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**Programa de Pós-Graduação em Geologia**

Janaina Rodrigues de Paula

**ESTRATIGRAFIA E GEOQUÍMICA DO SUPERGRUPO MINAS**  
**NA MINA DE SEGredo, QUADRILÁTERO FERRÍFERO, BRASIL**

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Orientador(a): Prof. Dr. Fabrício de Andrade Caxito

Coorientador(a): Dr. Diniz Tamantini Ribeiro

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## FOLHA DE APROVAÇÃO

**Estratigrafia e Geoquímica do Supergrupo Minas na Mina de Segredo,  
Quadrilátero Ferrífero, Brasil.**

**JANAINA RODRIGUES DE PAULA**

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Aprovada em 28 de abril de 2020, pela banca constituída pelos membros:

*Fabrizio de A. Caxito*

Prof. Fabrício de Andrade Caxito - Orientador  
UFMG

*gabriel*

Prof. Gabriel Jubé Uhlein  
UFMG

*Carlos Alberto Spier*

Prof. Carlos Alberto Spier  
The University of Queensland

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## RESUMO

O pacote metassedimentar do Supergrupo Minas no Quadrilátero Ferrífero (QFe), leste do Brasil, possui importantes formações de ferro do tipo Lago Superior, com até 400m de espessura (Formação Cauê). A unidade é sobreposta pelos carbonatos da Formação Gandarela (aprox. 2.4 Ga). Essas unidades paleoproterozoicas registraram significativas mudanças das condições de redox da atmosfera e oceano e provavelmente, o Grande Evento de Oxigenação (GOE) do Paleoproterozoico. O depósito de Segredo está localizado na parte SW do QFe e a complexidade estrutural e a descontinuidade das camadas são desafios para estudos sobre a evolução sedimentar da Bacia de Minas. Nesse depósito, a sequência estratigráfica invertida do Supergrupo Minas compõe o flanco inverso do Sinforme de Fábrica. Com base no mapeamento geológico e no estudo de um furo de sonda profundo (480 m) realizado no depósito de Segredo, propõe-se uma revisão litoestratigráfica dada pelo empilhamento dos grupos Itabira, Piracicaba, Sabará e Itacolomi. As unidades basais do Supergrupo Minas (Grupo Caraça) não estão expostas. As unidades do Grupo Itabira compreendem formações ferríferas bandadas (BIF), diamictitos e dolomitos com interdigitação lateral e vertical. Os diamictitos são interpretados como produtos de fluxos gravitacionais nas bordas da plataforma carbonática. Os dados químicos e isotópicos das formações Cauê e Gandarela definem variações das assinaturas químicas (ETR) e da razão isotópica de carbono. Com base nos resultados foi proposto um perfil de estratigrafia de sequência (2ª ordem) dado pela variação de tratos transgressivos e de mar alto. Quimicamente, BIFs dolomíticas mostram anomalias positivas de Eu e baixo conteúdo de elementos terrígenos, confirmando assim a contribuição de fluidos hidrotermais durante a precipitação das BIF's e dos carbonatos. Anomalias negativas de Ce refletem um oceano localmente oxigenado durante a precipitação de carbonatos (Formação Gandarela). Além disso, a ocorrência do Grupo Sabará foi definida de acordo com as fácies sedimentares e dados geocronológicos de U-Pb (zircão detrítico mais jovem a cerca de 2,1 Ga). Localmente, o Grupo Sabará sobrepõe-se diretamente o Grupo Itabira através de uma discordância angular.

**Palavras-chave:** Grande Evento de Oxigenação (GOE); Estratigrafia de Isótopos de Carbono e Oxigênio; Geocronologia em zircão detrítico U-Pb; Cráton São Francisco

## **ABSTRACT**

*The metasedimentary package of the Minas Supergroup in the Quadrilátero Ferrífero (QFe) region, eastern Brazil, bears important Lake Superior-type iron formations up to 400m thick in the Cauê Formation, superposed by dolomitic carbonates of the Gandarela Formation, deposited ca. 2.4 Ga ago and thus probably registering the Great Oxygenation Event (GOE) of the Paleoproterozoic. The deposit of Segredo is in the SW portion of the QFe. The structural complexity and the discontinuity of the layers are challenges to local studies on the sedimentary evolution of the Minas Basin. In this deposit, the inverted stratigraphic sequence of Minas Supergroup is arranged in the overturned limb of Fábrica Synform. Based on the geological mapping and the study of a deep drill hole core (480 m) performed at Segredo deposits, a lithostratigraphic review is proposed. The lithostratigraphic succession occurs through the stacking of the Itabira, Piracicaba, Sabará and Itacolomi groups, from the bottom up. The basal units of the Minas Supergroup (Grupo Caraça) are not exposed. The units of the Itabira Group comprise banded iron formation (BIF), diamictite and dolostone that have lateral and vertical interdigitation. The chemical and isotopic data from the Cauê and Gandarela formations are defined by variations of the chemical (REE) and C-isotopic signatures. Based on the defined lithostratigraphic configuration, an evolution of depositional tracts of 2<sup>nd</sup> order by transgressive and highstand system tracts is proposed. The diamictites are interpreted as gravity-driven flow products at the edges of the carbonate platform. Chemically, dolomitic BIFs show positive Eu anomalies and low terrigenous content, thus confirming the contribution of hydrothermal fluids during the precipitation of BIF and carbonates. Negative Ce anomalies reflect a locally oxygenated ocean during the carbonates precipitation (Gandarela Formation). In addition, the occurrence of the Sabará Group is defined in the region by the sedimentary facies and by U-Pb geochronological data (younger detrital zircon at ca. 2.1 Ga). The Sabará Group overlay directly the Itabira Group through an angular unconformity.*

**Keywords:** Great Oxygenation Event (GOE); Carbon and Oxygen Isotope Stratigraphy; Detrital zircon U-Pb geochronology; São Francisco Craton

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## 1. INTRODUÇÃO

A abundância de rochas paleoproterozoicas no Quadrilátero Ferrífero (QFe) é um convite para a pesquisa das condições físico-químicas imperantes no Precambriano. O QFe é uma província metalogenética com inúmeras mineralizações de Ouro (Au), Ferro (Fe) e Manganês (Mn), que abrange uma área de cerca de 7.000 km<sup>2</sup>.

Desde os primeiros trabalhos publicados sobre a geologia do QFe, muitos estudos avançaram no conhecimento sobre a estratigrafia e contexto estrutural da região. No entanto, em certas áreas do QFe, o reconhecimento das sequências sedimentares e suas correlações ainda causam discussões.

O pacote metassedimentar dos supergrupos Minas e Estrada Real (Paleoproterozoico) na Mina de Segredo, SW do QFe, apresenta a sequência invertida das rochas pertencente aos grupos: Itabira, Piracicaba, Sabará e Itacolomi. A complexidade estrutural e a descontinuidade das camadas impõem desafios aos estudos sobre a evolução sedimentar da Bacia Minas, no local.

Na mina de Segredo, as formações ferríferas sustentam a fisiografia da área através de cristas e platôs de até 1.500 m de altitude. O alinhamento das cristas define o divisor das bacias hidrográficas do Rio das Velhas, a leste, e do Rio Paraopeba, a oeste. A mina foi adquirida pela Vale S/A em 2001, mas as primeiras operações de lavra no depósito iniciaram-se no começo do século XIX.

O mapeamento regional e a descrição de um furo de sonda (480 m) contribuíram para o refino do arcabouço estrutural e caracterização dos estratos sedimentares do depósito de ferro de Segredo. As amostras coletadas foram submetidas às análises mineralógica, química e de isótopos estáveis de C e O para caracterização mineral, elementar e isotópica das diversas fases de carbonatos e estudo das condições de sedimentação e dos processos sin a pós-diagenético. Além disso, grãos de zircão detrítico foram analisados (U-Pb) para análise de proveniência de rochas metassedimentares.

### 1.1 Localização e vias de acesso

A mina de Segredo se localiza na junção dos municípios de Belo Vale, Congonhas e Ouro Preto, e dista aproximadamente 60 km a sul de Belo Horizonte,

capital do Estado de Minas Gerais (Figura 1). O acesso, saindo de Belo Horizonte, se dá pela BR040 sentido Rio de Janeiro.

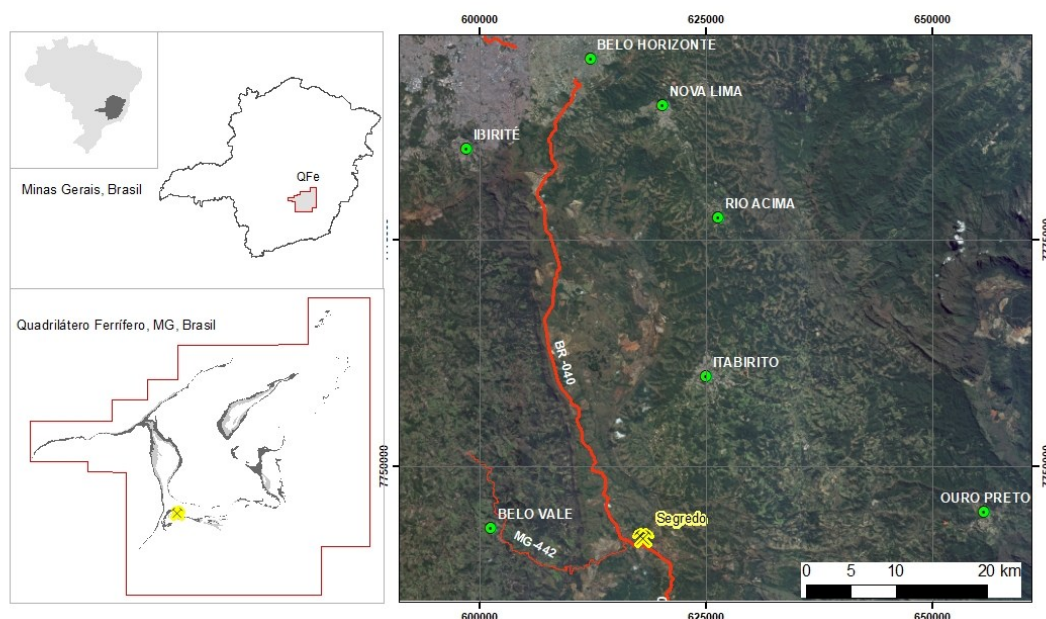


Figura 1 - Localização e acesso à Mina de Segredo.

## 1.2 Objetivos

A partir dos dados estratigráficos, geoquímicos e isotópicos ( $\delta^{13}\text{C}$  e  $\delta^{18}\text{O}$ ) em rochas químicas da Formação Cauê e datações U-Pb em grãos de zircão detrítico na rocha terrígena objetivou-se responder as seguintes questões:

- Quais as particularidades químicas e estratigráficas do Supergrupo Minas, na mina de Segredo?
- Qual a evolução sedimentar e estratigráfica da Bacia Minas, no âmbito da mina de Segredo?
- Há evidências das camadas pertencentes aos grupos Sabará e Caraça na mina de Segredo?

A mina foi utilizada nesse estudo por representar bem a complexidade estrutural e estratigráfica das jazidas de ferro do QFe, além de possuir grande diversidade de litotipos supergênicos e hipogênicos com valor econômico e boa cobertura por sondagem profunda.

## **2. MATERIAIS E MÉTODOS**

### **2.1 Descrição**

Para este estudo, foram mapeados 147 pontos nas minas de Segredo e João Pereira, bem como nas áreas próximas: Reserva Natural Poço Fundo e Serra do Pires. Os limites da Formação Cauê (escala 1: 5000) foram assinalados a partir do mapa geológico da mina, atualizado pelos geólogos de planejamento de curto prazo. As análises litoestratigráficas e estruturais dos dados foram a base para a revisão do mapa litoestrutural (escala 1: 10.000) e definição do arcabouço geológico.

Além disso, um furo de sonda profundo foi selecionado no depósito de Segredo e disponibilizado pela empresa VALE SA. O furo de sonda nomeado FDSP0046 foi executado no ano de 2005, na localização Lat: 20,42°S e Long. 91,86° (SAD69) e atingiu a profundidade de 480 metros. O furo possui diâmetro HW (ca. 76 mm) até a profundidade de 267 metros e depois, diâmetro NW (54 mm). A profundidade do manto de intemperismo no testemunho atinge a profundidade de 111 metros. A descrição do testemunho foi realizada no galpão de testemunhos da mina e detalhou-se os intervalos em escala centimétrica.

### **2.2 Amostragem**

A Tabela 1 relaciona as amostras coletadas para análises petrográficas, químicas e isotópicas. As amostras selecionadas para preparação de lâminas petrográficas e análise química objetivaram a representatividade dos diferentes litotipos interceptados no furo de sonda.

A análise de isótopos estáveis de C e O considerou alíquotas de carbonatos pertencentes ao dolomito, diamictito e ao itabirito dolomítico do furo em estudo. Ressalta-se que foram coletadas amostras da matriz e dos intraclastos do diamictitos, e 04 amostras de veios de carbonato. A coleta das amostras obedeceu a intervalos de 5 metros.

As amostras destinadas para geocronologia representam a coleta de vários incrementos em uma mesma litologia (metaconglomerado e quartzito) – tabela 2.

Essa ação visou a obtenção de massa suficiente para a concentração de cristais de zircão.

Foram realizados testes de reação com HCl (10%) para identificação dos tipos de calcitas e dolomitas e com H<sub>2</sub>O<sub>2</sub> para as zonas manganíferas.

Tabela 1 – Relação das amostras coletadas no testemunho de sonda.

| Método Analítico      | Quantidade | Suporte Amostral |
|-----------------------|------------|------------------|
| Lâminas Petrográficas | 29         | ~ 10 cm          |
| Análises Químicas     | 22         | ~ 10 cm          |
| Isótopos Estáveis     | 74         | ~ 10 cm          |
| Datação U-Pb          | 2          | Incremental      |

### 2.3 Preparação e Análise das amostras

As análises executadas nas amostras coletadas no testemunho foram sumarizadas na

## Tabela 2.

A preparação das amostras para confecção de lâmina petrográfica, difração de raios-X e análise química foram conduzidas nos laboratórios do Centro de Desenvolvimento de Pesquisa – VALE SA, em Santa Luzia/MG.

As análises multielementares foram realizadas através de digestão por água régia, multiácida, fusão com peróxido de sódio, metaborato de lítio e leitura por ICP-OES e ICP-MS e análise de Perda ao Fogo em Mufla. A empresa SGS – Geosol, Vespasiano/MG conduziu as análises.

As amostras destinadas para análise de isótopos estáveis de C e O, coletadas na sequência carbonática das formações Cauê e Gandarela, foram preparadas no Centro de Pesquisa Professor Manoel Teixeira da Costa/UFMG. Para a coleta de material pulverizado perfurou-se as amostras com uma broca diamantada de Ø 4 mm. As alíquotas coletadas foram encaminhadas para o laboratório NEG-LABISE, na Universidade Federal de Pernambuco.

Duas amostras para concentração de zircão foram destinadas para o Laboratório de Separação Mineral de Alta Pureza (SEPURA) do Centro de Pesquisa Professor Manoel Teixeira da Costa/UFMG. As amostras correspondem às camadas de metaconglomerado (AC01) e quartzito (AC02). A concentração dos minerais pesados considerou as etapas principais: cominuição, peneiramento, concentração com líquidos densos, separação magnética e catação com pinça na lupa binocular. A amostra AC02 apresentou apenas 8 zircões, logo a quantidade não foi suficiente para datação de proveniência (U-Pb).

A metodologia completa das análises encontra-se no artigo científico do Capítulo 4.

Tabela 2 – Listagem das amostras coletadas organizadas pela profundidade e metodologia aplicada.

| Amostra                | Prof.  | Litotipo             | Lâmina Petrográfica | Análise Química | Concentração de Zircão | Isótopos Estáveis | Difração de Raios-X | Análise Química |
|------------------------|--------|----------------------|---------------------|-----------------|------------------------|-------------------|---------------------|-----------------|
| SEG-2018-FDSP0046-A001 | 106.05 | Metaconglomerado     | x                   | x               | x                      | -                 | -                   | x               |
| SEG-2018-FDSP0046-A002 | 114.53 | Metaconglomerado     | x                   | -               | x                      | -                 | -                   | -               |
| SEG-2018-FDSP0046-A003 | 117.15 | Metaconglomerado     | x                   | -               | x                      | -                 | -                   | -               |
| SEG-2018-FDSP0046-A004 | 146.20 | Metaconglomerado     | -                   | -               | x                      | -                 | -                   | -               |
| SEG-2018-FDSP0046-A005 | 151.85 | Filito               | x                   | x               | -                      | -                 | x                   | x               |
| SEG-2018-FDSP0046-A006 | 161.55 | Quartzito            | x                   | -               | x                      | -                 | -                   | -               |
| SEG-2018-FDSP0046-A007 | 166.00 | Quartzito            | -                   | -               | x                      | -                 | -                   | -               |
| SEG-2018-FDSP0046-A008 | 183.45 | Black shale          | x                   | x               | -                      | -                 | -                   | x               |
| SEG-2018-FDSP0046-A009 | 183.60 | Black shale          | x                   | x               | -                      | -                 | -                   | x               |
| SEG-2018-FDSP0046-A010 | 184.00 | Black shale          | -                   | x               | -                      | -                 | -                   | x               |
| SEG-2018-FDSP0046-A011 | 187.21 | Dolomito             | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A012 | 192.20 | Itabirito Dolomítico | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A019 | 197.17 | Itabirito Dolomítico | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A020 | 202.05 | Itabirito Dolomítico | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A021 | 206.06 | Itabirito Dolomítico | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A022 | 216.86 | Dolomito             | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A023 | 221.64 | Dolomito             | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A024 | 230.00 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A025 | 235.68 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A026 | 244.71 | Dolomito             | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A027 | 245.92 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A028 | 266.74 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A029 | 269.02 | Dolomito             | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A030 | 275.00 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A031 | 277.85 | Dolomito             | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A032 | 283.00 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A033 | 287.87 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A034 | 292.88 | Itabirito Dolomítico | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A035 | 296.62 | Itabirito Dolomítico | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A036 | 298.84 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A037 | 302.21 | Itabirito Dolomítico | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A038 | 304.77 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A039 | 310.40 | Itabirito Dolomítico | x                   | -               | -                      | x                 | x                   | -               |
| SEG-2018-FDSP0046-A040 | 314.28 | Itabirito Dolomítico | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A041 | 318.81 | Itabirito Dolomítico | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A042 | 329.10 | Itabirito Dolomítico | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A043 | 335.78 | Metadiamictito       | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A044 | 340.79 | Metadiamictito       | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A045 | 345.73 | Metadiamictito       | x                   | -               | -                      | x                 | x                   | -               |
| SEG-2018-FDSP0046-A046 | 356.01 | Metadiamictito       | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A047 | 361.33 | Metadiamictito       | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A048 | 365.98 | Metadiamictito       | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A049 | 367.75 | Metadiamictito       | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A050 | 375.75 | Metadiamictito       | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A051 | 380.22 | Metadiamictito       | x                   | -               | -                      | x                 | x                   | -               |
| SEG-2018-FDSP0046-A052 | 385.69 | Metadiamictito       | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A053 | 389.08 | Metadiamictito       | x                   | -               | -                      | x                 | x                   | -               |
| SEG-2018-FDSP0046-A054 | 395.00 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A055 | 399.86 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A056 | 408.90 | Dolomito             | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A057 | 413.85 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A058 | 418.91 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A059 | 423.75 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A060 | 429.00 | Dolomito             | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A061 | 434.09 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A062 | 438.41 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A063 | 442.98 | Dolomito             | x                   | x               | -                      | x                 | x                   | x               |
| SEG-2018-FDSP0046-A064 | 447.96 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A065 | 452.74 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A066 | 457.46 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A067 | 462.40 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A068 | 467.40 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A069 | 472.50 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A070 | 476.95 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2018-FDSP0046-A071 | 480.07 | Dolomito             | -                   | -               | -                      | x                 | -                   | -               |
| SEG-2019-FDSP0046-A072 | 380.00 | Dolomito             | x                   | -               | -                      | -                 | -                   | -               |
| SEG-2019-FDSP0046-A073 | 165.00 | Quartzito            | x                   | x               | -                      | -                 | -                   | x               |
| SEG-2019-FDSP0046-A074 | 390.00 | Filito Clorítico     | x                   | x               | -                      | -                 | -                   | x               |

### 3. GEOLOGIA REGIONAL

A província metalogenética do QFe está localizada na porção leste do Brasil, no extremo sudeste do Cráton São Francisco (Almeida 1977) e é composta predominantemente por unidades arqueanas e paleoproterozoicas. A região é mundialmente reconhecida pelos gigantes depósitos de ferro, sendo que grande parte dessas formações ferríferas compõem a sucessão metassedimentar química da Formação Cauê, unidade estratigráfica paleoproterozoica do Supergrupo Minas (Dorr 1969). Sua localidade tipo foi definida no Pico do Cauê, distrito de Itabira, Minas Gerais.

#### 3.1 Estratigrafia

As unidades do Supergrupo Minas nas proximidades da mina de Segredo foram definidas, da base para o topo, pelos grupos: Itabira, Piracicaba, Sabará e Itacolomi (Figure 2 – artigo científico). Os afloramentos em frentes de lavra permitem a definição clara dos contatos geológicos. Já em áreas nos entornos das minas, são comuns espessas camadas de rochas intemperizadas, vegetação e estruturas físicas (ferrovias, rodovias, pilha de deposição de estéril, prédios e usinas) que recobrem as feições texturais e mineralógicas das rochas ou ocultam os contatos de topo e base da Formação Cauê. Localmente, a figura 2 destaca o mapa geológico da mina de Segredo nas proximidades do furo de sonda em estudo.

##### **Grupo Itabira**

Localmente, a Formação Cauê caracteriza-se predominantemente pela formação ferrífera bandada metamorfizadas (itabiritos) e seus produtos de enriquecimento supergênico além de, subordinadamente, lentes de metachert, dolomito e filito. De acordo com o critério composicional, pode-se classificar as formações ferríferas da Mina de Segredo em: hematítico, quartzo-itabirito, dolomita-quartzo-itabirito e itabirito dolomítico. O perfil de intemperismo dessas rochas pode atingir cerca de 300 m de profundidade, e seus principais produtos de alteração correspondem às formações ferríferas friáveis com teores de Fe, Al e perda ao fogo que diminuem em profundidade. A espessura da Formação Cauê é variável, com máxima de aproximadamente 500 metros, na zona de charneira e

com adelgaçamento na porção leste da mina, chegando a 50 metros. Essas mudanças ocorrem em função de variabilidades sin-deposicionais e do alto grau de deformação imposto a essas rochas.

A Formação Cauê grada lateralmente e verticalmente para a Formação Gandarela, sendo assim, tem-se o aumento dos carbonatos e diminuição dos óxidos de ferro. Dolomito, filito dolomítico, filito manganêsífero, metadiamicrito integram a sequência carbonática da Formação Gandarela. Em superfície, os principais produtos de intemperismo dessas rochas possuem teores variados de hidróxido de ferro, quartzo e aluminossilicatos. A presença de óxidos de Fe e Mn atribui a essas rochas a coloração marrom, feição conhecida como “borra de café”. A Formação Gandarela é descontínua e concentra-se predominantemente na porção leste da mina de Segredo, onde a camada pode atingir espessura de 100 metros.

