

Tracing magmatic footprints: Influence of a CO₂-rich melt on the mineral assemblage of the San José del Guaviare Syenite, SE Colombia

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ABSTRACT. A combined optical and electron microscopy (SEM, EDS, and EPMA) study was conducted on ten rock samples from the Proterozoic San José del Guaviare Syenite (SJGS), southeastern Colombia, to utilize minor and trace minerals in interpreting the magmatic evolution of these silica undersaturated rocks. The major minerals of the sampled syenites are nepheline, Fe-rich clinopyroxene, amphibole, alkali feldspar, and biotite. The minor minerals are titanite, calcite, cancrinite, and sodalite. Trace minerals are the niobium- or rare earth element-rich minerals pyrochlore, columbite, euxenite, britholite, ancylite-Ce and wöhlerite. Apatite, rhodochrosite, strontianite, fluorite, zircon, magnetite, ilmenite, and pyrite occur as traces as well.

Crystallization started with primary (magmatic) calcite and Nb-rich minerals pyrochlore, columbite, euxenite, and a first generation of apatite, which occur as inclusions in foids, feldspars, and Fe-rich clinopyroxenes. Calcite is enriched in light rare earth elements and Sr, with low Mg concentrations, while primary apatite has high Sr concentrations. Both minerals have a composition typical for minerals crystallized in carbonatites. The presence of calcite and high Fe and low Ti clinopyroxene point to CO₂-saturated conditions.

During cooling, fluorbritholite-Ce formed as individual grains or by a fluid-enhanced apatite-britholite transformation. The formation of Fe-rich amphibole, often at the expense of Fe-rich clinopyroxene, reveals a decreasing influence of CO₂ and temperature. Presumably, the transformation of orthoclase into microcline occurred simultaneously. Perthitic microcline as a second K-feldspar generation indicates slow cooling from high temperatures. A late stage of CO₂-rich hydrothermal-metasomatic processes is suggested by the growth of secondary cancrinite, Sr-Mn carbonates and ancylite-Ce. The composition of primary and early crystallized calcite and apatite makes their origin as residues of an early segregated or independently formed mantle-derived carbonatitic melt more likely than crystallization from a CO₂-rich syenitic melt. An origin from melted crustal carbonates is unlikely as well. Therefore, the presence of a carbonatitic melt at an early magmatic evolutive stage, as opposed to a non-carbonatitic melt at a late stage, seems possible for the SJGS rocks.

Keywords: Colombia, Amazonian Craton, San José del Guaviare Syenite, Syenites, Carbonatites, Accessory minerals.

RESUMEN. Rastreado las huellas magmáticas: Influencia de fluidos ricos en CO₂ en la composición mineralógica de la Sienita de San José del Guaviare, SE Colombia. Esta contribución presenta un estudio combinado de microscopía óptica y electrónica (SEM, EDS y EPMA) en diez muestras de roca de la unidad Sienita del San José del Guaviare (SJGS), de edad proterozoica, la cual aflora en el sureste de Colombia. Se utilizaron minerales accesorios y traza para interpretar la evolución magmática de estas rocas subsaturadas en sílice. Los principales constituyentes minerales de las sienitas analizadas son nefelina, clinopiroxeno rico en Fe, anfíbol, feldespato alcalino y biotita. Los minerales menores corresponden a titanita, calcita, cancrinita y sodalita. Los minerales traza son aquellos ricos en niobio o tierras raras, como pirocloro, columbita, euxenita, britolita, ancilita-Ce y wöhlerita. Apatito, rodocrosita, estroncianita, fluorita, circón, magnetita, ilmenita y piritita son minerales traza también.

La cristalización comenzó con calcita primaria (magmática) y minerales ricos en Nb tales como pirocloro, columbita, euxenita y una primera generación de apatito, los que forman inclusiones en feldespatoideos, feldespatos y clinopiroxenos ricos en Fe. La calcita se presenta enriquecida en tierras raras livianas y en Sr, con bajas concentraciones de Mg, mientras que el apatito primario posee altas concentraciones de Sr. Ambos minerales exhiben composiciones típicas de minerales cristalizados en carbonatitas. La presencia de calcita y clinopiroxeno rico en Fe y bajo en Ti apunta a condiciones saturadas en CO₂.

Durante el enfriamiento se formó fluorbritolita-Ce a manera de granos individuales o a partir de una transformación apatito-britolita favorecida por fluidos. La formación de anfíbol rico en Fe, a menudo a expensas del clinopiroxeno rico en Fe, revela una disminución de la influencia del CO₂ y de la temperatura. Posiblemente la transformación de ortoclasa en microclina ocurrió de manera simultánea. La microclina peritítica, como una segunda generación de feldespato potásico, indica un enfriamiento lento a partir de altas temperaturas. El crecimiento de cancrinita secundaria, de carbonatos de Sr-Mn y ancilita-Ce, sugieren un estadio tardío de procesos hidrotermales-metasomáticos ricos en CO₂.

La composición de la calcita y del apatito primarios, cristalizados tempranamente, implica que lo más probable es que su origen esté relacionado con residuos de un fundido carbonatítico derivado del manto, ya sea segregado tempranamente o formado de manera independiente, comparado con un origen a partir de la cristalización de un fundido sienítico rico en CO₂ o de carbonatos corticales fundidos. La presencia, por lo tanto, de un fundido carbonatítico en una etapa magmática temprana parece la alternativa más plausible para las rocas del SJGS.

Palabras clave: Colombia, Cratón Amazónico, Sienita de San José del Guaviare, Sienitas, Carbonatitas, Minerales accesorios.

1. Introduction

Nepheline syenites and their volcanic equivalents are part of the alkaline silica-undersaturated rock suites which are often associated with carbonatites (e.g., Keller, 1984a, b; Worley *et al.*, 1995; Woolley, 2001; Halama *et al.*, 2005). Melts which are parental to syenites and carbonatites are usually generated by low degrees of partial melting of lithospheric mantle (e.g., Bell and Simonetti, 2010; Yaxley *et al.*, 2022). The formation of carbonatites and their spatial proximity to silicate magmatites is explained by different models.

There is still an open discussion whether silicate and carbonatitic melts are cogenetic. Classical models on the common occurrence of both rock types are: I. The formation of two independent primary melts of a highly oxidized carbonate-metasomatized lithospheric mantle (e.g., Wallace and Green, 1988; Ying *et al.*, 2004; Braunger *et al.*, 2018). II. A primary melt from a metasomatized lithospheric mantle that fractionates and further decouples a carbonatitic melt by liquid immiscibility (e.g., Gittins, 1989;

Halama *et al.*, 2005; Brooker and Kjasgaard, 2011). Gittins and Mitchell (2023), however, state that, as yet no reliable experimental work is available that proves that nephelinitic melts evolve to such an extent that the separation of immiscible silicate and carbonate melts can take place. Furthermore, the different rheologies of both melts favor different intrusion levels. III. The possible formation of basic secondary syenites and ijolites through the metasomatic influence of carbonatitic melts on solid and partly acidic rocks (Vasyukova and Williams-Jones, 2022). In addition, Anenburg and Walters (2024) describe silica contamination from silica-oversaturated wall rocks by carbonatite melts behind the formation of silicocarbonatite-like assemblages. IV. Small carbonate accumulations in nepheline-bearing lava caused by melted crustal limestones, *i.e.*, anatectic carbonatites (Gozzi *et al.*, 2014).

Alkaline rock suites sometimes display both silica oversaturated and silica undersaturated trends (Bonin and Giret, 1984), which makes it possible for nepheline syenites to occur in close relationship with silica-saturated granitoids. The majority of the

world's rare earth elements (REEs) and Nb resources are concentrated in carbonatites and alkaline-silicate rocks (Chakhmouradian and Williams, 2004; Atanasova *et al.*, 2017; Anenburg *et al.*, 2021; Beard *et al.*, 2023). Therefore, syenites and carbonatites have increasingly come into the focus of exploration, either for alumina and alkalis for ceramic glass, enamels, fillers, paints, papers, plastics, and foam rubber or critical raw materials such as REEs, Nb, Ta, P, Zr and F (*e.g.*, Chakhmouradian and Wall, 2012; Jones *et al.*, 2013; Marks and Markl, 2017; Stoppa *et al.*, 2019; Anenburg *et al.*, 2021; Beard *et al.*, 2023). More recently, selected nepheline syenites have been studied because of their potential as alternative potash sources in fertilizers (*e.g.*, Chiwona *et al.*, 2020). Some of the world's first-class REEs and Nb deposits and resources are related to these rock associations (*e.g.*, Anenburg *et al.*, 2021; Beard *et al.*, 2023). Prominent examples are the nepheline-syenites of Norra Kärr, Sweden, the largest European deposit of heavy REEs (Atanasova *et al.*, 2017), and the Nb-Ta-rich, pyrochlore-bearing nepheline-syenites from Motzfeld, Greenland (Finch *et al.*, 2019). An example of co-existence of syenites and carbonatites is Bayan Obo, China, the world's largest production facility for light REEs (Yang *et al.*, 2019).

The present study explores the use of minor (1-5 vol.%) and trace (<1 vol.%) minerals as tracers to investigate the possible existence of a buried or eroded carbonatite in the vicinity of the Proterozoic San José del Guaviare Syenite (SJGS) in southeastern Colombia. Secondly, the study also focuses on assessing the abundance of critical elements such as Nb and REEs and their mineralogy in the SJGS. Although the SJGS has so far been reported as isolated outcrops and studied petrographically, geochronologically, and geochemically (whole rock) (Arango *et al.*, 2011; Franco-Victoria *et al.*, 2018; Larrota Rincón and Concha, 2018; Amaya López *et al.*, 2021), there are no in-depth studies on mineral chemistry yet.

2. Geological setting

2.1. The Amazonian Craton and its surroundings

The Amazonian Craton represents the largest and most diverse example of Precambrian continental crustal growth within the South American continent (Engler, 2009). It is subdivided into numerous

Neoproterozoic to Proterozoic domains (Fig. 1) with ages ranging from >2.6 Ga to *ca.* 0.95 Ga (Cordani and Teixeira, 2007). Teixeira *et al.* (2019) described the craton as a sequence of accreted continental slices of Paleo- to Mesoproterozoic continental and oceanic arcs with one or two Archean cores in the present northeast. These crustal domains were partially affected by the Brasiliano/Pan-African orogeny (peak *ca.* 0.61 Ga; Rodríguez-Corcho *et al.*, 2021).

According to Cordani and Teixeira (2007) and Engler (2009), the Amazonian craton is composed of provinces with different ages, starting with Central Amazonian (>2.6 Ga) and the Maroni-Itacaiúnas (2.26-1.95 Ga) domains at the east with four contiguous provinces to the west linked by orogenic events (Fig. 1). In Colombia, Ibáñez-Mejía *et al.* (2011) described the Putumayo Orogen, a Meso- to Neoproterozoic belt buried under the north Andean foreland basins at the suggested border between the Amazonian Craton and the Guiana Shield. Galvis *et al.* (1979) described Precambrian igneous and metamorphic rocks of the Mitú Migmatitic Complex, which builds up the crystalline basement of eastern Colombia, as the northwestern part of the Guiana Shield. Priem *et al.* (1982) reported a Rb-Sr age of 1.78 Ga for biotitic gneisses, suggesting a relationship to the Rio Negro-Juruena Province (1.82-1.60 Ga). Ibáñez-Mejía *et al.* (2020), however, indicated a discontinuous distribution of U-Pb crystallization ages of these rocks with four main age clusters: 1.99, 1.81-1.72, 1.59-1.50, and 1.41-1.39 Ga, therefore suggesting that the term "Mitú Migmatitic Complex" would now be inadequate and obsolete.

2.2. San José del Guaviare Syenite Unit (SJGS)

Galvis *et al.* (1979) were the first to describe silica-undersaturated rocks in the SJGS area of southeastern Colombia, found in the La Lindosa mountain range and the isolated hills of Cerritos and El Capricho (Fig. 2). The unit is composed of diverse syenites, like nepheline syenites, nepheline-monzosyenites, and nepheline-bearing alkali feldspar syenites, as well as quartz-bearing syenites, syenogranites, and quartz-rich granitoids (Amaya López *et al.*, 2021). Amaya López *et al.* (2021) stated that silica-saturated intrusions would be underrepresented in terms of volume and restricted to the southwestern hills (El Capricho and Cerritos; Fig. 2).

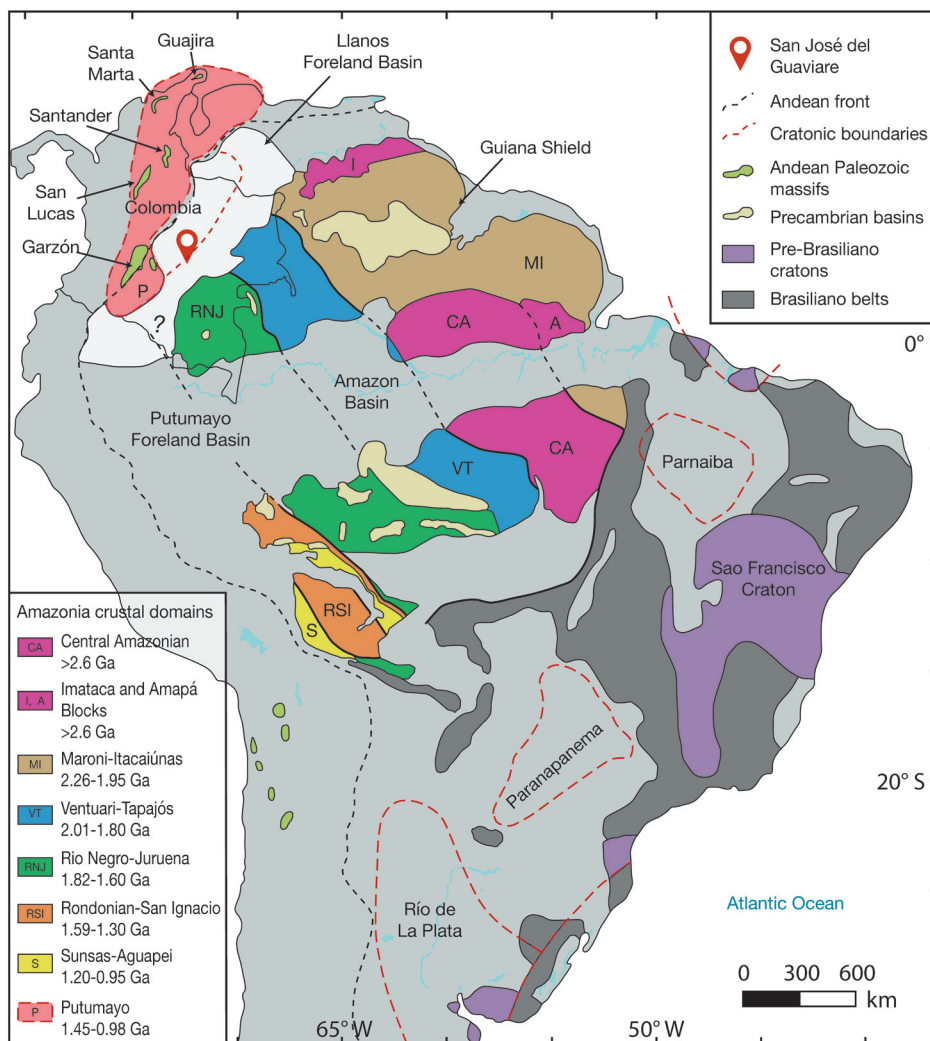


FIG. 1. Simplified geotectonic framework of South America highlighting the Amazonian Craton and the Guiana Shield. Modified from Ibáñez-Mejía *et al.* (2020).

