Petrography and geochemistry of the Mesoarchean Bikoula banded iron formation in the Ntem complex (Congo craton), Southern Cameroon: Implications for its origin

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Abstract

Precambrian banded iron formations (BIFs) represent an important source of mineable iron, as well as an archive recording secular changes in the chemistry of the Earth's early oceans. Here we report petrographic and geochemical characteristics of unweathered drill core samples from the Bikoula BIF, a virtually uncharacterized oxide facies iron formation, hosted in the Mesoarchean Ntem complex, southern Cameroon. The BIF is cross-cut with syenitic veins. The entire succession is highly deformed and metamorphosed under granulite facies conditions. The BIF is characterized by alternating micro-bands of magnetite, quartz and pyroxene. Sulfides (pyrite, pyrrhotite, and chalcopyrite), oligoclase, ferro-pargasite, biotite and ilmenite occur as minor phases. The presence of pyroxene, ferro-pargasite and oligoclase, relatively high contents of major elements such as Al_2O_3 (0.76 – 7.52 wt.%), CaO (1.95 – 4.90

wt.%), MgO (3.78 – 5.59 wt.%), as well as positive correlations among Al_2O_3, TiO_2, HFSEs, LILEs and transition metals (V, Cr, Ni, Cu and Zn), suggest that the BIF protolith included a significant amount of clastic material. Several samples have preserved seawater-like PAAS-normalized REE-Y patterns, including LREE depletion, and positive La and Y anomalies. Positive Eu anomalies observed in some of the analyzed samples indicate influx of hydrothermal fluids (possibly including Fe and Si) within the basin where the BIF precipitated. However, few samples show unusual negative Eu anomalies that likely result from a large proportion of clastic contamination. The lack of Ce anomalies suggests that the Bikoula BIF was deposited in a basin that was (at least partly) anoxic or suboxic, where it was possible to transport and concentrate dissolved Fe^{2+}.

Keywords: Bikoula BIF; Ntem complex; Granulite-facies metamorphism; Hydrothermal fluids; Seawater

1. Introduction

Banded iron formations (BIFs) are chemical sedimentary rocks that contain ≥ 15% iron and typically display banding consisting of iron-rich layers alternating with silica-rich layers (James, 1954; Trendall, 2002). BIFs are common in the Precambrian geological record, while an equivalent facies has never been observed in Phanerozoic sequences or modern environments (Klein, 2005). BIFs are of great interest due to their economic importance as the world's largest source of iron ore (Robb, 2005), and because the models proposed to explain their genesis are intimately linked to the evolution of the Earth's atmosphere, hydrosphere, and biosphere (Konhauser et al., 2009; Bontognali et al., 2013). Based on their depositional environment and co-occurring rock facies, BIFs have been subdivided into Superior- and Algoma-types (Gross, 1980). The former were deposited in near-shore continental shelf environments and are associated with carbonates, quartzites and black shales, whereas the latter are consistently associated with volcanic rocks and greywackes in greenstone belts. All BIFs have experienced some form of diagenetic and/or metamorphic overprinting (Klein, 2005), which makes it challenging to unambiguously reconstruct the precise depositional setting and the paleoenvironment in which the iron-bearing minerals originally precipitated.

Despite decades of research, many fundamental questions about the origin of BIFs remain unanswered and highly debated. However, some common concepts recur in most of the proposed hypotheses. It is commonly thought that, during the period of BIFs deposition, the oceans (at least at depth) were anoxic, and thus capable of transporting and accumulating dissolved ferrous iron (Cloud, 1968; Holland, 1973). The latter may have been oxidized to solid-phase iron oxyhydroxides through either biological (oxygenic or anoxygenic photosynthesis) or nonbiological (ultraviolet photo-oxidation) processes (Bekker et al., 2014). Alternatively, direct precipitation under anoxic conditions may have formed Fe-carbonates or mixed valence Fe-silicates. Based on REE distributions, it has been proposed that Fe and Si in most BIFs derive from hydrothermal sources (Holland, 1973; Bau and Möller, 1993; Morris and Horwitz, 1983), although Hamade et al. (2003) used Ge/Si ratios in BIFs to postulate a continental source for silica.

This study focuses on the Bikoula BIF, an Algoma-type iron formation hosted in the Mesoarchean Ntem complex, which constitutes the northwestern edge of the Congo craton (Maurizot et al., 1986). Several greenstone belt occurrences hosting BIFs of economic importance have been identified in the Ntem complex (Maurizot et al., 1986). However, previous studies of BIFs in this region exclusively focused on weathered BIFs that crop out at the surface (Lerouge et al., 2006; Suh et al., 2008, 2009; Nforba et al., 2011; Ilouga et al., 2013; Chombong et al., 2013; Anderson et al., 2014; Ganno et al., 2015, 2016), where weathering makes it difficult to reliably understand their petrogenesis. Here, we present the first petrographic and geochemical data on unweathered BIF and cross-cutting rocks of the Ntem complex, which were collected in the framework of a drilling project named the Bikoula Iron Ore Project (Aluvance Plc, 2014). The presented data are compared, discussed and interpreted with regard to previous studies of BIFs.

2. Geological setting

2.1. Regional geology

The Ntem complex corresponds to the northwestern border of the Congo craton in Southern Cameroon (Maurizot et al., 1986). It is bounded to the north by the Yaoundé Group which belongs to the Pan-African orogenic belt in Central Africa (Nédélec et al., 1986; Nzenti et al., 1988). The Ntem complex has been subdivided into three units: Ntem, Nyong and Ayna.

The Ntem unit contains the Bikoula BIF (Fig. 1) and comprises an intrusive series, a banded series and greenstone belts (Maurizot et al., 1986; Pouclet et al., 2007). The intrusive series occurs in the northern part and consists dominantly of magmatic charnockitic suite and TTG (Tonalite-Trondjemite-Granodiorite) suite (Pouclet et al., 2007). The banded series is represented by highly deformed granulitic gneisses (leptynites, enderbergites, granitic gneisses and charnockitic gneisses) that are distributed over the southern part of the Ntem unit (Maurizot et al., 1986; Takam et al., 2009).

Greenstones in the Ntem unit occur as disrupted belts and as xenoliths in the intrusive series, indicating an older age for their formation (Shang et al., 2004a, 2007). These supracrustal rocks consist of BIFs, metagraywackes, sillimanite-bearing paragneisses, garnet-bearing amphibolites and pyroxenites (Shang et al., 2004a; Tchameni et al., 2010). They were affected by granulite-facies metamorphism with estimated peak temperatures of 750 ± 50 °C at 5 – 6 kbar (Tchameni, 1997; Tchameni et al., 2001). Emplacement of the greenstone belts in the Ntem unit has been dated at ca. 3.1 Ga using the Pb-Pb zircon evaporation technique (Tchameni et al., 2004). Greenstone belts are highly dismembered and cross-cut by late syenitic plutons and doleritic veins (Tchameni et al., 2001).

The Ntem complex was affected by two major periods of deformation. The first involves successive diapiric emplacements of the Mesoarchean charnockites (~ 2.900 Ma) and TTGs (~ 2830 Ma). It is marked by vertical foliation and lineation, stretching and isoclinal folds (Shang et al., 2004a). This episode of deformation was synchronous with a regional granulite-facies metamorphism (Tchameni, 1997). This Archean event was followed, in the Paleoproterozoic, by a transcurrent deformation phase marked by the development of N-S to NE-SW trending sinistral shear zones and partial melting of the TTG suite and the greenstone belt country rocks, with generation of a variety of granites (Shang et al., 2007). Late syenitic plutons (~ 2.3 Ga) intruded the complex during this second tectonic episode (Tchameni et al., 2001). The Eburnean metamorphism affected all the Archean and Paleoproterozoic formations and was dated at ~ 2.05 Ga (Toteu et al., 1994).

2.2. Local geology and stratigraphy

In the Bikoula region, the BIF ore bodies occur in roughly NW-SE direction with steep dips 50–80° to the SW or NE (Fig. 2). The main ore body is ~0.5 km in width and extends ~4.8 km along strike. The country rocks in the Bikoula area are pyroxene-bearing granitoids (charnockites) of various orientations. Observations at outcrops typically reveal highly weathered BIF with characteristic light (silica) bands alternating with dark (iron oxide) bands (Fig. 3). Analysis of remote sensing data revealed E-W and NE-SW trending faults/shear zones that affected both ore bodies and country rocks, resulting in mylonitic structures observed in many outcrops.

A vertical drill core (BKLD030), of ~133.8 m deep, through the central part of the main ore body (Fig. 2) was chosen for this study. It comprises various iron ore formations cross-cut by syenitic veins (Fig. 4). The lower part of the core comprises unweathered BIF which grades upwards into partly oxidized and altered sheared BIF. The uppermost part of the sheared BIF has been affected by weathering and oxidation processes resulting in a sheared oxidized BIF. Close to the topographic surface, intense weathering and erosional processes prevailed and generated supergene high-grade ores namely the soft saprolitic and detrital ores. Because the middle and upper parts of the core were affected by secondary enrichment through intensive shearing and weathering processes, the present study exclusively focuses on the unweathered lower part of the drill core.

3. Sampling and analytical procedures

Samples were selected from a split diamond core and were then halved using a core cutting machine (quarter thickness of the whole original core). The length of samples was variable depending on the scale of banding, the compositional homogeneity and the thickness of individual rock units. From the sampled quarter, polished thin sections were cut perpendicular to the banding and the remainder of the core was crushed for geochemical analyses. A total of 12 unweathered BIF samples and 11 of the syenites were collected for petrographic and geochemical investigations (Fig. 4).

Detailed petrographic observations were undertaken using transmitted and reflected light microscopy on polished thin sections at ETH Zurich, Switzerland, where a JEOL JXA-8200 electron microprobe analyzer was utilized for mineral analyses. Natural and artificial silicates and oxides were used as standards. An acceleration voltage of 15 kV was used, along with 20 nA beam current and 20 μm beam diameter. Measuring time on the peak was 40 seconds, with 10 seconds on the background. The detection limit was approximately 0.01 wt.% for major and minor elements, and relative measurement errors did not exceed 1%. A Jeol JSM-6390 LA scanning electron microscope (SEM), equipped with a secondary electron (SE) and a backscatter electron detector (BSE), was used to examine textural relationships of extremely fine mineral phases.

Major element concentrations in BIF samples were analyzed using an Axios FAST X-ray fluorescence spectrometer with an RSD (Relative Standard Deviation) < 5% at the ALS laboratory (Ireland), and in the syenites with a wavelength dispersive X-ray fluorescence spectrometer (WD-XRF, PANalytical AXIOS) at ETH Zurich. Trace element analyses of BIF samples were performed using an ICP-MS (Element, Finnigan MAT) at ETH Zurich. Rare earth elements were acquired using a ThermoFisher XSeries 2 ICP-MS at University of Southampton. The RSD was < 2.5% for the trace and REE analyses.

4. Petrography

4.1. BIF

At the mesoscopic scale, BIF shows a conspicuous banding (Fig. 5a). Banding is generally irregular in thickness and obliterated in places. The BIF is generally characterized by intercalated quartz-rich grey-white and magnetite-rich dark bands or laminae. Between these bands (i.e. light and dark bands), a pyroxene-rich greenish brown layer often occurs, imparting a greenish coloration to the BIF. Contacts between the laminae are usually diffuse. The magnetite-rich and pyroxene-rich bands are highly magnetic. The main minerals are quartz (30 – 40 vol.%), magnetite (30 – 50 vol.%) and pyroxene (20 – 30 vol.%), with smaller amounts of plagioclase, amphibole, biotite, ilmenite and sulfides.

4.1.1. Quartz

Quartz occurs as aggregates in quartz-rich bands or individual grains within the magnetite- and pyroxene-rich bands, and is often found as inclusions in grains of pyroxene (Fig. 5b). In these bands, quartz occurs as anhedral, up to 2.5 mm in size, slightly elongated grains with moderate preferred orientation (Figs. 5c–d). Quartz is often intermixed with magnetite and pyroxene, resulting in a weaker banding of the BIF. Many quartz grains exhibit inequigranular interlobate texture, display undulose extinction and embayed to amoeboid grain boundaries. Larger grains commonly show patchy extinction resulting from the coalescence of smaller subgrains. All these deformational features are suggestive of dynamic recrystallization.

4.1.2. Pyroxene

Pyroxene occurs as orthopyroxene and clinopyroxene in approximately equal proportions. Orthopyroxene is brownish in color, anhedral to subhedral, and forms bands of variable thickness that appear to alternate with quartz and magnetite bands (Fig. 5b). The orthopyroxene bands range from 1.5 to 2 mm in thickness and are not continuous, often cross-cut by magnetite or quartz. Most orthopyroxene occurs as medium to coarse grains up to 4 mm in length and 2.4 mm wide and often show preferred orientation. The large grains contain inclusions of clinopyroxene, magnetite and sulfides. Grain boundaries are generally embayed to smoothly curved against other minerals. Smaller crystals can be found associated with both the magnetite and quartz-rich laminae. Exsolution lamellae of clinopyroxene as well as deformation twins are clearly visible in many grains (Fig. 5d).

Clinopyroxene is noticeably smaller, reaching 1.5 mm in length for the larger grains, and occurs as anhedral to subhedral crystals. In thin section, grains appear scattered, are commonly in contact with magnetite and orthopyroxene bands, and display a preferred orientation in places. Clinopyroxene is pale green, non pleochroic, with yellow-orange to blue-purple interference colors, and exhibits straight to curved grain outlines (Fig. 5d). Some clinopyroxene crystals display simple twinning. Extremely fine orthopyroxene exsolution lamellae are common in many crystals. Two generations of clinopyroxene occur, the first as porphyroblasts containing exsolution lamellae of orthopyroxene (Fig. 5d) and the second as small anhedral crystals in large cracks of orthopyroxene megacrysts (Fig. 5e).

4.1.3. Magnetite

Magnetite, the main iron mineral of the Bikoula BIF, occurs in 1.5–3.5 mm thick bands. Within the magnetite-rich layers, magnetite exhibits a texture consisting of continuously interlocking grains (Figs. 6a–b). Fe-rich layers display many cracks where magnetite is often partially replaced by pyrite (Fig. 6c). In quartz and pyroxene bands, magnetite grains are subhedral to euhedral in shape, and may be distributed rather uniformly, or interconnected to form aggregates of various configurations (see Fig. 5b). Grain boundaries shared with the other minerals are straight to smoothly curved. Magnetite is also found as inclusions or in contact with grains of quartz and pyroxene.

4.1.4. Minor mineral phases

Sulfides in the Bikoula BIF comprise pyrite, pyrrhotite and subordinate chalcopyrite. Pyrite occurs as subhedral to euhedral crystals interstitial to magnetite and pyroxene, and displays straight to smoothly curved contacts with the latter two minerals (Fig. 6a). Pyrite grains are irregularly shaped with a random arrangement, and may range up to 0.5 mm in size. Most pyrite crystals are partially to completely replaced by pyrrhotite (Figs. 6c–d), indicating sulphur release during progressive metamorphism (Craig and Vokes, 1993). Pyrite often contains very fine inclusions of chalcopyrite and magnetite. Chalcopyrite grains are anhedral to subhedral, $\leq$ 20 µm in size, and commonly associated with pyrite (Fig. 6d).

Plagioclase occurs as anhedral to subhedral grains, up to 4 mm, that display undulose extinction (Figs. 6e–f). It often contains minute inclusions of magnetite. Amphibole forms strongly pleochroic greenish to brownish colored individual crystals. Mineral grains present vary from anhedral to subhedral and reach up to 2.8 mm in size. Locally, the mineral is slightly altered to Fe-rich biotite (Fig. 6e), and often contains inclusions of magnetite and plagioclase. Biotite occurs mostly as aggregates that are bent or kinked, presumably due to tectonic overprint. Crystals are anhedral to subhedral in shape, and may reach up to 1.6 mm in length. Some biotite grains are altered to iron-rich biotite (Figs. 6e–f). Ilmenite and ulvöspinel mainly occur as lamellae in magnetite grains (Fig. 6b). Ilmenite also forms typically ≤ 0.3 mm individual anhedral grains that are associated with magnetite.

4.2. Syenites

Syenites (Fig. 7a) are medium- to coarse-grained, grey, and are composed of microcline (80-90%), plagioclase (3-5%), quartz (2-3%), clinopyroxene (1-3%), magnetite (1-2%), biotite (1%) and apatite (1%). Accessory phases include ilmenite, pyrite and chalcopyrite. The rock appears highly strained and recrystallized, mostly along microcline grain margins due to metamorphism (Figs. 7b–d). Microcline occurs as anhedral, up to 8 mm in length, perthitic grains with a weak to strong preferred orientation (Figs. 7b–c). Crystals display cross-hatched twins and, in general, embayment at the grain boundaries. Potassium feldspar crystals are partially sericitized and host inclusions of magnetite and apatite.

Albite phenocrysts, up to 8 mm in size, are commonly anhedral to subhedral with straight to curved grain outlines, and display undulose extinction (Fig. 7d). Plagioclase microcrystals and quartz with rare K-feldspar crystals, typically ≤ 0.1 mm in size, make up the fine-grained recrystallized groundmass (Fig. 7e). In the groundmass, quartz is less abundant than plagioclase. Quartz occurs as anhedral grains that show undulose extinction, commonly embayed crystal boundaries and rare inclusions of plagioclase and potassium feldspar. Quartz also fills micro-veinlets that traverse microcline or albite phenocrysts (Fig. 7d).

Mafic phases are smaller in size relative to K-feldspar crystals. Clinopyroxene occurs mainly as subhedral to euhedral grains up to 1.7 mm in length, most of which are isolated and preferentially oriented (Fig. 7c). These grains are usually interstitial between felsic minerals and rarely occur as inclusions in alkali feldspar megacrysts. The mineral commonly exhibits sharp and straight to smoothly curved grain boundaries with other minerals and is sometimes partially altered to anhedral amphibole, chlorite and/or biotite (Figs. 7f–h).

Biotite is present as fine-grained (< 0.5 mm in length), subhedral, pleochroic green to brownish flakes partly altered to chlorite (Fig. 7f). These flakes appear as interstitial isolated crystals with random orientation and rarely cluster to form aggregates. Biotite often overgrows or partly replaces clinopyroxene (Figs. 7f and 7i). It commonly shows straight to curved grain boundaries. All these replacement textures can be ascribed to local manifestations of a metamorphic overprint.

Magnetite and ilmenite form decussate aggregates, often slightly elongated, that are oriented approximately in the same direction as K-feldspar or pyroxene (Fig. 7j). They also occur as individual grains within the rock matrix. Crystals are subhedral to euheudral in shape and may reach up to 0.3 mm and 0.5 mm in length for magnetite and ilmenite, respectively. Apatite (0.02 to 0.4 mm in length) forms tiny hexagonal, rounded or rectangular grains that usually occur as inclusions in alkali feldspar, magnetite and pyroxene, or sometimes as isolated crystals. Pyrite and chalcopyrite were observed within the groundmass of the syenites or as inclusions in pyroxene.

5. Geochemistry

5.1. Mineral chemistry

5.1.1. Magnetite

Electron microprobe analyses of magnetite in the Bikoula BIF show that the magnetite has total iron content (expressed as FeO_t) between 92.06 and 93.98 % (Table 1). In contrast to magnetite from typical BIFs found in other regions worldwide (Dupuis and Beaudoin, 2011), it has high Al_2O_3 (0.18 to 0.59 %, average 0.34 %) and TiO_2 (0.09 to 0.56 %, average 0.21 %). In syenites (Appendix A.1), magnetite shows FeO_t content as high as in BIF (average 92.99 %), but is highly depleted in all the other elements.

5.1.2. Clinopyroxene

Clinopyroxene in syenites is diopsidic in composition (~$Wo_{40-42}En_{27-28}Fs_{19-22}$) with minor aegirine and jadeite component (~3.4–8.7 and ~0–4.3 mol.%, respectively) and has X_{Fe} ($Fe^{2+}/Mg+Fe^{2+}$) of ~0.41–0.45 (Fig. 8a, Appendix A.2). Clinopyroxene in the BIF is more iron rich and reaches less calcic and sodic compositions (Appendix B.1, Fig. 8a). The composition ranges from diopside (~$Wo_{43}En_{28}Fs_{29}$) to augite (~$Wo_{37}En_{26}Fs_{22}$) and with lower aegirine and jadeite contents (~3.6–7.1 and ~0–1.2 mol.%, respectively) and more FeO_t (X_{Fe} ~0.46 – 0.51) compared to the clinopyroxene in syenites.

5.1.3. Orthopyroxene

Orthopyroxene electron probe microanalyses are tabulated in Appendix B.2. Compared to the clinopyroxenes, the orthopyroxene is more iron-rich ($Wo_{1.2-1.6}En_{34-36}Fs_{59-62}$) (Fig. 8a) with significant concentrations of CaO and MnO (0.58 – 0.75 % and 1.23 – 1.55 %, respectively). Orthopyroxene grains have low Al_2O_3 and Cr_2O_3 contents (< 0.19 %) and high X_{Fe} (> 0.6).

5.1.4. Amphibole

The calculation of crystal formula for amphiboles shows the following characteristics: $(Ca+Na)_B = 1.597–1.789$ (≥ 1); $Ca_B = 1.597–1.789$ (≥ 1.5); Si = 6.341–6.470; Ti = 0.112–0.137 (< 0.5); $(Na+K)_A = 0.910–0.999$ (≥ 0.5) and Mg# = 0.455–0.471 (Appendix B.3). According to the international nomenclature of amphiboles (Leake et al., 1997), it classifies as ferro-pargasite (Fig. 8b), a member of the calcic group of amphiboles.