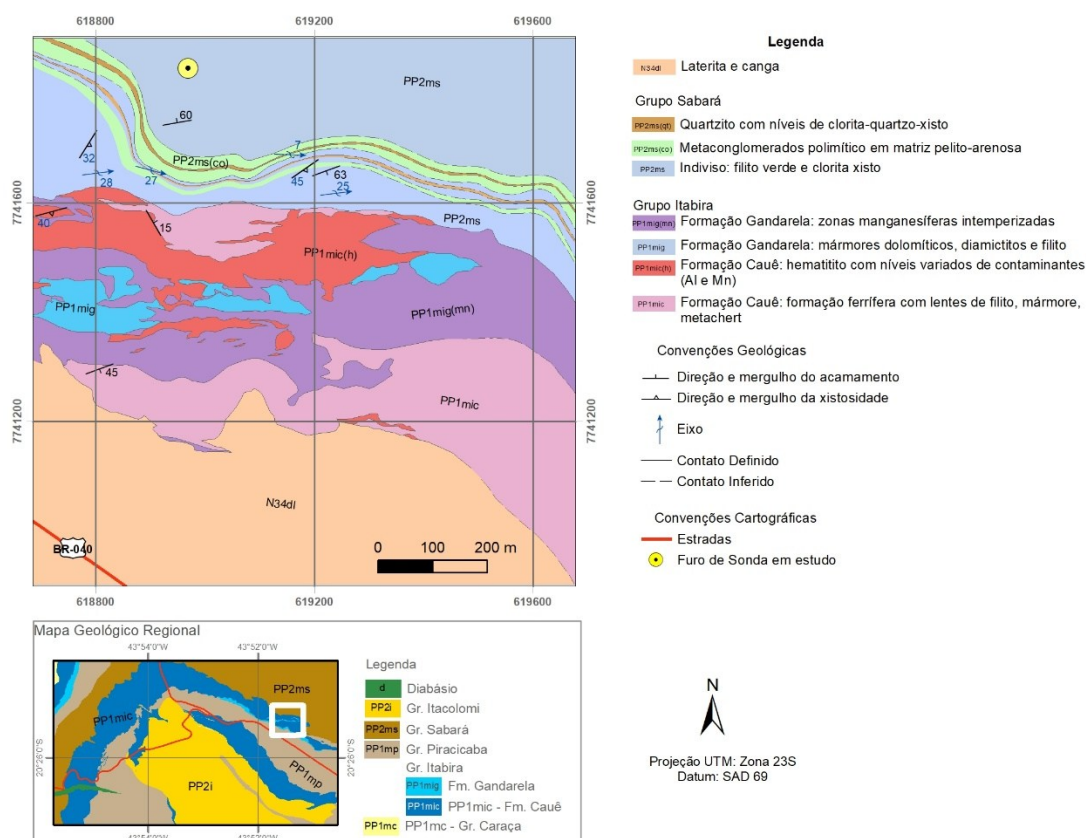


Figura 2 – Mapa Geológico Local. O polígono branco no mapa abaixo indica a localização da área mapeada no contexto regional.

### **Grupo Piracicaba**

Através de um contato brusco, o Grupo Piracicaba deposita-se sobre o Grupo Itabira. Ocorrem predominantemente filito sericítico e quartzito fino, ocasionalmente, quartzito ferruginoso e dolomito que foram identificados, apenas, em três furos de sonda. A cobertura cenozoica encobre os contatos de topo e base dessa sequência. No entanto, dados de furos de sonda indicam espessuras de até 450 metros.

### **Grupo Sabará**

A presença do Grupo Sabará foi definida apenas no extremo N-NE da área em estudo e encontra-se em contato abrupto com a sequência invertida do Supergrupo Minas. Há incerteza sobre a espessura dessa camada devido à natureza erosional do contato de base bem como, ao limite da área mapeada nesse estudo.

A camada guia do Grupo Sabará é dada por um metaconglomerado polimítico com clastos deformados de conglomerado, formação ferrífera, granitoide e quartzito. Ademais, ocorre, clorita-filito, quartzito e lentes de *blackshale*.

### **Grupo Itacolomi**

Já o Grupo Itacolomi não é abrangido no mapa local (Figura 2), pois localiza-se na porção sul da Mina de Segredo (Figure 3 do artigo científico), entretanto, possui expressiva representatividade no núcleo do Sinforme de Fábrica. Afloram quartzitos, e em menor expressão, filito e conglomerados.

O contato de base com o Grupo Piracicaba é abrupto e a espessura da camada, no núcleo do sinforme de Fábrica, supera 1000 metros.

## **3.2 Contexto Geotectônico**

A evolução tectônica do QFe é, ainda, alvo de discussão e estudo devido a sua alta complexidade e intensidade de deformação das rochas. Estudos anteriores de Dorr (1969), Chemale *et al.* (1991), Alkmim & Marshak (1998), Almeida (2004), Almeida *et al.* (2005) e Endo *et al.* (2005) demonstram diferenças nos modelos evolutivos do QFe. Entretanto, é consensual que pelo menos dois

eventos orogenéticos afetaram o QFe: i) Orogenia Riacciana (ca. 2.0 Ga) - Marshak and Alkmim (1989), Endo (1997) e ii) Orogenia Brasiliana, com sua fase principal - Tardicriogeniana-Eoediacarana (0,6 Ga) - Brito Neves *et al.* (2014).

A evolução tectônica ocorrida há cerca de 2.0 Ga, de acordo com Chemale *et al.* (1994), Alkmim & Marshak (1998), Rosière *et al.* (2000) e Rosière *et al.* (2008), abrange duas fases de deformação penecontemporâneas. Dessa forma, o primeiro conjunto de estruturas corresponde a dobramentos vergentes para noroeste e falhas de empurrão que afetaram a sequência de supracrustais. O padrão de deformação sugere a formação de um *fold-thrust belt* durante o fechamento da Bacia Minas. Já o segundo conjunto de estruturas configura-se pelo soerguimento de domos granito-gnáissicos e, por conseguinte, o colapso orogênico e conformação da arquitetura de domos e quilhas do QFe. Posteriormente, o evento Brasiliano atuou na inversão, amplificação, translação e rotação dos sinclinais ao redor dos domos cristalinos.

Almeida (2004), Almeida *et al.* (2005) e Endo *et al.* (2005) propõem distinta evolução do arcabouço estrutural do QFe (Figura 3). Nos trabalhos são definidas três gerações relacionadas ao grau hierárquico e período de formação: 1) Nappe Curral e dobras de segunda ordem associadas com vergência para N-NE; 2) Nappe Ouro Preto e dobras de segunda ordem associadas, vergência para S-SW, ambas fases associadas a idade Riacciana e 3) fase associada à amplificação de estruturas e redobramentos, correlacionada ao evento Ediacarano.

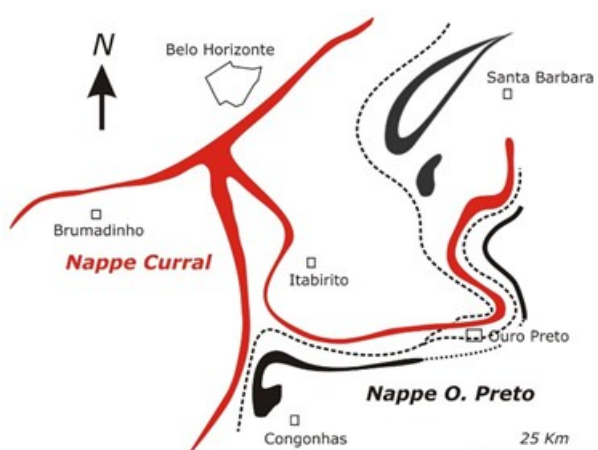


Figura 3 – Articulação das nappes Curral e Ouro Preto (Endo *et al.* 2005).

A nappe Curral constitui uma megadobra alóctone vergente para norte (Endo *et al.* 2005), cujo flanco normal se encontra redobrado formando o sinclinal Moeda e o flanco inverso se dispõe na Serra do Curral. A Nappe Ouro Preto, sobreposta à Nappe Curral, também constitui uma megadobra alóctone, porém vergente para SSW e instalada durante o Riachiano (Almeida 2004, Almeida *et al.* 2005 e Endo *et al.* 2005). As principais dobras de segunda ordem associadas a geração desta nappe são os sinclinais Gandarela, Ouro Fino e Santa Rita e os anticlinais Conceição, Santo Antônio e Mariana. A base do descolamento basal desta nappe é definida pela zona de cisalhamento São Vicente (Baltazar 1996, 1998).

### 3.3 Geologia Estrutural da região da Mina de Segredo

As unidades do Supergrupo Minas na mina de Segredo, orientam-se segundo direção principal ESE - WNW. O arranjo das camadas conforma o flanco inverso do Sinclinal de Fábrica (Figura 4), onde a Formação Cauê dispõe-se sobre a unidade carbonática da Formação Gandarela. Deste modo, o flanco normal da megadobra situa-se na mina de João Pereira (JPE), onde a direção das camadas inflete para NE-SW. A região da charneira do sinclinal dispõe-se na região conhecida por Almas e o eixo da dobra apresenta caimento de médio ângulo para leste.

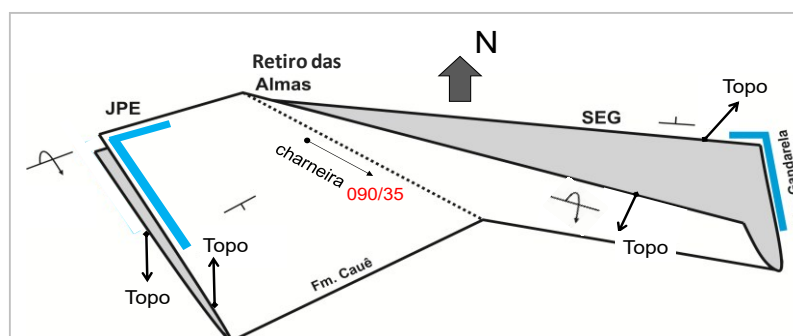


Figura 4 - Perfil esquemático do Sinforme de Fábrica, na mina de Segredo (SEG) localiza-se o flanco inverso e em João Pereira (JPE), o flanco normal, a zona da charneira abarca a região de Retiro das Almas.

A sobreposição de eventos deformacionais promoveu a deflexão das camadas na mina de Segredo. A direção principal das camadas inflete para a direção ESE-WNW- com mergulho médio para NNE (Figura 5a). Já, a foliação é representada pela direção NE-SW com mergulho para SE (Figura 5**Error!**

**Reference source not found.**b). Os eixos das dobras de segunda ordem são paralelos ao eixo do dobramento principal do Sinclinal de Fábrica (Figura 5c).

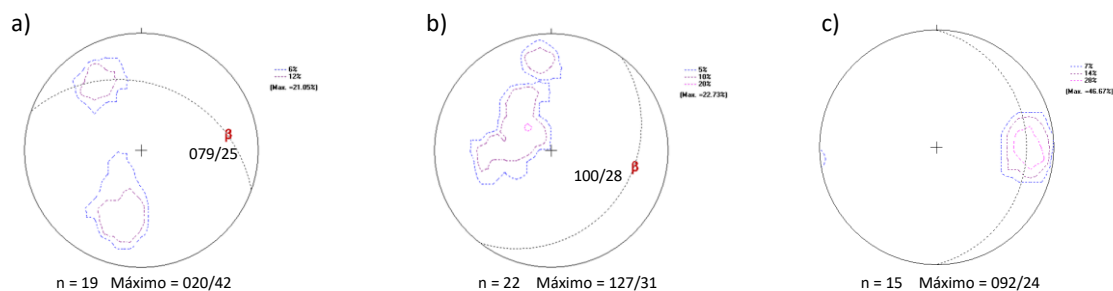


Figura 5 - Diagramas estereográficos isoareais de densidade de polos das estruturas: (a) acamamento (b) foliação e c) eixo de dobra

#### 4. ARTIGO CIENTÍFICO

Os resultados obtidos no presente estudo foram organizados no formato de um artigo intitulado *Carbon and Oxygen Isotope Stratigraphy and Geochemistry of Banded Iron Formations and carbonates of the Paleoproterozoic Minas Supergroup (Cauê and Gandarela formations) in the Segredo Mine, Quadrilátero Ferrífero, MG*.

O manuscrito foi submetido à revista *Brazilian Journal of Geology* em 09/03/2020 e atualmente, está na fase de revisão.

Nesse capítulo, o artigo científico é apresentado na íntegra e as referências de figuras e tabelas remetem somente ao artigo.

#### ***Carbon and Oxygen Isotope Stratigraphy and Geochemistry of Banded Iron Formations and carbonates of the Paleoproterozoic Minas Supergroup (Cauê and Gandarela formations) in the Segredo Mine, Quadrilátero Ferrífero, MG***

JANAINA R. PAULA<sup>1\*</sup>, FABRICIO A. CAXITO<sup>2</sup>, DINIZ T. RIBEIRO<sup>1</sup>, ALCIDES N. SIAL<sup>4</sup>, ANA RAMALHO ALKMIM<sup>5</sup>, CRISTIANO LANA<sup>5</sup>, ISSAMU ENDO<sup>5</sup>

<sup>1</sup>VALE SA, Nova Lima, Brazil, [janaina.rodrigues@vale.com](mailto:janaina.rodrigues@vale.com) and [diniz.ribeiro@vale.com](mailto:diniz.ribeiro@vale.com)

<sup>2</sup> Federal University of Minas Gerais, Belo Horizonte, Brazil, [caxito@ufmg.br](mailto:caxito@ufmg.br)

<sup>4</sup> Federal University of Pernambuco – LABISE, Pernambuco, Brazil, [sial@ufpe.br](mailto:sial@ufpe.br)

<sup>5</sup> Federal University of Ouro Preto, Ouro Preto, Brazil, [ana\\_alkmim@yahoo.com.br](mailto:ana_alkmim@yahoo.com.br), [cristiano.lana@ufop.edu.br](mailto:cristiano.lana@ufop.edu.br) and [issamu.endo@gmail.com](mailto:issamu.endo@gmail.com)

\*Corresponding author.

**Keywords:** Great Oxygenation Event (GOE), Carbon and Oxygen Isotope Stratigraphy, Detrital zircon U-Pb geochronology, São Francisco Craton

#### 4.1 Abstract

The metasedimentary package of the Minas Supergroup in the Quadrilátero Ferrífero (QFe) region, eastern Brazil, bears important Lake Superior-type iron formations up to 400m thick in the Cauê Formation, superposed by dolomitic carbonates of the Gandarela Formation, deposited ca. 2.4 Ga ago and thus probably registering the Great Oxygenation Event (GOE) of the Paleoproterozoic.

The deposit of Segredo is in the SW portion of the QFe. The structural complexity and the discontinuity of the layers are challenges to local studies on the sedimentary evolution of the Minas Basin. In this deposit, the inverted stratigraphic sequence of Minas Supergroup is arranged in the overturned limb of Fábrica Synform.

Based on the geological mapping and the study of a deep drill hole core (480 m) performed at Segredo deposits, a lithostratigraphic review is proposed. The lithostratigraphic succession occurs through the stacking of the Itabira, Piracicaba, Sabará and Itacolomi groups, from the bottom up. The basal units of the Minas Supergroup (Grupo Caraça) are not exposed.

The units of the Itabira Group comprise banded iron formation (BIF), diamictite and dolostone that have lateral and vertical interdigitation. The chemical and isotopic data from the Cauê and Gandarela formations are defined by variations of the chemical (REE) and C-isotopic signatures. Based on the defined lithostratigraphic configuration, an evolution of depositional tracts of 2<sup>nd</sup> order by transgressive and highstand system tracts is proposed. The diamictites are interpreted as gravity-driven flow products at the edges of the carbonate platform.

Chemically, dolomitic BIFs show positive Eu anomalies and low terrigenous content, thus confirming the contribution of hydrothermal fluids during the precipitation of BIF and carbonates. Negative Ce anomalies reflect a locally oxygenated ocean during the carbonates precipitation (Gandarela Formation).

In addition, the occurrence of the Sabará Group is defined in the region by the sedimentary facies and by U-Pb geochronological data (younger detrital zircon at ca. 2.1 Ga). The Sabará Group overlays directly the Itabira Group through an angular unconformity.

## 4.2 Introduction

The Paleoproterozoic Banded Iron Formations (BIFs) record geochemical changes of Earth's systems mainly marked by the increase of atmospheric oxygen during the Great Oxygenation Event (GOE) at ca. 2.4 Ga. The GOE shows a permanent change in the concentration of atmospheric oxygen content, in the volatile composition in the atmosphere-ocean system and increasing its oxidizing potential (Holland 1984; Holland 2002; Holland 2006; Bekker et al. 2010; Lyons et al. 2014). Increasing oxygen levels led to changes in atmospheric CH<sub>4</sub>/CO<sub>2</sub> ratios and a decrease in greenhouse warming by CH<sub>4</sub>, H<sub>2</sub>S and H<sub>2</sub> reduced gases (Pavlov et al. 2000; Kopp et al. 2005). Furthermore, Evans et al. (1997), Hoffman (2013) and Gumsley et al. (2017) postulated that the rise of atmospheric oxygen was not monotonic, but characterized by oscillations and may have contributed as a trigger for climate instability and cyclical global glacial events.

A useful tool for understanding the prevailing geochemical conditions on ancient Earth is the stable isotopes analysis. Their variations enable determining stratigraphic correlations worldwide (Beukes and Klein, 1990, Veizer et al. 1990, Veizer et al. 1992, Spier et al. 2007, Morgan et al. 2013, Gumsley et al. 2017). Although currently it has been well accepted that the C-isotopic data echoes the original composition of seawater during sedimentary deposition, several discussions are also being conducted about the preservation of original isotopic composition in Paleoproterozoic BIF (Veizer et al. 1992; Sial et al. 2000; Bekker et al. 2003; Morgan et al. 2013; Teixeira et al. 2017).

Another issue concerns the iron source for the genesis of huge BIF deposits during the Precambrian Era (Guild 1953; Holland 1984; Klein and Beukes 1992). Two genetic models have been discussed. The first advocated mobilization of Fe under continental weathering conditions (Borchert 1960). The second and more accepted invokes an iron-rich hydrothermal solution introduced by plumes (Isley 1995). In the same way, several authors (Isley 1995; Barley et al. 1997; Isley and Abbott 1999; Bekker et al. 2010) associated iron deposition to episodic mafic mantle plume magmatism, known as Large Igneous Province (LIPS). In this way, the ancient LIPs contributed to increase the expansion rate of oceanic crust leading to the production of flood basalts, dike swarms and layered intrusions. The

mafic volcanism could represent one of the main sources for dissolved ferrous iron for BIF deposition, as well as contribute to change in the oceanic redox state (Isley and Abbott 1999; Bekker et al. 2010).

The world's largest Paleoproterozoic iron deposits are in Brazil, Australia, South Africa, Russia and Ukraine. In Brazil, the main deposits are spread across the country and significantly different in genesis and age, such as the Archean Algoma-type BIFs of the Carajás Province in northern Brazil, the Paleoproterozoic Lake Superior-type deposits of the Quadrilátero Ferrífero (QFe) in southeastern Brazil, and the Neoproterozoic Rapitan-like iron formation of the Urucum district in western Brazil.

In QFe, the BIF deposits are related to metasedimentary rocks of the Itabira Group, which records a passive margin setting during a stage of regional marine transgression of the Minas Basin (Dorr 1969; Schorscher 1992; Canuto 2010). The basal unit of the Itabira Group is the Cauê Formation, that comprises quartz-rich, dolomitic and amphibolitic BIFs (Dorr 1969) known as quartz-itabirites, dolomitic itabirites and amphibolitic itabirites. Through a lateral and vertical transition lies the carbonate succession of the Gandarela Formation (Dorr 1969). The metasedimentary succession was submitted to greenschist facies metamorphism (e.g. Müller et al. 1982, Hoefs et al. 1982) and deformation related to Rhyacian (ca. 2.0 Ga) and Ediacaran/Cambrian (Brasiliana, ca. 0.5 Ga) orogenesis (e.g. Marshak and Alkmim 1989, Endo 1997).

Although several iron deposits have been intensively explored over the last 50 years, the QFe continues to be responsible for an annual production of 190 Mt, approximately 65% of Brazilian production (DNPM 2017). At the Segredo mine (Figure 1), southwest QFe, iron ore mining began in 1923. In 2001, the mine was acquired by Vale SA. Nevertheless, the area has been in the limelight since the early nineteenth century, when German engineer Wilhelm Ludwig Von Eschwege installed the first industrial-scale iron foundry in Brazil.

In addition to its historical and economic relevance, the Segredo Mine was studied in this work because it represents the structural and stratigraphic complexity of the QFe iron deposits, and it exhibits a variety of hypogenic and supergenic BIF types. We propose a lithostratigraphic review of Segredo deposits based on mapping, chemostratigraphy and geochronological data obtained from a

480 meters deep drill hole core. Finally, we expect to contribute to the debate on the evolution of the Minas Basin.

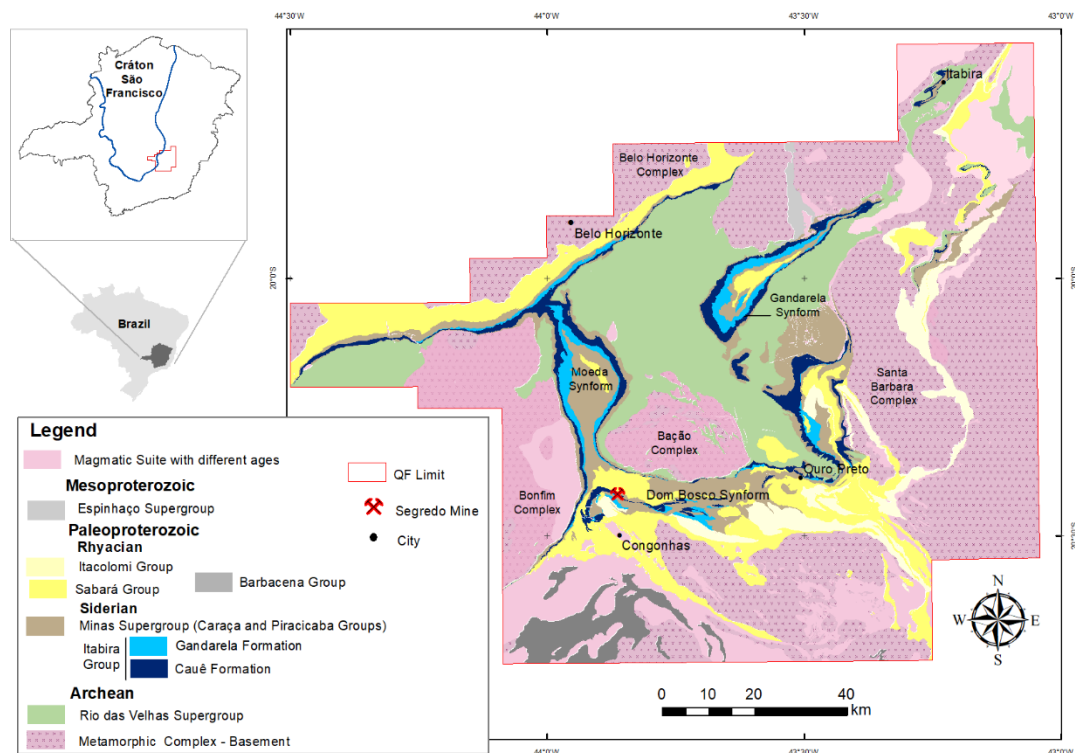


Figure 1: Location of Segredo Mine in the geologic map of Quadrilátero Ferrífero modified from Endo et al. (2019).