U-Pb zircon ages reported by Arango *et al.* (2011), Franco-Victoria *et al.* (2018), and Amaya López *et al.* (2021) indicate an Ediacaran age (~620–605 Ma) for the SJGS. The primary melts correspond to intraplate anorogenic alkaline magmas intruded into rift-like stretching zones during the fragmentation of Rodinia (Amaya López *et al.*, 2021), when the Iapetus Ocean opened and the northern Amazonian Craton separated from Laurentia and Baltica (Condie, 2011; Cawood and Pisarevsky, 2017).

The isotope signature of the products indicates a mantle origin and silica-saturated melts, resulting

in syenogranites and quartz-syenites with evidence of crustal assimilation (Amaya López *et al.*, 2021). The intrusions are hosted in the Mesoproterozoic metamorphic basement of the Guaviare Complex described by Maya *et al.* (2018), which is locally affected by contact metamorphism producing hornfels aureoles, well exposed in the southern Cerritos hill (Fig. 2). Syenites of this unit are overlain unconformably by the Cretaceous sedimentary sequence of the San José Formation in the La Lindosa mountain range and by Neogene mudstones of the La Caja Formation (Arango *et al.*, 2011).

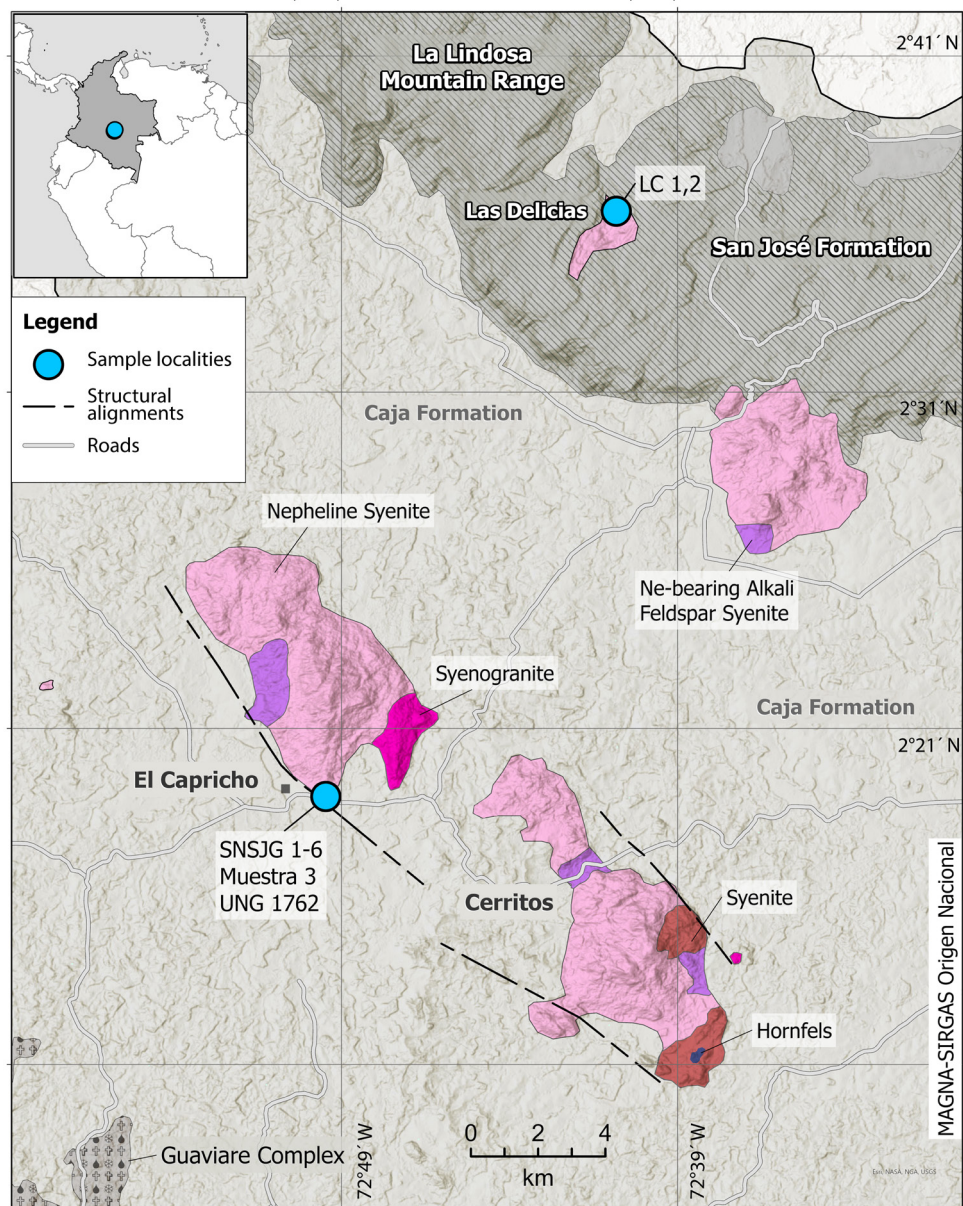


FIG. 2. Geological map of the SJGS area, after Amaya López *et al.* (2021). Blue circles refer to sample localities.

3. Methods

Eight thin sections from El Capricho and two from Las Delicias were studied with a petrographic microscope. Of these, seven were examined by electron probe microanalyzer (EPMA) and scanning electron microscopy (SEM) with energy-dispersive spectroscopy (EDS).

Coated thin sections were analyzed using a JEOL JXA-8200 EPMA. Natural and synthetic silicates, oxides, and phosphates were used as reference materials. For the major elements, natural reference materials from Astimex Standards Ltd (MINM25-53) were used: almandine-rich garnet for Fe, Mg, Si, Al, Ta, Th, U; albite for Na, plagioclase for Ca; bustamite for Mn; celestine for Sr; tugtupite for Cl. The REEs

were calibrated with element phosphates, Ba, and Ti as silicates from the Smithsonian Institution/Washington. For major elements, F, and Cl, the X-ray lines $\text{K}\alpha_1$ were analyzed; $\text{La}\alpha_1$ lines for Sr, La, Y, Ce, Eu, Gd, and Ta; $\text{Lb}\alpha_1$ lines for Pr and Nd; and the $\text{Ma}\alpha_1$ line for Th and U. Raw X-ray intensities were corrected using a ZAF (atomic number, absorption, fluorescence) correction procedure. Matrix corrections were performed using the software supplied by JEOL. An acceleration voltage of 20 kV was used for REEs, while 15 kV were used for all the other elements. A beam current of 15/20 nA with a beam size of 1–15 μm was used. The counting time was 10–30 s on peaks for major elements and 50 s for REEs and other trace elements with 5 to 15 s on background. Na, K, and F, as least-stable components were analyzed first during the analytical process. To reduce migration, counting times were reduced to 6 s on peaks and 3 s on backgrounds. Total iron shown as FeO was calculated to Fe^{2+} cations in the mineral formula. Fe^{3+} was calculated by charge balance or other procedures (see table captions). In addition, detailed images and a first semi-quantitative analysis were provided by a JEOL JSM-651 equipped with an Oxford INCA x-act spectrometer.

4. Petrography

The studied samples are all classified as nepheline-syenites, composed of alkali feldspar (29–65 vol.%), nepheline (15–35 vol.%), biotite (2–9 vol.%), amphibole (0–18 vol.%), and clinopyroxene (0–10 vol.%). The minor minerals are titanite (0–8 vol.%), calcite (0–3 vol.%), cancrinite (0–4 vol.%), and sodalite (0–3 vol.%). Trace minerals with <1 vol.% are restricted to individual samples and consist of pyrochlore, columbite, euxenite, apatite, britholite, ancylite-Ce, wöhlerite, rhodochrosite, strontianite, fluorite, zircon, magnetite, ilmenite, and pyrite.

All rocks are hololeucocratic to leucocratic with colors that vary from white to gray. They are massive and phaneritic. In general, crystal sizes range from <1 mm to 4.5 mm but some samples present a coarser-grained and inequigranular texture. Samples SNSJG 2, LC 1, and LC 2 (see figure 2 for locations) show alkali feldspar tabular crystals of up to ~2 cm. Some samples (SNSJG 4 and 5a from El Capricho and LC 1 and LC 2 from Las Delicias) display an inequigranular texture with oriented alkali feldspar phenocrysts (up to 1.5 cm), suggesting a sub-solidus

magmatic flow orientation in a stress field (see Stein, 2000).

Whereas nepheline-syenites from El Capricho have feldspar abundance ranging from 55 to 60 vol.% (K-feldspar > Albite) and nepheline between 15 and 35 vol.%, the Las Delicias samples contain ~30 vol.% feldspars, ~35 vol.% nepheline, and have higher concentrations of clinopyroxene and amphibole. In all samples biotite is present with ~2–9 vol.%, independent of the sampling area.

In order to determine the importance of minor and trace minerals in the relation of Nb- and REE-rich syenites to a possible carbonatite occurrence, detailed description of the composition and fabric of major, minor, and trace minerals is necessary.

K-feldspar (Kfs) occurs either as orthoclase or microcline (Fig. 3A–E). Microcline often forms rims around orthoclase, indicating a second generation of Kfs, as shown in figure 3B. The transformation is often continuous or due to dynamic or static recrystallization (Fig. 3B). Both minerals show frequent perthitic exsolutions with cord-, patch- or vein-like morphology (Fig. 3A–E). Orthoclase and microcline appear mostly with lath-shaped forms. Microcline shows the typical tartan twinning (Fig. 3A, B) and orthoclase Carlsbad twinning (Fig. 3C). Inclusions of nepheline and magnetite are frequently observed (Fig. 3D, E), but pyrochlore and other trace minerals are common inclusions too. Kfs itself also occurs as inclusions in nepheline and apatite. The composition of Kfs, independent of microcline or orthoclase lattice, is very limited with $\text{Or}_{94-99}\text{Ab}_{93-95}\text{An}_{0-0.1}$ (Supplementary Table S1). Unlike nepheline, Kfs remains nearly unaffected by kaolinite.

Albite ($\text{Ab}_{94-99}\text{An}_{0.3-6}\text{Or}_{0.4-0.5}$; Supplementary Table S1) occurs as corona (rims) around nepheline (Fig. 3D) and in Kfs or as individual grains (Fig. 3A, 3E, 4A–D), commonly in contact with nepheline, clinopyroxene, microcline, amphibole, and locally with primary calcite (Fig. 3A).

Nepheline is the dominant feldspathoid. It occurs as anhedral to subhedral (hexagonal) crystals (Fig. 5A) and as inclusion in microcline and orthoclase. It contains inclusions of Kfs and rarely magnetite, biotite or calcite. In sample LC 2, large crystals with numerous inclusions of biotite and titanite are present. Inclusions of pyrite are rare. Nepheline is altered to cancrinite or intergrown in symplectites with cancrinite (Fig. 3F). Nepheline is sometimes also altered to kaolinite ranging from

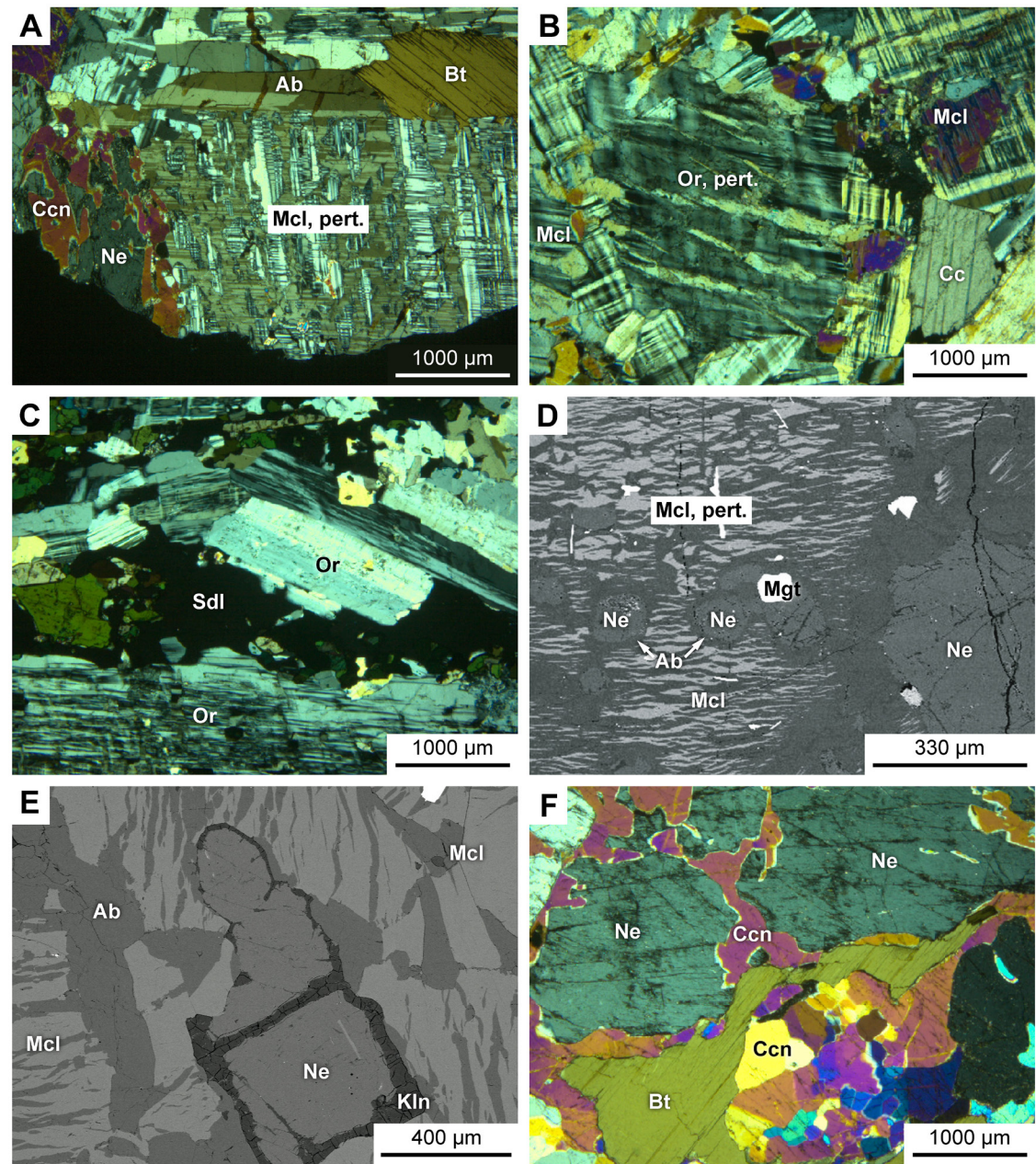


FIG. 3. Photomicrographs and BSE images of some SJGS samples showcasing the main constituent minerals and some accessory minerals of relevance. **A.** Subhedral microcline (Mcl) with perthitic exsolutions (pert), albite (Ab), biotite (Bt), cancrinite (Ccn), and nepheline (Ne). Sample UNG 1762, crossed nicols. **B.** Orthoclase (Or) with partial tartan twinning and a rim of microcline (recrystallized K-feldspar) near to calcite (Cc). Sample SNSJG 1, crossed nicols. **C.** Oriented orthoclase with sodalite (Sdl) in the center. Sample LC 2, crossed nicols. **D.** Microcline with perthitic exsolutions and magnetite (Mgt) inclusions. Albite rims formed around nepheline inclusions. Sample SNSJG 6, BSE image. **E.** Nepheline with a kaolinite (Kln) rim as inclusion in microcline. Sample SNSJG 5, BSE image. **F.** Reaction of nepheline and biotite to form cancrinite. Sample UNG 1762, crossed nicols.

