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# Characteristics of djerfisherite from fluid-rich, metasomatized alkaline intrusive environments and anhydrous enstatite chondrites and achondrites

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**Running Title:** *Formation of terrestrial and extraterrestrial djerfisherite*

## Abstract

Djerfisherite is a K-Cl bearing sulfide that is present in both ultra-reduced extraterrestrial enstatite meteorites (E chondrites and enstatite achondrites or aubrites) and reduced terrestrial alkaline intrusions, kimberlites, ore deposits and skarns. Major element chemistry of two terrestrial occurrences of djerfisherite (from the Ilímaussaq and Khibina alkaline igneous suites) and three extraterrestrial examples of djerfisherite have been determined and combined with petrographic characterization and element mapping to unravel three discrete modes of djerfisherite formation. High Fe/Cu is characteristic of extraterrestrial djerfisherite and low Fe/Cu is typical of terrestrial djerfisherite. Ilímaussaq djerfisherite, which has high Fe contents (~55 wt%) is the exception. Low Ni contents are typical of terrestrial djerfisherite due to preferential incorporation of Fe and/or Cu over Ni, but Ni contents of up to 2.2 wt% are measured in extraterrestrial djerfisherite. Extensive interchange between K and Na is evident in extraterrestrial samples, though Na is limited (<0.15 wt%) in terrestrial djerfisherite. We propose three setting-dependent mechanisms of djerfisherite formation: primitive djerfisherite as a product of nebula condensation in the unequilibrated E chondrites; formation by extensive K-metasomatism in Khibina djerfisherite; and as a product of primary 'unmixing' due to silicate-sulfide immiscibility for Ilímaussaq djerfisherite. There are several important reasons why a deeper understanding of the petrogenesis of this rare and unusual mineral is valuable: (1) Its anomalously high K-contents make it a potential target for Ar-Ar geochronology to constrain the timing of metasomatic alteration; (2) typically high Cl-contents (~1.1 wt%) mean it can be used as a valuable tracer of fluid evolution during metasomatic alteration; and (3) it may be a potential source of K and magmatic Cl in the sub-continental lithospheric mantle (SCLM), which has implications for metal solubility and the generation of ore deposits.

**Keywords:** djerfisherite, metasomatism, alkaline intrusions, enstatite chondrite, sulfide immiscibility

## Introduction

Djerfisherite, ((Na, K)$_6$(Fe, Cu, Ni)$_{25}$S$_{26}$Cl), a potassium-bearing sulfide mineral, was first reported in meteorites by Ramdohr (1963) and later described in the enstatite (E) chondrite St. Mark's (high-Fe subgroup 'EH' and petrologic type 5 'EH5'; Fuchs, 1966). Since then, it has been recognized as a minor sulfide-phase in other E chondrites, the aubrites (or enstatite achondrites), and rarely in iron meteorites (e.g., Toluca; El Goresy et al., 1971**)**. The anhydrous E chondrites are some of the most reduced materials in the solar system, evidenced by the presence of FeO-poor silicates, metallic Fe-Ni phases, and Si-bearing metal. These ultra-reducing conditions also resulted in the formation of unusual sulfide mineral assemblages, where predominantly lithophile elements (e.g., K, Na, Ca) behave in a chalcophile manner. The formation of djerfisherite and other sulfides in these primitive meteorites is not yet well understood. Several modes of formation have been suggested for djerfisherite and other sulfides in E chondrites: (*i*) a primitive nebular condensate from gas of solar composition in a reducing environment (C/O>1; Lin and El Goresy, 2002; Lehner, et al, 2010**;** Ebel and Sack, 2013), (*ii*) sulfidization of metal by $H_2S$ in the solar nebula (as for troilite; Grossman, 2010; Lauretta et al., 1997; Lauretta et al., 1998) or Fe-O bearing silicates (as for niningerite ((Mg,Fe)S); Lehner et al., 2013), *(iii)* a non-nebular sulfidization process (Jacobsen et al. 2013) or (*iv*) the result of post-accretionary heating of the EH parent body or bodies under reducing conditions (e.g., the result of thermal metamorphic events; Müller and Jessberger, 1985) or impact melting (Van Niekerk and Keil, 2011).

An overview of djerfisherite formed in terrestrial and extraterrestrial environments is provided in **Figure A1** in the Supplementary Materials. Djerfisherite was first described in detail in terrestrial rocks from the Cu-Ni-sulfide deposit of Talnakh (Noril'sk, Siberia; Genkin et al., 1971). Terrestrial occurrences of accessory djerfisherite are rare and are typically restricted to silica-undersaturated rocks, such as alkaline igneous complexes (e.g., Khibina, Guli Dunite Complex; Korobeinikov et al., 1998; Zaccarini et al., 2007) and kimberlites (e.g., Elwin Bay, Udachnaya; Clarke et al., 1994; Sharygin et al., 2007) but have also been documented in mafic diatremes (Czamanske and Moore, 1977), Cu-ore sulfide deposits (Genkin et al., 1971) and metamorphosed calcareous rocks (Jamtveit et al., 1997; Beard and Drake, 2007).