### 4.3 Geological settings

The QFe, located in southeastern Brazil, is an important polymetallic province and contains economically important deposits of gold, iron and manganese. The regional geomorphological features exhibit an approximately square geometric arrangement framed by Paleoproterozoic BIF (Figure 1). The metallogenic district is situated at the southernmost São Francisco Craton (Almeida 1977), where four regional lithostratigraphic units are recognized (Figure 2): i) Metamorphic Complex: Archean gneisses, migmatites and granitoids; ii) Rio das Velhas Supergroup: Archean greenstone belt; iii) Minas Supergroup: Paleoproterozoic metasedimentary rocks composed of clastic and chemical sediments; and iv) Itacolomi Group: Paleoproterozoic supracrustal sequence formed by quartzites and metaconglomerates (Alkmim and Marshak 1998; Dorr 1969; Renger et al. 1994). The tectonic history of QFe is characterized by multiple phases that produced a complex deformation pattern. Regional metamorphism

ranges from greenschist facies to amphibolite facies (Herz 1978; Hoefs et al. 1982; Müller *et al.* 1982; Pires and Bertolino 1991; Olivo et al. 1996; Pires 1995; Quéméneur et al. 2003; Rosière et al. 2008; Neri 2012).

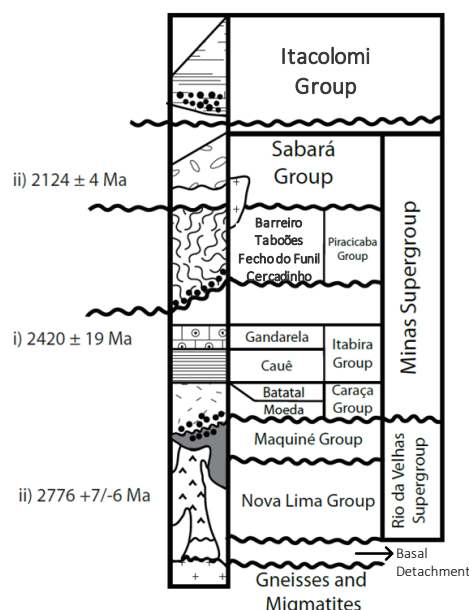


Figure 2: Stratigraphic column of the Minas Supergroup, modified from Morgan et al. (2013) and Rosière et al. (2008). References for age are from: (i) Babinski et al. (1995) (Pb-Pb whole-rock isochron) and (ii) Machado et al. (1992) (younger detrital zircon U-Pb age).

The Minas Supergroup comprises metasedimentary rocks, approximately 6 km thick (Alkmim and Marshak 1998), deposited from ca. 2600 to 2100 Ma (Renger et al. 1994; Machado et al. 1996; Babinski et al. 1995; Hartmann et al. 2006; Cabral et al. 2012; Brueckener et al. 2014; Koglin et al. 2014; Mendes et al. 2014). The sedimentation unconformably overlies the Archean basement and records a complete Wilson Cycle (Schorscher 1992; Alkmim and Marshak 1998; Canuto 2010). As a consequence, the stages of evolution of the Minas basin include the installation of passive margin until the development of syn-orogenic basin during a Rhyacian accretionary orogeny (Dorr 1969; Schorscher 1992; Renger et al. 1995; Alkmim and Marshak 1998; Hartmann et al. 2006; Canuto, 2010; Farina et al. 2016).

The Segredo mine, located on the southwest of QFe (Figure 1), comprises part of an allochthonous succession placed between the Dom Bosco and Moeda synclines (Guild 1957; Dorr 1969; Lobato et al. 2005; Endo et al. 2019). The lithostratigraphic record, from the bottom up, of the Itabira, Piracicaba, Sabará and Itacolomi groups is recognized (Figure 3), but some lithostratigraphic uncertainties

remain under discussion (e.g. Guild et al. 1957; Lobato et al. 2005; Endo et al. 2019).

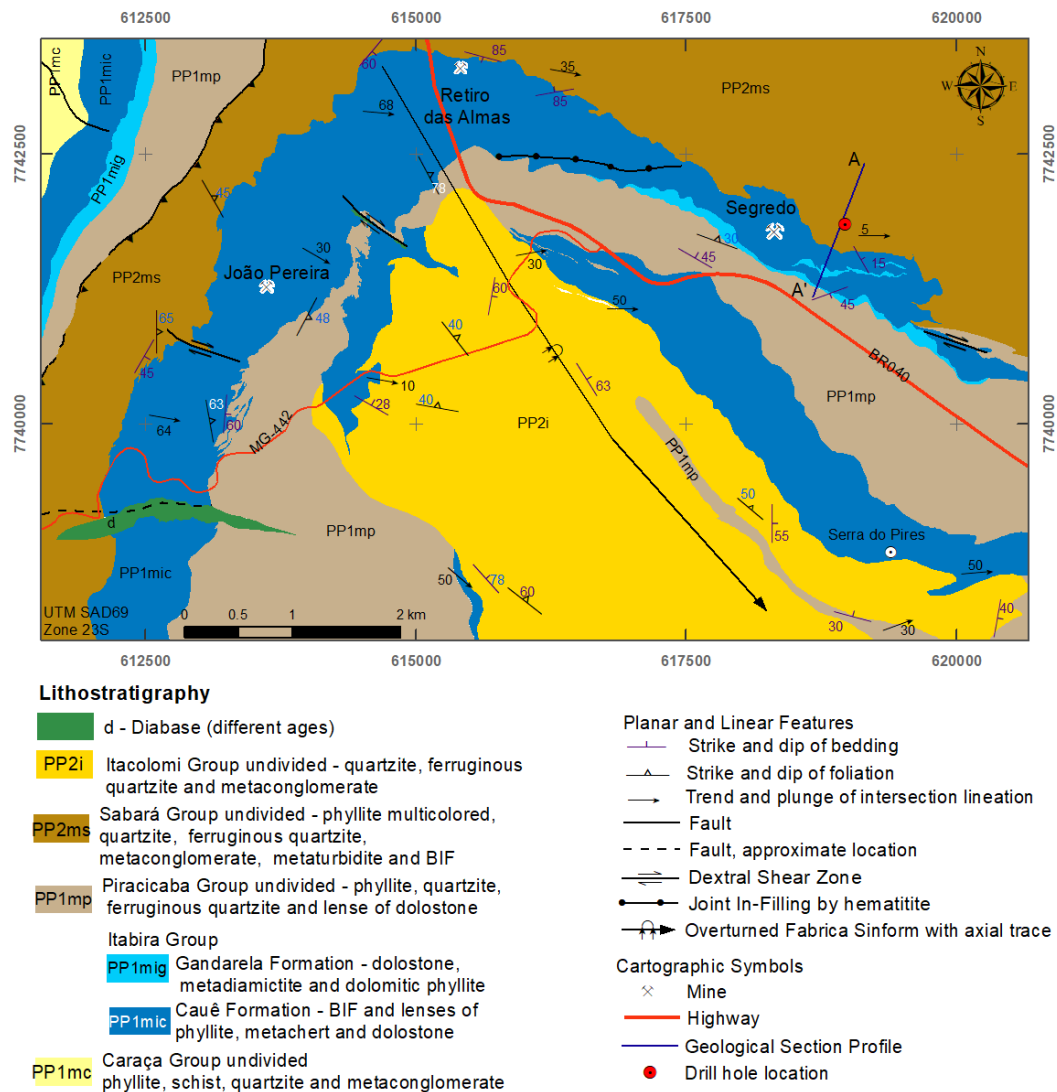


Figure 3: Geologic Map of Segredo mine and region modified of Endo et al. (2019).

The Caraça Group, a basal unit of the Minas Supergroup, is a siliciclastic sequence subdivided into the Moeda Formation, composed of quartzites and phyllites and the Batatal Formation, represented by phyllites and quartz-muscovite schist with minor black shale lens (Dorr et al. 1957; Dorr 1969). The nearest occurrence is restricted to Serra da Moeda.

The Itabira Group conformably overlies the Caraça Group and is dominantly composed of chemical sediments, subdivided into the Cauê and Gandarela formations (Dorr 1958 a, b). The Cauê Formation is mainly composed of BIF, with common phyllite, metachert and dolostone lenses, and has physical

expressiveness and economic importance due to iron ore exploitation. The thickness of the BIF ranges from 100 to 900 meters, the maximum thickness being found in the hinge zone of regional-scale folds (Figure 3). Furthermore, the variation in thickness is due to syn-depositional factors and the high degree of deformation. In the eastern part of the Segredo mine, the proto ore is dolomitic BIF intercalated with dolostone in a structurally controlled system, and its main supergenic products include high grade iron ore (> 64% wt.  $\text{Fe}_2\text{O}_3$ ).

The Gandarela Formation, in turn, consists mostly of carbonate rocks, predominantly of dolomitic composition (Dorr 1969). An old and unsolved issue is the delimitation of these two formations in the entire area of the QFe, due to the intergradational characteristic and the effects of weathering on their contact zone (Dorr 1969), suggesting that these layers could possibly be grouped into a single formation (Simmons 1968).

The Piracicaba Group (Dorr et al. 1957; Dorr 1969) is characterized by shallow to deep sea metasedimentary rocks overlying the Itabira Group over an erosional unconformity. It has significant spatial distribution and comprises gray phyllite, quartzite, ferruginous quartzite, iron formation and dolostone lenses. The lithologies are individualized into the Cercadinho, Fecho do Funil, Taboões and Barreiro formations.

The Sabará Group is positioned at the top of the Minas Supergroup and overlies the Piracicaba Group through an erosive surface (Gair 1958; Dorr 1969; Renger et al. 1995; Reis et al. 2002; Almeida et al. 2005). The clastic metasedimentary rocks of the Sabará Group represent flysch-type deposits (e.g. Barbosa 1968, Dorr 1969, Chemale et al. 1994, Alkmim and Marshak 1998). The predominant lithotypes are: multicolored phyllite, chlorite-schist, metaconglomerate, quartzite, metadiamicite, metaturbidite and BIF (Almeida et al. 2005). The metaconglomerate exhibits granite and gneiss pebbles, indicating important changes in paleogeography, with the emergence of new source areas, increased erosion and transport gradient (Renger et al. 1995). There is still no consensus on the delimitation of the unit in the region.

The younger sequence, the Itacolomi Group, overlies the lower units by angular unconformity (Dorr 1969). The sequence predominantly comprises quartzite and ferruginous quartzite. Lenticular phyllites and metaconglomerates

occur in restricted areas. The sediments represent an erosion of Minas Supergroup and the deposition in a marine and continental environment (Dorr 1969).

Subsequent studies conducted by Endo et al. (2019) grouped the younger units (Sabará and Itacolomi groups) into the Estrada Real Supergroup. This was proposed in the geological map of Endo et al. (2019) and will be clarified in future works.

Normally, the Paleoproterozoic rocks are partially covered by Cenozoic sediments or by a thick layer of weathered rock that can reach hundreds of meters.

The region was subjected to a complex deformation pattern, with superimposition of at least two orogenic events: i) Rhyacian Orogeny, acting from 2.1 to 1.8 Ga and ii) Brasiliana Orogeny, comprising the period between 0.63 and 0.56 Ga (Almeida et al. 1973; Cordani et al. 1968; Cordani et al. 1973; Almeida and Hasui 1984; Cordani and Sato 1999; Ávila et al. 2010; Brito Neves 2011; Seixas et al. 2013; Brito Neves et al. 2014). The origin and tectonic evolution of the Segredo deposits are still the subject of debate by several authors (e.g. Barbosa 1949; Guild 1957; Dorr 1969; Trzaskos et al. 2011; Endo et al. 2019). Despite the different evolution proposals, it is a matter of consensus that the region integrates a mega allochthonous structure.

The geological structure of Segredo deposits is geometrically arranged in a km-scale fold called Fábrica Synform (Figure 3). This structural framework makes up an asymmetric fold with hinge line dipping towards E (095/35) and verging SW.

The fold geometry (Figure 3) exhibits the overturned limb of Fábrica Synform in the Segredo mine. Consequently, the Paleoproterozoic units are arranged in an inverted stratigraphic succession. The bedding planes are oriented according to the ESE-WNW direction and dipping to NNE with different angles (range 30° to sub vertical). The hinge is in the region known as Retiro das Almas (Figure 3). The normal limb of the Fábrica Synform is in the João Pereira (JPE) mine, where the direction of the layers inflects to NE-SW. Penetrative regional schistosity and brittle structures crosscut the area through normal, reverse and strike-slip faults.

## **4.4 Sampling and analytical Methods**

### **4.4.1 Drill Hole Core**

A 480 meters deep drill hole core was selected in Segredo mine and made available by VALE S.A. The drill hole intercepts an inverted lithostratigraphy sequence of Minas Supergroup. At 110 meters, the rocks are well preserved from weathering, and black shale, metadiamictite, dolostone, dolomitic BIF, metaconglomerate, phyllite and quartzite have been identified (Figure 4). The rocks were submitted to greenschist facies metamorphism and show hydrothermal overprint, such as veins and carbonate remobilization. After detailed description of the drill hole core, 64 samples were selected for petrographic, chemical and geochronological analysis.

### **4.4.2 Analytical Methods**

A total of 29 thin sections from the drill hole were studied by optical microscopy (Zeiss, model Imager Z1 - reflected and transmitted light). Four thin sections were submitted to microstructure morphology examination and chemical composition characterization by scanning microscopy (SEM, HITACHI SU3500). The images were obtained by the Back-Scattering Electron Technique (BSE) with a 20.0 kV beam at the CDM - Vale Mineralogy Laboratory.

For qualitative analysis of the mineral phases, 11 samples were analyzed by X-ray diffraction. The Bruker D8 Advance diffractometer with Linxeye XE cobalt radiation detector was used through the powder method in the CDM - Vale Mineralogy Laboratory. The collected diffractograms were treated by Diffrac.EVA software and database, PDF2-2003.

Major, trace and rare earth elements analysis were realized at SGS Geosol Laboratory Ltd., Minas Gerais, Brazil. A total of 22 samples were analyzed by ICP-MS or ICP-OES after fusion with lithium metaborate or multi acid digestion (nitric, hydrochloric, hydrofluoric and perchloric acid). The volatile content (Loss On Ignition - LOI) was determined by the mass difference after ignition at 1000 °C.

Stable isotope analyses of C and O were performed on 74 aliquots of dolostone, metadiamictite (clast and matrix) and dolomitic BIF, as well as 05

samples of carbonate veins. Sampling was done at the drill hole core, where carbonate samples were collected at each five meters. The analyses were conducted at the NEG-LABISE Laboratory at the Federal University of Pernambuco (UFPE/Brazil). For extraction of CO<sub>2</sub> gas in a high vacuum line, 20 mg of powdered carbonates were attacked with 100% orthophosphoric acid at 25°C for three days. The duration of reaction is due to the Ca-Mg carbonate composition of most samples. The obtained CO<sub>2</sub> gas was analyzed for O and C isotopes in a ThermoFinnigan Delta V Advantage mass spectrometer. Results are expressed in the notation  $\delta$  in permil (‰) relative to the Vienna Pee Dee Belemnite (VPDB) standard, with accuracy better than  $\pm 0.1\text{‰}$ .

For detrital zircon dating, samples were collected from different intervals of metaconglomerate in the drill hole core (drill hole depth ranges: 106.05 to 106.23, 114.53 to 114.85, 117.15 to 117.50 and 146.20 to 146.42 meters deep). Nearly 65 zircon grains were acquired through heavy minerals concentration at the SEPURA laboratory, CPMTIC Research Center, at Federal University of Minas Gerais (UFMG/Brazil). Analysis of cathodoluminescence imaging enabled the investigation of internal structures of the zircon. U-Pb isotope determinations by LA-SF-ICP-MS, ThermoFinnigan Element 2 coupled to a CETAC laser 213nm, were carried out at the laboratories of Federal University of Ouro Preto (UFOP/Brazil). For the full U-Pb analytical procedures followed in this study and machine parameters, see Lana et al. (2017).

## **4.5 Results**

### **4.5.1 Local Geology**

The Paleoproterozoic succession at the Segredo Mine integrates an overturned limb of Fábrica Synform, where the inverse stratigraphic sequence aligns in the ESE-WNW direction and dips towards NNE. The cross section (Figures 3 and 4) exhibits the dip around 30° NNE and the contact is refined by geological mapping and collected data of a drill hole core. Normally, the surface is subjected to weathering process, thereby, the weathering horizon can reach about 300 m deep.

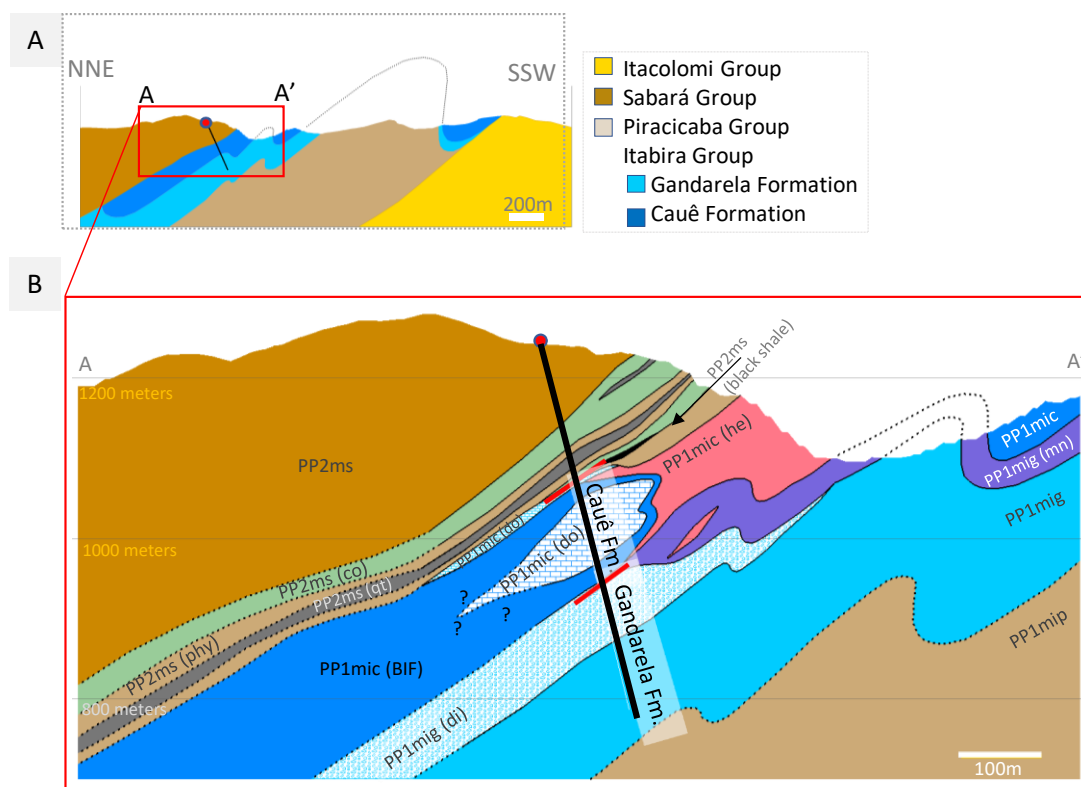


Figure 4: A - Regional NNE-SSE cross section of the Segredo Mine demonstrating the inverse stratigraphy sequence. The red polygon delimits the area from figure 4 - B, where detailed cross section and the black line indicates the studied drill hole.

Key: PP2ms – Sabará Group undivided, conglomerate (co), quartzite (qt), phyllite (phy); PP1mic – Cauê Formation, hematite (he), dolomitic BIF (BIF), dolostone (do); PP1mig – Gandarela Formation: dolostone, diamictite (di) e manganese zone (mn) e PP1mip – Piracicaba Group: phyllite and quartzite.

The Minas Supergroup succession is incomplete at the Segredo mine, due to the absence of the basal unit, the Caraça Group.

The base of Itabira Group comprises the Cauê Formation sedimentary rocks, characterized principally by BIF, although dolostone, chert and phyllite lenses are observed. Compositionally, different BIF types are recognized: hematite, quartz-itabirite (Figure 5A), dolomite-quartz-itabirite and dolomitic itabirite. Among the BIF, their main supergenic product corresponds to friable iron ore, where the quartz content is lower (<5%) and Ca-Mg carbonates are absent.

From the transitional contact, the chemical sedimentary rocks of Gandarela Formation are gradually interleaved with the iron formation of Cauê Formation, both laterally and vertically. Apart from that, the contact is generally covered by sediments of Cenozoic basins that can reach 150 meters thick. Dolostone (Figure 5B) and metadiamictite (Figures 5C and 5D) are dominant rocks. Besides these, irregular layers of dolomitic phyllite and manganeseiferous phyllite are recognized.

Its main weathering products have different levels of iron hydroxide, quartz and aluminosilicates, but the presence of Mn oxides is common and characterizes a typical brown color known as "coffee grounds" ("borra de café"). Locally, the discontinuity of carbonate layers promotes an unconformable contact between BIF (Cauê Formation) and metasedimentary rocks of the Piracicaba Group.

The Piracicaba Group display wide area distribution and consists of monotonous sericitic phyllite strata with rare quartzite, ferruginous quartzite and dolostone. Unfortunately, the metasedimentary rocks are severely weathered. For these reasons, the individualization of its formations has become difficult.

The upper part of Minas Supergroup stratigraphy, related with the Sabará Group, is restricted to the N-NE portion of the deposits, and it overlies the Cauê Formation through an unconformity contact. Lithologies are diverse: green phyllite, quartzite, ferruginous quartzite and polymict metaconglomerate constitute this unit. Phyllite is a characteristic rock of the group, and when not weathered, it shows green color due to the presence of chlorite. In fact, the lithostratigraphic classification of phyllite is difficult, because it is a common rock of both the Sabará and Piracicaba groups and their weathered products are very similar. For these reasons, the polymict metaconglomerate is used as guide layer of the Sabará Group. Normally, polymict metaconglomerate is matrix-supported, poorly sorted and shows deformed clasts of quartzite, iron formation, granite and gneiss (Figure 5E) immersed in a fine-grained matrix.

Lastly, the younger unit is the clastic sedimentary rocks of Itacolomi Group, restricted to the southern portion of the Segredo Mine. The clastic sedimentary rocks unconformably overlie the Piracicaba Group through sheared contacts. The most abundant rock is quartzite and, elsewhere in the region, minor lenses of phyllite and monomict metaconglomerate are found (Figure 5F).



Figure 5: A - Folded quartz-itabirite layers from Cauê Formation; B - Drill core sample of brecciated dolostone; C –Metadiamictite with cobble of carbonates immersed in matrix ferruginous and carbonatic; D – Different shapes of carbonate clasts in metadiamictite; E - Matrix-supported metaconglomerate with diversified and deformed clasts associated with the Sabará Group; F - Drill core sample of metaconglomerates with clasts of quartzite and BIF from Itacolomi Group.

#### 4.5.2 Petrography

The studied drill hole core represents the overturned limb of Segredo Mine, where the inverted lithostratigraphic sequence of Minas Supergroup was recognized. Two lithological domains can be defined: i) clastic and ii) chemical: dolomitic BIF and dolostone (Figure 6).

