-03D	SAP 1601-69.00	16.830	0.018	0.638	0.043	4.116	24.40	27.24	9.54	0.003696	± 0.000004	0.023	1.96E-16	0.25	1.0016	0.0018
S13	2660-03E	SAP 1601-69.00	11.478	0.012	0.057	-0.001	11.799	102.80	77.00	4.96	0.003696	± 0.000004	0.030	2.57E-16	0.27	1.0016	0.0018
S13	2660-03F	SAP 1601-69.00	9.427	0.009	0.121	-0.005	10.991	116.60	71.84	4.65	0.003696	± 0.000004	0.025	2.15E-16	0.30	1.0016	0.0018
S13	2660-03G	SAP 1601-69.00	8.430	0.011	0.076	-0.001	8.776	104.10	57.59	3.01	0.003696	± 0.000004	0.035	3.05E-16	0.35	1.0016	0.0018
S13	2660-03H	SAP 1601-69.00	7.879	0.013	0.093	0.004	6.628	84.10	43.66	2.48	0.003696	± 0.000004	0.038	3.28E-16	0.45	1.0016	0.0018
S13	2660-03I	SAP 1601-69.00	8.998	0.016	0.355	0.010	6.090	67.70	40.16	3.21	0.003696	± 0.000004	0.040	3.51E-16	0.54	1.0016	0.0018
S13	2660-03J	SAP 1601-69.00	10.660	0.017	0.358	0.016	6.108	57.30	40.28	4.29	0.003696	± 0.000004	0.033	2.89E-16	0.69	1.0016	0.0018
S13	2660-03K	SAP 1601-69.00	18.077	0.020	0.128	0.011	14.799	81.90	96.07	6.46	0.003696	± 0.000004	0.033	2.84E-16	0.99	1.0016	0.0018
S13	2660-03L	SAP 1601-69.00	53.199	0.048	1.407	0.105	22.211	41.70	142.34	29.60	0.003696	± 0.000004	0.024	2.05E-16	2.47	1.0016	0.0018
S14	2656-01A	SAP 2499-83.10	9.003	0.014	0.007	0.014	4.783	53.10	31.61	0.93	0.003696	± 0.000004	0.214	1.86E-15	0.10	1.0025	0.0018
S14	2656-01B	SAP 2499-83.10	6.848	0.012	0.002	0.002	6.309	92.10	41.59	0.26	0.003696	± 0.000004	0.488	4.25E-15	0.20	1.0025	0.0018
S14	2656-01C	SAP 2499-83.10	7.121	0.012	0.000	0.001	6.956	97.70	45.79	0.22	0.003696	± 0.000004	0.668	5.83E-15	0.22	1.0025	0.0018
S14	2656-01D	SAP 2499-83.10	7.165	0.012	0.000	0.000	7.129	99.50	46.92	0.21	0.003696	± 0.000004	0.738	6.47E-15	0.25	1.0025	0.0018

AppendixI (Continued)

Sample	Gain ID#	Drill Hole - Depth	⁴⁰ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar	Age (Ma)	± (Ma)	J	% ⁴⁰ Ar	⁴⁰ Ar (Moles)	Laser Power (W)	⁴⁰ Ar/ ³⁶ Ar Discr.	±	
S14	2656-01E	SAP 2499-83.10	7.273	0.012	0.000	0.000	7.273	100.00	47.85	0.24	0.003696	± 0.000004	0.601	5.25E-15	0.27	1.0025	0.0018
S14	2656-01F	SAP 2499-83.10	7.258	0.012	0.000	0.000	7.218	99.50	47.50	0.29	0.003696	± 0.000004	0.424	3.68E-15	0.30	1.0025	0.0018
S14	2656-01G	SAP 2499-83.10	7.243	0.012	0.000	0.000	7.336	101.30	48.26	0.34	0.003696	± 0.000004	0.356	3.13E-15	0.35	1.0025	0.0018
S14	2656-01H	SAP 2499-83.10	7.289	0.011	0.000	0.000	7.299	100.10	48.02	0.42	0.003696	± 0.000004	0.255	2.24E-15	0.45	1.0025	0.0018
S14	2656-01I	SAP 2499-83.10	6.857	0.012	0.006	0.000	6.991	102.00	46.02	0.41	0.003696	± 0.000004	0.288	2.51E-15	0.99	1.0025	0.0018
S14	2656-01J	SAP 2499-83.10	7.506	0.013	0.000	0.000	7.405	98.70	48.71	0.76	0.003696	± 0.000004	0.144	1.26E-15	2.47	1.0025	0.0018
S14	2656-02A	SAP 2499-83.10	10.835	0.018	0.000	0.019	5.133	47.40	33.90	1.64	0.003696	± 0.000004	0.139	1.21E-15	0.10	1.0025	0.0018
S14	2656-02B	SAP 2499-83.10	8.070	0.013	0.001	0.007	5.864	72.70	38.68	0.55	0.003696	± 0.000004	0.316	2.75E-15	0.20	1.0025	0.0018
S14	2656-02C	SAP 2499-83.10	7.182	0.012	0.021	0.001	6.804	94.70	44.81	0.64	0.003696	± 0.000004	0.176	1.53E-15	0.22	1.0025	0.0018
S14	2656-02D	SAP 2499-83.10	7.380	0.012	0.015	0.000	7.296	98.90	48.01	0.54	0.003696	± 0.000004	0.206	1.80E-15	0.25	1.0025	0.0018
S14	2656-02E	SAP 2499-83.10	7.310	0.012	0.011	0.000	7.381	101.00	48.56	0.46	0.003696	± 0.000004	0.257	2.25E-15	0.27	1.0025	0.0018
S14	2656-02F	SAP 2499-83.10	7.291	0.012	0.005	0.000	7.160	98.20	47.12	0.37	0.003696	± 0.000004	0.329	2.88E-15	0.30	1.0025	0.0018
S14	2656-02G	SAP 2499-83.10	7.267	0.013	0.013	0.001	7.081	97.50	46.61	0.22	0.003696	± 0.000004	0.636	5.56E-15	0.35	1.0025	0.0018
S14	2656-02H	SAP 2499-83.10	7.268	0.012	0.005	0.000	7.138	98.20	46.98	0.20	0.003696	± 0.000004	0.922	8.02E-15	0.45	1.0025	0.0018
S14	2656-02I	SAP 2499-83.10	7.385	0.012	0.002	0.001	7.213	97.70	47.46	0.26	0.003696	± 0.000004	0.584	5.08E-15	0.99	1.0025	0.0018
S14	2656-02J	SAP 2499-83.10	7.703	0.013	0.013	0.002	7.134	92.60	46.95	0.62	0.003696	± 0.000004	0.214	1.88E-15	2.47	1.0025	0.0018
S14	2656-03A	SAP 2499-83.10	10.181	0.015	0.001	0.019	4.526	44.50	29.93	1.23	0.003696	± 0.000004	0.197	1.72E-15	0.10	1.0025	0.0018
S14	2656-03B	SAP 2499-83.10	7.555	0.013	0.004	0.006	5.766	76.30	38.04	0.41	0.003696	± 0.000004	0.418	3.66E-15	0.20	1.0025	0.0018
S14	2656-03C	SAP 2499-83.10	6.982	0.012	0.023	0.003	6.196	88.80	40.85	0.80	0.003696	± 0.000004	0.146	1.27E-15	0.22	1.0025	0.0018
S14	2656-03D	SAP 2499-83.10	6.906	0.011	0.004	0.000	7.018	101.60	46.20	0.73	0.003696	± 0.000004	0.132	1.15E-15	0.25	1.0025	0.0018
S14	2656-03E	SAP 2499-83.10	7.054	0.011	0.027	0.000	6.969	98.80	45.88	0.64	0.003696	± 0.000004	0.171	1.49E-15	0.27	1.0013	0.0018
S14	2656-03F	SAP 2499-83.10	7.106	0.012	0.018	0.000	7.075	99.60	46.57	0.42	0.003696	± 0.000004	0.296	2.59E-15	0.30	1.0013	0.0018
S14	2656-03G	SAP 2499-83.10	7.166	0.011	0.000	0.001	6.993	97.60	46.03	0.24	0.003696	± 0.000004	0.585	5.12E-15	0.35	1.0013	0.0018
S14	2656-03H	SAP 2499-83.10	7.284	0.012	0.008	0.001	7.099	97.50	46.72	0.18	0.003696	± 0.000004	1.523	1.33E-14	0.45	1.0013	0.0018
S14	2656-03I	SAP 2499-83.10	10.369	0.013	0.011	0.003	9.525	91.90	62.42	0.25	0.003696	± 0.000004	1.486	1.30E-14	0.99	1.0013	0.0018
S14	2656-03J	SAP 2499-83.10	12.929	0.011	0.023	0.007	10.803	83.60	70.64	0.72	0.003696	± 0.000004	0.384	3.35E-15	2.47	1.0013	0.0018
S15	2666-01A	SAP 0999-75.70	31.208	0.033	0.000	0.042	18.832	60.30	121.39	10.32	0.003696	± 0.000004	0.043	3.77E-16	0.10	1.0012	0.0017
S15	2666-01B	SAP 0999-75.70	8.326	0.011	0.000	0.004	7.179	86.20	47.24	2.60	0.003696	± 0.000004	0.041	3.54E-16	0.20	1.0012	0.0017
S15	2666-01C	SAP 0999-75.70	7.976	0.017	0.094	0.003	7.208	90.40	47.43	5.73	0.003696	± 0.000004	0.016	1.35E-16	0.22	1.0012	0.0017
S15	2666-01D	SAP 0999-75.70	7.817	0.011	0.000	-0.002	8.472	108.40	55.63	7.08	0.003696	± 0.000004	0.013	1.02E-16	0.25	1.0012	0.0017
S15	2666-01E	SAP 0999-75.70	8.603	0.024	0.000	-0.013	12.399	144.10	80.83	10.55	0.003696	± 0.000004	0.009	6.96E-17	0.27	1.0012	0.0017
S15	2666-01F	SAP 0999-75.70	8.750	0.019	0.000	-0.014	12.786	146.10	83.30	11.11	0.003696	± 0.000004	0.009	6.57E-17	0.30	1.0012	0.0017
S15	2666-01G	SAP 0999-75.70	9.866	0.018	0.000	-0.004	10.916	110.60	71.35	9.22	0.003696	± 0.000004	0.012	8.69E-17	0.35	1.0012	0.0017
S15	2666-01H	SAP 0999-75.70	22.350	0.019	0.141	0.005	20.969	93.80	134.66	25.47	0.003696	± 0.000004	0.010	6.82E-17	0.45	1.0012	0.0017
S15	2666-01I	SAP 0999-75.70	69.514	0.023	2.177	0.006	68.098	97.80	405.00	12.50	0.003696	± 0.000004	0.059	4.93E-16	0.99	1.0012	0.0017
S15	2666-01J	SAP 0999-75.70	208.084	0.016	1.806	-0.063	227.044	109.00	1099.24	57.02	0.003696	± 0.000004	0.035	2.83E-16	2.47	1.0012	0.0017
S15	2666-02A	SAP 0999-75.70	19.900	0.020	0.115	0.046	6.362	32.00	41.93	3.24	0.003696	± 0.000004	0.147	1.28E-15	0.10	1.0012	0.0017
S15	2666-02B	SAP 0999-75.70	8.921	0.013	0.091	0.002	8.203	92.00	53.88	0.59	0.003696	± 0.000004	0.244	2.14E-15	0.20	1.0012	0.0017
S15	2666-02C	SAP 0999-75.70	8.724	0.012	0.083	0.002	8.073	92.50	53.04	0.86	0.003696	± 0.000004	0.143	1.24E-15	0.22	1.0012	0.0017
S15	2666-02D	SAP 0999-75.70	7.722	0.012	0.120	0.002	7.054	91.30	46.43	1.27	0.003696	± 0.000004	0.078	6.76E-16	0.25	1.0012	0.0017
S15	2666-02E	SAP 0999-75.70	7.121	0.009	0.024	0.002	6.666	93.60	43.91	2.17	0.003696	± 0.000004	0.040	3.54E-16	0.27	1.0012	0.0017
S15	2666-02F	SAP 0999-75.70	6.676	0.010	0.016	0.003	5.661	84.80	37.35	2.76	0.003696	± 0.000004	0.029	2.59E-16	0.30	1.0012	0.0017
S15	2666-02G	SAP 0999-75.70	6.048	0.012	0.000	0.001	5.865	97.00	38.69	2.30	0.003696	± 0.000004	0.031	2.73E-16	0.35	1.0012	0.0017
S15	2666-02H	SAP 0999-75.70	5.823	0.009	0.101	-0.001	6.057	104.00	39.94	2.64	0.003696	± 0.000004	0.025	2.22E-16	0.45	1.0012	0.0017
S15	2666-02I	SAP 0999-75.70	10.672	0.012	0.066	0.003	9.643	90.40	63.18	2.17	0.003696	± 0.000004	0.056	4.84E-16	0.99	1.0012	0.0017
S15	2666-02J	SAP 0999-75.70	14.763	0.004	0.900	0.010	11.738	79.50	76.62	13.93	0.003696	± 0.000004	0.012	1.07E-16	2.47	1.0012	0.0017

