A review of mineral assemblages of agpaitic rocks from the Poços de Caldas alkaline massif, southeastern Brazil

Celso de Barros Gomes[1]* , Andrezza de Almeida Azzi[1] , Daniel Atencio[1]

Abstract

This study revises the early-magmatic, late-magmatic, and hydrothermal mineral assemblages occurring in rocks of agpaitic affinity, mainly represented by nepheline syenites and phonolites, from the Poços de Caldas alkaline massif. Mostly composed of different types of silicates, these rocks include rare minerals of of distinct groups, such as sulfides, oxides, carbonates, phosphates, sulfates, niobates, and notably halides, with villiaumite (NaF) as an important phase indicative of extreme alkali enrichment. Hydrothermal alteration products of nepheline and alkali feldspar typically consist of feldspathoids and zeolites. The rare minerals are of varied origin, from magmatic crystallization to hydrothermal and weathering processes. In general, they tend to occur interstitially or form euhedral crystals, especially when filling cavities or growing out from their walls. Petrological conditions involving the formation of the agpaitic rocks and their mineral assemblages are discussed.

KEYWORDS: igneous petrology; alkaline rocks; agpaitic rocks; mineral chemistry.

INTRODUCTION

The Late Cretaceous isolated circular structure referred to in literature as the Poços de Caldas massif represents the second largest known alkaline igneous occurrences worldwide, extending over an area of more than 800 km^2 in southeastern Brazil (Fig. 1). Emplaced into a Neoproterozoic basement mainly composed of granitic and gneissic rocks, probably as a caldera-like structure, the Poços de Caldas massif also includes significant amounts of aeolian sandstones of the Cretaceous Botucatu Formation (Ellert 1959). Tectonically, it is associated with the Cabo Frio magmatic lineament, a curved, 60 km wide, and 1,150 km long WNW-ESE-trending belt encompassing several alkaline intrusions from the east of Poços de Caldas to the oceanic margin near Cabo Frio (Almeida 1991, Riccomini *et al.* 2005). Lying in a singular position, this isolated massif is distant from the alkaline occurrences that form the Alto Paranaíba Igneous Province to the northeast and the Serra do Mar Province (Thompson *et al.* 1998) to the east. Being quite distinctive in terms of petrographic composition, Poços de Caldas can be briefly described as consisting of two main suites: a felsic and a mafic-ultramafic one (Ulbrich 1984, Ulbrich *et al.* 2005). The felsic suite comprises nepheline syenites, tinguaites (subvolcanic pyroxene phonolites), and volcanic phonolites. The syenitic rocks mostly form discrete bodies, accounting for 17% of the entire district, whereas the most abundant tinguaites and altered vesicular phonolites represent 80% of the outcropping areas (Ulbrich and Ulbrich 2000). The mafic-ultramafic lithologies, in turn, are composed of a variety of fragmented volcanoclastic material (agglomerates, lapilli, and tuffs) and poorly exposed lava flows filling the depressed area of Vale do Quartel, a narrow, irregular, N-S-trending structure at the western border of the massif. Additional rock types include phonolites and lamprophyres cropping out as dikes cutting syenitic rocks in areas such as the Osamu Utsumi open pit uranium mine (Ulbrich 1984, Ulbrich *et al.* 2005) or in the Minas Pedras quarry, outside the complex, where they are penetrating into basement gneisses (Vlach *et al.* 1996, 1998, Ulbrich *et al.* 1998). Dikes of alnoitic and silico-carbonatitic affinity are described as small bodies lying peripherally to the massif and have been investigated geochemically by Vlach *et al.* (1996, 1998).

Abundant geochronological data obtained by different methods are available for the massif and apparently confirm their long magmatic history (K/Ar age between 64 and 83 Ma, with a median value of 77 Ma, Ulbrich *et al.* 2005). These authors also reported Rb/Sr measurements giving an isochron age of 78.6 ± 6.6 Ma, and more recent work by Vlach *et al.* (2018) yielded an Ar/Ar plateau age of 87 (*ca.*) Ma for phlogopite crystallization in conduit breccia. This value is older than the "best" presumed (*ca.* 79 Ma) age proposed by Ulbrich *et al.* (2002) for the main magmatic event of the massif.

Significant areas of the district, especially those associated with felsic rocks, show evidence of being affected in variable degrees by strong subvolcanic magmatic-related hydrothermal alteration and brecciation, as evidenced by the large number of mineralized occurrences (mainly U, Th, Mo, and Zr), some of them already economically exploited in past decades (Ulbrich 1984, Lapido-Loureiro 1994, Ulbrich *et al.* 2005).

[1]Instituto de Geociências, Universidade São Paulo – São Paulo (SP), Brazil.
E-mail: cgomes@usp.br; andrezzazzi@gmail.com; datencio@usp.br

*Corresponding author.

The unusual composition of the felsic rocks and the geological processes that influenced the magmatic evolution of the Poços de Caldas massif are responsible for mineral assemblages, mainly associated with rocks of agpaitic affinity, presenting remarkable diversity and generally having complex chemical compositions. Thus, the main purpose of the present study was to review the data available on that mineralogy, describing the different minerals so far identified in the massif that include some well-known and others that still need additional information for a better characterization.

PETROGRAPHY

The dominant felsic suite in Poços de Caldas is represented by highly evolved SiO_2-undersaturated rocks of syenitic (either intrusive or fine-grained) composition, giving rise to the formation of two distinct petrographic lineages based on their alkali content and mineralogy: a transitional agpaitic (a paragenesis proposed by Marks and Markl 2017, and also adopted by Guarino *et al.* 2019, showing the presence of minerals typical of miaskitic rocks) and an agpaitic one. Ulbrich *et al.* (2005) and Vlach *et al.* (2018) also defined the former association as "intermediate miaskitic varieties." The miaskitic lineage is clearly more abundant (118.7 km² of outcrops vs. 24.8 km²) and older than the agpaitic, as reported by Ulbrich (1984), Ulbrich and Ulbrich (2000), and Ulbrich *et al.* (2005). Revising the global agpaitic rocks, Marks and Markl (2017) concluded that in a composite magmatic complex consisting of several miaskitic intrusive units, the agpaitic units are mostly younger compared to the miaskitic ones. In general, according to these authors, miaskitic rocks usually contain zircon, baddeleyite, and titanite as their main accessory phases, whereas the agpaitic ones are characterized by a more complex mineral composition, including aenigmatite, astrophyllite, eudialyte, lamprophyllite, F-disilicates, and wadeite. However, apparently, the Poços de Caldas miaskites mostly contain titanite as a frequent accessory phase, being the mineral of early crystallization in the assemblages (Guarino *et al.* 2021). In their review on agpaitic rocks, Marks and Markl (2017) stated that the quite unusual mineralogy of the agpaitic rocks is due to the presence of some specific elements in their composition, such as large ion lithophile elements (K, Rb), halogens (F, Cl), volatiles (CO_2, H_2O), rare earth elements (lanthanides), and high field strength elements (Zr, Ti, Nb, U-Th). Also, the assemblages result from the enrichment of alkalies (particularly Na) and iron in major mafic constituents and the occurrence of accessory phases of high Na-Ca content. All such chemical evidence is found in Poços de Caldas minerals and has been confirmed by studies performed by Ulbrich *et al.* (2005), Gomes *et al.* (2021), and Guarino *et al.* (2021). Similar characteristics are commonly noted in other well-known agpaitic occurrences around the world (Sørensen 1997, Andersen *et al.* 2010, 2018, Marks and Markl 2017). Yet the agpaitic mineral assemblages in Poços de Caldas comprise mainly silicate phases (the eudialyte group being the most typical minerals) and species belonging to other groups, such as oxides, phosphates, carbonates, and fluorocarbonates, more scarcely, sulfates, and niobates.