5.1.5. Feldspar

Feldspar in the syenites (Appendices A.3 and A.4) is dominated by perthitic microcline (orthoclase > 96 %) exsolving albite (An = 5.4–8.6 %). Feldspar in the BIF is a plagioclase of oligoclase composition (An = 17.0–19.7 %) and relatively homogeneous in chemical composition (Appendix B.4).

5.1.6. Biotite

In the BIF, biotite is characterized by X_{Fe} = 0.452–0.487, Al^{IV} = 1.076–1.120, Mg# = 0.513–0.548 and Ti = 0.216–0.256 (Appendix B.5). Alteration-type biotite shows higher iron contents and is depleted in TiO_2.

5.1.7. Ilmenite

Major element analyses for ilmenite show TiO_2 of 50.17 – 51.32 % in syenites and of 51.06 – 52.05 % in BIF (Appendices A.5 and B.6). Ilmenite in BIF has lower FeO_t than ilmenite in syenites (average 40.88 % compared to 43.83 %, respectively), while average MnO is higher (7.02 % in BIF compared to 4.38 % in syenites).

5.2. Bulk rock geochemistry

5.2.1. BIF

Major and trace element data of the BIF samples are listed in Table 2. The Fe_2O_3 content varies from 42.79 to 57.89 wt.% (average 49.97 wt.%), SiO_2 32.3 to 42 wt.% (average 37.77 wt.%) and Al_2O_3 0.76 to 7.52 wt.% (average 2.88 wt.%) (Table 2). The contents of other major oxides are also quite significant, i.e. CaO 1.95 – 4.90 wt.%, K_2O 0.13 – 1.96 wt.%, Na_2O 0.19

– 2.05 wt.% and MgO 3.78 – 5.59 wt.%. The BIF is also characterized by low contents of TiO_2 (0.11 – 0.88 wt.%), MnO (0.39 – 0.56 wt.%) and P_2O_5 (0.09 – 0.13 wt.%).

Variations in some transition elements are as follows; V 7.58 – 49.56 ppm, Cr 8 – 225.67 ppm, Ni 5.05 – 84.63 ppm, Cu 3.07 – 32.27 ppm and Zn 55.32 – 150.71 ppm. Among the High Field Strength Elements (HFSE), Y, Zr and Sc vary from 10.99 – 28.99 ppm, 7.44 – 111.46 ppm and 0.78 – 6.19 ppm, respectively (Table 2). The contents of Large Ion Lithophile Elements (LILE; Rollinson, 1993) Rb, Sr and Ba vary from 5.09 to 153.73 ppm, 21.45 to 210.09 ppm and 16.82 to 200.46 ppm, respectively. Mo abundances are low (< 6 ppm, Table 2) as expected in older BIFs (Stern et al., 2013; Scott et al., 2008).

Samples analyzed from the Bikoula BIF show variable REE contents with ΣREE ranging from 8.90 to 111.54 ppm (Table 2). All the samples are characterized by high LREE relative to HREE (LREE/HREE ranges from 5.06 and 19.69). PAAS-normalized REE-Y patterns (Fig. 9) show depletion of LREE ($La/Yb_{PAAS} < 1$) except in one sample (i.e. sample L271), strong positive Y anomalies ($Y/Y^*_{PAAS} = 0.98 – 6.25$) and weak negative Ce anomalies ($Ce/Ce^*_{PAAS} = 0.85 – 0.99$). Of the twelve BIF samples analyzed, five display strongly positive Eu anomalies ($Eu/Eu^*_{PAAS} = 1.19 – 3.45$), another five display slightly negative Eu anomalies (0.58 – 0.86) while two do not show any anomaly (samples L273 and L282).

5.2.2. Syenites

Whole-rock compositions of the studied syenites are presented in Table 3. SiO_2 contents range from 58.29 to 65.73 wt.%, Al_2O_3 15.29 to 18.91 wt.% and Fe_2O_3 1.15 to 7.82 wt.%. K_2O and Na_2O contents are relatively high and similar, both varying between 4.83 and 7.07 wt.% (Table 3). There are significant contents of CaO (0.76 – 3.30 wt.%; average 1.59 wt.%) and MgO (0.22 – 1.32 wt.%; average 0.69 wt.%). Other major oxide components are minor in abundance, namely TiO_2 (0.02 – 0.74 wt.%), P_2O_5 (0.03 – 0.50 wt.%) and MnO (0.02 – 0.13

wt.%). On the total alkali (Na_2O+K_2O) vs. silica diagram (Cox et al., 1979), the syenites plot in the alkaline fields (syenite and nepheline syenite fields, Fig. 10).

6. Discussion

6.1. Mineral paragenesis and effects of metamorphism

The major mineral assemblage of the Bikoula BIF is magnetite-quartz-orthopyroxene-clinopyroxene (see Fig. 5). This mineralogy, which was observed in all samples, is characteristic of iron formations that have undergone granulite-facies metamorphism (Klein, 2005). As mentioned in section 2.1, the Ntem complex experienced multiple phases of deformation and metamorphism. Thus, the two generations of clinopyroxene identified in the BIF (see Figs. 5d–e), the presence of secondary biotite (see Figs. 6e–f), and the retrogressive reaction textures in the cross-cutting syenites likely result from multistage metamorphism with regressive post-peak events.

In general, exsolution lamellae in pyroxene occur in many igneous and metamorphic rocks as the result of slow cooling from the highest equilibration temperature. This unmixing phenomenon is usually a fossil indicator of very high temperature prevailing during crystallization. Exsolution lamellae in ortho- and clinopyroxene are commonly reported in high-grade metamorphosed BIFs, resulting either from contact metamorphism (e.g., Bonnischen, 1969, 1975; Vaniman et al., 1980) or regional metamorphism (e.g., Sandiford and Powell, 1986a; Gole and Klein, 1981; Harley, 1987; Bhattacharya et al., 1990; Fonarev et al., 2006). Outcrop observation, petrographic analysis and bulk rock composition have shown that the Bikoula iron occurrences are typical of sedimentary banded iron formations (BIFs). The assemblages of the Bikoula BIF do not have hornfelsic textures. Rather, existing studies exclusively point to a regional high-grade metamorphism that prevailed during or soon after emplacement of charnockite (Toteu et al., 1994; Tchameni et al., 2000; Pouclet et al., 2007).

Thus, despite the close spatial relationship between the greenstones and charnockitic country rocks (see Figs. 1 and 2), the metamorphic assemblages in the Bikoula BIF are most likely not the result of contact metamorphism. The peak of the regional metamorphism was constrained at 750 °C ± 50 °C and 5 – 6 Kb (Tchameni, 1997). Therefore, exsolution textures in the Bikoula BIF may likely result from a regional granulite-facies metamorphism affecting the greenstones and magmatic rocks of the Ntem complex.

In the currently observable assemblage, magnetite is the dominant Fe-rich mineral of the Bikoula BIF. Due to the high metamorphic degree and the recrystallized habit of the magnetite crystals, it is not possible to precisely link the evolution of this mineral to the primary process of iron precipitation from seawater. As proposed in many models for BIF formation, the primary iron mineral that precipitated directly from seawater was most likely a Fe^{3+} oxyhydroxide, a mixed valence Fe-silicate or a Fe^{2+}-carbonate (e.g., ferrihydrite, greenalite, and siderite) (Fischer and Knoll, 2009). Studies of low grade metamorphosed BIF indicates that such primary minerals commonly transform through a large variety of possible abiotic or microbially mediated process into magnetite, hematite, iron carbonates (siderite and ankerite), and various iron-silicate phases (Posth et al., 2013; Smith et al., 2013; Bontognali et al., 2013). Therefore, the magnetite present in the Bikoula BIF may be a recrystallized diagenetic product or, alternatively, it may have formed during a later metamorphic process during which one of the abovementioned primary or diagenetic phase (e.g., siderite, ankerite, Fe-silicate) was transformed into magnetite.

Fukada et al. (2001) proposed that Ti in magnetite from the Superior-type BIF in the Hamersley basin may have originated from hydrothermal solutions, while Ti in silicates was introduced from terrigenous sources. Such explanation for the origin of Ti may also apply to the Bikoula BIF. Ti may have reacted with magnetite during metamorphism to form a Ti-bearing magnetite. Depending on the oxygen fugacity during the cooling process that followed the peak of metamorphism, some Ti-rich magnetite grains may have been oxidized to ilmenite lamellae while the un-oxidized portions exolved ulvöspinel (Simmons et al., 1974).

Quartz occurs as inclusions in pyroxene, suggesting that it was a phase that crystallized early. Quartz in iron formations is regarded as resulting from recrystallization of initial amorphous silica precipitate (i.e., chert) during metamorphism (Klein, 2005). In the Bikoula BIF, textural analysis revealed that quartz was most likeky dynamically recrystallized through bulging, subgrain rotation and grain boundary migration, suggesting its crystallization during prograde metamorphism (Passchier and Trouw, 2005).

Metamorphic Al-bearing phases in the Bikoula BIF comprise of ferro-pargasite, bitotite and oligoclase. Oligoclase inclusions in ferro-pargasite suggest that the latter crystallized after plagioclase. Ferro-pargasite is considered as the product of the reaction between Al-rich clastic material in the BIF and a Ca-Mg-Fe bearing silicate precursor during prograde metamorphism (Wang et al., 2014).

Banding in iron formations may exist on a range of scales: macrobands (meter thick rock types), mesobands (centimeter in thickness) and microbands (millimeter to sub-millimeter) (Trendall and Blockley, 1970). Explanations for banding in BIF include microbial blooms (Trendall and Blockey, 1970), silica precipitation interrupted by pulses of Fe-rich waters (Hamade et al., 2003), density flow deposition (Lascelles, 2007), temperature fluctuation in the oceanic photic zone (Posth et al., 2008), internal dynamics of the geochemical system (Wang et al., 2009), and episodic re-sedimentation of Fe-silicates alternating with periods of non-deposition (Rasmussen et al., 2013). Due to the extensive recrystallization that occurred during metamorphism, it would be too speculative to propose any hypothesis regarding the origin of banding in the Bikoula BIF. In the studied core, it is even difficult to conclude whether some of the laminations correspond to primary sedimentary layers or represent a banding of purely metamorphic origin.

6.2. Detrital input into BIF

Banded iron formations have long been considered as chemically precipitated sediments. However, many authors agree that, in several cases, precipitation and accumulation of chemical sediments was influenced by the simultaneous deposition of detrital components (Arora et al., 1995; Horstmann and Hälbich, 1995; Basta et al., 2011; Kato et al., 1996; Bolhar et al., 2005b; Sunder Raju, 2009). Elevated Al_2O_3 and TiO_2 are considered as indicators of detrital influx during BIF deposition. Similarly, Si, Mg, Ca and K are thought to be commonly present in detrital sediments (Hatton and Davidson, 2004). Thus, the relatively high abundance of Al_2O_3 (0.76 – 7.52 wt.%), TiO_2 (0.11 – 0.88 wt.%), MgO (3.78 – 5.59 wt.%), CaO (1.95 – 4.90 wt.%), K_2O (0.13 – 1.96 wt.%) and Na_2O (0.19 – 2.05 wt.%) suggest detrital influx during deposition of the Bikoula BIF. Furthermore, Al_2O_3 and TiO_2 vary sympathetically, with a correlation coefficient $R^2 = 0.34$ (see Table 4), suggesting incorporation of detrital components to the chemical precipitate (González et al., 2009; Pecoits et al., 2009; Lan et al., 2014). Clastic contamination of the Bikoula BIF is further supported by a plot of Y/P_2O_5 as a function Zr/Cr (Marchig et al., 1982). On this diagram, the samples plot either in the deep-sea sediment field or between the latter and the hydrothermal field (Fig. 11).

Trace elements such as Zr, Hf, Y, Rb and Sr are commonly derived from weathering of crustal felsic rocks, whereas Cr, Ni, Co, V and Sc commonly have a mafic source (Rao and Naqvi, 1995). Table 4 displays significant positive correlations of Al_2O_3 with LILEs, HFSEs and transition metals. The correlation coefficients (R^2) are: Al_2O_3 vs. V ($R^2 = 0.50$), vs. Ni (0.39), vs. Zn (0.42), vs. Sc (0.44), vs. Y (0.41), vs. Zr (0.53), vs. Th (0.65), vs. U (0.58), vs. Pb (0.97), vs. Rb (0.73), vs. Sr (0.41) and vs. Ba (0.46) (Table 4). All these relationships may indicate involvement of clastic materials and further suggest that this detritus might have been derived from weathering of both felsic and mafic (bimodal) sources.

The Th/U ratio can also be used to trace the sources of contaminants in BIF. Possible syn-depositional contaminants of iron formations include volcanic ash, sedimentary detritus and material of uncertain origin such as phosphate grains (Thurston et al., 2012). Phosphate contamination is generally associated to a Th/U > 5 (Thurston et al., 2012), while other contaminants (i.e. clastic or volcanic) have Th/U ratios of ca. 3 – 5 (Condie, 1993; Thurston et al., 2012). Thus, the incorporation of phosphates in iron formation raises the Th/U ratio. In the Bikoula BIF samples, the Th/U ratio lies between 2.93 and 6.92 (average 4.44), indicating little or no phosphate contamination. Zr contents vary sympathetically with the Th/U ratios (R^2 = 0.61, Table 4), consistently with clastic contamination.

6.3. Sources of chemical components

Several discrimination diagrams have been used by many workers to constrain the influence of seawater, hydrothermal, biologic and detrital sources on BIF genesis (e.g., Wonder et al., 1988; Stern et al., 2013; Xu et al., 2014). On the Fe-Mn-Al diagram (Bonatti et al., 1979), the Bikoula BIF samples fall in the hydrothermal field (Fig. 12). Similarly, the Al_2O_3-SiO_2 discrimination diagram (Wonder et al., 1988) shows that most of the BIF samples plot in the hydrothermal field (Fig. 13). This may indicate that Si and Fe were likely derived from hydrothermal sources. However, two samples plot in the hydrogenous field (Fig. 13), suggesting chemical precipitation from seawater with insignificant hydrothermal input. The seawater input is also suggested by the low CaO/(CaO+MgO) ratios ranging from 0.31 to 0.53 (Table 2), indicative of sediments that precipitated from seawater (Dasgupta et al., 1999).

Bostrom (1973) described a method for assessing dilution by clastic or volcanic detritus of hydrothermal/hydrogenous input and proposed a plot of Fe/Ti versus Al/(Al+Fe+Mn) to quantify the hydrothermal input relative to the detrital component. Aluminum and titanium cannot be introduced in solution (Ewers and Morris, 1981) and are immobile during hydrothermal, diagenetic and weathering processes (Kato et al., 1996). These two elements can thus be used as proxies to quantify clastic input. Fe and Mn are enriched in components of hydrothermal fluids (Gurvich, 2006), and therefore serve as hydrothermal proxies. Pure hydrothermal sediments are characterized by high Fe/Ti ratio (> 7000) while pure clastic sediments are enriched in Al resulting in Al/(Al+Fe+Mn) > 0.6 (Peter and Goodfellow, 1996; Hatton and Davidson, 2004). On the Al/(Al+Fe+Mn) diagram of Bostrom (1973), the Bikoula BIF samples plot within or close to the field of hydrothermal Soldier Cap Group iron formations (Hatton and Davidson, 2004) and far from the region occupied by modern pelagic-terrigenous sediments (Fig. 14). Figure 14 also suggests quite significant contribution of hydrothermal processes (over 70 vol.%) to the deposition of the Bikoula BIF.

Positive correlations between Al_2O_3 or TiO_2 versus Na_2O, K_2O, MgO and CaO (see Table 4) suggest a common origin for these elements, which were likely present in detrital particles.

Measurements of rare earth elements (REE) in BIFs have often been used to infer the chemical evolution of early oceans and, in particular, to detect the influx of submarine hydrothermal emanations within the basin-waters from where BIFs were precipitated (Derry and Jacobsen, 1990; Bau and Möller, 1993; Kato et al., 1998). Indeed, REE are only minimally fractionated during adsorption onto ferric iron oxyhydroxides precipitates (Bekker et al., 2014) and, due to closed-system conditions for the REE and low fluid/rock ratios, the REE distribution is usually not affected in BIFs that have undergone low- to high-grade regional or contact metamorphism (Bau, 1993). Petrographic analyses suggest that the Bikoula BIF samples studied have experienced high-grade metamorphism with only minor infiltration metasomatism and, therefore, may record quite original REE signals. PAAS-normalized REE-Y patterns (Fig.

9) show that some BIF samples have preserved seawater-like features such as LREE depletion, and positive La and Y anomalies (Alibo and Nozaki, 1999; Bolhar et al., 2004), which points to precipitation from seawater.

Positive Eu anomalies in BIFs have been interpreted as evidence that submarine hydrothermal fluids –that may be source not only of the REE but also of Fe and Si– were important component of the solution from where the Fe-minerals were precipitated (Derry and Jacobsen, 1990; Slack et al., 2007). In the Bikoula BIF, five samples display positive Eu anomalies ($Eu/Eu*_{PAAS}$ = 1.19 – 3.45), pointing to fluxes of high-temperature (> 350°C) hydrothermal fluids. However, seven samples display no or weakly negative Eu anomalies (Fig. 9). The negative Eu anomaly (rarely seen in BIFs) suggests that REE patterns in the Bikoula BIF were also influenced by the heterogeneous input of clastic materials within the depositional basin (Arora et al., 1995; Manikyamba et al., 1993; Manikyamba and Naqvi, 1997b).

Dymek and Klein (1988) and subsequently Alexander et al. (2008) introduced conservative two component mixing diagrams to assess the proportions of seawater and high-*T* hydrothermal fluids. According to the Sm/Yb-Eu/Sm and Y/Ho-Eu/Sm diagrams (Figs. 15a and b, respectively), extremely small amounts of submarine high-*T* hydrothermal fluids (< 0.1 %) were enough to cause positive Eu anomalies in the Bikoula BIF. Therefore, as observed in other BIFs, it can be deduced that relatively small inputs of high-*T* hydrothermal fluids may have been sufficient to account for REE-Y distribution in the Bikoula BIF.

6.4. Redox state of ocean water at the time of the Bikoula BIF deposition

Ce concentrations in BIFs provide information helpful for constraining paleoredox conditions of ancient seawater. In general, modern oxygenated marine settings show a strong negative Ce anomaly when normalized to shale compositions. This arises from the oxidation of Ce^{3+} to Ce^{4+} and incorporation into Fe-Mn oxyhydroxides, clay particles and organic matter

(Byrne and Sholkovitz, 1996). In contrast, suboxic and anoxic marine waters lack large Ce anomalies as a result of reductive dissolution of the Fe-Mn particles (German et al., 1991). However, it can be challenging to identify Ce anomalies because of anomalous abundances of La. Bau and Dulski (1996) proposed a discrimination diagram that compares $(Ce/Ce^*)_{SN}$ calculated as $Ce_{SN}/(0.5La_{SN} + 0.5Pr_{SN})$ to $(Pr/Pr^*)_{SN}$ calculated as $Pr_{SN}/(0.5Ce_{SN} + 0.5Nd_{SN})$ to identify ‘’real’’ La and Ce anomalies in BIFs. As it is the case with other Archean and early Paleoproterozoic BIFs (Planavsky et al., 2010), the Bikoula BIF samples lack negative Ce anomalies (Fig. 16). The lack of evidence for Ce oxidation (implying that the reservoir of Fe^{2+} is not fully oxidized) is consistent and supports the commonly held view that, during the Mesoarchean, oceans were (at least partly) anoxic or suboxic, allowing for the transport and accumulation of Fe^{2+} (Lyon et al., 2014). Under these conditions, various mechanisms may have caused the progressive mineralization of the Fe^{2+} reservoir, leading to the formation of the Bikoula BIF, including: oxidation with O_2 produced by photosynthetic microbes or oxidation through abiotic photochemical reactions (Cairns-Smith, 1978), microbial oxidation through anoxygenic photosynthesis (Widdel et al., 1993), or even through direct precipitation from anoxic seawater as ferrous or mixed valences minerals (e.g., siderite, iron-rich clay minerals) (Rasmussen et al., 2014).

Conclusion

The Bikoula BIF is located within the Mesoarchean Ntem complex, South Cameroon, and it is included in a ~3.1 Ga greenstone belt hosted by charnockitic granites. The BIF sequence is locally cross-cut by late syenitic veins.

Petrographic analysis revealed that the BIF mainly consists of magnetite, quartz, orthopyroxene and clinopyroxene. BIF suffered high-grade metamorphism that caused intense recrystallization of precursor precipitates. The presence of minor amounts of Al-rich phases (ferro-pargasite, biotite and oligoclase) and high contents of Al_2O_3, TiO_2, Na_2O, K_2O, MgO and CaO suggest that the primary chemical precipitate was contaminated by a significant amount of clastic material.

REE-Y patterns of the Bikoula BIF display positive Eu anomaly, which indicates that seawater from which the BIF precipitated was influenced by hydrothermal solutions. In some samples, Eu anomalies are very low or even slightly negative, likely as the result of variable amount of clastic contamination. Finally, the lack of Ce anomalies in the studied BIF suggests that its deposition occurred in a basin that was not fully oxic (i.e., at least partly anoxic or suboxic), where it was possible to transport and concentrate dissolved Fe^{2+}.