Appendix I (Continued)

Sample	Gain ID#	Drill Hole - Depth	⁴⁰ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar	Age (Ma)	± (Ma)	J	% ⁴⁰ Ar	⁴⁰ Ar (Moles)	Laser Power (W)	⁴⁰ Ar/ ³⁶ Ar Discr.	±	
S15	2666-03A	SAP 0999-75.70	8.847	0.014	0.000	0.011	5.509	82.30	36.36	2.80	0.003696	± 0.000004	0.038	3.33E-16	0.10	1.0012	0.0017
S15	2666-03B	SAP 0999-75.70	7.858	0.012	0.014	0.003	6.944	88.40	45.72	1.02	0.003696	± 0.000004	0.097	8.46E-16	0.20	1.0012	0.0017
S15	2666-03C	SAP 0999-75.70	7.450	0.012	0.000	0.000	7.331	98.40	48.23	1.65	0.003696	± 0.000004	0.053	4.67E-16	0.22	1.0012	0.0017
S15	2666-03D	SAP 0999-75.70	7.326	0.011	0.207	0.002	6.853	93.50	45.13	2.25	0.003696	± 0.000004	0.040	3.43E-16	0.25	1.0012	0.0017
S15	2666-03E	SAP 0999-75.70	6.791	0.013	0.000	-0.001	7.143	105.20	47.01	3.43	0.003696	± 0.000004	0.021	1.78E-16	0.27	1.0012	0.0017
S15	2666-03F	SAP 0999-75.70	6.948	0.009	0.000	-0.003	7.745	111.50	50.92	5.70	0.003696	± 0.000004	0.014	1.19E-16	0.30	1.0012	0.0017
S15	2666-03G	SAP 0999-75.70	7.865	0.012	0.000	0.008	5.502	70.00	36.32	5.06	0.003696	± 0.000004	0.018	1.54E-16	0.35	1.0012	0.0017
S15	2666-03H	SAP 0999-75.70	9.396	0.014	0.000	0.011	6.046	64.40	39.87	4.10	0.003696	± 0.000004	0.026	2.19E-16	0.45	1.0012	0.0017
S15	2666-03I	SAP 0999-75.70	9.542	0.012	0.209	0.004	8.295	86.90	54.48	2.14	0.003696	± 0.000004	0.051	4.38E-16	0.99	1.0012	0.0017
S15	2666-03J	SAP 0999-75.70	15.331	0.060	0.495	0.044	2.452	16.00	16.27	29.67	0.003696	± 0.000004	0.006	4.92E-17	2.47	1.0012	0.0017
S16	2667-01A	SAP 3702-60.55	-1.191	-0.057	0.000	0.062	-19.387	%1627.2	-134.14	154.25	0.003696	± 0.000004	0.000	4.32E-18	0.10	1.0012	0.0017
S16	2667-01B	SAP 3702-60.55	23.434	0.029	0.000	0.075	1.253	5.30	8.34	7.45	0.003696	± 0.000004	0.045	4.08E-16	0.20	1.0012	0.0017
S16	2667-01C	SAP 3702-60.55	5.569	0.014	0.000	0.011	2.253	40.50	14.96	5.89	0.003696	± 0.000004	0.013	1.31E-16	0.22	1.0012	0.0017
S16	2667-01D	SAP 3702-60.55	4.522	0.006	0.000	0.007	2.327	51.50	15.45	5.56	0.003696	± 0.000004	0.010	1.14E-16	0.25	1.0012	0.0017
S16	2667-01E	SAP 3702-60.55	6.020	0.010	0.000	0.014	1.957	32.50	13.00	7.09	0.003696	± 0.000004	0.011	1.26E-16	0.27	1.0012	0.0017
S16	2667-01F	SAP 3702-60.55	8.829	0.015	0.000	0.031	-0.205	-2.30	-1.37	6.16	0.003696	± 0.000004	0.018	1.93E-16	0.30	1.0012	0.0017
S16	2667-01G	SAP 3702-60.55	14.179	0.017	0.131	0.040	2.382	16.80	15.81	4.83	0.003696	± 0.000004	0.047	4.51E-16	0.35	1.0012	0.0017
S16	2667-01H	SAP 3702-60.55	10.712	0.014	0.078	0.015	6.231	58.20	41.07	1.02	0.003696	± 0.000004	0.223	2.00E-15	0.45	1.0012	0.0017
S16	2667-01I	SAP 3702-60.55	11.470	0.014	0.086	0.022	4.917	42.90	32.49	0.99	0.003696	± 0.000004	0.302	2.68E-15	0.99	1.0012	0.0017
S16	2667-01J	SAP 3702-60.55	61.359	0.040	0.000	0.188	5.830	9.50	38.46	11.80	0.003696	± 0.000004	0.121	1.11E-15	2.47	1.0012	0.0017
S16	2667-02A	SAP 3702-60.55	843.672	1.169	0.000	2.809	13.626	1.60	88.64	3649.07	0.003696	± 0.000004	0.018	1.54E-16	0.10	1.0012	0.0017
S16	2667-02B	SAP 3702-60.55	407.985	0.411	0.000	1.200	53.408	13.10	325.00	453.45	0.003696	± 0.000004	0.030	2.67E-16	0.20	1.0012	0.0017
S16	2667-02C	SAP 3702-60.55	61.565	0.239	0.000	0.104	30.752	50.00	194.21	271.33	0.003696	± 0.000004	0.003	1.82E-17	0.22	1.0012	0.0017
S16	2667-02D	SAP 3702-60.55	70.826	0.537	0.000	0.639	117.951	-166.5	-1033.03	944.32	0.003696	± 0.000004	0.002	1.44E-17	0.25	1.0012	0.0017
S16	2667-02E	SAP 3702-60.55	66.626	0.195	3.892	0.515	-85.473	-127.9	-684.94	652.29	0.003696	± 0.000004	0.002	1.24E-17	0.27	1.0012	0.0017
S16	2667-02F	SAP 3702-60.55	88.003	0.246	0.000	0.207	26.724	30.40	169.93	349.18	0.003696	± 0.000004	0.003	1.83E-17	0.30	1.0012	0.0017
S16	2667-02G	SAP 3702-60.55	79.060	0.234	0.000	0.376	-32.056	-40.50	-227.51	342.10	0.003696	± 0.000004	0.004	2.14E-17	0.35	1.0012	0.0017
S16	2667-02H	SAP 3702-60.55	145.301	0.057	0.000	0.436	16.410	11.30	106.23	276.10	0.003696	± 0.000004	0.008	5.90E-17	0.45	1.0012	0.0017
S16	2667-02I	SAP 3702-60.55	367.791	0.242	0.000	0.837	120.497	32.80	664.55	256.44	0.003696	± 0.000004	0.030	2.50E-16	0.99	1.0012	0.0017
S16	2667-02J	SAP 3702-60.55	423.218	0.618	9.909	0.752	203.283	47.70	1010.97	539.77	0.003696	± 0.000004	0.014	1.04E-16	2.47	1.0012	0.0017
S16	2667-03A	SAP 3702-60.55	4.364	0.023	0.000	0.004	3.255	74.60	21.58	5.61	0.003696	± 0.000004	0.009	7.91E-17	0.10	1.0012	0.0017
S16	2667-03B	SAP 3702-60.55	5.080	0.014	0.065	0.001	4.838	95.20	31.97	2.91	0.003696	± 0.000004	0.023	1.97E-16	0.20	1.0012	0.0017
S16	2667-03C	SAP 3702-60.55	3.668	0.012	0.000	-0.015	8.075	220.20	53.06	12.57	0.003696	± 0.000004	0.003	2.50E-17	0.22	1.0012	0.0017
S16	2667-03D	SAP 3702-60.55	3.457	0.038	0.350	0.003	2.627	76.00	17.43	15.95	0.003696	± 0.000004	0.003	1.72E-17	0.25	1.0012	0.0017
S16	2667-03E	SAP 3702-60.55	4.085	0.013	0.004	0.005	2.495	61.10	16.56	13.48	0.003696	± 0.000004	0.004	2.41E-17	0.27	1.0012	0.0017
S16	2667-03F	SAP 3702-60.55	4.748	0.030	0.425	-0.006	6.632	139.70	43.69	21.65	0.003696	± 0.000004	0.003	1.43E-17	0.30	1.0012	0.0017
S16	2667-03G	SAP 3702-60.55	4.346	0.021	0.098	-0.007	6.496	149.50	42.80	19.45	0.003696	± 0.000004	0.002	1.23E-17	0.35	1.0012	0.0017
S16	2667-03H	SAP 3702-60.55	11.773	0.097	0.000	-0.058	28.983	246.20	183.59	69.63	0.003696	± 0.000004	0.002	2.64E-18	0.45	1.0012	0.0017
S16	2667-03I	SAP 3702-60.55	9.814	0.020	2.771	0.065	-9.141	-93.00	-62.00	39.33	0.003696	± 0.000004	0.003	2.49E-17	0.99	1.0007	0.0017
S16	2667-03J	SAP 3702-60.55	27.314	-0.044	0.000	-0.081	51.175	187.40	312.53	106.66	0.003696	± 0.000004	0.003	1.78E-17	2.47	1.0007	0.0017
S17	2673-01A	SAP 3702-62.00B	11.961	0.024	0.063	0.036	1.313	11.00	8.80	3.48	0.003722	± 0.000004	0.057	4.97E-16	0.10	1.0014	0.0018
S17	2673-01B	SAP 3702-62.00B	4.145	0.014	0.028	0.009	1.348	32.50	9.03	1.18	0.003722	± 0.000004	0.059	5.09E-16	0.20	1.0014	0.0018
S17	2673-01C	SAP 3702-62.00B	3.303	0.011	0.015	0.002	2.684	81.30	17.94	0.53	0.003722	± 0.000004	0.107	9.32E-16	0.22	1.0014	0.0018
S17	2673-01D	SAP 3702-62.00B	3.149	0.011	0.050	0.001	2.712	86.10	18.12	0.95	0.003722	± 0.000004	0.047	4.12E-16	0.25	1.0014	0.0018
S17	2673-01E	SAP 3702-62.00B	3.034	0.013	0.148	0.001	2.804	92.40	18.73	1.45	0.003722	± 0.000004	0.028	2.43E-16	0.27	1.0014	0.0018
S17	2673-01F	SAP 3702-62.00B	2.967	0.012	0.227	0.006	1.329	44.80	8.90	1.71	0.003722	± 0.000004	0.024	2.04E-16	0.30	1.0014	0.0018
S17	2673-01G	SAP 3702-62.00B	3.206	0.014	0.087	0.007	1.216	37.90	8.15	1.18	0.003722	± 0.000004	0.040	3.49E-16	0.35	1.0014	0.0018