The goals of the present study are three-fold: (1) provide an overview of terrestrial and extraterrestrial djerfisherite occurrences in the context of new data from the Ilímaussaq alkaline igneous complex (SW Greenland), the Khibina Massif (Kola Peninsula, Russia) and three meteorite samples, ALH 77295 (Alan Hills, Transantarctic Mountains, Antarctica), SAH 97096 (Sahara Desert, Africa) and Peña Blanca Spring; (2) characterize the petrography and mineral chemistry of djerfisherite from samples of distinct provenance, and (3) examine the contrasting sample sets and discuss common elements of djerfisherite formation across different, yet extreme petrological environments. More broadly, we show that this unusual accessory phase has the potential to be (i) a useful tracer of metasomatic activity in alkaline intrusions, (ii) an essential source of K and Cl in the lower crust and upper sub-continental lithospheric mantle (SCLM), and finally (iii) a unique and valuable tool to fingerprint extreme and ultra-reducing conditions in both extraterrestrial and terrestrial systems.

## Sample Descriptions and Geologic Setting

A brief summary of all sample descriptions is given in **Table 1** and representative photomicrographs are presented in **Figure 1**. Thick sections (50 −100 μm) of all samples were examined in reflected light using a Nikon Eclipse LV150 microscope with integrated digital camera. The full area of each of the sections was optically mapped at 5-10x magnification. Areas containing sulfide assemblages were mapped further at 20x and 50x magnification. This included six target areas in Ilímaussaq, three in Khibina, 23 areas in ALH 77295, two areas in SAH 97096 (though many occurrences of djerfisherite in SAH 97096 were identified but not mapped due to their much smaller size of ~10−30 μm grainsize), and one area in Peña Blanca Spring.

*Terrestrial Samples: The Ilímaussaq Complex (SW Greenland) and Khibina (Kola Peninsula, Russia)*

The Ilímaussaq intrusion is an ~18 x 8 $km^2$ elongate alkaline to peralkaline intrusion predominantly comprising syenitic and nepheline-syenitic rocks (Marks and Markl, in press). A U-Pb baddeleyite age of 1160 ± 5 Ma assigns the intrusion to the mid-Proterozoic (Krumrei et al., 2006). The Ilímaussaq rocks are typically highly differentiated and peralkaline, as well as rich in the alkalis (Na, K, Rb, etc.), the halogens (F, Cl; Marks and Markl, in press) and show extreme enrichment in the REE-minerals, making the intrusion of great economic interest. The unique assemblages in the Ilímaussaq rocks are believed to be the result of low oxygen fugacity, low $SiO_2$ activity and very low $H_2O$ activity in the Ilímaussaq parental melt, which is thought to have resembled a highly fractionated alkali basalt (Larsen and Sørensen, 1987). The rocks are also extensively metasomatized and the late-stage hydrothermal alteration of cumulate by agpaitic fluids (molar proportions of (Na+K)/Al>1) has led to a diverse and very unusual mineral assemblage (Upton and Emeleus, 1987; Marks and Markl, in press).

Three principal intrusive suites in the Ilímaussaq intrusion have been identified and consist of (a) metaluminous augite-bearing syenites, (b) peralkaline granites and quartz syenites and (c) peralkaline nepheline-bearing syenites (Larsen and Sørensen, 1987; Upton and Emeleus, 1987). The latter, an agpaitic suite, is highly differentiated and is the host of the djerfisherite-bearing cumulates (naujaites) that are the focus of this study (Larsen and Sørensen, 1987). Crystallization is believed to have occurred at approximately 1 kbar (2-3 km; Markl et al., 2001) though there is some suggestion from work on sodalite-hosted fluid inclusions that estimates crystallization at 3-4 kbar (10-12 km; (Markl, et al., 2001; Krumrei et al., 2006; Markl et al., 2010). There is one reported occurrence of djerfisherite in the Ilímaussaq (Karup-Møller, 1978), in association with K-free thallium-sulfide, thalcusite ($Tl_2(Cu,Fe)_4S_4$;Karup-Møller and Makovicky, 2001). The sample studied here is a sulfide-bearing analcime-pegmatite from Kvanefjeld. Approximately 1-10 μm anhedral djerfisherite grains (**Fig. 1a**) are concentrated around or close to the margins of anhedral 3-5 mm long aenigmatite crystals. The djerfisherite and other sulfides are often closely associated with small (<50 μm) non-stoichiometric sulfide minerals with pronounced exsolution textures (**Fig. 1b**).

