

Lithogeochemistry and 3D geological modeling of the apatite-bearing Mesquita Sampaio beforosite, Jacupiranga alkaline complex, Brazil

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Abstract

The Mesquita Sampaio beforosite is a mineral exploration area with apatite mineralization occurring near the northern portion of the Morro da Mina apatite deposit (Cajati Mine), in the Jacupiranga Alkaline Complex. This study presents the mineralogical, geochemical and 3D geological modeling data of this target. Four lithotypes are presented for Mesquita Sampaio: the fine-grained beforosite (FGB), the coarse-grained beforosite (CGB), the xenolith zone (XEN), and the jacupirangite (JAC). The 3D geological model shows the Mesquita Sampaio beforosite as a vertical body with an NNW direction and approximately 350 meters in length, 150 meters in width, and 400 meters of depth, with open extensions. The main mineral assemblage of the beforosite is dolomite, apatite, phlogopite, serpentine, calcite, and magnetite, in order of abundance. The distribution of major elements for both types of beforosites (FGB and CGB) indicates the same composition with only a small variation in the mineral proportions. Although no direct contact relation between Mesquita Sampaio and Morro da Mina is known, both may be the same carbonatite body with a gradual compositional variation, or the Mesquita Sampaio beforosite could be a distinct late or even earlier carbonatite pipe.

KEYWORDS: carbonatite; Jacupiranga Alkaline Complex; Cajati Mine; beforosite; Mesquita Sampaio; apatite; lithogeochemistry; 3D geological modeling.

INTRODUCTION

The Jacupiranga Alkaline Complex is a classical Brazilian occurrence of mineral deposit in alkaline rocks province with associated carbonatite, congregating facilities of mine and a chemical-industrial complex. These facilities refer to the company Mosaic Fertilizantes, which currently develops mining activity in the main carbonatite body for the apatite extraction as an ore for phosphate production. The Mesquita Sampaio area is located approximately at latitude 24°40'33.0" S and longitude 48°08'04.0" W, in the vicinity of the northern portion of the Morro da Mina, the name given to the Cajati mine, and presents mineral resources that are in the mineral exploration stage. The Morro da Mina phosphate deposit is located in the Cajati town, Vale do Ribeira region, in the southeast of São Paulo State, close to the border with Paraná State and about 240 km from the city of São Paulo.

This work is the first geological description of the Mesquita Sampaio beforosite, bringing the initial mineralogical, geochemical, and 3D modeling aspects. This paper introduces and

discusses the first data available from the Mesquita Sampaio, which were obtained from drill hole samples, and compares the mineralogical, textural, and geochemical aspects of the beforosite with the available data in the literature from the contiguous Morro da Mina apatite deposit.

GEOLOGIC SETTING

Jacupiranga Alkaline Complex

Morro da Mina and Mesquita Sampaio are inserted in the Jacupiranga Alkaline Complex, a classic Brazilian occurrence of alkaline and ultrabasic rocks with associated carbonate manifestations that contemplate a phosphate deposit of magmatic affiliation. The main carbonate body presents a structure interpreted as a diatreme, discovered by Bauer (1877) and preliminarily investigated at the end of the nineteenth century by Derby (1891) and Hussak (1892). More detailed studies (Melcher 1965, 1966) came with the removal of the weathering mantle with the open-pit mining activities on the Morro da Mina carbonate body. The mining of high-grade weathered ore (> 25% P₂O₅) lasted until the mid-1960s, when the economic base of the deposit began to undergo changes, initiating the mining of the non-weathering carbonate body mineralized to apatite, with average contents around 5% of P₂O₅. Thus, more detailed studies on the deposit structural geology and mineralogy became possible (Gaspar and Wyllie 1983a, 1983b, Menezes and Martins 1984, Gaspar 1989). K-Ar radiometric analysis on

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carbonatites of the complex yield an age of 130 ± 5 Ma (Amaral 1978), subsequently confirmed by Rb-Sr age of 131 ± 3 Ma (Roden *et al.* 1985), and by $^{40}\text{Ar}/^{39}\text{Ar}$ ages for different lithotypes of Jacupiranga Alkaline Complex ranging from 133.7 ± 0.5 to 131.4 ± 0.5 Ma (Chmyz *et al.* 2017). In relation to the tectonics, several authors such as Almeida (1983), Ruberti *et al.* (2005), and Gomes *et al.* (2011), among others, point out an association between the rocks of the Jacupiranga Alkaline Complex and the Guapiara Lineament, where the Mesozoic alkaline magmatic activity would have been conditioned by the

Ponta Grossa Arch (Fig. 1). Germann *et al.* (1987) presents a geological map in which the complex shows an oval shape of approximately 70 km^2 , with NNW direction, and is completely embedded into the Precambrian rocks of the Açungui Group (550 Ma) (Fig. 2). The carbonatite host rocks are mafic alkaline rocks, represented by jacupirangite and dunite, bordered by a zone of assimilation in the northern region. It is worth mentioning that the jacupirangite, originally defined by Derby (1891), designates a pyroxenite constituted essentially by titanian augite, magnetite, and nepheline, with biotite and