The massif is also marked by the presence of strongly agpaitic petrographic types described in literature as lujavrites and khibinites (eudialyte-bearing nepheline syenites variable in color index, texture, and grain size; Ulbrich and Ulbrich 2000) that are particularly abundant in the northern ring area known as Pedra Balão and also occur at the western side of the district (Morro do Serrote) and at its eastern margin (Morro do Taquari), as shown in Fig. 1.
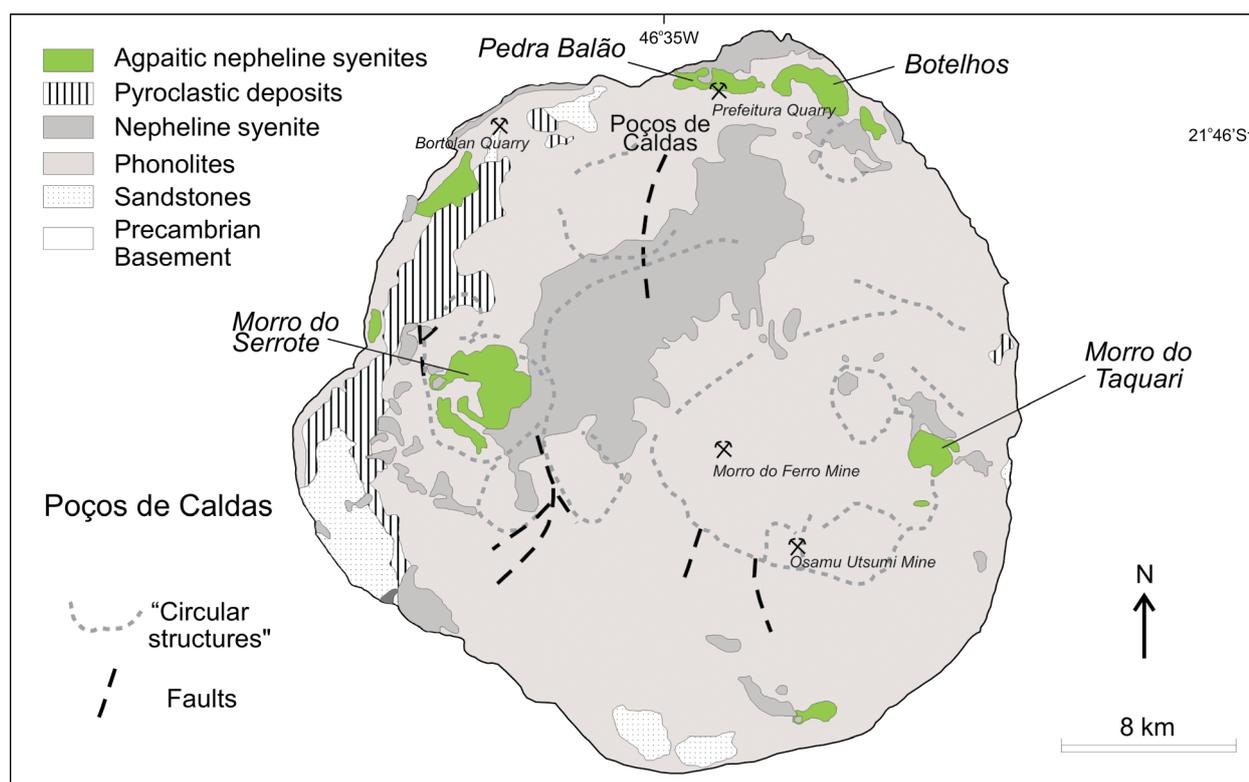
Source: modified from Ulbrich *et al.* (2005).
Figure 1. Geological map of the Poços de Caldas massif and its areas of prevailing agpaitic rocks.

MINERAL COMPOSITION

Poços de Caldas agpaitic minerals are classified based mainly on their chemical composition, which is mostly determined through wavelength dispersive spectrometry (WDS) microprobing and energy dispersive spectrometry (EDS) methods. Additional information for the chrystalochemical characterization of such constituents derives from optical studies, x-ray crystallography, Raman, and infrared spectrographic analysis; all techniques were routinely used by Azzi (2019) in the systematical investigation of Poços de Caldas minerals to confirm their identification and to help distinction between phases of similar characteristics.

Some rare, exotic mineral phases in Poços de Caldas agpaitic rocks are due to crystallization from highly evolved magmas enriched in HFSEs and other incompatible elements and halogens (Gomes *et al.* 2021). In general, as mainly suggested by the studies of Ulbrich and co-workers over the years and by Guarino *et al.* (2021), these minerals occur as euhedral phases in the rock groundmass or as irregular, fibrous, or prismatic aggregates. They are usually early- to late-magmatic minerals (mostly represented by different types of silicates), and the assemblages also contain phases originated from hydrothermal and typical weathering processes (carbonates and clay minerals).

The Prefeitura and Bortolan quarries (decommissioned in the 1980s), both including nepheline syenites and fine-grained equivalents (phonolites), respectively, as their main rock types, were the most important sources of samples for the investigation of Poços de Caldas mineralogy. A Th-REE supergene deposit covering a stockwork of magnetite dykes and dykelets at Morro do Ferro has also provided samples for mineralogical studies in the past (Waber 1990, 1992, Lapido-Loureiro 1994, Ulbrich *et al.* 2005).

Chemical data on the agpaitic minerals are listed in Tables 1–13, arranged according to their chemical classification into different groups as it is traditionally adopted in literature. Except for polezhaevaite (Table 1) and chlorbartonite (Table 2), both minerals analyzed by the EDS method, all the chemical data were determined by the WDS technique and mostly reported in wt% of oxide concentrations.

Table 1. Chemical composition (wt%) of polezhaevaite in the Poços de Caldas massif.

	[1]	[2]
Sample	P7 123	P7 123
Na	2.53	3.23
Ca	1.31	0.86
Sr	22.5	25.52
La	14.22	19.92
Ce	22.71	17.33
Nd	3.32	1.21
Pr	1.86	0.95
F	30.98	30.24
Total	99.43	99.26

[1]: Polezhaevaite-(Ce); [2]: Polezhaevaite-(La).
Source: Azzi (2019).

Halides

This mineral group is represented in the Poços de Caldas massif by **villiaumite** $\{NaF\}$, a low-temperature hydrothermal phase forming commonly euhedral crystals that vary in color from deep red to colorless (Fig. 2). Villiaumite is a crystallization phase of the so-called hyperagpaitic assemblages formed during the final stages of agpaitic systems, indicating extreme alkali enrichment (Marks and Markl 2017). The mineral contains a high Na content of 51.72%, as reported for the Poços de Caldas phonolitic rocks by Azzi (2019).

Other hydrothermal constituents of the massif are members of the fluorite group, especially the Sr-bearing **strontiofluorite** $\{SrF_2\}$, with an abundant Sr concentration (59.11%), and the associated **polezhaevaite-(Ce)** and the undescribed La-dominant equivalent, **"polezhaevaite-(La),"** which occurs as white aggregates of diminute crystals (Fig. 3). Data on the latter two species, described by EDS in Brazilian rocks for the first time, are shown in Table 1.

Sulfides

Sulfide minerals of unusual composition are rare, with **chlorbartonite** $\{K_6Fe_{24}S_{26}(Cl,S)\}$ being the only species identified so far that presents as irregular aggregates and microcrystals (Fig. 4). EDS analyses by Azzi (2019) revealed the high K content of the mineral (Table 2). Common sulfides in the miaskitic and agpaitic rocks are galena, molibdenite, pyrite,

Table 2. Chemical composition (wt%) of chlorbartonite in the Poços de Caldas massif.

Sample	P7 297	P7 297
S	32.32	37.41
Fe	52.72	51.37
K	9.04	10.11
Si	0.19	b.d.l.
Na	0.07	b.d.l.
Zr	0.46	b.d.l.
Cl	1.1	1.53
Total	95.90	100.42

b.d.l.: below detection limits.
Source: Azzi (2019).
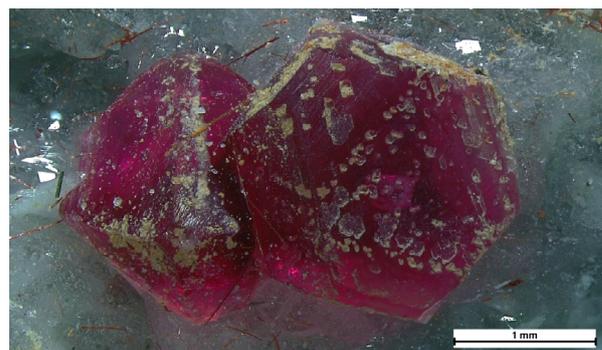
Source: Azzi (2019).
Figure 2. Deep red in color villiaumite forming euhedral crystals of cubic habit. Image taken by magnifying glass.

pyrrhotite, and sphalerite, as reported by Biondi (2005) and Ulbrich *et al.* (2005) at the Osamu Utsumi mine and the mineralized deposits of Agostinho and Morro do Ferro, and are linked to intense hydrothermal alteration processes responsible for the formation of mineral deposits of U, Zr, Mo, and Th.

Oxides

The oxide minerals found in the Poços de Caldas massif are of varied composition and origin; the phases they constitute bear different cations that occupy structural sites either in isolated form or combined with other elements. Known minerals include **baddeleyite** $\{ZrO_2\}$, found in the Osamu Utsumi mine (Biondi 2005); **cerianite-(Ce)** $\{CeO_2\}$, reported by authors including Frondel and Marwin (1959), Fujimori (1982, 1984), and Lapido-Loureiro (1994); sporadic **loparite-(Ce)** $\{(Na,Ce,Ca)(Ce,Th)(Ti,Nb)_2O_6\}$ cited by Guarino *et al.* (2021) as tiny crystals in the groundmass of nepheline syenites; **manganoan ilmenite** $\{Fe^{2+}TiO_3\}$ (Atencio *et al.* 1999); **pyrochlore**-group mineral $\{(Ca,Na)_2Nb_2O_6(OH,F)\}$ (Ulbrich *et al.* 2005, Guarino *et al.* 2021); and **pyrophanite** $\{Mn^{2+}TiO_3\}$ forming either isolate grains or botryoidal aggregates (Fig. 5). Chemical data for loparite-(Ce) and pyrophanite are listed in Table 3, indicating a complex composition for the former mineral containing high amounts of REE and abundant MnO in the latter. Additional oxide minerals include U-Th-Ti-bearing phases, such as **anatase** $\{TiO_2\}$, **brannerite** $\{UTiO_6\}$, **thorianite** $\{ThO_2\}$, and **uraninite** $\{UO_2\}$, mainly found in rocks of the Osamu Utsumi or Cercado areas. Most minerals are genetically related to hydrothermal processes in tinguaitic breccias and phonolitic lavas and have been mentioned by Lapido-Loureiro (1994) and Ulbrich *et al.* (2005) in association with the mineralized bodies of the central regions of the complex.

Carbonates

Carbonates are widespread minerals typically present in late phases, originated by hydrothermal or deuteric alteration. In the Poços de Caldas massif, they occupy rock interstices or cavities and are generally associated with different rock types, especially syenitic ones. The carbonate species vary considerably in terms of chemical composition, being represented by two groups, one including Fe- and Sr-bearing varieties and another with important amounts of REE-carbonates. The Fe- and

Source: Azzi (2019).