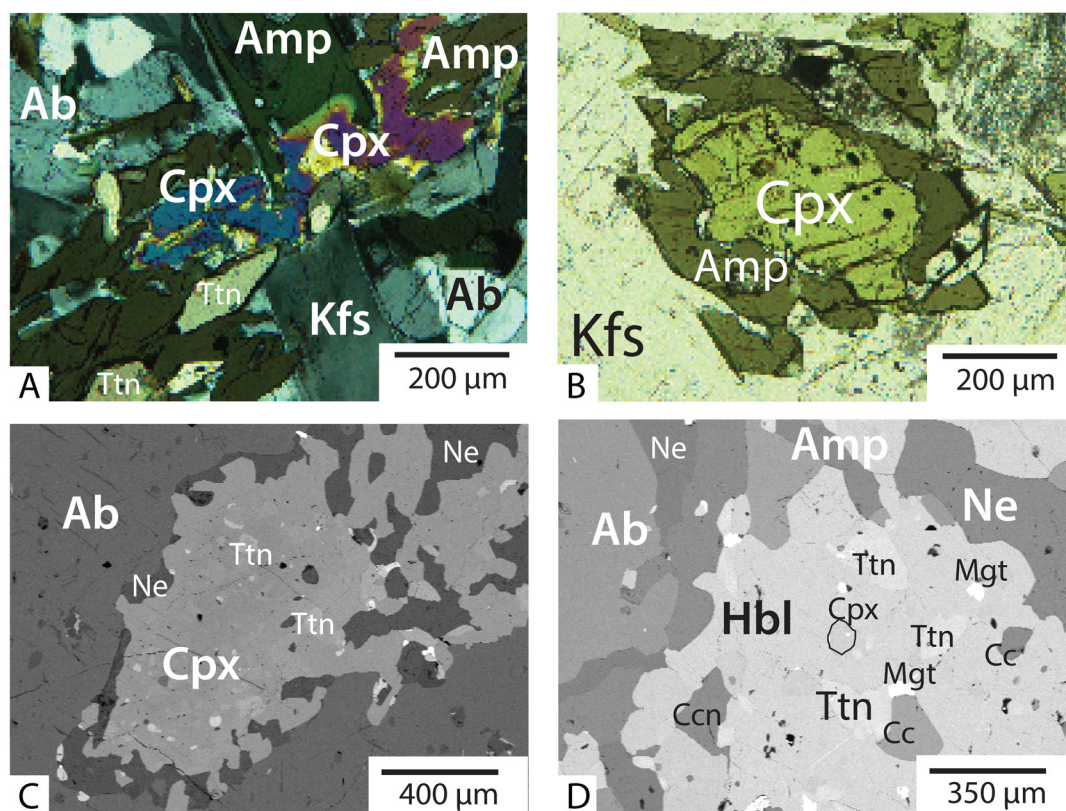


FIG. 4. Photomicrographs and BSE images of some SJGS samples showcasing the main constituent minerals and some accessory minerals of relevance. **A.** Anhedral clinopyroxene (Cpx), titanite (Ttn), amphibole (Amp), albite (Ab), and K-feldspar (Kfs). Sample SNSJG 4, crossed nicols. **B.** Amphibole (Amp) overgrown on clinopyroxene. Sample SNSJG 4, parallel nicols. **C.** Anhedral clinopyroxene with inclusions of titanite, rimmed by albite and intergrown with nepheline. Sample LC 2, BSE image. **D.** Anhedral hornblende (Hbl) with relics of clinopyroxene and inclusions of calcite (Cc), cancrinite (Ccn), titanite, and magnetite (Mgt). Sample SNSJG 4, BSE image.

kaolinite rims to complete pseudomorphs (Fig. 3E). The chemical composition of nepheline is shown in Supplementary Table S2.

Sodalite is restricted to a few samples (LC 2 and UNG 1762) and in low concentration. It forms anhedral to euhedral grains with a maximum grain size of ~ 0.8 mm (Fig. 3C). It contains up to 10 wt% Cl (Supplementary Table S2). It commonly has inclusions of euhedral pyrochlore.

Cancrinite with the general formula $(\text{Na}, \text{Ca}, \square)_8(\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3, \text{SO}_4)_2 \cdot 2\text{H}_2\text{O})$ is formed both as a primary phase and interstitial anhedral crystals associated with calcite, nepheline, and sodalite. More common are polycrystalline aggregates growing at the expense of nepheline (Fig. 3F, 5A), occasionally with calcite aggregates. The analyzed

grains contain ~ 4.7 wt% SO_3 (Supplementary Table S2). Cancrinite is particularly abundant in coarse-grained samples with up to 4 vol.%.

Clinopyroxene occurs in thin sections as intense green crystals (Fig. 4B), that are commonly rimmed by amphibole $\pm$ titanite (Fig. 4A, B). Additionally, calcite, titanite and magnetite are common inclusions (Fig. 4C). Clinopyroxene is often overgrown by amphibole (Fig. 4B, D). The composition of clinopyroxene depends on the sampled rocks, although all are rich in FeO_{tot} (total Fe as FeO) and Na_2O with concentrations of 16 to 25 wt% FeO_{tot} and 3.3 to 4.8 wt% Na_2O , and low in TiO_2 (< 0.7 wt%) (Supplementary Table S3). The calculated components indicate that most are aegirine-augite (Supplementary Table S3).

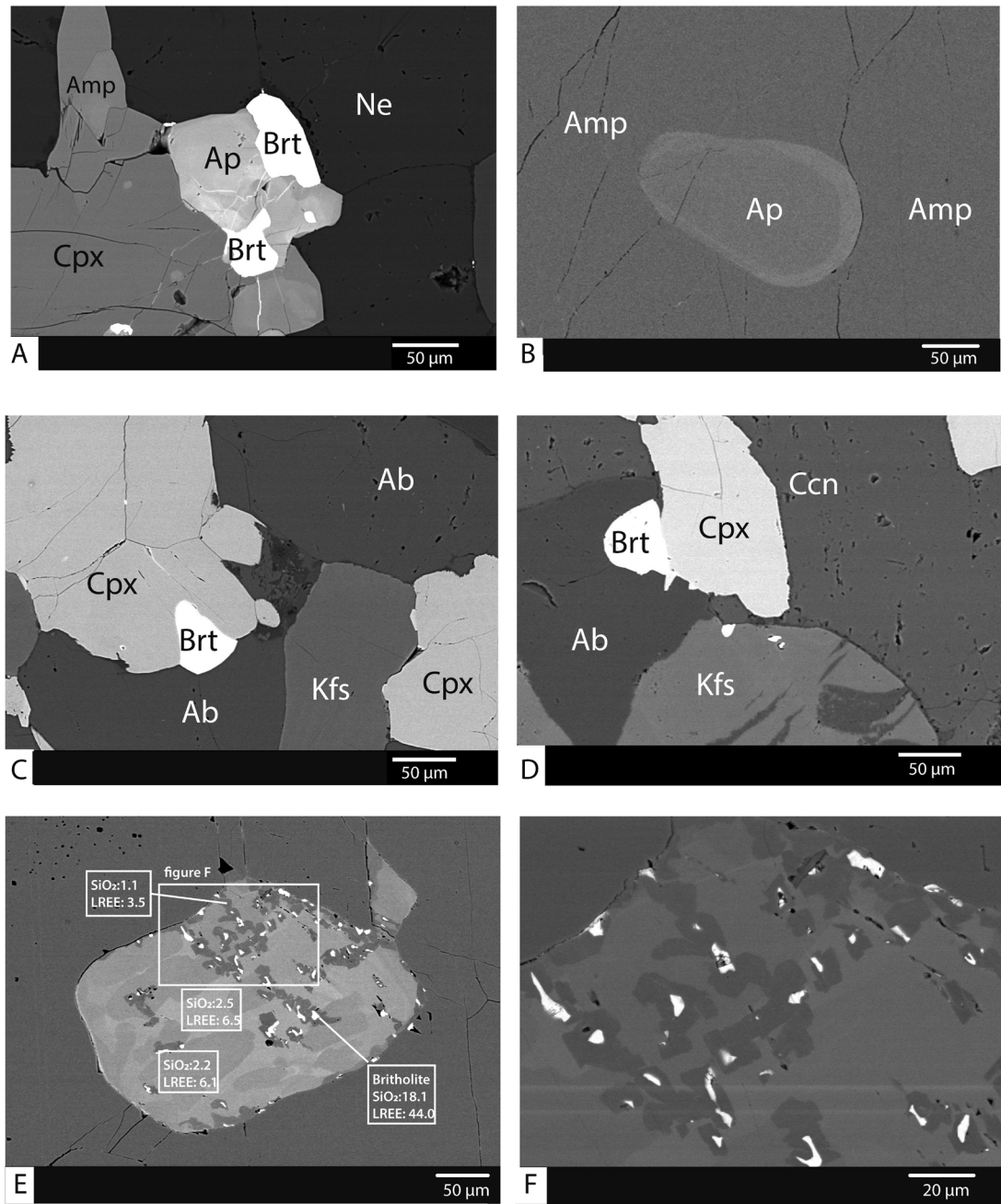
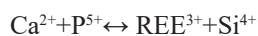


FIG. 5. Apatite (Ap) and britholite (Brt) in the syenite SJGS rock suite, BSE images. **A.** Coexisting apatite and britholite between clinopyroxene (Cpx) and nepheline (Ne). Sample LC 2. **B.** Zoned apatite with a REE-rich rim. Sample LC 1. **C.** Britholite intergrown with clinopyroxene. Sample LC 2. **D.** Britholite single crystal between albite (Ab) and clinopyroxene. Cancrinite (Ccn) on the right and K-feldspar (Kfs) below. Sample LC 2. **E.** Small grain of apatite, overgrown by an apatite matrix, and exsolution of britholite from apatite. Sample LC 1. **F.** Zoom-in from e, different hues indicate different SiO₂ and REE concentration domains.

Amphibole is present in most samples. In thin sections they show very dark green to slightly bluish colors (Fig. 4B). Chemically they are rich in FeO, Na₂O, and K₂O (Supplementary Table S4). The amphiboles (general formula A₀₋₁B₂C₅T₈O₂₂(OH)₂) in the syenites can be classified either as a member of the sodium-calcium amphiboles defined with ^B(Mg, Fe²⁺, Mn²⁺, Li) ≤ 0.5, ^B(Ca, Na) ≥ 1, and 0.5 ≤ ^BNa < 1.5, or as a member of the Ca-amphiboles with ^B(Mg, Fe²⁺, Mn²⁺, Li) ≤ 0.5, ^B(Ca, Na) ≥ 1, and ^BNa < 0.5 (all values in atoms per formula unit; apfu) (Leake *et al.*, 1997, 2004). According to the nomenclature of Leake *et al.* (1997), the analyzed Na-Ca-amphiboles can be named as potassian taramites (sample LC 1) and the Ca-amphiboles potassian-sodian hastingsites (samples LC 2 and SNSJG 4) (Supplementary Table S4). Both types are chemically and optically very similar. These amphiboles are probably comparable with the already described, but not chemically analyzed “arfvedsonite-like amphibole” of Amaya López *et al.* (2021). The amphiboles occur solitary as euhedral to subhedral crystals (Fig. 4A) but more commonly as anhedral rims around greenish to brownish clinopyroxenes (Fig. 4B, D) and contain inclusions of microcline, biotite, and titanite.

Biotite occurs as isolated crystals and as intergrowths with titanite and amphibole (Fig. 3A, F). It often contains microcline inclusions, opaque minerals, zircons and pyrochlore, the latter producing pleochroic halos. Biotites are also found as inclusions in microcline and nepheline. It has low concentrations of F and high concentrations of FeO (Supplementary Table S5). Biotite shows a Fe/Fe+Mg value of about 0.86. Sample SNSJG 4 reveals lower concentrations of Fe and Fe/Fe+Mg values (Supplementary Table S5), possibly due to secondary processes.