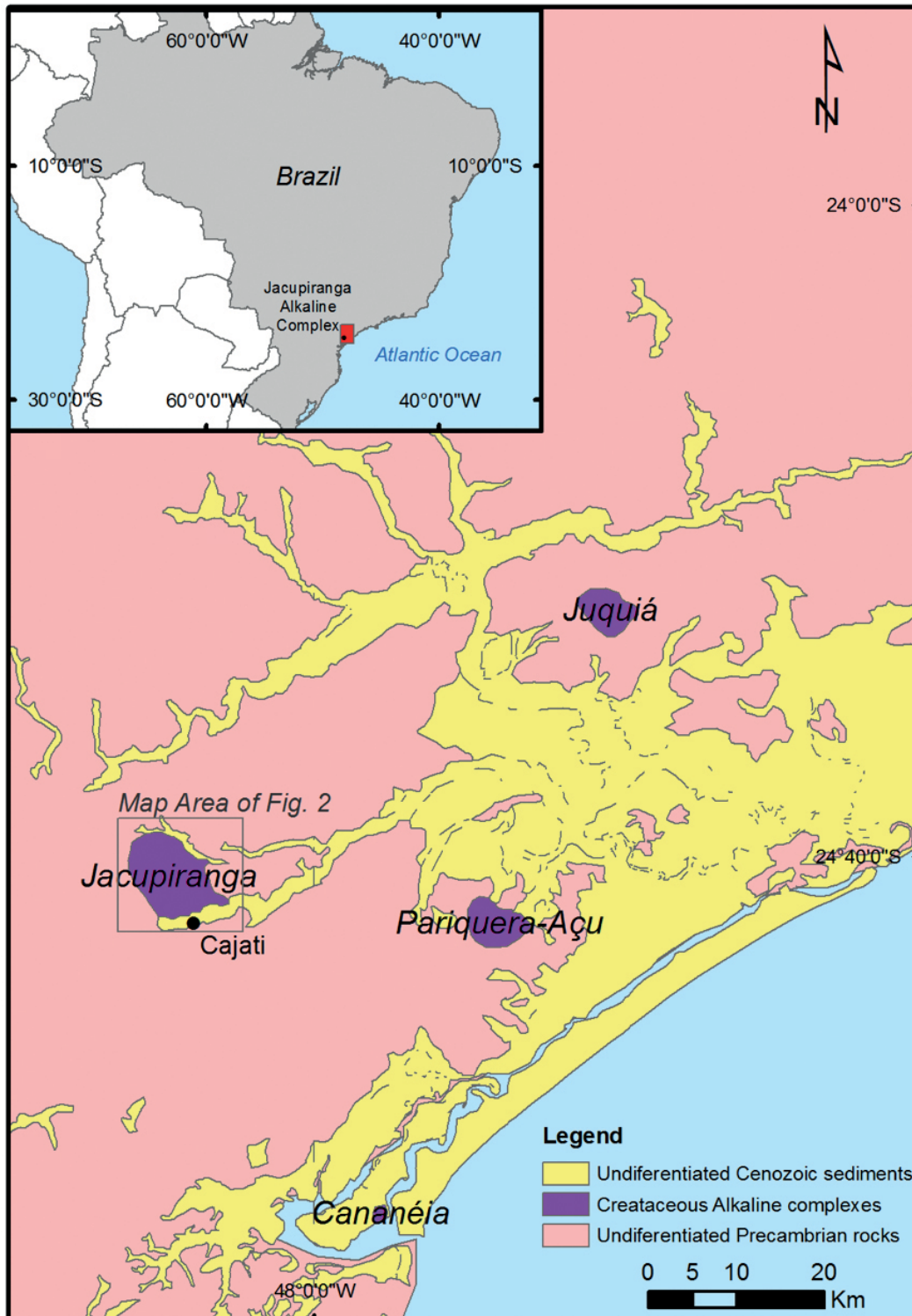


Figure 1. Schematic regional geological map of Jacupiranga, Juquiá, Pariquera-Açu, and Cananéia alkaline complexes at the Guapiara Lineament (after Ruberti *et al.* 2005).

olivine as accessories, being the presence of such pyroxene in the rock is a fundamental characteristic for its definition. In this work, all pyroxenite hosting the carbonatite in Morro da Mina and Mesquita Sampaio areas are treated indistinctly as jacupirangite, due to the widespread use of the term in the mine. The alkaline intrusion also presents other types of pyroxenites, serpentinized peridotite, ijolite, nepheline syenite, fenite and, more in the center, carbonatite, the object of this work, in addition to other types of alkaline rocks of lesser expression, that occur mainly in the form of dikes, like melteigite and phonolite.

Morro da Mina carbonatite (Cajati apatite mine)

Specifically considering carbonatite, the portion of the Jacupiranga Alkaline Complex where the apatite mine is installed, perhaps the first work of major importance are Gaspar and Wyllie (1983a, 1983b), which identified five phases of carbonatitic intrusions, and not only two (Melcher 1965, 1966), and their chronological sequence, having the jacupirangite as host rock.

Thus, this magmatic structure is interpreted as a volcanic chimney breccia, with narrow and inverted conical shape, resulting from the subvolcanic explosion of carbonate volcanic magma that, when reaching shallow depths of the crust, caused the sudden gas expansion as fluidized magma, involving fragments of the ducts, in this case, of jacupirangite xenoliths, and of the carbonatite itself. A striking feature of this contact is the presence of reaction zones or fenitization, corresponding to a layer of carbonate minerals and newly formed silicates, generated from the interaction of carbonatite and jacupirangite, whose thickness varies from millimeters to centimeters, and can reach around 30 centimeters. Morbidelli *et al.* (1986) elaborate a detailed study on reaction zone describing a sequence from the jacupirangite to the carbonatite, which begins with the amphibole-rich band (A), then the phlogopite-rich band (P), and finally olivine-rich band (O). The A band occurs in the jacupirangite contact, where the amphibole is a pyroxene pseudomorph. It has a variable thickness of 1 to 5 centimeters, dark green color, interspersed with millimeter bands of

carbonates, in a well-defined banding, with the occurrence of phlogopite and magnetite. The most developed P band consists essentially of phlogopite, in addition to ilmenite and magnetite, the banded structure does not occur regularly in some portions as spots, and it presents a variable thickness from a few centimeters to 1 meter and red wine color. The external O band contains, in addition to abundant olivine, phlogopite, magnetite, and ilmenite, centimetric to decimetric band thickness with a very dark color, almost black, and the banded structure is less regular than in previous phases, commonly olivine crystals are strongly affected by serpentinization. The carbonate phase can occur as bands, spots or veins, and are essentially of calcitic composition. In general, they present associated apatite, well developed in the P band, in addition to phlogopite and amphibole.

Menezes and Martins (1984) divided the mineral assemblage of the Morro da Mina deposit into two groups: those found in carbonatite and those found in jacupirangite. The complete list consists of 53 species. In carbonatite, these authors observed: ancylite, aragonite (secondary), baddeleyite, barite, brucite, calcite (primary and secondary), chalcocopyrite, titanclinochumite, dolomite, strontianite, phlogopite, fluorapatite, forsterite, galena, geikielite, magnetite, manasseite, pyrite, pyrrhotite, quartz (secondary), quintinite, serpentine group minerals, uranpyrochlore, and valerite. In turn, the minerals found in jacupirangite, according to these authors, are: aegirine, titan-andradite, titan-augite, barite, biotite, calcite, calzirtite, diopside, dolomite, edingtonite, phlogopite, fluorapatite, forsterite, hornblende, magnesium-ilmenite, magnetite, natrolite, nepheline, perovskite, pyrite, pyrrhotite, richterite, schorlomite, tazheranite, titanite, tochilinite, tremolite, vesuvianite, vigezzite, wollastonite, zircon, zirconolite, and zirkelite.

With the geological and chemical control of the mining activities and the detailed mapping of the mining fronts, it was possible to elaborate a map with detail of structural features (magmatic foliation and mineral lineation) of five intrusive phases, and the development of a structural model of the main carbonatite body in geometric and evolutionary terms (Gaspar and Wyllie 1983b). The intrusions of the southern portion were denominated: C₁, C₂, C₃ and those of the northern portion: C₄ and C₅. The intrusions of the southern portion were subdivided into two parts: north and south. The sequence of carbonate intrusions, from the oldest to the newest, is C₁, C₂, C₃, C₄, and C₅.