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References

Alexander, B.W., Bau, M., Andersson, P., Dulski, P., 2008. Continentally-derived solutes in shallow Archean seawater: rare earth element and Nd isotope evidence in iron formation from the 2.9 Ga Pongola Supergroup, South Africa. Geochim. Cosmochim. Acta 72, 378–394.

Alibo, D.S., Nozaki, Y., 1999. Rare earth elements in seawater: particle association, shale-normalization, and Ce oxidation. Geochim. Cosmochim. Acta 63, 363–372.

Aluvance Plc, 2014. http://aluvance.com/ (Accessed 15 October 2014).

Anderson, K.F.E., Wall, F., Rollinson, G.K., Moon, C.J., 2014. Quantitative mineralogical and chemical assessment of the Nkout iron ore deposit, Southern Cameroon. Ore Geol. Rev. 62, 25–39.

Arora, M., Govil, P., Charan, S., Uday Raj, B., Balaram, V., Manikyamba, C., Chatterjee, A., Naqvi, S., 1995. Geochemistry and origin of Archaean banded iron formation from Bababudan Belt, India. Econ. Geol. 90, 2040–2057.

Basta, F.F., Maurice, A.E., Fontbote, L., Favarger, P.-Y., 2011. Petrology and geochemistry of the banded iron formation (BIF) of Wadi Karim and Um Anab, Eastern Desert, Egypt: implications for the origin of Neoproterozoic BIF. Prec. Res. 187, 277–292.

Bau, M., 1993. Effects of syn- and post-depositional processes on the rare-earth element distribution in Precambrian Iron-formations. Eur. J. Mineral. 5, 257–267.

Bau, M., Dulski, P., 1996. Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron-formations, Transvaal Supergroup, South Africa. Prec. Res. 79, 37–55.

Bau, M., Dulski, P., 1999. Comparing yttrium and rare earths in hydrothermal fluids from the Mid-Atlantic Ridge: implications for Y and REE behaviour during near-vent mixing and for the Y/Ho ratio of Proterozoic seawater. Chem. Geol. 155, 77–90.

Bau, M., Möller, P., 1993. Rare earth element systematics of the chemically precipitated component in early Precambrian iron formations and the evolution of the terrestrial atmosphere–hydrosphere–lithosphere system. Geochim. Cosmochim. Acta 57, 2239–2249.

Bekker, A., Planavsky, N.J., Krapez, B., Rasmussen, B., Hofman, A., Slack, J.F., Rouxel, O.J., Konhauser, K.O., 2014. Iron Formations: Their Origins and Implications for Ancient Seawater Chemistry. In Mackenzie, F.T. (volume ed.), Sediments, Diagenesis and Sedimentary Rocks (Treatise on Geochemistry), Amsterdam: Elsevier, pp. 561–628.

Bhattacharya, A., Spiering, B., Sen, S.K., Natarajan, R., Mazumdar, A.C., 1990. Compositional characteristics and phase equilibria in manganiferous iron formations from a high-grade terrain near Satnuru, Karnataka, India. J. Metam. Geol. 8, 525–538.

Bolhar, R., Kamber, B.S., Moorbath, S., Fedo, C.M., Whitehouse, M.J., 2004. Characterisation of early Archaean chemical sediments by trace element signatures. Earth Planet. Sci. Lett. 222, 43–60.

Bolhar, R., Van Kranendonk, M.J., Kamber, B.S., 2005b. A trace element study of siderite–jasper banded iron formation in the 3.45 Ga Warrawoona Group, Pilbara Craton—Formation from hydrothermal fluids and shallow seawater. Prec. Res. 137, 93–114.

Bonatti, E., Kolla, V., Moore, W.S., Stern, C., 1979. Metallogenesis in marginal basins: Fe-rich basal deposits from the Philippine Sea. Marine Geology 32, 21–37.

Bonnichsen, B., 1969. Metamorphic pyroxenes and amphiboles in the Biwabik iron formation, Dunka River area, Minnesota. Mineral. Soc. Amer. Spec. Pap. 2, 217–239.

Bonnischen, B., 1975. Geology of the Biwabik iron formation, Dunka River area, Minnesota. Econ. Geol. 70, 319–340.

Bontognali, T.R.R., Fischer, W.W., Föllmi, K.B., 2013. Siliciclastic associated banded iron formation from the 3.2 Ga Moodies Group, Barberton Greenstone Belt, South Africa. Prec. Res. 226, 116–124.

Bostrom, K., 1973. The origin and fate of ferromanganoan active ridge sediments. Stockholm Contribution of Geology 27, 149–243.

Byrne, R.H., Sholkovitz, E.R., 1996. Marine chemistry and geochemistry of the lanthanides, in Gschneidner, K.A., Jr., and Eyring, L., eds., Handbook on the physics and chemistry of the rare earths, Volume 23: Amsterdam, Elsevier Ltd., p. 497–593.

Cairns-Smith, A.G., 1978. Precambrian solution photochemistry, inverse segregation, and banded iron formations. Nature 276, 807–808.

Chombong, N.N., Suh, C.E., Ilouga, D.C.I., 2013. New detrital zircon U-Pb ages from BIF-related metasediments in the Ntem Complex (Congo craton) of southern Cameroon, West Africa. Natural Sciences 5 (7), 835–847.

Cloud, P., 1968. Atmospheric and hydrospheric evolution on the primitive Earth. Science 160, 729–736.

Condie, K.C., 1993. Chemical composition and evolution of the upper continental crust; contrasting results from surface samples and shales. Chem. Geol. 104, 1–37.

Cox, K.G., Bell, J.D., Pankhurst, R.J., 1979. The Interpretation of Igneous Rocks. George Allen & Unwin, London, United Kingdom, 445 pp.

Craig, J.R., Vokes, F.M., 1993. The metamorphism of pyrite and pyritic ores: an overview. Mineralogical Magazine 57, 3–18.

Dasgupta, H.C., Sambasiva Rao, V.V., Krishna, C., 1999. Chemical environments of deposition of ancient iron- and manganese-rich sediments and cherts. Sediment. Geol. 125, 83–98.

Derry, L.A., Jacobsen, S.B., 1990. The chemical evolution of Precambrian seawater: Evidence from REEs in banded iron formations. Geochem. Cosmochim. Acta 54, 2965–2977.

Dymek, R.F., Klein, C., 1988. Chemistry, petrology and origin of banded iron-formation lithologies from the 3800 Ma Isua supracrustal belt, West Greenland. Prec. Res. 39, 247–302.

Ewers, W.E., Morris R.C., 1981. Studies of the Dales Gorge Member of the Brockman Iron Formation, Western Australia. Econ. Geol. 76, 1929–1953.

Fischer, W.W., Knoll, A.H., 2009. An iron shuttle for deep-water silica in Late Archean and Early Paleoproterozoic iron formation. Geological Society of America Bulletin 121, 222–235.

Fonarev, V.I., Pilugin, S.M., Savko, K.A., Novikova, M.A., 2006. Exsolution textures of orthopyroxene and clinopyroxene in high-grade BIF of the Voronezh Crystalline Massif: evidence of ultrahigh-temperature metamorphism. J. Metam. Geol. 24, 135–151.

Fukuda, K., Matsunaga, M., Kato, Y., Nakai, I., 2001. Chemical speciation of trace titanium in Hamersley banded iron formations by X-ray fluorescence imaging and xanes analysis. J. Trace Microprobe Tech. 19, 509–519.

Ganno, S., Ngnotue T., Kouankap Nono, G.D., Nzenti, J.P., Notsa, F.M., 2015. Petrology and geochemistry of the banded iron-formations from Ntem complex greenstones belt, Elom area, Southern Cameroon: Implications for the origin and depositional environment. Chem. Erde 75, 375–387.

Ganno, S., Moudioh, C., Nchare, N.A., Kouankap Nono, G.D., Nzenti, J.P., 2016. Geochemical Fingerprint and Iron Ore Potential of the Siliceous Itabirite from Palaeoproterozoic Nyong Series, Zambi Area, Southwestern Cameroon. Resource Geology 66, No. 1, 71–80.

German, C.R., Holliday, B.P., Elderfield, H., 1991. Redox cycling of rare earth elements in the suboxic zone of the Black Sea. Geochim. Cosmochim. Acta 55, 3553–3558.

Gole, M.J., Klein, C., 1981. High-grade metamorphic Archean banded iron-formations, Western Australia: assemblages with coexisting pyroxenes ± fayalite. Am. Mineral. 66, 87–99.

González, P.D., Sato, A.M., Llambías, E.J., Petronilho, L.A., 2009. Petrology and geo-chemistry of the banded iron formation in the Eastern Sierras Pampeanas of San Luis (Argentina): implications for the evolution of the Nogolí Metamorphic Complex. J. S. Am. Earth Sci. 28, 89–112.

Gross, G.A., 1980. A classification of iron formations based on depositional environments. Canadian Mineralogist 18, 215–222.

Gurvich, E.G., 2006. Metalliferous Sediments of the World Ocean: Fundamental Theory of Deep-Sea Hydrothermal Sedimentation. Springer Berlin, 416p.

Hamade, T., Konhauser, K.O., Raiswell, R., Goldsmith, S., Morris, R.C., 2003. Using Ge/Si ratio to decouple iron and silica fluxes in Precambrian banded iron formations. Geology 31, 35–38.

Harley, S.L., 1987. A pyroxene-bearing meta-ironstone and other pyroxene granulites from Tonagh Island, Enderby Land, Antarctica: further evidence for very high temperature (> 980°C) Archean regional metamorphism in the Napier Complex. Journal of Metamorphic Geology 5, 341–356.

Hatton, O., Davidson, G., 2004. Soldiers Cap Group iron-formations, Mt. Isa Inlier, Australia, as windows into the hydrothermal evolution of a base-metal-bearing Proterozoic rift basin. Australian J. Earth Sci. 51, 85–106.

Holland, H.D., 1973. The oceans: a possible source of iron in iron formations. Econ. Geol. 68, 1169–1172.

Horstmann, U.E., Hälbich, I.W., 1995. Chemical composition of banded iron formations of the Griqualand West Sequence, Northern Cape Province, South Africa, in comparison with other Precambrian iron formations. Prec. Res. 72, 109–145.

Ilouga, D.C.I., Suh C.E., Ghogomu, R.T., 2013. Textures and Rare Earth Elements Composition of Banded Iron Formations (BIF) at Njweng Prospect, Mbalam Iron Ore District, Southern Cameroon. International Journal of Geosciences 4, 146–165.

James, H.L., 1954. Sedimentary facies of iron-formation. Econ. Geol. 49, 235–293.

Kato, Y., Kawakami, T., Kano, T., Kunugiza, K., Swamy, N.S., 1996. Rare-earth element geochemistry of banded iron formations and associated amphibolite from the Sargur belts, south India. J. Southeast Asian Earth Sci. 14, 161–164.

Kato, Y., Ohta, I., Tsunematsu, T., Watanabe, Y., Isozaki, Y., Maruyama, S., Imai, N., 1998. Rare earth element variations in mid-Archean banded iron formations: implications for the chemistry of ocean and continent and plate tectonics. Geochim. Cosmochim. Acta 62, 3475–3497.

Klein, C., 2005. Some Precambrian banded iron-formations (BIFs) from around the world: their age, geologic setting, mineralogy, metamorphism, geochemistry, and origins. Am. Mineral. 90, 1473–1499.

Konhauser, K.O., Pecoits, E., Lalonde, S.V., Papineau, D., Nisbet, E.G., Barley, M.E., Arndt, N.T., Zahnle, K., Kamber, B.S., 2009. Oceanic nickel depletion and a methanogen famine before the great oxidation event. Nature 458, 750–753.

Lan, T.G., Fan, H.R., Santosh, M., Hu, F.F., Yang, K.F., Yang, Y.H., Liu, Y.S., 2014. U–Pb zircon chronology, geochemistry and isotopes of the Changyi banded iron formation in eastern Shandong Province: constraints on BIF genesis and implications for Paleoproterozoic tectonic evolution of the North China Craton. Ore Geol. Rev. 56, 472–486.

Lascelles, D.F., 2007. Black smokers and density currents: an uniformitarian model for the genesis of banded iron-formations. Ore Geol. Rev. 32, 381–411.

Leake, B.E., Woolley, A.R., Arps, C.E.S., Birch, W.D., Gilbert, M.C., Grice, J.D., Hawthorne, F.C., Kato, A., Kisch, H.J., Krivovichev, V.G., Linthout, K., Laird, J., Mandarino, J., Maresch, W.V., Nickel, E.H., Rock, N.M.S., Schumacher, J.C., Smith, D.C., Stephenson, N.C.N., Ungaretti, L., Whittaker, E.J.W., Guo, Y.Z., 1997. Nomenclature of amphiboles: report of the subcommittee on amphiboles of the International Mineralogical Association, Commission on New Minerals and Mineral Names. Eur. J. Mineral. 9, 623–651.

Lerouge, C., Cocherie, A., Toteu, S.F., Milesi, J.P., Penaye, J., Tchameni, R., Nsifa, N.E., Fanning, C.M., 2006. SHRIMP U–Pb zircon dating for the Nyong Series, South West Cameroon. J. Afri. Earth Sci. 44, 413–427.

Lyons, T.W., Reinhard, C.T., Planavsky, N.J., 2014. The rise of oxygen in Earth's early ocean and atmosphere. Nature 506, 307–315.

Manikyamba, C., Balaram, V., Naqvi, S.M., 1993. Geochemical signatures of polygenetic origin of a banded iron formation (BIF) of the Archaean Sandur greenstone belt (schist belt) Karnataka nucleus, India. Prec. Res. 61, 137–164.

Manikyamba, C., Naqvi, S.M., 1997b. Mineralogy and geochemistry of Archaean greenstone belt-hosted Mn formations and deposits of the Dharwar Craton: redox potential of proto-oceans. Geological Society Special Publication No. 119, 91–103.

Marchig, V., Gundlach, H., Möller, P., Schley, F., 1982. Some geochemical indicators for discrimination between diagenetic and hydrothermal metalliferous sediments. Mar. Geol. 50, 241–256.

Maurizot, P., Abessolo, A., Feybesse, J.L., Johan Lecomte, P., 1986. Etude de prospection minière du Sud-Ouest Cameroun : Synthèse des travaux de 1978 à 1985. Rapp. BRGM. 85, CMR 066.

Morimoto, N., Fabries, J., Ferguson, A.K., Ginzburg, I.V., Ross, M., Seifert, F.A., Zussman, J., Aoki, K., Gottardi, G., 1989. Nomenclature of pyroxenes. Can. Mineral. 27, 143‑156.

Morris, R.C., Horwitz, R.C., 1983. The origin of the iron-formation-rich Hamersley Group of Western Australia–Deposition on a platform. Prec. Res. 21, 273–297.

Nédélec, A., Macaudière, J., Nzenti, J.P., Barbey, P., 1986. Evolution structurale et métamorphique des schistes de Mbalmayo (Cameroun): implications pour la structure de la zone mobile panafricaine d'Afrique centrale au contact du craton du Congo. C. R. Acad. Sci., Paris, Tome 303 (Série II 1), 75–80.

Nforba, M.T., Kabeyene, V.K., Suh, C.E., 2011. Regolith Geochemistry and Mineralogy of the Mbalam Itabirite-Hosted Iron Ore District, South Eastern Cameroon. Open Journal of Geology 1, 17–36.

Nzenti, J.P., Barbey, P., Macaudière, J., Soba, D., 1988. Origin and evolution of the late Precambrian high grade Yaoundé gneisses (Cameroon). Prec. Res. 38, 91–109.

Passchier, C.W., Trouw, R.A.J., 2005. Microtectonics, second ed. Springer Verlag, Berlin, 366p.

Pecoits, E., Gingras, M.K., Barley, M.E., Kappler, A., Posth, N.R., Konhauser, K.O., 2009. Petrography and geochemistry of the Dales Gorge banded iron formation: paragenetic sequence, source and implications for palaeo-ocean chemistry. Prec. Res. 172, 163–187.

Peter, J.M., Goodfellow, W.D., 1996. Mineralogy, bulk and rare earth element geochemistry of massive sulphide-associated hydrothermal sediments of the Brunswick Horizon, Bathurst Mining Camp, New Brunswick. Can. J. Earth Sci. 33, 252–283.

Planavsky, N.J., Bekker, A., Rouxel, O.J., Kamber, B.S., Hofmann, A.W., Knudsen, A., Lyons, T.W., 2010. Rare earth element and yttrium compositions of Archean and paleoproterozoic Fe formations revisited: new perspectives on the significance and mechanisms of deposition. Geochim. Cosmochim. Acta 74, 6387–6405.

Posth, N.R., Hegler, F., Konhauser, K.O., Kappler, A., 2008. Alternating Si and Fe deposition caused by temperature fluctuations in Precambrian oceans. Nat. Geosci. 1, 703–708.

Posth, N.R., Köhler, I., Swanner, E.D., Schröder, C., Wellmann, E., Binder, B., Konhauser, K.O., Neumann, U., Berthold, C., Nowak, M., Kappler, A., 2013. Simulating Precambrian banded iron formation diagenesis. Chem. Geol. 362, 66–73.

Pouclet, A., Tchameni, R., Mezger, K., Vidal, M., Nsifa, N.E., Penaye, P., 2007. Archaean crustal accretion at the northern border of the Congo Craton (South Cameroon). The charnockite-TTG link. Bulletin de la Société Géologique de France 178 (5), 3–14.

Rao, T.G., Naqvi, S.M., 1995. Geochemistry, depositional environment and tectonic setting of the BIF's of the late Archean Chitradurga schist belt, India. Chem. Geol. 121, 217–243.

Rasmussen, B., Krapez, B., Meier, D.B., 2014. Replacement origin for hematite in 2.5 Ga banded iron formation: Evidence for postdepositional oxidation of iron-bearing minerals. Geological Society of America Bulletin 126, 438–446.

Rasmussen, B., Meier, D.B., Krapez, B., Muhling, J.R., 2013. Iron silicate microgranules as precursor sediments to 2.5-billion-year-old banded iron formations. Geology 41, 435–438.

Robb, L., 2005. Introduction to Ore-Forming Processes. Blackwell Publishing, 373p.

Robertson, A.H.F., Hudson, J.D., 1973. Cyprus umbers: chemical precipitates on a Tethyan ocean ridge. Earth Planet. Sci. Lett. 18, 93–101.

Rollinson, H.R., 1993. Using Geochemical Data: Evaluation, Presentation, Interpretation. Longmann Group UK, 352p.

Sandiford, M., Powell, R., 1986a. Pyroxene exsolution in granulites from Fyfe Hills, Enderby Land, Antarctica: evidence for 1000°C metamorphic temperatures in Archean continental crust. American Mineralogist 71, 946–954.

Scott, C., Lyons, T.W., Bekker, A., Shen, Y., Poulton, S.W., Chu, X., Anbar, A.D., 2008. Tracing the stepwise oxygenation of the Proterozoic ocean. Nature 452, 456–459.

Shang, C.K., Satir, M., Nsifa, E.N., Liegeois, J.P., Siebel, W., Taubald, H., 2007. Archaean high-K granitoids produced by remelting of the earlier Tonalite–Trondhjemite–Granodiorite (TTG) in the Sangmelima region of the Ntem complex of the Congo craton, southern Cameroon. Int. J. Earth Sci. 96, 817–842.

Shang, C.K., Satir, M., Siebel, W., Nsifa, E.N., Taubald, H., Liegeois, J.P., Tchoua, F.M., 2004a. TTG magmatism in the Congo craton; a view from major and trace element geochemistry, Rb–Sr and Sm–Nd systematics of TTG magmatism in the Congo craton: case of the Sangmelima region, Ntem complex, southern Cameroon. J. Afri. Earth Sci. 40, 61–79.

Simmons, E.C., Lindsley, D.H., Papike, J.J., 1974. Phase Relations and Crystallization Sequence in a Contact-Metamorphosed Rock from the Gunflint Iron Formation, Minnesota. J. Petrol. 15, 539–565.

Slack, J.F., Grenne, T., Bekker, A., Rouxel, O.J., and Lindberg, P.A., 2007. Suboxic deep seawater in the late Paleoproterozoic: Evidence from hematitic chert and iron formation related to seafloor-hydrothermal sulfide deposits, central Arizona, USA. Earth Planet. Sci. Lett. 255, 243–256.

Smith, A.J.B., Beukes, N.J., and Gutzmer, J., 2013, The composition and depositional environments of Mesoarchean iron formations of the West Rand Group of the Witwatersrand Supergroup, South Africa. Economic Geology and the Bulletin of the Society of Economic Geologists 108, 111–134.

Stern, R.J., Mukherjee, S.K., Miller, N.R., Ali, K., Johnson, P.R., 2013. ~750 Ma banded iron formation from the Arabian-Nubian Shield – Implications for understanding neoproterozoic tectonics, volcanism, and climate change. Prec. Res. 239, 79–94.

Suh, C.E., Cabral, A.R., Ndime, E., 2009. Geology and ore fabrics of the Nkout high-grade hematite deposit, southern Cameroon. In: P.J. Williams et al. (editors), Smart Science for Exploration and Mining, Proceedings of the Tenth Biennial SGA Meeting of The Society for Geology Applied to Mineral Deposits, Townsville, Australia, pp. 558–560.

Suh, C.E., Cabral, A.R., Shemang, E.M., Mbinkar, L., Mboudou, G.G.M., 2008. Two contrasting iron deposits in the Precambrian mineral belt of Cameroon, West Africa. Exploration and Mining Geology 17, 197–207.