Figure 3. White aggregates of polezhaevaite-(Ce) associated with stronadelphite and strontiofluorite in gray shades. Image taken by magnifying glass.
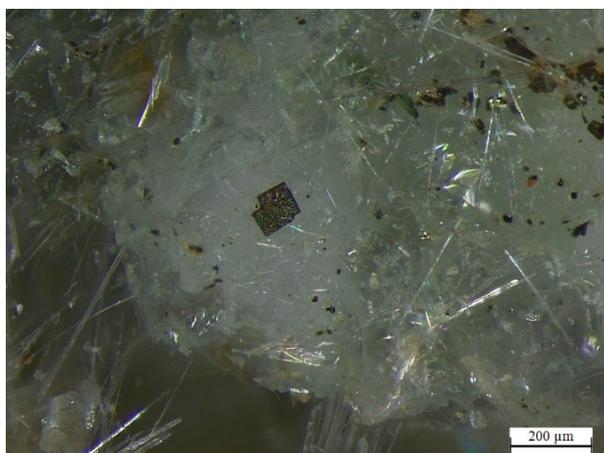
Source: Azzi (2019).

Figure 4. Chlorbartonite forming dark irregular aggregates at the center of the section associated with natrolite in gray to the right and plagioclase in white to the left. Image taken by magnifying glass.

Source: Azzi (2019).

Figure 5. Very fine crystals of pyrophanite forming dark botryoidal aggregates on the top of aegirine. Image taken by magnifying glass.

Table 3. Chemical composition (wt%) of loparite-(Ce) (Guarino *et al.* 2021) and pyrophanite (Azzi 2019) in the Poços de Caldas massif.

	Loparite-(Ce)	Pyrophanite
Sample	PC 40	P7 513
TiO_2	43.79	49.17
FeO	0.28	6,42
MnO		40.27
Nb_2O_5	3.54*	1.48
CaO	7.04	
Na_2O	5,57	
SrO	16.20	
La_2O_3	6.06	
Ce_2O_3	12.69	
Nd_2O_3	3.15	
ThO_2	0.35	
UO_2	b.d.l.	
Total	98.67	97.34

b.d.l.: below detection limits; blank rows: not analyzed; *Chemical data on niobium are expressed as weight % of the element.

Sr-bearing group of minerals includes **ankerite** $\{(CaFe^{2+},Mg)(CO_3)_2\}$ (Atencio *et al.* 1999), **kutnohorite** $\{(Ca,Mn^{2+})(CO_3)_2\}$ (Schorscher and Shea 1992), and the very common **strontianite** $\{SrCO_3\}$, which presents in white to green tones and a botryoidal habit. The second, REE-bearing mineral group is represented by light rose, anhedral to euhedral crystals of **ancylite-(Ce)** $\{CeSr(CO_3)_2(OH).H_2O\}$ (Fig. 6) and **ancylite-(La)** $\{LaSr(CO_3)_2(OH).H_2O\}$, in addition to fine white-to-colorless aggregates of **burbankite** $\{(Na,Ca)_3(Sr,Ba,Ce)_3(CO_3)_5\}$. A Ba-free variety has been described on some sites by Matioli *et al.* (1994). Initially identified in Poços de Caldas rocks by Wedow Jr. (1967), a **bastnäsite** $\{(Ce,La,REE(CO_3)F\}$-group mineral was pointed out by Ulbrich *et al.* (2005) as a primary mineral associated with thorite, monazite, pyrochlore, zircon, oxide secondary phases, and several other minerals. **Thorbastnäsite** $\{ThCa(CO_3)_2F_2.3H_2O\}$ was described in the Th-REE-(Nb) deposit of Morro do Ferro by Lapido-Loureiro (1994). Chemical data on ancylite and Ba-free-burbankite are presented in Table 4, showing variable contents of REE, CaO, and SrO for both these minerals. Burbankite is also distinguished by its abundant Na$_2$O and low BaO content. An occurrence of a **lanthanite** $\{(La,Nd)_2(CO_3)_3.8H_2O\}$-group mineral (Waber 1990) has been discovered in the Morro do Ferro deposit, but no quantitative chemical data are available for such a constituent. However, an energy dispersive spectrum obtained by Waber (1990) suggests a Nd:La ratio near 1:1, indicating an intermediate mineral between lanthanite-(Nd) and lanthanite-(La) (Atencio 1990).

Phosphates

Secondary phosphate minerals mainly formed from hydrothermal alteration are found in syenitic rocks of miaskitic to agpaitic affinity, massive to scoriaceous lavas, and lamprophyres of the district and are marked by variable proportions of Sr, reaching a maximum value of 58.66% SrO in **stronadelphite** $\{Sr_5(PO_4)_3F\}$ (Azzi 2019). Guarino *et al.* (2021) reported stronadelphite with up to 64.3% SrO and additional phosphatic accessory phases such as **strontium-bearing apatite** $\{(Ca,Sr)_5(PO_4)_3F\}$, **fluorcaphite** $\{SrCaCa_3(PO_4)_3F\}$,

and **phosphate-bearing britholite-(Ce)** $\{(Ce,Ca)_5(SiO_4,PO_4)_3(OH,F)\}$ in rocks of the massif. Britholite is the only phosphosilicate mineral identified so far, occupying cavities in association with pectolite and götzenite crystals (Fig. 7). Representative analyses for sample P7 297 for both Ce- and La-rich britholite are listed in Table 5, britholite-(Ce) showing a slight enrichment in SrO. Conversely, the rare crystals of britholite analyzed by Guarino *et al.* (2021) in nepheline syenites present a low SrO content (1.1%). Within the apatite supergroup, Azzi (2019) recognized **belovite-(Ce)** $\{NaCeSr_3(PO_4)_3\}$ described in rocks of the Bortolan quarry as fine colorless to light gray aggregates. Except for the F content of 2.42% in the first analysis, EDS results for two grains of sample P7 123 (Table 5) indicate a relatively homogeneous composition for this mineral. The occurrence of phosphatic minerals such as **cheralite** $\{CaTh(PO_4)_2\}$, previously identified by Fujimori (1984), **lithiophyllite** $\{LiMn^{2+}(PO_4)\}$, and **xenotime-(Y)** $\{Y(PO_4)\}$ in the Osamu Utsumi mine (Cercado and Agostinho deposits) and Morro do Ferro deposits (Morro Alto and Conquista) areas is also mentioned by Neves and Atencio (2019). **Florencite-(Ce)** $\{Ce,Al_3(PO_4)_2(OH)_6\}$ was noticed by Ulbrich *et al.* (2005) and Azzi *et al.* (2017).

Sulfates

Mostly hydrated in composition, sulfate minerals are secondary phases resulting from weathering and alteration processes. Waber (1992) mentioned the occurrence of **alunite** $\{KAl_3(SO_4)_2(OH)_6\}$ and **jarosite** $\{KFe^{3+}(SO_4)_2(OH)_6\}$ in the Morro do Ferro deposit, whereas Waber *et al.* (1992) recorded the presence of the same minerals in the oxidized zone of the Osamu Utsumi mine. In this mine, Atencio *et al.* (1994) described different sulfates, such as **rozenite** $\{FeSO_4.4H_2O\}$, **aluminocopiapite** $\{Al_{2/3}Fe^{3+}_4(SO_4)_6(OH)_2.20H_2O\}$ (and perhaps other copiapite group-minerals), **alunogen** $\{Al_2(SO_4)_3.17H_2O\}$, **coquimbite** $\{Al,Fe_3(SO_4)_6(H_2O)_{12}.6(H_2O)\}$, a **halotrichite** $\{FeAl_2(SO)_4.22H_2O\}$-group mineral, and **gypsum** $\{CaSO_4.2H_2O\}$. Botryoidal aggregates of blue coquimbite,

Figure 6. Light orange pseudo-octahedral crystals of ancylite-(Ce) associated with white aggregate mainly of alkali feldspar and natrolite. Image taken by magnifying glass.

Source: Azzi (2019).

Table 4. Partial chemical composition (wt%) of ancylite-(Ce), ancylite-(La), and burbankite in the Poços de Caldas massif.

	[1]	**[2]**	**[3]**	**[4]**
Sample	**P7 445**	**P7 338**	**P7 338**	**P7 338**
La$_2$O$_3$	15.67	27.28	13.24	0.84
Pr$_2$O$_3$	1.81	2.06	0.78	b.d.l.
SrO	18.06	10,61	31.23	43.07
CaO	1.06	2.82	1.47	13.43
ThO$_2$	3.06	0.30	b.d.l.	0.38
Ce$_2$O$_3$	24.39	24,29	12.12	0.50
Nd$_2$O$_3$	5.09	5.42	1.53	0.15
BaO	b.d.l.	b.d.l.	b.d.l.	0.32
Na$_2$O	b.d.l.	b.d.l.	10.53	8.58
F	0.66	0.56	0.16	0.01
Total	69.80	73.34	71.06	67.29

[1]: Ancylite-(Ce); [2]: Ancylite-(La); [3, 4]: Burbankite; b.d.l.: below detection limits.