Britholite and apatite are members of the apatite supergroup M₃(TO₄)₃X [M: Ca, Pb, Ba, Sr, Mn, Na, Ce, La, Y; T: P, V, Si, S; X: F, OH, Cl]. It includes the britholite group with the general formula (REE,Ca)₅[(Si,P)O₄]₃(OH, F) (Pasero *et al.*, 2010). Transformation of apatite into britholite is possible by the coupled substitution mechanism (*e.g.*, Ronsbø, 1989; Zozulya *et al.*, 2015, 2017):



In the analyzed syenites, apatite crystals occur in grain sizes of up to ~450 μm (Figs. 5A, 5B, 6). They are classified as fluorapatites with 0.6-0.7 apfu F (Fig. 7A) and are characterized by high SrO₂ (0.19-0.51 wt%) and Y₂O₃ (0.03-0.51 wt%) concentrations

(Table 1). Apatite grains occur independently (Fig. 5B), rimmed by fluorbritholite (Fig. 5A) or in complex intergrowth with britholite (Figs. 5E, F, 6). Britholite occurs as fluorbritholite-Ce with 1-1.2 apfu Ce and 0.5-0.7 apfu F, discarding a possible inaccuracy of F contents due to beam migration. Electron microscopy and EPMA analyses reveal a complex growth history for the larger apatites (Fig. 6; Table 1). BSE images display several small grains, with very low SiO₂ and high light REE concentrations, overgrown by a later generation of merged apatites with slightly higher SiO₂ and light REE concentrations (Fig. 5E). These grains then underwent transformation, forming a third apatite and britholite generation by the reaction:

REE-rich apatite → REE-poor apatite + REE-rich britholite (Figs. 5E, 5F, 7B)

which is here interpreted as an exsolution texture during changing physical or chemical conditions, confirming the miscibility gap between apatite and britholite described by Melluso *et al.* (2012), Zozulya *et al.* (2017), and Lorenz *et al.* (2019). Anenburg *et al.* (2018) showed that these exsolutions are a high-temperature process. The reaction or exsolution took place in channels transecting the apatite, which can be clearly seen in the element distribution map (Fig. 6). The process is accompanied by an increase in Sr, pointing to an influx of a Sr-bearing fluid (Fig. 6F). According to Chakhmouradian *et al.* (2017), the abundance of Mg and Fe in mantle-derived melts can increase the partitioning of Sr and the Ca-Sr substitution in apatite. The newly crystallized britholite forms ~2-10 μm sized grains (Fig. 5E, F). However, britholite occurs more frequently as isolated, <50 μm-sized single crystals or as inclusions in nepheline, albite or clinopyroxene. Compared to apatites, britholites have lower F contents, dismissing a possible inaccuracy of F contents (as described above), higher ThO₂ concentrations, and similar Sr contents. When present as isolated grains, britholite often appears in contact with clinopyroxene, nepheline, apatite, or albite.

Pyrochlore occurs as a common inclusion in orthoclase, nepheline, sodalite, amphibole, biotite, and albite (Fig. 8). It typically forms euhedral grains with a size of ~50-100 μm, and only in rare cases crystal sizes of up to 250 μm are reached, which exhibit metamictic alteration (Fig. 8C). Few crystals show poikilitic structures with open euhedral cavities (Fig. 9), forming so-called negative crystals, where faces of the cavities within the crystal are planes of the host.

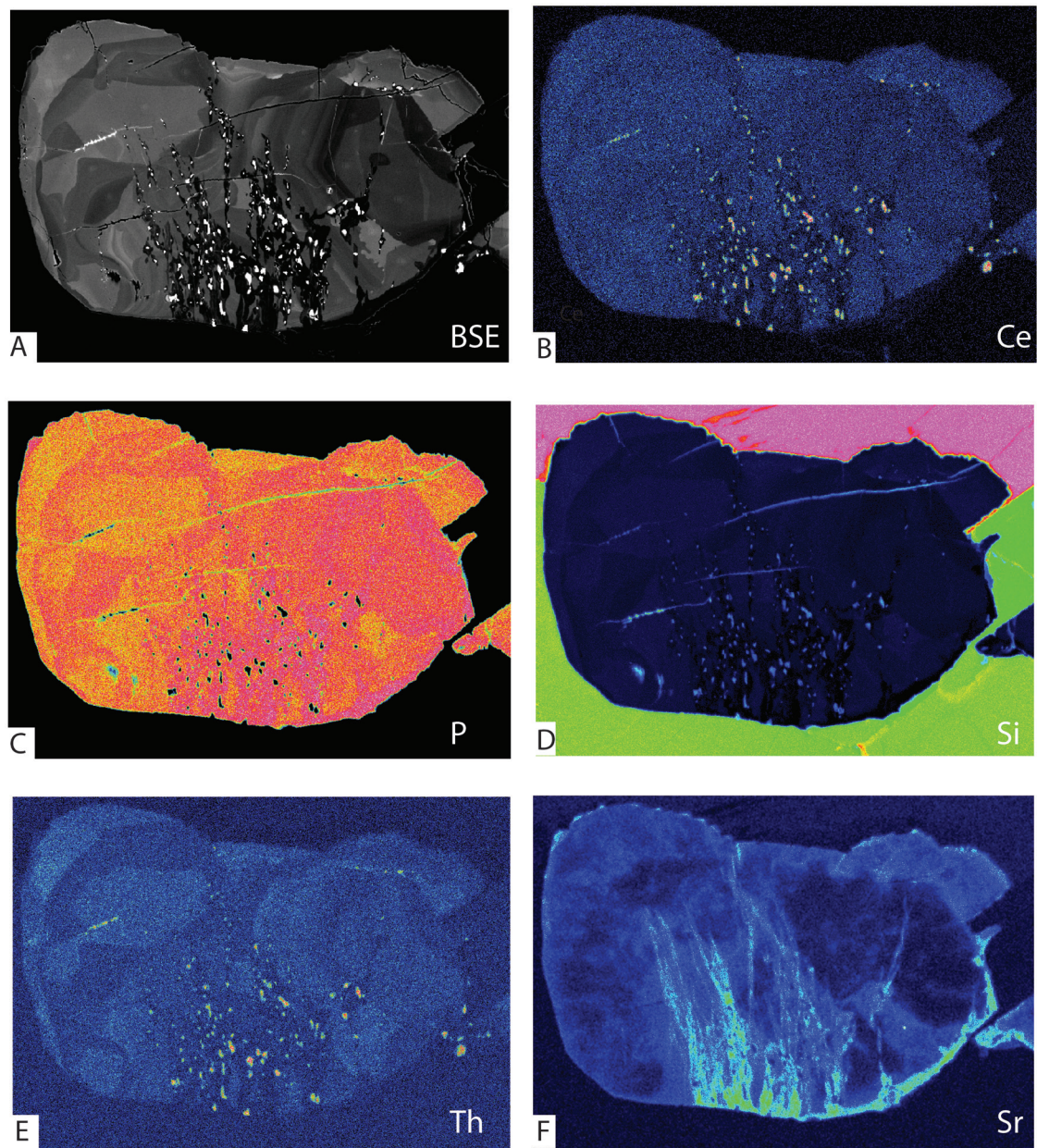


FIG. 6. BSE image and element distribution maps in an SJGS apatite crystal and delineation of britholite-rich domains: **A.** Exsolution of britholite (light colors), comparable to figure 5E. **B.** Britholite can be identified by its higher light REE concentrations, here exemplified by Ce. **C-D.** Apatite and britholite are easily distinguishable by their different P and Si concentrations. **E.** Higher Th concentrations can help differentiate britholite from apatite. **F.** Sr map indicating the metasomatic ingress of Sr into the britholite-bearing zone. Sample LC 1 (all images). Horizontal side of the image: 400 μm .

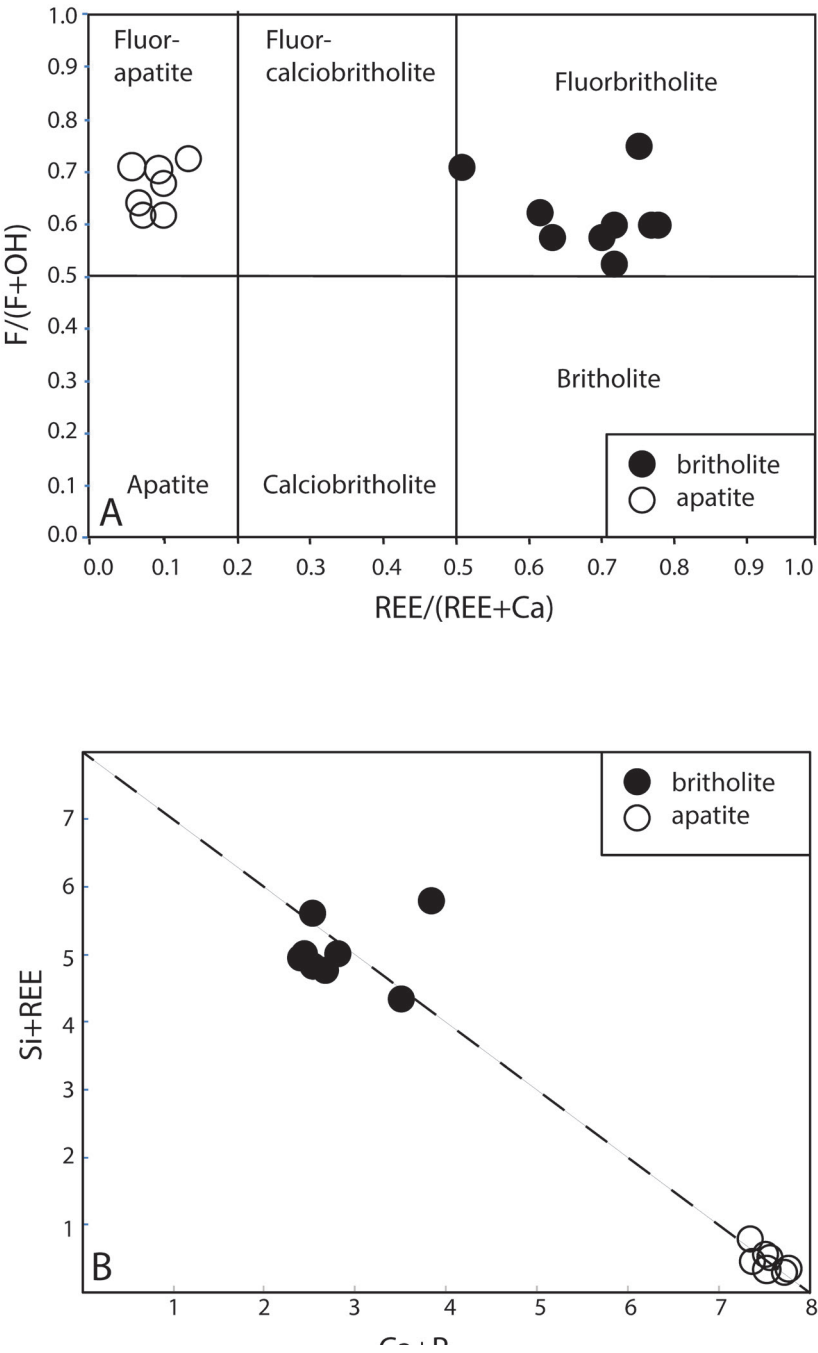


FIG. 7. EPMA analyses of SJGS apatite and britholite crystals. **A.** REE/(REE+Ca) versus F/(F+OF) diagram. **B.** Ca+P versus Si+REE diagram. Dashed line shows the ideal substitution Si+REE ↔ Ca + P. All units in apfu (atoms per formula unit).

TABLE 1. COMPOSITION OF APATITES AND BRITHOLITES. ANALYSES BY ELECTRON PROBE MICROANALYZER (EPMA).

Sample		Britholite									Apatite						
wt%		LC 2						LC 1			SNSJG 1		LC 2	LC 2	LC 1	LC 1	LC 1
P ₂ O ₅	5.58	6.52	6.39	6.68	6.51	9.73	5.72	13.97	5.11	33.82	36.31	38.54	36.96	37.17	35.90	37.66	
SiO ₂	19.15	17.93	18.16	16.12	15.84	18.36	18.19	13.92	17.83	3.96	2.77	1.16	1.82	1.77	2.28	1.59	
ThO ₂	1.78	1.93	1.95	3.19	3.19	1.91	2.68	1.94	2.13	0.23	0.15	0.06	0.08	0.17	0.17	0.08	
Al ₂ O ₃	0.28	2.13	2.02	1.88	1.88	-	2.91	1.10	-	-	0.01	-	0.01	-	-	-	
Y ₂ O ₃	2.44	2.73	2.71	2.57	2.78	1.92	3.06	2.12	2.33	0.51	0.33	0.08	0.06	0.18	0.27	0.03	
La ₂ O ₃	11.96	10.22	11.05	10.55	10.65	12.37	11.74	10.10	16.21	2.40	1.69	0.7128	1.88	1.15	1.66	1.75	
Ce ₂ O ₃	24.56	22.58	22.94	24.26	22.87	22.85	24.76	22.00	26.12	5.04	3.70	1.84	2.85	2.51	3.25	2.58	
Pr ₂ O ₃	2.36	2.18	2.20	2.47	2.27	2.07	2.16	1.86	2.35	0.42	0.39	0.17	0.30	0.32	0.36	0.21	
Nd ₂ O ₃	7.50	7.35	7.22	7.85	8.08	6.16	6.41	5.66	7.53	1.72	1.22	0.71	0.72	0.98	1.14	0.69	
Sm ₂ O ₃	0.84	0.92	0.83	0.84	0.90	0.57	0.81	0.68	0.64	0.22	0.17	0.09	0.05	0.11	0.10	0.00	
Eu ₂ O ₃	0.35	0.40	0.47	0.33	0.43	0.47	0.40	0.41	0.36	0.11	0.07	0.05	0.03	0.05	0.09	0.01	
Gd ₂ O ₃	3.39	3.06	3.16	3.43	3.15	3.05	3.24	2.86	3.21	0.73	0.48	0.30	0.41	0.38	0.47	0.35	
CaO	15.79	13.74	14.23	11.28	11.40	20.31	12.24	20.01	14.44	47.84	50.14	51.61	49.46	50.48	49.27	50.24	
FeO	-	0.08	0.01	0.26	0.05	0.02	0.08	0.04	0.10	0.05	0.19	-	0.06	0.02	-	0.02	
SrO	-	-	-	-	-	0.58	0.03	0.72	0.67	0.19	0.30	0.20	0.51	0.23	0.25	0.43	
Na ₂ O	-	0.01	0.01	0.03	0.03	0.01	0.11	0.03	-	0.02	0.03	0.10	0.17	0.12	0.18	0.19	
F	1.39	1.24	1.42	1.33	1.29	1.52	1.80	1.64	0.61	2.48	2.42	2.27	2.19	2.17	2.14	2.23	
Cl	0.04	93.01	0.15	0.13	0.14	0.06	0.06	0.01	0.10	-	-	-	-	-	-	-	
Total	97.43	91.01	94.92	93.21	91.45	101.96	96.40	99.06	99.66	99.75	100.37	97.19	97.67	97.80	97.54	98.07	
corr. -O=F	0.59	0.52	0.60	0.56	0.54	0.64	0.76	0.69	0.26	1.04	1.02	0.96	0.92	0.91	0.90	0.94	
corr. -O=Cl	0.01	0.00	0.03	0.03	0.03	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Total corr.	96.83	90.49	94.32	92.65	90.91	101.32	95.64	98.38	99.40	98.70	99.35	96.23	96.75	96.88	96.64	97.13	

table 1 continued.