Sunder Raju, P.V., 2009. Petrography and geochemical behaviour of trace element, REE and precious metal signatures of sulphidic banded iron formations from the Chikkasiddavanahalli area, Chitradurga schist belt, India. J. Asi. Earth Sci. 34, 663-673.

Takam, T., Arima, M., Kokonyangi, J., Dunkley, D.J., Nsifa, E.N., 2009. Paleoarchaean charnockites in the Ntem complex, Congo craton, Cameroon: insights from SHRIMP zircon U–Pb ages. Journal of Mineralogical and Petrological Sciences 104, 1–11.

Tchameni, R., 1997. Géochimie et géochronologie des formations de l'Archéen et du Paléoproterozoïque du Sud-Cameroun (Groupe du Ntem, Craton du Congo). Thèse de l'Univérsité d'Orléans, France, 395p.

Tchameni, R., Lerouge, C., Penaye, J., Cocherie, A., Milesi, J.P., Toteu, S.F., Nsifa, E.N., 2010. Mineralogical constraint for metamorphic conditions in a shear zone affecting the Archean Ngoulemakong tonalite, Congo craton (Southern Cameroon) and retentivity of U–Pb SHRIMP zircon dates. J. Afri. Earth Sci. 58, 67–80.

Tchameni, R., Mezger, K., Nsifa, N.E., Pouclet, A., 2000. Neoarchaean evolution in the Congo Craton: evidence from K rich granitoids of the Ntem complex, Southern Cameroon. J. Afri. Earth Sci. 30, 133–147.

Tchameni, R., Mezger, K., Nsifa, E.N., Pouclet, A., 2001. Crustal origin of Early Proterozoic syenites in the Congo craton (Ntem complex), South Cameroon. Lithos 57, 23–42.

Tchameni, R., Pouclet, A., Mezger, K., Nsifa, E.N., Vicat, J.P., 2004. Monozircon and Sm–Nd whole rock ages from the Ebolowa greenstone belts: evidence for the terranes older than 2.9 Ga in the Ntem Complex (Congo craton, South Cameroon). Journal of the Cameroon Academy of Sciences 4 (3), 213–224.

Thurston, P.C., Kamber, B.S., Whitehouse, M., 2012. Archean cherts in banded iron formation: insight into Neoarchean ocean chemistry and depositional processes. Prec. Res. 214, 227–257.

Toteu, S.F., Van Schmus, W.R., Penaye, J., Nyobe, J.B., 1994. U–Pb and Sm–Nd evidence for Eburnean and Pan-African high grade metamorphism in cratonic rocks of Southern Cameroon. Prec. Res. 67, 321–347.

Trendall, A.F., 2002. The significance of iron-formation in the Precambrian stratigraphic record. Spec. Publs int. Ass. Sediment. 33, 33–66.

Trendall, A.F., Blockley, J.G., 1970. The iron formations of the Precambrian Hamersley Group Western Australia with special reference to the crocidolite. Geological Survey of Western Australia Bulletin, Perth 365 p.

Vaniman, D. T., Papike, J. J. & Labotka, T., 1980. Contact metamorphic effect of the Stillwater Complex, Montana: the concordant iron formation. American Mineralogist, 65, 1087–1102.

Wang, C.L., Zhang, L.C., Lan, C.Y., Dai, Y.P., 2014. Petrology and geochemistry of the Wangjiazhuang banded iron formation and associated supracrustal rocks from the Wutai greenstone belt in the North China Craton: Implications for their origin and tectonic setting. Prec. Res. 255, 603–626.

Wang, Y., Xu, H., Merino, E., Konishi, H., 2009. Generation of banded iron formations by internal dynamics and leaching of oceanic crust. Nature Geoscience 2, 781–784.

Whitney, D.L., Evans, B.W., 2010. Abbreviations for names of rock-forming minerals. American Mineralogist 95, 185–187.

Widdel, F., Schnell, S., Heising, S., Ehrenreich, A., Assmus, B., Schink, B., 1993. Ferrous iron oxidation by anoxygenic phototrophic bacteria. Nature 362, 834‑836.

Wonder, J., Spry, P., Windom, K., 1988. Geochemistry and origin of manganese-rich rocks related to iron-formation and sulfide deposits, western Georgia. Econ. Geol. 83 (5), 1070–1081.

Xu, D.R., Wang, Z.L., Chen, H.Y., Hollings, P., Jansen, N.H., Zhang, Z.C., Wu, C.J., 2014. Petrography and geochemistry of the Shilu Fe–Co–Cu ore district, South China: Implications for the origin of a Neoproterozoic BIF system. Ore Geol. Rev. 57, 322–350.

Zhang, J., Nozaki, Y., 1996. Rare earth elements and yttrium in seawater: ICP-MS determinations in the East Caroline, Coral Sea, and South Fiji basins of the western South Pacific Ocean. Geochim. Cosmochim. Acta 60, 4631–4644.

Table captions

Table 1. Electron microprobe analyses of magnetite from the Bikoula BIF.

Table 2. Major (wt.%) and trace (ppm) element contents in the Bikoula BIF.

Table 3. Major element contents (wt.%) in syenites.

Table 4. Linear inter-element correlations (R^2) for all BIF samples ($n = 12$).

Appendix A. Electron microprobe analyses of minerals in syenites.

A.1. Magnetite

A.2. Clinopyroxene

A.3. Microcline

A.4. Albite

A.5. Ilmenite

Appendix B. Electron microprobe analyses of minerals from the Bikoula BIF.

B.1. Clinopyroxene

B.2. Orthopyroxene

B.3. Ferro-pargasite

B.4. Oligoclase

B.5. Biotite

B.6. Ilmenite

Figure captions

Fig. 1. Geological map of SW Cameroon (modified after Pouclet et al., 2007). The star indicates the position where the studied BIF occurs.

Fig. 2. Geological map showing the location where the core intersecting the studied BIF was drilled.

Fig. 3. Field photos of the Bikoula BIF. (a and b) Weathered outcrops of BIF occurring in the study area. (c) Hand sample collected from an outcrop, showing dark iron-rich bands and light quartz-rich bands as well as yellowish goethite or limonite resulting from supergene weathering.

Fig. 4. Stratigraphy of the Bikoula BIF with sample locations.

Fig. 5. Core section (a) and photomicrographs (b–e) of the Bikoula BIF, (c) and (d) taken with crossed polars. (a) Unweathered BIF drill core sample showing black Fe-rich bands alternating with whitish silica bands and greenish silicate bands. (b) BIF consisting of alternating magnetite

(Mag), quartz (Qtz) and pyroxene (Opx and Cpx) bands. (c) BIF showing magnetite, pyroxene and quartz bands; some quartz grains show preferred orientation and are dynamically recrystallized. (d) BIF showing pyroxene exsolution textures; orthopyroxene (Opx) exsolving clinopyroxene (Cpx) lamellae and first generation of clinopyroxene (Cpx^{I}) exsolving Opx lamellae. (e) Photomicrograph showing later generation of clinopyroxene (Cpx^{II}) developed in the interstices of large Opx grains. Mineral abbreviations according to Whitney and Evans (2010).

Fig. 6. Photomicrographs and SEM image of the Bikoula BIF; red arrows indicate alteration/replacement texture. (a) Reflected light photomicrograph illustrating magnetite band with cracks; pyrite (Py) grains are associated with magnetite. (b) SEM image illustrating interlocking magnetite grains containing ilmenite (Ilm) and ulvöspinel (fine, dark) lamellae. (c) Reflected light photomicrograph of pyrite and magnetite; pyrite replaces magnetite along cracks. (d) Reflected light photomicrograph of pyrite, pyrrhotite (Po) and chalcopyrite (Ccp); pyrrhotite replaces pyrite. (e–f) Cross polarized light photomicrograph of BIF consisting of oligoclase (Olg), ferro-pargasite (Fp), magnetite, biotite (Bt) and iron-rich biotite; iron-rich biotite (Fe-Bt) occurs as alteration phase which replacing ferro-pargasite or biotite as shown with red arrows.

Fig. 7. Petrographic characteristics of the syenites intercalated with the BIF, red arrows indicate alteration/replacement textures. (a) Drill core sample showing macroscopic features. (b–c) Syenite consisting of microcline (Mc) and clinopyroxene in a fine recrystallized groundmass; grains show a preferred orientation. (d) Albite (Ab) and microcline phenocrysts surrounded by groundmass; groundmass fills interstices and fractures of phenocrysts. (e) Groundmass consisting of quartz, polysynthetic twinned plagioclase and k-feldspar (Kfs). (f) Photomicrograph showing chlorite (Chl) replacing biotite (left red arrow) and biotite and chlorite replacing clinopyroxene (right red arrow) (Plane polarized light). (g–h) Plane polarized

light (g) and crossed polarized light (h) photomicrographs showing replacement reaction texture of clinopyroxene by amphibole (Amp) and chlorite. (i) Photomicrograph of syenite consisting of microcline, clinopyroxene, biotite and magnetite-ilmenite aggregate; biotite overgrowths clinopyroxene. (j) Magnetite-ilmenite aggregates, preferentially oriented; note some fine rounded apatite grains (Reflected light microscopy).

Fig. 8. (a) Compositional ranges of pyroxenes (Morimoto et al., 1989) including clinopyroxene in syenite, clinopyroxene and orthopyroxene in BIF. (b) Amphibole compositions (diamonds) plotted on Si vs. Mg# diagram (Leake et al., 1997).

Fig. 9. PAAS-normalized REE-Y patterns of the Bikoula BIF. Seawater data: average of 0, 9 and 30 m depth samples of station SA-5 (Zhang and Nozaki, 1996).

Fig. 10. Compositions of the syenites (black diamonds) plotted in a total alkalis vs. silica (TAS) diagram (after Cox et al., 1979).

Fig. 11. Compositions of the Bikoula BIF plotted in a bivariate diagram of Y/P_2O_5 vs. Zr/Cr. Deep-sea, diagenetic and metalliferous fields are based on data from Marchig et al. (1982).

Fig. 12. Ternary Fe–Mn–Al plot showing hydrothermal and non-hydrothermal fields for modern marine ferromanganese deposits (Bostrom, 1973). The Bikoula BIF plots within the hydrothermal field. Fields for metalliferous sediments from the East Pacific Rise (EPR) (Bostrom, 1973), Deep Sea Drilling Project (DSDP) Leg 31 (Bonatti et al., 1979), Cyprus umbers (Robertson and Hudson, 1973) and other oceanic sediments are also included.

Fig. 13. Plot of Al_2O_3 vs. SiO_2 (after Wonder et al., 1988) to illustrate the origin of primary chemical precipitates of the Bikoula BIF samples (Filled triangles).

Fig. 14. Composition of the Bikoula BIF (Filled triangles) plotted on the Fe/Ti vs. Al/(Al+Fe+Mn) discrimination diagram (after Bostrom, 1973). This diagram is proposed for

estimating the relative contribution from hydrothermal inputs in the fluid from where BIF precipitated. Hydrothermal chemical sediment of the Soldier Cap Group iron formations (Hatton and Davidson, 2004) is plotted to show the hydrothermal input.

Fig. 15. Composition of the Bikoula BIF (triangles) plotted in an elemental ratio diagram with two-component conservative mixing lines for Eu/Sm, Sm/Yb, and Y/Ho (after Alexander et al., 2008). The high-*T* (>350°C) hydrothermal fluids follow Bau and Dulski (1999) and the Pacific seawater follow Alibo and Nozaki (1999). (a) Plot of Sm/Yb vs. Eu/Sm showing a $\leq 0.1\%$ high-*T* hydrothermal fluid contribution. (b) Plot of Y/Ho vs. Eu/Sm showing a $\leq 0.1\%$ high-*T* hydrothermal fluid contribution.

Fig. 16. Composition of the Bikoula BIF plotted in a $(Ce/Ce^*)_{SN}$ vs. $(Pr/Pr^*)_{SN}$ diagram after Bau and Dulski (1996).

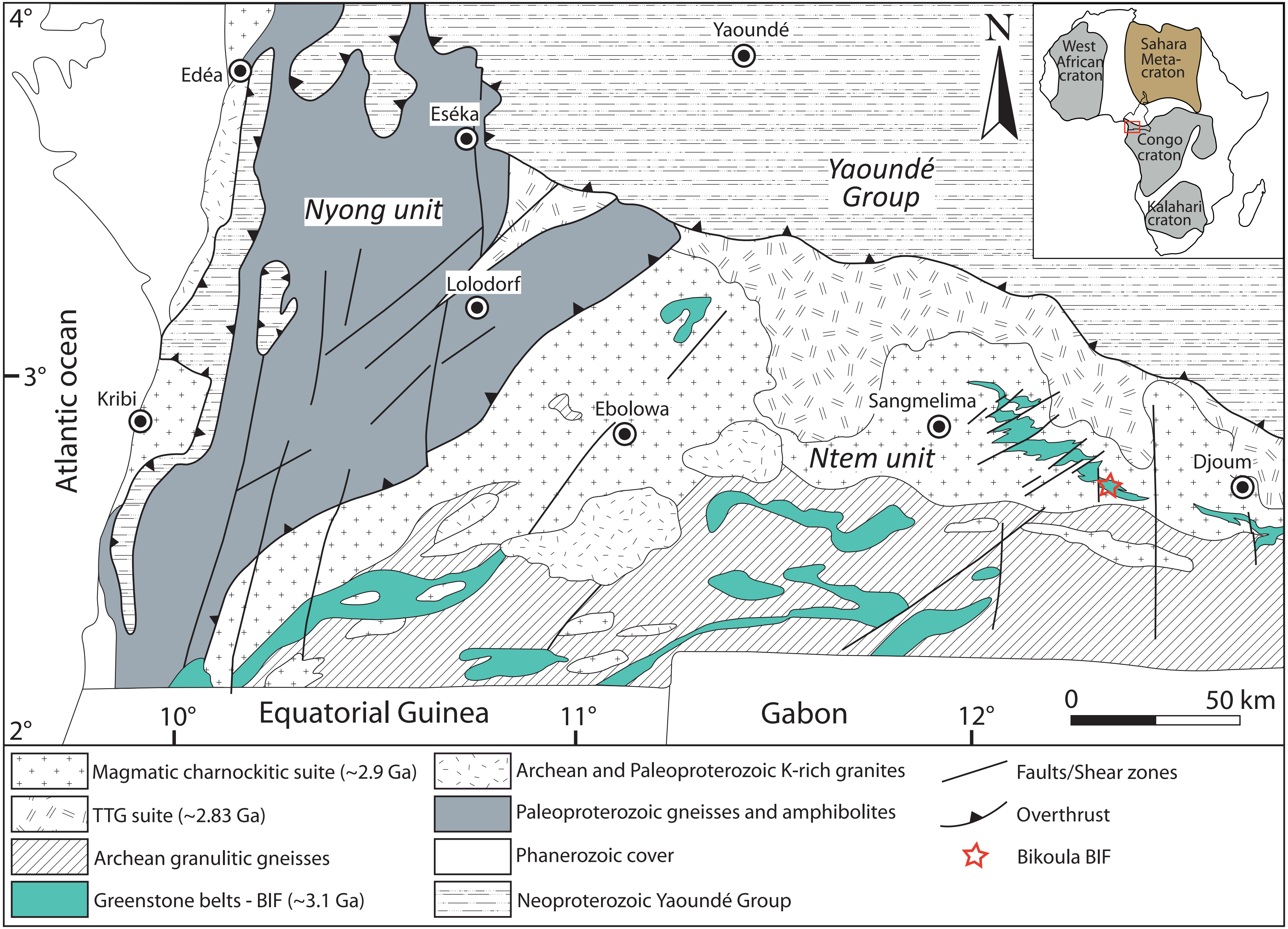

Fig. 1
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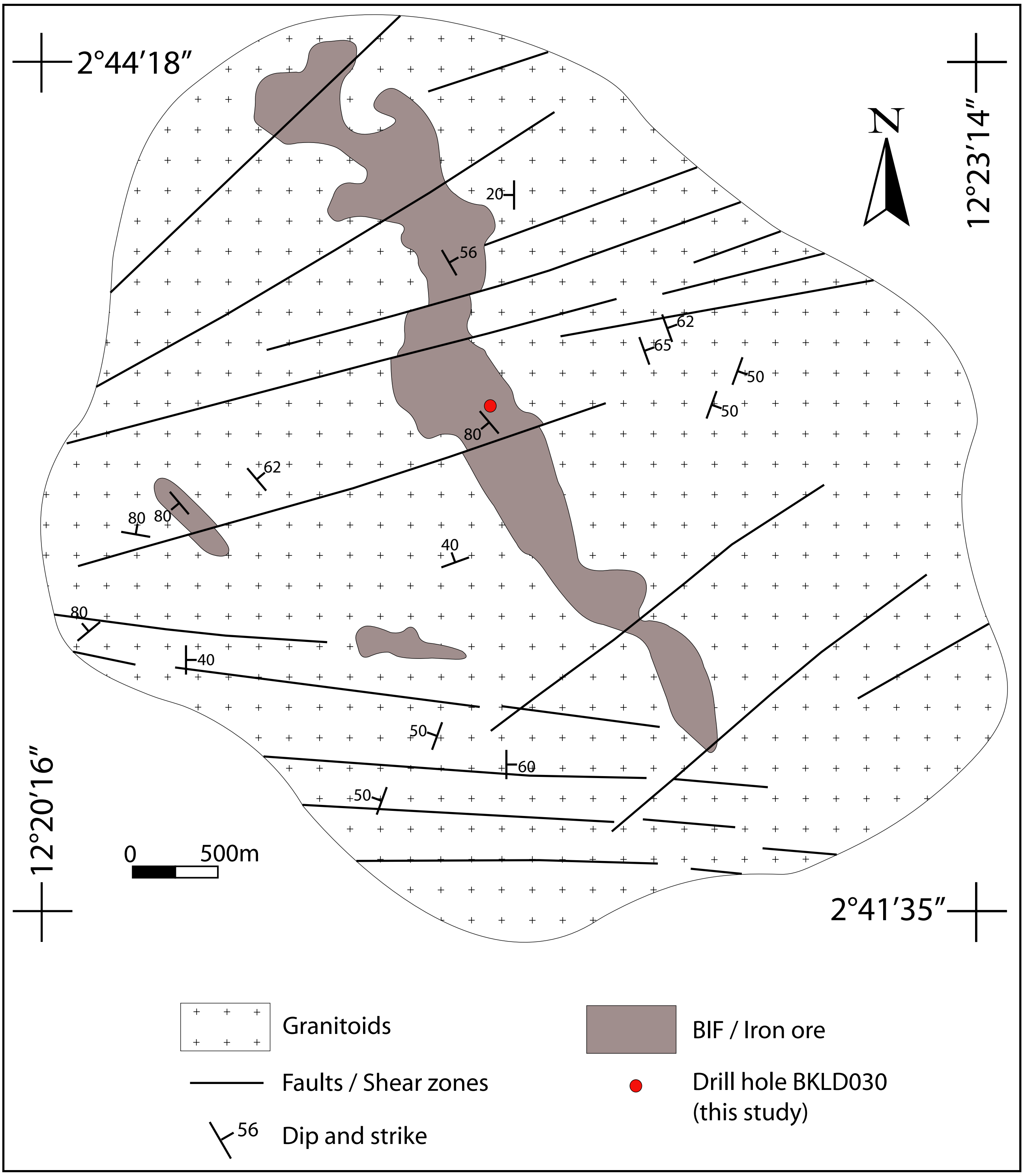

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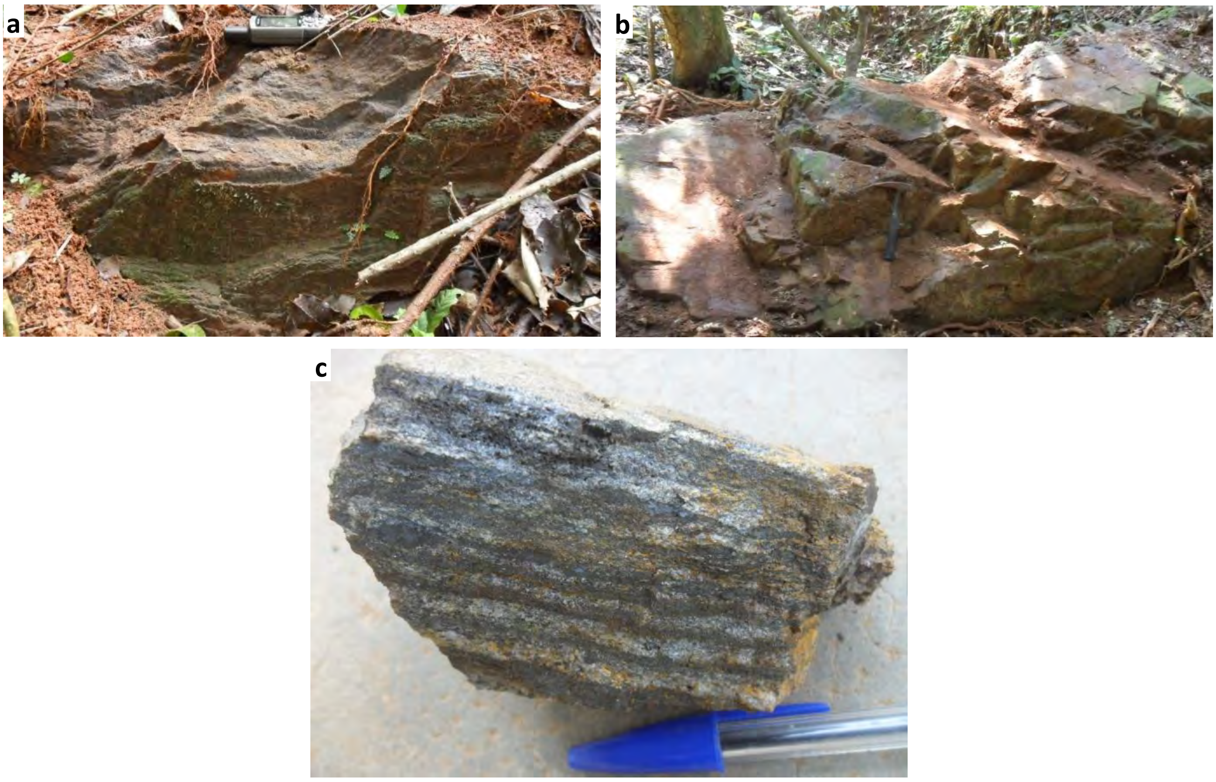