Source: Azzi (2019).

which turn white with increasing relative humidity, were cited by Atencio and Coutinho (1997). The blue color returns, however, when the mineral is kept at approximately 100°C. Chemical analysis revealed the presence of 0.49% Mo, which is apparently responsible for the blue color of the mineral. Despite the incorrect name [coquimbite-(Mo)], coquimbite was described by Ulbrich *et al.* (2005) in rocks of the U-Zr-Mo deposit of Campo do Cercado. **Thenardite** $\{Na_2(SO_4)\}$ is listed by Azzi (2019) as a mineral whose complete description in the massif still lacks supporting data. The rare presence of **baryte** $\{Ba(SO_4)\}$ in phonolites and lamprophyres and **celestine** $\{Sr(SO_4)\}$ in phonolites is pointed out by Guarino *et al.* (2021).

Niobates

Fersmite $\{(Ca,Ce,Na)(Nb,Ta,Ti)_2(O,OH,F)_6\}$ is the only niobate species known, identified by Fujimori (1984) in rocks of the Morro do Ferro deposit, where it occurs in association with other rare accessory thoriferous minerals, such as "bastnäsite," cerianite-(Ce), cheralite, coffinite, and thorbastnäsite.

Silicates

The silicates are early- to late-stage magmatic accessory phases, with F-silicates (sorosilicates) being the most typical group mineral in agpaitic rocks.

Nesosilicates

Only a few nesosilicate minerals occur in the Poços de Caldas massif, namely **coffinite** $\{U(SiO_4).nH_2O\}$ and **thorogummite** (discredited as a valid species in 2014, IMA14-B). This name has been used to characterize heterogeneous mixtures of secondary, non-crystalline minerals originated by the alteration, hydration, and metamictization of **thorite** $\{Th(SiO_4)\}$, both identified in the Morro do Ferro deposit, and a new Fe^{3+}-rich **cerite** group mineral under study, present in the Bortolan quarry. Coffinite is a rare uraniferous mineral initially described by Fujimori (1982) and later confirmed by Lapido-Loureiro (1994) as an ore primary mineral set in a gangue bearing thorogummite and other minerals (allanite, bastnäsite, and cerianite) associated with the Morro do Ferro deposit.

F-Disilicates

F-disilicates form a mineral assemblage with a great number of phases, mostly already described in Poços de Caldas agpaitic rocks. They are highly complex in composition, contain Na-Ca-HFSE (Ti, Zr, and Nb)-halogen (F) as important and characteristic elements, and occur in the groundmass of phonolites or in the interstices of nepheline syenites. The F-disilicates are represented in the Brazilian and Paraguayan agpaitic rocks by the rinkite-(Ce) and wöhlerite (or cuspidine) groups (Table 6, modified; Gomes *et al.* 2021). In bold are endmembers known to occur in the Poços de Caldas district. Tables 7 and 8 list chemical composition data available for several of these minerals.

Based on its optical properties, **fersmanite** was first recognized in Poços de Caldas by Ashry (1962) in the eudialyte syenites (khibinites) of the northern border of the massif.

However, despite being more recently listed by Atencio *et al.* (1999) as a local secondary accessory phase occupying vugs and fractures within phonolitic rocks, no data are available on the mineral's composition. The minerals described as "giannettite" or "hainite" correspond today to götzenite or bortolanite, according to the current classification of seidozerite-group minerals (Sokolova and Camara 2017). Light yellow **götzenite** and **bortolanite** occur as prismatic crystals up to 2 cm long. Bortolanite (Day *et al.* 2022) is a type of mineral from Brazil. Representative chemical analyses of both minerals are given in Table 7. They do not differ greatly in composition, with the götzenite crystals being slightly enriched in CaO and impoverished in ZrO$_2$ and Na$_2$O with respect to the bortolanite. **Lamprophyllite** is a typical mineral, long

Source: Azzi (2019).

Figure 7. Diminute britholite-(Ce) grains filling cavities and microfissures in prismatic götzenite crystal. Britholite-(Ce) of white color is better distinguished on BSE image to the right.

Table 5. Representative chemical composition (wt%) of britholite-(Ce) and britholite-(La) and EDS values for belovite-(Ce) in the Poços de Caldas massif.

Sample	*Britholite*		*Belovite-(Ce)*	
	P7 297	**P7 297**	**P7 123**	**P7 123**
Y$_2$O$_3$	b.d.l.	b.d.l.		
SiO$_2$	22.24	19.34		
La$_2$O$_3$	22.37	30.17	11.73	12.61
CaO	5.17	5.13	3.87	2.16
ThO$_2$	1.23	1.37		
SrO	8.50	7.32	38.15	36.2
TiO$_2$	0.28	0.31		
Ce$_2$O$_3$	25.78	26.36	13.22	14.92
Pr$_2$O$_3$			0.73	1.1
Nd$_2$O$_3$	2,95	3.86	1.17	1.86
Na$_2$O	1,56	0.95	2.69	3.12
F	1.89	1.05	2.42	b.d.l.
P$_2$O$_5$	1.46	1.54	28.92	29.24
Total	97.60	100.08	102.9	101.21

b.d.l.: below detection limits; blank rows: not analyzed.
Source: Azzi (2019).

known to occur in Poços de Caldas eudialyte syenites (khibinites) either as fine isolate tabular crystals or as fibroradial aggregates (Ashry 1962), being promptly distinguished from

other species by its peculiar yellowish-honey (dominant) to brown-reddish shades. The mineral was studied to some extent by Gualda (1998), and Gualda and Vlach (1998), and by Azzi (2019) and Guarino *et al.* (2021) years later. Chemical analysis results obtained by all these authors reveal lamprophyllite to be a Ti-silicate with high concentrations of SrO and Na_2O (Table 7). MnO is present in varying amounts. BaO contents are significant as well. **Fluorlamprophyllite** is a type of mineral from Brazil (Andrade *et al.* 2018). It occurs in nepheline syenites at the Morro do Serrote. **Rinkite-(Ce)** is found in the syenitic rocks in association with **mosandrite-(Ce)**, which is another mineral of the same group. Both phases consist of Ca-Ti-Na-F-rich silicates of slightly different composition. CaO is more present in rinkite-(Ce), while REE is more abundant in mosandrite (Table 8). **Normandite**, a mineral also bearing Ca, Ti, Na, and F as major elements, is distinguished from the latter by the higher amounts of TiO_2, MnO, and FeO and the lower quantities of CaO and REE. Comparing the composition of some F-disilicate minerals from the Poços de Caldas massif and the nearby alkaline complexes of Itatiaia and Passa

Table 6. Rinkite-(Ce) and wöhlerite minerals.

Bortolanite	$Ca_2(Ca_{1.5}Zr_{0.5})Na(NaCa)Ti(Si_2O_7)_2(OF)F_2$
Fersmanite	$Ca_4(Na,Ca)_4(Ti,Nb)_4(Si_2O_7)_2O_8F_3$
Fluorlamprophyllite	$(SrNa)Ti_2Na_3Ti(Si_2O_7)_2O_2F_2$
Götzenite	$Ca_4NaCa_2Ti(Si_2O_7)_2(OF)F_2$
Hiortdahlite	$(Na,Ca)_2Ca_4Zr(Mn,Ti,Fe)(Si_2O_7)_2(F,O)_4$
Kochite	$Ca_2MnZrNa_3Ti(Si_2O_7)_2(OF)F_2$
Lamprophyllite	$(SrNa)Ti_2Na_3Ti(Si_2O_7)_2O_2(OH)_2$
Låvenite	$(Na,Ca)_4(Mn,Fe)_2(Zr,Ti,Nb)_2(Si_2O_7)_2(O,F)_4$
Mosandrite-(Ce)	$(Ca_3REE)(H_2O)_2Ca_{0.5}\square_{0.5}Ti(Si_2O_7)_2$
Normandite	$Na_2Ca_2(Mn,Fe)(Ti,Nb,Zr)_2(Si_2O_7)_2O_2F_2$
Rinkite-(Ce)	$(Ca_3REE)Na(NaCa)Ti(Si_2O_7)_2(OF)F_2$
Rosenbuschite	$Ca_6Zr_2Na_6ZrTi(Si_2O_7)_4(OF)_2F_4$
Wöhlerite	$Na_2Ca_4Zr(Nb,Ti)(Si_2O_7)_2(OF)_4$

Table 7. Average chemical composition (wt%) values for F-disilicate minerals in the Poços de Caldas massif.