Sample		Britholite										Apatite				
wt%		LC 2					LC 1			SNSJG 1		LC 2	LC 2	LC 1	LC 1	LC 1
Cations (apfu)																
P	0.61	0.73	0.70	0.78	0.77	0.97	0.63	1.40	0.58	2.64	2.76	2.81	2.75	2.86	2.80	2.88
Si	2.48	2.36	2.36	2.21	2.21	2.17	2.35	1.64	2.30	0.36	0.25	0.10	0.16	0.16	0.21	0.14
sum T	3.10	3.09	3.06	2.99	2.98	3.14	2.98	3.04	2.88	3.00	3.01	2.91	2.91	3.02	3.01	3.03
Th	0.05	0.06	0.06	0.10	0.10	0.05	0.08	0.05	0.63	-	-	-	-	-	-	-
Al	0.04	0.33	0.31	0.30	0.31		0.44	0.15	-	-	-	-	-	-	-	-
Y	0.17	0.19	0.19	0.19	0.21	0.12	0.21	0.13	0.16	0.03	0.02	-	-	0.01	0.01	0.00
La	0.57	0.50	0.53	0.53	0.55	0.54	0.56	0.44	0.72	0.08	0.06	0.02	0.06	0.04	0.06	0.06
Ce	1.17	1.09	1.09	1.22	1.17	0.99	1.17	0.95	1.23	0.17	0.12	0.06	0.09	0.08	0.11	0.09
Pr	0.11	0.10	0.10	0.12	0.12	0.09	0.10	0.08	0.11	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Nd	0.35	0.35	0.33	0.38	0.40	0.26	0.30	0.24	0.95	0.06	0.04	0.02	0.02	0.03	0.04	0.02
Sm	0.04	0.04	0.04	0.04	0.04	0.02	0.04	0.03	0.03	0.01	0.01	-	-	-	-	-
Eu	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	-	-	-	-	-	-	-
Gd	0.15	0.13	0.14	0.16	0.15	0.12	0.14	0.11	0.14	0.02	0.01	0.01	0.01	0.01	0.01	0.01
Ca	2.19	1.94	1.98	1.66	1.70	2.57	1.70	2.53	1.95	4.72	4.82	4.76	4.67	4.91	4.86	4.87
Sr	-	-	-	-	-	0.04	-	0.10	0.10	0.01	0.02	0.01	0.03	0.01	0.01	0.05
Na	-	-	-	-	-	-	0.02	0.01	-	0.01	0.01	0.17	0.03	0.02	0.03	0.03
Fe	-	0.01	-	0.03	0.01	-	0.01	-	0.02		0.01	-	-	-	-	-
sum M	4.86	4.76	4.79	4.76	4.78	4.82	4.79	4.82	4.79	5.12	5.13	5.06	4.92	5.14	5.16	5.11
F	0.57	0.52	0.58	0.58	0.57	0.57	0.74	0.60	0.61	0.72	0.70	0.62	0.61	0.62	0.62	0.64
Cl	0.01	0.03	0.03	0.03	0.03	0.01	0.01	-	0.01	-	-	-	-	-	-	-
OH, calc.	0.42	0.45	0.38	0.39	0.40	0.42	0.25	0.40	0.38	0.28	0.31	0.38	0.39	0.38	0.38	0.36
sum X	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-	1.00	1.00	1.00	-	-	1.00	1.00	1.00

Formulae were calculated on the basis of 13O and 8 cations. OH was calculated from OH=1-(F+Cl), according to Pasero *et al.* (2010) and Lorenz *et al.* (2019). See text for the definition of T, M, and X. apfu=atoms per formula unit.

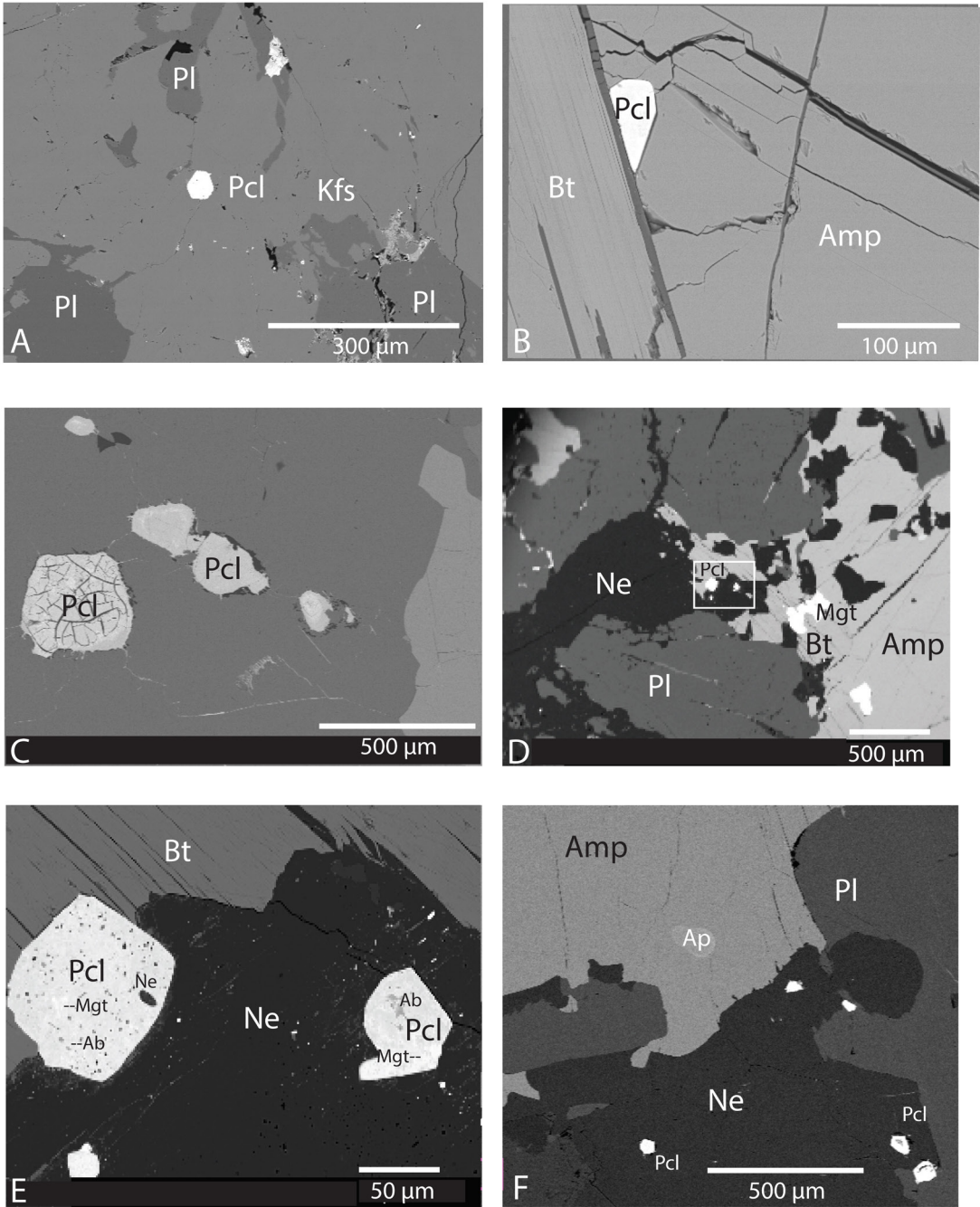


FIG. 8. BSE images of SJGS pyrochlore crystals. **A.** Euhedral pyrochlore (Pcl) in K-feldspar (Kfs). Pl=plagioclase. Sample UNG 1762. **B.** Subhedral pyrochlore in amphibole (Amp). Bt=Biotite. Sample LC 1. **C.** Subhedral to euhedral and partially fractured pyrochlore in feldspar. Sample LC 1. **D.** Euhedral pyrochlore in biotite. Ne=Nepheline; Mgt=Magnetite. Sample LC 1. **E.** Detail from D, pyrochlore in nepheline shows inclusions of magnetite (light), albite (Ab, gray), nepheline (dark), and holes (dark). **F.** Euhedral pyrochlore in nepheline. Ap=Apatite. Sample UNG 1762.

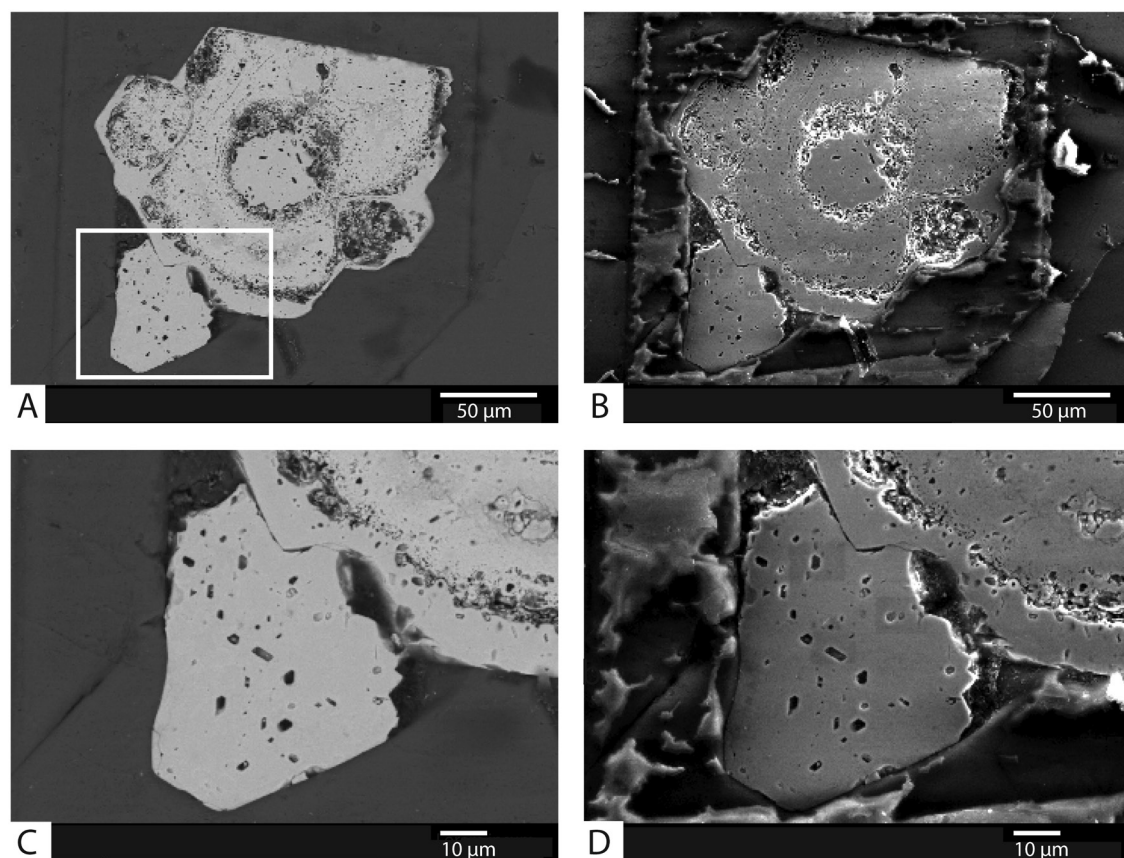


FIG. 9. BSE (A, C) and SE (B, D) images of SJGS pyrochlore crystals. Zoom-ins from A and B are shown in C and D, respectively. Sample UNG 1762.

The analyzed pyrochlores are characterized by $\text{Nb} + \text{Ta} > 2\text{Ti}$ and $\text{Nb} > \text{Ta}$ (Table 2), being therefore pyrochlores following the classification of Hogarth (1977). The general formula of the pyrochlore supergroup is $\text{A}_2\text{B}_2\text{X}_6\text{Y}$, where the A site contains the large Na, Ca, Mn, Sr, Y, and REE cations in 8-fold coordination, and the B site contains the smaller 6-fold coordinated Ta, Nb, Ti, Fe^{3+} , Mg, Al, and Si.

The classical pyrochlore nomenclature of Hogarth (1977) was modified by Atencio *et al.* (2010) and approved by the Commission on New Minerals Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA). According to this new nomenclature, the high Na/Ca and Nb/Ta ratios, and the high fluorine content indicate

that the crystals analyzed are fluornatropyrochlores. The EPMA analytical total is low (around 91–93 wt%) and the A site is below 2 apfu, which points to the presence of H_2O (Atencio *et al.*, 2010). In addition, the crystals have light REEs of ~ 1 wt%. The composition of pyrochlore varies depending on the samples analyzed. For example, sample UNG 1762 has more Na, Sr, and F, and less U, Ti, and Si than those in sample LC 1. Element mapping shows that some pyrochlores are zoned, with an inner core and an outermost rim significantly richer in Na and F and poorer in U and Th (Fig. 10). The cavities between the core and inner regions (black colors) help explain the lower concentrations in the element distribution maps.

TABLE 2. COMPOSITION OF PYROCHLORES. ANALYSES BY ELECTRON PROBE MICROANALYZER (EPMA).

Sample	UNG 1762						LC 1		
wt%									
Na ₂ O	7.33	8.35	8.54	7.68	8.25	2.99	0.01	0.49	0.73
CaO	9.44	11.34	10.20	10.83	10.22	16.29	11.54	9.32	12.33
SrO	2.83	2.14	2.46	2.33	2.46	-	-	-	-
Ce ₂ O ₃	1.06	0.81	1.12	0.94	1.07	0.56	1.92	1.85	0.10
ThO ₂	0.98	1.34	1.36	1.39	1.29	1.69	0.87	1.57	0.10
FeO	0.25	2.09	1.83	1.88	1.92	1.21	1.43	-	0.97
SiO ₂	0.77	4.50	3.16	4.07	3.61	-	14.45	3.55	14.60
MnO	0.09	0.65	0.50	0.69	0.31	0.29	-	-	-
TiO ₂	2.95	4.32	4.45	4.43	3.98	8.41	7.40	12.40	9.35
Nb ₂ O ₅	61.14	51.10	52.54	51.31	52.09	53.74	54.80	55.32	53.68
Ta ₂ O ₅	1.48	1.98	1.56	1.62	1.82	0.63	0.01	1.36	0.10
Al ₂ O ₃	0.06	0.16	0.08	0.16	0.14	-	-	-	-
UO ₂	0.02	0.02	0.02	0.02	0.02	5.47	1.66	3.55	4.13
F	5.51	4.42	4.01	4.27	4.36	2.22	-	-	
sum	93.91	93.22	91.83	91.62	91.54	93.50	94.09	93.40	96.10
Cations (apfu)									
Na	0.91	0.97	1.02	0.91	1.00	0.36	-	0.04	0.06
Ca	0.65	0.73	0.68	0.71	0.68	1.10	0.54	0.47	0.57
Sr	0.10	0.07	0.09	0.08	0.09	0.00	-	-	-
Ce	0.02	0.02	0.03	0.02	0.03	0.01	0.06	0.06	-
Th	0.01	0.02	0.02	0.02	0.02	0.02	0.01	0.02	-
Fe ²⁺	0.01	0.10	0.09	0.10	0.10	0.06	0.05	-	0.03
Si	0.05	0.27	0.20	0.25	0.23	-	0.63	0.36	0.62
Mn	-	0.03	0.03	0.04	0.02	0.02	-	-	-
Ti	0.14	0.20	0.21	0.20	0.18	0.40	0.24	0.44	0.30
Nb	1.77	1.39	1.47	1.41	1.53	1.53	1.08	1.18	1.06
Ta	0.02	0.03	0.03	0.03	0.03	0.01	-	0.03	-
Al	-	0.01	0.01	0.01	0.01	-	-	-	-
U	-	-	-	-	-	0.05	0.01	0.03	0.03
F	0.93	0.84	0.78	0.82	0.89	0.44	-	-	-
sum	4.61	4.68	4.66	4.60	4.81	4.00	2.62	2.63	2.68

Formulae were calculated on the basis of 2 B-site cations. apfu=atoms per formula unit.