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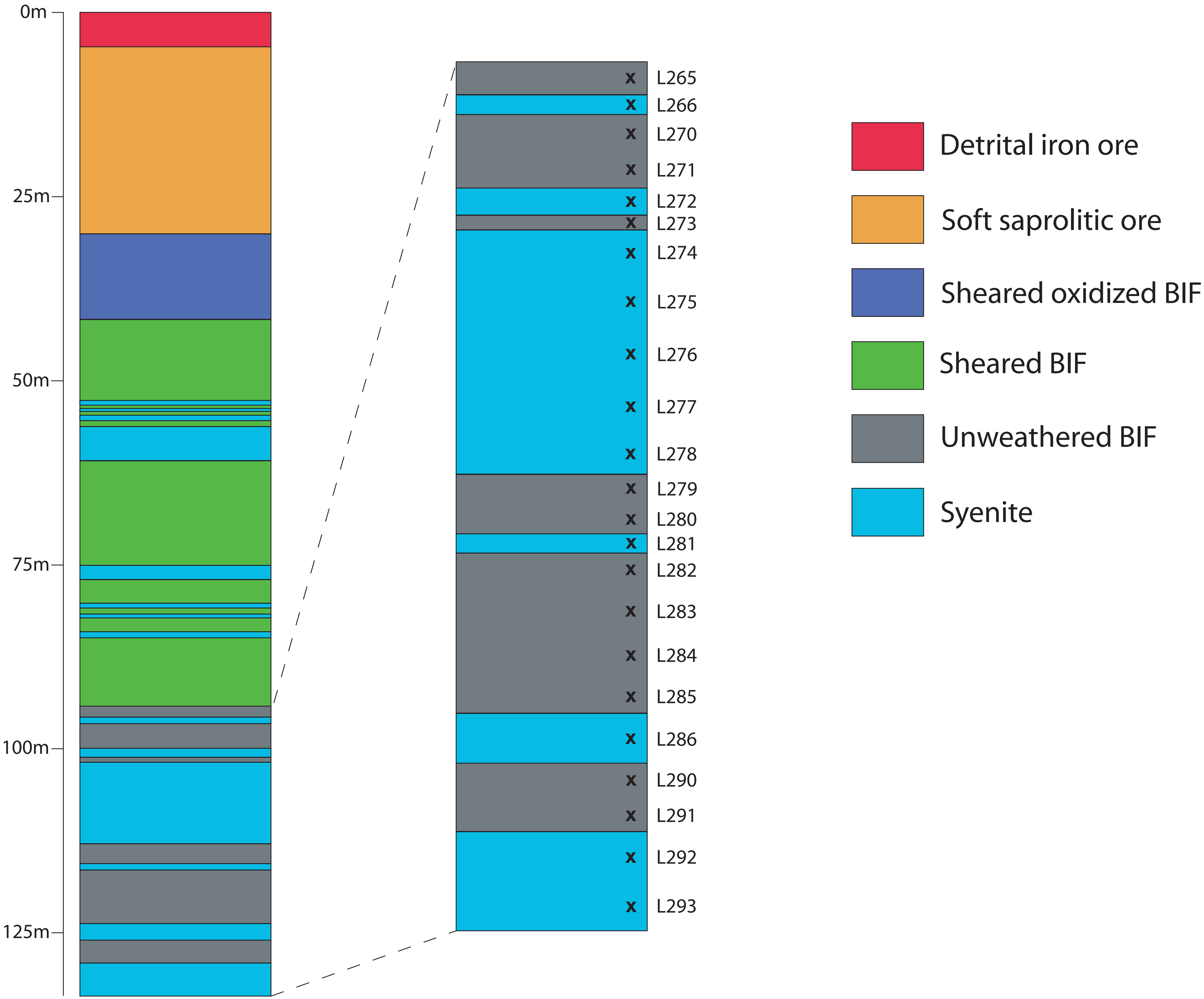

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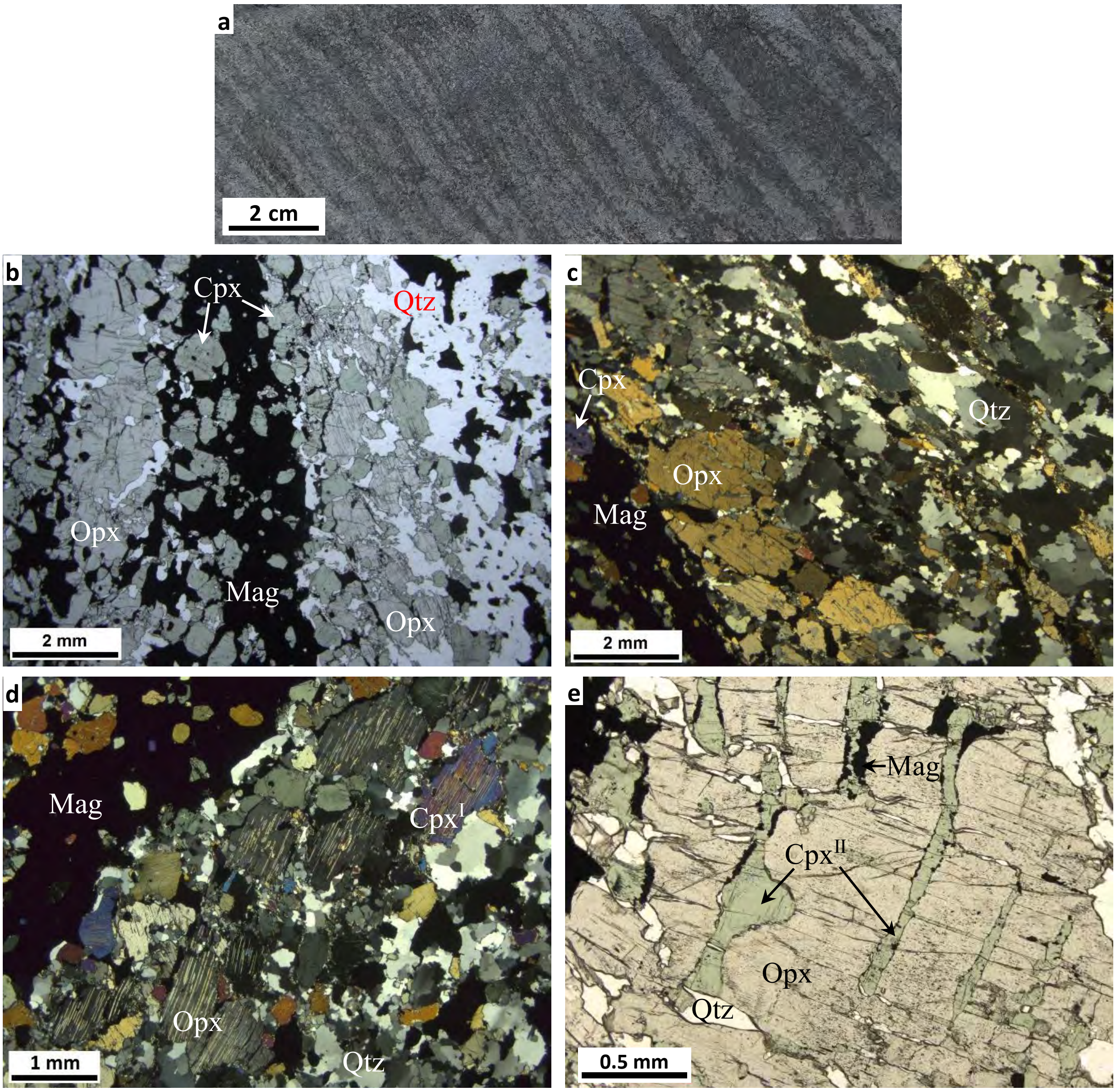

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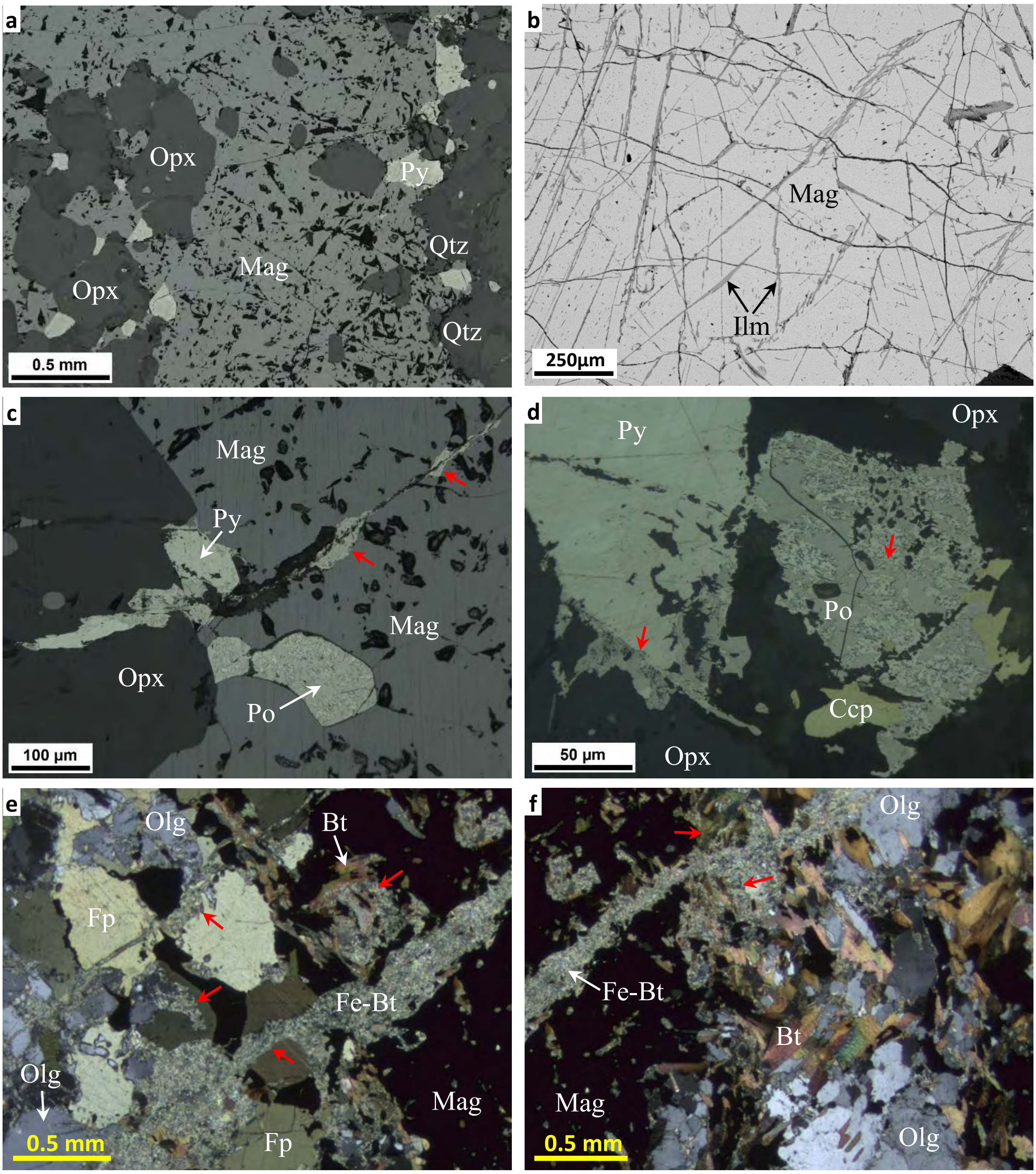

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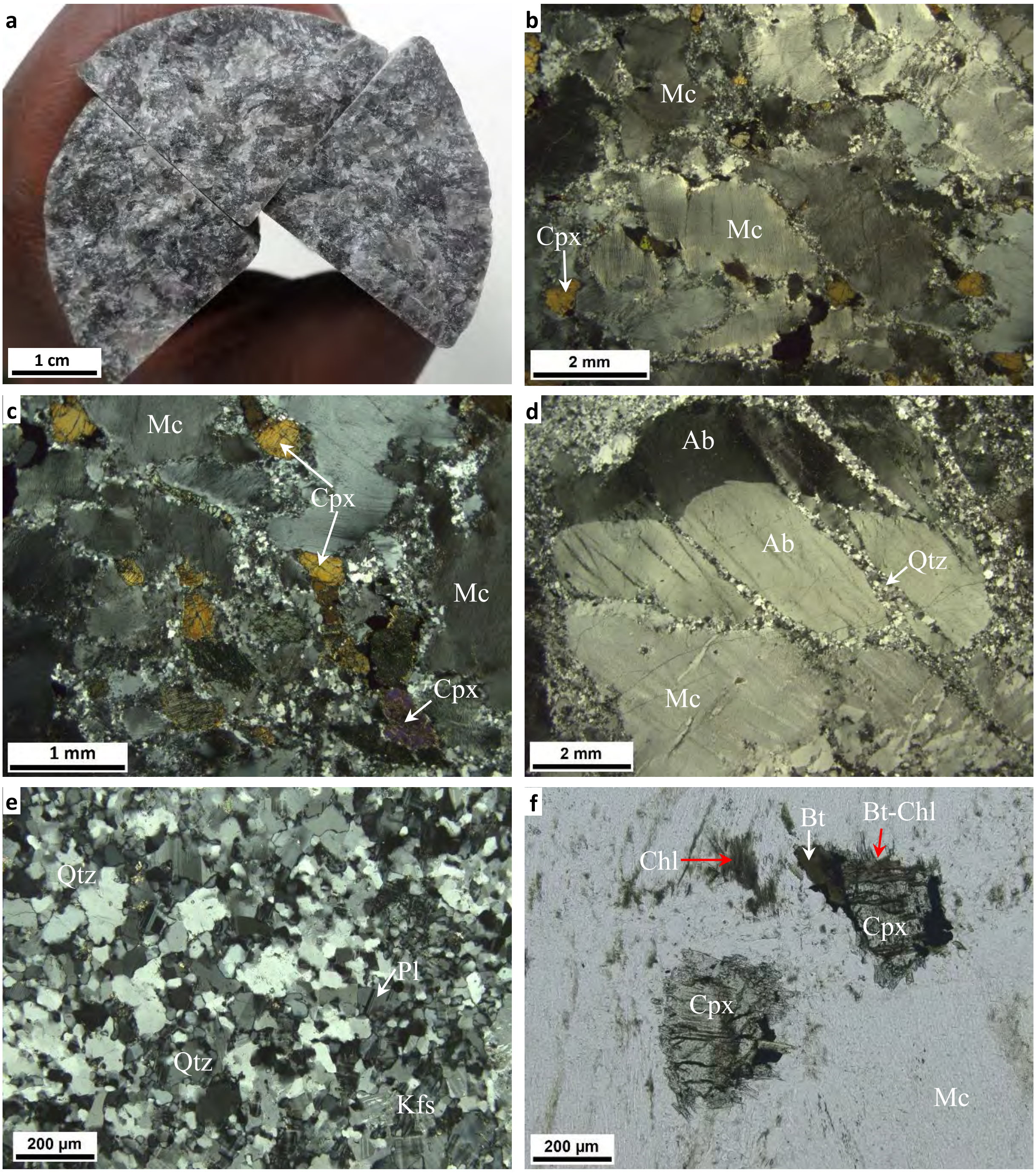

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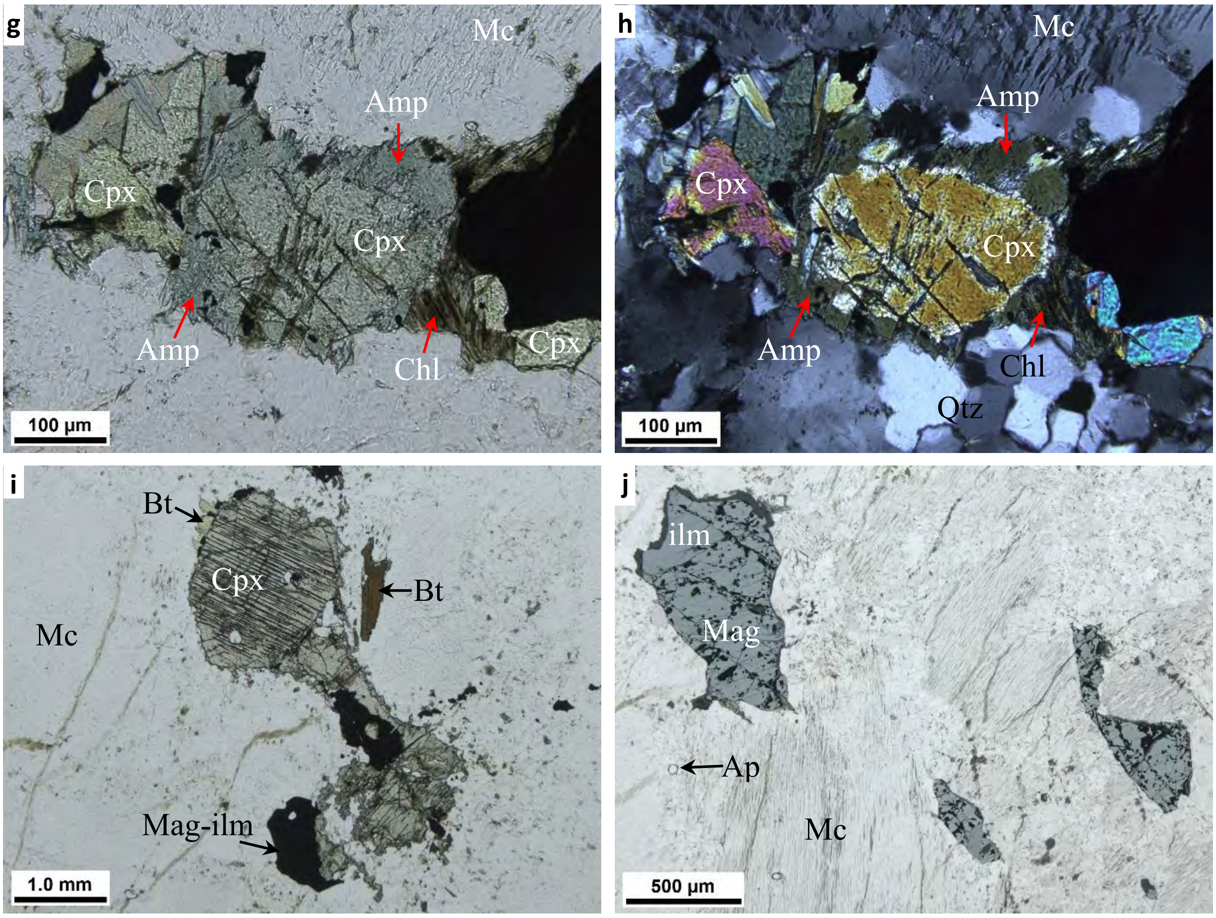

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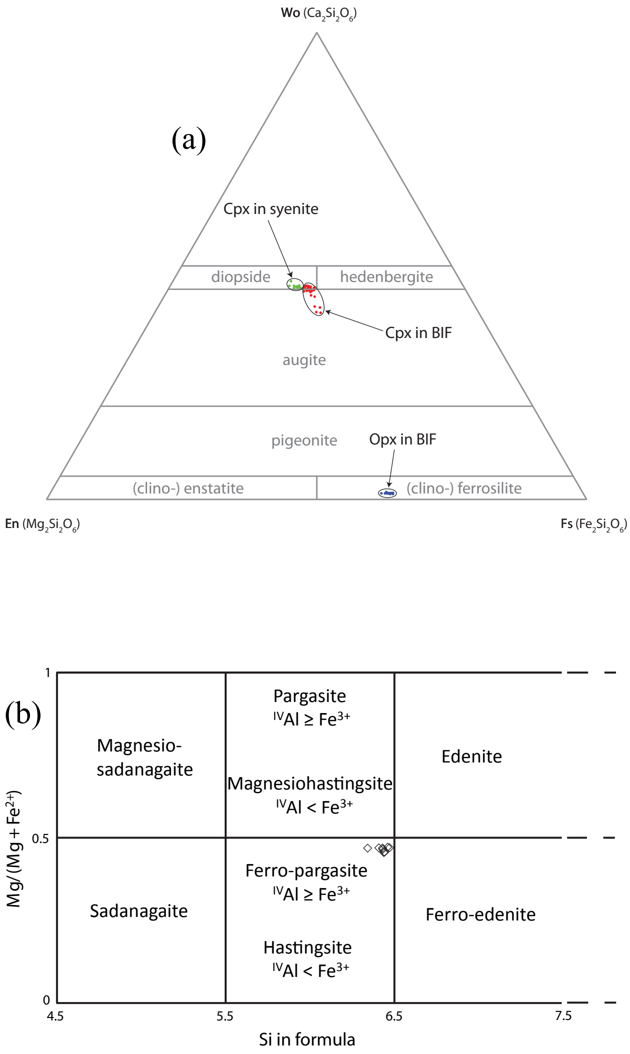