Sample	Bortolanite				Götzenite		Lamprophyllite				
	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]
								P7 391	P7 391		
SiO_2	31.16	30.30	31.85	31.54	30.09	31.44	30.87	26.41	28.55	30.88	30.34
TiO_2	9.01	9.23	9.17	8.80	8.92	9.83	29.06	27,22	27.82	26.74	27.56
ZrO_2	5.09	4.91	7.09	5.21	3.43	2.33					
HfO_2	0.1		b.d.l.	0.01	0.06						
Al_2O_3	0.03	0.02	0.11	0.12			0.04	0,23	0.03	0.15	0.26	0.24
Nb_2O_5	1.01	1.21	1.25	1.45	1.01	0.82	0.48	1.5	0.89	0.77	0.82
MnO	1.53	1.49	1.79	1.91	0.75	0.92	5.23	1.44	6.97	4.66	4.31
MgO		0.02	0.02	0.02		0.03	0.30	0.1	0.04	0.51	0.35
FeO	0.36	0.64	0.54	0.64	0.79	0.75	1.59	0.41	1.09	2.83	2.78
CaO	32.47	32.36	30.97	31.91	34.21	36.03	0.52	1.14	0.06	1.08	0.95
SrO	1.36	0.75	1.43	1.51	0.44	0.79	16.96	16	13.06	15.79	16.41
La_2O_3	0.63		0.76	1.04	1.38	1.17	0.04			0.44	0.80
Ce_2O_3	0.91	1.64	0.94	1.65	2.50	1.96	0.03	0.5	b.d.l.	0.22	0.38
Pr_2O_3						0.18					
Nd_2O_3	0.24		0.30	0.41		0.39				0.30	0.45
Y_2O_3	0.04	0.16	0.11	0.18	0.94	0.11				0.70	
ThO_2			0.10	0.12		0.11				0.18	0.22
Na_2O	7.68	7.44	8.40	7.81	6.30	6.17	10.99	10.91	11.51	11.01	11.03
K_2O		0.03					0.77	1.29	0.82	0.75	0.54
BaO								6.54		1.30	1.26
H_2O						2.43					
F	6.27	7.73	7.02	7.06	9.22	5.13	0.98	1.86	0.61	2.05	1.48
Cl		0.01									
O=F		3.26	2.95	2.97	3.87	2.16	0.22			0.86	0.62
Total	97.89	97.94	99.16	98.73	100.03	100.63	97.97	95.68	94.35	98.49	97.72

[1-4]: **Bortolanite** (respectively, Bortolan quarry, Azzi 2019; Morro do Cristo, Soubiès *et al.* 1991, average of 8 analyses; Guarino *et al.* 2021, average of 25 analyses in nepheline syenites and of 34 in phonolites); [5-6]: **Götzenite** (Prefeitura quarry, Schorscher and Shea 1992; Bortolan quarry, Atencio *et al.* 1999, average of 3 analyses). [7-11]: **Lamprophyllite** (respectively, Gualda 1998, average of 10 analyses; Azzi 2019, sample P7 391; Guarino *et al.* 2021, average of 13 analyses in nepheline syenites and of 11 in phonolites). b.d.l.: below detection limits; blank rows: not analyzed.

Quatro, investigated by Melluso *et al.* (2017) and Guarino *et al.* (2019), respectively, Guarino *et al.* (2021) drew attention to the presence of mosandrite and normandite and the absence of låvenite in the former. However, normandite, the Ti-equivalent of låvenite, was reported in Poços de Caldas rocks by Gualda and Vlach (1998), Atencio *et al.* (1999), and Ulbrich *et al.* (2005).

Cyclosilicates

Cyclosilicates are important constituents of agpaitic rocks in the massif, mainly represented by members of the eudialyte group. Table 9 lists all phases reported in the Poços de Caldas massif. Table 10 presents the chemical compositions determined for some minerals.

The chemical composition of **catapleiite,** a mineral of bright yellow color and granular habit found in Poços de Caldas rocks, was analyzed by Azzi (2019) and Guarino *et al.* (2021). It is a replacement mineral in agpaitic and transitional agpaitic nepheline syenites (Guarino *et al.* 2021). Table 10 shows analyses

regarding two samples studied by Azzi (2019), whose composition varies as indicated by their ZrO_2 and alkali content. Recent data on the mineral by Guarino *et al.* (2021) are very consistent, showing a high presence of ZrO_2 (29.20–32.22%)

Table 9. Cyclosilicate minerals in rocks from the Poços de Caldas massif.

Catapleiite	$Na_2Zr(Si_3O_9).2H_2O$
Eudialyte	$Na_{15}Ca_6Fe_3Zr_3Si(Si_{25}O_{73})$ $(O,OH,H_2O)_3(Cl,OH)_2$
Ferrokentbrooksite	$Na_{15}Ca6Fe_3Zr_3Nb(Si_{25}O_{73})$ $(O,OH,H_2O)_3(F,Cl)_2$
Gaidonnayite	$Na_2Zr(Si_3O_9).2H_2O$
Georgechaoite	$NaKZr(Si_3O_9).2H_2O$
Hilairite	$Na_2Zr(Si_3O_9).3H_2O$
Manganoeudialyte	$Na_{14}Ca_6Mn_3Zr_3(Si_{26}O_{72})$ $(OH)_2(H_2O,Cl,O,OH)_6$
Kentbrooksite	$(Na,REE)_{15}(Ca,REE)_6Mn_3Zr_3Nb(Si_{25}O_{73})$ $(O,OH,H_2O)_3(F,Cl)_2$
Wadeite	$K_2Zr(Si_3O_9)$

Table 8. Average chemical composition (wt%) values for F-disilicate minerals in the Poços de Caldas massif.

	Rinkite-(Ce)		Mosandrite-(Ce)		Normandite		
	[1]	[2]	[3]	[4]	[5]	[6]	[7]
SiO_2	30.32	30.15	27.99	31.55	32.90	32.26	31.57
TiO_2	8.79	8.48	9.07	9.22	19.00	16.83	18.04
ZrO_2	1.04	2.15	0.13	1.62	1.42	3.70	2.36
HfO_2							
Al_2O_3	0.10	0.13	0.33	1.09	0.04	0.07	0.11
Nb_2O_3	1.31	1.36	2.18	3.55	1.83	2.52	1.53
Ta_2O_3							
MnO	0.49	0.66	0.26	0.48	6.78	8.34	7.02
MgO	0.05	0.01	0.03	0.04	0.27	0.19	0.27
FeO	0.36	0.31	0.15	0.47	7.46	7.08	8.69
CaO	31.98	31.80	23.16	26.50	17.00	15.61	16.58
SrO	1.59	2.58	1.40	3.99	0.10	0.59	1.06
La_2O_3	3.29	2.55	5.60	6.12	0.01	0.39	0.08
Ce_2O_3	5.15	4.07	8.88	8.29	0.02	0.22	0.06
Pr_2O_3					0.01		
Nd_2O_3	1.01	1.11	1.42	1.57	0.01	0.10	0.25
Sm_2O_3	0.13	0.09	0.13	0.65		0.25	0.14
Y_2O_3	0.08	0.15	0.11	0.64			
ThO_2	0.29	0.32	0.68	1.41		0.07	0.07
UO_2	0.13	0.11	0.34	b.d.l.		0.10	0.10
Na_2O	7.03	7.01	4.27	7.35	8.80	9.91	8.73
K_2O					0.02		
BaO							
H_2O							
F	6.48	6.59	3.93	5.40	3.03	3.46	4.66
Cl							
$O=F$	2.73	2.78	1.65	2.28	0.68	2.30	1.96
Total	96.89	96.84	88.41	97.96	98.01	101.36	99.37

[1, 2]: **Rinkite-(Ce)** (Guarino *et al.* 2021, average of 55 analyses in nepheline syenites and of 14 in phonolites); [3, 4]: **Mosandrite-(Ce)** (Guarino *et al.* 2021, average of 36 analyses in nepheline syenites and of 4 in phonolites; [5-7]: **Normandite** (respectively, Gualda 1998, average of 10 analyses; Guarino *et al.* 2021, average of 7 analyses in nepheline syenites and of 8 in phonolites); b.d.l.: below detection limits; blank rows: not analyzed.

and Na_2O (9.05–17.00%). **Eudialyte**, which occurs in bright reddish pink to pinkish purple shades, is the most important rare metal silicate presenting as a primary or secondary (mainly formed as anhedral crystals after titanite in phonolites, Guarino *et al.* 2021) phase, in high modal amounts in lujavrites and khibinites (9–12%, Ulbrich *et al.* 2005). In these rocks, it represents a rock-forming mineral that appears concentrated in centimeter- to decimeter-sized patches. Eudialyte forms a complex solid solution with manganoeudialyte, ferrokentbrooksite, and kentbrooksite as endmembers. As noted by Guarino *et al.* (2021), the mineral exhibits a pronounced variability in the concentration of MnO, FeO, SrO, ΣREE, and Cl in nepheline syenites in relation to phonolites. Chemical data on the eudialyte group was first made available by Gualda and Vlach (1996). **Manganoeudialyte**, a type-mineral from Brazil, is found in rose to violet shades in lujavrite-khibinite bodies outcropping at the northern edge of the massif, concentrated in centimeter-sized patches interstitial to the main minerals of the rocks (Nomura *et al.* 2010). Compared to eudialyte, the available manganoeudialyte analyses (Table 10) have a lower SiO_2 and CaO and a

higher SrO and MnO content that reaches a maximum value of 9.56%. Small amounts of Nb_2O_5 and REE are also present. **Gaidonnayite**, which was preliminarily studied by Matioli and Atencio (1994), forms isolate bright yellow subhedral crystals. Small polycrystalline spherules of variable color have also been described. Partial chemical analyses demonstrate that the mineral is a Zr-silicate containing significant amounts of alkalies, especially Na_2O (Table 10). **Wadeite** crystals were described by Guarino *et al.* (2021) as occupying the interstices of some nepheline syenites. The homogeneous representative chemical composition of sample PC39b grains is presented in the above-mentioned table. The mineral, which corresponds to a Zr-silicate, is enriched in K_2O with a low ΣREE_2O_3 (0.35%) content. Rare crystals of an ill-defined phase having SiO_2 (42.24%), ZrO_2 (26.83%), K_2O (10.44%), and Na_2O (6.94%) as major constituents were tentatively identified by Guarino *et al.* (2021) as **georgechaoite**. Briefly mentioned by Atencio *et al.* (1999) is **hilairite**, while ferrobrooksite and kentbrooksite are reported by Atencio *et al.* (2000). Little information exists in the literature on the latter three minerals.

Table 10. Average chemical composition (wt%) values for cyclosilicate minerals in the Poços de Caldas massif.