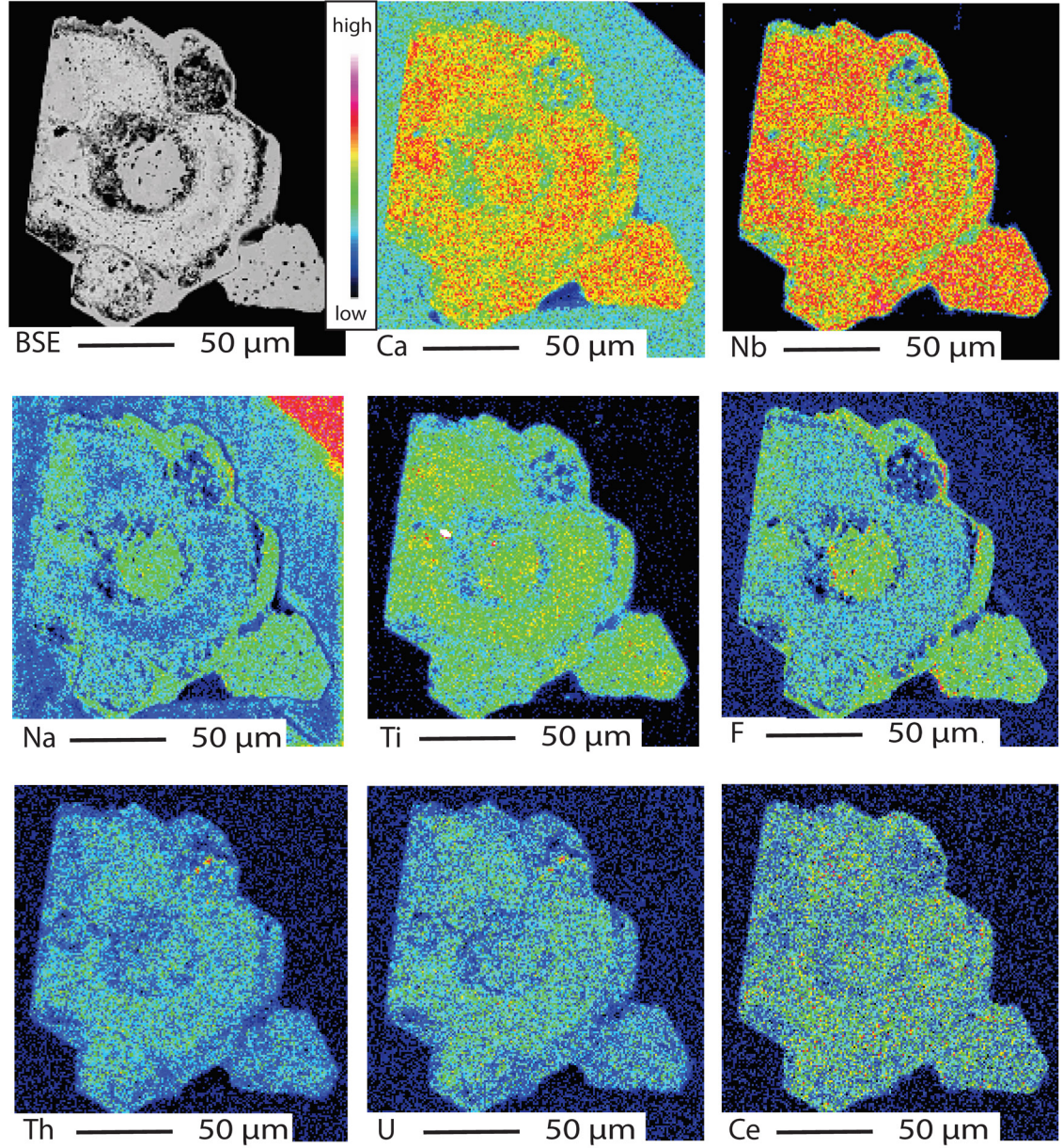


FIG. 10. BSE image (upper left) and element distribution maps of a pyrochlore crystal from sample UNG 1762 shown in figure 9. The strong zonation is due to an increase in Na, Ti and F concentrations. A false zonation is also given by the holey structure. Same color code for all element concentrations.

Calcite is usually found as isolated primary crystals in nepheline, microcline, and biotite or in contact with nepheline and albite (Fig. 11A, B). In addition, microcrystalline calcite aggregates are associated with cancrinite altering nepheline. However, in the latter case calcite shows high-temperature grain boundaries in contact with albite. Primary calcite is rich in light REEs with a total of up to 1,290 ppm (Table 3). La is up to 2,300 times and Ce up to 1,000 times above the chondrite-normalized concentrations. Additionally, primary calcite contains up to 3 wt% SrO, but is poor in MnO (≤ 0.84 wt%) and MgO (≤ 0.07 wt%), with low MgO/MnO ratios (0.06-0.08). The FeO concentrations are also low (≤ 0.35 wt%) (Table 3).

Rhodochrosite occurs rarely. It forms up to 80 μm -long, anhedral to subhedral inclusions in amphibole. Itself contains μm -sized inclusions of columbite (Fig. 11C), which are probable exsolutions. The chemical composition of a SJGS rhodochrosite crystal is shown in table 3.

Ancylite-Ce appears as individual grains with sizes <200 μm and <400 μm as aggregates (Fig. 11D). It typically occurs as inclusions, but due to its (OH) content it is probably of secondary origin, so the interpretation of an earlier crystallized phase would possibly be a mistake result of a cut effect. The chemical composition of a SJGS ancylite-Ce crystal is shown in table 3.

Strontianite with up to 12 wt% CaO occurs as an alteration product in Fe-rich amphiboles and K-feldspar (Fig. 11E, F; Table 3).

Columbite occurs as euhedral inclusion or exsolution with a grain size of up to 10 μm in rhodochrosite (Fig. 11C). Columbite inclusions in the rhodochrosite represent chemically a Ta-poor (0.003 apfu Ta) manganocolumbite (or columbite-Mn) with a Mn+Fe value of 1.34 apfu (Table 4).

Euxenite occurs in sample LC 1 as a <50 μm -long euhedral inclusion in nepheline. It contains up to 4.2 wt% UO_2 and 2.3 wt% Ce_2O_3 (Table 4). The presence of euxenite as an inclusion in nepheline indicates an early crystallization in the magmatic evolution.

Wöhlerite occurs as very rare grains (Fig. 12A). Crystals are typically <250 μm -long, anhedral to subhedral, and form grain boundaries with clinopyroxene. The chemical composition of a SJGS wöhlerite crystal is shown in table 4.

Titanite is frequently associated with opaque minerals (ilmenite-magnetite) and can be found as inclusions in clinopyroxene, amphibole, nepheline, biotite, and K-feldspar. It exhibits single polysynthetic twinning and is commonly euhedral, indicating early growth (Fig. 4A, C, D). It contains up to 2.2 wt% FeO (0.062 apfu) and traces of MnO, MgO, and Na_2O (Table 5).

Iron Oxide minerals in the syenites are commonly magnetite and ilmenite. They occur as individual grains or as ilmenite exsolutions in magnetite. The composition these iron oxides is very similar, independent of their occurrence as host grains, exsolutions or as individual grains (Table 6). The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of magnetite is constant around ~ 0.5 . Ilmenite is Mn-rich with up to 15 wt% MnO (~ 0.3 apfu). Both minerals have mostly anhedral shapes although some exhibit cubic shapes (Fig. 12C, D). Ilmenite-magnetite pairs sometimes contain nepheline inclusions (Fig. 12c).

Pyrite is very rare and detectable as inclusions in nepheline (Fig. 11A).

Fluorite appears rarely as up to 100 μm -large purplish inclusions in nepheline (Fig. 12B). It contains 0.56 wt% SrO, and 0.135 wt% FeO (Table 5). The REE concentrations are below the detection limit of the EPMA, except for Ce (250 ppm), Nd (350 ppm), and Gd (170 ppm).

Zircon appears in the studied samples very rarely and will not be discussed here (one grain in three thin sections of one rock sample). Larger zircons in the SJGS rock suite are described by Amaya López *et al.* (2021).

Kaolinite is a common secondary mineral, which in our samples is seen altering exclusively nepheline (Fig. 3E). The kaolinite forms rims around nepheline as well as complete substitutions.

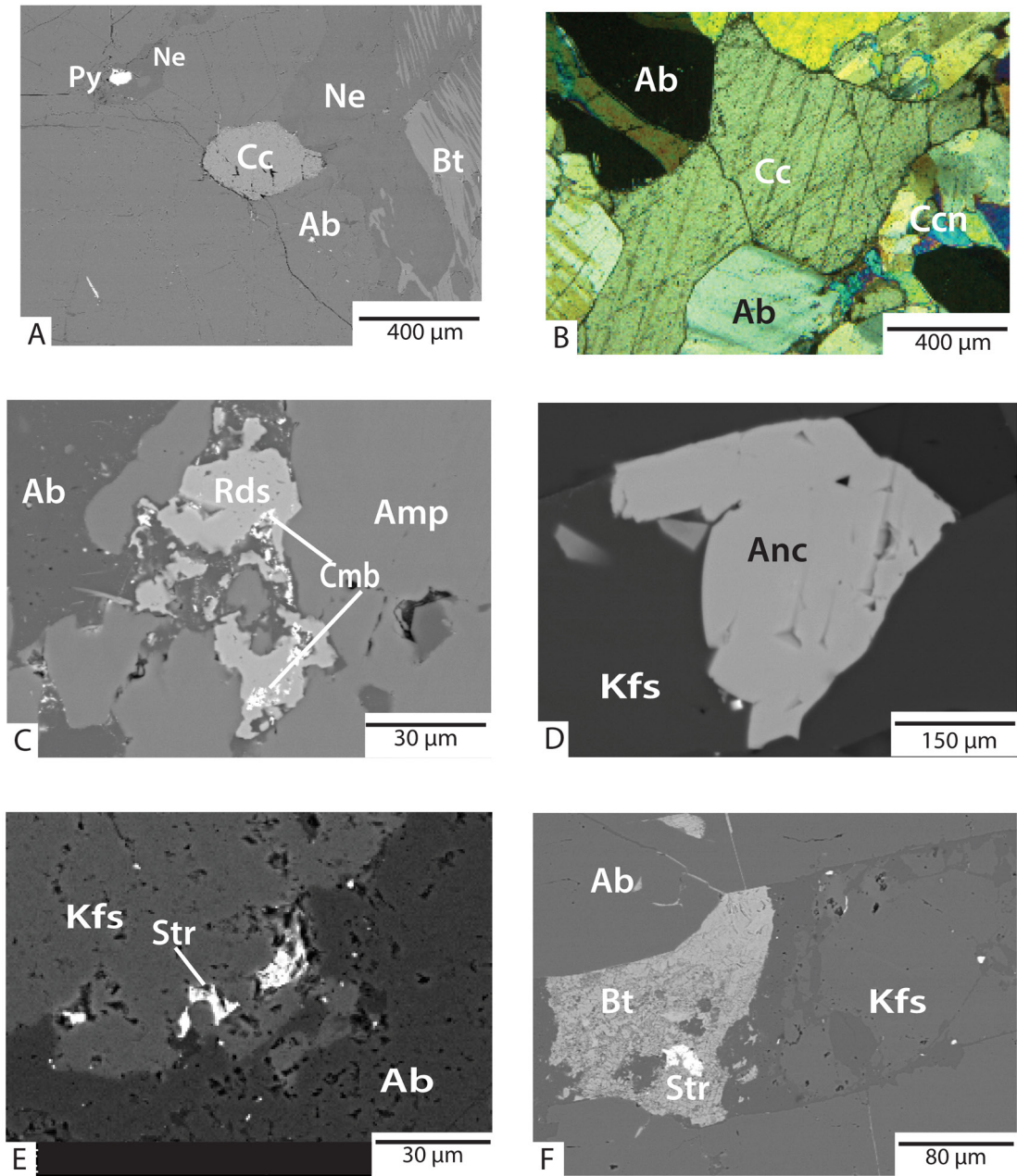


FIG. 11. Photomicrographs and BSE images of some SJGS samples showcasing carbonates. **A.** Euhedral primary calcite (Cc) at the albite-nepheline (Ab-Ne) interface. Bt=Biotite. Py=Pyrite. Sample SNSJG 6. **B.** Primary calcite between albite and recrystallized cancrinite (Ccn). Sample SNSJG 1. **C.** Rhodochrosite (Rds) with Mn-rich columbite (Cmb). Amp=Amphibole. Sample UNG 1762. **D.** Ancyrite-Ce aggregate (Anc) in K-feldspar (Kfs). Sample UNG 1762. **E.** Strontianite (Str) as secondary product at the contact between albite and K-feldspar. Sample UNG 1762. **F.** Strontianite in fractured biotite. Sample UNG 1762.

TABLE 3. COMPOSITION OF CARBONATES. ANALYSES BY ELECTRON PROBE MICROANALYZER (EPMA).