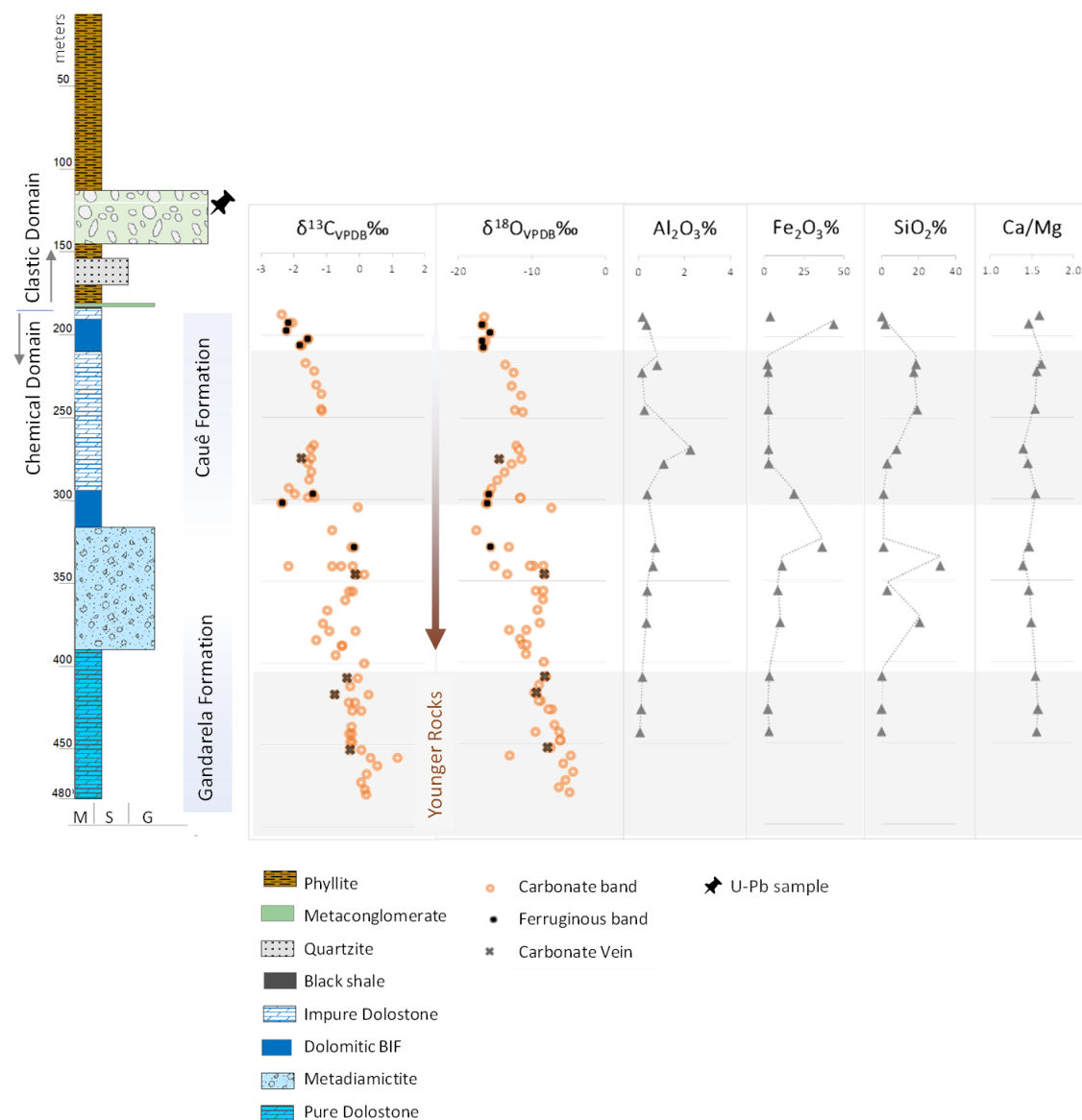


Figure 6 – Details of the drill hole core studied in Segredo Mine, a plot of C and O isotopic ratios for carbonate rocks and variation profile of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{Ca/Mg}$  ratios.

### Clastic Domain

The clastic domain is predominantly composed of phyllites and is 185m thick (Figure 6), where approximately 60% is weathered. The mineralogy consists mainly of chlorite, quartz and muscovite (Figure 7 A). The green phyllite layer displays uniform color, laminated on a fine scale, lepidoblastic texture and pervasive schistosity. Discrete levels of oligomict metaconglomerate with quartzite fragments are interbedded. Clearly, two folding phases are recognized, with a crenulation cleavage, pressure shadows, and associated quartz veinlets.

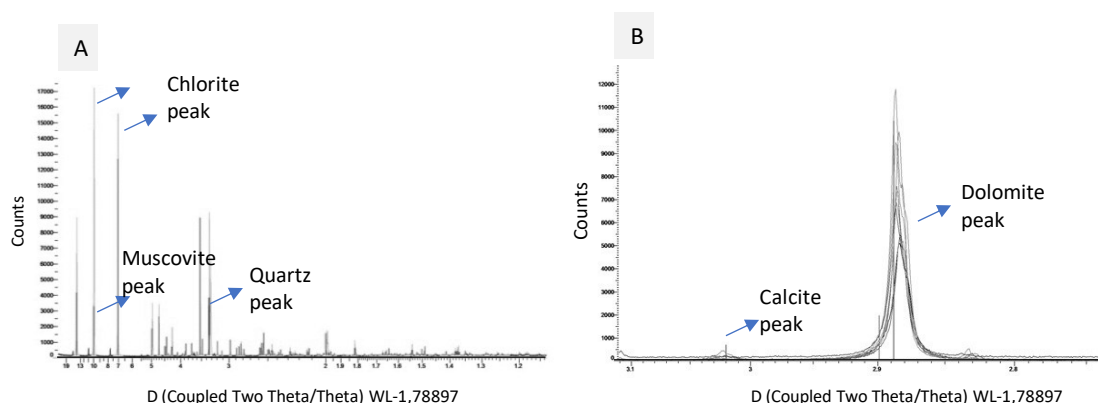


Figure 7 - X-ray diffraction analysis A - clastic domain represent by phyllite (sample: A05) and B – chemical domain: dolostone and dolomitic BIF (samples: A11, A22, A23, A26, A29, A31, A35, A60 e A63). Calcite peak was identified in A22 sample.

From 114 m, the drill hole core exhibits a 30-meter thick matrix-supported metaconglomerate (Figure 6). This rock presents rounded and low-sphericity clasts composed mostly of quartzite, although BIF clasts and others lithic fragments are found elsewhere (Figures 8 A and B). The layer is poorly sorted, and the size of clasts ranges from sand to pebble, occasionally larger than the diameter of the drill hole core (6.3 cm). The matrix maintains the same composition and texture of green phyllite. Crenulated lepidoblastic texture is pervasive in the interval.

The phyllite with magnetite porphyroblasts occurs over an angular discordance at 145m depth (Figures 8 C and D). Layers of chlorite alternate with layers mostly composed of quartz and form a fine lamination texture. Porphyroblasts of euhedral magnetite with millimeter size with pressure shadow and discrete rutile grains are found. Deformational structures such as a crenulated to anastomosed foliation are displayed.

An impure quartzite bed (17 meters thick) occurs between the phyllite (Figure 6), where gradational contact is observed, but the rocks may interfinger on a small scale. Compositionally, coarse grained quartz and fine-grained clay minerals prevail. The pervasive foliation is defined by chlorite-rich laminae.

A gradational contact is defined by appearance of clasts of quartzite and conglomeratic quartzite in a quartz-chlorite-phyllite matrix. The lenses of matrix-supported metaconglomerate extend for 2 meters of thickness.

Finally, the last part of the clastic domain comprises a thin black shale stratum (0.65 meters thick) over the metaconglomerate through an angular

discordance (Figures 8 E and F). Mineralogically, the black shale is composed by carbonaceous matter, quartz, muscovite and disseminated microcrystals of aluminosilicate minerals, chalcopryite, chlorite, goethite, graphite, hematite, Ti oxide and pyrite, as accessory phases. The shale shows a brecciated texture, like mud cracks. The fractures are filled by quartz with granoblastic texture, and Fe-hydroxide and graphite occur in the cleavage.

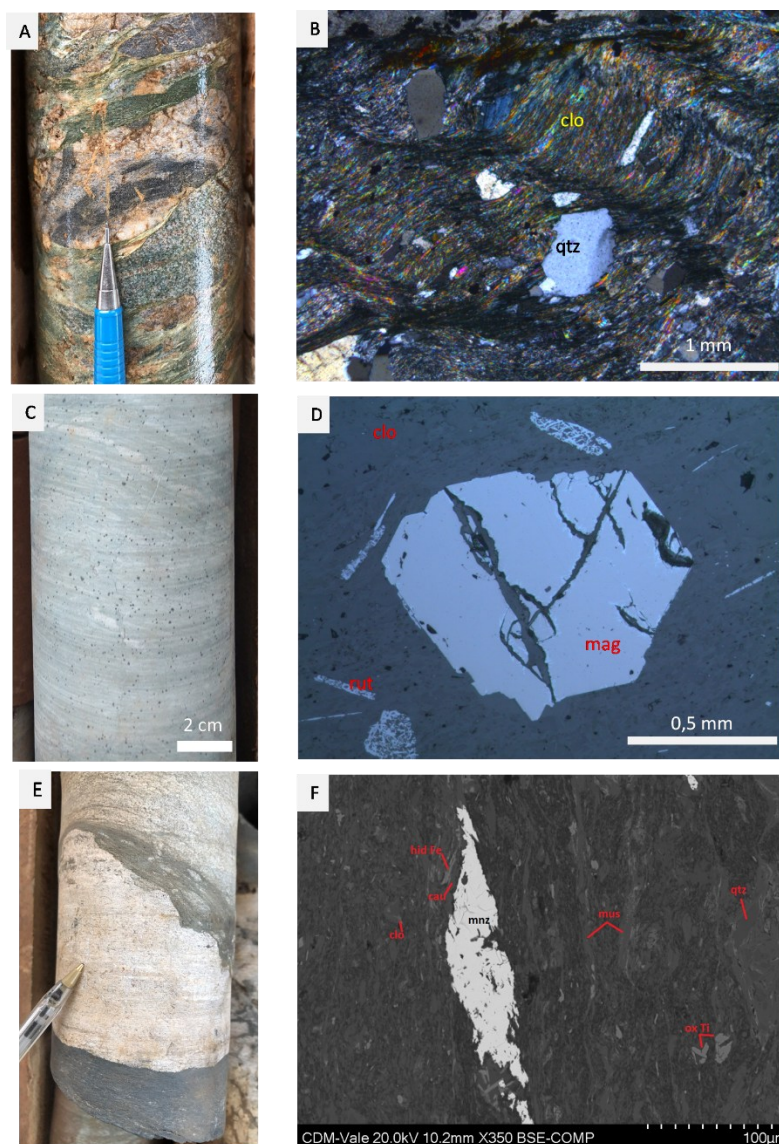


Figure 8: A – Drill core of metaconglomerate (132m depth); B – Photomicrograph of crenulated matrix composed by chlorite (clo) and quartz (qtz). Cross-polarized transmitted light. C – Chlorite phyllite (174m depth); D – Photomicrograph of magnetite porphyroblast (mag) and rutile (rut). Reflected light. E – Contact of phyllite, quartz vein and black shale; F – Monazite (mnz), kaolinite (kau), chlorite (clo), iron hydroxide (hid Fe), quartz (qtz), Titanium oxide (ox Ti) in black shale layer (SEM–EDX).

### **Chemical Domain: dolomitic BIF, dolostone and metadiamicctite**

The carbonate sequence comprises at least 295 meters (Figure 6). The uncertainty of thickness is due to the drill hole not having crosscut the top contact of the carbonate rocks. The sequence consists largely of dolostone and, secondarily, dolomitic BIF and metadiamicctite. Dolomite is the main carbonate mineral (Figure 6 and 7B) and mostly displays triple junctions ( $120^\circ$ ) at grain boundaries.

From 185 to 316 meters, impure dolostone strata alternate with dolomitic BIF (Figure 6), where the iron formation corresponds to approximately 30% of this thickness. Impure dolostone strata exhibits white to red color, the variation corresponding to the amount of iron oxide. Chlorite laminae and rare solution surfaces (stylolites) are found. Hematite appears as an accessory mineral in the dolostone, as well as in micrometric inclusions. Texturally, it displays fine-grained and locally banded textures. Alternation between the mesobands of iron oxide and dolomite defines the dolomitic BIF (Figure 9A and B). Microscopically, grey iron-oxide bands comprise micro hematite crystals, while micritic dolomite compounds the carbonate bands. Generally, dolomite is in close association with the ferruginous bands (Figure 10A). Accessory minerals include talc, apatite and calcite (Figure 10B). All the sequence is highly deformed and has undergone folding and shearing (Figure 9B). Apart from that, veins of various compositions (dolomite, calcite, quartz, chlorite and Fe oxide) crosscut the chemical sedimentary succession.

From a gradual contact, given by the appearance of intraclasts in the dolomitic BIF, the metadiamicctite is formed (Figure 6). The metadiamicctite layer is 74m thick and is an exception to strictly chemical sedimentary processes in this part of the drill hole core. The term diamicctite define the texture of the rock and does not imply a glacial deposition process. The matrix is thin (Figures 9 D) and is composed mainly of dolomite and Fe oxide, with carbonate composition prevailing in depth. The rock is poorly sorted and clast size is mostly of millimetric length, rarely overcoming 5 centimeters. Compositionally, it is oligomict and is mainly formed by intraclasts of the dolomite. Locally, beds with contribution of quartz clasts occur (Figure 9E) and lithoclasts such as iron formation are rare. Clasts borders are closely associated with overgrowth of chlorite or hematite. Two

different carbonates can be identified by SEM–EDX (HITACHI SU3500 microscopic model): a brighter Fe-Mn dolomite associated with recrystallized borders, and a darker, pure dolomite, preserved in crystal cores (Figure 10C).

Overlying the sequence, a discrete chlorite phyllite (0.07m thick), composed by chlorite and hematite, interrupts a metadiamicrite through sharp contact (Figure 9G). White dolostone concordantly overlies the chlorite phyllite. Dolostone, the top of the Gandarela Formation, extends approximately 90 meters or more (Figure 6). Basically, it is composed of dolomite, thus characterizing a different type of dolostone from the one found at 185 to 316 meters deep. The inaccuracy of thickness is due to the edge of the drill hole core being at 480m and not cross-cutting the whole layer. In terms of texture, there are brecciated levels and banded strata. The color varies between white, gray and rosy, promoted by concentrations of iron oxides or chlorite. Generally, millimetric veins of carbonates and quartz crosscut the sedimentary package (Figure 9H). Accessory minerals include biotite, calcite and hematite dispersed throughout the dolomitic matrix (Figure 10D).

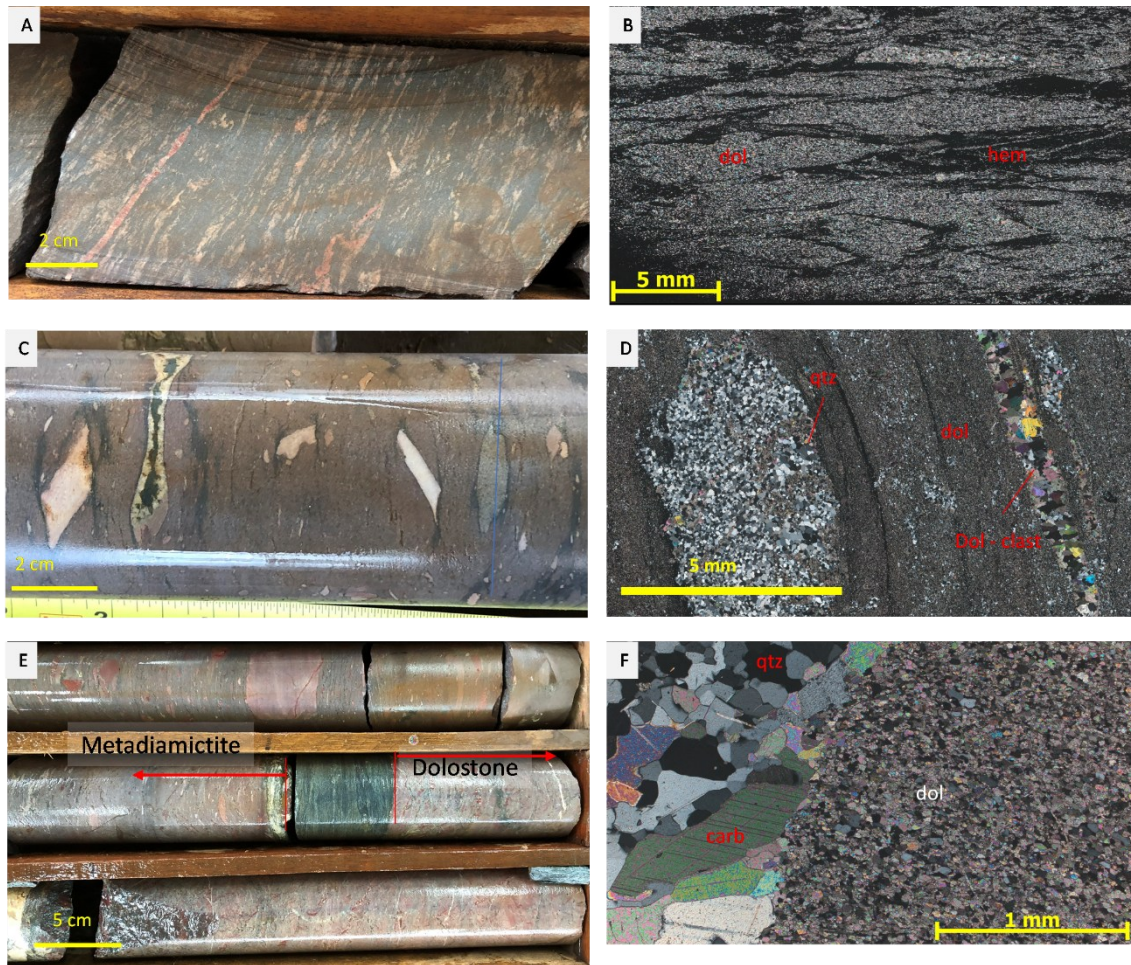


Figure 9: A – Dolomitic BIF drill hole core. The banding is defined by alternating layers of dolomite and iron oxide. B - Photomicrograph of superposed folding and internal shearing strata of dolomite (dol) and hematite (hem). Cross-polarized transmitted light. C - Drill core of metadiamictite. D – Photomicrograph by cross-polarized transmitted light of dolomite clasts (dol clast) and quartz (qtz) immersed in dolomitic matrix (dol). E - Contact between metadiamictite, phyllite and dolostone in drill hole core. And, F – Different texture between dolostone (dol) and vein composed by carbonate (carb) and quartz (qtz). Photomicrography parallel-polarized transmitted light.

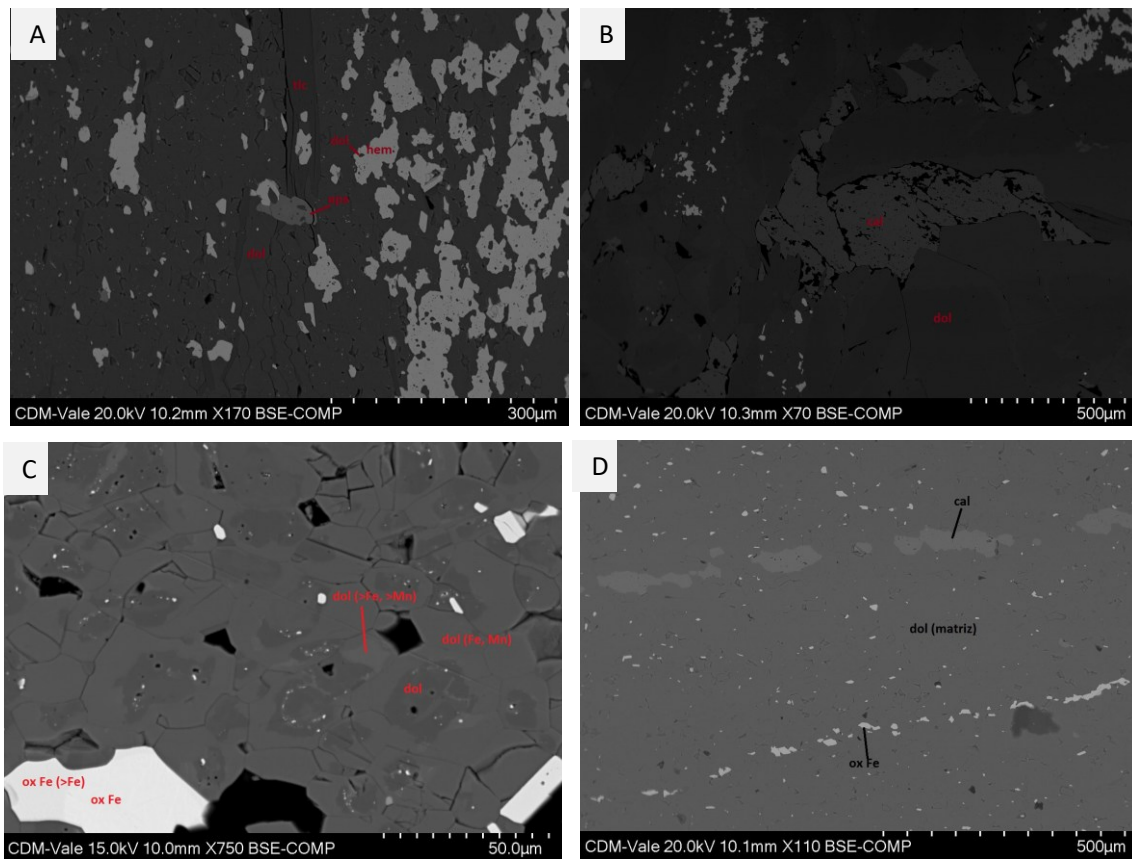


Figure 10: Imaging of SEM, signal backscattered electrons (BSE) A - Close association between hematite (hem) and dolomite (dol), talc veinlet (tlc) and overgrown apatite (apa). B – Calcite vein as a secondary carbonate. C - Different composition of dolomite crystals: core: pure dolomite - dol and borders: Fe and Mn-dolomites. D –Hematite laminae (ox Fe) and calcite veins in dolostone.

### 4.5.3 Geochemistry

#### Major, minor and trace elements

The chemical analyses relative to the major, minor and trace elements for each sedimentary rock domain (clastic and chemical) are presented in Table 1.

#### Clastic Domain

The chemical components  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  make up most of the composition of this domain (Figure 11), and  $\text{MgO}$  can reach a maximum value of 3.33 wt% (sample A010). The black shale layer shows high LOI; the average value is 15.50 wt% due to the presence of carbonaceous matter. Low contents of Ca (range 0.04 to 0.90 wt%) and Mn (0.03 to 0.10 wt%) were obtained for this group. Anomalous NaO values (2.62 wt%) were obtained in a metaconglomerate sample (sample A001). High content of terrigenous elements (Figure 12), for example:  $\text{Al}_2\text{O}_3 \leq 18.23$  wt.%,  $\text{TiO}_2 \leq 1.03$  wt.%,  $\text{Hf} \leq 4.26$  ppm,  $\text{Nb} \leq 11.46$  ppm,  $\text{Th} \leq 14.6$  ppm and  $\text{Zr} \leq 172$  ppm.