Appendix (Continued)

Sample	Gain ID#	Drill Hole - Depth	⁴⁰ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar	Age (Ma)	± (Ma)	J	% ⁴⁰ Ar	⁴⁰ Ar (Moles)	Laser Power (W)	⁴⁰ Ar/ ³⁶ Ar Discr.	±	
S17	2673-01H	SAP 3702-62.00B	3.530	0.015	0.082	0.009	0.910	25.80	6.10	0.95	0.003722	± 0.000004	0.060	5.21E-16	0.45	1.0014	0.0018
S17	2673-01I	SAP 3702-62.00B	3.328	0.016	0.247	0.010	0.302	9.10	2.02	3.52	0.003722	± 0.000004	0.013	1.07E-16	0.99	1.0014	0.0018
S17	2673-01J	SAP 3702-62.00B	10.483	0.027	1.127	0.043	-2.049	-19.50	-13.81	11.66	0.003722	± 0.000004	0.013	1.01E-16	2.47	1.0014	0.0018
S17	2673-02A	SAP 3702-62.00B	5.653	0.009	0.000	0.012	2.067	36.60	13.82	4.54	0.003722	± 0.000004	0.015	1.34E-16	0.10	1.0014	0.0018
S17	2673-02B	SAP 3702-62.00B	3.426	0.012	0.000	0.002	2.829	82.60	18.90	0.85	0.003722	± 0.000004	0.053	4.63E-16	0.20	1.0014	0.0018
S17	2673-02C	SAP 3702-62.00B	3.335	0.008	0.000	-0.001	3.569	107.00	23.81	1.95	0.003722	± 0.000004	0.019	1.71E-16	0.22	1.0014	0.0018
S17	2673-02D	SAP 3702-62.00B	3.126	0.012	0.000	0.003	2.154	68.90	14.41	3.06	0.003722	± 0.000004	0.012	1.08E-16	0.25	1.0014	0.0018
S17	2673-02E	SAP 3702-62.00B	2.781	0.015	0.014	0.006	1.075	38.70	7.21	4.12	0.003722	± 0.000004	0.008	7.52E-17	0.27	1.0014	0.0018
S17	2673-02F	SAP 3702-62.00B	2.663	0.010	0.173	0.005	1.064	40.00	7.13	5.38	0.003722	± 0.000004	0.006	5.60E-17	0.30	1.0014	0.0018
S17	2673-02G	SAP 3702-62.00B	2.491	0.010	0.097	0.004	1.196	48.00	8.01	5.36	0.003722	± 0.000004	0.006	5.08E-17	0.35	1.0014	0.0018
S17	2673-02H	SAP 3702-62.00B	3.999	0.008	0.000	-0.002	4.532	113.30	30.18	16.75	0.003722	± 0.000004	0.002	2.33E-17	0.45	1.0014	0.0018
S17	2673-02I	SAP 3702-62.00B	3.731	0.012	0.021	-0.006	5.406	144.90	35.94	8.66	0.003722	± 0.000004	0.005	4.54E-17	0.99	1.0014	0.0018
S17	2673-02J	SAP 3702-62.00B	6.764	-0.002	0.000	-0.017	11.701	173.00	76.91	65.67	0.003722	± 0.000004	0.001	1.17E-17	2.47	1.0014	0.0018
S17	2673-03A	SAP 3702-62.00B	28.161	0.032	0.000	0.076	5.612	19.90	37.30	8.49	0.003722	± 0.000004	0.051	4.47E-16	0.10	1.0014	0.0018
S17	2673-03B	SAP 3702-62.00B	6.741	0.014	0.000	0.016	2.036	30.20	13.62	1.88	0.003722	± 0.000004	0.055	4.88E-16	0.20	1.0014	0.0018
S17	2673-03C	SAP 3702-62.00B	2.943	0.013	0.000	0.001	2.566	87.20	17.15	0.70	0.003722	± 0.000004	0.053	4.66E-16	0.22	1.0014	0.0018
S17	2673-03D	SAP 3702-62.00B	2.895	0.012	0.000	0.001	2.561	88.50	17.11	1.00	0.003722	± 0.000004	0.031	2.72E-16	0.25	1.0014	0.0018
S17	2673-03E	SAP 3702-62.00B	3.376	0.013	0.000	0.000	3.448	102.10	23.00	2.22	0.003722	± 0.000004	0.016	1.43E-16	0.27	1.0014	0.0018
S17	2673-03F	SAP 3702-62.00B	4.680	0.013	0.000	0.011	1.503	32.10	10.06	3.38	0.003722	± 0.000004	0.015	1.36E-16	0.30	1.0014	0.0018
S17	2673-03G	SAP 3702-62.00B	4.876	0.016	0.000	0.012	1.382	28.30	9.25	2.10	0.003722	± 0.000004	0.028	2.40E-16	0.35	1.0014	0.0018
S17	2673-03H	SAP 3702-62.00B	3.321	0.012	0.000	0.002	2.729	82.20	18.23	1.68	0.003722	± 0.000004	0.022	1.89E-16	0.45	0.9986	0.0019
S17	2673-03I	SAP 3702-62.00B	3.682	0.014	0.000	0.009	1.080	29.30	7.24	3.11	0.003722	± 0.000004	0.013	1.12E-16	0.99	0.9986	0.0019
S17	2673-03J	SAP 3702-62.00B	18.956	0.040	0.000	0.089	-7.268	-38.30	-49.48	24.27	0.003722	± 0.000004	0.009	7.64E-17	2.47	0.9986	0.0019
S18	2674-01A	SAP 3702-62.50	4.456	0.018	0.000	0.000	4.478	100.50	29.82	16.00	0.003722	± 0.000004	0.003	3.10E-17	0.10	0.9986	0.0019
S18	2674-01B	SAP 3702-62.50	4.688	0.015	0.000	0.010	1.831	39.10	12.25	1.45	0.003722	± 0.000004	0.045	3.98E-16	0.20	0.9986	0.0019
S18	2674-01C	SAP 3702-62.50	2.567	0.012	0.000	0.003	1.643	64.00	11.00	2.04	0.003722	± 0.000004	0.016	1.47E-16	0.22	0.9986	0.0019
S18	2674-01D	SAP 3702-62.50	2.865	0.013	0.000	0.002	2.339	81.70	15.64	2.91	0.003722	± 0.000004	0.012	1.18E-16	0.25	0.9986	0.0019
S18	2674-01E	SAP 3702-62.50	2.999	0.012	0.000	0.000	2.875	95.90	19.21	3.36	0.003722	± 0.000004	0.011	1.06E-16	0.27	0.9986	0.0019
S18	2674-01F	SAP 3702-62.50	3.020	0.013	0.000	0.003	2.271	75.20	15.19	2.55	0.003722	± 0.000004	0.015	1.41E-16	0.30	0.9986	0.0019
S18	2674-01G	SAP 3702-62.50	2.782	0.012	0.000	0.002	2.103	75.60	14.07	0.89	0.003722	± 0.000004	0.038	3.56E-16	0.35	0.9986	0.0019
S18	2674-01H	SAP 3702-62.50	2.409	0.013	0.000	0.001	2.125	88.20	14.21	0.14	0.003722	± 0.000004	0.264	2.33E-15	0.45	0.9986	0.0019
S18	2674-01I	SAP 3702-62.50	2.807	0.014	0.003	0.003	1.930	68.80	12.91	0.25	0.003722	± 0.000004	0.236	2.07E-15	0.99	0.9986	0.0019
S18	2674-01J	SAP 3702-62.50	7.992	0.014	0.049	0.021	1.828	22.90	12.24	2.24	0.003722	± 0.000004	0.053	4.88E-16	2.47	0.9986	0.0019
S18	2674-02A	SAP 3702-62.50	342.740	0.221	1.480	1.161	-0.367	-0.10	-2.47	110.64	0.003722	± 0.000004	0.190	1.65E-15	0.10	0.9986	0.0019
S18	2674-02B	SAP 3702-62.50	69.491	0.064	0.024	0.231	1.119	1.80	7.50	16.91	0.003722	± 0.000004	0.097	8.46E-16	0.20	0.9986	0.0019
S18	2674-02C	SAP 3702-62.50	91.966	0.057	0.000	0.266	13.426	14.60	87.97	21.33	0.003722	± 0.000004	0.081	7.21E-16	0.25	0.9986	0.0019
S18	2674-02D	SAP 3702-62.50	23.493	0.022	0.223	0.067	3.635	15.50	24.25	5.32	0.003722	± 0.000004	0.083	7.35E-16	0.30	0.9986	0.0019
S18	2674-02E	SAP 3702-62.50	21.525	0.022	0.000	0.057	4.609	21.40	30.69	7.35	0.003722	± 0.000004	0.042	3.76E-16	0.35	0.9986	0.0019
S18	2674-02F	SAP 3702-62.50	28.956	0.023	0.231	0.065	9.735	33.60	64.21	11.37	0.003722	± 0.000004	0.036	3.30E-16	0.40	0.9986	0.0019
S18	2674-02G	SAP 3702-62.50	32.590	0.030	1.175	0.082	8.596	26.40	56.81	15.88	0.003722	± 0.000004	0.029	2.66E-16	0.45	0.9986	0.0019
S18	2674-02H	SAP 3702-62.50	19.091	0.022	0.063	0.042	6.589	34.50	43.71	10.59	0.003722	± 0.000004	0.022	2.09E-16	0.54	0.9986	0.0019
S18	2674-02I	SAP 3702-62.50	25.151	0.022	0.452	0.073	3.753	14.90	25.03	6.89	0.003722	± 0.000004	0.063	5.67E-16	0.99	0.9986	0.0019
S18	2674-02J	SAP 3702-62.50	197.296	0.102	1.742	0.569	29.371	14.90	187.16	82.60	0.003722	± 0.000004	0.051	4.73E-16	2.47	0.9986	0.0019
S18	2674-03A	SAP 3702-62.50	23.984	0.027	0.287	0.071	3.014	12.60	20.13	6.07	0.003722	± 0.000004	0.096	8.42E-16	0.10	0.9986	0.0019
S18	2674-03B	SAP 3702-62.50	8.870	0.016	0.133	0.017	3.874	43.70	25.83	1.61	0.003722	± 0.000004	0.096	8.35E-16	0.20	0.9986	0.0019
S18	2674-03C	SAP 3702-62.50	7.475	0.013	0.092	0.001	7.050	94.30	46.73	0.81	0.003722	± 0.000004	0.135	1.17E-15	0.25	0.9986	0.0019