Sample	Calcite		Rhodochrosite	Strontianite	Ancylite-Ce	
	SNSJG 6		UNG 1762	UNG 1762	SNSJG 6	
wt%						
CaO	59.56	59.89	1.60	11.89	2.96	3.63
MgO	0.05	0.07	0.49	-	-	-
MnO	0.81	0.84	54.06	-	-	-
FeO	0.25	0.35	9.98	-	-	-
SrO	2.85	2.94	3.07	41.86	20.78	18.95
CO ₂	36.29	35.72	24.32	46.25	28.73	29.44
F					0.55	0.55
ppm					wt%	wt%
La	530	510	-	-	12.73	12.97
Ce	610	630	-	-	21.19	21.21
Pr	-	-	-	-	1.92	1.85
Nd	150	150	-	-	5.53	4.86
Sm	-	-	-	-	0.51	0.43
Eu	-	-	-	-	0.44	0.34
Gd	-	-	-	-	2.93	2.89
sum	99.81	99.79	93.50	99.98	98.28	97.13
Cations (apfu)						
Ca	1.93	1.93	0.06	0.77	-	-
Mg	0.003	0.003	0.03	-	-	-
Mn	0.02	0.02	1.56	-	-	-
Fe ²⁺	0.01	0.01	0.28	-	-	-
Sr	0.04	0.04	0.06	1.23	-	-
C	2.00	2.00	2.00	2.00	-	-
O	6.00	6.00	6.00	6.00	-	-
Components						
mol%						
CaCO ₃	96.51	96.29	3.17	38.31	-	-
MgCO ₃	0.14	0.17	1.59	-	-	-
MnCO ₃	0.96	0.98	78.24	-	-	-
FeCO ₃	0.29	0.40	14.21	-	-	-
SrCO ₃	2.11	2.16	2.79	61.69	-	-
Total	100.00	100.00	100.00	100.00	-	-

Number of cations were calculated on the basis of 6O. apfu=atoms per formula unit.

TABLE 4. COMPOSITION OF EUXENITES, COLUMBITES, AND WÖHLERITES. ANALYSES BY ELECTRON PROBE MICROANALYZER (EPMA).

Sample	euxenite			columbite	wöhlerite	
	LC 1			UNG 1762	LC 2	
wt%					wt%	
Nb ₂ O ₅	58.82	55.10	71.13	68.49	Nb ₂ O ₅	15.36
Ta ₂ O ₅	1.45	0.10	-	0.20	SiO ₂	29.55
SiO ₂	8.02	14.99	1.75	0.84	TiO ₂	1.15
TiO ₂	13.18	9.50	11.60	1.77	ZrO ₂	15.90
ThO ₂	1.67	0.10	-	-	MnO	0.55
UO ₂	3.77	4.24	6.13	-	CaO	30.16
Ce ₂ O ₃	1.97	0.1	2.31	-	Na ₂ O	4.82
FeO	0.02	1.00	0.02	6.15	F	2.49
MnO	-	-	-	21.96	-	-
CaO	9.91	12.66	7.82	0.59	-	-
Na ₂ O	0.52	0.75	-	-	-	-
sum	99.33	98.54	100.76	100.00	sum	99.98
Cations (apfu)				Cations (apfu)		
Nb	1.361	1.208	1.682	1.748	Nb	4.49
Ta	0.020	0.001	0.000	0.003	Si	3.83
Si	0.410	0.727	0.092	0.047	Ti	0.11
Ti	0.507	0.346	0.456	0.075	Zr	4.02
Th	0.019	0.001	0.000	0.000	Mn	0.06
U	0.043	0.046	0.071	0.000	Ca	4.18
Ce	0.012	0.001	0.015	0.000	Na	1.21
Fe ²⁺	0.001	0.041	0.001	0.290	F	1.02
Mn	0.000	0.000	0.000	1.050	sum	17.82
Ca	0.543	0.658	0.438	0.036		
Na	0.052	0.070	0.000	0.000		
sum	2.969	3.100	2.819	3.250		

Number of cations in euxenite and columbite were calculated on the basis of 6O. Number of cations in wöhlerite were calculated on the basis of 18O. apfu=atoms per formula unit.

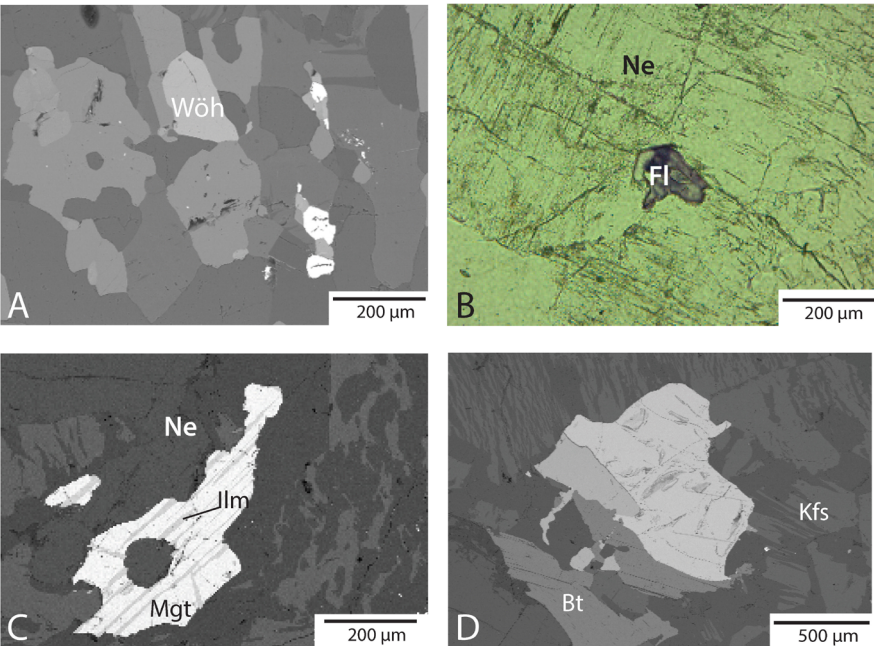


FIG. 12. Photomicrographs and BSE images of some SJGS samples showing wöhlerite and iron oxides. **A.** Wöhlerite (Wöh). Sample LC 2. **B.** Fluorite (Fl) in nepheline (Ne). Sample Muestra 3. **C.** Magnetite (Mgt, white domains) with exsolution lamellae of ilmenite (Ilm, gray elongated domains) as inclusion in nepheline. Sample SNSJG 5a. **D.** Magnetite and ilmenite in Kfs. Sample SNSJG 5a.

TABLE 5. COMPOSITION OF TITANITES AND FLUORITES. ANALYSES BY ELECTRON PROBE MICROANALYZER (EPMA).

Sample		Titanite SNSJG 6		SNSJG 4	Fluorite SNSJG 4	
wt%					ppm	
SiO ₂	30.51	30.35	29.96	30.27	Ce ₂ O ₃	254
TiO ₂	37.04	37.71	38.72	36.36	Nd ₂ O ₃	350
Al ₂ O ₂	0.04	0.02	1.52	1.27	Gd ₂ O ₃	176
FeO	2.24	1.58	1.29	1.95	wt%	
MgO	0.04	0.02	0.02	0.09	FeO	0.14
MnO	0.16	0.12	0.13	0.02	CaO	73.72
CaO	28.99	28.56	28.65	28.01	SrO	0.56
Na ₂ O	0.17	0.23	0.18	0.27	F	25.27
sum	100.49	99.78	100.48	99.24	sum	99.78
Cations (apfu)					Cations (apfu)	
Si	1.02	1.013	0.979	1.012	Ce	0.001
Ti	0.928	0.947	0.952	0.915	Nd	0.001
Al	0.002	0.001	0.059	0.05	Gd	0.001
Fe ²⁺	0.005	0.004	0.004	0.001	Fe	0.002
Mn	0.002	0.002	0.001	0.004	Ca	0.99
Mg	0.002	0.002	0.001	0.004	Sr	0.005
Ca	1.035	1.022	1.004	1.003	sum	1.000
Na	0.001	0.015	0.011	0.018		
sum	3.06	3.06	3.05	3.06		

Number of cations were calculated on the basis of 50. apfu=atoms per formula unit.

TABLE 6. COMPOSITION OF MAGNETITES AND ILMENITES. ANALYSES BY ELECTRON PROBE MICROANALYZER (EPMA).

Sample	Magnetite			Ilmenite		
	SNSJG 5a with ilmenite exsolutions	SNSJG 4 individual grain	SNSJG 5a* individual grain	SNSJG 5a exsolved from magnetite	SNSJG 5a individual grain	SNSJG 5a* individual grain
wt%						
TiO ₂	0.06	0.09	0.17	52.55	52.41	52.57
Al ₂ O ₃	0.05	0.14	-	-	-	-
FeO	95.43	97.34	99.40	32.79	32.55	34.24
MgO	0.03	0.93	-	-	-	-
MnO	0.13	0.04	0.14	14.18	14.92	13.19
CaO	0.01	0.02	-	-	-	-
sum	95.71	98.56	100.00	99.55	99.88	100.00
Cations (apfu)						
Ti	0.002	0.002	0.005	1.00	1.00	1.00
Al	0.003	0.006	-	-	-	-
Fe ²⁺	0.99	0.95	1.00	0.69	0.68	0.72
Fe ³⁺	1.99	1.99	1.99	-	-	-
Mg	0.002	0.05	-	-	-	-
Mn	0.003	0.001	0.004	0.31	0.32	0.28
Ca	0.001	0.001	-	-	-	-
sum	3	3	3	2	2	2

Number of cations were calculated on the basis of 4O. apfu=atoms per formula unit.
Analyses by electron probe microanalyzer (EPMA) unless where * (EDS analyses).

5. Discussion and conclusions

Numerous accessory minerals, several dominated by so-called critical elements such as Nb and REEs, are present in the SJGS samples. These accessory minerals typically present along with mostly major mineral phases, such as nepheline, potassium feldspar, albite, biotite, titanite, Fe-rich clinopyroxenes, and Fe-rich amphiboles. In the study area, accessory minerals can be used as tracers to evaluate fluid and melt interactions during the SJGS magmatic evolution.

The textural and compositional characteristics of the SJGS minerals suggest different magmatic stages. We propose an early high-temperature crystallization stage dominated by the growth of nepheline, sodalite, potassium feldspar (orthoclase), Fe-rich clinopyroxene, albite, apatite, amphibole, and biotite. Inclusions of calcite and Nb-rich minerals

(pyrochlore, columbite, and euxenite) indicate that they were formed during this early stage as well.

We suggest a large proportion of SJGS calcite is primary in origin. The high abundance of light REEs (~1,290 ppm) in calcite is similar to those observed in calcites from experiments on silica-rich carbonatites (sövites) of Oka (Canada), Kaiserstuhl (Germany), and Alnö (Sweden), which vary between 300 and 1,100 ppm (*e.g.*, Hornig-Kjarsgaard, 1998). This abundance contrasts usually lower light REE concentrations in sedimentary and hydrothermal calcite. Sedimentary calcites, like the late Devonian reefal calcites (Australia), have light REE concentrations below 10 ppm (Nothdurft *et al.*, 2004). Likewise, hydrothermally formed calcites show lower light REE concentrations than those from calcites in carbonatites (Stipp *et al.*, 2006). Furthermore, the SJGS calcites have low MgO (≤ 0.07 wt%) and

high SrO (~2.9 wt%) concentrations (Table 3), which is typical for calcites that crystallized from experimental silica-rich carbonatite melts (e.g., Hornig-Kjarsgaard, 1998). Additionally, the very low MgO/MnO ratios (0.062-0.083) are comparable to magmatic calcite, in contrast to hydrothermally formed calcites (Chakhmouradian *et al.*, 2016). Calcite crystallization textures (Fig. 11A, B) suggest formation at high temperatures (e.g., Philpotts and Ague, 2021), and albite rims around nepheline (Fig. 3D) indicate high pressures during the crystallization of these mineral phases (*i.e.*, fractionation of albite after nepheline), all in accordance with experimental studies (e.g., Philpotts and Ague, 2021). The high SrO concentrations in apatite (0.2-0.5 wt%) are typical for apatite crystallized from carbonatitic melts as well (Belousova *et al.*, 2002), whereas apatite from mafic rocks has significant lower SrO concentrations (<0.13 wt%; Belousova *et al.*, 2002). Finally, the high FeO and low TiO₂ contents in clinopyroxene (Supplementary Table S3) point to high CO₂ activities in the free volatile phase, *i.e.*, CO₂-saturated conditions (e.g., Dolfi, 1996; Gozzi *et al.*, 2014).

A decrease in temperature and an increase in P_{H_2O} ($P_{H_2O} > P_{CO_2}$) is indicated by the transition of Fe-rich clinopyroxene into Fe-rich amphibole. Another process that possibly takes place simultaneously is the deformation-enhanced triclinization of orthoclase, forming microcline (some feldspars with shape-preferred orientation also show evidence of deformation during an early intrusion stage under an active stress field). Exsolution of albite from alkali feldspar during the formation of perthitic microcline as a second alkali feldspar generation also points to slow cooling from high temperatures. Britholite, a solid solution member of the apatite supergroup (higher Si and REE contents; see table 1), forms as overgrowths on apatite, or replace it as a product of the $Ca+P \leftrightarrow REE+Si$ exchange reaction. Britholite has primarily been described from nepheline syenites (e.g., Ilimaussaq intrusive complex, Greenland; Winther, 1901), carbonatites (e.g., Angola; Torró *et al.*, 2012; Anenburg *et al.*, 2018), and metasomatized halos around alkaline intrusions (e.g., Kola Peninsula; Zozulya *et al.*, 2015, 2017). According to the phase diagram of Anenburg *et al.* (2018), britholite can crystallize during cooling and redistribution of REEs from apatite, still at high (400-700 °C) temperatures. From Nolans Bore, a P-REE-Th-rich vein-style

deposit in Australia, Anenburg *et al.* (2018) described exsolution of britholite from fluorapatite at a solvus under high CO₂ and Si activities. Synchronous, and probable reaction-enhanced, was the ingress of (possibly internally derived) Sr-rich fluids into the studied apatites.

As the cooling progressed, late magmatic hydrothermal-metasomatic processes dominated by fluids with variable P_{CO_2}/P_{H_2O} are represented by secondary cancrinite, Sr- and Mn-carbonates and ancylite-Ce. Ancylite is a typical hydrothermal alteration product (e.g., Larsen and Gault, 2002). Cancrinite occurs as a primary magmatic phase with calcite, nepheline, and sodalite, but more often as polycrystalline aggregates in nepheline. In the samples analyzed, the secondary growth of cancrinite probably occurred synchronously with the formation of the late magmatic carbonates strontianite (Sr) and rhodochrosite (Mn), which grew at the expense of feldspars and amphiboles. The influx of Sr into the system, transforming apatite and forming Sr-carbonates, possibly occurred coevally and had the same source.