Apart from that, the domain is relatively enriched in  $\text{K} \leq 2.96\%$ ,  $\text{Ba} \leq 1,348$  ppm,  $\text{Ce} \leq 159.9$  ppm,  $\text{Rb} \leq 135.4$  ppm,  $\text{V} \leq 265$  ppm,  $\text{Cr} \leq 157$  ppm (except sample A073) and  $\text{U} \leq 11.7$  ppm.

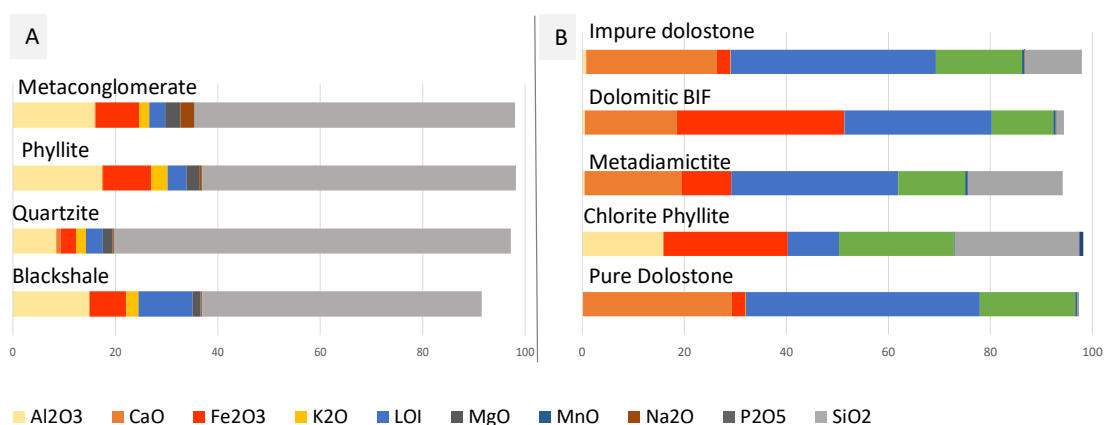


Figure 11: Composition of major elements in the drill hole core. A – Clastic domain (samples: A001, A005, A073 and average of: A008, A009, A010). B – Chemical domain shows different contribution of hematite and quartz. The plot shows the average of the lithological groups: Impure dolostone (samples: A011, A022, A023, A026, A029 and A031), Dolomitic BIF (samples: A012, A035 and A042), Metadiamictite (sample: A044, A046 and A050), Chlorite Phyllite (sample: A074) and pure dolostone – Gandarela Formation (sample: A056, A060 and A063).

Table 1: Chemical analyses of samples from Segredo Mine.

| Clastic Domain                 |                  |               |               |               |               |               | Chemical Domain |               |               |               |               |               |               |               |               |                |                |                |                   |               |               |               |  |
|--------------------------------|------------------|---------------|---------------|---------------|---------------|---------------|-----------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|----------------|----------------|----------------|-------------------|---------------|---------------|---------------|--|
| Sample<br>Depth (m)            | A001<br>106.1    | A005<br>151.9 | A073<br>165.0 | A008<br>183.5 | A009<br>183.6 | A010<br>184.0 | A011<br>187.2   | A012<br>192.2 | A022<br>216.9 | A023<br>221.6 | A026<br>244.7 | A029<br>269.0 | A031<br>277.9 | A035<br>296.6 | A042<br>329.1 | A044<br>340.8  | A046<br>356.0  | A050<br>375.8  | A074<br>390.0     | A056<br>408.9 | A060<br>429.0 | A063<br>443.0 |  |
| Lithology                      | Metaconglomerate | Phyllite      | Quartzite     | Black Shale   | Black Shale   | Black Shale   | Dolostone       | Dolomitic BIF | Dolostone     | Dolostone     | Dolostone     | Dolostone     | Dolostone     | Dolomitic BIF | Dolomitic BIF | Metadiamictite | Metadiamictite | Metadiamictite | Chlorite Phyllite | Dolostone     | Dolostone     | Dolostone     |  |
| Major Elements (%)             |                  |               |               |               |               |               |                 |               |               |               |               |               |               |               |               |                |                |                |                   |               |               |               |  |
| Al <sub>2</sub> O <sub>3</sub> | 15.94            | 17.45         | 8.44          | 18.23         | 12.34         | 14.06         | 0.16            | 0.35          | 0.81          | 0.15          | 0.26          | 2.26          | 1.1           | 0.38          | 0.72          | 0.64           | 0.37           | 0.34           | 15.82             | 0.16          | 0.11          | 0.06          |  |
| CaO                            | 0.22             | 0.12          | 0.9           | 0.05          | 0.04          | 0.16          | 28.71           | 14.22         | 23.89         | 24.23         | 23.93         | 25.71         | 27.38         | 23.95         | 15.98         | 15.05          | 23.88          | 18.04          | 0.17              | 28.79         | 29.12         | 29.59         |  |
| Fe <sub>2</sub> O <sub>3</sub> | 8.44             | 9.42          | 3             | 6.12          | 4.21          | 11.04         | 3.66            | 43.61         | 1.98          | 2.39          | 2.3           | 2.54          | 2.67          | 18.58         | 36.19         | 11             | 8.38           | 9.87           | 24.32             | 3.23          | 2.03          | 2.86          |  |
| K <sub>2</sub> O               | 1.99             | 3.23          | 1.9           | 3.56          | 2.28          | 1.49          | 0.06            | <0.01         | 0.11          | 0.06          | 0.08          | 0.13          | 0.07          | 0.05          | <0.01         | <0.01          | 0.01           | <0.01          | <0.01             | <0.01         | 0.07          | 0.06          |  |
| LOI                            | 3.16             | 3.64          | 3.31          | 15.5          | 11.74         | 4.32          | 45.2            | 22.76         | 36.71         | 37.93         | 37.4          | 40.35         | 43.61         | 37            | 26.88         | 26.31          | 34.37          | 37.48          | 10                | 45.49         | 46.25         | 45.96         |  |
| MgO                            | 2.88             | 2.53          | 1.78          | 1.09          | 0.15          | 3.33          | 18.03           | 9.73          | 14.81         | 15.55         | 15.57         | 18.46         | 18.88         | 15.52         | 10.92         | 10.85          | 16.35          | 12.13          | 22.52             | 18.67         | 18.51         | 19            |  |
| MnO                            | 0.09             | 0.04          | 0.1           | 0.04          | 0.03          | 0.06          | 0.98            | 0.4           | 0.32          | 0.36          | 0.28          | 0.34          | 0.26          | 0.64          | 0.46          | 0.44           | 0.58           | 0.69           | 0.08              | 0.25          | 0.43          | 0.27          |  |
| Na <sub>2</sub> O              | 2.62             | 0.47          | 0.27          | 0.34          | 0.2           | 0.16          | <0.01           | <0.01         | <0.01         | <0.01         | 0.01          | 0.04          | 0.02          | <0.01         | <0.01         | <0.01          | <0.01          | <0.01          | <0.01             | <0.01         | <0.01         | <0.01         |  |
| P <sub>2</sub> O <sub>5</sub>  | 0.15             | 0.09          | 0.03          | 0.09          | 0.13          | 0.1           | 0.02            | 0.24          | 0.06          | 0.05          | 0.07          | 0.06          | 0.01          | 0.11          | <0.01         | <0.01          | <0.01          | <0.01          | 0.11              | <0.01         | 0.01          | <0.01         |  |
| S                              | <0.01            | <0.01         | <0.01         | 0.01          | 0.01          | 0.01          | <0.01           | <0.01         | <0.01         | <0.01         | <0.01         | <0.01         | <0.01         | <0.01         | <0.01         | <0.01          | 0.01           | <0.01          | <0.01             | <0.01         | <0.01         | <0.01         |  |
| SiO <sub>2</sub>               | 62.56            | 61.23         | 77.48         | 44.9          | 55.98         | 62.89         | 0.16            | 1.84          | 18.75         | 17.42         | 19.37         | 8.17          | 2.95          | 0.99          | 1.09          | 31.83          | 2.97           | 20.53          | 24.44             | 0.27          | <0.01         | <0.01         |  |
| TiO <sub>2</sub>               | 0.67             | 0.75          | 0.18          | 1.03          | 0.64          | 0.88          | <0.01           | 0.04          | 0.06          | <0.01         | <0.01         | 0.13          | 0.05          | 0.08          | 0.04          | 0.05           | 0.03           | 0.03           | 0.77              | 0.03          | <0.01         | <0.01         |  |
| Trace Elements (ppm)           |                  |               |               |               |               |               |                 |               |               |               |               |               |               |               |               |                |                |                |                   |               |               |               |  |
| Ag                             | <0.02            | 0.08          | <0.02         | <0.02         | <0.02         | <0.02         | 0.17            | 0.62          | 0.26          | 0.27          | 0.16          | 0.13          | 0.31          | 0.65          | 0.5           | <0.02          | <0.02          | <0.02          | 0.59              | 0.22          | 0.32          | 0.45          |  |
| As                             | 14               | <1            | 1             | 11            | 17            | 23            | <1              | 1             | <1            | <1            | <1            | <1            | <1            | 3             | 1             | 1              | 1              | 1              | 4                 | <1            | <1            | <1            |  |
| Ba                             | 428              | 873           | 574           | 1348          | 844           | 689           | <10             | <10           | 214           | <10           | 17            | 47            | <10           | 22            | <10           | <10            | <10            | <10            | 13                | <10           | <10           | <10           |  |
| Be                             | 1.3              | 2.2           | 0.4           | 3.4           | 2.9           | 1.8           | 0.2             | 0.2           | 0.5           | 0.2           | 0.2           | 0.7           | 0.6           | 1.1           | 0.6           | 0.2            | 0.3            | 0.3            | 2.1               | 0.1           | 0.1           | 0.2           |  |
| Bi                             | 0.13             | 0.11          | 0.11          | 0.25          | 0.11          | 0.15          | <0.04           | 0.04          | 0.04          | 0.05          | 0.06          | <0.04         | <0.04         | 0.07          | 0.07          | <0.04          | 0.07           | 0.13           | 0.15              | <0.04         | <0.04         | <0.04         |  |
| Cd                             | 0.18             | 0.07          | 0.11          | <0.02         | 0.05          | 0.03          | 0.14            | 0.18          | 0.06          | 0.12          | 0.07          | 0.1           | 0.1           | 0.38          | 0.13          | 0.08           | 0.06           | 0.03           | 0.04              | 0.04          | 0.03          | 0.12          |  |
| Co                             | 29.5             | 37.6          | 199.6         | 35.6          | 78.9          | 71.7          | 6.3             | 46.3          | 229.6         | 109.3         | 108.6         | 35.8          | 33.2          | 47.9          | 39.4          | 94.1           | 21.2           | 44.9           | 67.5              | 12            | 1.3           | 1.6           |  |
| Cr                             | 125              | 134           | 19            | 157           | 101           | 106           | 2               | <1            | 2             | <1            | 2             | 3             | 1             | <1            | <1            | 3              | 7              | <1             | 977               | 4             | 3             | 3             |  |
| Cs                             | 3.98             | 6.36          | 4.86          | 9.99          | 5.65          | 2.31          | <0.05           | 0.08          | 1.15          | 0.17          | 0.33          | 0.44          | 0.06          | <0.05         | <0.05         | <0.05          | 0.09           | <0.05          | 0.73              | <0.05         | <0.05         | <0.05         |  |
| Cu                             | 61.4             | 12.4          | 7.9           | 37.9          | 55.1          | 15.1          | 4.9             | 13            | <0.5          | 0.7           | 1.2           | 2.7           | 1             | <0.5          | 8.6           | 15.5           | 15.4           | 24.2           | 13.9              | 4             | <0.5          | 0.7           |  |
| Ga                             | 18.4             | 22.4          | 11.6          | 27            | 17.5          | 20.3          | 1.5             | 2.5           | 1.7           | 0.8           | 0.9           | 3.1           | 1.4           | 2.1           | 4.6           | 2.1            | 3.2            | 2.1            | 24.5              | 1.6           | 0.7           | 0.5           |  |
| Ge                             | 0.4              | 0.3           | <0.1          | <0.1          | <0.1          | <0.1          | <0.1            | 0.2           | <0.1          | <0.1          | <0.1          | <0.1          | <0.1          | 0.3           | 0.2           | <0.1           | <0.1           | <0.1           | 0.6               | <0.1          | <0.1          | <0.1          |  |
| Hf                             | 3.23             | 3.17          | 2.94          | 4.26          | 2.58          | 3.25          | 0.11            | 0.17          | 0.51          | 0.1           | 0.17          | 0.71          | 0.37          | 0.43          | 0.28          | 0.22           | 0.13           | 0.14           | 4.22              | 0.09          | 0.07          | 0.11          |  |
| In                             | 0.06             | 0.09          | 0.03          | 0.08          | 0.07          | 0.05          | <0.02           | <0.02         | <0.02         | <0.02         | <0.02         | 0.02          | <0.02         | <0.02         | <0.02         | <0.02          | <0.02          | <0.02          | 0.06              | <0.02         | <0.02         | <0.02         |  |
| Li                             | 68               | 72            | 28            | 20            | 5             | 58            | <1              | 2             | 16            | 4             | 4             | 28            | 14            | 2             | 3             | 6              | 5              | 4              | 140               | 6             | 4             | <1            |  |
| Mo                             | 1.28             | 1.94          | 0.73          | 0.63          | 0.83          | 0.23          | 0.46            | 1.62          | 0.19          | 0.19          | 0.22          | 0.18          | 0.22          | 1.07          | 0.58          | 0.3            | 0.34           | 0.45           | 0.73              | 0.16          | 0.32          | 0.26          |  |
| Nb                             | 9.98             | 11.4          | 10.63         | 11.46         | 6.95          | 7.84          | 1.13            | 0.55          | 1.7           | 0.47          | 0.89          | 2.07          | 0.92          | 2.14          | 0.62          | 0.61           | 0.29           | 0.34           | 22.59             | 0.06          | 0.24          | 0.22          |  |
| Ni                             | 111.5            | 115.3         | 43.5          | 25.3          | 12.3          | 121.8         | 4.3             | <0.5          | 2.8           | 2.5           | 1.6           | 3.6           | 4.8           | 6.4           | <0.5          | 0.9            | <0.5           | 0.9            | 194               | <0.5          | 1.5           | 2.5           |  |
| Pb                             | 50.1             | 41.3          | 4.9           | 5.2           | 4.3           | 3.1           | 12              | 3.8           | 5.2           | 4.1           | 6.9           | 8.2           | 10.3          | 10.5          | 1.7           | 1              | 1.7            | 2.3            | <0.5              | 1.7           | 6.8           | 29.6          |  |
| Rb                             | 80.4             | 120.3         | 77            | 135.4         | 84.7          | 49.6          | 0.4             | <0.2          | 2.8           | 0.9           | 1.1           | 3.3           | 0.5           | <0.2          | 0.2           | <0.2           | 1              | <0.2           | 1                 | 0.3           | 0.9           | <0.2          |  |
| Sb                             | 1.14             | 2.82          | 4.76          | 5.47          | 23.23         | 4.08          | 0.47            | 7.64          | 5.2           | 0.17          | 0.45          | 13.7          | 6.98          | 4.4           | 4.75          | 1.13           | 1.42           | 2.03           | 6.69              | 0.71          | 0.65          | 0.83          |  |
| Sc                             | 11.1             | 15.7          | 3.9           | 28.4          | 21            | 19.9          | 0.8             | 1             | 1.5           | <0.5          | 0.5           | 3.2           | 3             | 3.8           | 2.5           | 1.3            | 1              | 1              | 15.7              | <0.5          | <0.5          | <0.5          |  |
| Se                             | <2               | <2            | <2            | <2            | <2            | <2            | <2              | <2            | <2            | <2            | <2            | <2            | <2            | <2            | <2            | <2             | <2             | <2             | <2                | <2            | <2            | <2            |  |
| Sn                             | <0.3             | <0.3          | 0.9           | 4.1           | 2.4           | 2.3           | <0.3            | <0.3          | <0.3          | <0.3          | <0.3          | <0.3          | <0.3          | <0.3          | <0.3          | 0.7            | <0.3           | <0.3           | 2.1               | <0.3          | <0.3          | <0.3          |  |
| Sr                             | 97               | 80            | 65            | 45            | 25            | 19            | 93              | <10           | 76            | 65            | 57            | 78            | 62            | 59            | 52            | 31             | 40             | 32             | <10               | <10           | 40            | 49            |  |
| Ta                             | 0.71             | 1.23          | 0.28          | 0.96          | 0.67          | 0.72          | <0.05           | 0.09          | 0.22          | 0.1           | 0.07          | 0.25          | <0.05         | 0.11          | 0.16          | 0.13           | <0.05          | <0.05          | 1.21              | 0.12          | <0.05         | <0.05         |  |
| Te                             | 0.1              | 0.09          | 0.08          | 0.25          | 0.09          | 0.06          | <0.05           | <0.05         | <0.05         | <0.05         | <0.05         | <0.05         | <0.05         | <0.05         | <0.05         | <0.05          | <0.05          | <0.05          | 0.2               | <0.05         | <0.05         | <0.05         |  |
| Th                             | 9.1              | 13.5          | 10.2          | 14.6          | 7.6           | 7.9           | 2.5             | 0.4           | 1.2           | 0.5           | 0.5           | 1.9           | 0.7           | 1.2           | 0.7           | 0.7            | 0.4            | 0.4            | 10.1              | 0.2           | 0.2           | 0.2           |  |
| Tl                             | <0.5             | <0.5          | <0.5          | <0.5          | <0.5          | <0.5          | <0.5            | <0.5          | <0.5          | <0.5          | <0.5          | <0.5          | <0.5          | <0.5          | <0.5          | <0.5           | <0.5           | <0.5           | 0.8               | <0.5          | <0.5          | <0.5          |  |
| U                              | 1.7              | 6.5           | 2.1           | 8             | 9.7           | 11.7          | 2.7             | 3             | 1             | 0.5           | 0.8           | 1.4           | 0.9           | 4.4           | 9.9           | 1.4            | 1.6            | 1.2            | 7.5               | 0.4           | 0.3           | 0.4           |  |
| V                              | 110              | 141           | 57            | 265           | 172           | 166           | <5              | 55            | <5            | <5            | <5            | <5            | 26            | 9             | 59            | <5             | <5             | 5              | 157               | 28            | <5            | <5            |  |
| W                              | 10               | 12.3          | 712.4         | 100.4         | 304.6         | 161.4         | 2.6             | 145.7         | 378.2         | 326.8         | 285.3         | 115.4         | 96.4          | 102.5         | 110.2         | 462.5          | 68.6           | 165            | 12.5              | 39            | 1.9           | 2.2           |  |
| Zn                             | 150              | 120           | 43            | 43            | 22            | 120           | 17              | 35            | 12            | 7             | 10            | 20            | 24            | 33            | 22            | 24             | 12             | 13             | 129               | 5             | 11            | 28            |  |
| Zr                             | 128              | 130           | 80            | 172           | 93            | 131           | 13              | 36            | 38            | 13            | 18            | 38            | 20            | 29            | 26            | 11             | 20             | 23             | 148               | 28            | 14            | 14            |  |

### Chemical Domain: carbonate rocks and metadiamictite

The main mineral in the chemical domain is dolomite (Figure 7B). Generally, calcite corresponds to different vein generations. Chemical analyses identified LOI, CaO and MgO average contents of 37.58, 23.50 and 15.53 wt%, respectively, except for the chlorite phyllite. The domain was subdivided into impure dolostone, dolomitic BIF, metadiamictite, chlorite phyllite, and pure dolostone (Figure 10B). The samples show low content of terrigenous elements (Figure 11).

Impure dolostone, such as those sampled in A022, A023, A026 and A029, has an SiO<sub>2</sub> contribution (average composition 15.93 wt.% SiO<sub>2</sub>). In addition, they have low Fe<sub>2</sub>O<sub>3</sub> ≤ 2.54 wt%, MnO ≤ 0.36 wt% and K<sub>2</sub>O ≤ 0.13 wt%.

The carbonates in the dolomitic BIF, given by the sum of the CaO, MgO and LOI contents, range from 46.71 to 76.47 wt%. Compositionally, there are Fe<sub>2</sub>O<sub>3</sub> ≤ 43.61 wt%, SiO<sub>2</sub> ≤ 1.84 wt%, Al<sub>2</sub>O<sub>3</sub> ≤ 0.72 wt%, MnO ≤ 0.64 wt% and P<sub>2</sub>O<sub>5</sub> ≤ 0.24 wt%.

In the metadiamictite layer, the signature of the major elements shows significant variations due to the heterogeneous composition of the matrix and clasts. The level with the highest contribution of quartz clasts has SiO<sub>2</sub> ≤ 31.83 wt%, while the predominant levels of carbonate intraclasts have a value of 2.97 wt% SiO<sub>2</sub>. The iron content in the matrix decreases with depth and shows average values of 9.75 wt% of Fe<sub>2</sub>O<sub>3</sub>. And the carbonate composition (CaO + MgO + LOI) ranges from 52.21 to 74.60 wt% and the MnO content is less than 0.69 wt%.

The sample A074 collected in the thin layer of chlorite phyllite (0.65 meters thick) showed Fe<sub>2</sub>O<sub>3</sub> (24.32 %wt), SiO<sub>2</sub> (24.32 %wt), MgO (24.44 %wt) and Al<sub>2</sub>O<sub>3</sub> (22.52 %wt) as main constituents. Among the smaller elements, the sample shows relatively high levels of Cr, Ga, Hf, Li, Nb, Ni, Ti and Th.

Pure dolostone collected from samples A056, A060 and A63 shows homogeneous carbonate composition, exceeding 92.95% wt of CaO + MgO + LOI. These rocks are characterized by low Fe<sub>2</sub>O<sub>3</sub> ≤ 3.23 wt%, MnO ≤ 0.43 wt%, SiO<sub>2</sub> ≤ 0.27 wt% and Al<sub>2</sub>O<sub>3</sub> ≤ 0.16 wt%.

Dolostone and dolomitic BIF show low contents of Ba (except sample A22), Hf, K, Na, Ni Th and Zr. Additionally, it displays U/Th average value of 3.09 and outlier reach up 14.14 (sample A042).

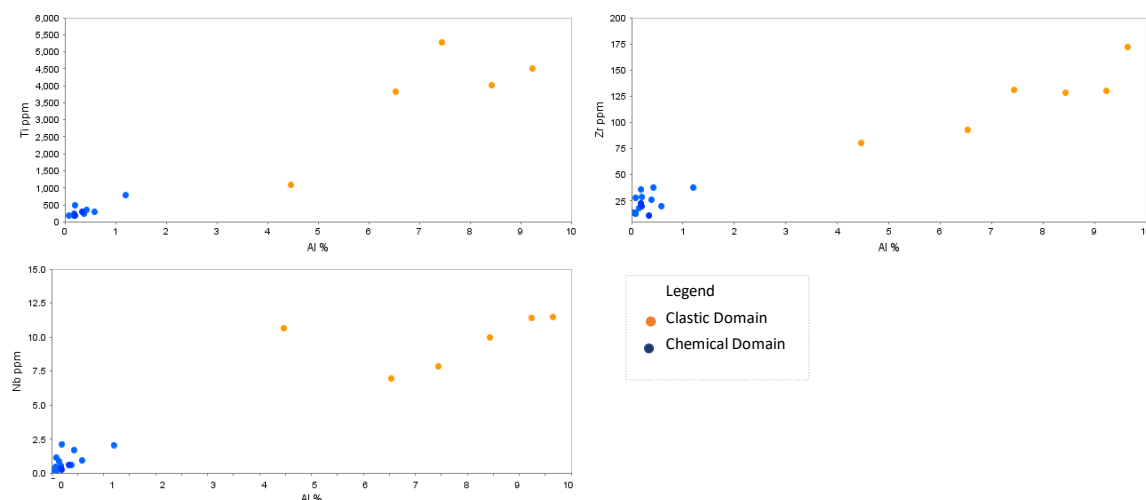


Figure 12: Plot of Ti, Nb and Zr versus Al for the clastic and chemical domain. All studied samples presented positive correlation, and terrestrial contribution is significant only in the clastic domain.