Appendix (Continued)

Sample	Core ID#	Drill Hole - Depth	⁴⁰ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar	Age (Ma)	± (Ma)	J	% ⁴⁰ Ar	⁴⁰ Ar (Moles)	Laser Power (W)	⁴⁰ Ar/ ³⁶ Ar Discr.	±	
S18	2674-03D	SAP 3702-62.50	8.826	0.013	0.142	0.004	7.727	87.50	51.15	1.35	0.003722	± 0.000004	0.081	7.06E-16	0.30	0.9986	0.0019
S18	2674-03E	SAP 3702-62.50	9.358	0.013	0.468	0.007	7.323	78.20	48.51	3.20	0.003722	± 0.000004	0.038	3.28E-16	0.35	0.9986	0.0019
S18	2674-03F	SAP 3702-62.50	8.643	0.011	0.688	0.013	4.740	54.80	31.55	7.18	0.003722	± 0.000004	0.017	1.38E-16	0.40	0.9986	0.0019
S18	2674-03G	SAP 3702-62.50	8.946	0.016	0.736	0.014	4.793	53.60	31.90	8.88	0.003722	± 0.000004	0.013	1.06E-16	0.45	0.9986	0.0019
S18	2674-03H	SAP 3702-62.50	8.168	0.013	0.869	0.012	4.556	55.70	30.33	5.63	0.003722	± 0.000004	0.018	1.48E-16	0.54	0.9986	0.0019
S18	2674-03I	SAP 3702-62.50	10.519	0.011	0.144	0.015	6.082	57.80	40.38	3.84	0.003722	± 0.000004	0.037	3.07E-16	0.99	0.9986	0.0019
S18	2674-03J	SAP 3702-62.50	31.387	0.038	1.327	0.109	-0.692	-2.20	-4.65	34.18	0.003722	± 0.000004	0.013	9.58E-17	2.47	0.9986	0.0019
S19	2676-01A	SAP 5102-120.60	89.612	0.060	0.000	0.230	21.749	24.30	140.43	26.75	0.003722	± 0.000004	0.060	5.30E-16	0.10	0.9986	0.0019
S19	2676-01B	SAP 5102-120.60	46.825	0.036	0.042	0.129	8.613	18.40	56.93	6.47	0.003722	± 0.000004	0.215	1.88E-15	0.20	0.9986	0.0019
S19	2676-01C	SAP 5102-120.60	13.008	0.016	0.253	0.010	10.086	77.50	66.49	3.48	0.003722	± 0.000004	0.044	3.82E-16	0.22	0.9986	0.0019
S19	2676-01D	SAP 5102-120.60	10.173	0.011	0.303	0.006	8.466	83.20	55.97	3.64	0.003722	± 0.000004	0.034	2.94E-16	0.25	0.9986	0.0019
S19	2676-01E	SAP 5102-120.60	10.618	0.015	0.427	0.010	7.744	72.90	51.27	3.80	0.003722	± 0.000004	0.034	2.91E-16	0.27	0.9986	0.0019
S19	2676-01F	SAP 5102-120.60	8.280	0.010	0.171	0.004	7.257	87.60	48.08	3.71	0.003722	± 0.000004	0.029	2.50E-16	0.30	0.9986	0.0019
S19	2676-01G	SAP 5102-120.60	7.244	0.011	0.114	0.003	6.281	86.70	41.69	2.06	0.003722	± 0.000004	0.046	3.99E-16	0.35	0.9986	0.0019
S19	2676-01H	SAP 5102-120.60	7.270	0.015	0.084	0.005	5.824	80.10	38.69	1.82	0.003722	± 0.000004	0.055	4.78E-16	0.45	0.9986	0.0019
S19	2676-01I	SAP 5102-120.60	13.157	0.015	0.084	0.012	9.560	72.70	63.08	2.19	0.003722	± 0.000004	0.085	7.41E-16	0.99	0.9986	0.0019
S19	2676-01J	SAP 5102-120.60	85.606	0.031	0.000	0.134	45.940	53.70	284.77	35.92	0.003722	± 0.000004	0.031	2.69E-16	2.47	0.9986	0.0019
S19	2676-02A	SAP 5102-120.60	78.476	0.054	0.066	0.228	10.989	14.00	72.32	14.02	0.003722	± 0.000004	0.135	1.18E-15	0.10	0.9986	0.0019
S19	2676-02B	SAP 5102-120.60	17.564	0.016	0.176	0.022	11.068	63.00	72.83	3.33	0.003722	± 0.000004	0.083	7.19E-16	0.20	0.9986	0.0019
S19	2676-02C	SAP 5102-120.60	9.229	0.016	0.230	0.005	7.684	83.20	50.87	3.68	0.003722	± 0.000004	0.032	2.83E-16	0.22	0.9986	0.0019
S19	2676-02D	SAP 5102-120.60	7.528	0.015	0.011	0.004	6.403	85.10	42.49	3.88	0.003722	± 0.000004	0.025	2.17E-16	0.25	0.9986	0.0019
S19	2676-02E	SAP 5102-120.60	6.584	0.017	0.189	0.003	5.838	88.70	38.78	4.23	0.003722	± 0.000004	0.021	1.82E-16	0.27	0.9986	0.0019
S19	2676-02F	SAP 5102-120.60	5.976	0.016	0.181	0.002	5.520	92.40	36.69	3.93	0.003722	± 0.000004	0.019	1.69E-16	0.30	0.9986	0.0019
S19	2676-02G	SAP 5102-120.60	6.759	0.011	0.000	0.004	5.658	83.70	37.60	3.69	0.003722	± 0.000004	0.021	1.89E-16	0.35	0.9986	0.0019
S19	2676-02H	SAP 5102-120.60	9.056	0.021	0.219	0.009	6.389	70.50	42.40	4.52	0.003722	± 0.000004	0.024	2.14E-16	0.45	0.9986	0.0019
S19	2676-02I	SAP 5102-120.60	14.520	0.019	0.096	0.004	13.415	92.40	87.90	6.39	0.003722	± 0.000004	0.026	2.33E-16	0.99	0.9986	0.0019
S19	2676-02J	SAP 5102-120.60	50.597	0.027	0.000	0.038	39.344	77.80	246.54	64.47	0.003722	± 0.000004	0.009	7.85E-17	2.47	0.9986	0.0019
S19	2676-03A	SAP 5102-120.60	26.754	0.027	0.010	0.071	5.721	21.40	38.01	4.92	0.003722	± 0.000004	0.090	7.83E-16	0.10	0.9986	0.0019
S19	2676-03B	SAP 5102-120.60	10.452	0.014	0.143	0.007	8.535	81.70	56.42	1.71	0.003722	± 0.000004	0.083	7.21E-16	0.20	0.9986	0.0019
S19	2676-03C	SAP 5102-120.60	8.204	0.012	0.051	0.001	7.908	96.40	52.33	1.30	0.003722	± 0.000004	0.095	8.31E-16	0.25	0.9986	0.0019
S19	2676-03D	SAP 5102-120.60	7.124	0.013	0.105	0.000	7.007	98.40	46.45	1.06	0.003722	± 0.000004	0.082	7.14E-16	0.30	0.9986	0.0019
S19	2676-03E	SAP 5102-120.60	8.041	0.013	0.050	0.002	7.407	92.10	49.06	1.21	0.003722	± 0.000004	0.085	7.44E-16	0.45	0.9986	0.0019
S19	2676-03F	SAP 5102-120.60	11.122	0.014	0.003	0.002	10.643	95.70	70.08	2.84	0.003722	± 0.000004	0.049	4.34E-16	0.99	0.9986	0.0019
S19	2676-03G	SAP 5102-120.60	34.582	0.038	3.302	0.072	13.482	38.90	88.33	36.06	0.003722	± 0.000004	0.010	9.48E-17	2.47	0.9986	0.0019
Sapacado Deposit																	
S20	2679-01A	AN 0802-33.20	16.163	0.015	0.000	0.034	6.195	38.30	41.12	4.04	0.003722	± 0.000004	0.055	4.80E-16	0.10	1.0006	0.0018
S20	2679-01B	AN 0802-33.20	8.935	0.012	0.000	0.006	7.182	80.40	47.59	0.86	0.003722	± 0.000004	0.172	1.50E-15	0.20	1.0006	0.0018
S20	2679-01C	AN 0802-33.20	7.192	0.011	0.107	0.002	6.477	90.10	42.97	1.42	0.003722	± 0.000004	0.068	5.92E-16	0.22	1.0006	0.0018
S20	2679-01D	AN 0802-33.20	5.641	0.011	0.140	-0.006	7.312	129.60	48.44	3.76	0.003722	± 0.000004	0.018	1.58E-16	0.25	1.0006	0.0018
S20	2679-01E	AN 0802-33.20	3.698	0.011	0.000	-0.010	6.545	177.00	43.42	5.91	0.003722	± 0.000004	0.007	6.15E-17	0.27	1.0006	0.0018
S20	2679-01F	AN 0802-33.20	2.674	0.013	0.013	-0.009	5.395	201.80	35.87	4.97	0.003722	± 0.000004	0.006	5.07E-17	0.30	1.0006	0.0018
S20	2679-01G	AN 0802-33.20	2.301	0.016	0.104	0.002	1.644	71.40	11.00	3.85	0.003722	± 0.000004	0.006	5.79E-17	0.35	1.0006	0.0018
S20	2679-01H	AN 0802-33.20	2.364	0.012	0.000	-0.002	3.003	127.10	20.05	2.75	0.003722	± 0.000004	0.010	8.52E-17	0.45	1.0006	0.0018
S20	2679-01I	AN 0802-33.20	26.506	0.015	0.000	0.007	24.534	92.60	157.65	3.76	0.003722	± 0.000004	0.083	7.30E-16	0.99	1.0006	0.0018
S20	2679-01J	AN 0802-33.20	183.880	0.025	0.058	0.048	169.795	92.30	883.62	9.00	0.003722	± 0.000004	0.439	3.83E-15	2.47	1.0006	0.0018
S20	2679-02A	AN 0802-33.20	18.031	0.023	0.122	0.033	8.147	45.20	53.89	4.79	0.003722	± 0.000004	0.054	4.71E-16	0.10	1.0006	0.0018
S20	2679-02B	AN 0802-33.20	9.041	0.011	0.093	0.006	7.169	79.30	47.51	1.18	0.003722	± 0.000004	0.116	1.01E-15	0.20	1.0006	0.0018