The magmatic evolution of the SJGS rocks can be summarized as follows: a CO₂-rich environment during the early and late stages with variable contributions of (OH) and CO₂. The presence of magmatic calcite and apatite in the earliest stages of the SJGS nepheline-syenites can be addressed using different models:

- I. The formation of two primary, independent melts derived from a highly oxidized carbonate-metasomatized lithospheric mantle (e.g., Wallace and Green, 1988; Ying *et al.*, 2004; Braunger *et al.*, 2018). In the case of the SJGS, this would imply a mingling stage of the two melts, resulting in larger carbonatite bodies, nodules or spheres. These textures are not observed; however, this process cannot be completely ruled out.
- II. The more commonly discussed model suggests a single primary melt derived from a contaminated lithospheric mantle that fractionates and further decouples a carbonatitic residual melt by liquid immiscibility (Gittins, 1989; Beccaluva *et al.*, 1992; Bell and Rukhlov, 2004; Downes *et al.*, 2005; Halama *et al.*, 2005; Brooker and Kjarsgaard, 2011). Gittins and Mitchell (2023), however, discuss that there is still no reliable experimental work proving that a nephelinitic magma can develop to such an extent that separation of immiscible

silicate and carbonate melts takes place. In our case study, the SJGS would be the carbonate-bearing silicate (syenite) residuum, with calcite, apatite, pyrochlore, and/or cancrinite. Due to its low density, the decoupled carbonatite melt reaches shallow intrusion levels more rapidly than silicate melts. Mineralogically speaking, this model fits with the syenites analyzed here.

- III. “Simple” crystallization differentiation of a primary magma derived from contaminated mantle (Gittins and Mitchell, 2023). In this case, calcite is part of the silicate melt fractionation, and large carbonatite volumes decoupled from the evolving melt are lacking. Although the calcite textures observed favor this model, the apatite and pyrochlore compositions (U-rich) do not (Vasyukova and Williams-Jones, 2023).
- IV. Crystallization under the metasomatic influence of carbonatitic melts on solid rocks, forming secondary syenites (Vasyukova and Williams-Jones, 2022). The low abundance of calcite in the syenites and the absence of a convincing evidence for additional metasomatic processes render this model unlikely. Although the presence of U-rich pyrochlores could be due to interaction with carbonate melts (Vasyukova and Williams-Jones, 2022), no other evidence has been found in the SJGS that points to a metasomatic influence, such as biotite or phoscorite formation as described by Vasyukova and Williams-Jones (2022).
- V. Melting of carbonated crustal rocks. The typical light REE and Sr concentrations in calcites from melted crustal carbonates are significantly lower (>10 times lower light REE, >2 times lower Sr), than in the SJGS calcites, so this model is rendered as unlikely as well (see Gozzi *et al.*, 2014).

In conclusion, the particular calcite and apatite compositions in the SJSG area suggest a previous coexistence with a carbonatitic melt. Cancrinite (Maravic and Morteani, 1980), britholite (Djeddi *et al.*, 2021) and ancylite (Eby, 1975; Hornig-Kjarsgaard, 1998) reported from syenites coexisting with carbonatites elsewhere probably formed during the cooling or hydrothermal stages. We therefore favor model II, *i.e.*, a single melt derived from a contaminated lithospheric mantle that upon advanced fractionation decoupled a carbonatitic residual melt by liquid immiscibility. Model I (two independent primary

melts), although less likely, cannot be completely ruled out. The SJGS rocks possibly represent an older member of a nepheline-syenite-carbonatite association, such as those reported from the Southern Victoria Land, Antarctica (Worley *et al.*, 1995) and the chemically equivalent phonolites associated with carbonatites in Kaiserstuhl (Germany) (Wimmenauer, 1962; Braunger *et al.*, 2018). The unmixed carbonatite melts that coexisted with and decoupled from the parent melt possibly intruded shallow crustal levels and was subsequently eroded.

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TABLE S1. COMPOSITION OF FELDSPARS. ANALYSES BY ELECTRON PROBE MICROANALYZER (EPMA).

K-feldspar							Albite			
Sample	LC 1			LC 2		LC 1			SNSJG 4	
wt%	core	core	core	Inclusion in apatite	core	Recrystallized grain	Exsolution in orthoclase	Recrystallized grain	core	core
SiO ₂	64.15	64.03	64.78	64.53	63.54	67.04	67.50	67.08	67.19	66.19
TiO ₂	0.03	0.02	0.02	-	-	0.01	-	0.01	0.02	0.01
Al ₂ O ₃	18.0	18.78	19.01	19.34	19.32	19.93	20.10	19.74	20.03	21.48
FeO	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.02
CaO	0.01	0.01	0.01	-	-	0.01	0.10	0.09	0.15	1.11
Na ₂ O	0.65	0.69	0.49	0.81	0.77	11.57	11.34	11.36	11.23	10.51
K ₂ O	15.25	15.41	15.45	15.52	15.54	0.08	0.07	0.08	0.09	0.06
sum	98.88	98.99	99.93	100.15	99.24	98.81	99.24	98.51	98.83	99.40
Cations (apfu)										
Si	2.98	2.97	2.96	2.97	2.96	2.97	2.97	2.98	2.97	2.91
Al	1.03	1.04	1.06	1.05	1.06	1.04	1.04	1.03	1.04	1.11
Fe	-	-	0.01	-	-	-	-	-	-	-
Ca	0.001	0.001	0.001	-	-	0.002	0.004	0.003	0.005	0.05
Na	0.06	0.06	0.04	0.07	0.07	0.99	0.07	0.98	0.96	0.90
K	0.92	0.93	0.93	0.90	0.92	-	-	-	-	-
sum	4.99	5.0	5.0	5.0	5.01	5.01	4.99	5.0	5.0	4.98
Components mol%										
an	0.1	0.01	0.1	-	-	0.3	0.5	0.5	0.7	5.5
ab	6.1	6.40	4.6	7.4	7.0	99.2	99.1	99.0	98.8	94.1
or	93.8	93.5	95.3	92.6	93.0	0.5	0.4	0.5	0.5	0.4

Number of cations were calculated on the basis of 8O. apfu=atoms per formula unit.

TABLE S2. COMPOSITION OF FOIDS. ANALYSES BY ELECTRON PROBE MICROANALYZER (EPMA) UNLESS WHERE * (EDS ANALYSES).

Sample	Nepheline				Sodalite			Cancrinite	
	UNG 1762		SNSJG 1	LC 2*	LC 2*		UNG 1762*	SNSJG 6*	
wt%									
SiO ₂	42.86	43.36	43.37	44.45	48.31	40.80	40.60	41.29	38.56
TiO ₂	-	-	0.02	0.03	-	-	-	-	-
Al ₂ O ₃	32.89	35.11	34.98	34.82	31.48	29.91	30.06	29.98	27.44
FeO	0.16	0.16	0.14	0.10	-	-	-	-	0.43
MnO	0.01	0.01	0.02	-	-	-	-	-	-
CaO	-	-	-	0.02	-	-	-	-	6.14
Na ₂ O	16.00	15.87	15.79	15.89	13.02	20.40	19.85	17.90	14.72
K ₂ O	6.61	6.52	6.46	6.04	7.20	-	-	0.75	
SO ₃	-	0.01	-	0.02	-	-	-	-	4.71
Cl	-	-	-	-	-	8.90	9.49	10.08	-
F	-	-	0.01	-	-	-	-	-	-
sum	98.53	101.10	100.9	101.4	100	100	100.00	100	92.00
Cations (apfu)									
Si	8.37	8.24	8.25	8.37	9.12	5.54	5.52	5.58	6.53
Ti	-	-	0.003	0.004	-	-	-	-	-
Al	7.58	7.86	7.85	7.73	7.01	4.80	4.85	4.78	5.47
Fe ²⁺	0.03	0.03	0.02	0.02	-	-	-	-	0.06
Mn	0.002	0.002	0.003	-	-	-	-	-	-
Ca	-	-	-	-	-	-	-	-	1.16
Na	6.06	5.84	5.83	5.83	4.77	5.38	5.23	5.20	4.84
K	1.65	1.58	1.57	1.45	1.73	-	-	0.13	-
sum	23.69	23.55	23.53	23.40	22.63	15.72	15.60	15.69	18.06

Number of cations in nepheline were calculated on the basis of 32O and in sodalite on the basis of 21O. Number of cations in cancrinite were calculated on the basis of 12(Si+Al) and 8 wt% H₂O. apfu=atoms per formula unit.

TABLE S3. COMPOSITION OF CLINOPYROXENES. ANALYSES BY ELECTRON PROBE MICROANALYZER (EPMA).

Sample	LC 2	SNSJG 4		SNSJG 6	
wt%	Inclusion in amphibole	Core	Inclusion in amphibole	Core	Core
SiO ₂	49.09	49.95	50.02	50.11	50.91
TiO ₂	0.50	0.61	0.67	0.61	0.5
Al ₂ O ₃	2.12	2.97	2.92	3.34	2.45
FeO	24.80	17.36	16.26	17.06	18.05
MnO	1.80	1.26	1.19	1.13	1.25
MgO	2.21	6.66	7.46	6.61	6.06
CaO	18.21	17.24	18.39	16.65	15.62
Na ₂ O	3.28	3.95	3.57	4.32	4.77
K ₂ O	0.01	-	-	0.01	0.01
sum	101.00	100.00	100.50	99.57	99.57
Cations (apfu)					
Si	1.9	1.89	1.88	1.89	1.93
Al ^{IV}	0.10	0.1	0.11	0.11	0.07
Al ^{VI}	-	0.03	0.01	0.04	0.04
Ti	0.02	0.02	0.02	0.02	0.01
Fe ³⁺	0.32	0.34	0.33	0.34	0.35
Fe ²⁺	0.48	0.21	0.18	0.19	0.23
Mg	0.13	0.38	0.42	0.37	0.34
Mn	0.06	0.04	0.04	0.04	0.04
Ca	0.75	0.70	0.74	0.67	0.64
Na	0.25	0.29	0.26	0.32	0.35
K	0.001	-	-	-	-
sum	4.01	4.00	3.99	3.99	4.00
Components mol%					
Jd%	0.00	2.58	1.12	4.4	4.3
Ac(Aeg)	25.13	27.00	25.41	27.9	31.2
Ca.FeTs	0.0	0.0	0.0	0.0	0.0
Ca.TiTs	1.48	1.78	2.01	1.8	1.4
Ca.Ts	3.44	3.68	4.03	3.6	2.0
Woll%	36.02	32.92	34.80	31.6	30.4
En%	6.49	19.16	21.34	19.0	17.3
Fs%	27.44	12.89	11.29	11.7	13.4

Number of cations were calculated on the basis of 6O. End members are from the method of Cawthorn and Collerson (1974). Jd: jadeite; Ac: acmite; Aeg: aegirine; Ca.FeTs: ferro-calcic Tschermak's end-member; Ca.TiTs: titanium-calcium Tschermak's end-member; Ca.Ts: Ca-Tschermak's end-member; Woll: wollastonite; En: enstatite; Fs: ferrosilite. Fe³⁺ calculation after Droop (1987). apfu=atoms per formula unit.

TABLE S4. COMPOSITION OF AMPHIBOLES. ANALYSES BY ELECTRON PROBE MICROANALYZER (EPMA).

Sample	LC 1		LC 2	SNSJG 4	
wt%	Core	Rim	Core	Rims around clinopyroxene	
SiO ₂	39.93	38.82	38.42	38.86	38.34
TiO ₂	1.96	1.53	1.04	11.08	0.96
Al ₂ O ₃	9.11	9.79	11.08	12.22	12.12
FeO	31.30	31.18	31.68	24.73	25.00
MnO	1.98	1.84	1.66	1.63	1.66
MgO	0.94	0.9	1.80	5.73	5.47
CaO	7.65	7.51	9.54	9.07	9.04
Na ₂ O	4.31	4.22	3.37	3.77	3.91
K ₂ O	1.85	1.98	1.93	2.06	1.94
sum	98.49	97.76	100.53	99.23	98.44
Cations (apfu)					
Si	6.63	6.27	6.028	5.96	5.95
Al ^{IV}	1.66	1.73	1.971	2.04	2.05
Al ^{VI}	0.06	0.13	0.076	0.17	0.16
Ti	0.024	0.19	0.124	0.14	0.11
Fe ³⁺	0.78	0.90	1.02	1.09	1.11
Fe ²⁺	3.43	3.32	3.12	2.08	2.14
Mn	0.27	0.25	0.22	0.21	0.22
Mg	0.23	0.22	0.42	1.31	1.27
Ca	1.32	1.30	1.60	1.49	1.50
Na	1.34	1.32	1.02	1.12	1.17
K	0.38	0.41	0.386	0.43	0.38
sum	16.12	16.04	15.99	16.04	16.06

Number of cations were calculated on 23O oxygens with Fe²⁺/Fe³⁺ estimation assuming 13 cations. apfu=atoms per formula unit.

TABLE S5. COMPOSITION OF BIOTITES. ANALYSES BY ELECTRON PROBE MICROANALYZER (EPMA).

Sample		UNG 1762				SNSJG 1	Muestra 3	SNSJG 4
wt%								
SiO ₂	33.23	33.73	33.88	33.88	32.84	34.07	32.78	35.41
TiO ₂	3.88	3.58	4.17	4.01	3.51	4.05	4.09	1.15
Al ₂ O ₃	13.89	14.03	13.94	13.68	14.65	14.01	14.31	15.30
FeO	32.13	32.81	32.23	33.35	33.68	32.26	32.99	23.40
MnO	1.02	1.00	1.05	1.04	0.28	0.50	0.64	2.04
MgO	2.92	3.05	3.23	3.24	3.02	3.15	3.11	9.59
CaO	0.01	-	-	0.02	0.47	-	-	0.07
Na ₂ O	0.14	0.11	0.10	0.12	0.14	0.14	0.12	0.11
K ₂ O	9.21	9.52	9.53	9.31	8.29	9.69	9.81	9.34
F	0.34	0.29	0.4	0.39	0.30	0.30	0.22	0.20
sum	96.77	97.83	98.53	99.04	97.18	98.17	98.07	96.61
Cations (apfu)								
Si	5.42	5.43	5.42	5.41	5.32	5.45	5.30	5.51
Ti	0.48	0.43	0.50	0.48	0.43	0.49	0.50	0.13
Al	2.67	2.66	2.63	2.58	2.80	2.64	2.73	2.81
Fe ²⁺	4.38	4.42	4.31	4.46	4.57	4.32	4.46	3.05
Mn	0.14	0.14	0.14	0.14	0.04	0.07	0.09	0.27
Mg	0.71	0.73	0.77	0.77	0.73	0.75	0.75	2.23
Ca	-	-	-	-	0.08	-	-	0.01
Na	0.04	0.03	0.03	0.04	0.04	0.04	0.04	0.03
K	1.92	1.95	1.94	1.90	1.71	1.98	2.02	1.85
sum	15.75	15.80	15.75	15.78	15.73	15.75	15.87	15.89
Fe/(Fe+Mg)	0.86	0.86	0.85	0.85	0.86	0.85	0.86	0.58

Number of cations were calculated on the basis of 24 (O, OH, F). apfu=atoms per formula unit.