A second terrestrial sample from a well-documented djerfisherite-bearing locality in the Khibina Massif (also Khibny), Kola Peninsula (Russia), was examined (Sokolva et al., 1970). The Paleozoic Khibina Massif is located in the central portion of the Kola Alkaline province. It comprises a suite of 24 alkaline-carbonatitic-ultrabasic complexes (ca. 360-380 Ma; Zaitsev et al., 1998; Ageeva et al., 2012) and covers an area >1300 $km^2$. The suite of intrusions can be broadly divided into agpaitic nepheline-syenites, ijolite-urtites and rischorrites (feldspathoid-bearing syenites). The sample studied here was obtained from Excalibur Minerals Ltd. (New York) and contains three djerfisherite grains (roughly 1-5 mm in diameter, see **Fig. A2 in the Supplementary Materials**) within a pegmatitic groundmass (in a sample of approximately 3.5 $cm^2$ in size).

*Extraterrestrial Samples*

Two unequilibrated EH chondrites (petrologic type 3, ALH 77295 and SAH 97096) and one aubrite (Peña Blanca Spring) were selected for this study (**Table 1**). The EH3 samples were selected as they are the most primitive of the E chondrites and have experienced the least amount of secondary processing (e.g., thermal metamorphism) on the EH chondritic parent body(ies), with no visible evidence of hydrothermal alteration. They are pristine, unaltered and contain relatively abundant djerfisherite (up to 0.1 vol%). Peña Blanca Spring, an aubrite, provides an igneous counterpart from a differentiated parent body, of similar chemical composition to the EH chondrites, for comparison with the 'primitive' djerfisherite found in the EH chondrites.

*ALH 77295.* Four sections of ALH 77295 were examined. ALH 77295 is comprised of enstatite, kamacite (α-(Fe-Ni)) and troilite (FeS) ± niningerite ((Mg,Fe)S) ± oldhamite (CaS) ± daubrèelite ($FeCr_2S$) ± djerfisherite ($(Na,K)_6(Fe,Cu,Ni)_{25}S_{26}Cl$) ± graphite. Chondrules, ferromagnesian silicate-rich igneous spherules which formed early (e.g., 1-4 Ma after solar system formation), and likely in a different region to the chondrites (Alexander et al., 2008), are abundant, often rimmed by metal or sulfide and have a maximum diameter of ~ 1.4 mm. Djerfisherite is not present in chondrules, but chondrules may be rimmed externally by sulfides. Sulfides are texturally distributed in two principal ways: (1) in the interstices of the enstatite crystals, disseminated throughout the groundmass as small grains and (2) associated with concentrically layered metal-sulfide (often troilite) nodules (with chondrule-like accretionary textures; **Fig. 1c**). Djerfisherite is the dominant lithophile-bearing sulfide with minor troilite in clasts of oblong kamacite-rich nodules (**Fig. 1d**). A large (~ 500 μm x 20-50 μm) vein-like structure of djerfisherite is also present (**Fig. 1e**) and is the only such vein observed in an extraterrestrial sample in this study.

*SAH 97096.* Three sections of SAH 97096 were examined. The mineral assemblage consists of enstatite, kamacite and troilite ± niningerite ± oldhamite ± daubrèelite ± djerfisherite ± graphite and a secondary djerfisherite 'breakdown' assemblage of 'porous troilite' or 'Qinzhen' texture (**Fig. 1f**). The 'Qinzhen' texture has been previously described by Lin and El Goresy (2002) and suggested to be indicative of Ar-loss from djerfisherite during a transformation to troilite upon heating (El Goresy, pers. comm). No other djerfisherites in the section exhibit this particular texture. Unlike ALH 77295, no djerfisherite veins were found but the modal proportion of sulfide (not including djerfisherite) is generally higher and the mineral assemblage more diverse. Opaque veins (kamacite) are common and in some cases cross-cut existing sulfides (oldhamite and niningerite; **Fig. 1g**). Concentrations of small amounts of sulfide (often troilite) occur along chondrule rims and linear trails of troilite leading to small sulfide grains in the matrix, and interstices are also observed. Chondrules are often oblong and are up to 1.3 mm in diameter. The mineralogy and proportions of the small sulfides around the chondrule rims is similar to that of the bulk section. Exsolution lamellae are present in some sulfides and there are complex intergrowths of kamacite-troilite myrmekites and Fe-FeS intergrowth textures present in small patches (5-60 μm) in the matrix (**Fig. 1h).**

*Peña Blanca Spring*. Two sections of Peña Blanca Spring were analyzed. The sections are almost entirely comprised of enstatite with a brecciated texture. Sulfides are sparse, consisting of oldhamite, alabandite (MnS), troilite, djerfisherite and niningerite. The distribution of djerfisherite is limited to several small (<20 μm) grains, typically as part of a larger cluster of other sulfides (e.g., oldhamite) or rimming multi-sulfide clasts (e.g., refer to **Fig. 2g**).