Appendix (Continued)

Sample	Core ID#	Drill Hole - Depth	⁴⁰ Ar/ ³⁹ Ar	³⁸ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar	Age (Ma)	± (Ma)	J	% ⁴⁰ Ar	⁴⁰ Ar (Moles)	Laser Power (W)	⁴⁰ Ar/ ³⁶ Ar Discr.	±	
S20	2679-02C	AN 0802-33.20	7.240	0.010	0.075	-0.001	7.485	103.40	49.57	2.30	0.003722	± 0.000004	0.037	3.26E-16	0.22	1.0006	0.0018
S20	2679-02D	AN 0802-33.20	5.929	0.014	0.382	0.008	3.520	59.40	23.48	5.64	0.003722	± 0.000004	0.013	1.12E-16	0.25	1.0006	0.0018
S20	2679-02E	AN 0802-33.20	4.292	0.010	0.224	-0.014	8.376	195.10	55.38	7.70	0.003722	± 0.000004	0.006	5.12E-17	0.27	1.0006	0.0018
S20	2679-02F	AN 0802-33.20	3.089	0.010	0.119	-0.003	4.103	132.80	27.34	7.28	0.003722	± 0.000004	0.005	3.57E-17	0.30	1.0006	0.0018
S20	2679-02G	AN 0802-33.20	3.206	0.015	0.000	-0.008	5.451	170.10	36.24	7.28	0.003722	± 0.000004	0.005	4.03E-17	0.35	0.9988	0.0017
S20	2679-02H	AN 0802-33.20	3.320	0.017	0.000	-0.017	8.260	248.90	54.63	7.50	0.003722	± 0.000004	0.005	3.78E-17	0.45	0.9988	0.0017
S20	2679-02I	AN 0802-33.20	19.630	0.017	0.000	0.001	19.280	98.20	125.02	5.83	0.003722	± 0.000004	0.041	3.57E-16	0.99	0.9988	0.0017
S20	2679-02J	AN 0802-33.20	126.460	0.025	0.000	0.030	117.606	93.00	655.00	10.10	0.003722	± 0.000004	0.186	1.63E-15	2.47	0.9988	0.0017
S20	2679-03A	AN 0802-33.20	12.915	0.016	0.000	0.025	5.451	42.20	36.24	3.35	0.003722	± 0.000004	0.055	4.84E-16	0.10	0.9988	0.0017
S20	2679-03B	AN 0802-33.20	8.438	0.012	0.025	0.005	6.923	82.00	45.89	0.83	0.003722	± 0.000004	0.165	1.44E-15	0.20	0.9988	0.0017
S20	2679-03C	AN 0802-33.20	6.743	0.012	0.000	0.001	6.532	96.90	43.33	1.59	0.003722	± 0.000004	0.052	4.56E-16	0.22	0.9988	0.0017
S20	2679-03D	AN 0802-33.20	4.423	0.018	0.000	0.000	4.281	96.80	28.52	3.84	0.003722	± 0.000004	0.014	1.24E-16	0.25	0.9988	0.0017
S20	2679-03E	AN 0802-33.20	2.983	0.018	0.002	0.000	2.859	95.90	19.10	5.33	0.003722	± 0.000004	0.007	6.06E-17	0.27	0.9988	0.0017
S20	2679-03F	AN 0802-33.20	2.277	0.012	0.198	0.002	1.828	80.30	12.23	5.51	0.003722	± 0.000004	0.005	4.20E-17	0.30	0.9988	0.0017
S20	2679-03G	AN 0802-33.20	2.725	0.012	0.000	-0.003	3.635	133.40	24.24	5.33	0.003722	± 0.000004	0.006	5.47E-17	0.35	0.9988	0.0017
S20	2679-03H	AN 0802-33.20	2.831	0.014	0.085	-0.003	3.770	133.20	25.14	6.90	0.003722	± 0.000004	0.005	4.41E-17	0.45	0.9988	0.0017
S20	2679-03I	AN 0802-33.20	29.312	0.014	0.121	0.004	28.056	95.70	179.19	4.90	0.003722	± 0.000004	0.070	6.10E-16	0.99	0.9988	0.0017
S20	2679-03J	AN 0802-33.20	74.773	0.017	0.000	0.034	64.864	86.70	390.15	7.82	0.003722	± 0.000004	0.157	1.37E-15	2.47	0.9988	0.0017
S21	2680-01A	AN 0802-84.15	8.572	0.014	0.000	0.018	3.213	37.50	21.44	7.90	0.003722	± 0.000004	0.013	1.18E-16	0.10	0.9988	0.0017
S21	2680-01B	AN 0802-84.15	6.682	0.015	0.096	0.010	3.634	54.40	24.24	1.71	0.003722	± 0.000004	0.054	4.76E-16	0.20	0.9988	0.0017
S21	2680-01C	AN 0802-84.15	6.713	0.013	0.177	0.004	5.511	82.10	36.63	1.94	0.003722	± 0.000004	0.045	4.02E-16	0.22	0.9988	0.0017
S21	2680-01D	AN 0802-84.15	8.037	0.013	0.076	0.002	7.540	93.80	49.93	0.99	0.003722	± 0.000004	0.110	9.61E-16	0.25	0.9988	0.0017
S21	2680-01E	AN 0802-84.15	7.599	0.012	0.052	0.000	7.699	101.30	50.97	1.00	0.003722	± 0.000004	0.102	9.03E-16	0.27	0.9988	0.0017
S21	2680-01F	AN 0802-84.15	7.283	0.011	0.061	0.000	7.312	100.40	48.44	1.43	0.003722	± 0.000004	0.066	5.90E-16	0.30	0.9988	0.0017
S21	2680-01G	AN 0802-84.15	7.130	0.012	0.000	-0.002	7.769	109.00	51.43	1.05	0.003722	± 0.000004	0.078	6.93E-16	0.35	0.9988	0.0017
S21	2680-01H	AN 0802-84.15	6.217	0.012	0.106	-0.002	6.781	109.10	44.97	0.97	0.003722	± 0.000004	0.080	7.10E-16	0.45	0.9988	0.0017
S21	2680-01I	AN 0802-84.15	5.328	0.014	0.165	0.004	4.191	78.70	27.92	0.59	0.003722	± 0.000004	0.152	1.34E-15	0.99	0.9988	0.0017
S21	2680-01J	AN 0802-84.15	8.000	0.014	0.218	0.006	6.240	78.00	41.42	3.44	0.003722	± 0.000004	0.032	2.97E-16	2.47	0.9988	0.0017
S21	2680-02A	AN 0802-84.15	10.627	0.015	0.084	0.019	4.876	45.90	32.45	4.24	0.003722	± 0.000004	0.032	2.84E-16	0.10	0.9988	0.0017
S21	2680-02B	AN 0802-84.15	6.758	0.014	0.112	0.010	3.957	58.60	26.38	1.62	0.003722	± 0.000004	0.061	5.31E-16	0.20	0.9988	0.0017
S21	2680-02C	AN 0802-84.15	8.355	0.014	0.109	0.006	6.556	78.50	43.50	2.43	0.003722	± 0.000004	0.044	3.85E-16	0.22	0.9988	0.0017
S21	2680-02D	AN 0802-84.15	9.106	0.012	0.139	0.005	7.569	83.10	50.12	1.85	0.003722	± 0.000004	0.064	5.59E-16	0.25	0.9988	0.0017
S21	2680-02E	AN 0802-84.15	7.719	0.012	0.081	0.002	7.078	91.70	46.91	1.20	0.003722	± 0.000004	0.085	7.44E-16	0.27	0.9988	0.0017
S21	2680-02F	AN 0802-84.15	6.842	0.011	0.130	0.000	6.830	99.80	45.29	1.14	0.003722	± 0.000004	0.070	6.19E-16	0.30	0.9988	0.0017
S21	2680-02G	AN 0802-84.15	5.893	0.012	0.078	0.001	5.721	97.10	38.01	1.02	0.003722	± 0.000004	0.072	6.38E-16	0.35	0.9988	0.0017
S21	2680-02H	AN 0802-84.15	5.103	0.012	0.133	0.001	4.810	94.30	32.01	0.92	0.003722	± 0.000004	0.074	6.51E-16	0.45	0.9988	0.0017
S21	2680-02I	AN 0802-84.15	5.064	0.013	0.256	0.004	3.923	77.50	26.15	0.82	0.003722	± 0.000004	0.099	8.69E-16	0.99	0.9988	0.0017
S21	2680-02J	AN 0802-84.15	13.770	0.017	0.000	0.037	2.749	20.00	18.36	5.20	0.003722	± 0.000004	0.039	3.49E-16	2.47	0.9988	0.0017
S21	2680-03A	AN 0802-84.15	6.078	0.048	0.000	0.011	2.955	48.60	19.74	44.55	0.003722	± 0.000004	0.002	1.79E-17	0.10	0.9988	0.0017
S21	2680-03B	AN 0802-84.15	8.065	0.016	0.027	0.015	3.618	44.90	24.13	2.75	0.003722	± 0.000004	0.042	3.65E-16	0.20	0.9988	0.0017
S21	2680-03C	AN 0802-84.15	4.526	0.013	0.000	-0.001	4.941	109.20	32.88	2.81	0.003722	± 0.000004	0.019	1.73E-16	0.22	0.9988	0.0017
S21	2680-03D	AN 0802-84.15	7.427	0.013	0.000	-0.001	7.766	104.60	51.41	4.35	0.003722	± 0.000004	0.021	1.90E-16	0.25	0.9988	0.0017
S21	2680-03E	AN 0802-84.15	9.615	0.015	0.082	0.008	7.122	74.10	47.20	4.59	0.003722	± 0.000004	0.029	2.61E-16	0.27	0.9988	0.0017
S21	2680-03F	AN 0802-84.15	8.885	0.011	0.004	-0.001	9.243	104.00	61.02	3.51	0.003722	± 0.000004	0.031	2.88E-16	0.30	0.9988	0.0017
S21	2680-03G	AN 0802-84.15	8.403	0.012	0.033	0.001	8.254	98.20	54.59	1.07	0.003722	± 0.000004	0.101	8.89E-16	0.35	0.9988	0.0017
S21	2680-03H	AN 0802-84.15	6.284	0.012	0.114	0.000	6.347	101.00	42.12	0.66	0.003722	± 0.000004	0.132	1.17E-15	0.45	0.9988	0.0017
S21	2680-03I	AN 0802-84.15	4.734	0.014	0.062	0.005	3.307	69.90	22.07	0.57	0.003722	± 0.000004	0.152	1.35E-15	0.99	0.9988	0.0017