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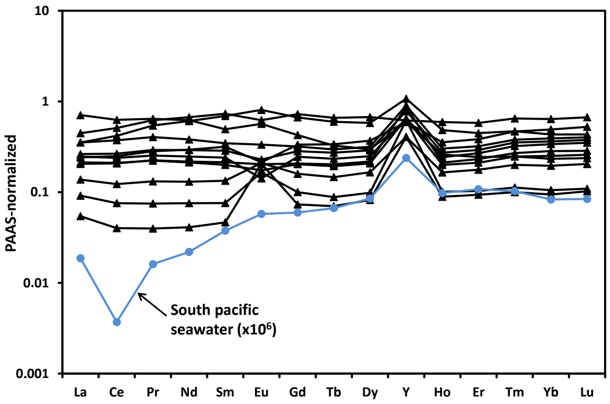

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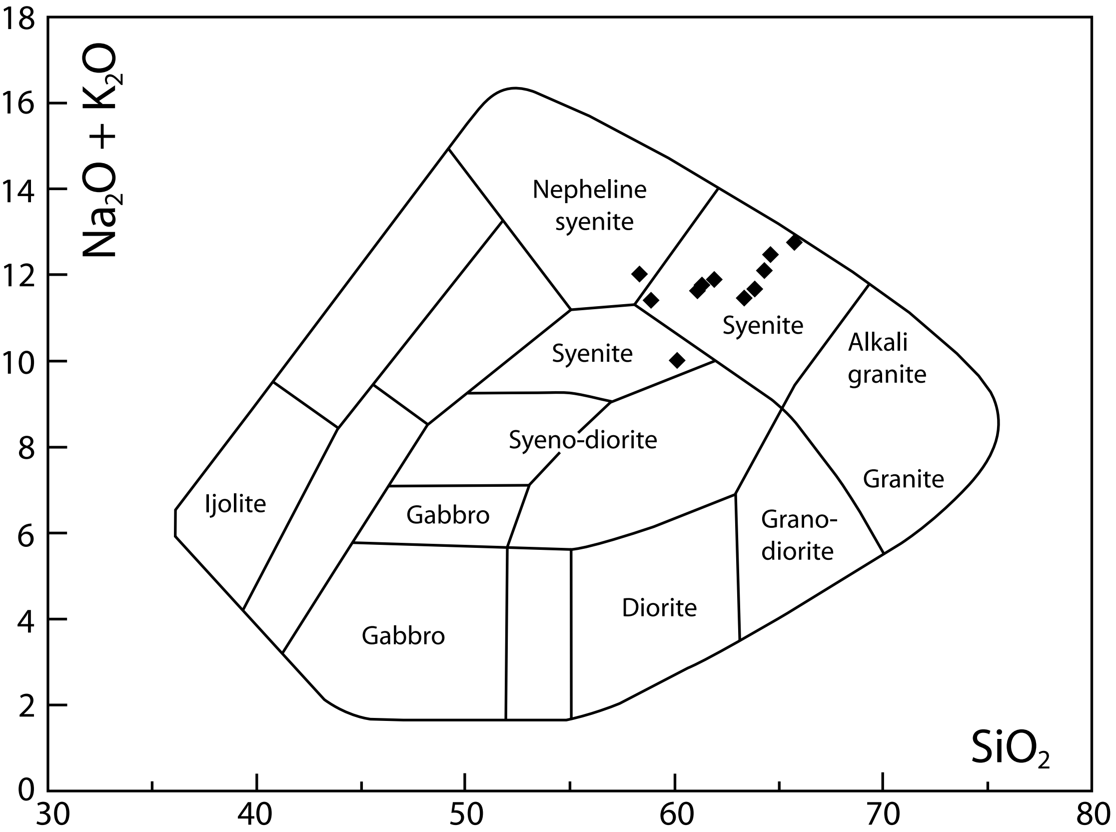

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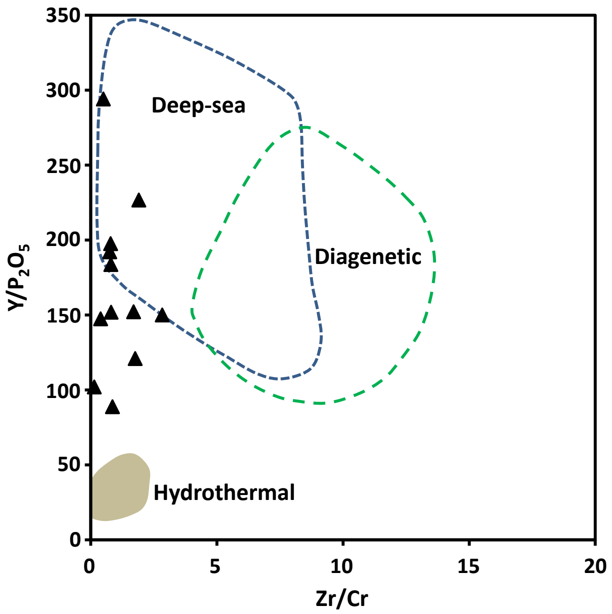

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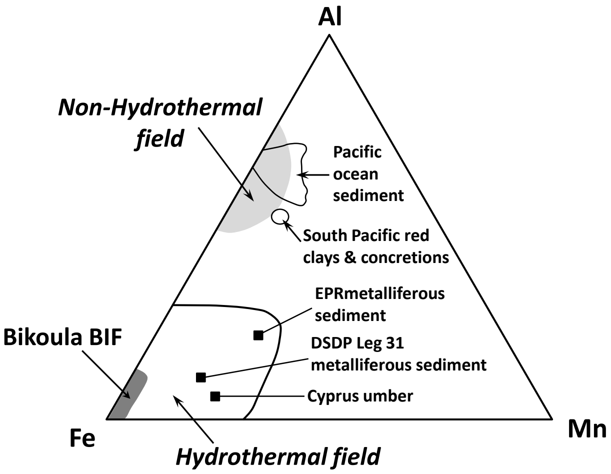

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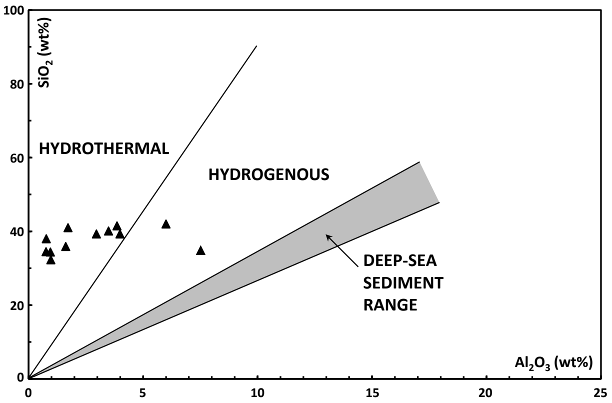

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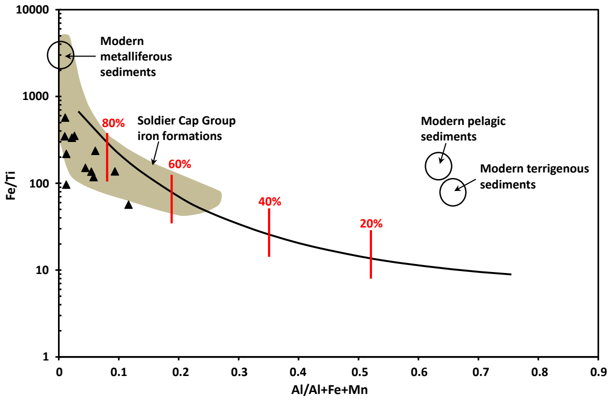

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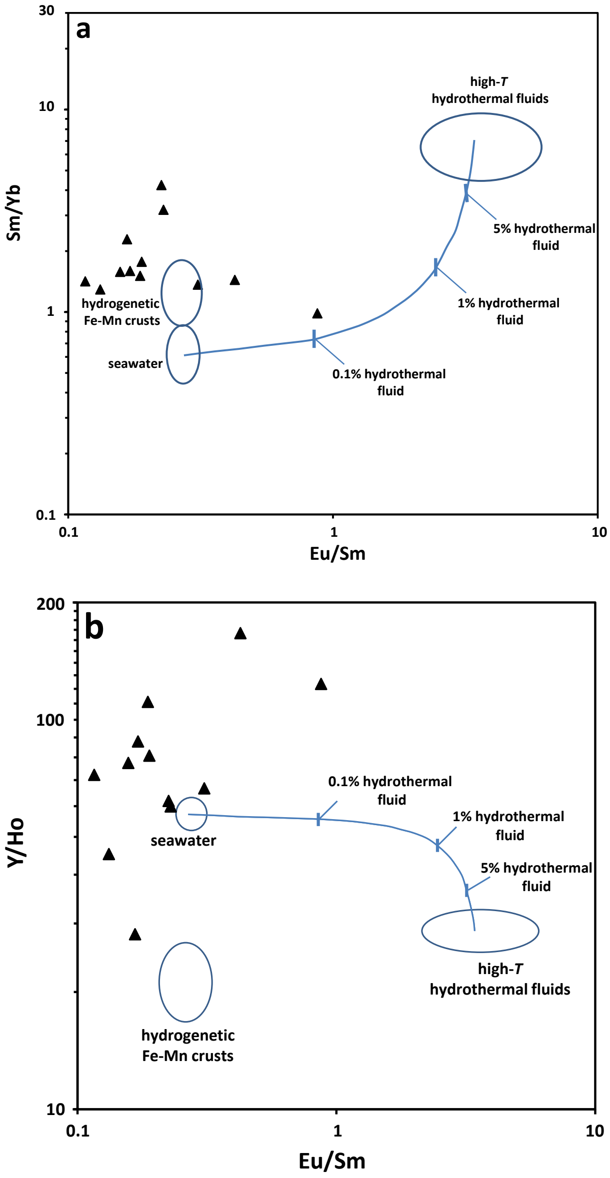

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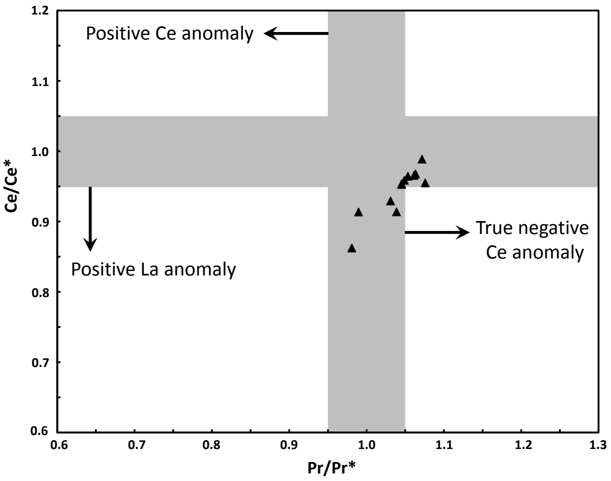

Fig. 16

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Table 1

No.	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO_t	MnO	MgO	CaO	Na_2O	K_2O	Total
1	0.07	0.10	0.25	0.00	93.98	0.07	0.02	0.02	0.04	0.01	94.56
2	0.07	0.09	0.25	0.00	93.75	0.07	0.04	0.20	0.00	0.01	94.48
3	0.09	0.11	0.28	0.00	93.45	0.04	0.00	0.16	0.04	0.01	94.18
4	0.06	0.09	0.18	0.00	93.70	0.07	0.00	0.09	0.01	0.00	94.20
5	0.10	0.13	0.35	0.00	93.02	0.07	0.01	0.00	0.05	0.00	93.72
6	0.11	0.10	0.31	0.00	93.09	0.04	0.04	0.02	0.00	0.00	93.72
7	0.12	0.12	0.35	0.00	92.95	0.07	0.01	0.01	0.00	0.00	93.64
8	0.11	0.12	0.37	0.00	92.41	0.03	0.03	0.01	0.00	0.00	93.07
9	0.11	0.13	0.35	0.01	93.14	0.01	0.00	0.01	0.05	0.00	93.81
10	0.10	0.12	0.35	0.00	93.10	0.05	0.01	0.00	0.08	0.02	93.83
11	0.10	0.10	0.31	0.00	93.02	0.06	0.00	0.01	0.00	0.01	93.63
12	0.11	0.11	0.38	0.02	93.13	0.07	0.01	0.02	0.00	0.00	93.86
13	0.12	0.13	0.37	0.04	92.92	0.03	0.00	0.01	0.03	0.00	93.65
14	0.14	0.10	0.31	0.01	93.29	0.05	0.00	0.01	0.03	0.00	93.95
15	0.11	0.09	0.37	0.00	93.25	0.09	0.00	0.00	0.03	0.01	93.95
16	0.07	0.10	0.27	0.01	92.96	0.00	0.03	0.05	0.00	0.00	93.48
17	0.09	0.11	0.59	0.01	92.31	0.04	0.02	0.00	0.00	0.01	93.19
18	0.14	0.21	0.25	0.02	92.45	0.08	0.00	0.00	0.00	0.00	93.16
19	0.13	0.36	0.54	0.01	92.06	0.10	0.02	0.00	0.01	0.00	93.22
20	0.13	0.35	0.47	0.00	92.83	0.09	0.01	0.00	0.00	0.01	93.88
21	0.14	0.45	0.25	0.02	92.54	0.07	0.01	0.01	0.00	0.02	93.51
22	0.10	0.22	0.22	0.00	93.11	0.02	0.02	0.00	0.07	0.00	93.77
23	0.10	0.49	0.22	0.04	92.72	0.12	0.00	0.02	0.01	0.00	93.72
24	0.08	0.48	0.53	0.01	92.66	0.08	0.01	0.01	0.03	0.00	93.90
25	0.09	0.43	0.50	0.00	92.47	0.04	0.02	0.00	0.00	0.00	93.55
26	0.13	0.39	0.40	0.00	93.08	0.10	0.00	0.00	0.00	0.00	94.10
27	0.12	0.25	0.25	0.00	93.16	0.03	0.01	0.02	0.00	0.01	93.85
28	0.14	0.56	0.40	0.00	92.96	0.13	0.02	0.00	0.04	0.00	94.27
29	0.15	0.16	0.22	0.01	93.26	0.04	0.00	0.00	0.00	0.00	93.84
Av.	0.11	0.21	0.34	0.01	92.99	0.06	0.01	0.02	0.02	0.00	93.78

Table 2

	L265	L270	L271	L273	L279	L280	L282	L283	L284	L285	L290	L291	Av.
SiO_2	34.90	32.30	41.50	40.10	35.90	39.30	39.30	42.00	34.40	34.50	38.00	41.00	37.77
TiO_2	0.88	0.70	0.22	0.39	0.19	0.37	0.48	0.37	0.30	0.19	0.11	0.16	0.36
Al_2O_3	7.52	0.97	3.86	3.49	1.62	2.96	3.99	6.00	0.95	0.76	0.77	1.72	2.88
Fe_2O_3	42.79	57.89	44.61	45.48	54.46	47.72	48.48	43.48	56.09	56.60	53.80	48.22	49.97
MnO	0.39	0.51	0.41	0.51	0.56	0.49	0.51	0.45	0.53	0.49	0.44	0.42	0.48
MgO	5.59	4.95	4.28	4.43	4.94	4.17	3.93	3.99	4.64	4.28	4.26	3.78	4.44
CaO	4.33	3.95	4.63	4.90	2.34	2.34	3.25	2.04	3.01	2.80	1.95	2.21	3.15
Na_2O	2.05	0.32	1.16	1.22	0.42	0.88	1.19	1.74	0.26	0.19	0.22	0.56	0.85
K_2O	1.96	0.17	0.97	0.98	0.43	0.86	1.03	1.76	0.18	0.15	0.13	0.53	0.76
P_2O_5	0.10	0.09	0.13	0.11	0.11	0.12	0.12	0.12	0.11	0.11	0.11	0.12	0.11
LOI	0.02	-1.83	-0.87	-1.08	-1.73	-1.55	-1.39	-1.13	-1.87	-1.83	-1.71	-1.07	-1.34
Total	100.53	100.02	100.90	100.52	99.23	97.67	100.89	100.81	98.60	98.24	98.07	97.65	99.43
Li	34.58	7.92	15.03	9.40	4.78	6.06	9.31	11.91	6.05	5.43	4.52	3.93	9.91
Sc	6.19	1.94	0.91	2.13	1.34	1.58	2.09	1.43	1.76	1.45	0.78	1.37	1.91
V	49.56	15.29	8.80	14.53	9.95	17.77	15.99	13.63	13.58	10.57	7.58	9.82	15.59
Cr	225.67	23.91	8.00	10.83	16.14	81.76	56.55	10.65	45.85	18.81	93.59	8.71	50.04
Ni	84.63	10.41	5.21	6.42	10.82	10.17	6.90	7.00	9.81	10.47	7.62	5.05	14.54
Cu	16.64	32.27	5.63	9.96	6.61	10.23	13.53	5.60	5.84	3.07	6.58	8.53	10.38
Zn	150.71	121.95	56.55	121.25	93.06	117.21	131.10	128.64	91.73	67.19	55.32	60.54	99.60
Rb	153.73	9.25	26.36	16.41	9.64	26.04	24.03	52.18	5.84	8.78	5.09	9.26	28.88
Sr	67.80	21.45	204.71	92.63	33.74	74.46	139.13	210.09	25.36	23.29	46.19	50.66	82.46
Y	28.99	16.84	16.08	24.41	16.04	17.58	23.55	17.54	21.14	16.72	11.00	10.99	18.41
Zr	111.46	19.08	14.04	20.64	27.31	32.03	44.59	30.12	34.23	15.15	12.80	7.44	30.74
Ba	75.26	16.82	152.90	147.08	43.24	89.29	133.28	200.46	20.50	24.61	34.91	93.38	85.98
Pb	3.28	0.66	1.51	1.73	0.76	1.70	1.91	2.47	0.61	0.47	0.67	0.90	1.39
Hf	4.53	0.87	0.67	1.07	1.07	1.28	1.73	1.23	1.21	0.77	0.44	0.26	1.26
Mo	3.49	5.62	2.05	2.74	3.18	3.07	4.42	2.65	3.10	2.22	1.84	0.78	2.93
Th	2.72	0.31	0.44	0.42	0.49	0.83	0.73	1.03	0.58	0.43	0.34	0.22	0.71
U	0.39	0.08	0.10	0.08	0.17	0.22	0.19	0.24	0.14	0.14	0.11	0.06	0.16
Cd	0.27	0.16	0.13	0.17	0.09	0.13	0.20	0.14	0.16	0.13	0.10	0.10	0.15
W	0.32	0.21	0.15	0.12	0.23	0.12	0.13	0.09	0.24	0.24	0.20	0.37	0.20
Re	1.90	1.45	2.23	1.89	1.10	0.23	1.55	1.52	1.83	1.16	1.49	1.90	1.52
Th/U	6.92	3.76	4.58	5.15	2.95	3.76	3.79	4.30	4.23	3.16	2.93	3.49	4.44
La	13.43	3.48	26.90	13.43	9.18	8.11	7.80	9.40	10.00	17.00	5.23	2.07	10.50
Ce	33.46	6.06	50.21	29.92	19.94	16.83	16.61	19.12	21.26	40.86	9.84	3.21	22.28
Pr	4.83	0.67	5.73	3.60	2.52	1.98	2.01	2.26	2.60	5.54	1.17	0.35	2.77
Nd	19.47	2.42	19.91	12.21	9.42	6.80	6.95	7.90	9.33	21.47	4.18	1.31	10.11
Sm	3.88	0.43	2.77	1.94	1.78	1.12	1.20	1.35	1.60	4.11	0.75	0.26	1.76
Eu	0.89	0.18	0.62	0.37	0.24	0.19	0.22	0.16	0.25	0.69	0.23	0.23	0.36
Gd	3.14	0.47	2.01	1.50	1.57	0.96	0.98	1.15	1.33	3.41	0.75	0.34	1.47
Tb	0.46	0.07	0.25	0.23	0.26	0.15	0.16	0.18	0.21	0.51	0.11	0.05	0.22
Dy	2.55	0.43	1.31	1.39	1.63	0.91	0.96	1.10	1.27	2.96	0.73	0.36	1.30
Ho	0.48	0.10	0.26	0.30	0.36	0.20	0.21	0.24	0.27	0.59	0.17	0.09	0.27
Er	1.30	0.30	0.71	0.93	1.11	0.61	0.67	0.78	0.85	1.69	0.51	0.27	0.81
Tm	0.19	0.05	0.10	0.15	0.19	0.10	0.11	0.13	0.14	0.26	0.08	0.04	0.13
Yb	1.21	0.30	0.65	1.10	1.38	0.70	0.79	0.95	1.02	1.80	0.55	0.26	0.89
Lu	0.19	0.05	0.10	0.17	0.23	0.11	0.12	0.15	0.16	0.29	0.09	0.04	0.14
LREE	75.96	13.24	106.15	61.47	43.08	35.04	34.78	40.18	45.04	89.66	21.40	7.43	47.78
HREE	9.52	1.76	5.39	5.77	6.72	3.75	4.00	4.68	5.25	11.51	2.99	1.47	5.23
Σ REE	85.48	15.00	111.54	67.25	49.79	38.79	38.78	44.86	50.29	101.17	24.38	8.90	53.02
LREE/HREE	7.98	7.52	19.69	10.65	6.41	9.36	8.69	8.58	8.58	7.79	7.17	5.06	8.96
$(Eu/Eu^*)_{SN}$	1.19	1.87	1.23	1.01	0.66	0.86	0.97	0.58	0.80	0.85	1.43	3.45	1.24
$(Ce/Ce^*)_{SN}$	0.93	0.91	0.93	0.99	0.95	0.96	0.96	0.95	0.96	0.95	0.91	0.85	0.94
$(Y/Y^*)_{SN}$	2.02	6.25	2.14	2.92	1.64	3.19	4.06	2.64	2.78	0.98	2.46	4.76	2.99
Y/Ho	59.89	166.73	61.86	80.84	45.20	87.92	111.09	72.17	77.44	28.14	66.64	123.52	81.79
$(La/Yb)_{SN}$	0.82	0.87	3.03	0.90	0.49	0.85	0.72	0.73	0.73	0.70	0.70	0.58	0.93

$(Eu/Eu^*)_{SN} = [2Eu/(Sm+Gd)]_{SN}$; $(Ce/Ce^*)_{SN} = [2Ce/(La+Pr)]_{SN}$; $(Y/Y^*)_{SN} = [2Y/(Dy+Ho)]_{SN}$.