Sample	1	2	3	4	5	6	7	8	9	10
	P7 398	P7 164		PC39b	PC16	P7 398	P7 49	P7 A4	P7 513	PC39b
SiO_2	45.04	45.36	49.95	50.34	42.76	44.01	46.81	45.2	43.99	44.98
TiO_2	0.5	0.07	0.52	0.13	0.25	0.06	0.97	b.d.l.	0.29	0.82
ZrO_2	29.6	35.13	12.01	11.11	10.32	10.99	9.88	30.36	28.03	29.30
HfO_2	0.37	0.41	0.21				0.17	b.d.l.		
Al_2O_3			0.12	0.10						
Nb_2O_3			1.02	1.88	3.97	3.29	2.42	b.d.l.	3.2	0.57
MnO			2.56	1.77	9.56	6.04	2.07			
MgO			0.04	b.d.l.						
FeO			4.11	5.55	0.55	0.52	4.21			
CaO	0.07	0.67	10.30	11.58	6.09	9.73	10.98			0.00
SrO	b.d.l.	0.32	2.59	2.47	4.68	6.54	5.38			1.88
La_2O_3			0.13		2.62	1.52	0.98			0.00
Ce_2O_3			0.16		3.35	1.49	1.13			0.00
Pr_2O_3										
Nd_2O_3			0.01	0.10	0.29	0.18	0.21			0.00
Sm_2O_3				0.87						0.35
Y_2O_3										
ThO_2				0.20		0.14	0.13			
UO_2										
Na_2O	b.d.l.	9.09	13.05	10.48	10.23	8.31	10.22	12.93	8.07	0.44
K_2O	23.71	0.06	0.59	2.72	0.41	1.13	1.26	2.15	5.74	21.63
BaO										
H_2O										
F					0.73	0.06	0.54			
Cl			1.22	0.71	0.37	0.27	0.15			
O=F			0.27							
Total	99.29	91.11	98.07	100.6	96.4	94.54	97.75	90.64	89.32	99.96

[1, 2]: **Catapleiite** (Azzi 2019); [3, 4]: **Eudialyte** (respectively, Gualda 1998, average of 20 analyses; Guarino *et al.* 2021, reported 55 analyses, but only one with lower MnO is here listed); [5-7]: **Manganoeudialyte** (respectively, Guarino *et al.* 2021, single analysis; P7 398 and P7 49, Azzi 2019); [8, 9]: **Gaidonnayite** (Azzi 2019); [10]: **Wadeite** (Guarino *et al.* 2021, representative analysis). b.d.l.: below detection limits; blank rows: not analyzed.

Except for niobophyllite, which is only known to be present in phonolitic rocks of the Bom Repouso alkaline occurrence (Rosa 2012), all the other inosilicate members are found in Poços de Caldas rocks (Table 11). **Aenigmatite**, a Ti-Na silicate with abundant FeO and important amounts of MnO, occurs in the groundmass of phonolites. **Astrophyllite** was described for the first time in Poços de Caldas by Ashry (1962) in khibinites of the northern border of the massif, presenting as fine lamellar aggregates yellow-brownish in color. Chemically, it is characterized by the high proportions of TiO_2, MnO, and K_2O and the abundance of FeO. **Lorenzenite**, first described by Gualda and Vlach (1997) in nepheline syenites, is present as colorless euhedral isolate crystals that are mostly prismatic in shape. It is distinguished by its unusual chemical composition, with a marked prevalence of TiO_2 (43.46%) and abundant Na_2O (17.4%). Initially mentioned by Atencio *et al.* (1997), **narsarsukite** was only identified in sample P7 A6 by Azzi (2019) as having an irregular and variable habit and exhibiting yellow to yellow-brownish shades. As evidenced by the chemical composition reported in Table 12, the mineral corresponds to a Na-Ti-silicate bearing high amounts of FeO. **Pectolite** crystals are colorless to white and tabular in shape, appearing either in isolated form or as fibroradial aggregates. Subordinate to pectolite, **serandite** was identified in only two samples by Azzi (2019). Both minerals were first identified by Gualda and Vlach (1997). Pectolite is richer in CaO, while serandite shows a higher MnO content. The amount of Na_2O is almost constant in both species (Table 12). Recent analyses of pectolite by Guarino *et al.* (2021) present high CaO (21.15–30.36%) and Na_2O (8.94–10.19%) contents and a quite variable amount of MnO (1.84–14.94%). However, as noticed in Poços de Caldas rocks by Atencio *et al.* (1999), the information on calciohilairite (hilairite), kupletskite, and elpidite is incomplete and needs to be confirmed by further investigations.

Phyllosilicates

Phyllosilicate minerals are not abundant in the Poços de Caldas massif, being represented by only three members: **neptunite** $\{KNa_2LiFe^{2+}_2Ti_2(Si_8O_{24})\}$, **tainiolite** $\{KLiMg_2(Si_4O_{10})F_2\}$, and **tuperssuatsiaite** $\{Na_2(Fe^{3+},Mn^{2+})_3(Si_8O_{20})(OH)_2.4H_2O\}$. A few alteration minerals are also present,

namely **berthierine 1M** $\{(Fe^{2+},Fe^{3+},Al)_3(Si,Al)_2O_5(OH)_4\}$ and **chamosite** $\{(Fe^{2+}Mg,Al,Fe^{3+})_6(SiAl)_4O_{10}(OH,O)_8\}$, both reported by Atencio *et al.* (1999), and **fluorapophyllite** $\{(Na,K)Ca_4Si_8O_{20}F.8H_2O)\}$, referred to by Azzi (2019).

Neptunite exhibits an intense red color, occurring as subhedral prismatic crystals. EDS chemical data shown in Table 13 indicate that the mineral corresponds to a Ti-Fe-rich silicate with significant alkali content. Present as a colorless to white material in tabular, acicular, or finely aggregated habit, tainiolite is a rare Li-rich phase so far known to occur in two Brazilian localities, Araxá (Traversa *et al.* 2001) and Poços de Caldas. Partial compositional values for tainiolite from the Poços de Caldas massif are also included in Table 13. No chemical data are available for Li_2O. The chemical composition of the mineral includes high concentrations of MgO and K_2O, which is quite similar to that determined for the Araxá phase. Tuperssuatsiaite fibers and needles form isolate crystals or aggregates of different shapes, such as rosettes and tuffs. Irregular forms are also present. Although reported by various authors, a full description of the minerals in the massif is only presented by Atencio *et al.* (2005). Chemical compositions are reported in Table 13, with the most complete analysis revealing that the hydrated mineral (12.63% of H_2O) is a Fe-rich silicate with important alkali concentrations.

Alteration products

They are mainly referred to as different products that originated from late-magmatic activities developed under hydrothermal and/or weathering conditions. In general, the revised literature does not provide much information on the behavior of these products, which have been mainly identified based on optical features; no detailed investigation is presently available for such minerals.

Hydrothermal minerals

The breakdown of **nepheline** $\{(Na,K)Al_2Si_4O_{16}\}$ (and subordinate **sodalite** $\{(Na,K)AlSiO_4\}$ as a primary constituent), as a result of alteration processes that took place mainly in central areas of the massif, gives formation to secondary phases mostly represented by distinct feldspathoids, zeolites, and some carbonates.

Feldspathoids usually include **analcime** $\{NaAlSi_2O_6.H_2O\}$, **leucite** $\{KAlSi_2O_6\}$, **haüyne** $\{Na_3Ca(Si_3O_8)O_{12}(SO_4)\}$, **nosean** $\{Na_8(Si_6Al_6)O_{24}SO_4.H_2O\}$, **cancrinite** $\{(Na,Ca,\square_8)Al_6Si_6)O_{24}(CO_3,SO_4)_2.2H_2O\}$, and a rare member of the cancrinite group, **vishnevite** $\{Na_8(Al_6Si_6)O_{24}(SO_4).2H_2O\}$. This last variety, which is found as fine brown-reddish aggregates, was analyzed by Azzi (2019), with the data indicating high contents of SiO_2 (39.47%), Al_2O_3 (33.79%), alkalies (Na_2O 12.41% and K_2O 7.96%), and SO_3 (7.13%).

Zeolites, usually present as prismatic crystals or aggregates filling cavities, have **natrolite** $\{Na_2Al_2Si_3O_{10}.3H_2O\}$ and **mesolite** $\{Na_2Ca_2Si_8O_{16}O_{30}.8H_2O\}$ as their most frequent phases. A few rare varieties, such as **gonnardite** $\{(Na,Ca)_2(Si,Al)_5O_{10}.3H_2O\}$ and both thomsonite, **thomsonite-(Ca)** $\{(Na,Ca)(Al_5Si_5)O_{20}.6H_2O\}$ and **thomsonite-(Sr)** $\{(Na,Sr_2)(Al_5Si_5)O_{20}.6-7H_2O\}$, were recognized in rocks of the Bortolan quarry by Azzi (2019).

Table 11. Inosilicate minerals.