Appendix (Continued)

Appendix (Continued)																	
Sample	Gain ID#	Drill Hole - Depth	⁴⁰ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	³⁷ Ar/ ³⁹ Ar	³⁶ Ar/ ³⁹ Ar	⁴⁰ Ar/ ³⁹ Ar	% ⁴⁰ Ar	Age (Ma)	± (Ma)	J	% ⁴⁰ Ar	⁴⁰ Ar (Moles)	Laser Power (W)	⁴⁰ Ar/ ³⁶ Ar Discr.	±	
S21	2680-03J	AN 0802-84.15	11.943	0.025	0.401	0.026	4.287	35.90	28.56	6.31	0.003722	± 0.000004	0.030	2.82E-16	2.47	0.9988	0.0017
S22	2681-01A	AN 1502-53.30	11.948	0.018	0.101	0.023	5.154	43.10	34.28	1.74	0.003722	± 0.000004	0.119	1.04E-15	0.10	0.9988	0.0017
S22	2681-01B	AN 1502-53.30	5.463	0.012	0.027	0.002	4.763	87.20	31.70	0.43	0.003722	± 0.000004	0.225	1.96E-15	0.20	0.9988	0.0017
S22	2681-01C	AN 1502-53.30	5.159	0.012	0.026	0.001	4.954	96.00	32.97	0.21	0.003722	± 0.000004	0.441	3.85E-15	0.22	0.9988	0.0017
S22	2681-01D	AN 1502-53.30	5.286	0.012	0.026	0.001	5.121	96.90	34.06	0.27	0.003722	± 0.000004	0.329	2.85E-15	0.25	0.9988	0.0017
S22	2681-01E	AN 1502-53.30	5.565	0.012	0.043	0.000	5.426	97.50	36.07	0.36	0.003722	± 0.000004	0.207	1.78E-15	0.27	0.9988	0.0017
S22	2681-01F	AN 1502-53.30	5.932	0.012	0.058	0.001	5.669	95.60	37.67	0.53	0.003722	± 0.000004	0.151	1.29E-15	0.30	0.9988	0.0017
S22	2681-01G	AN 1502-53.30	6.145	0.012	0.033	0.000	6.247	101.70	41.47	0.56	0.003722	± 0.000004	0.150	1.29E-15	0.35	0.9988	0.0017
S22	2681-01H	AN 1502-53.30	5.319	0.014	0.064	0.000	5.218	98.10	34.70	0.76	0.003722	± 0.000004	0.094	8.07E-16	0.45	0.9988	0.0017
S22	2681-01I	AN 1502-53.30	4.888	0.012	0.052	0.000	4.828	98.80	32.13	1.18	0.003722	± 0.000004	0.049	4.08E-16	0.99	0.9988	0.0017
S22	2681-01J	AN 1502-53.30	9.772	0.018	0.000	0.012	6.102	62.40	40.51	4.13	0.003722	± 0.000004	0.029	2.32E-16	2.47	0.9988	0.0017
S22	2681-02A	AN 1502-53.30	27.932	0.026	0.142	0.071	7.042	25.20	46.68	4.07	0.003722	± 0.000004	0.170	1.48E-15	0.10	0.9988	0.0017
S22	2681-02B	AN 1502-53.30	5.926	0.012	0.068	0.003	5.035	85.00	33.50	0.53	0.003722	± 0.000004	0.160	1.40E-15	0.20	0.9988	0.0017
S22	2681-02C	AN 1502-53.30	5.690	0.012	0.042	0.000	5.565	97.80	36.98	0.64	0.003722	± 0.000004	0.131	1.15E-15	0.22	0.9988	0.0017
S22	2681-02D	AN 1502-53.30	6.073	0.012	0.014	0.000	5.945	97.90	39.48	0.63	0.003722	± 0.000004	0.131	1.15E-15	0.25	0.9988	0.0017
S22	2681-02E	AN 1502-53.30	5.822	0.012	0.022	0.000	5.839	100.30	38.79	0.25	0.003722	± 0.000004	0.381	3.33E-15	0.27	0.9988	0.0017
S22	2681-02F	AN 1502-53.30	5.931	0.012	0.015	0.000	5.877	99.10	39.04	0.18	0.003722	± 0.000004	0.712	6.23E-15	0.30	0.9988	0.0017
S22	2681-02G	AN 1502-53.30	6.149	0.012	0.015	0.000	6.038	98.20	40.09	0.18	0.003722	± 0.000004	0.716	6.27E-15	0.35	0.9988	0.0017
S22	2681-02H	AN 1502-53.30	6.643	0.012	0.023	0.000	6.541	98.50	43.40	0.23	0.003722	± 0.000004	0.663	5.82E-15	0.45	0.9988	0.0017
S22	2681-02I	AN 1502-53.30	5.540	0.013	0.063	0.001	5.267	95.10	35.02	0.63	0.003722	± 0.000004	0.115	1.03E-15	0.99	0.9988	0.0017
S22	2681-02J	AN 1502-53.30	8.070	0.016	0.000	0.012	4.494	55.70	29.92	1.99	0.003722	± 0.000004	0.057	5.32E-16	2.47	0.9988	0.0017
S22	2681-03A	AN 1502-53.30	144.136	0.090	0.031	0.466	6.302	4.40	41.83	17.20	0.003722	± 0.000004	0.431	3.75E-15	0.10	0.9988	0.0017
S22	2681-03B	AN 1502-53.30	8.714	0.014	0.131	0.010	5.912	67.90	39.27	1.77	0.003722	± 0.000004	0.073	6.41E-16	0.20	0.9988	0.0017
S22	2681-03C	AN 1502-53.30	8.042	0.012	0.148	0.006	6.399	79.60	42.47	1.87	0.003722	± 0.000004	0.059	5.13E-16	0.22	0.9988	0.0017
S22	2681-03D	AN 1502-53.30	9.771	0.012	0.139	0.006	8.111	83.00	53.66	1.65	0.003722	± 0.000004	0.095	8.31E-16	0.25	0.9988	0.0017
S22	2681-03E	AN 1502-53.30	9.873	0.012	0.048	0.004	8.783	89.00	58.03	0.69	0.003722	± 0.000004	0.236	2.06E-15	0.27	0.9988	0.0017
S22	2681-03F	AN 1502-53.30	8.320	0.011	0.059	0.000	8.331	100.10	55.09	0.68	0.003722	± 0.000004	0.177	1.55E-15	0.30	0.9988	0.0017
S22	2681-03G	AN 1502-53.30	6.189	0.011	0.078	-0.002	6.765	109.30	44.87	1.45	0.003722	± 0.000004	0.053	4.85E-16	0.35	0.9988	0.0017
S22	2681-03H	AN 1502-53.30	4.774	0.011	0.000	0.000	4.651	97.50	30.97	1.22	0.003722	± 0.000004	0.049	4.43E-16	0.45	0.9988	0.0017
S22	2681-03I	AN 1502-53.30	5.194	0.014	0.039	0.001	4.796	92.30	31.92	0.39	0.003722	± 0.000004	0.222	1.95E-15	0.99	0.9988	0.0017
S22	2681-03J	AN 1502-53.30	6.699	0.014	0.053	0.007	4.724	70.50	31.45	1.11	0.003722	± 0.000004	0.098	8.73E-16	2.47	1.0012	0.0017
S23	2682-01A	AN 1502-87.65	26.455	0.026	0.065	0.079	3.144	11.90	20.99	2.16	0.003722	± 0.000004	0.510	4.45E-15	0.10	1.0012	0.0017
S23	2682-01B	AN 1502-87.65	5.413	0.012	0.003	0.005	3.937	72.70	26.24	0.54	0.003722	± 0.000004	0.201	1.75E-15	0.20	1.0012	0.0017
S23	2682-01C	AN 1502-87.65	4.618	0.012	0.051	0.002	4.140	89.60	27.58	0.49	0.003722	± 0.000004	0.142	1.24E-15	0.22	1.0012	0.0017
S23	2682-01D	AN 1502-87.65	5.089	0.013	0.010	0.001	4.806	94.40	31.98	0.38	0.003722	± 0.000004	0.203	1.78E-15	0.25	1.0012	0.0017
S23	2682-01E	AN 1502-87.65	5.008	0.012	0.028	0.001	4.812	96.10	32.03	0.22	0.003722	± 0.000004	0.330	2.88E-15	0.27	1.0012	0.0017
S23	2682-01F	AN 1502-87.65	4.918	0.012	0.012	0.000	4.807	97.80	31.99	0.16	0.003722	± 0.000004	0.590	5.15E-15	0.30	1.0012	0.0017
S23	2682-01G	AN 1502-87.65	4.927	0.012	0.007	0.000	4.798	97.40	31.93	0.14	0.003722	± 0.000004	0.760	6.63E-15	0.35	1.0012	0.0017
S23	2682-01H	AN 1502-87.65	4.964	0.012	0.010	0.001	4.808	96.90	32.00	0.15	0.003722	± 0.000004	0.718	6.29E-15	0.45	1.0012	0.0017
S23	2682-01I	AN 1502-87.65	4.909	0.013	0.006	0.001	4.645	94.60	30.92	0.22	0.003722	± 0.000004	0.440	3.85E-15	0.99	1.0012	0.0017
S23	2682-01J	AN 1502-87.65	6.104	0.012	0.012	0.007	4.147	67.90	27.63	0.96	0.003722	± 0.000004	0.116	1.04E-15	2.47	1.0012	0.0017
S23	2682-02A	AN 1502-87.65	4.160	0.011	0.000	0.001	3.912	94.00	26.08	1.78	0.003722	± 0.000004	0.030	2.67E-16	0.10	1.0012	0.0017
S23	2682-02B	AN 1502-87.65	3.747	0.011	0.010	0.000	3.895	104.00	25.97	0.42	0.003722	± 0.000004	0.133	1.17E-15	0.20	1.0012	0.0017
S23	2682-02C	AN 1502-87.65	3.701	0.013	0.009	0.000	3.788	102.40	25.26	0.38	0.003722	± 0.000004	0.137	1.20E-15	0.22	1.0012	0.0017
S23	2682-02D	AN 1502-87.65	4.233	0.013	0.008	0.000	4.241	100.20	28.26	0.32	0.003722	± 0.000004	0.205	1.79E-15	0.25	1.0012	0.0017
S23	2682-02E	AN 1502-87.65	4.714	0.012	0.004	0.000	4.578	97.10	30.48	0.19	0.003722	± 0.000004	0.450	3.94E-15	0.27	1.0012	0.0017