## Electron Microprobe Analysis

Element mapping and quantitative analyses of all samples was carried out using a Cameca SX 100 Electron Microprobe at the University of Manchester (UK) and a Cameca SX100 at the Open University (Milton Keynes, UK). Further details of the analytical protocols are provided in the Supplementary Materials. The results of Cl, K, Cu and S element mapping of representative sections of Ilímaussaq, Khibina, SAH 97096 and ALH 77295 are illustrated in **Figure 2**. Peña Blanca Spring was mapped, but the overall element map is not shown due to djerfisherite scarcity (at the resolution of the map scale djerfisherite is not easily visible). A representative sulfide assemblage from Peña Blanca Spring is shown in **Figure 2g** instead. Element maps were collated into a single color-coded map using *ImageJ* and a manual image processing protocol (Joy et al. 2011). Areas of high intensity color are djerfisherite and notable examples of djerfisherite are highlighted by rectangular outlines in each panel. Examples of backscattered electron images for extraterrestrial djerfisherite-bearing assemblages are shown in **Figure 2e-g**. The djerfisherite compositional data for all samples are provided in the Supplementary Materials and plotted in **Figures 3 and 4.** The generalized structure of djerfisherite was first determined by Dmitrieva and Ilyukhin (1975) and reported by (Evans and Clark, 1981) as: $A_{6-x}BM_{24-y}S_{26}X_{1-x}$, where the M site (tetrahedral) may contain Fe, Cu or Ni; the B site (octahedral) may contain Cu, Na, or Li; A may be K or Na; and X is Cl (refer to **Supplementary Materials Figure A1** for a review). Representative (calculated) mineral formulae are given in **Supplementary Materials Table A2** and further discussion of chemical variation and substitutions is provided below.

The overall major element chemistry of djerfisherite is internally consistent for each sample but variations exist between samples, both terrestrial and extraterrestrial. Extraterrestrial djerfisherite shows considerable compositional variation, with the djerfisherite in ALH 77295 distinct from SAH 97096. ALH 77295 djerfisherite contains 51.0–53.9 wt% Fe and 31.5–34.4 wt% S. Nickel is significantly higher than in any of the terrestrial samples measured in this study (typically 0.1 wt%), reaching concentrations up to 2.2 wt% with Cu showing a slightly higher range of 1.5-2.7 wt%. Potassium shows some variation between analyses, from 6.4 to 8.5 wt%, while Cl is consistent with an average concentration of 1.4 wt. %. SAH 97096 djerfisherite is Fe-poor compared to ALH 77295 at 47.3–51.5 wt%, with relatively constant S at 33.5–34.9 wt%. Nickel contents are comparable to ALH 77295, reaching concentrations of 1.5 wt% and Cu concentrations exceed those measured in ALH 77295, ranging from 3.9–4.8 wt%. Potassium ranges from 7.2–7.9 wt%, while Cl is consistent for each measurement at 1.4 wt%. Peña Blanca Spring has average Fe content of 48 wt% and average S contents of 35 wt%. Nickel contents are comparable to the E chondrites at 1.3 wt%. Potassium concentrations are the highest measured in this study, reaching up to 9.8 wt%, while Cl is again comparable to all other samples at 1.5 wt%.

Terrestrial djerfisherite also shows considerable variation and distinct populations are apparent between Ilímaussaq and Khibina djerfisherite. Ilímaussaq djerfisherite is Fe-rich at 52.8–55.0 wt% and shows relatively constant S at 32.7–33.8 wt%. Nickel and Cu contents are consistently low, from below detection to ~0.24 wt%, respectively. Potassium ranges from 7.7–8.3 wt%, while Cl is consistent at 1.4 wt%. In contrast, Khibina djerfisherite has approximately 10 wt% less Fe than Ilímaussaq djerfisherite, with Fe-contents ranging from 40.3 to 43.5 wt%. Sulfur is constant at 32.0–33.2 wt%. Nickel is low with maximum concentrations of 0.13 wt% but Cu is variable and very high at 12.6 to 14.5 wt%; the highest djerfisherite Cu concentrations measured in this study. Khibina djerfisherite K concentrations are higher than in the Ilímaussaq djerfisherite at 8.7–8.9 wt%, but Cl is similar (~1.4 wt%).

## Discussion

*Mineral-chemical relationships between djerfisherite populations*

All measured djerfisherite compositions are plotted together with previously published terrestrial and extraterrestrial djerfisherite compositions in **Figure 3.** In general, extraterrestrial examples tend towards high Fe and Ni contents (**Fig. 3a, c**). However, Ilímaussaq djerfisherite exceeds even the high Fe contents measured in the EH3 chondrites and is amongst the most Fe-rich of all previously reported djerfisherite compositions (**Fig. 3a, b**). It has been previously noted that djerfisherite derived from evolved complexes (e.g., Khibina pegmatite, Guli alkali carbonatite; Henderson et al., 1999) is significantly Fe-enriched, and the Fe-contents of Ilímaussaq djerfisherite even exceed these values. Published djerfisherite data in kimberlite samples (Clarke et al., 1977; Clarke et al., 1994; Sharygin et al., 2007) show the largest variation in Fe content. Djerfisherite is variably present in megacrysts, xenoliths, kimberlite groundmass and as inclusions within diamonds (though most commonly sited in megacrysts and pyroclasts; Clarke et al., 1994; Logvinova et al. 2008).