### Rare Earth Elements and Yttrium

The Rare Earth Elements and Yttrium (REEY) values, normalized to Post Archean Average Australian Shale (PAAS; Taylor and McLennan, 1985), are shown in Table 2. Generally, rocks are depleted in trace elements (average 5 ppm REE) but can reach an anomalous value of 159.9 ppm Ce in sample A008 (black shale). Distinct REEY signatures were identified in the domains, as shown in Figures 13 A and B.

The clastic domain indicated discrete enrichment in heavy rare earth elements (Figure 13A), except for samples A008 and A073, which correspond to black shale and quartzite, respectively. Measurements of the Tm element were not obtained in the black shale samples (A008, A009 and A010). Values below the detection limit ( $<0.05$ ) were suppressed in the plots.

Among the chemical domain, all samples show enrichment in the heavier REE with respect to light REE (Figure 13B). The mean values of impure dolostone present intermediate REEY composition between dolomitic BIF and dolostone associated with Gandarela Formation. In addition, Gandarela Formation dolostone is more depleted in the REEY in relation to the chemical domain. On the other hand, the chlorite phyllite (390m deep in the drill hole core) has a different REEY behavior and enrichment in the heavy REE is more prominent (Figure 13C).

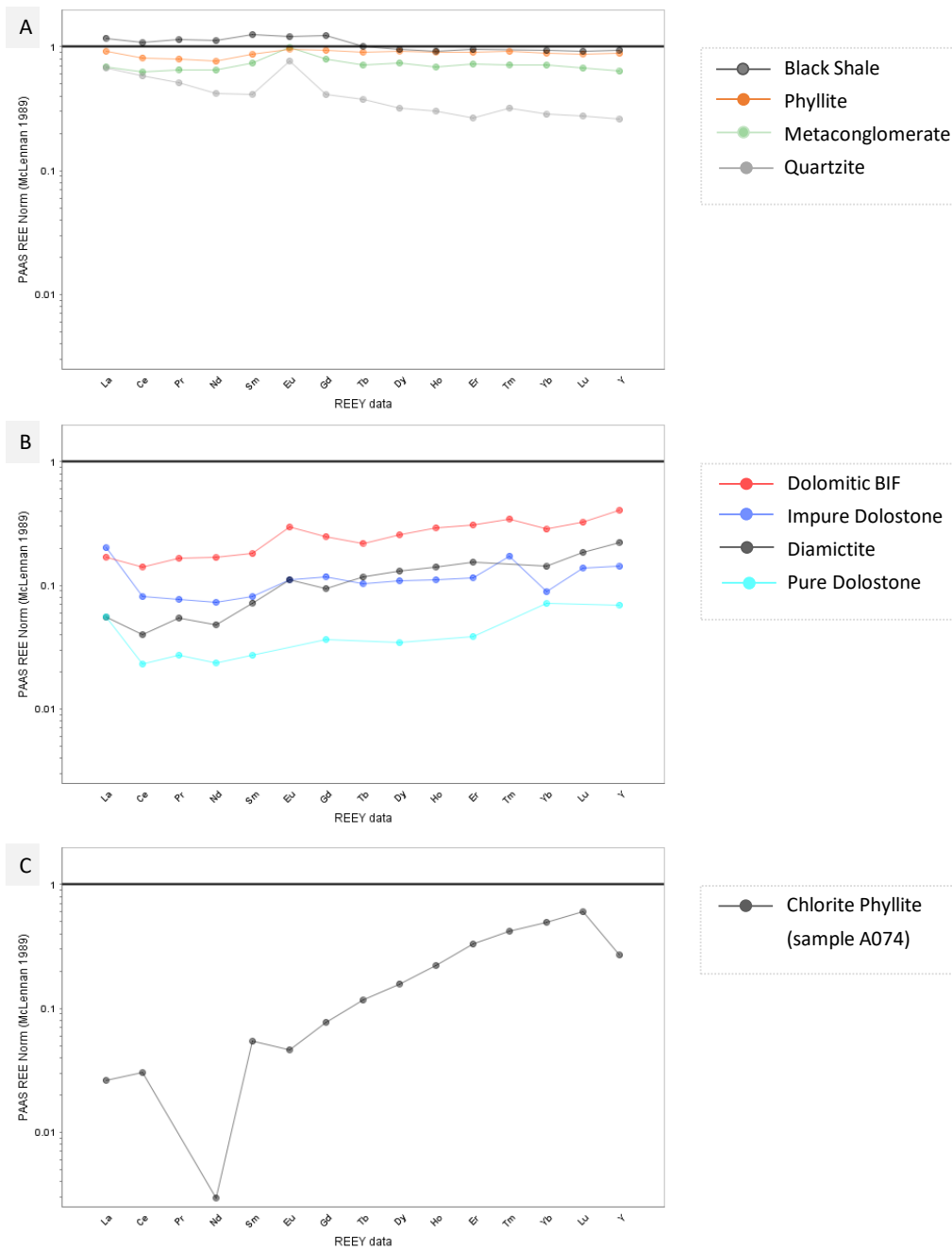


Figure 13 – PAAS - normalized REEY data (Taylor and McLennan 1985) for clastic domain (A) and chemical domain (B). Average values were calculated for black shale (n=3), diamictite (n=3), dolomitic itabirite (n=3), impure dolostone (n=6) and pure dolostone (n=3). (C) Chlorite Phyllite between metadiamictite and dolostones layers (depth in the drill hole: 390m).

Positive Eu anomaly (average 1.25) characterizes the dolomitic BIF and dolostone. This anomaly is calculated as  $Eu/Eu^* = Eu_{PAAS} / (Sm_{PAAS} \times Gd_{PAAS})^{0.5}$ , where  $Eu^*$  is the hypothetical concentration of  $Eu^{+3}$  (Taylor and McLennan, 1985). Figure 14 displays a diagram used to calculate Ce anomaly (Bau and Dulski 1996). For this purpose, the abundance of Ce and Pr were calculated from the formulas: Ce ( $Ce/Ce^* = Ce_{PAAS} / (0.5 \times (La_{PAAS} + Pr_{PAAS}))$ ) and Pr ( $Pr/Pr^* = Pr_{PAAS} /$

$(0.5 \times (\text{Ce}_{\text{PAAS}} + \text{Nd}_{\text{PAAS}}))$ ). As a result, a Ce negative anomaly was identified mainly in pure dolostones (Gandarela Formation) and in a dolomitic BIF sample. In contrast, impure dolostone (Cauê Formation) exhibits positive La anomaly, and a single dolomitic BIF sample plot within the negative La anomaly field. Additionally, dolomitic BIF and dolostone shows Y/Ho ratios ranging from 31.0 to 46.0.

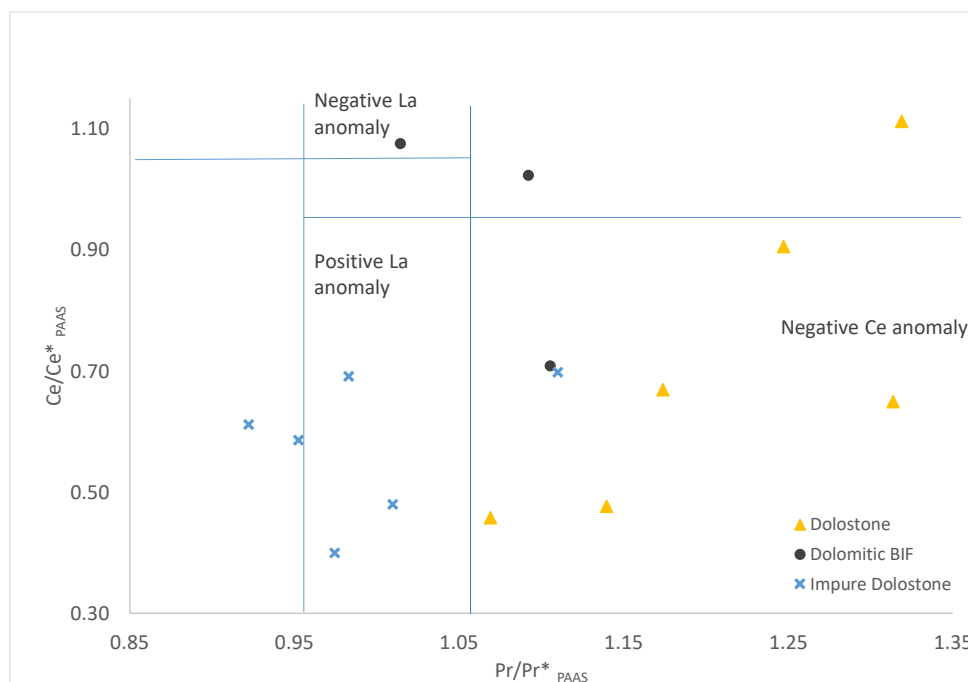


Figure 14 – Plots of Ce/Ce\* versus Pr/Pr\* (Bau and Dulski 1996) for samples from the chemical domain.

Table 2: REE + Y data and relevant ratios from drill hole core in Segredo Mine.

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#### 4.5.4 Carbon and Oxygen Isotopes

The overall isotopic data, summarized in table 3, shows the variation of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for Ca-Mg carbonates. Isotopic data were calibrated to the Vienna PeeDee Belemnite (VPDB), an international marine carbonate standard. The 74 samples of dolostone, dolomitic BIF, metadiamictite and carbonate veins show  $\delta^{13}\text{C}_{\text{VPDB}}$  values ranging from -2.40 to 1.15‰ and negative values of  $\delta^{18}\text{O}_{\text{VPDB}}$  spread between -17.60 to -4.47‰. The O-isotopic ratio becomes less negative with increasing drill hole depth, whereas  $\delta^{13}\text{C}_{\text{VPDB}}$  values approach zero. The dolomitic BIF is depleted in  $^{13}\text{C}$  and  $^{18}\text{O}$  and dolostone layers comprise a distinct grouping (Figure 6). Remarkably, the results obtained in the carbonate veins are like the proximal rocks, besides the isotopic ratio  $\delta^{18}\text{O}$  varies from -9.40 to -7.89‰ and just one result reach to -14.46‰.

Table 3: Carbon and oxygen isotope values for drill hole core in study. The precision of isotopic measurements is better than  $\pm 0.1\text{‰}$ .

| Sample  | Depth (m) | $\delta^{13}\text{C}_{\text{VPDB}}\text{‰}$ | $\delta^{18}\text{O}_{\text{VPDB}}\text{‰}$ | Analyzed Rock                    |
|---------|-----------|---------------------------------------------|---------------------------------------------|----------------------------------|
| A011    | 187.2     | -2.38                                       | -16.52                                      | Dolostone                        |
| A012-C  | 192.2     | -2.06                                       | -16.66                                      | Dolomitic BIF - Carbonate band   |
| A012-F  | 192.2     | -2.18                                       | -16.76                                      | Dolomitic BIF - Ferruginous band |
| A019-F  | 197.2     | -2.24                                       | -15.72                                      | Dolomitic BIF - Ferruginous band |
| A020-C  | 202.1     | -1.59                                       | -16.37                                      | Dolomitic BIF - Carbonate band   |
| A020-F  | 202.1     | -1.59                                       | -16.75                                      | Dolomitic BIF - Ferruginous band |
| A021-C  | 206.1     | -1.78                                       | -16.71                                      | Dolomitic BIF - Carbonate band   |
| A021-F  | 206.1     | -1.83                                       | -16.6                                       | Dolomitic BIF - Ferruginous band |
| A022    | 216.9     | -1.66                                       | -13.67                                      | Dolostone                        |
| A023    | 221.6     | -1.39                                       | -12.52                                      | Dolostone                        |
| A024    | 230.0     | -1.33                                       | -12.77                                      | Dolostone                        |
| A025    | 235.7     | -1.17                                       | -11.51                                      | Dolostone                        |
| A026    | 244.7     | -1.19                                       | -12.39                                      | Dolostone                        |
| A027    | 245.9     | -1.16                                       | -11.3                                       | Dolostone                        |
| A028    | 266.7     | -1.4                                        | -12.13                                      | Dolostone                        |
| A029    | 269.0     | -1.5                                        | -11.75                                      | Dolostone                        |
| A030-C1 | 275.0     | -1.47                                       | -11.46                                      | Dolostone                        |
| A030-C2 | 275.0     | -1.78                                       | -14.46                                      | Carbonate Vein                   |
| A031    | 277.9     | -1.59                                       | -12.82                                      | Dolostone                        |
| A032    | 283.0     | -1.48                                       | -13.74                                      | Dolostone                        |
| A033    | 287.9     | -1.55                                       | -14.75                                      | Dolostone                        |
| A034-C  | 292.9     | -2.17                                       | -15.56                                      | Dolomitic BIF - Carbonate band   |
| A035-C  | 296.6     | -1.98                                       | -16.04                                      | Dolomitic BIF - Carbonate band   |
| A035-F  | 296.6     | -1.43                                       | -15.88                                      | Dolomitic BIF - Ferruginous band |
| A036-M  | 298.8     | -1.38                                       | -11.59                                      | Dolostone                        |
| A036-C  | 298.8     | -1.58                                       | -11.62                                      | Dolostone                        |
| A037-C  | 302.2     | -2.4                                        | -16.28                                      | Dolomitic BIF - Carbonate band   |
| A037-F  | 302.2     | -2.36                                       | -16.05                                      | Dolomitic BIF - Ferruginous band |
| A038    | 304.8     | -0.06                                       | -7.44                                       | Dolostone                        |
| A041-C  | 318.8     | -0.84                                       | -17.6                                       | Dolomitic BIF - Carbonate band   |
| A042-C  | 329.1     | -0.25                                       | -13.17                                      | Dolomitic BIF - Carbonate band   |
| A042-F  | 329.1     | -0.17                                       | -15.66                                      | Dolomitic BIF - Ferruginous band |
| A044-M  | 340.8     | -0.84                                       | -8.49                                       | Diamictite - Matrix              |
| A044-C1 | 340.8     | -2.18                                       | -15.13                                      | Diamictite - Siliciclastic Clast |
| A044-C2 | 340.8     | -0.57                                       | -9.82                                       | Diamictite - Siliciclastic Clast |
| A044-C3 | 340.8     | -0.22                                       | -10.3                                       | Diamictite - Dolomitic BIF Clast |
| A045-C1 | 345.7     | -0.106                                      | -8.39                                       | Diamictite - Matrix              |
| A045-C2 | 345.7     | 0.14                                        | -13.39                                      | Diamictite - Matrix              |
| A045-V  | 345.7     | -0.13                                       | -8.31                                       | Carbonate Vein                   |
| A046-M  | 356.0     | -0.32                                       | -9.5                                        | Diamictite - Matrix              |
| A046-C  | 356.0     | -0.22                                       | -8.48                                       | Diamictite - Carbonate Clast     |
| A047    | 361.3     | -0.44                                       | -8.54                                       | Diamictite - Matrix              |
| A049    | 367.8     | -0.99                                       | -9.27                                       | Diamictite - Matrix              |
| A050-C  | 375.8     | -1.12                                       | -8.99                                       | Diamictite - Siliciclastic Clast |
| A051-M  | 380.2     | -0.93                                       | -10.8                                       | Diamictite - Matrix              |
| A051-C  | 380.2     | -0.13                                       | -13.12                                      | Diamictite - Carbonate Clast     |
| A052    | 385.7     | -1.33                                       | -11.68                                      | Diamictite - Matrix              |
| A053-M  | 389.1     | -0.54                                       | -11.31                                      | Diamictite - Matrix              |
| A053-C  | 389.1     | -0.54                                       | -10.75                                      | Diamictite - Carbonate Clast     |
| A054    | 395.0     | -0.74                                       | -10.87                                      | Dolostone                        |
| A055    | 399.9     | 0.14                                        | -8.44                                       | Dolostone                        |
| A056-C1 | 408.9     | -0.06                                       | -8.1                                        | Dolostone                        |
| A056-C2 | 408.9     | -0.39                                       | -8.25                                       | Carbonate Vein                   |
| A057    | 413.9     | -0.29                                       | -9.1                                        | Dolostone                        |
| A058-C1 | 418.9     | 0.27                                        | -9.73                                       | Dolostone                        |
| A058-C2 | 418.9     | -0.76                                       | -9.4                                        | Carbonate Vein                   |
| A059-C1 | 423.8     | -0.14                                       | -8.79                                       | Dolostone                        |
| A059-C2 | 423.8     | -0.34                                       | -9.13                                       | Dolostone                        |
| A060-C1 | 429.0     | -0.23                                       | -7.33                                       | Dolostone                        |
| A060-C2 | 429.0     | 0.05                                        | -7.79                                       | Dolostone                        |
| A062    | 438.4     | -0.25                                       | -6.99                                       | Dolostone                        |
| A063-C1 | 443.0     | -0.24                                       | -6.36                                       | Dolostone                        |
| A063-C2 | 443.0     | -0.33                                       | -9.58                                       | Dolostone                        |
| A064-C1 | 448.0     | -0.29                                       | -6.16                                       | Dolostone                        |
| A064-C2 | 448.0     | -0.23                                       | -6.23                                       | Dolostone                        |
| A065-C1 | 452.7     | 0.05                                        | -7.46                                       | Dolostone                        |
| A065-C2 | 452.7     | -0.29                                       | -7.89                                       | Carbonate Vein                   |
| A066-C1 | 457.5     | 0.33                                        | -4.78                                       | Dolostone                        |
| A066-C2 | 457.5     | 1.15                                        | -13.08                                      | Dolostone                        |
| A067    | 462.4     | 0.53                                        | -5.82                                       | Dolostone                        |
| A068    | 467.4     | 0.21                                        | -4.47                                       | Dolostone                        |
| A069    | 472.5     | 0.04                                        | -5.49                                       | Dolostone                        |
| A070    | 477.0     | 0.16                                        | -6.41                                       | Dolostone                        |
| A071    | 480.1     | 0.2                                         | -4.94                                       | Dolostone                        |

#### 4.5.5 U-Pb dating

From the metaconglomerate belonging to the clastic domain (Figure 6), a total of 65 zircon crystals (sample AC01) were recovered. Images of zircon grains obtained by Cathodoluminescence (CL) are shown in Figure 15. The grain sizes ranges from 65 to 260  $\mu\text{m}$  in length and exhibit anhedral to euhedral shapes.

|                                                                                    |                                                                                    |                                                                                    |                                                                                    |                                                                                    |                                                                                      |                                                                                      |
|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
|   |   |   |   |   |   |   |
| Sample 11a<br>2818 $\pm$<br>31 Ma                                                  | Sample 12a<br>2212 $\pm$<br>44 Ma<br>Sample 13<br>2212 $\pm$<br>36 Ma              | Sample 16a<br>3393<br>$\pm$ 30 Ma                                                  | Sample 12<br>2621<br>$\pm$ 39 Ma                                                   | Sample 28<br>2193<br>$\pm$ 49 Ma                                                   | Sample 31<br>2141<br>$\pm$ 45 Ma                                                     | Sample 34<br>2222<br>$\pm$ 41 Ma                                                     |
|  |  |  |  |  |  |  |
| Sample 35<br>2191<br>$\pm$ 52 Ma                                                   | Sample 49<br>3441<br>$\pm$ 34 Ma                                                   | Sample 50<br>2909<br>$\pm$ 62 Ma                                                   | Sample 51<br>2231<br>$\pm$ 46 Ma                                                   | Sample 53<br>2613<br>$\pm$ 38 Ma                                                   | Sample 76<br>2254<br>$\pm$ 37 Ma<br>Sample 77<br>2202<br>$\pm$ 39 Ma                 | Sample 80<br>3011<br>$\pm$ 40 Ma                                                     |

200 $\mu\text{m}$

Figure 15: Photomicrography by Cathodoluminescence with the location of some of the spots performed by LA-SF-ICPMS in concordant zircon grains (within 90-110%) and the measured  $^{207}\text{Pb}/^{206}\text{Pb}$  ages.

Measurements were obtained from 71 spots, avoiding microfractures and weakly zoned. Among the measures obtained, 17 yielded concordant ages using only the zircon grains that show concordance within 90-110% concordance. The complete dataset is provided in table 4. The results are shown in  $^{207}\text{Pb}/^{206}\text{Pb}$  age histograms (bin size: 40 Ma) and probability density plots (Figure 16), calculated using the Isoplot 3.6 software by Ludwig (2008).