Appendix (Continued)

Sample	Core ID#	Drill Hole - Depth	$^{40}\text{Ar}/^{39}\text{Ar}$	$^{38}\text{Ar}/^{39}\text{Ar}$	$^{37}\text{Ar}/^{39}\text{Ar}$	$^{36}\text{Ar}/^{39}\text{Ar}$	$^{40}\text{Ar}/^{39}\text{Ar}$	% ^{40}Ar	Age (Ma)	$\pm$ (Ma)	J	% ^{40}Ar	^{40}Ar (Moles)	Laser Power (W)	$^{40}\text{Ar}/^{36}\text{Ar}$ Discr.	$\pm$
S23	2682-02F	AS 1502-87.65	4.799	0.012	0.002	0.000	4.758	99.20	31.67	0.14	0.003722	± 0.000004	0.728	6.36E-15	0.30	1.0012 0.0017
S23	2682-02G	AS 1502-87.65	4.844	0.012	0.002	0.000	4.825	99.60	32.11	0.11	0.003722	± 0.000004	1.223	1.07E-14	0.35	1.0012 0.0017
S23	2682-02H	AS 1502-87.65	4.973	0.011	0.002	0.000	4.971	100.00	33.07	0.11	0.003722	± 0.000004	1.559	1.36E-14	0.45	1.0012 0.0017
S23	2682-02I	AS 1502-87.65	5.030	0.012	0.000	0.000	4.925	97.90	32.77	0.12	0.003722	± 0.000004	1.419	1.24E-14	0.99	1.0012 0.0017
S23	2682-02J	AS 1502-87.65	5.608	0.013	0.000	0.004	4.526	80.70	30.13	0.54	0.003722	± 0.000004	0.162	1.43E-15	2.47	1.0012 0.0017
S23	2682-03A	AS 1502-87.65	3.996	0.011	0.000	-0.007	6.156	154.10	40.87	2.65	0.003722	± 0.000004	0.019	1.66E-16	0.10	1.0012 0.0017
S23	2682-03B	AS 1502-87.65	3.851	0.012	0.000	0.000	3.924	101.90	26.16	0.41	0.003722	± 0.000004	0.149	1.29E-15	0.20	1.0012 0.0017
S23	2682-03C	AS 1502-87.65	4.693	0.012	0.000	0.000	4.670	99.50	31.09	0.23	0.003722	± 0.000004	0.310	2.70E-15	0.22	1.0012 0.0017
S23	2682-03D	AS 1502-87.65	4.812	0.012	0.000	0.000	4.881	101.40	32.48	0.22	0.003722	± 0.000004	0.415	3.62E-15	0.25	1.0012 0.0017
S23	2682-03E	AS 1502-87.65	4.828	0.012	0.000	0.000	4.829	100.00	32.14	0.16	0.003722	± 0.000004	0.537	4.68E-15	0.27	1.0012 0.0017
S23	2682-03F	AS 1502-87.65	4.947	0.012	0.000	0.000	5.013	101.40	33.35	0.20	0.003722	± 0.000004	0.457	3.97E-15	0.30	1.0012 0.0017
S23	2682-03G	AS 1502-87.65	4.982	0.011	0.000	0.000	5.065	101.70	33.70	0.22	0.003722	± 0.000004	0.378	3.30E-15	0.35	1.0012 0.0017
S23	2682-03H	AS 1502-87.65	4.929	0.011	0.000	0.000	4.821	97.80	32.09	0.43	0.003722	± 0.000004	0.179	1.55E-15	0.45	1.0012 0.0017
S23	2682-03I	AS 1502-87.65	4.927	0.011	0.000	0.001	4.771	96.80	31.76	1.07	0.003722	± 0.000004	0.059	5.01E-16	0.99	1.0012 0.0017
S23	2682-03J	AS 1502-87.65	5.504	0.012	0.081	0.004	4.198	76.30	27.97	1.13	0.003722	± 0.000004	0.065	5.53E-16	2.47	1.0012 0.0017
Typical full system blank			^{40}Ar (nA)	$\pm$	^{39}Ar (nA)	$\pm$	^{38}Ar (nA)	$\pm$	^{37}Ar (nA)	$\pm$	^{36}Ar (nA)	$\pm$	Air pipette $^{40}\text{Ar}/^{36}\text{Ar}$		$\pm$	
			0.00661	0.00007	0.000065	0.00001	0.000032	0.000004	0.00032	0.00001	0.00011	0.000004	1.0010		0.0018	

Anexo 5 – Relação da Amostras, Coordenadas e Procedimentos Analíticos Aplicados

Amostras Coletadas em Afloramentos													
Amostra	Coordenadas Locais (m)			Tipo	Petrografia	MEV	DR-X	Rietveld	Mössbauer	MES	Análise Química		Isótopos C e O
	Este	Norte	Altitude								MBR	ACTLAB	
Amostras do Grupo 1													
MAC121	2450	-820	1022	DA	X								
MAC122	2250	-800	960	FS	X								
MAC130	2425	-830	1002	DA	X	X	X					X	
MAC131	2429	-829	1003	DA	X		X					X	
MAC132	2435	-827	1003	DA	X		X					X	
MAC133	2440	-823	1004	MC	X		X					X	
MAC134	2443	-818	1004	DA	X		X			X		X	
MAC135	2448	-815	1005	DA	X	X	X					X	
MAC136	2449	-814	1005	MC	X		X					X	
MAC137	2452	-812	1006	DA	X		X			X		X	
MAC138	2456	-812	1006	DA	X		X					X	
MAC139	2460	-809	1006	DA	X		X			X		X	
MAC140	2370	-837	997	FS	X	X	X					X	
MAC141	2400	-840	998	FS	X	X	X					X	
Amostras do Grupo 2													
MAC1	2340	-650	920	ID-DL	X							X	
MAC4	2426	-805	1008	ID	X		X				X	X	
MAC5	2461	-789	1012	ID	X		X				X	X	
MAC5A	2461	-789	1012	ID-HM								X	
MAC6	2464	-763	1011	ID-HM		X						X	
MAC6A	2464	-763	1011	ID-HM						X		X	
MAC7	2481	-731	1011	ID	X		X				X	X	
MAC7A	2481	-731	1011	ID-HM								X	
MAC8	2489	-699	1012	ID	X		X				X	X	
MAC8A	2489	-699	1012	ID-HM								X	
MAC9	2506	-659	1012	ID	X		X				X	X	
MAC10	2511	-618	1010	ID	X		X				X	X	
MAC10A	2511	-618	1010	ID-HM								X	
MAC11	2509	-584	1012	ID	X		X				X	X	
MAC11A	2509	-584	1012	ID-HM								X	
MAC16	1980	-530	917	ID-DL		X						X	
MAC81	2040	-490	954	ID-DL								X	
MAC96	1980	-500	932	ID	X	X	X		X	X	X	X	
MAC100	2436	-793	1009	ID-DL					X			X	
MAC101	2476	-512	1017	ID-DL	X					X			
MAC102	2420	-810	1008	ID-DL	X					X		X	
MAC103	2422	-810	1008	ID-DL	X							X	
ISO1	2420	-810	1008	ID-DL	X								X
ISO2	2422	-808	1007	ID-DL	X								X
ISO3	2423	-807	1009	ID-DL	X								X
ISO4	2430	-804	1009	ID-DL	X								X
ISO6	2434	-797	1009	ID-DL	X								X
ISO8	2448	-793	1014	ID-DL	X								X
ISO9	2462	-791	1014	ID-DL	X								X
ISO11	2464	-783	1012	ID-DL	X					X			X
ISO12	2467	-775	1012	ID-DL	X								X
ISO14	2470	-770	1014	ID-DL	X								X
ISO15	2470	-768	1015	ID-DL	X								X
ISO16	2464	-765	1013	ID-DL	X								X
ISO18	2476	-752	1012	ID-DL	X					X			X
ISO19	2479	-745	1013	ID-DL	X					X			X
ISO20	2480	-742	1012	ID-DL	X					X			X
ISO21	2482	-734	1012	ID-DL	X					X			X
ISO23	2487	-722	1013	ID-DL	X					X			X
ISO24	2488	-717	1013	ID-DL	X					X			X
ISO25	2492	-709	1015	ID-DL	X								X
ISO26	2496	-696	1013	ID-DL	X					X			X
ISO27	2497	-692	1013	ID-DL	X								X
ISO28	2501	-680	1012	ID-DL	X								X
ISO29	2504	-669	1012	ID-DL	X					X			X
ISO30	2506	-660	1012	ID-DL	X								X
ISO32	2508	-647	1011	ID-DL	X								X
ISO34	2509	-640	1011	ID-DL	X	X				X			X