There is a strong negative correlation between Cu and Fe contents in all samples measured in this study, except the aubrite Peña Blanca Spring (**Fig. 3b**). This negative correlation appears to be the result of exchange between divalent Cu and Fe on the tetrahedral site. There is also a strong bimodal distribution between extraterrestrial djerfisherite (which tends towards high Fe and low

Cu) and terrestrial djerfisherite, which tends towards low Fe and high Cu. The Ilímaussaq djerfisherite is inconsistent with those of other igneous complexes, including the Khibina djerfisherite, instead plotting nearer to extraterrestrial djerfisherite in Fe-Cu space. The very low Cu (average of 0.16 wt) therefore likely occurs at the expense of high Fe in Ilímaussaq djerfisherite. This might represent preferential incorporation of $Fe^{2+}$ over $Cu^{2+}$ into the tetrahedral M site of djerfisherite or Cu partitioning behavior, whereby Cu is instead partitioned into neighboring Cu-sulfides (e.g., chalcopyrite). Markl and Marks (in press) note that fractionation of olivine-augite-ulvöspinel in the Ilímaussaq intrusion greatly increases the molar fraction of Fe (in mafic minerals), enriching Fe and stabilizing Fe- and Na-rich phases, such as djerfisherite. Djerfisherite in kimberlites shows a large spread in both Cu and Fe contents. As all kimberlite djerfisherites plotted in **Figure 3** and **Figure 4** (e.g., Frank Smith kimberlite, Clarke et al., 1977; Elwin Bay, Clarke et al., 1994; and Udchanaya, Sharygin et al., 2007) come from Type I kimberlites (enriched by OIB mantle source) and is thus purported to originate from the SCLM, no distinction between the overall chemistry and kimberlite classification is attempted here. However, the presence of djerfisherite in groundmass, xenoliths, inclusions in xenocrysts (e.g., in diamond) and pyroclasts suggests high Cl and K concentrations in both kimberlites and the xenocrystic material or melts that originate at depth and are transported to the surface under localized, strongly reducing conditions.

All djerfisherite measured in this study (and all published analyses) show a very restricted range in Ni contents (<5 wt%) in the tetrahedral site, with the exception of those from kimberlites. No correlation is observed between K and Ni in all measured extraterrestrial djerfisherite (**Fig. 3c**) though a trend is seen in the published E-chondrite and aubrite data. We also observe a very limited spread in the Ni contents in most measured djerfisherite (from 0.08 to 0.13 in terrestrial samples), except djerfisherite in kimberlites where higher Ni contents (up to 20 wt%) are typical (Henderson et al., 1999). No correlation is observed between K and Ni in the extraterrestrial djerfisherite measured in this work (**Fig. 3c**), though published E chondrite and aubrite data show a negative correlation (Fuchs 1966; El Goresy et al 1971, 1988; Lin & El Gorsey 2002). Khibina and Ilímaussaq djerfisherites are Ni-poor (<0.13 wt%), suggesting either limited availability of Ni or a preference for incorporation of Fe and Cu into the tetrahedral site instead. We speculate that the differences in Ni-content between djerfisherite derived from kimberlites and the other terrestrial occurrences of djerfisherite reflects the difference between ‘mantle’ (i.e., kimberlitic) djerfisherite and crustal (i.e., Cu-S ores, alkaline complexes) djerfisherite. Sodium versus K distribution is shown in **Figure 4e**, suggesting that there is evidence of significant exchange between Na and K. Data for djerfisherite in E chondrites (Fuchs, 1966; El Goresy et al., 1971; El Goresy et al., 1988; Lin and El Goresy, 2002) support this view. Those data also show the highest Na contents (up to 1.5 wt%), much higher than the samples measured in this study. The extraterrestrial samples generally contain more Na than the terrestrial samples measured in this study. In terrestrial djerfisherite, Na-K exchange could be attributed to differences in source rock, initial magma chemistry or metasomatizing fluid compositions (e.g., Na vs. K metasomatism) depending upon the mode of djerfisherite formation (see discussion below).