Table 4 – U-Pb data for detrital zircons of the metaconglomerate sample number AC01. Concordance calculated as  $(^{206}\text{Pb}/^{238}\text{U} \text{ age}/^{207}\text{Pb}/^{206}\text{Pb} \text{ age}) \times 100$ . Total systematic uncertainties (ssys):  $^{206}\text{Pb}/^{238}\text{U} = 2.0\%$ ,  $^{207}\text{Pb}/^{206}\text{Pb} = 0.55\%$  (2sigma). The blue line indicates concordant date; the yellow line shows the dates utilized in discordia, and the green line shows a sample used in both diagrams.

| Spot Number | f <sup>206</sup> | <sup>206</sup> Pb cps | U ppm    | Th/U | Ratios                               |        |                                     |        |                                     |        |      |                                      |      |                                     | Ages (Ma) |                                     |      |        |  |  |  |
|-------------|------------------|-----------------------|----------|------|--------------------------------------|--------|-------------------------------------|--------|-------------------------------------|--------|------|--------------------------------------|------|-------------------------------------|-----------|-------------------------------------|------|--------|--|--|--|
|             |                  |                       |          |      | <sup>207</sup> Pb/ <sup>206</sup> Pb | 2s (%) | <sup>207</sup> Pb/ <sup>235</sup> U | 2s (%) | <sup>206</sup> Pb/ <sup>238</sup> U | 2s (%) | Rho  | <sup>207</sup> Pb/ <sup>206</sup> Pb | 2s ± | <sup>206</sup> Pb/ <sup>238</sup> U | 2s ±      | <sup>207</sup> Pb/ <sup>235</sup> U | 2s ± | % conc |  |  |  |
| 07a         | 0.12             | 2367549               | 635.7897 | 0.60 | 0.1304                               | 2.02   | 5.2889                              | 2.67   | 0.2941                              | 1.74   | 0.65 | 2104                                 | 35   | 1662                                | 26        | 1867                                | 23   | 89     |  |  |  |
| 08a         | 0.10             | 2016384               | 533.807  | 2.46 | 0.1238                               | 1.96   | 5.0935                              | 2.63   | 0.2983                              | 1.74   | 0.66 | 2012                                 | 35   | 1683                                | 26        | 1835                                | 23   | 92     |  |  |  |
| 09a         | 0.28             | 1958229               | 459.0961 | 1.83 | 0.1352                               | 2.23   | 6.2812                              | 2.95   | 0.3369                              | 1.93   | 0.66 | 2167                                 | 39   | 1872                                | 32        | 2016                                | 26   | 93     |  |  |  |
| 10a         | 0.23             | 1574618               | 851.8338 | 3.52 | 0.1033                               | 2.42   | 2.0799                              | 2.95   | 0.1460                              | 1.68   | 0.57 | 1685                                 | 45   | 878                                 | 14        | 1142                                | 21   | 77     |  |  |  |
| 11a         | 0.16             | 1888376               | 275.3773 | 1.65 | 0.1990                               | 1.90   | 14.8577                             | 2.67   | 0.5416                              | 1.88   | 0.70 | 2818                                 | 31   | 2790                                | 43        | 2806                                | 26   | 100    |  |  |  |
| 12a         | 1.00             | 510183.1              | 99.70736 | 0.66 | 0.1388                               | 2.56   | 7.7326                              | 3.13   | 0.4041                              | 1.79   | 0.57 | 2212                                 | 44   | 2188                                | 34        | 2200                                | 29   | 100    |  |  |  |
| 13a         | 0.00             | 410220                | 79.70513 | 0.76 | 0.1388                               | 2.07   | 7.7790                              | 2.72   | 0.4065                              | 1.75   | 0.64 | 2212                                 | 36   | 2199                                | 33        | 2206                                | 25   | 100    |  |  |  |
| 14a         | 0.27             | 2059849               | 767.8102 | 2.41 | 0.1197                               | 1.97   | 3.4971                              | 2.72   | 0.2119                              | 1.87   | 0.69 | 1952                                 | 35   | 1239                                | 21        | 1527                                | 22   | 82     |  |  |  |
| 15a         | 3.29             | 2079148               | 3067.527 | 1.36 | 0.2901                               | 3.09   | 2.1414                              | 12.64  | 0.0535                              | 12.26  | 0.97 | 3418                                 | 48   | 336                                 | 41        | 1162                                | 92   | 29     |  |  |  |
| 16a         | 0.01             | 2379240               | 274.8946 | 2.99 | 0.2855                               | 1.93   | 26.9088                             | 2.67   | 0.6836                              | 1.84   | 0.69 | 3393                                 | 30   | 3358                                | 49        | 3380                                | 26   | 100    |  |  |  |
| 07          | 5.67             | 1966293               | 1245.475 | 1.36 | 0.4010                               | 4.51   | 17.5008                             | 6.09   | 0.3165                              | 4.09   | 0.67 | 3913                                 | 68   | 1773                                | 63        | 2963                                | 60   | 60     |  |  |  |
| 08          | 0.49             | 1484571               | 1591.549 | 1.43 | 0.1214                               | 2.09   | 3.1311                              | 2.87   | 0.1870                              | 1.97   | 0.69 | 1977                                 | 37   | 1105                                | 20        | 1440                                | 22   | 77     |  |  |  |
| 09          | 1.00             | 1756928               | 2717.729 | 0.83 | 0.1144                               | 2.72   | 2.0449                              | 3.63   | 0.1296                              | 2.41   | 0.66 | 1871                                 | 49   | 786                                 | 18        | 1131                                | 25   | 69     |  |  |  |
| 10          | 3.95             | 1407782               | 1109.837 | 1.80 | 0.3135                               | 3.50   | 10.9933                             | 5.04   | 0.2543                              | 3.63   | 0.72 | 3538                                 | 54   | 1461                                | 47        | 2523                                | 48   | 58     |  |  |  |
| 11          | 0.66             | 1072553               | 674.9201 | 0.94 | 0.1297                               | 2.11   | 5.6982                              | 2.92   | 0.3186                              | 2.01   | 0.69 | 2094                                 | 37   | 1783                                | 31        | 1931                                | 25   | 92     |  |  |  |
| 12          | 1.00             | 873160.5              | 346.4124 | 2.05 | 0.1766                               | 2.36   | 12.3023                             | 3.04   | 0.5054                              | 1.92   | 0.63 | 2621                                 | 39   | 2637                                | 41        | 2628                                | 29   | 100    |  |  |  |
| 13          | 1.00             | 171045.8              | 75.24873 | 2.44 | 0.1736                               | 2.40   | 10.9085                             | 3.09   | 0.4557                              | 1.94   | 0.63 | 2593                                 | 40   | 2421                                | 39        | 2515                                | 29   | 96     |  |  |  |
| 14          | 0.07             | 744970.9              | 504.2569 | 0.97 | 0.1285                               | 2.24   | 5.2490                              | 2.90   | 0.2962                              | 1.84   | 0.64 | 2078                                 | 39   | 1672                                | 27        | 1861                                | 25   | 90     |  |  |  |
| 15          | 1.78             | 1531072               | 1868.107 | 0.98 | 0.2136                               | 2.69   | 4.8395                              | 3.92   | 0.1643                              | 2.85   | 0.73 | 2933                                 | 44   | 981                                 | 26        | 1792                                | 33   | 55     |  |  |  |
| 16          | 1.42             | 852322.7              | 1530.352 | 2.82 | 0.1415                               | 2.80   | 2.1781                              | 4.25   | 0.1117                              | 3.19   | 0.75 | 2245                                 | 48   | 682                                 | 21        | 1174                                | 30   | 58     |  |  |  |
| 17          | 0.40             | 1542301               | 1352.861 | 0.72 | 0.1633                               | 2.20   | 5.1456                              | 2.88   | 0.2286                              | 1.87   | 0.65 | 2490                                 | 37   | 1327                                | 22        | 1844                                | 25   | 72     |  |  |  |
| 18          | 1.16             | 1249016               | 1755.684 | 3.06 | 0.1479                               | 2.51   | 2.9089                              | 3.55   | 0.1426                              | 2.52   | 0.71 | 2322                                 | 43   | 860                                 | 20        | 1384                                | 27   | 62     |  |  |  |
| 19          | 2.10             | 699735.4              | 437.1664 | 0.43 | 0.2630                               | 2.76   | 11.6375                             | 3.58   | 0.3209                              | 2.27   | 0.64 | 3265                                 | 43   | 1794                                | 35        | 2576                                | 34   | 69     |  |  |  |
| 20          | 0.96             | 1492847               | 1564.589 | 1.19 | 0.1475                               | 2.30   | 3.8911                              | 3.21   | 0.1913                              | 2.23   | 0.70 | 2317                                 | 39   | 1128                                | 23        | 1612                                | 26   | 70     |  |  |  |
| 27          | 0.90             | 1330235               | 1549.505 | 0.99 | 0.1417                               | 2.37   | 3.3624                              | 3.24   | 0.1721                              | 2.20   | 0.68 | 2248                                 | 41   | 1024                                | 21        | 1496                                | 26   | 68     |  |  |  |
| 28          | 1.00             | 179089.1              | 88.73375 | 1.84 | 0.1373                               | 2.84   | 7.6590                              | 3.46   | 0.4047                              | 1.99   | 0.57 | 2193                                 | 49   | 2190                                | 37        | 2192                                | 32   | 100    |  |  |  |
| 29          | 0.13             | 577693.5              | 479.4644 | 2.19 | 0.1217                               | 1.93   | 4.0542                              | 2.74   | 0.2416                              | 1.94   | 0.71 | 1982                                 | 34   | 1395                                | 24        | 1645                                | 23   | 85     |  |  |  |
| 30          | 0.52             | 355394.3              | 202.7906 | 1.74 | 0.1335                               | 2.35   | 6.4656                              | 3.02   | 0.3514                              | 1.90   | 0.63 | 2144                                 | 41   | 1941                                | 32        | 2041                                | 27   | 95     |  |  |  |
| 31          | 1.00             | 498812.1              | 252.1849 | 2.38 | 0.1332                               | 2.56   | 7.2835                              | 3.22   | 0.3966                              | 1.96   | 0.61 | 2141                                 | 45   | 2153                                | 36        | 2147                                | 29   | 100    |  |  |  |
| 32          | 0.47             | 1110303               | 708.2636 | 1.59 | 0.1306                               | 2.08   | 5.6596                              | 2.88   | 0.3143                              | 1.99   | 0.69 | 2106                                 | 36   | 1762                                | 31        | 1925                                | 25   | 91     |  |  |  |
| 33          | 0.84             | 370747.7              | 262.622  | 2.43 | 0.1761                               | 2.32   | 6.8719                              | 3.12   | 0.2830                              | 2.09   | 0.67 | 2616                                 | 39   | 1607                                | 30        | 2095                                | 28   | 76     |  |  |  |
| 34          | 0.19             | 681428                | 327.9661 | 1.54 | 0.1396                               | 2.39   | 8.0166                              | 3.08   | 0.4166                              | 1.94   | 0.63 | 2222                                 | 41   | 2245                                | 37        | 2233                                | 28   | 100    |  |  |  |
| 35          | 0.50             | 262527.9              | 128.2043 | 2.23 | 0.1371                               | 2.96   | 7.7629                              | 3.55   | 0.4106                              | 1.95   | 0.55 | 2191                                 | 52   | 2217                                | 36        | 2204                                | 32   | 100    |  |  |  |
| 36          | 4.97             | 327283.9              | 264.1939 | 3.73 | 0.3993                               | 3.29   | 13.6738                             | 5.55   | 0.2484                              | 4.47   | 0.81 | 3906                                 | 49   | 1430                                | 57        | 2727                                | 54   | 52     |  |  |  |
| 37          | 0.17             | 1395503               | 1204.967 | 0.26 | 0.1250                               | 1.85   | 4.0010                              | 2.76   | 0.2322                              | 2.05   | 0.74 | 2028                                 | 33   | 1346                                | 25        | 1634                                | 23   | 82     |  |  |  |
| 38          | 1.00             | 219994.1              | 160.586  | 1.70 | 0.1597                               | 2.39   | 6.0482                              | 3.26   | 0.2747                              | 2.22   | 0.68 | 2453                                 | 41   | 1564                                | 31        | 1983                                | 29   | 79     |  |  |  |
| 39          | 0.32             | 667790.6              | 368.0409 | 2.14 | 0.1356                               | 1.99   | 6.8019                              | 2.85   | 0.3638                              | 2.04   | 0.72 | 2172                                 | 35   | 2000                                | 35        | 2086                                | 25   | 96     |  |  |  |
| 40          | 0.02             | 1649409               | 726.6904 | 1.18 | 0.1728                               | 1.98   | 10.8441                             | 2.80   | 0.4551                              | 1.98   | 0.71 | 2585                                 | 33   | 2418                                | 40        | 2510                                | 26   | 96     |  |  |  |
| 47          | 0.02             | 700596.6              | 460.374  | 2.19 | 0.1350                               | 2.12   | 5.6811                              | 2.86   | 0.3051                              | 1.92   | 0.67 | 2165                                 | 37   | 1717                                | 29        | 1929                                | 25   | 89     |  |  |  |
| 48          | 0.00             | 231446                | 105.0306 | 2.14 | 0.1731                               | 1.99   | 10.5447                             | 2.86   | 0.4418                              | 2.05   | 0.72 | 2588                                 | 33   | 2359                                | 40        | 2484                                | 27   | 95     |  |  |  |
| 49          | 0.01             | 1345943               | 377.2558 | 2.87 | 0.2944                               | 2.21   | 29.0351                             | 2.93   | 0.7153                              | 1.92   | 0.65 | 3441                                 | 34   | 3478                                | 52        | 3455                                | 29   | 100    |  |  |  |
| 50          | 1.00             | 359886.7              | 125.8378 | 1.69 | 0.2104                               | 3.85   | 16.6365                             | 4.38   | 0.5734                              | 2.10   | 0.48 | 2909                                 | 62   | 2922                                | 49        | 2914                                | 43   | 100    |  |  |  |
| 51          | 1.00             | 368094.1              | 177.8925 | 1.33 | 0.1403                               | 2.68   | 8.0257                              | 3.36   | 0.4149                              | 2.02   | 0.60 | 2231                                 | 46   | 2237                                | 38        | 2234                                | 31   | 100    |  |  |  |
| 52          | 0.50             | 866134                | 724.055  | 1.69 | 0.1289                               | 2.13   | 4.2624                              | 2.99   | 0.2398                              | 2.10   | 0.70 | 2083                                 | 37   | 1386                                | 26        | 1686                                | 25   | 82     |  |  |  |
| 53          | 0.20             | 726823.1              | 289.0991 | 1.50 | 0.1758                               | 2.26   | 12.2157                             | 2.96   | 0.5041                              | 1.90   | 0.64 | 2613                                 | 38   | 2631                                | 41        | 2621                                | 28   | 100    |  |  |  |
| 54          | 2.26             | 1747592               | 2878.776 | 0.53 | 0.1669                               | 3.33   | 2.8007                              | 5.42   | 0.1217                              | 4.28   | 0.79 | 2527                                 | 56   | 740                                 | 30        | 1356                                | 41   | 54     |  |  |  |
| 55          | 0.38             | 1270666               | 642.6569 | 2.08 | 0.2166                               | 1.97   | 11.8390                             | 2.79   | 0.3964                              | 1.97   | 0.71 | 2956                                 | 32   | 2153                                | 36        | 2592                                | 26   | 83     |  |  |  |
| 56          | 0.11             | 1028962               | 841.0188 | 1.40 | 0.1296                               | 2.18   | 4.3820                              | 2.93   | 0.2453                              | 1.95   | 0.67 | 2092                                 | 38   | 1414                                | 25        | 1709                                | 24   | 82     |  |  |  |
| 57          | 0.53             | 477408.2              | 509.34   | 3.91 | 0.1401                               | 2.27   | 3.6295                              | 3.04   | 0.1879                              | 2.02   | 0.67 | 2228                                 | 39   | 1110                                | 21        | 1556                                | 24   | 71     |  |  |  |
| 58          | 0.43             | 1079619               | 1839.673 | 1.52 | 0.0993                               | 2.18   | 1.6114                              | 3.03   | 0.1177                              | 2.11   | 0.70 | 1612                                 | 41   | 717                                 | 14        | 975                                 | 19   | 73     |  |  |  |
| 59          | 0.37             | 726557.5              | 1370.725 | 3.62 | 0.0925                               | 2.55   | 1.3550                              | 3.32   | 0.1063                              | 2.13   | 0.64 | 1477                                 | 48   | 651                                 | 13        | 870                                 | 20   | 75     |  |  |  |
| 60          | 0.15             | 1237412               | 1586.374 | 1.21 | 0.1373                               | 2.08   | 2.9597                              | 2.86   | 0.1564                              | 1.97   | 0.69 | 2193                                 | 36   | 937                                 | 17        | 1397                                | 22   | 67     |  |  |  |
| 67          | 0.26             | 287258.9              | 175.6452 | 2.27 | 0.1383                               | 2.36   | 6.2504                              | 3.16   | 0.3279                              | 2.11   | 0.67 | 2205                                 | 41   | 1828                                | 33        | 2012                                | 28   | 91     |  |  |  |
| 68          | 0.46             | 560096.7              | 248.6652 | 4.85 | 0.2492                               | 2.14   | 15.5190                             | 2.91   | 0.4516                              | 1.97   | 0.68 | 3180                                 | 34   | 2402                                | 39        | 2848                                | 28   | 84     |  |  |  |
| 69          | 1.66             | 1070468               | 1635.02  | 1.54 | 0.1867                               | 3.03   | 3.3793                              | 4.40   | 0.1313                              | 3.20   | 0.73 | 2713                                 | 50   | 795                                 | 24        | 1500                                | 35   | 53     |  |  |  |
| 70          | 0.16             | 514889.9              | 392.1644 | 2.59 | 0.1311                               | 2.06   | 4.7576                              | 2.87   | 0.2632                              | 1.99   | 0.70 | 2112                                 | 36   | 1506                                | 27        | 1777                                | 24   | 84     |  |  |  |
| 71          | 0.19             | 1104091               | 391.5197 | 1.30 | 0.1797                               | 2.27   | 14.0126                             | 3.00   | 0.5654                              | 1.97   | 0.65 | 2651                                 | 38   | 2889                                | 46        | 2751                                | 29   | 105    |  |  |  |
| 72          | 0.34             | 1231415               | 955.8345 | 1.62 | 0.1284                               | 2.17   | 4.5742                              | 2.95   | 0.2583                              | 2.01   | 0.68 | 2077                                 | 38   | 1481                                | 26        | 1745                                | 25   | 85     |  |  |  |
| 73          | 0.63             | 999689.2              | 1824.591 | 0.57 | 0.0960                               | 2.71   | 1.4533                              | 3.54   | 0.1099                              | 2.28   | 0.64 | 1547                                 | 51   | 672                                 | 14        | 911                                 | 21   | 74     |  |  |  |
| 74          | 0.67             | 721218.2              | 1279.935 | 0.98 | 0.0910                               | 2.50   | 1.4179                              | 3.48   | 0.1130                              | 2.42   | 0.70 | 1447                                 | 48   | 690                                 | 16        | 896                                 | 21   | 77     |  |  |  |
| 75          | 0.68             | 1355628               | 787.3516 | 0.52 | 0.1878                               | 2.12   | 8.9401                              | 2.     |                                     |        |      |                                      |      |                                     |           |                                     |      |        |  |  |  |

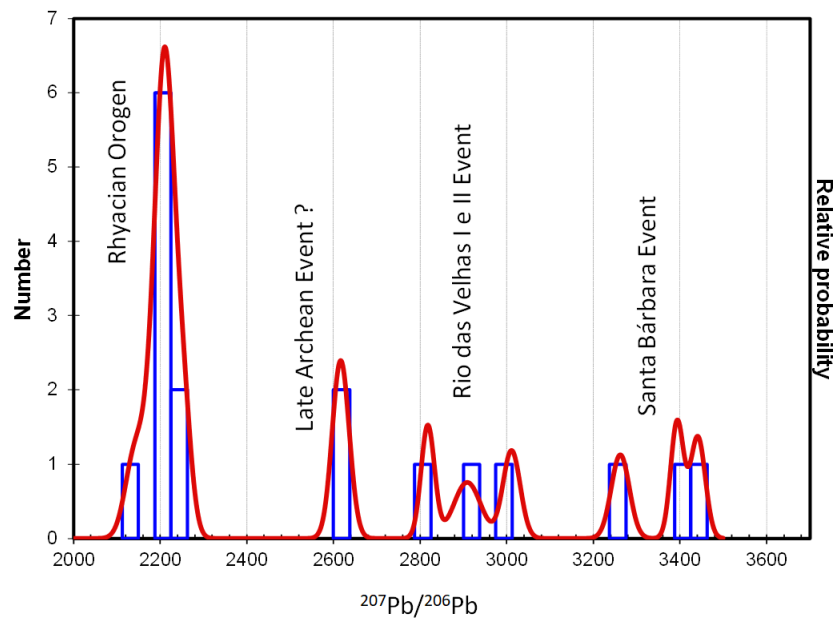


Figure 16 - Relative probability density plot of U–Pb detrital zircon ages obtained from metaconglomerate (sample AC01). For comparison, the age distributions of different tectonic-magmatic events in the QFe region are marked (Farina et al. 2016; Aguilar et al. 2017).

Although only the concordant grains are used in the provenance analysis and relative probability density plot of Figure 16, it is noteworthy that some of the discordant grains align in a Discordia (Figure 17) with an upper intercept at ca. 2.8 Ga and a lower intercept at  $573 \pm 39$  Ma (MSWD 6.9).

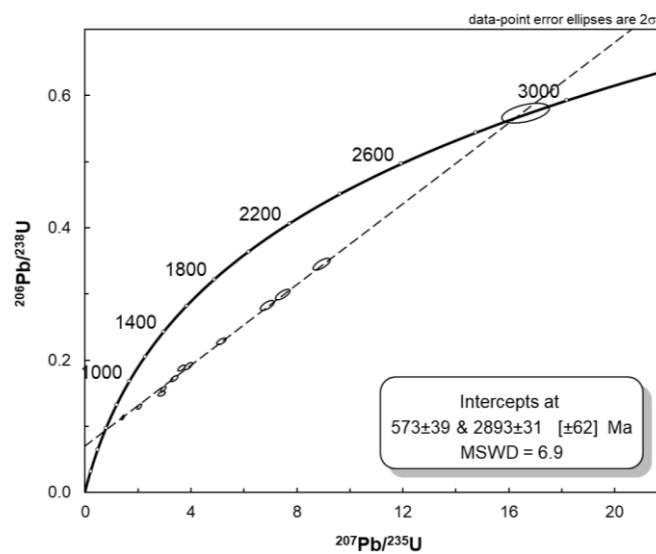


Figure 17 – Concordia diagram for metaconglomerate (sample AC01) showing discordant zircon grains that align in a Discordia with an upper intercept at ca. 2.9 Ga and a lower intercept at 573 Ma.

## 4.6 Discussion

### 4.6.1 Depositional environments of the Itabira Group

The discussion about the preservation of original isotopic composition is important to Precambrian carbonates because, generally, ancient rocks were subject to post-depositional changes during diagenesis, metamorphism, surficial weathering and/or hydrothermalism (Kaufman and Knoll 1995; Jacobsen and Kaufman 1999; Caxito et al. 2019). Nevertheless, C and O isotopic ratios values obtained in this study are like values obtained for QFe rocks in other works (Figure 18).

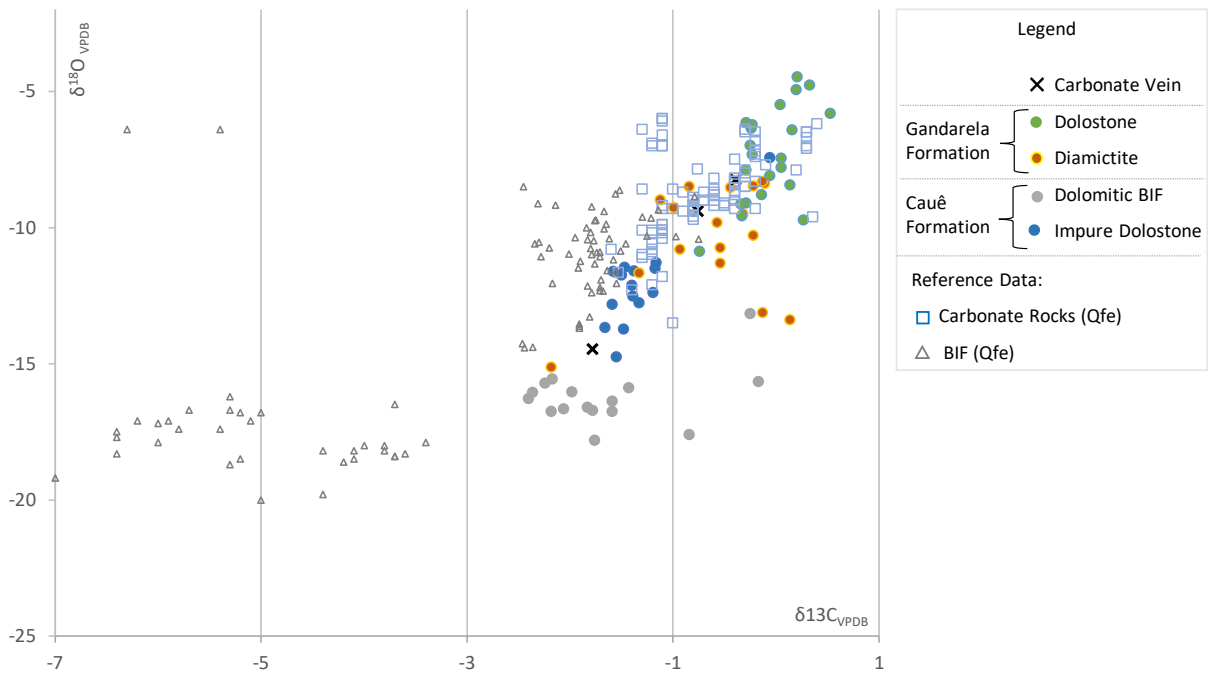


Figure 18: Carbon and oxygen isotopes of BIF and carbonate rock of the Segredo Mine. For comparison, data collected in the QFe for other works is also plotted.