Amostra	Coordenadas Locais (m)			Tipo	Petrografia	MEV	DR-X	Rietveld	Mössbauer	MES	Análise Química		Isótopos C e O
	Este	Norte	Altitude								MBR	ACTLAB	
ISO36	2511	-619	1011	ID-DL	X	X							X
ISO37	2511	-619	1011	ID-DL	X					X			X
ISO38	2512	-600	1012	ID-DL	X	X							X
ISO39	2513	-587	1013	ID-DL	X	X				X			X
ISO40	2507	-577	1013	ID-DL	X	X							X
ISO42	2511	-567	1013	ID-DL	X	X							X
ISO43	2509	-562	1013	ID-DL	X					X			X
ISO45	2503	-547	1015	ID-DL	X								X
ISO46	2500	-541	1014	ID-DL	X								X
ISO47	2498	-535	1014	ID-DL	X					X			X
ISO48	2492	-527	1015	ID-DL	X								X
ISO49	2489	-524	1015	ID-DL	X								X
ISO50	2484	-519	1015	ID-DL	X					X			X
ISO51	2476	-512	1017	ID-DL	X								X
ISO52	2471	-507	1019	ID-DL	X								X
ISO53	2469	-505	1020	ID-DL	X					X			X
Amostras do Grupo 3													
MAC2	1589	-511	1050	HO	X		X			X	X	X	
MAC3A	2272	-753	939	PB	X		X				X	X	
MAC12	2300	-720	920	SO	X		X				X		
MAC13	2280	-720	920	PB	X						X		
MAC14	2464	-610	920	SO	X		X				X		
MAC14A	2464	-610	969	MB							X	X	
MAC14B	2464	-610	969	PB							X	X	
MAC15	1965	-529	917	PB	X		X						
MAC17	2270	-735	931	SO	X		X				X	X	
MAC18	2308	-717	928	SO	X		X				X		
MAC19	2483	-655	978	SO	X	X	X				X		
MAC20	1943	-500	929	SO	X		X				X	X	
MAC44	1930	-530	899	HO	X						X	X	
MAC49	2930	-450	1210	SO	X						X		
MAC54	1859	-623	908	SO	X	X	X				X		
MAC55	1847	-572	914	SO	X						X		
MAC56	1883	-578	908	SO	X						X		
MAC57	2181	-543	925	SO	X	X					X		
MAC58	2235	-560	925	SO	X						X		
MAC59	2413	-636	954	SO	X	X	X				X		
MAC59H	2413	-636	954	MB							X	X	
MAC59I	2413	-636	954	PB							X	X	
MAC60	2930	-450	1210	SO	X		X				X	X	
MAC62	1230	-410	1229	HO	X	X	X			X	X		
MAC63	1435	-578	1155	SO							X		
MAC67	2289	-579	918	HO	X		X	X	X		X	X	
MAC68	1862	-499	965	HO	X		X		X		X	X	
MAC69	2320	-568	918	SO	X						X		
MAC77	2356	-642	920	SO	X						X		
MAC84	2380	-670	922	HO	X						X	X	
MAC97	1980	-500	932	HO	X	X	X	X	X		X	X	
MAC105A	1400	-425	1167	HO	X		X		X		X	X	
MAC105B	1400	-425	1167	HO	X						X	X	
MAC107	2350	-650	928	PB	X						X	X	
MAC112	1300	-410	1210	HO	X						X		
MAC115	1350	-420	1208	HO	X						X	X	
MAC126A	2425	-603	957	MB			X		X		X	X	
MAC126B	2425	-603	957	PB			X		X		X	X	
MAC127A	2423	-625	956	MB			X	X	X	X	X	X	
MAC127B	2423	-625	956	PB			X	X	X		X	X	
MAC128A	2418	-649	951	MB			X		X		X	X	
MAC128B	2418	-649	951	PB			X		X		X	X	
MAC129A	2459	-594	966	MB			X		X		X	X	
MAC129B	2459	-594	966	PB			X		X		X	X	

Amostras Coletadas em Furos de Sonda

Furo de Sonda	Profundidade de Coleta da Amostra (m)	Tipo	Petrografia	Densidade	MEV	DR-X	Rietveld	Mössbauer	MES	Análises Químicas	
										MBR	ACTLAB
Amostras do Grupo 1											
PZ-03	69.0	QD	X		X	X					X
PZ-03	83.0	QD	X			X					X
PZ-03	103.0	QD	X			X			X		X
PZ-03	122.0	QD	X		X	X					X
PZ-03	138.0	QD	X			X					X
PZ-03	152.0	QD	X			X			X		X
PZ-03	170.0	QD	X			X					X
PZ-03	185.0	QD	X			X			X		X
PZ-03	196.0	QD	X			X					X
Amostras do Grupo 2											
PZ-55	27.0	ID		X							X
PZ-55	37.0	ID		X							
PZ-55	61.0	ID		X							X
PZ-55	150.0	ID		X							
PZ-55	151.0	ID		X							
PZ-55	168.0	ID		X							
PZ-55	176.0	ID		X							
PZ-03	18.0	QI	X			X					X
PZ-03	23.0	QI	X		X	X					X
PZ-03	36.0	QI	X			X					X
PZ-03	50.0	QI	X			X					X
PZ-54	80.0	QI	X			X					X
PZ-54	85.0	QI	X			X					X
PZ-54	120.0	QI	X		X	X					X
PZ-54	124.0	QI	X			X					X
FSD09-99	29.5	ID	X							X	
FSD09-99	32.7	ID	X			X				X	
FSD09-99	32.8	ID	X							X	
FSD09-99	33.2	ID	X			X				X	
FSD09-99	46.0	ID	X							X	
Amostras do Grupo 3											
FSD08-99	2.20	SO		X						X	
FSD08-99	4.80	SO		X						X	X
FSD08-99	7.30	SO		X						X	X
FSD08-99	12.50	SO		X						X	X
FSD08-99	13.20	SO		X						X	
FSD08-99	14.70	SO		X						X	X
FSD08-99	14.80	SO		X						X	
FSD08-99	16.80	SO		X						X	X
FSD08-99	17.00	SO		X						X	
FSD08-99	19.00	SO		X						X	X
FSD09-99	3.50	SO		X						X	X
FSD09-99	4.10	SO		X						X	
FSD09-99	8.60	SO		X						X	X
FSD09-99	10.50	SO		X						X	X
FSD09-99	12.50	SO		X						X	
FSD09-99	13.50	SO		X						X	
FSD09-99	19.70	SO		X						X	
FSD09-99	20.90	SO		X						X	
FSD09-99	24.70	SO		X						X	X
FSD09-99	27.70	SO		X						X	X
FSD09-99	28.70	SO		X						X	X
FSD11-99	2.50	SO	X	X	X					X	
FSD11-99	4.80	SO		X						X	X
FSD11-99	5.50	SO		X						X	
FSD11-99	5.70	SO		X						X	X
FSD11-99	5.80	SO		X						X	
FSD11-99	6.50	SO		X						X	
FSD11-99	6.80	SO		X						X	
FSD11-99	7.00	SO		X						X	
FSD11-99	7.10	SO		X						X	X
FSD11-99	8.30	SO		X						X	

Furo de Sonda	Profundidade de Coleta da Amostra (m)	Tipo	Petrografia	Densidade	MEV	DR-X	Rietveld	Mössbauer	MES	Analises Químicas	
										MBR	ACTLAB
FSD11-99	8.50	SO		X						X	
FSD11-99	8.60	SO		X						X	
FSD11-99	8.90	SO		X						X	
FSD11-99	9.20	SO		X						X	
FSD11-99	12.40	SO		X						X	X
FSD11-99	13.40	SO		X						X	X
FSD11-99	20.40	SO		X						X	X
FSD11-99	22.80	SO		X						X	
FSD11-99	25.50	SO		X						X	
FSD11-99	25.70	SO		X						X	X
FSD11-99	26.30	SO		X						X	
FSD11-99	26.50	SO		X						X	
FSD11-99	26.70	SO		X						X	X
FSD11-99	28.30	SO		X						X	X
PZ-55	170.00	HO		X							X

Grupo 1: DA=Dolomito argiloso, FS=Filito sericítico, MC= Metachert.

Grupo 2: ID=Itabirito dolomítico, QI=Quartzito itabirito, ID-HM=Banda hematítica do itabirito dolomítico, ID-DL= Banda dolomítica do itabirito dolomítico.

Grupo 3: HO=Minério compacto, SO=Minério friável, MB=Banda maciça do minério friável, PB=Banda porosa do minério friável.

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