*Extraterrestrial djerfisherite: Formation of a nebular sulfide*

Extraterrestrial djerfisherite occurs as isolated anhedral grains in the groundmass, monomineralic djerfisherite vein structures (**Fig. 1e** and highlighted in **Fig. 2d**) and as part of metal sulfide clasts (**Fig. 1c,d, f**) but it does not occur in chondrules (chondrules are represented by the dark areas on the element map of ALH 77295, **Fig. 2d,** whereas metal-sulfide clasts are represented by white). While the formation of terrestrial djerfisherite is largely ascribed to secondary processes, djerfisherite in E chondrites has been suggested to be of primitive solar nebular origin (e.g., Lin and El Goresy 2002) and a potentially important source of K in the nebular condensation sequence (based on recent thermodynamic calculations; Ebel et al., 2012; Ebel and Sack, 2013). Textural observations and age constraints support the idea that djerfisherite formed in the solar nebula as a condensate. These constraints include the presence of djerfisherite in and accreted around concentric metal-sulfide nodules (which are suggested to be pre-accretionary objects; Weisberg and Prinz, 1998; Weisberg et al., 2013), the presence of euhedral grains in the groundmass, and 'old' djerfisherite $^{129}I$-$^{129}Xe$ ages in ALH 77295 (4564.2 ± 1.1 Ma; King et al., 2013)**,** attesting to their primitive nature. The occurrence of a large (100's of μm long) and laterally continuous vein of djerfisherite, unique to the ALH 77295 section examined in this study (**Fig. 1e**) is interesting. This textural mode of occurrence could suggest a secondary, parent body origin due to the elevated temperatures that may be required to produce such a feature. Veins can indicate melting or shock processes if high pressure assemblages are observed (cf. Chen et al., 1996). Though sulfide veins in EH chondrites are common, they typically consist of <1 mm veins of kamacite or troilite (e.g., **Fig. 1g**; or Lin and El Goresy, 2002). These features have been attributed to shock-induced melting (shock stage S3, 15-20 GPa; Lin and El Goresy, 2002). However, the djerfisherite vein observed here in ALH 77295 lacks the characteristic fine-grained metal intergrowths of such textures and shows no evidence of the typical darkening of surrounding silicates from dispersion and inclusion of metal droplets that are characteristic of shock processes (Rubin et al., 1997). Moreover, we observe no evidence of high-pressure phases, nor is there evidence of hydrous phases that would be required to 'enrich' a pre-existing sulfide (e.g., fluid-troilite reactions) with mobile elements such as K, Na and Cl at elevated temperature during thermal metamorphism. It is difficult to envisage the formation of djerfisherite on an anhydrous EH3 parent body without proposing an alternative (and significant) volatilization process during heating. Therefore, we currently rule out any secondary shock-induced or metamorphic occurrence of the mineral, and propose that the vein-like structure formed via accretion in the solar nebula as suggested for similar opaque veins in other EH chondrites instead (e.g., Qingzhen, EH3; Lin and El Goresy, 2002).

*Terrestrial djerfisherite: The role of silicate-sulfide immiscibility and metasomatism*

Occurrences of terrestrial djerfisherite are varied in setting, chemistry and likely, mode of formation. Djerfisherite from the Ilímaussaq (**Fig. 1a-b** and **Fig. 2a**) naujaites shows a discrete and restricted spatial distribution of typically small (<0.2 mm) grains with highly variable subhedral-anhedral morphologies (**Fig. 1a-b**). The occurrence of vermiform or globular sulfide textures comprised of non-stoichiometric sulfide (**Fig. 1b**) could indicate formation by ‘unmixing’ due to sulfide immiscibility. The schematic phase diagram in **Figure 5** illustrates the region of silicate-sulfide immiscibility in the FeO-FeS-$SiO_2$ system (MacLean, 1969). Remnant textures of unmixed melts may be preserved if the immiscible liquids separate due to density differences often evidenced by the presence of relict sulfide ‘globules’, as above. Indeed, recent work by Guzmics et al. (2012) suggests that the Cu-Fe-S system may be characteristic of immiscible sulfide melts that are unmixed from alkaline-silicate parent compositions. The separation of sulfide from silicate melt is envisaged to occur at crustal pressures (e.g., 5-10 kbar). The small, isolated and globular sulfide morphologies observed in the Ilímaussaq sample (**Fig. 1b**) contrast starkly with the Khibina djerfisherite grains, which occur as large (1-3 mm) and polygonal grains (shown in detail in **Fig. A2 of the Supplementary Materials**). Extensive K-veining is also present in the thin section images and element maps of the Khibina sample, as (**Fig. A2a** and **Fig. 2b,** respectively), though quantitative compositional data could not be obtained due to the fine-grained and composite nature of the material. The djerfisherite grains are intimately spatially associated with the K-rich veins, suggesting a genetic relationship between the grains and the pervasive vein structures (**Fig. A2a**). It is possible that K was delivered to pre-existing alkali-poor or alkali-free sulfides, such as chalcopyrite, via these vein networks, essentially converting a K-free sulfide into a K-rich sulfide. Alternatively, these K-enriched veins could trace the path of fluid fracture networks, where the most extreme compositions of the metasomatizing fluid front interacted with the host rock to form djerfisherite, possibly influenced by the presence of fluid inclusions (**Fig. A2d**). The ~120° internal grain boundary junctions observed between some djerfisherite grains (e.g., **Fig. A2b, c**) is a sub-solidus equilibration texture and requires a sustained thermal input, suggesting textural maturation over a relatively protracted (but unknown) time period.