Table 3

	L266	L272	L274	L275	L276	L277	L278	L281	L286	L292	L293	Av.
SiO_2	65.73	64.27	61.90	61.30	61.09	58.84	58.29	60.14	63.82	63.31	64.60	62.12
TiO_2	0.02	0.06	0.31	0.42	0.48	0.74	0.66	0.62	0.15	0.06	0.10	0.33
Al_2O_3	18.39	18.91	17.35	17.10	17.75	17.88	17.29	15.29	17.79	16.98	18.81	17.59
Fe_2O_3	1.15	2.02	4.91	4.75	4.87	7.82	7.33	7.34	2.97	3.51	1.72	4.40
MnO	0.02	0.02	0.07	0.08	0.07	0.07	0.08	0.13	0.08	0.08	0.04	0.07
MgO	0.22	0.22	0.52	0.64	0.83	1.21	1.00	1.32	0.67	0.66	0.33	0.69
Na_2O	5.88	7.07	5.63	5.55	6.03	6.21	4.98	5.20	5.91	5.60	6.57	5.88
CaO	0.76	1.18	1.72	1.94	1.80	1.11	1.68	3.30	1.07	1.72	1.19	1.59
K_2O	6.89	5.05	6.28	6.20	5.62	5.21	7.05	4.83	5.78	5.87	5.92	5.88
P_2O_5	0.04	0.03	0.21	0.21	0.37	0.06	0.50	0.34	0.14	0.06	0.04	0.18
LOI	0.51	0.59	0.66	0.41	0.68	0.46	0.74	0.73	0.84	0.83	0.55	0.64
Total	99.62	99.43	99.56	98.62	99.58	99.60	99.63	99.23	99.23	98.69	99.85	99.37

Table 4

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Li	Sc	V	Cr	Ni
TiO_2	0.15															
Al_2O_3	0.13	0.34														
Fe_2O_3	0.52	0.07	0.77													
MnO	0.12	0.02	0.23	0.34												
MgO	0.50	0.40	0.05	0.02	0.00											
CaO	0.01	0.28	0.12	0.09	0.01	0.19										
Na_2O	0.19	0.32	0.98	0.82	0.22	0.02	0.15									
K_2O	0.18	0.29	0.99	0.80	0.22	0.02	0.08	0.98								
P_2O_5	0.65	0.30	0.01	0.21	0.08	0.55	0.02	0.02	0.02							
LOI	0.11	0.25	0.74	0.72	0.53	0.08	0.23	0.73	0.70	0.02						
Li	0.01	0.54	0.69	0.36	0.33	0.37	0.30	0.63	0.60	0.04	0.76					
Sc	0.11	0.69	0.44	0.14	0.11	0.50	0.20	0.39	0.38	0.21	0.52	0.78				
V	0.08	0.70	0.50	0.18	0.15	0.46	0.15	0.43	0.44	0.17	0.53	0.80	0.97			
Cr	0.09	0.37	0.25	0.08	0.19	0.34	0.02	0.19	0.20	0.13	0.30	0.55	0.68	0.76		
Ni	0.12	0.51	0.39	0.12	0.21	0.56	0.11	0.31	0.32	0.19	0.51	0.81	0.91	0.93	0.79	
Cu	0.22	0.58	0.00	0.03	0.00	0.20	0.15	0.00	0.00	0.36	0.00	0.06	0.15	0.14	0.05	0.07
Zn	0.02	0.71	0.42	0.13	0.03	0.17	0.09	0.42	0.42	0.19	0.13	0.28	0.44	0.46	0.19	0.25
Rb	0.00	0.52	0.73	0.38	0.31	0.32	0.10	0.65	0.67	0.05	0.72	0.92	0.82	0.88	0.65	0.87
Sr	0.58	0.00	0.41	0.55	0.12	0.15	0.03	0.46	0.43	0.40	0.19	0.08	0.01	0.00	0.03	0.02
Y	0.04	0.55	0.41	0.15	0.01	0.27	0.39	0.41	0.36	0.09	0.26	0.48	0.62	0.57	0.27	0.40
Zr	0.07	0.59	0.53	0.17	0.08	0.43	0.09	0.44	0.46	0.12	0.44	0.76	0.89	0.92	0.75	0.86
Ba	0.74	0.00	0.46	0.72	0.09	0.20	0.03	0.55	0.53	0.35	0.26	0.06	0.00	0.00	0.04	0.01
Pb	0.12	0.40	0.97	0.75	0.21	0.05	0.11	0.96	0.96	0.00	0.71	0.67	0.49	0.56	0.33	0.42
Hf	0.07	0.63	0.56	0.19	0.08	0.45	0.13	0.48	0.48	0.14	0.48	0.80	0.92	0.95	0.73	0.88
Mo	0.31	0.52	0.01	0.06	0.21	0.23	0.11	0.01	0.00	0.35	0.02	0.04	0.11	0.10	0.03	0.04
Th	0.02	0.52	0.65	0.28	0.19	0.35	0.06	0.56	0.59	0.07	0.56	0.83	0.84	0.91	0.74	0.88
U	0.01	0.37	0.58	0.21	0.07	0.22	0.00	0.47	0.55	0.04	0.32	0.57	0.59	0.70	0.62	0.65
Th/U	0.00	0.52	0.64	0.44	0.20	0.28	0.47	0.64	0.58	0.03	0.72	0.82	0.71	0.70	0.37	0.60
ΣREE	0.00	0.00	0.11	0.08	0.04	0.07	0.28	0.10	0.09	0.04	0.14	0.23	0.06	0.06	0.01	0.09
Eu/Eu*	0.01	0.01	0.06	0.00	0.20	0.05	0.00	0.05	0.05	0.01	0.02	0.02	0.00	0.01	0.01	0.00

	Cu	Zn	Rb	Sr	Y	Zr	Ba	Pb	Hf	Mo	Th	U	Th/U	ΣREE
Zn	0.27													
Rb	0.04	0.35												
Sr	0.06	0.02	0.05											
Y	0.06	0.61	0.42	0.01										
Zr	0.06	0.48	0.84	0.00	0.62									
Ba	0.05	0.07	0.05	0.84	0.04	0.00								
Pb	0.01	0.50	0.74	0.33	0.45	0.57	0.41							
Hf	0.07	0.50	0.87	0.00	0.66	0.99	0.00	0.60						
Mo	0.61	0.48	0.02	0.01	0.24	0.12	0.04	0.02	0.13					
Th	0.03	0.41	0.96	0.02	0.49	0.93	0.02	0.69	0.94	0.04				
U	0.00	0.44	0.77	0.03	0.38	0.82	0.02	0.62	0.80	0.06	0.88			
Th/U	0.05	0.35	0.71	0.07	0.64	0.61	0.11	0.65	0.66	0.03	0.64	0.36		
ΣREE	0.14	0.01	0.12	0.09	0.16	0.07	0.03	0.07	0.09	0.02	0.10	0.06	0.19	
Eu/Eu*	0.07	0.13	0.02	0.06	0.20	0.07	0.01	0.06	0.07	0.10	0.06	0.18	0.01	0.23

Appendix A.

A.1.

No.	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO_t	MnO	MgO	CaO	Na_2O	K_2O	Total
1	0.05	0.09	0.06	0.00	92.56	0.02	0.00	0.01	0.02	0.02	92.84
2	0.09	0.07	0.00	0.00	91.04	0.00	0.03	0.03	0.05	0.02	91.33
3	0.09	0.07	0.03	0.03	92.15	0.00	0.00	0.05	0.10	0.01	92.52
4	0.09	0.07	0.07	0.02	92.51	0.01	0.01	0.00	0.01	0.00	92.80
5	0.13	0.17	0.04	0.02	92.89	0.01	0.01	0.02	0.05	0.01	93.34
6	0.08	0.10	0.07	0.00	92.61	0.01	0.00	0.00	0.00	0.01	92.88
7	0.12	0.07	0.04	0.00	92.66	0.02	0.00	0.00	0.03	0.00	92.95
8	0.08	0.07	0.08	0.00	92.92	0.01	0.02	0.01	0.07	0.01	93.25
9	0.07	0.10	0.09	0.00	93.06	0.03	0.00	0.00	0.00	0.00	93.36
10	0.08	0.12	0.08	0.02	92.77	0.00	0.00	0.01	0.00	0.00	93.08
11	0.07	0.09	0.07	0.00	92.84	0.01	0.00	0.00	0.03	0.00	93.11
12	0.09	0.08	0.10	0.02	92.68	0.01	0.00	0.01	0.04	0.00	93.03
13	0.13	0.07	0.12	0.01	92.90	0.02	0.00	0.00	0.01	0.00	93.27
14	0.07	0.09	0.05	0.01	93.04	0.01	0.00	0.02	0.00	0.01	93.30
15	0.06	0.08	0.08	0.02	93.05	0.00	0.00	0.03	0.06	0.00	93.39
16	0.05	0.11	0.05	0.00	93.03	0.03	0.00	0.00	0.00	0.01	93.28
17	0.10	0.05	0.15	0.04	92.45	0.03	0.00	0.09	0.01	0.00	92.94
18	0.07	0.07	0.05	0.01	92.73	0.02	0.00	0.03	0.02	0.01	93.01
19	0.03	0.10	0.07	0.00	92.88	0.00	0.00	0.05	0.06	0.01	93.21
Av.	0.08	0.09	0.07	0.01	92.67	0.01	0.00	0.02	0.03	0.01	92.99

A.2.

No.	1	2	3	4	5	6	7	8	9	10	11	12	Av.
SiO_2	51.26	51.70	51.55	51.73	51.31	52.02	52.15	52.43	52.43	52.25	52.37	52.14	51.95
TiO_2	0.09	0.09	0.10	0.11	0.08	0.06	0.07	0.09	0.06	0.14	0.13	0.14	0.10
Al_2O_3	0.72	0.91	0.80	0.91	0.79	0.77	0.71	0.71	0.59	1.08	1.01	0.92	0.83
Cr_2O_3	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00
FeO_t	15.24	14.81	15.03	15.24	14.87	14.87	15.20	15.08	14.86	15.00	14.84	15.09	15.01
MnO	0.70	0.68	0.65	0.68	0.67	0.65	0.68	0.67	0.64	0.67	0.66	0.70	0.67
MgO	9.81	9.68	9.96	9.53	9.63	9.89	9.83	9.78	9.79	9.62	9.77	9.78	9.76
CaO	20.01	19.97	20.31	20.09	20.48	20.38	20.29	20.35	20.60	20.19	20.45	20.36	20.29
Na_2O	1.02	1.05	1.10	1.13	1.16	1.06	1.06	1.02	0.96	1.07	1.05	1.05	1.06
K_2O	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Total	98.86	98.90	99.52	99.42	99.00	99.70	99.98	100.13	99.93	100.02	100.29	100.20	99.66
Cations per 6 oxygens													
Si	1.980	1.995	1.974	1.987	1.976	1.990	1.991	2.000	2.004	1.995	1.992	1.987	1.989
Ti	0.003	0.003	0.003	0.003	0.002	0.002	0.002	0.003	0.002	0.004	0.004	0.004	0.003
Al	0.033	0.042	0.036	0.041	0.036	0.035	0.032	0.032	0.027	0.049	0.046	0.041	0.037
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe^{3+}	0.079	0.042	0.092	0.063	0.094	0.061	0.060	0.039	0.034	0.034	0.040	0.055	0.058
Fe^{2+}	0.413	0.436	0.390	0.427	0.386	0.415	0.425	0.443	0.441	0.445	0.432	0.426	0.423
Mn	0.023	0.022	0.021	0.022	0.022	0.021	0.022	0.022	0.021	0.022	0.021	0.023	0.022
Mg	0.565	0.557	0.569	0.546	0.553	0.564	0.559	0.556	0.558	0.547	0.554	0.555	0.557
Ca	0.828	0.826	0.833	0.827	0.845	0.835	0.830	0.832	0.844	0.826	0.834	0.831	0.832
Na	0.077	0.079	0.082	0.084	0.086	0.078	0.078	0.075	0.071	0.079	0.078	0.078	0.079
K	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Wo	0.405	0.411	0.405	0.408	0.412	0.413	0.412	0.416	0.422	0.412	0.415	0.411	0.412
En	0.282	0.278	0.284	0.273	0.276	0.282	0.280	0.278	0.279	0.274	0.277	0.278	0.278
Fs	0.207	0.218	0.195	0.213	0.193	0.207	0.212	0.221	0.220	0.223	0.216	0.213	0.212
Ae	0.077	0.042	0.082	0.063	0.087	0.061	0.060	0.039	0.034	0.034	0.040	0.055	0.056
Jd	0.000	0.036	0.000	0.022	0.000	0.017	0.018	0.032	0.027	0.043	0.038	0.023	0.021
Mg#	0.577	0.561	0.593	0.561	0.589	0.576	0.568	0.557	0.558	0.551	0.562	0.566	0.568
XFe	0.423	0.439	0.407	0.439	0.411	0.424	0.432	0.443	0.442	0.449	0.438	0.434	0.432

A.3.

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	Av.
SiO_2	64.20	63.61	63.71	63.23	64.29	64.15	64.66	64.60	64.43	64.64	64.00	64.58	64.45	64.51	64.51	64.51	64.26
TiO_2	0.03	0.02	0.06	0.06	0.05	0.04	0.03	0.03	0.04	0.06	0.03	0.05	0.05	0.03	0.03	0.03	0.04
Al_2O_3	18.53	18.25	18.26	18.23	18.53	18.39	18.09	18.51	18.25	18.25	18.28	18.45	18.21	18.24	18.23	18.19	18.31
Cr_2O_3	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.02	0.02	0.01	0.00	0.01
FeO_t	0.00	0.07	0.06	0.17	0.07	0.19	0.06	0.01	0.01	0.05	0.02	0.25	0.21	0.03	0.06	0.02	0.00
MnO	0.01	0.00	0.01	0.01	0.01	0.00	0.02	0.00	0.01	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.01
MgO	0.00	0.00	0.00	0.00	0.01	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.02	0.01
CaO	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Na_2O	0.32	0.37	0.32	0.21	0.35	0.24	0.23	0.28	0.32	0.30	0.29	0.26	0.26	0.28	0.32	0.31	0.29
K_2O	16.81	16.52	16.77	16.78	16.66	16.87	16.89	16.94	16.80	16.86	16.84	17.03	16.80	16.93	16.72	16.89	16.82
Total	99.90	98.85	99.19	98.69	99.98	99.91	99.99	100.38	99.86	100.21	99.48	100.65	100.00	100.04	99.88	99.97	99.82
Cations per 8 oxygens																	
Si	2.969	2.973	2.968	2.962	2.971	2.969	2.991	2.974	2.982	2.982	2.973	2.967	2.982	2.981	2.986	2.982	2.976
Ti	0.001	0.001	0.002	0.002	0.002	0.002	0.001	0.001	0.001	0.002	0.001	0.002	0.002	0.001	0.001	0.001	0.001
Al	1.010	1.005	1.003	1.007	1.009	1.003	0.986	1.004	0.995	0.992	1.001	0.999	0.993	0.993	0.994	0.991	0.999
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.001	0.000	0.000	0.000
Fe^{3+}	0.000	0.003	0.002	0.007	0.003	0.007	0.002	0.000	0.000	0.002	0.001	0.010	0.008	0.001	0.002	0.001	0.003
Fe^{2+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mg	0.000	0.000	0.000	0.000	0.001	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.001	0.000
Ca	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.028	0.033	0.029	0.020	0.031	0.021	0.021	0.025	0.029	0.027	0.026	0.023	0.023	0.025	0.028	0.028	0.026
K	0.992	0.985	0.997	1.003	0.982	0.996	0.997	0.995	0.992	0.992	0.998	0.998	0.991	0.998	0.987	0.996	0.994
Xan	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Xab	0.028	0.032	0.028	0.019	0.031	0.021	0.021	0.025	0.028	0.026	0.025	0.023	0.023	0.024	0.028	0.027	0.026
Xor	0.972	0.967	0.972	0.981	0.969	0.979	0.979	0.975	0.972	0.972	0.975	0.977	0.977	0.975	0.972	0.973	0.974

A.4.

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	Av.
SiO_2	67.65	66.64	67.65	67.08	74.33	66.82	66.26	66.58	67.22	67.14	67.37	67.21	67.29	67.63
TiO_2	0.03	0.03	0.04	0.03	0.04	0.04	0.06	0.04	0.01	0.04	0.00	0.02	0.03	0.03
Al_2O_3	20.74	20.13	20.28	20.59	13.69	21.37	21.62	21.35	21.11	20.61	21.09	20.77	21.22	20.35
Cr_2O_3	0.01	0.00	0.00	0.01	0.02	0.01	0.00	0.02	0.01	0.01	0.03	0.00	0.02	0.01
FeO_t	0.02	0.08	0.02	0.12	0.06	0.05	0.13	0.04	0.10	0.26	0.07	0.05	0.05	0.08
MnO	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.03	0.02	0.00	0.00	0.01	0.00	0.01
MgO	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.02	0.01	0.00	0.00
CaO	1.56	1.29	1.05	1.31	1.08	1.71	1.50	1.62	1.35	1.31	1.29	1.35	1.21	1.36
Na_2O	9.12	10.28	10.16	10.34	7.86	10.09	10.16	10.21	10.38	10.37	10.43	10.39	10.47	10.02
K_2O	0.07	0.06	0.07	0.07	0.07	0.07	0.07	0.11	0.08	0.08	0.08	0.09	0.08	0.08
Total	99.20	98.51	99.27	99.56	97.15	100.18	99.80	99.99	100.28	99.83	100.39	99.90	100.37	99.57
Cations per 8 oxygens														
Si	3.031	2.979	3.006	2.967	3.472	2.941	2.924	2.933	2.951	2.963	2.954	2.961	2.949	3.002
Ti	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.000	0.001	0.000	0.001	0.001	0.001
Al	1.095	1.061	1.062	1.073	0.754	1.109	1.125	1.108	1.092	1.072	1.090	1.079	1.096	1.063
Cr	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.001	0.000	0.000	0.001	0.000	0.001	0.000
Fe^{3+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe^{2+}	0.001	0.003	0.001	0.005	0.002	0.002	0.005	0.001	0.004	0.010	0.003	0.002	0.002	0.003
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000
Mg	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.001	0.001	0.000	0.000
Ca	0.075	0.062	0.050	0.062	0.054	0.081	0.071	0.077	0.064	0.062	0.061	0.064	0.057	0.064
Na	0.792	0.891	0.875	0.887	0.712	0.861	0.869	0.872	0.884	0.887	0.887	0.888	0.890	0.861
K	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.006	0.005	0.005	0.005	0.005	0.005	0.004
Xan	0.086	0.065	0.054	0.065	0.070	0.085	0.075	0.080	0.067	0.065	0.064	0.067	0.060	0.069
Xab	0.909	0.932	0.942	0.931	0.924	0.911	0.921	0.914	0.928	0.930	0.931	0.928	0.936	0.926
Xor	0.005	0.004	0.004	0.004	0.005	0.004	0.004	0.006	0.005	0.005	0.005	0.005	0.005	0.005

A.5.

No.	1	2	3	4	5	6	7	8	Av.
SiO_2	0.02	0.02	0.03	0.03	0.03	0.02	0.02	0.01	0.02
TiO_2	50.17	50.59	50.29	51.32	51.18	50.83	50.77	50.36	50.69
Al_2O_3	0.01	0.02	0.00	0.00	0.01	0.00	0.03	0.00	0.01
Cr_2O_3	0.02	0.01	0.00	0.02	0.01	0.01	0.00	0.00	0.01
FeO_t	43.55	44.38	44.79	42.74	42.58	44.01	44.11	44.45	43.83
MnO	4.14	4.22	4.01	5.03	4.96	4.25	4.21	4.19	4.38
MgO	0.07	0.03	0.04	0.01	0.01	0.03	0.06	0.01	0.03
CaO	0.08	0.00	0.01	0.09	0.14	0.01	0.00	0.01	0.04
Na_2O	0.05	0.02	0.02	0.04	0.00	0.00	0.00	0.02	0.02
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Total	98.09	99.28	99.19	99.29	98.92	99.17	99.21	99.07	99.03

Appendix B.

B.1.