According to Gaspar and Wyllie (1983b), C₁ is a coarsely-banded sovite composed of calcite, apatite, magnetite, olivine, phlogopite, dolomite, and sulfides, with all mineralogy being described in abundance order. The banding is usually subvertical dipping north. The apatite lineation is always subhorizontal. Two southern regions can be individualized because they are poor in non-carbonaceous minerals. However, outside these regions, the sovite is rich in olivine, magnetite, and apatite, and inside these regions, it contains apatite and phlogopite. The C₂ intrusion was described as a finely banded sovite consisting of calcite, apatite, magnetite, olivine, phlogopite, dolomite, and sulfides. It has a vertical dip, parallel to the contact with C₁, and the apatite lineation is subhorizontal. Sovite and beforeite with diffuse banding were observed in the contact between C₂

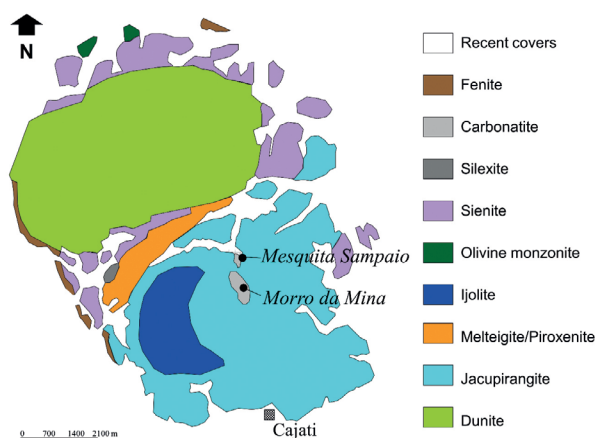


Figure 2. Geological map of the Jacupiranga Alkaline Complex (compiled and modified from Melcher 1966, Germann *et al.* 1987, Faleiros and Pavan 2013) with the Mesquita Sampaio and the Morro da Mina carbonatites locations.

and C_3 . The C_3 intrusion is a medium-to-thick grained sovite, with a less evident banding, composed of calcite, apatite, magnetite, phlogopite, dolomite, olivine, and sulfide. The C_3 body has a different characteristic from the other places: in its center, the dip varies from 20 to 40° to the north, it becomes steeper in the edges, and vertical in other places. The apatite lineation is usually parallel to the main magmatic foliation dip. In the northern part, the C_4 body was described as a sovite composed of calcite, apatite, magnetite, olivine, phlogopite, dolomite, and sulfides in the form of a cylindrical intrusion with vertical banding parallel to the edges, and with subhorizontal mineral lineation. Finally, the C_5 intrusion, which was described as a medium- to coarse-grained rauhaugite, is composed of dolomite, apatite, phlogopite, magnetite, sulfides, and calcite. C_5 cuts C_4 intrusion and has banded with a dip near 80° to the north. The apatite lineation is parallel to the dip.

Due to difficulties in mineral processing associated with the necessity to reevaluate the deposit, Saito *et al.* (2004) present a refinement of the Morro da Mina carbonatite body, identifying a total of twelve geological units that take into account not only geological characteristics but also relevant characteristics of the rock as ore in the beneficiation plant (Fig. 3). In addition to the definitions by Gaspar and Wyllie (1983b), the authors distinguished seven exclusively carbonate units (1, 2, 3, 6, 7, 8, and 9) with distinct petrographic characteristics, mappable contacts, and a distinct internal organization with concentric flow foliation and presence of xenoliths in the contact regions. Correlating the twelve units from Saito *et al.* (2004) with the five intrusions of Gaspar and Wyllie (1983b), carbonatite units 1 to 3 correspond to the C_1 intrusion, units 6 to 8 correspond to the C_2 intrusion, unit 6 also corresponds to C_3 , unit 9 corresponds to C_4 , and apparently, dolomite carbonatite (unit 11) corresponds to C_5 . In addition to them, Saito *et al.* (2004) defined some isolated metric lenses of phoscorite in the north and south mine regions (units 4 and 10), and a coarse-grained dolomite carbonatite (unit 11) occurring as late carbonate alteration products

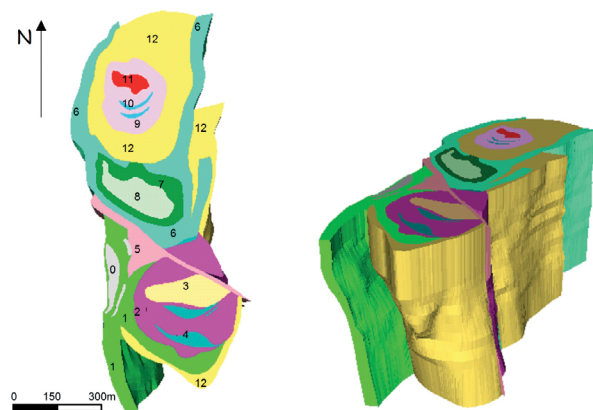


Figure 3. 3D geological model of Morro da Mina deposit (Saito *et al.* 2004). Geological units: 1) South Peripheral Carbonatite; 2) South Calcitic Carbonatite; 3) Oxidized Carbonatite; 4) South Phoscorite Zone; 5) Fault Zone; 6) Intermediate Carbonatite; 7) Foliated Carbonatite; 8) White Carbonatite; 9) North Carbonatite; 10) North Phoscorite Zone; 11) Dolomite Carbonatite; 12) Xenolith Zones; 0) Jacupirangite.

(dolomitization). In addition to the north xenolith zone mapped by Gaspar (1989), two other regions were identified in the east and south zones, where the centimetric to metric xenoliths are jacupirangite with metasomatized borders, sometimes supported by a carbonaceous matrix. The fault zone (unit 5) corresponds to the main fault of a brittle shear regime that produced the main fault system and subsidiary faults, with N75W/subvertical direction with a sinistral shear component. The fault zone produced a series of products such as breccias, cataclasites, and gouges, in addition to allowing the pervasive to fissural alteration and oxidation of the carbonatite in different intensities.