Key: Carbonate Rocks (QFe) - calcites, dolomites, limestones and dolomitic limestone from Extramil Quarry, Hargreaves Quarry, Gandarela Farm and Socorro Quarry, (Bekker et al. 2003; Morgan et al. 2013). And BIF (QFe) - result obtained in Águas Claras Mine and Alegria Mine (Spier et al. 2007; Morgan et al. 2013; Teixeira et al. 2017).

For instance, Bekker et al. (2003), Spier et al. (2007) and Morgan et al. (2013) analyze the stable isotopes (C and O) in the dolomitic BIF and dolostone samples from Cauê and Gandarela formations, respectively. In comparison, a coincident isotopic behavior was found, where the results show a slightly positive trend of  $\delta^{13}\text{C}$

toward the top stratigraphic sequence (Gandarela Formation). On the other hand, dispersed values are presented by Teixeira et al. (2017), where the values of  $\delta^{13}\text{C}$  are relatively lower than the others and reach a minimum of  $-10.0\text{‰}$ . These authors related the scattering C-isotopic ratios with the high  $\delta^{56}\text{Fe}$  values and suggested the influence of microorganism activity in the dissimilatory iron reduction of the precursor ferric oxides.

Another important factor in the C-isotopic analysis considers the results of carbonate vein samples. Those results indicate similar  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values to the proximal layers. This reinforces that processes of carbonate recrystallization and interaction with fluids did not promote extensive alteration of the C-isotopic composition, except for samples with lower  $\delta^{18}\text{O} < -10\text{‰}$ . In addition, the  $\delta^{18}\text{O}$  isotopic ratios obtained in Segredo deposits show negative values reaching a minimum of  $-17.6\text{‰}$ . Yet, the values are consistent with other well-preserved Paleoproterozoic carbonate sequences (Veizer et al. 1989, 1990, 1992; Bekker et al. 2003).

Kaufman and Knoll (1995) suggest the Mn/Sr index to analyze the degree of alteration of the samples and thus evaluate the representativeness of the results in relation to primary C-isotope values. According to the authors, the  $\text{Mn/Sr} < 10$  demonstrates the substitution of Sr by Mn due to percolation of meteoric fluid in carbonates. The values for dolostone in Segredo mine is  $\text{Mn/Sr} > 32$ . Nevertheless, the index of alteration is not easily applied to Paleoproterozoic rocks (Veizer et al. 1992, Bekker 2003).

In the face of the complex deformation and metamorphic grades of the Segredo mine, carbon isotope fluctuations and REEY signatures clearly define a stratigraphic correlation between impure dolostone and dolomitic BIF. Therefore, a syngenetic character for this lithological arrangement is interpreted (intervals of 184.75 to 316.45 meters depth in the drill hole core), whose dolomitic BIF is intercalated with impure dolostones (Figure 6). Thus, the lithological arrangement is grouped into Cauê Formation succession and it is associated with precipitation in a shallow-water basin.

In the  $\delta^{18}\text{O}$  versus  $\delta^{13}\text{C}$  diagram proposed by Hudson (1977) and modified by Nelson and Smith (1996) the identification of different carbonate origins is assessed. The diagram considers values of  $\delta^{18}\text{O} > -10\text{‰}$  because lower values may indicate the fractionation of oxygen isotopes during diagenesis or other post-depositional

process. The samples are from the Gandarela Formation dolostone plot within the marine limestone field. This origin is consistent with regional understanding of depositional systems evolution in the carbonate precipitation of Gandarela Formation. Furthermore, the contribution of Nogueira et al. (2019) indicates a marine limestone origin for other samples of the Gandarela Formation.

The definition of the marine limestone field suggests that dolomite was formed diagenetically, as a product of dolomitization processes. Alternative explanations for mechanisms of dolomite formation are argued by several authors, for example: reactions with seawater (Machel 2003), bacterial mediation (Warren 2002; Spier et al. 2007), or primary abiotic precipitation from a CO<sub>2</sub>-rich hydrothermal-seawater fluid (Morgan et al. 2013).

All dolomitic BIF and dolostone present in Segredo Mine exhibit a uniform average Ca/Mg ratio = 1.5 (Figure 6) and CaMgCO<sub>3</sub> composition (Figure 7B). Some alteration halos composed of Fe-Mn dolomite were identified. The alteration is restricted to the crystal borders and probably results of hydrothermal overprinting. In addition, dolomites have a homogeneous texture, in contrast to the granular texture of the dolomite veins. Beukes et al. (2003) proposed a hydrothermal process in the QFe able to promote the replacement of chert bands by dolomite. This proposal is incompatible to the Segredo mine samples. All evidence points to a diagenetic origin of dolomite. Moreover, homologous ideas are presented in the development of regional works in the QFe (Spier et al. 2007, Rosière et al. 2008, Teixeira et al. 2017).

No alteration was identified in  $\delta^{13}\text{C}$  values from decarbonatization reactions, a process responsible for the formation of Ca-Mg silicates in the presence of siliciclastic rocks and <sup>12</sup>C rich - CO<sub>2</sub> release due to kinetic fractionation (Kaufman and Knoll 1995). This process could be responsible for the formation of chlorite, a common accessory mineral at the Segredo mine. However, this mineral is interpreted as a product of the greenschist facies metamorphism.

Several studies (Kaufman, 1997; Hoffman, 1998; Bekker et al., 2003; Gumsley et al., 2017; Caxito et al., 2019) use stable isotope proxies to investigate the drastic climate changes during the Proterozoic eon. These studies include the discussion about the coexistence of cap carbonates and glacial events in low latitude terrains around the world. In Brazil, isotopic composition obtained at the QFe region reveals that Minas Supergroup may record a global glaciation during Paleoproterozoic

evolution (Bekker et al. 2003, Nogueira et al. 2019). Bekker et al. (2003) argued that isotopic changes are correlated with North American glacial events, although no evidence of glaciation has been identified in the Minas Basin. The lack of evidence was associated with erosional processes. On the other hand, the ranges of C isotopes in Segredo deposits show no evidence of glacial events concurrently with the formation of Itabira Group.

The discussion of REE signatures, considering variations in the Ce (III and IV) and Eu (III and II) elements, contributes to the analysis of marine redox conditions and the fluid-rock interaction in the Minas Basin (e.g. Derry and Jacobsen 1990; German and Elderfield 1990; Byrne and Sholkovitz, 1996; Slack et al. 2007). Contributions of Graf (1977) and Fryer et al. (1979) indicate that the REE pattern of chemical precipitates is subject to change by terrigenous input. In the Segredo mine, low  $\text{Al}_2\text{O}_3$  values found in the chemical domain, except sample A074 - chlorite phyllite, indicate that the chemical sediments are devoid of detrital input. It should be noted that the metadiamictite matrix, belonging to the chemical domain, shows no clastic contribution. This characteristic, associated with their oligomict composition and C-isotope pattern, suggests that their formation results from sediment-gravity flows in a slope wedge. Therefore, no evidence was found for glacial records.

The behavior of Y/Ho, Ce/Ce\* and Pr/Pr\* in BIF and dolostones at Cauê Formation is compatible with Paleoproterozoic and Archean Fe formations (e.g. Planavsky et al. 2010). The positive Eu anomaly found in some of the Segredo mine rocks is consistent with the enrichment of most Early Proterozoic and Archean BIFs. This is interpreted as resulting from a mixing of sea water and submarine hydrothermal iron-bearing fluids. Fryer et al. (1979) discussed whether the anomaly comes from a local hydrothermal input related to BIF precipitation or is reflected in marine chemistry in ancient times. Negative Ce anomalies reflect a locally oxygenated ocean during carbonate precipitation (Gandarela Formation). Dolostones associated with the Cauê Formation have Ce values masked by the positive La anomaly. The dolomitic BIF Ce/Ce\* anomalies are scattered and not conclusive.

The chlorite phyllite (sample A074), located between the Gandarela Formation metadiamictites and dolostones, is rich in  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and MgO. Correlation between Cr and Ti contents defines an ocean floor basalt protolith for the sample (Suckau et al. 2005). This rock could be interpreted as mafic volcanic, but this possibility must be assessed through further studies.

#### 4.6.2 Sequence Stratigraphy of Itabira Group

The Itabira Group sedimentary evolution involves transitions between transgressive and regressive depositional sequences through interplays of base-level changes, shoreline shifts and variations in the rate of precipitation and accommodation of chemical sediments. This evolution implies a stacking pattern interpreted as a first order sequence driven towards the top of sequence (Figure 19).

This proposal is coherent with previous works (Dorr 1969; Barbosa 1979) where the authors suggested that sea level fluctuations and marine regressions took place during the formation of the Itabira Group. Based on the definition of the first order tract system, we sought to detail the local stacking pattern of the Itabira Group (Figure 19). As a result, two second-order stratigraphic sequences were individualized within the lithological framework exposed by the studied drill hole core.

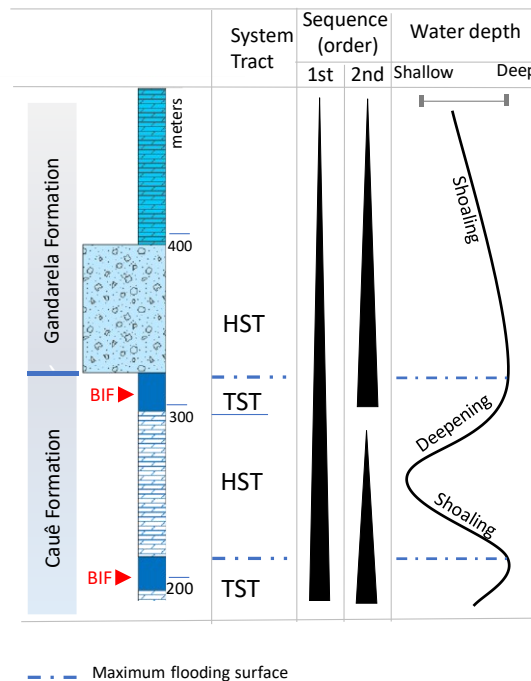


Figure 19: Proposal of stratigraphy column showing depositional cycles of Itabira Group. The drill hole profile was rotated to represent the normal sequence of group. Abbreviation: TST – transgressive systems tract and HST – highstand system tract.

#### Stratigraphy Sequence of Cauê Formation

The base of Cauê Formation starts at 185 meters deep in the drill hole core and the rocks comprise interdigitations of carbonates and dolomitic BIF. This stacking pattern extends to 295 meters and is characterized as a syn-depositional feature associated to the Cauê Formation. This association is motivated by stratigraphic relationships between the layers and the chemical signatures (C-isotope and RREY), already discussed in the previous topic. Likely, the sedimentary succession was influenced by variations in base-level, geometry of the basin margin and the shallower-water environment.

In order to detail, Cauê Formation was interpreted as a superposition of three systems tracts (2<sup>nd</sup>):

- 1) From zero to 185 meters deep in the studied drill hole - Continuity of the transgressive system tract (TST) already installed in the Minas Basin during the sedimentation of Caraça Group (basal contact of Itabira Group).
- 2) From 185 to 210 meters deep in the studied drill hole - The accommodation of carbonates is recorded in a highstand system tract (HST). This stratigraphic evolution corresponds to a normal regression which triggers the progradation to the sediment advance towards the seafloor.
- 3) From 210 to 294 meters deep in the studied drill hole - The top of Cauê Formation marks the return to TST. The BIF deposition represents the return of a transgressive stage and a relative deepening of sea water.

The stacking pattern found in the drill hole core may be discussed in light of an aggradation cycle. Catuneanu (2006) proposed that 'pure' carbonate systems can sustain aggradation process within the basin if the supply of sediment by extra-basinal sources is restricted and dominates for chemical or biochemical precipitation of carbonates. However, further studies are needed to expand this interpretation at the regional level.

### **Stratigraphy Sequence of Gandarela Formation**

The metasedimentary rocks of Gandarela Formation represent a subsequent system tract defined as highstand system tract, from 316 meters deep in the drill hole and downwards.

Firstly, the contact of the Cauê and Gandarela formations is marked by the formation of diamictites, which corresponds to an abrupt change in strictly chemical sedimentation.

In this proposal, the metadiamictite represents an accumulation of clastic carbonates on the slope and on the basin floor, according to the model discussed by Neumann and Land (1975) and Catuneanu (2006). This process can be driven by a decrease in base-level rise, where the volume of carbonate sediment is higher than available accommodation space, allowing the reworking of sediment through mechanical erosion (e.g. waves, currents and storms) and bioerosion (Hine et al. 1981, 1992; Catuneanu 2006).

Finally, the progradation of sedimentation patterns in the Highstand System Tract (HST) is maintained until the end of the hole.

#### **4.6.3 Model for deposition of the Sabara Group in the Segredo region**

One of the final stages of the Wilson cycle in the Minas Basin is represented by the inversion of the basin and deposition of the Sabará Group. This supracrustal sequence was deposited in a foreland synorogenic basin related to the Rhyacian accretionary orogeny. In the drill hole core studied, the initial sequence reaches 184.75 meters deep and exhibits various levels of polymict conglomerate. The zircon crystals provenance was based on the U/Pb frequency histogram (Figure 15), that shows ages related to Archean basement and to the volcanic arcs installed during supercontinent amalgamation in Paleoproterozoic times.

Therefore, the clastic sequence defined in the present study is associated with the Sabará Group. Contrary to expectations for a lithostratigraphy sequence, the Sabará Group is in contact with the Itabira Group, according to an angular discordance. According to the lithostratigraphic units, two explanations are suggested:

- i) Sabará Group deposition directly above the Itabira Group:

This hypothesis considers the deposition of Sabará Group over ancient rocks already subjected to deformation related to the closure process of Minas Basin (Figure 20). Thereby, relative block movement due to thrust fault would allow the Sabará Group to be deposited according to tectonic contacts.

This proposal may be interpreted as a favorable evidence for the lithostratigraphic review proposed by Endo et al. (2019), where the Sabará Group was separated from the Minas Supergroup and reclassified into Estrada Real Supergroup. The separation is based in the distinction of two main divisions bound by unconformities and characterized by distinct sedimentary facies, associations and environments.

ii) Sabará Group-related fault-displaced allochthonous rocks.

In this proposal, the juxtaposition of the Sabará Group rocks onto the Itabira Group rocks would have occurred through thrusting. However, during the mapping, no faults were identified that could have displaced the Sabará Group to the region studied.

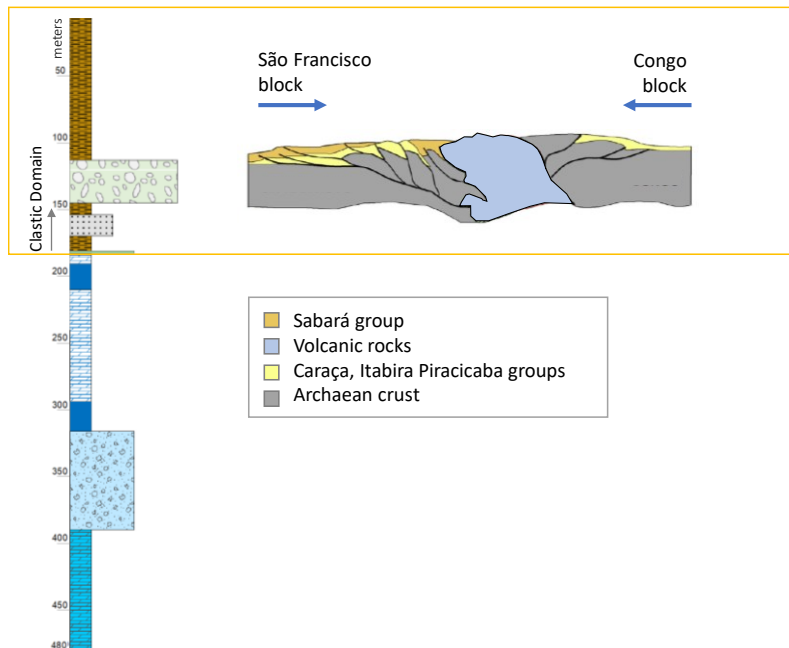


Figure 20: Simplified models for the deposition of Sabará Group in the studied area. Modified from Aguiar et al. (2017).

#### 4.6.4 Post-Depositional Processes

The metamorphism age in the Segredo Mine reach up  $573 \pm 39$  Ma, as suggested by the lower intercept of the Concordia diagram in Figure 16. The value corresponds to linear regression of 14 discordant zircon crystals obtained in this study. Ahren (1955), Wetherill (1956), Goldich and Mudrey (1972) advocate that the lower intersection of the Discordia line corresponds to the effects of partial lead loss due to irregularities in the crystalline structure, such as microfractures or micro-capillary network.

This age is consistent with the regional thermal event known as Brasiliana Orogeny, related to West Gondwana amalgamation. Thus, the results evidence the importance of the last significant disturbance in the rocks of the QFe registered at the Brasiliana collage or “Pulse” 3 (590 – 560 Ma) stage in which several collisional and metamorphic events took place, according to Brito Neves et al. (2014).

Other post-depositional processes to which the Minas Supergroup rocks were submitted might promote iron enrichment of the BIF. At Segredo deposits, the close association between high grade iron ore and dolomites (Figure 3) suggests that carbonate leaching processes might lead to residual iron oxide concentration. Morris (1985) and Ribeiro (2002) elucidate the role of weathering in the enrichment of BIF, through the processes of dissolution, transport and collapse of the residual layers. In addition to this process, the area exhibits evidences of post-depositional hydrothermal fluids circulation (carbonate veins) that may contribute to the transformation of the proto ore.

## 4.7 Conclusion

The carbon isotopic composition of the Itabira Group in the Segredo mine enables the characterization of the Cauê and Gandarela formations, marked by a gradual increase of  $\delta^{13}\text{C}$  towards the most recent rocks. The REEY signature differentiates the dolomites from the Cauê and Gandarela formations. Thus, the present study confirmed the syndepositional character of the precipitation of BIF and dolostones in the Cauê Formation. Consequently, chemical signatures (ETRY and C-isotope ratio) are useful tools for geological modeling of carbonate-rich successions of the Minas Supergroup.

From the perspective of the stratigraphic sequences, the Itabira Group comprises a sequence (2<sup>st</sup>) defined by cycles of transgressive tract (TST) to the

highstand tract (HST). Therefore, the records of the stratigraphic sequence found in Segredo deposits provide signs of a shallow water setting during the deposition of chemical sediments belonging to Cauê and Gandarela formations.

The deposition of diamictites at ca.  $\sim 2.4$  Ga in the Itabira Group was associated with debris flows in areas of slope resedimentation at the edges of the carbonate platform. No evidence of glaciation was identified in the diamictite layer.

The lithostratigraphic review at the Segredo mine defines the occurrence of siliciclastic rocks from the Sabará Group, characterized by ca. 2.0 Ga younger detrital zircons, deposited directly above the Itabira Group in the area. This evidence reinforces the proposal to incorporate the Sabará and Itacolomi Groups into the Estrada Real Supergroup (Endo et al., 2019).

Dolostone interleaved with BIF can be used as an exploratory guide for the formation of supergenic high grade iron deposits. Iron enrichment might occur due to carbonate leaching and, consequently, residual concentration of microhematite crystals and recrystallization of Fe-Mn impurities of dolomite crystals as oxides and hydroxides in the weathering zones.

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## 5. CONCLUSÕES E SUGESTÕES PARA TRABALHOS FUTUROS

A revisão litoestratigráfica baseada nos dados de mapeamento geológico na mina de Segredo e nas análises químicas (elementos maiores, traços e ETR), isotópicas (C e O) e geocronológicas (U-Pb) obtidas em um testemunho de sonda levaram a conclusões a respeito da sedimentação na Bacia Minas, sua estratigrafia e proveniência sedimentar.

As unidades litoestratigráficas pertencentes aos supergrupos Minas e Estrada Real conformam o Sinforme de Fábrica, que é dado por uma dobra assimétrica vergente para SW e eixo mergulhando para leste. Na mina de Segredo, a litoestratigrafia é dada pela seguinte sucessão da base para o topo: Grupo Itabira, Grupo Piracicaba, Grupo Sabará e Grupo Itacolomi. Não há registro do Grupo Caraça, que provavelmente foi erodido, ou não depositado na região.

O Grupo Itabira subdivide-se na base pelos dolomitos e BIFs da Formação Cauê, e no topo, pelos dolomitos e diamictitos da Formação Gandarela. A distinta assinatura química (ETR) e isotópica (C e O) entre os carbonatos do grupo Itabira permitiu o refino no agrupamento litoestratigráfico, uma vez que os dolomitos e BIFs da Formação Cauê apresentam-se enriquecidos em ETR e  $^{13}\text{C}$  em relação aos dolomitos da Formação Gandarela. Já o processo de formação da camada de diamictito, uma exceção à origem estritamente química do Grupo Itabira, foi associada a erosão de sedimentos químicos recém precipitados e transporte subaquático por processos gravitacionais nas margens das plataformas carbonáticas da Bacia Minas. As análises petrográficas, químicas e isotópicas não evidenciaram uma origem glacial para a rocha.

O estudo estratigráfico do Grupo Itabira permitiu a proposição de uma sequência de 2ª ordem para o arranjo das rochas da região estudada. A base da Formação Cauê representa a manutenção do trato de sistema transgressivo já instalado na Bacia Minas. Em seguida, o sistema migra para um trato de mar alto, com a progradação de carbonatos sobre as BIFs da Formação Cauê. Já no topo da Formação Cauê, retoma-se o sistema de trato transgressivo com a deposição da BIF e o avanço da linha de costa no sentido da margem da Bacia Minas. Finalmente, a sobreposição dos diamictitos e carbonatos associados à Formação Gandarela representa um novo ciclo progradante (sistema de trato de Mar Alto).

Na região, o Grupo Sabará foi definido a partir da petrografia e dos dados isotópicos (U-Pb) obtidos em cristais de zircão detrítico (2,1 Ga – grão mais jovem).

O grupo deposita-se diretamente sobre o Grupo Itabira através de uma superfície de discordância angular. Essa relação reforça o caráter sin-orogênico do Grupo Sabará, isto é, a sua deposição sobre camadas alóctones mais antigas da Bacia Minas, que poderiam ter se deslocado por falhas.

Com isso, ao finalizar o presente estudo, incluo novas dúvidas acerca do Grupo Itabira no QFe, onde os principais questionamentos recaem sobre a metalogênese do ferro e à estratigrafia da Bacia Minas:

- Poderiam existir registros da Glaciação paleoproterozoica global, como os reconhecidos na África do Sul (Sg. Transvaal), Canadá (Sg. Huroniano) e EUA (Sg. Snowy Pass)?
- Qual a fonte de Fe para a formação da BIF no Quadrilátero Ferrífero?
- No QFe existem registros das grandes províncias ígneas conforme identificado nos depósitos mundiais de idades semelhantes?
- Sob o aspecto estratigráfico, as camadas de dolomitos, *blackshales* e diamictitos que ocorrem no QFe podem ser camadas guias para a construção de um modelo deposicional para a Bacia Minas?

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