The occurrence of halogen-rich sulfides that are spatially related to alkali metal sulfide mineralization in association with igneous intrusions is well documented worldwide (Karup-Møller, 1978; Kogarko, 1987; Korobeinikov et al., 1998; Henderson et al., 1999; Zaccarini et al., 2007). The presence of such halogen- and alkali-rich minerals suggests an important role of fluids and brines in transporting and concentrating such elements during syn- and post-magmatic metasomatism for forming unusual halogen-rich sulfides, including djerfisherite. In the case of Khibina, late metasomatic activity seems likely to be responsible for the generation of djerfisherite, as observed in both mineral chemistry and textural relationships. Chemically, Khibina djerfisherite is comparable to published djerfisherite compositions from numerous alkaline intrusions (Czamanske et al., 1979; Korobeinikov et al., 1998; Zaccarini et al., 2007;

**Fig. 3 and 4).** Texturally, the veining coupled with the presence of numerous sulfides and inclusions spatially associated with the K-rich veins suggests djerfisherite formation via late-stage metasomatism. In contrast, djerfisherite from the Ilímaussaq intrusion not only lacks such textural evidence (i.e., it is not associated with veins or pervasive fluid inclusion trails) indicative of formation by metasomatism, but the ubiquitous presence of globular and vermiform sulfide textures spatially associated with the djerfisherite instead favors its formation by the unmixing of sulfide-silicate melt. Therefore, Ilímaussaq djerfisherite is texturally and compositionally distinct from all other examples of classic metasomatic djerfisherite reported from other alkaline intrusions (**Fig. 3**).

*Origin of K-Cl-rich fluids and insights into metasomatism in the SCLM*

Efforts to advance our understanding of the origin of alkaline and halogen-rich mantle fluids currently constitute an area of very active research (e.g., Logvinova et al., 2008; Klein-BenDavid et al., 2009 and references therein). Important motivations in this respect include links to fluid-inclusion diamond research (e.g., Turner et al., 1990), characterization of the halogen budget of the mantle (e.g., Johnson et al., 2000; Burgess et al., 2002; Joachim et al., 2013), and facilitating an understanding of the transportation and availability of these elements at mantle depths. Potassium-Cl-rich fluids are of central importance to the production of phases like djerfisherite in the mantle. Hence, kimberlites present an opportunity to study the origin of primary 'mantle djerfisherite', owing to their deep origin and potassic composition. The presence of djerfisherite in deep (170-220 km) sheared garnet peridotitic xenoliths in the Udachnaya-East pipe kimberlite (Sharygin et al., 2012 and references within) suggests a deep-magmatic origin of djerfisherite in some kimberlites. The presence of alkali-rich Cl-bearing micro-inclusions in kimberlitic diamonds could represent the (as of yet) hypothetical initial K-Cl-rich fluid from which djerfisherite may have formed via interaction with Fe-Ni-Cu sulfides (e.g., Logvinova et al., 2008 and references therein). We speculate that the presence of high-alkali Cl-rich fluids, hypothesized to result from K-infiltration of peridotite during injection of saline fluid into the mantle wedge, might be an important contributing to factor for the generation of the Ilímaussaq (djerfisherite-bearing) naujaites, (Marks and Markl, in press). Mungall and Brenan (2003) demonstrated experimentally that in the absence of aqueous fluid, sulfide melt is capable of dissolving and transporting significant quantities of the halogens, particularly Cl. The formation of alkali- and halogen-rich sulfides in igneous bodies via purely primary magmatic processes is therefore possible in theory. Indeed, the Ilímaussaq intrusion preserves evidence for some of the most reducing conditions in any terrestrial magmatic environment (Marks and Markl, 2001). Under such conditions, an alkali-halogen-rich sulfide, such as djerfisherite, could plausibly form via silicate-sulfide immiscibility (Guzmics et al., 2012). However, the generation of the alkaline parent melt likely arose from an initially metasomatized mantle (Edgar, 1987; Larsen and Sorensen, 1987), enriched in REE and incompatible elements. Despite its low abundance, djerfisherite could, therefore, be an important source/carrier of K and Cl in the lower crust or the upper SCLM. For example, whole rock data from metasomatized garnet peridotite from Udachnaya (Siberia; Doucet et al., 2013) exhibits K contents of up to 0.4 wt%, despite K being below detection limits in all measured mineral phases (including garnet, clinopyroxene, orthopyroxene and olivine). While no sulfide abundance was reported for these particular rocks, a simple mass balance calculation indicates that djerfisherite containing 9.5 wt% K could account for all of the whole rock K when present in only 0.05 modal % abundance. Moreover, the incorporation of high concentrations (~10 wt%) of fluid-mobile K makes djerfisherite a useful phase for dating metasomatic activity by the $^{40}Ar/^{39}Ar$ method (as suggested for bartonite;

see Czamanske et al., 1978). Owing to the significant concentrations (up to 1.5 wt%) of hydrophilic Cl present, djerfisherite is also a potentially valuable geochemical tracer of fluid evolution in alkaline intrusions, as well as an indicator of magmatic Cl-activity.