MATERIALS AND METHODS

The Mesquita Sampaio is a mineral exploration area right in the northern portion of the Morro da Mina carbonatite body, the Cajati apatite mine (Fig. 4). This study is based on core samples of the first eleven exploratory drillholes, which are all inclined at 45°, and distributed around the Mesquita Sampaio area in a regular spacing of 100 meters. Three drillholes were performed in the 2000 drilling campaign, identified as SP21, SP22, and SP24, and eight drillholes, SP42, SP43, SP44, SP45, SP46, SP47, SP48, and SP50, in the 2003 campaign, totaling 4,428 meters in the study area. The database provided by the company contains the drillhole log data and chemical analysis. All whole-rock core samples (with an average length of three meters) were analyzed by X-ray fluorescence (XRF), for CaO, MgO, SiO₂, Al₂O₃, Fe₂O₃, P₂O₅, TiO₂, SrO, MnO, and loss on ignition (LOI), with pressed powder samples, using an Axios Advanced spectrometer with sequential wavelength detector and the SuperQ software, both from PANalytical, in the internal mine laboratory, following routine procedures of the company (Sant'Agostino *et al.* 2001). Not all database samples were analyzed for all elements. Four beforosite samples with chemical analysis were selected for petrographic studies on thin sections using a Leica DM750P optical microscope.



Figure 4. Aerial photo with the location of the Morro da Mina open pit and the Mesquita Sampaio exploration target (approximate scale).

X-ray diffraction (XRD) analyses were performed on eighteen Mesquita Sampaio carbonatite samples, macroscopically selected as the most representative of the two beforisites, on Philips-MPD 1880 equipment, with PW1710 controller and X'Pert Data Collector software in the *Laboratório de Caracterização Tecnológica at Universidade de São Paulo (LCT-USP)*. The operating conditions were standardized in a step scan of $0,02^\circ$ with a time/step of 40 s, range from 2θ 2.5 to 70.0, analysis time per sample of 20 min, Cu ($K\alpha_1 = 1.5405981 \text{ \AA}$), 45 kV voltage, 40 mA current, spinner on, and graphite monochromator. The identification of the present phases was carried out using X'Pert High Score Plus software and International Center for Diffraction Data (ICDD) PDF-2 database.

MESQUITA SAMPAIO LITHOTYPES

The classification in lithotypes presented here originates from the geological model elaborated by the research team of the company, which followed the same standards applied to the geological model of Morro da Mina apatite deposit (Sant'Agostino *et al.* 2001, Bonas 2007). The classification presents the main characteristics of the rocks that influence the current ore beneficiation process, such as rock grain size, amount of macroscopically recognizable mineral species, and grain size of these minerals, highlighting apatite and carbonates as ore minerals, and magnetite and phlogopite as gangue ones (Tab. 1). Four lithotypes were defined, three of them for ore units: the fine-grained beforisite (FGB), the coarse-grained beforisite (CGB), and the xenolith zone (XEN), and one for barren material: the jacupirangite (JAC), described in detail below. The most notable attribute that differentiates the two carbonatite lithotypes is grain size, defining so, the FGB and the CGB. In addition to the grain size, another distinctive feature between these two units is the color, the FGB exhibits a more grayish color compared to the CGB, which is whiter (Fig. 5).

Table 1. Mesquita Sampaio lithotypes definition parameters.

Lithotype	Grain size	Mineralogy		
		Mineral	Grain size	Amount
Fine-grained beforisite (FGB)	2 mm	Carbonates	2 mm	70 ~ 90%
		Apatite	1 mm	5 ~ 10%
		Magnetite	3 mm	5 ~ 15%
		Phlogopite	2 mm	5%
		Accessories: olivine locally and disseminated sulfide associated with magnetite.		
Coarse-grained beforisite (CGB)	4 ~ 7 mm	Mineral	Grain size	Amount
		Carbonates	3 ~ 5 mm	65 ~ 85%
		Apatite	1mm	10 ~ 15%
		Magnetite	5 mm	5%
		Phlogopite	3 mm	5%
Accessories: sulfide locally				
Xenolith zone (XEM)	2 ~ 5 mm	Mineral	Grain size	Amount
		Silicates	1 mm	60 ~ 80%
		Fe oxides	2 mm	10 ~ 20%
		Carbonates	1 ~ 3 mm	20 ~ 30%
		Apatite	1 mm	5%
Accessories: sulfide locally				

Coarse-grained beforisite (CGB)

CGB is a coarse-grained white dolomite carbonatite, with fine-grained apatite, fine-grained magnetite sometimes ragged in small amount, and fine-grained phlogopite with sulfides locally (Fig. 5A). There are also small portions with very fine-grained concentrated greenish apatite with a common association of large magnetite crystals. The lineation of these minerals is not as marked as observed in the FGB.

Fine-grained beforisite (FGB)

The FGB comprises a fine-grained white to gray dolomite carbonatite with fine-grained apatite, fine-grained phlogopite locally with sulfides associated with magnetite, and glimmerite stains (Fig. 5B). The apatite is mostly euhedral, with greenish color, usually concentrated in small portions locally, and sometimes presents association with magnetite in a well-marked subvertical lineation.

Xenolith Zone (XEN)

This unit is characterized by the predominance of decimetric to metrics jacupirangite intercalations (Fig. 5C), with reaction edges (finitization), sometimes stained or flocked, marked by the alternation of millimetric to centimetric levels of grayish calcitic carbonatite with glimmerite, serpentine, and olivine. Both these silica phases and the grayish calcitic carbonatite levels may occur very thick locally.

Jacupirangite (JAC)

It is very similar to the jacupirangite described in Morro da Mina, a dark green to black color rock, composed of mafic minerals (pyroxenes and magnetite). In regions of contact with carbonatites, there are small portions composed of phlogopite, magnetite, and olivine, with zones of reaction reaching up one meter in thickness.

RESULTS

3D geological modeling

The three-dimensional (3D) digital geological modeling has the main objective to compartmentalize rock units in the space,

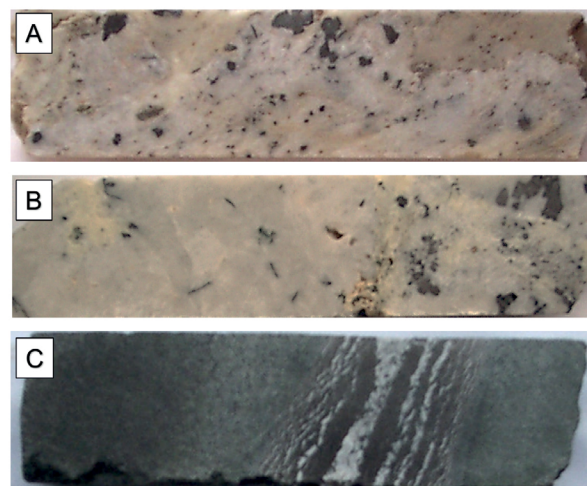


Figure 5. Drill core photos with a diameter of 47.6 mm. (A) Coarse-grained beforisite, (B) Fine-grained beforisite, and (C) Jacupirangite with reaction zone (finitization).

aiming for their technical and economic exploitation. The study carried out in the Mesquita Sampaio area was based on previous mineral exploration data performed by Bunge Fertilizantes (now Mosaic Fertilizantes) in 2003, where, in the first stage, gravimetric geophysical surveys were executed in sections with 250 meters spacing, and station locations spaced 25 meters along each section (Shukowsky *et al.* 2003). The results served as indicative of initial targets guiding for the location of the first drillholes and a second gravimetric survey, carried out in a regular spacing of 25 by 25 meters. The geological interpretation of drillhole data was performed through parallel vertical sections that delimited the contacts of the recognized geological units. Then, using the software Gems 5.5, the interpretations were generated in horizontal sections spaced 10 by 10 meters. To obtain the wireframe solid, the extrusion technique (Gems 5.5) was applied, which consists of extrapolating the information generated in the plant and then joining it level-by-level, obtaining a continuous solid that represents the dimensional model (Fig. 6).