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO_2	51.69	51.35	51.12	48.95	51.39	51.35	50.55	52.00	52.05	52.12	52.00	52.01	51.92	52.08	51.90
TiO_2	0.01	0.03	0.04	0.04	0.04	0.06	0.04	0.06	0.05	0.04	0.01	0.06	0.06	0.05	0.06
Al_2O_3	0.26	0.24	0.23	0.28	0.25	0.20	0.22	0.32	0.28	0.26	0.27	0.29	0.28	0.25	0.30
Cr_2O_3	0.00	0.00	0.00	0.00	0.01	0.00	0.03	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00
FeO_t	17.55	17.60	17.36	21.75	17.54	20.06	18.96	16.48	19.33	17.53	17.48	18.76	17.14	18.15	17.35
MnO	0.49	0.55	0.50	0.50	0.54	0.58	0.55	0.50	0.60	0.54	0.54	0.57	0.52	0.54	0.49
MgO	9.33	9.24	9.27	9.18	9.33	9.51	9.20	9.41	9.38	9.36	9.13	9.76	9.43	9.70	9.24
CaO	20.85	20.30	20.59	19.22	20.43	18.28	19.47	20.71	18.94	19.83	20.55	18.19	20.67	18.84	20.44
Na_2O	0.73	0.69	0.73	0.70	0.71	0.58	0.70	0.69	0.69	0.72	0.70	0.77	0.74	0.73	0.74
K_2O	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.02	0.02	0.02	0.01	0.00	0.00
Total	100.92	100.00	99.83	100.62	100.26	100.62	99.73	100.18	101.33	100.42	100.73	100.43	100.76	100.35	100.52
Cations per 6 oxygens															
Si	1.974	1.981	1.973	1.891	1.976	1.979	1.961	1.996	1.988	2.001	1.992	1.998	1.984	2.001	1.990
Ti	0.000	0.001	0.001	0.001	0.001	0.002	0.001	0.002	0.001	0.001	0.000	0.002	0.002	0.002	0.002
Al	0.012	0.011	0.011	0.013	0.011	0.009	0.010	0.015	0.013	0.012	0.012	0.013	0.013	0.011	0.014
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000
Fe^{3+}	0.095	0.078	0.096	0.257	0.088	0.073	0.119	0.041	0.059	0.039	0.057	0.046	0.072	0.038	0.059
Fe^{2+}	0.466	0.490	0.464	0.446	0.476	0.574	0.496	0.488	0.559	0.524	0.503	0.557	0.476	0.545	0.497
Mn	0.016	0.018	0.017	0.016	0.018	0.019	0.018	0.016	0.020	0.018	0.018	0.019	0.017	0.018	0.016
Mg	0.531	0.531	0.533	0.528	0.535	0.546	0.532	0.538	0.534	0.536	0.521	0.559	0.537	0.555	0.528
Ca	0.853	0.839	0.851	0.795	0.842	0.755	0.809	0.852	0.775	0.816	0.843	0.749	0.846	0.776	0.840
Na	0.054	0.052	0.054	0.053	0.053	0.044	0.053	0.052	0.051	0.054	0.052	0.057	0.055	0.055	0.055
K	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.000	0.001	0.001	0.001	0.000	0.000	0.000
Wo	0.421	0.414	0.421	0.392	0.416	0.374	0.400	0.425	0.382	0.408	0.418	0.374	0.418	0.388	0.415
En	0.265	0.266	0.267	0.264	0.267	0.273	0.266	0.269	0.267	0.268	0.261	0.279	0.268	0.278	0.264
Fs	0.233	0.245	0.232	0.223	0.238	0.287	0.248	0.244	0.279	0.262	0.252	0.278	0.238	0.272	0.249
Ae	0.054	0.052	0.054	0.053	0.054	0.044	0.053	0.041	0.051	0.039	0.053	0.046	0.055	0.038	0.055
Jd	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.011	0.000	0.012	0.000	0.011	0.000	0.011	0.000
Mg#	0.533	0.520	0.534	0.542	0.529	0.488	0.517	0.525	0.489	0.505	0.509	0.501	0.530	0.505	0.515
XFe	0.467	0.480	0.466	0.458	0.471	0.512	0.483	0.475	0.511	0.495	0.491	0.499	0.470	0.495	0.485

B.1. (Continued)

No.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	Av.
SiO_2	51.83	51.96	51.90	51.58	51.94	52.12	51.77	52.01	51.97	51.96	51.88	51.65	51.66	51.89	51.38	51.67
TiO_2	0.06	0.07	0.05	0.09	0.05	0.07	0.07	0.06	0.07	0.09	0.07	0.07	0.06	0.07	0.07	0.06
Al_2O_3	0.27	0.30	0.32	0.27	0.25	0.24	0.25	0.27	0.26	0.59	0.56	0.53	0.56	0.56	0.56	0.32
Cr_2O_3	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.03	0.00	0.02	0.01	0.00	0.00	0.01
FeO_t	17.39	16.83	17.34	17.14	16.80	16.89	16.99	17.14	17.33	16.60	16.91	16.49	16.82	16.87	16.76	17.58
MnO	0.50	0.50	0.51	0.49	0.50	0.51	0.52	0.50	0.52	0.60	0.55	0.56	0.61	0.64	0.56	0.54
MgO	9.39	9.33	9.24	9.18	9.24	9.11	9.04	9.42	9.25	9.36	9.42	9.35	9.32	9.24	9.21	9.32
CaO	20.76	20.73	20.55	20.47	20.75	20.70	20.60	20.49	20.83	20.15	20.50	20.42	20.00	20.42	20.60	20.18
Na_2O	0.71	0.77	0.77	0.75	0.72	0.71	0.69	0.72	0.79	0.94	0.87	0.91	0.95	0.80	0.86	0.75
K_2O	0.00	0.00	0.00	0.00	0.01	0.01	0.04	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.01
Total	100.93	100.50	100.67	99.99	100.27	100.38	99.97	100.61	101.02	100.31	100.78	100.00	100.00	100.51	99.99	100.42
Cations per 6 oxygens																
Si	1.979	1.989	1.986	1.988	1.995	2.001	1.997	1.990	1.982	1.989	1.978	1.983	1.985	1.987	1.975	1.983
Ti	0.002	0.002	0.001	0.003	0.002	0.002	0.002	0.002	0.002	0.003	0.002	0.002	0.002	0.002	0.002	0.002
Al	0.012	0.013	0.014	0.012	0.011	0.011	0.012	0.012	0.012	0.027	0.025	0.024	0.026	0.025	0.025	0.015
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.000
Fe^{3+}	0.079	0.062	0.068	0.063	0.051	0.036	0.044	0.058	0.079	0.059	0.080	0.073	0.072	0.057	0.085	0.073
Fe^{2+}	0.476	0.477	0.487	0.489	0.489	0.507	0.504	0.491	0.473	0.473	0.459	0.456	0.468	0.483	0.454	0.492
Mn	0.016	0.016	0.016	0.016	0.016	0.017	0.017	0.016	0.017	0.020	0.018	0.018	0.020	0.021	0.018	0.017
Mg	0.534	0.532	0.527	0.527	0.529	0.521	0.520	0.537	0.526	0.534	0.535	0.535	0.534	0.527	0.528	0.533
Ca	0.849	0.850	0.843	0.845	0.854	0.852	0.851	0.840	0.851	0.827	0.837	0.840	0.823	0.838	0.849	0.830
Na	0.052	0.057	0.057	0.056	0.054	0.053	0.052	0.054	0.058	0.069	0.064	0.068	0.071	0.060	0.064	0.056
K	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Wo	0.419	0.421	0.415	0.418	0.425	0.426	0.425	0.416	0.421	0.409	0.409	0.412	0.405	0.413	0.413	0.410
En	0.267	0.266	0.264	0.264	0.264	0.261	0.260	0.269	0.263	0.267	0.268	0.267	0.267	0.264	0.264	0.267
Fs	0.238	0.238	0.243	0.245	0.244	0.253	0.252	0.245	0.237	0.236	0.230	0.228	0.234	0.242	0.227	0.246
Ae	0.052	0.058	0.057	0.056	0.051	0.036	0.044	0.054	0.058	0.059	0.065	0.068	0.071	0.057	0.064	0.053
Jd	0.000	0.000	0.000	0.000	0.003	0.011	0.008	0.000	0.000	0.011	0.000	0.000	0.000	0.003	0.000	0.003
Mg#	0.529	0.528	0.520	0.519	0.520	0.507	0.508	0.523	0.526	0.530	0.538	0.540	0.533	0.522	0.537	0.521
XFe	0.471	0.473	0.480	0.481	0.480	0.493	0.492	0.477	0.474	0.470	0.462	0.460	0.467	0.478	0.463	0.480

B.2.

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Av.
SiO_2	49.13	49.80	49.44	49.90	49.23	50.08	50.17	50.11	50.36	50.06	50.19	50.12	50.10	50.06	50.05	49.97	50.17	50.34	49.96
TiO_2	0.06	0.06	0.04	0.03	0.05	0.08	0.06	0.05	0.07	0.03	0.05	0.04	0.05	0.03	0.07	0.06	0.07	0.10	0.06
Al_2O_3	0.04	0.03	0.03	0.02	0.02	0.07	0.10	0.07	0.09	0.05	0.03	0.08	0.07	0.15	0.14	0.18	0.15	0.14	0.08
Cr_2O_3	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00
FeO_t	38.14	37.92	37.95	37.99	37.49	37.18	37.25	37.62	37.24	37.37	37.38	37.42	37.12	36.71	36.67	36.71	36.95	36.96	37.34
MnO	1.27	1.28	1.26	1.26	1.25	1.28	1.35	1.30	1.24	1.25	1.24	1.26	1.23	1.55	1.54	1.53	1.47	1.52	1.34
MgO	11.68	11.94	11.67	11.65	12.05	11.84	11.65	11.69	11.89	11.51	11.60	11.54	11.54	11.81	11.88	11.73	11.80	11.75	11.73
CaO	0.61	0.62	0.63	0.61	0.61	0.63	0.67	0.65	0.61	0.66	0.68	0.58	0.64	0.75	0.60	0.61	0.65	0.58	0.63
Na_2O	0.01	0.03	0.02	0.04	0.01	0.01	0.02	0.03	0.02	0.02	0.01	0.05	0.03	0.05	0.00	0.00	0.02	0.00	0.02
K_2O	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.00
Total	100.93	101.68	101.05	101.53	100.72	101.17	101.27	101.52	101.52	100.96	101.21	101.09	100.80	101.11	100.97	100.78	101.29	101.39	101.17
Cations per 6 oxygens																			
Si	1.960	1.969	1.969	1.978	1.963	1.988	1.992	1.985	1.992	1.995	1.995	1.994	1.999	1.987	1.990	1.992	1.989	1.995	1.985
Ti	0.002	0.002	0.001	0.001	0.002	0.002	0.002	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.002	0.003	0.002
Al	0.002	0.001	0.001	0.001	0.001	0.003	0.005	0.003	0.004	0.002	0.002	0.004	0.004	0.007	0.007	0.008	0.007	0.006	0.004
Cr	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe^{3+}	0.076	0.061	0.060	0.044	0.071	0.017	0.010	0.026	0.010	0.008	0.008	0.010	0.000	0.021	0.010	0.005	0.012	0.000	0.025
Fe^{2+}	1.196	1.193	1.204	1.215	1.179	1.218	1.227	1.220	1.222	1.238	1.234	1.236	1.239	1.198	1.210	1.219	1.214	1.225	1.216
Mn	0.043	0.043	0.043	0.042	0.042	0.043	0.045	0.044	0.042	0.042	0.042	0.042	0.042	0.052	0.052	0.052	0.049	0.051	0.045
Mg	0.694	0.703	0.693	0.688	0.716	0.701	0.689	0.690	0.701	0.684	0.687	0.684	0.686	0.699	0.704	0.697	0.697	0.694	0.695
Ca	0.026	0.026	0.027	0.026	0.026	0.027	0.029	0.028	0.026	0.028	0.029	0.025	0.028	0.032	0.026	0.026	0.028	0.025	0.027
Na	0.001	0.003	0.002	0.003	0.000	0.001	0.002	0.003	0.001	0.002	0.001	0.004	0.002	0.004	0.000	0.000	0.001	0.000	0.002
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.000
Wo	0.013	0.013	0.013	0.013	0.013	0.013	0.014	0.014	0.013	0.014	0.014	0.012	0.014	0.016	0.013	0.013	0.014	0.012	0.013
En	0.347	0.352	0.346	0.344	0.358	0.350	0.344	0.345	0.350	0.342	0.343	0.342	0.343	0.348	0.351	0.347	0.348	0.347	0.347
Fs	0.598	0.596	0.602	0.607	0.589	0.608	0.613	0.609	0.610	0.618	0.617	0.617	0.619	0.597	0.603	0.608	0.605	0.612	0.607
Mg#	0.367	0.371	0.365	0.362	0.378	0.365	0.360	0.361	0.364	0.356	0.358	0.356	0.357	0.368	0.368	0.364	0.365	0.362	0.364
XFe	0.633	0.629	0.635	0.638	0.622	0.635	0.640	0.639	0.636	0.644	0.642	0.644	0.644	0.632	0.632	0.636	0.635	0.638	0.636

B.3.

No.	1	2	3	4	5	6	7	8	9	Av.
SiO_2	41.81	41.67	41.93	41.81	41.86	42.17	40.92	41.94	41.89	41.78
TiO_2	1.18	1.13	1.14	1.10	1.11	1.11	1.02	1.07	0.97	1.09
Al_2O_3	10.65	10.68	10.89	10.66	10.75	10.42	10.85	10.42	10.82	10.68
Cr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeO_t	19.59	19.49	19.45	19.45	19.23	19.32	20.69	19.10	19.41	19.53
MnO	0.69	0.74	0.71	0.64	0.67	0.61	0.64	0.62	0.67	0.67
MgO	9.19	9.20	9.18	9.59	9.53	9.61	9.51	9.56	9.48	9.43
CaO	10.76	10.56	10.70	10.81	10.69	10.72	9.62	10.84	10.66	10.60
Na_2O	2.14	2.19	2.13	2.23	2.24	2.25	2.01	2.20	2.23	2.18
K_2O	1.72	1.69	1.57	1.68	1.62	1.68	1.55	1.74	1.64	1.65
Total	97.73	97.35	97.71	97.97	97.70	97.89	96.81	97.50	97.77	97.60
Cations per 23 oxygens										
Si	6.436	6.440	6.442	6.407	6.429	6.470	6.341	6.459	6.430	6.428
Al^{IV}	1.564	1.560	1.558	1.593	1.571	1.530	1.659	1.541	1.570	1.572
Sum T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Al^{VI}	0.369	0.385	0.413	0.332	0.375	0.354	0.323	0.351	0.387	0.365
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000
Ti	0.137	0.131	0.132	0.127	0.128	0.129	0.118	0.124	0.112	0.126
Fe^{3+}	0.000	0.000	0.000	0.016	0.000	0.000	0.189	0.000	0.000	0.023
Mg	2.109	2.119	2.102	2.190	2.181	2.197	2.196	2.194	2.169	2.162
Fe^{2+}	2.522	2.519	2.499	2.477	2.470	2.479	2.492	2.460	2.492	2.490
Sum C	5.136	5.154	5.146	5.142	5.155	5.159	5.319	5.130	5.159	5.167
Mn	0.089	0.097	0.093	0.083	0.087	0.079	0.084	0.082	0.087	0.087
Ca	1.775	1.749	1.761	1.775	1.759	1.762	1.597	1.789	1.753	1.747
Na	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum B	1.864	1.845	1.854	1.858	1.846	1.841	1.681	1.870	1.841	1.833
Na	0.639	0.656	0.634	0.663	0.667	0.669	0.604	0.657	0.664	0.650
K	0.338	0.333	0.308	0.329	0.317	0.329	0.307	0.342	0.321	0.325
Sum A	0.977	0.990	0.942	0.991	0.985	0.998	0.910	0.999	0.985	0.975
Total	15.977	15.989	15.941	15.991	15.985	15.998	15.911	15.999	15.984	15.975
Mg#	0.455	0.457	0.457	0.469	0.469	0.470	0.468	0.471	0.465	0.465
XFe	0.545	0.543	0.543	0.531	0.531	0.530	0.532	0.529	0.535	0.535

B.4.

No.	1	2	3	4	5	6	7	Av.
SiO_2	63.41	63.49	63.54	63.33	64.09	63.67	64.06	63.66
TiO_2	0.04	0.04	0.01	0.04	0.05	0.03	0.05	0.04
Al_2O_3	22.37	22.18	21.99	21.99	22.12	22.12	22.18	22.14
Cr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeO_t	0.15	0.08	0.10	0.11	0.03	0.03	0.09	0.08
MnO	0.02	0.02	0.00	0.02	0.00	0.01	0.00	0.01
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	4.03	3.66	3.34	3.83	3.51	3.57	3.68	3.66
Na_2O	8.84	8.84	8.84	8.65	9.04	9.11	8.89	8.89
K_2O	0.32	0.31	0.24	0.33	0.24	0.31	0.25	0.29
Total	99.18	98.63	98.06	98.31	99.08	98.85	99.20	98.76
Cations per 8 oxygens								
Si	2.836	2.854	2.873	2.861	2.866	2.851	2.865	2.858
Ti	0.001	0.001	0.000	0.002	0.002	0.001	0.002	0.001
Al	1.179	1.175	1.172	1.171	1.166	1.167	1.169	1.171
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe^{3+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe^{2+}	0.006	0.003	0.004	0.004	0.001	0.001	0.003	0.003
Mn	0.001	0.001	0.000	0.001	0.000	0.001	0.000	0.000
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ca	0.193	0.176	0.162	0.185	0.168	0.171	0.176	0.176
Na	0.767	0.771	0.775	0.758	0.784	0.791	0.771	0.774
K	0.018	0.018	0.014	0.019	0.014	0.018	0.014	0.016
Xan	0.197	0.183	0.170	0.193	0.174	0.175	0.183	0.182
Xab	0.784	0.799	0.815	0.787	0.812	0.807	0.802	0.801
Xor	0.018	0.019	0.015	0.020	0.014	0.018	0.015	0.017

B.5.

	Biotite						Iron-rich biotite		
No.	1	2	3	4	5	Av.	1	2	Av.
SiO_2	37.18	37.15	37.50	37.09	37.02	37.19	37.61	38.28	37.95
TiO_2	4.36	4.31	4.17	3.80	3.70	4.07	0.25	0.13	0.19
Al_2O_3	13.11	13.28	13.42	13.00	13.02	13.17	12.81	12.62	12.72
Cr_2O_3	0.01	0.04	0.00	0.05	0.00	0.02	0.03	0.03	0.03
FeO_t	19.52	19.08	18.92	18.71	18.69	18.98	23.14	22.87	23.01
MnO	0.37	0.34	0.35	0.33	0.31	0.34	0.34	0.40	0.37
MgO	11.55	11.88	11.55	12.56	12.71	12.05	11.43	11.70	11.57
CaO	0.00	0.06	0.06	0.00	0.01	0.03	0.18	0.04	0.11
Na_2O	0.05	0.08	0.10	0.10	0.11	0.09	0.00	0.00	0.00
K_2O	10.45	10.28	10.13	10.08	10.09	10.21	10.09	10.15	10.12
Total	96.61	96.49	96.21	95.71	95.67	96.14	95.89	96.22	96.05
Cations per 11 oxygens									
Si	2.899	2.889	2.924	2.887	2.880	2.896	2.938	2.971	2.955
Ti	0.256	0.252	0.244	0.222	0.216	0.238	0.015	0.008	0.011
Al^{IV}	1.101	1.111	1.076	1.113	1.120	1.104	1.062	1.029	1.046
Al^{VI}	0.104	0.106	0.157	0.079	0.073	0.104	0.118	0.126	0.122
Cr	0.001	0.002	0.000	0.003	0.000	0.001	0.002	0.002	0.002
Fe^{3+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe^{2+}	1.273	1.241	1.234	1.218	1.216	1.236	1.512	1.485	1.498
Mn	0.025	0.022	0.023	0.021	0.021	0.022	0.023	0.026	0.024
Mg	1.342	1.377	1.342	1.457	1.474	1.398	1.331	1.354	1.342
Ca	0.000	0.005	0.005	0.000	0.001	0.002	0.016	0.003	0.009
Na	0.008	0.013	0.016	0.016	0.016	0.014	0.000	0.000	0.000
K	1.039	1.020	1.007	1.001	1.001	1.014	1.006	1.005	1.005
H	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Mg#	0.513	0.526	0.521	0.545	0.548	0.531	0.468	0.477	0.473
XFe	0.487	0.474	0.479	0.455	0.452	0.469	0.532	0.523	0.527

B.6.

No.	1	2	3	4	5	Av.
SiO_2	0.09	0.02	0.01	0.05	0.03	0.04
TiO_2	51.78	51.78	51.06	52.05	51.71	51.68
Al_2O_3	0.02	0.00	0.00	0.00	0.02	0.01
Cr_2O_3	0.00	0.03	0.02	0.00	0.00	0.01
FeO_t	40.71	40.37	40.79	41.22	41.33	40.88
MnO	7.28	7.11	6.89	7.01	6.79	7.02
MgO	0.00	0.03	0.00	0.00	0.00	0.01
CaO	0.03	0.01	0.05	0.00	0.00	0.02
Na_2O	0.03	0.00	0.04	0.00	0.01	0.01
K_2O	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.93	99.36	98.85	100.33	99.89	99.67