Aenigmatite	$Na_4(Fe^{2+}_{10}Ti_2)O4(Si_{12}O_{36})$
Astrophyllite	$K_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O(OH)_4F$
Calciohilairite	$CaZr(Si_3O_9).3H_2O$
Kupletskite	$K_2NaMn^{2+}_7(Si_4O_{12})_2O(OH)_4F$
Lorenzenite	$Na_2Ti_2O_3(Si_2O_6)$
Narsarsukite	$Na_4(Ti,Fe)_2(Si_8O_{20})(O,OH,F)_2$
Niobophyllite	$K_2NaFe^{2+}_7(Nb,Ti)_2(Si_4O_{12})_2O(OH)_4(O,F)$
Pectolite	$NaCa_2(Si_3O_8)(OH)$
Serandite	$NaMn^{2+}_2(Si_3O_8)(OH)$
Elpidite	$Na_2Zr(Si_6O_{15}).3H_2O$

Hydrothermal processes are also responsible for the origin of mineral deposits in the massif, mined in the past for elements such as U-Th-Zr-REE. Strong hydrothermal activities promoted the circulation of fluids, leading to the formation of sulfides and oxides as well as a gangue consisting of minerals of varied composition.

Weathering minerals

Deuteric conditions result in the origin of minerals that are chemically variable in composition and have a wide distribution within the massif. Weathering assemblages contain sulfates such as barite and celestine (Guarino *et al.* 2021), Al-rich phases formed by the alteration of feldspars and feldspathoids from nepheline syenites and their fine-grained equivalents, and secondary phosphate minerals. According to Ulbrich *et al.* (2005), the main laterite minerals identified in Poços de Caldas bauxites are **gibbsite** $\{Al(OH)_3\}$ and **goethite** $\{aFeO(OH)\}$, whereas **kaolinite** $\{Al_2Si_2O_5(OH)_4\}$ and **halloysite** $\{Al_2Si_2O_5(OH)_4\}$

are less abundant ones. Other aluminous minerals reported by these authors comprise **boehmite** $\{AlO(OH)\}$ and **litiophorite** $\{(Al,Li)(Mn^{4+},Mn^{3+})_2(OH)_2\}$.

PETROLOGICAL REMARKS

The Poços de Caldas massif is mainly formed by peralkaline igneous rocks showing (Na + K/Al) ratios > 1. The massif's highly evolved rocks are predominantly SiO$_2$-undersaturated in composition (mainly nepheline syenites and their fine-grained equivalents), referred to as agpaitic suites based on the geochemistry of its major and trace elements and the presence of typical minerals, such as eudialyte, F-disilicates, aenigmatite, and lamprophyllite (Gerasimovskii 1956, Sørensen 1960, 1997, Marks and Markl 2017). Intermediate rock types showing characteristics common to both miaskitic and agpaitic rocks are relatively frequent (Ulbrich *et al.* 2005) and might correspond to the "transitional agpaitic" type proposed by Marks and Markl

Table 12. Average chemical composition (wt%) values for inosilicate minerals in the Poços de Caldas massif.

Sample	[1] PC1b	[2] P7 A09	[3] P7 297	[4] P7 A6	[5]	[6] P7 29	[7] P7 100
SiO$_2$	39.79	33.91	34.31	68	52.10	54.27	51.84
TiO$_2$	9.39	10.90	43.46	12.1	0.02		
ZrO$_2$		0.64					
HfO$_2$							
Al$_2$O$_3$	1.13	1.57	0.04	0.72	0.01		
Nb$_2$O$_3$		0.61		1.28	b.d.l.		
MnO	4.99	11.82		0.38	14.08	1.47	21.70
MgO	0.75	2.36		0.06	0.05		
FeO	36.29	20.66	0.60	6.04	0.78	0.47	0.56
CaO	0.29	2.10	0.04		20.41	30.63	13.12
SrO		0.45			0.03	0.06	1.05
La$_2$O$_3$					0.04		
Ce$_2$O$_3$					0.11	0.02	0.43
Pr$_2$O$_3$							
Nd$_2$O$_3$							
Sm$_2$O$_3$							
Y$_2$O$_3$							
ThO$_2$							
UO$_2$							
Na$_2$O	7.40	1.57	17.40	14.64	8.92	9.51	7.89
K$_2$O		7.03	0.03	0.06			
BaO							
H$_2$O							
F		0.79		1.31			
Cl							
O=F							
Total	100.0	94.4	96.8	104.39	96.59	96.43	96.59

[1]: **Aenigmatite**, average of 23 analyses in phonolite (Guarino *et al.* 2019); [2]: **Astrophyllite** (Azzi 2019); [3]: **Lorenzenite** (Azzi 2019); [4]: **Narsarsukite** (Azzi 2019); [5, 6]: **Pectolite**, average of 16 analyses Gualda (1998); (Azzi 2019), respectively; [7]: **Serandite**, EDS analysis (Azzi 2019). b.d.l.: below detection limits; blank rows: not analyzed.

(2017), whose members include HFSE minerals that are typical of both associations (e.g., titanite from miaskitic rocks and eudialyte from agpaitic ones). More recently, the latter authors suggested that "agpaitic rocks" might be referred to as a descriptive term involving the distinction of igneous rocks based on their primary magmatic HFSE mineralogy, regardless of their whole-rock composition. They also suggested that agpaitic mineral assemblages should only be applied to igneous rocks characterized by the presence of early and late magmatic minerals. Thus, miaskitic rocks bearing agpaitic minerals only in hydrothermal veins or as clef fillings should not be called agpaitic.

The field relations between miaskitic and agpaitic rocks in composite complexes are generally variable. Only in a few places do agpaitic rocks constitute the dominant rock units within such complexes. Field relations, as discussed in Poços de Caldas by Ulbrich (1984) and Ulbrich et al. (2005), indicate that the massif might be placed into group 1 of Marks and Markl (2017), which includes plutonic to (sub)volcanic rocks with or without volcanic surface expression. Regarding the relations involving miaskitic and associated agpaitic rocks of those authors, they fall into the type B group, which is more typical, consisting of minor agpaitic units of an otherwise miaskitic complex.

Except for three large areas, namely Pedra Balão, Morro do Serrote, and Morro Taquari (Fig. 1), agpaitic rocks in Poços de Caldas usually occur as small bodies that are subordinate and younger than miaskitic units (Ulbrich 1984, Ulbrich et al. 2005). They are believed to have been derived from an independent magmatic pulse (Guarino et al. 2021). Such agpaitic rocks are thought to crystallize from highly evolved magmas that are enriched in HFSE and other incompatible elements and halogens (Ulbrich 1984, Ulbrich et al. 2005, Guarino et al. 2021). Rocks seem to originate from low-degree partial melting of slowly, fractionally crystallized alkaline basic-ultrabasic melts deriving from an enriched parental mantle source of basanitic (plagioclase-bearing) and/or nephelinitic (plagioclase-free) composition, which evolved by removal of olivine, clinopyroxene, and oxides toward high Sr- and high Ba-phonolitic magma compositions (Guarino et al. 2021). Continued fractional crystallization resulted in peralkaline phonolite compositions through the removal of nepheline syenites assemblages in subsequent stages, with late and post-magmatic processes playing an important role that leads to the enrichment of residual magmatic liquids in incompatible elements. Late-stage mineral phases are represented by REE-carbonates and REE-fluorocarbonates, bearing CO_2 and H_2O in their composition. According to Marks and Markl (2017), the varying timing of evolution processes in agpaitic magmas is responsible for mineral assemblage sequences that can be distinguished as orthomagmatic, late magmatic/pegmatitic, and hydrothermal (OM, LM, and HY associations, respectively). Specific parameters must be met so that different evolution stages are reached, with magmatic-agpaitic assemblages only formed under early magmatic crystallization conditions involving low enough oxygen fugacity (fO_2) and relatively dry magmas (low aH_2O). Such conditions enable subsequent requirements of Fe enrichment, increase in peralkalinity, retention of halogens, and extreme enrichment in HFSEs to be fulfilled. Textural evidence shown by mineral assemblages of Poços de Caldas rocks (Ulbrich 1984, Ulbrich et al. 2005, Guarino et al. 2021) is indicative that they have been affected by processes giving rise to the formation of variable phases that are typical of the diverse stages of evolution of agpaitic rocks (OM, LM, and HY) described by Marks and Markl (2017). Particularly, as observed by Gomes et al. (2021), the great number of late-stage magmatic specimens recognized in transitional agpaitic to agpaitic rocks belonging to the eudialyte-group and F-disilicate-group minerals drew attention. Additionally, the presence of other characteristic phases is common to agpaitic assemblages, such as aenigmatite and astrophyllite. Alteration parageneses are mainly represented by analcime and other feldspathoids, whereas hydrothermal activities, especially affecting tinguaites and phonolites of large areas of

Table 13. Average chemical composition (wt%) values for phyllosilicate minerals in the Poços de Caldas massif.

Sample	[1][*]	[2]	[3]	[4]
	P7 178	P7 A6		P7 433
SiO_2	52.48	58.56	55.13	47.89
TiO_2	17.39			0.13
ZrO_2				
HfO_2				
Al_2O_3	b.d.l.	0.04	0.33	0.12
Fe_2O_3			25.45	
Nb_2O_3				
Ta_2O_3				
MnO	0.56	0.04	0.43	0.43
MgO		19.94	0.15	
FeO	14.66	0.71	0.5	22.78
CaO			0.12	0.22
SrO				
La_2O_3				
Ce_2O_3				
Pr_2O_3				
Nd_2O_3				
Sm_2O_3				
Y_2O_3				
ThO_2		0.15		
UO_2				
Na_2O	6.67	0.4	4.26	5.22
K_2O	5.38	11.76	0.77	2.19
BaO		0.03		
H_2O			12.63**	
F		5.74		
Cl				
O=F				
Total	97.14	97,37	100	79.41

[1]: **Neptunite** (Azzi 2019); [2]: **Tainiolite** (Azzi 2019); [3, 4]: **Tuperssuatsiaite** (Atencio et al. 2005 and Azzi 2019, respectively); *EDS analysis; **calculated; b.d.l.: below detection limits; blank rows: not analyzed.