Of the four lithotypes defined for Mesquita Sampaio, only the XEN could not be represented in the 3D geological model due to a scale matter, as these zones are commonly centimetric and the model reproduces geological units at least on the metric scale. The 3D geological model shows the Mesquita Sampaio beforites as a vertical body with an NNW direction with approximately 350 meters in length and 150 meters in width of known dimensions. CGB is predominant in the northern portion of the pipe, while in the southern, FGB is (Fig. 6). Two jacupirangite

xenoliths of approximately 100 meters in length could be individualized within the beforite bodies (Fig. 6). With current knowledge, the Mesquita Sampaio carbonatite body reaches 400 m in depth with open continuity. The shape of the Mesquita Sampaio carbonatite suggests a secondary pipe or diatreme structure concerning the main Morro da Mina carbonatite body, although the temporal relations between them are still not clear due to the small number of drillholes.

Mineralogy and petrography

The identification of the 26 mineral species for Mesquita Sampaio beforite (Tab. 2) was obtained by comparing the sample diffractograms to the ICDD database. From the total identified mineral phases, only eight mineral species (dolomite, fluorapatite, phlogopite, lizardite, calcite, magnetite, hydroxylapatite, and kinoshitalite) occur in all eighteen samples analyzed by XRD. The three members, fluorapatite, hydroxylapatite, and chlorapatite are not easily distinguishable from XRD data, as well as in petrography. Menezes and Martins (1984) described fluorapatite in the Morro da Mina carbonatite. In this study, the minerals of the apatite group are treated as apatite indistinctly. The same occurs for serpentine group minerals, being treated in this work as serpentine. A representative main mineral assemblage of the Mesquita Sampaio beforite is dolomite, apatite, phlogopite, serpentine, calcite, and magnetite, being described from greater to smaller abundance. Ilmenite, pyrite, quartz, and titanomagnetite were identified in several

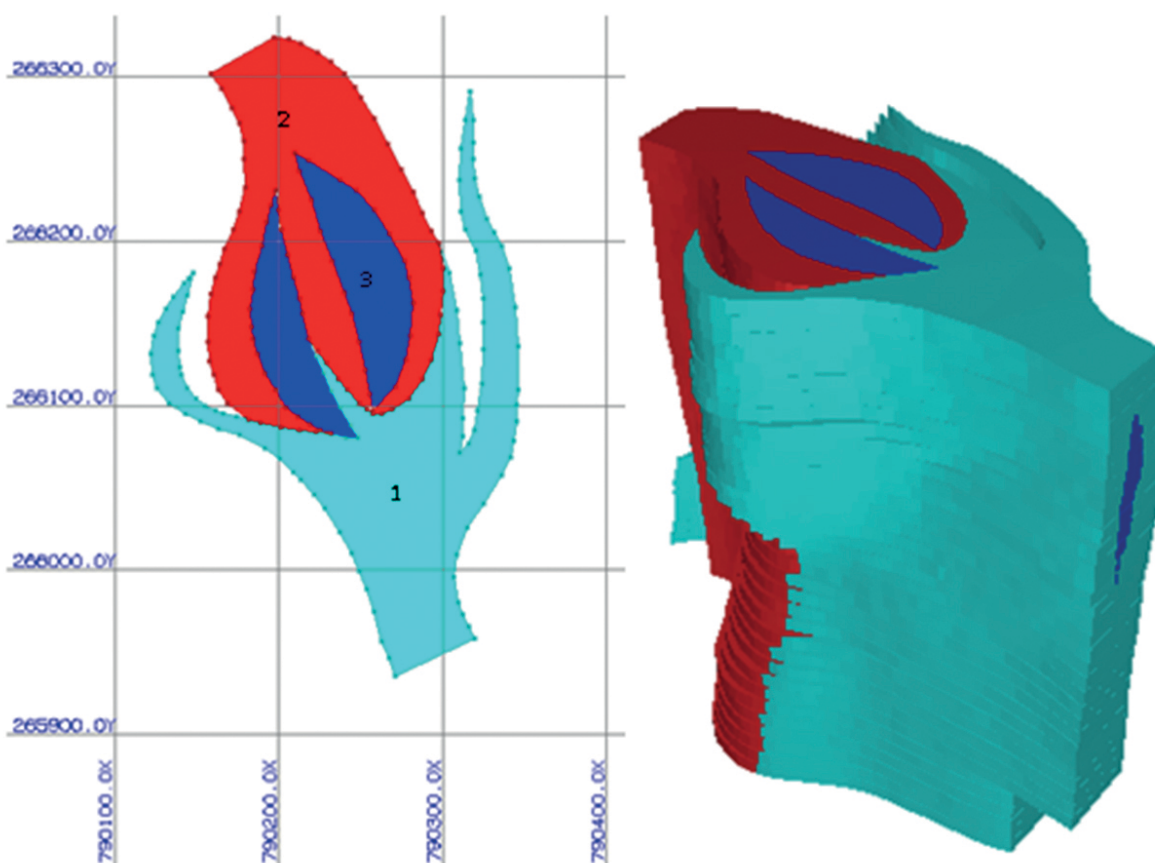


Figure 6. 3D geological model of Mesquita Sampaio. (1) Fine-grained beforite (FGB), (2) Coarse-grained beforite (CGB), and (3) Jacupirangite (JAC).

samples, being frequent accessories, while the other mineral phases were not confirmed by petrography studies and were identified in only one or two samples each, requiring other more specific studies for their confirmation.

Considering the modal estimation of the mineral phases occurring in the dolomite carbonatites of Mesquita Sampaio, between 75 and 85% of the ore-forming minerals are dolomite (mainly) and calcite. The second mineral that most occurs in these rocks is apatite (on average 10%), followed by opaque minerals, mainly magnetite (6%), and phlogopite (2%), which generally presents inverted pleochroism in orange-brown to greenish tones. The apatite occurs in fine-grained size, variably concentrated in small portions or along magmatic flow foliation. Perovskite and minerals of the pyrochlore group occur as trace minerals and were not identified in XRD studies. The carbonates presented in general medium grain size, with crystallization in two phases, from crystals of 0.02 to 5 mm.

In both beforites (FGB and CGB), the apatite occurs elongated, sometimes in a magmatic flow foliation, concentrated in local portions without preferential orientation. Both apatite as carbonates seem to have been simultaneously crystallized, from initial stages until later. Opaque occurs involving carbonates and filling interstices, suggesting that they are subsequent to them (Figs. 7A and 7B). The phlogopite occurs brownish euhedral with a pseudohexagonal habit, suggesting a stage of primary crystallization, and also occurs from orange-brown to

greenish with carbonates and opaque inclusions, presenting features that suggest a post-alteration, generating an aggregate material as light green spots (Figs. 7C and 7D).

The reaction zones, which are characteristic of borders of XEN, have centimetric bands of dolomite associated with apatite in a similar texture to that found in carbonatites. Pseudomorphs of colorless olivine and amphiboles with a fibrous appearance are also characteristic, highlighting the serpentine generation (Figs. 7E and 7F).

The jacupirangite in the Mesquita Sampaio area is a clinopyroxenite formed by opaque minerals (mainly magnetite) in a grain size smaller than the pyroxenes and included or interstitial to them (Figs. 7G and 7H). Phlogopite occurs in orange color, in small amounts, and fine-grained. Perovskite occurs in brown tones normally subhedral in association with opaque minerals.

Litho geochemistry

The whole-rock chemical compositions are tabulated by lithotype in Table 3. Mesquita Sampaio carbonatite data are plotted on the International Union of Geological Sciences (IUGS) classificatory diagram (Le Maitre *et al.* 2002), shown in Figure 8. Samples of Morro da Mina carbonatite from Huang *et al.* (1995) and Beccaluva *et al.* (2017) were considered for comparison. All Mesquita Sampaio beforite data, whether FGB or CGB, lies on the magnesio carbonatite field. The three Morro da Mina carbonatite samples (HB005, HB010, and HB011) from Huang *et al.* (1995) plot on the iron carbonatite field, while the two samples from Beccaluva *et al.* (2017) plot on the calcium carbonatite field (Fig. 8). Major elements scatter plots for the Mesquita Sampaio beforites are shown in Figure 9. The variations of SiO₂ reflect the modal proportions of olivine, micas, and serpentine, in addition to the Fe₂O₃ content, which also reflects magnetite proportions and some sulfides. The CaO, as well as the carbonates, are in the chemical structure of apatite. The MgO content is closely linked with the proportions of dolomite but also to the main silicates previously mentioned. The Al₂O₃ is related to the micas proportions and the TiO₂ to titanomagnetite and ilmenite mainly. In general, in all geochemical scatter plots of Figure 9, a small variability of mineral amounts could be noted for the two lithotypes of the Mesquita Sampaio area.

In addition to having higher MgO values than Morro da Mina carbonatites, the Mesquita Sampaio beforites have chemical compositions between mine carbonatite ranges intervals reported in the literature (Huang *et al.* 1995, Beccaluva *et al.* 2017). The Mesquita Sampaio beforite has CaO values from 31.3 to 32.7% and Fe₂O₃ values from 0.83 to 4.23%, while in the Morro da Mina carbonatite the values range from 28.6 to 50.7% and from 0.10 to 43.1%, respectively. These values reflect variations on dolomite, calcite and ankerite amounts or even the absence of one of these carbonates within the two contiguous carbonatites. The Al₂O₃ values vary from 0.18 to 0.34% in the Mesquita Sampaio beforites and the Morro da Mina carbonatites the values vary from 0.10 to 1.20% reflecting different proportions in micas, mainly phlogopite. The P₂O₅ and TiO₂ values in the beforites (3.07 to 6.00%; 0.17 to 0.62%, respectively) are also contained within the value ranges of the

Table 2. Identified minerals by X-ray diffraction (XRD) in the Mesquita Sampaio beforite, with International Centre for Diffraction Data (ICDD) card number.

ICDD	Mineral	Chemical formula
00-036-0426	Dolomite	CaMg(CO ₃) ₂
01-086-2348	Magnesite	MgCO ₃
00-012-0088	Ankerite	Ca(Mg, Fe)(CO ₃) ₂
01-081-2027	Calcite	CaCO ₃
01-070-0796	Fluorapatite	Ca _{4.895} (PO ₄) _{2.995} Cl _{0.23} F _{0.77} (OH) _{0.35}
01-082-1429	Hydroxylapatite	Ca _{10.084} (PO ₄) _{5.94} (OH) _{3.39}
01-073-1728	Chloroapatite	Ca ₅ (PO ₄) ₃ Cl
00-024-0867	Phlogopite	KMg ₃ AlSi ₃ O ₁₀ F ₂
01-083-1366	Biotite	K ₂ (Fe _{2.786} Mg _{2.321} Ti _{0.550}) (Al _{2.413} Si _{5.587} O ₂)(OH) ₄
00-034-0166	Vermiculite	(Mg, Al) ₃ (Si, Al) ₄ O ₁₀ (OH) _{2.4} H ₂ O
00-043-1491	Cebollite	Ca ₂ MgSi ₂ (O, OH) ₇
00-050-1606	Lizardite	(Mg, Fe) ₃ Si ₂ O ₅ (OH) ₄
00-052-1572	Antigorite	Mg ₃ Si ₂ O ₅ (OH) ₄
01-071-1140	Ilmenite	FeTiO ₂
01-075-1376	Titanomagnetite	Fe _{2.5} Ti _{0.5} O ₄
01-089-0951	Magnetite	Fe ₃ O ₄
00-001-1292	Rutile	TiO ₂
00-048-1873	Microlite	(Ca, Na) ₂ (Ta, Nb) ₂ O ₆ (OH, F)
01-071-0053	Pyrite	FeS ₂
00-046-1045	Quartz	SiO ₂
00-029-0180	Kinoshitalite	BaMg ₃ Si ₂ Al ₂ O ₁₀ (OH) ₂