Caldas (MG-SP): Caracterização mineralógica e petrográfica. In: Congresso Brasileiro de Geologia, 40., 1998, Belo Horizonte. *Resumos...* p. 284.

Guarino V., De Gennaro R., Melluso L., Ruberti E., Azzone R.G. 2019. The transition from miaskitic to agpaitic rocks, as highlighted by the accessory phase assemblages in the Passa Quatro alkaline complex (Southeastern Brazil). *The Canadian Mineralogist*, **57**(3):339-361. https://doi.org/10.3749/canmin.1800073

Guarino V., Lustrino M., Zanetti A., Tassinari C.C., Ruberti E., De Gennaro R., Melluso L. 2021. Mineralogy and geochemistry of a giant agpaitic reservoir: the Late Cretaceous Poços de Caldas potassic alkaline complex (SE Brazil). *Lithos*, 398-399, 106330. https://doi.org/10.1016/j.lithos.2021.106330

Lapido-Loureiro F.V. 1994. *Terras Raras no Brasil: depósitos, recursos identificados, reservas*. MCT-CNPq-CETEM, 189 p. Estudos e Documentos, n. 21.

Marks A.W.M., Markl G. 2017. A global review on agpaitic rocks. *Earth-Science Reviews*, **173**:229-258. https://doi.org/10.1016/j.earscirev.2017.06.002

Matioli D., Atencio D. 1994. Gaidonnayite from Poços de Caldas, Minas Gerais, Brazil. *Anais da Academia Brasileira de Ciências*, **66**(4):500-501.

Matioli D., Atencio D., Coutinho J.M.V. 1994. Barium-free burbankite from Poços de Caldas, Minas Gerais, Brazil. In: General Meeting of the International Mineralogical Association, 16., 1994, Pisa. *Abstracts...* p. 268.

Melluso L., Guarino V., Lustrino M., Morra V., De Gennaro R. 2017. The REE- and HFSE-bearing phases in the Itatiaia alkaline complex (Brazil) and geochemical evolution of feldspar-rich felsic melts. *Mineralogical Magazine*, **81**(2):217-250. https://doi.org/10.1180/minmag.2016.080.122

Neves P.C.P., Atencio D. 2019. *Enciclopédia dos minerais do Brasil:* elementos nativos e halogenetos. 2ª ed. Canoas: Ulbra, 344 p.

Nomura S.F., Atencio D., Chukanov N.V., Rastsvetaeva R.K., Coutinho J.M.V., Karipidis T.K. 2010. Manganoeudialyte – A new mineral from Poços de Caldas, Minas Gerais, Brazil. *Zapiski RMO (Proceedings of the Russian Mineralogical Society)*, **139**(4):35-47.

Riccomini C., Velázquez V.F., Gomes C.B. 2005. Tectonic controls of the Mesozoic and Cenozoic alkaline magmatism in the Central-Southeastern Brazilian Platform. In: Comin-Chiaramonti P., Gomes C.B. (eds.). *Mesozoic to Cenozoic alkaline magmatism in the Brazilian Platform*. São Paulo: Edusp/Fapesp, p. 31-56.

Rosa P.A.S. 2012. *Geologia e petrologia da suíte alcalina de Bom Repouso, MG.* Master Dissertation, Institute of Geosciences, Universidade de São Paulo, São Paulo.

Schorscher H.D., Shea M.D. 1992. The regional geology of the Poços de Caldas alkaline complex: mineralogy and geochemistry of selected nepheline syenites and phonolites. *Journal of Geochemical Exploration*, **45**(1-3):25-51. https://doi.org/10.1016/0375-6742(92)90121-N

Sokolova E., Camara E. 2017. The seidozerite supergroup of TS-Block Minerals: nomenclature and classification, with change of the following names - rinkite to rinkite-(Ce), mosandrite to mosandrite-(Ce), hainite to hainite-(Y) and innelite-1T to innelite 1A. *Mineralogical Magazine*, **81**(6):1457-1484. https://doi.org/10.1180/minmag.2017.081.010

Sørensen H. 1960. On the agpaitic rocks. In: International Geological Congress, 21., 1960, Copenhagen. *Proceedings...* **13**:319-327.

Sørensen H. 1997. The agpaitic rocks: an overview. *Mineralogical Magazine*, **61**(407):483-498. https://doi.org/10.1180/minmag.1997.061.407.02

Soubiès F., Melfi A.J., Delvigne J., Sardela I.A. 1991. Mobilidade do zircônio na bauxitização de rochas alcalinas do maciço de Poços de Caldas, Minas Gerais. *Revista Brasileira de Geociências*, **21**(1):17-22.

Thompson R.N., Gibson S.A., Mitchell J.G., Dickin, A.P., Leonardos O.H., Brod J.A., Greenwood J.C. 1998. Migrating Cretaceous-Eocene magmatism in the Serra do Mar alkaline province, SE Brazil: melts from the deflected

Trindade mantle plume? *Journal of Petrology*, **39**(8):1493-1526. https://doi.org/10.1093/petroj/39.8.1493

Traversa G., Gomes C.B., Brotzu P., Buraglini N., Morbidelli L., Principato M.S., Ronca S., Ruberti E. 2001. Petrography and mineral chemistry of carbonatites and mica-rich rocks from the Araxá complex (Alto Paranaíba Province, Brazil). *Anais da Academia Brasileira de Ciências*, **73**(1):71-98. https://doi.org/10.1590/S0001-37652001000100008

Ulbrich H.H. 1984. *A petrografia, a estrutura e o quimismo de nefelina sienitos do maciço alcalino de Poços de Caldas, MG-SP*. Habilitation Thesis, Institute of Geosciences, Universidade de São Paulo, São Paulo.

Ulbrich H.H., Ulbrich M.N.C. 2000. The lujavrite and khibinite bodies in the Poços de Caldas alkaline massif, southeastern Brazil: a structural and petrographic study. *Revista Brasileira de Geociências*, **30**:615-622. https://doi.org/10.25249/0375-7536.2000304615622

Ulbrich H.H., Vlach S.R.F., Demaiffe D., Ulbrich M.N.C. 2005. Structure and origin of the Poços de Caldas alkaline massif. In: Comin-Chiaramonti P., Gomes C.B. (eds.). *Mesozoic to Cenozoic alkaline magmatism in the Brazilian Platform*. São Paulo: Edusp/Fapesp, p. 367-418.

Ulbrich H.H., Vlach S.R.F., Ulbrich M.N.C., Kawashita K. 2002. Penecontemporaneous syenite-phonolite and basic-ultrabasic-carbonatitic rocks at the Poços de Caldas Alkaline Massif, SE Brazil. *Revista Brasileira de Geociências*, **32**(1):15-26.

Ulbrich M.N.C., Vlach S.R.F., Ulbrich H.H. 1998. Geoquímica de diques de rochas máfico-ultranáficas do maciço de Poços de Caldas (MG-SP). In: Congresso Brasileiro de Geologia, 40., Belo Horizonte. *Resumos...* p. 469.

Vlach S.R.F., Ulbrich H.H., Ulbrich M.N.C. 1998. Isótopos radiogênicos (Sr,Nd) e estáveis (C,O) de rochas máfico-ultramáficas potássicas da região de Poços de Caldas, MG-SP: inferências sobre a natureza do manto litosférico mesozoico. In: Congresso Brasileiro de Geologia, 40., 1998, Belo Horizonte. *Anais...* p. 475.

Vlach S.R.F., Ulbrich H.H., Ulbrich M.N.C., Gualda G.A.R. 1996. Rochas de afinidades alnoíticas e sílico-carbonatíticas periféricas ao maciço alcalino de Poços de Caldas (M-SP). In: Congresso Brasileiro de Geologia, 39., 1996, Salvador. *Anais...* **2**:128-130.

Vlach S.R.F., Ulbrich H.H., Ulbrich M.N.C., Vasconcelos P.M. 2018. Melanite-bearing nepheline syenite fragments and $^{39}Ar/^{40}Ar$ age of phlogopite megacrysts in conduit breccia from the Poços de Caldas alkaline massif (MG-SP), and implications. *Brazilian Journal of Geology*, **48**(2):391-402. https://doi.org/10.1590/2317-4889201820170095

Waber N. 1990. Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil: II. Morro do Ferro, Poços de Caldas. *Poços de Caldas Report*, **3**, 121 p.

Waber N. 1992. The supergene thorium and rare earth element deposit at Morro do Ferro, Poços de Caldas, Minas Gerais, Brazil. In: Chapman N.A., McKinley I.G., Shea M.E., Smellie J.A.T. (eds.). The Poços de Caldas project: natural analogues of processes in a radioactive waste repository. *Journal Geochemical Exploration*, **45**:113-157.

Waber N., Schorscher H.D., Peters T. 1992. Hydrothermal and supergene uranium mineralization at the Osamu Utsumi mime, Poços de Caldas, Minas Gerais, Brazil. In: Chapman N.A., McKinley I.G., Shea M.E., Smellie J.A.T. (eds.). The Poços de Caldas project: natural analogues of processes in a radioactive waste repository. *Journal Geochemical Exploration*, **45**:53-112.

Wedow Jr. H. 1967. The Morro do Ferro, Thorium and Rare-Earth ore deposits, Poços de Caldas district, Brazil. *United States Geological Survey Bulletin*, n. 1195-D, 34 p.