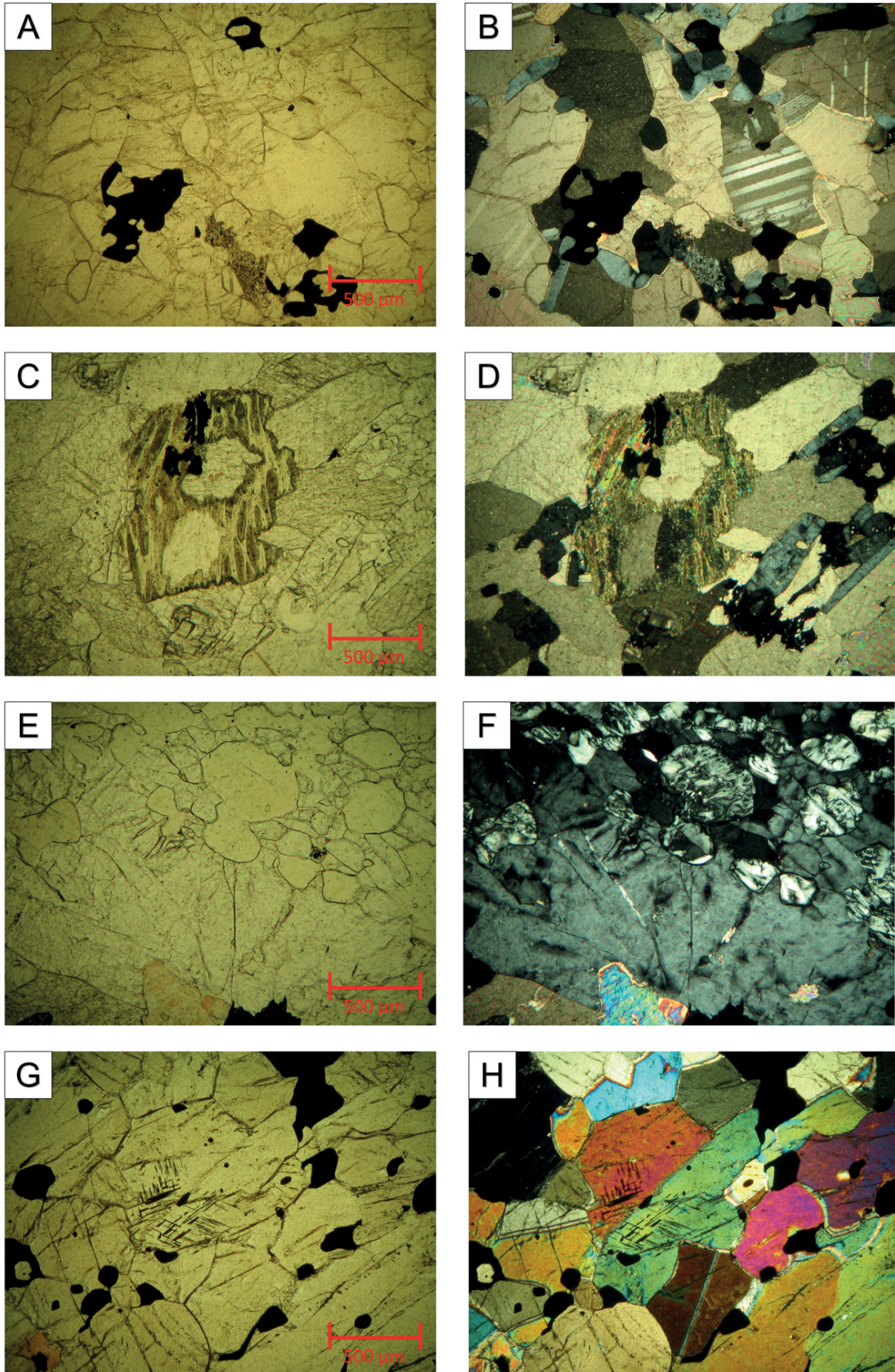
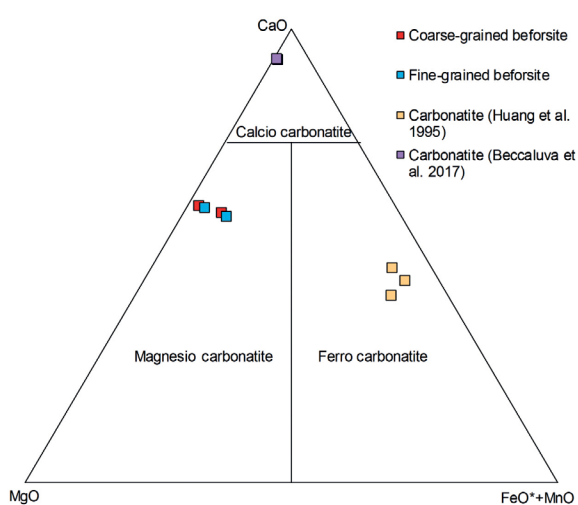


Figure 7. Photomicrographs of the Mesquita Sampaio lithotypes. Befsorsite with geminate carbonates (dolomite mostly) and opaque (magnetite mostly) both involving carbonates and interstitial to them with (A) open nicol and with (B) cross nicol. Befsorsite with corroded phlogopite in reaction with carbonates and with associated opaque, apatite (gray color) in magmatic flow foliation with (C) open nicol and with (D) cross nicol. Reaction zone between carbonates and phlogopite with greenish reaction stains (lower portion) and pseudomorphs of colorless olivine (upper portion) (E) open nicol and with (F) cross nicol. Jacupirangite with clinopyroxenes (yellow to green interference color) in granular texture with associated opaque minerals (magnetite mostly) with (G) open nicol and with (H) cross nicol.

Table 3. Bulk rock major element compositions of the Mesquita Sampaio beforosite. In blank, not determined elements.

	SP45-440.00 m Fine-grained beforosite	SP46-212.65 m Fine-grained beforosite	SP43-177.30 m Coarse-grained beforosite	SP50-400.00 m Coarse-grained beforosite
SiO ₂	0.59	1.57	1.70	0.23
CaO	32.70	31.26	32.50	32.70
MgO	19.37	17.56	18.20	19.70
Al ₂ O ₃	0.21	0.34	0.18	
Fe ₂ O ₃	1.56	4.23	3.52	0.83
P ₂ O ₅	3.07	4.01	6.00	3.14
TiO ₂		0.62	0.17	
SrO	0.60	0.57	0.66	0.65
MnO	0.24	0.26	0.25	0.27
LOI	41.11	39.74	37.10	42.30

**Figure 8.** Ternary IUGS classification diagram for carbonatites (Le Maitre *et al.* 2002) with samples from the Mesquita Sampaio beforosite.

Morro da Mina carbonatites (0.10 to 9.80%; 0.01 to 1.30%, respectively), reflecting different proportions in the accessory minerals identified in petrography and XRD analysis, such as apatite, titanomagnetite, and ilmenite.

DISCUSSION

The 3D geological modeling delineates a beforosite pipe with significant dimensions (350 x 150 meters), though smaller than the Morro da Mina carbonatite, which has at least 1 km of extension along its main strike. The main feature of the Mesquita Sampaio carbonatite is its magnesian composition. Dolomite carbonatites are described in the Morro da Mina as a product of late processes (Gaspar and Wyllie 1983b, Gaspar 1989, Saito *et al.* 2004). In some mine regions, it appears to be a swarm of beforosite dikes intruding the sovites, but in other regions, the increase in dolomite could be attributed to a metasomatic process of dolomitization of the sovite (Gaspar and Wyllie 1983b). The textures observed in the Mesquita Sampaio beforosite are not from veins or replacement, but rather primary and not similar to the dolomite carbonatites

described in the mine. The normal sequence of cationic abundances in the carbonatite rock is: Ca > Mg > Fe > (Na + K) (Le Bas 1981). One hypothesis would be that considering the Mesquita Sampaio as a late intrusion, it could be the generator of the Morro da Mina dolomite carbonatite dikes and dolomitization, due also to the proximity of these dolomitic occurrences, present in the northern portion of the mine, to the Mesquita Sampaio area. For while no direct contact relation between Mesquita Sampaio and Morro da Mina is known, both may be the same carbonatitic body with a gradual variation of the composition, or the Mesquita Sampaio is a distinct late or even earlier carbonatite pipe.

The Mesquita Sampaio beforosite subdivision in two lithotypes based on rock grain size do not reflect great chemical differences (Tab. 3), which means that both lithotypes have the same mineralogy, but in different modal proportions. The same occurs when comparing the chemical composition and mineralogy of the Mesquita Sampaio beforosite with the data in the literature for the Morro da Mina carbonatite (Menezes and Martins 1984, Gaspar 1989, Huang *et al.* 1995, Beccaluva *et al.* 2017). The similarities of geochemical and mineralogical data for the carbonatites in the Mesquita Sampaio with the Morro da Mina data suggest a parental relationship between both. However, geochemical studies with trace elements and isotopes are necessary to confirm this hypothesis. At the present stage of knowledge, the overlapped major elements compositions only indicate similar mineralogical compositions for the two carbonatites.

The apatite-bearing Mesquita Sampaio beforosite, although with small dimensions, is a potentially additional ore source to the phosphate mine, however detailed economic studies are still necessary to confirm its economic viability.

CONCLUSIONS

- The 3D geological modeling based on the first eleven drill-holes defined a subvertical carbonatite body of hundreds of meters scale in an NNW direction with depth extension confirmed until 400 meters. The 3D model of the Mesquita Sampaio also differentiated a coarse-grained beforosite

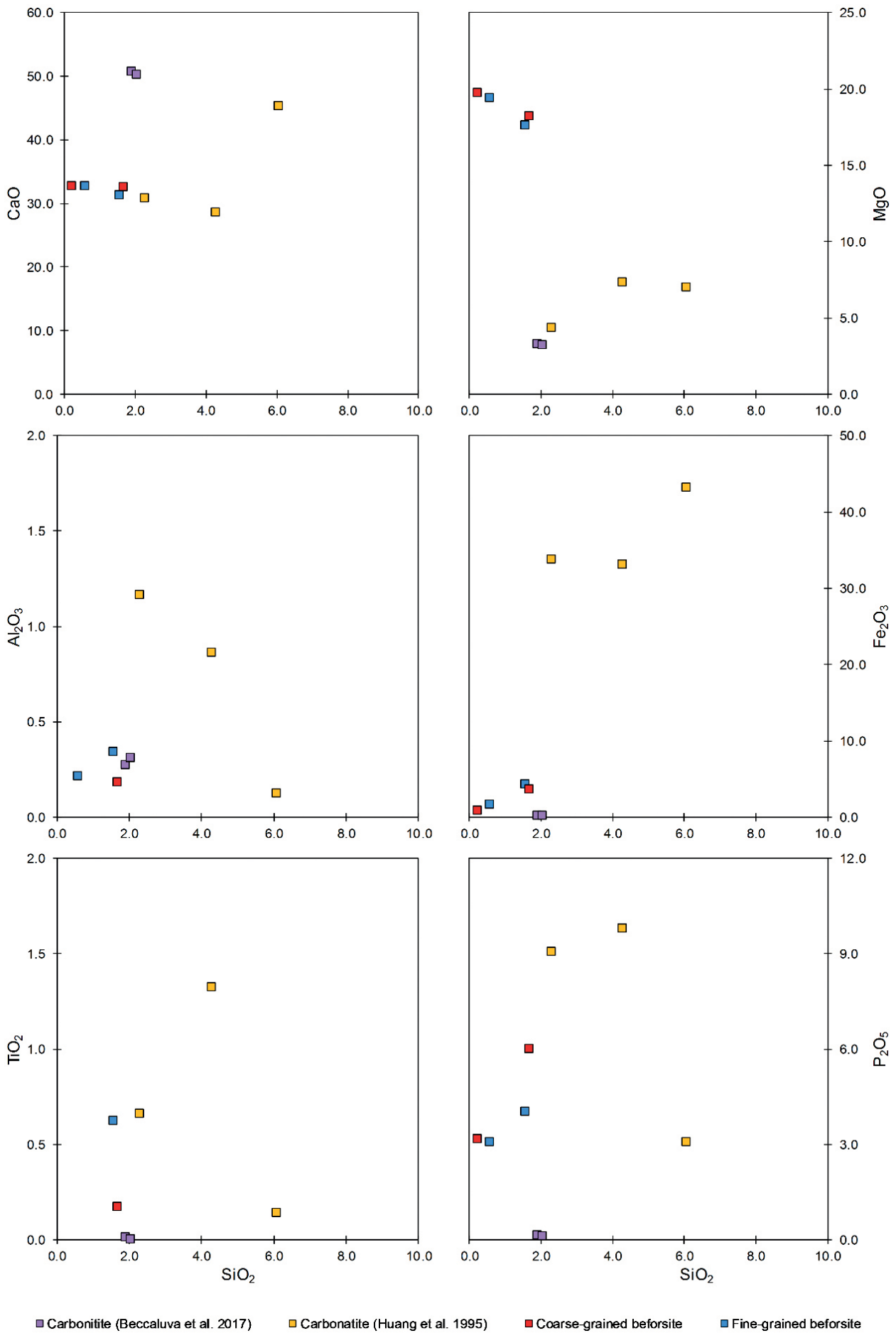


Figure 9. Selected Harker diagrams for the Mesquita Sampaio befsite.

(CGB) in the northern portion of the pipe structure, and a fine-grained beforosite (FGB) in the southern portion;

- A representative main mineral assemblage of the Mesquita Sampaio beforosite is dolomite, apatite, phlogopite, serpentine, calcite, and magnetite, in abundance order. All these minerals have also been described in the contiguous Morro da Mina carbonatite;
- The temporal relation between the Mesquita Sampaio and the Morro da Mina carbonatites are still not clear, but the close results of mineralogy, geochemistry, the direction of

intrusion, and spatial location suggest a parental relationship between both.

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