## Implications

In summary, three modes of djerfisherite formation have been documented in extraterrestrial and terrestrial djerfisherite populations: (1) a product of nebular condensation (E chondrites), (2) the result of late-metasomatic activity (Khibina alkaline intrusion), and (3) the product of sulfide-immiscibility (Ilímaussaq intrusion). We emphasize the underlying importance of *initial* metasomatism in the generation of terrestrial incompatible element-enriched alkaline melts capable of producing unusual minerals, such as djerfisherite, under conditions of suitable $f_{O2}$. It is also suggested that the highly varied compositions of mantle-derived djerfisherite reported from kimberlites are likely due to unique localized fluid and rock compositions and is distinct from crustal djerfisherite. Though volumetrically a minor sulfide phase, djerfisherite's unusually high K-content makes it a valuable target for Ar/Ar geochronology and could be particularly useful for constraining the timing of metasomatism of igneous intrusions. In addition, the high Cl concentration (and probably other halogens) means that djerfisherite, in conjunction with fluid inclusions in other phases, could be a valuable tracer of fluid evolution during metasomatic alteration, as the halogens are sensitive tracers due to their incompatible and hydrophilic nature. The potential for djerfisherite to act as a sensitive indicator of Cl-activity in magmatic environments is also emphasized as this bears on metal solubility and the generation of ore deposits. Characterizing the importance of djerfisherite as a potential source of K and Cl in the

SCLM is highlighted as an avenue for future work. Efforts to determine the stability djerfisherite over a range of relevant P-T conditions, as well as characterizing the partitioning behavior of K and the halogens between djerfisherite (other sulfides?) and fluid/melt phases will be useful in better determining the role of djerfisherite as a K and halogen source in the SCLM.

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## Figure Captions

**Figure 1** Reflected light photomicrographs of samples. (a) Ilímaussaq djerfisherite showing large euhedral-subhedral grain with sulfide inclusions and (b) example of sulfide exsolution texture characteristic of the Ilímaussaq. (c) Metal-sulfide nodule in enstatite chondrite (EH3) ALH 77295. Central portion of the clast is troilite and kamacite surrounded by djerfisherite and exterior troilite in a concentric structure. The metal-sulfide nodule is set in the sample matrix of enstatite, metal and small sulfides. (d) Metal-sulfide nodule in ALH 77295 where djerfisherite is central to the clast, surrounded by troilite and kamacite in a concentric structure set in an enstatite, metal and sulfide matrix. (e) Portion of extensive djerfisherite vein in ALH 77295. (f) Metal-sulfide clast consisting of central djerfisherite and kamacite surrounded by porous troilite, characteristic of the 'Qingzhen' breakdown reaction described by Lin and El Goresy (2002). The oblong clast is set in a matrix of enstatite, metal and sulfides. (g) Kamacite vein cross-cutting through sulfide assemblage in SAH 97096. (h) Complex intergrowth of Fe-FeS (djr, djerfisherite; kam, kamacite; tro, troilite). Please see the online edition for the color version.

**Figure 2** Sulfur (pink), potassium (blue), copper and chlorine mapping of sample from **(a)** Ilímaussaq alkaline complex, **(b)** Khibina section, **(c)** ALH 77295 and **(d)** SAH 97096. Examples of djerfisherite grains are highlighted in the black box on each panel. BSE images of extraterrestrial examples of djerfisherite, **(e)** ALH 77295: complex metal-sulfide clast or metal 'chondrule'. Note the concentric accretionary-like texture of the metal and sulfide nodules. **(f)** SAH 97096: djerfisherite and kamacite clast surrounded by 'porous' troilite. **(g)** Peña Blanca

Spring: small djerfisherite grain included in larger metal-sulfide clast. (djr, djerfisherite; kam, kamacite; daub, daubréelite; tro, troilite). Please see the online edition for the color version.

**Figure 3 (a)** Sulfur vs. Fe content , (b) Copper vs. Fe content, (c) Potassium vs. Ni content, (d) Potassium vs. Fe content ,and (e) Sodium vs. K content in terrestrial and extraterrestrial djerfisherite compared to published djerfisherite analyses (all concentrations in wt%). Symbols are given in the figure key. Refer to text for discussion. References: Guli Dunite Complex (Zaccarini et al., 2007); Khibina, Kola (Czamanske et al., 1979); Salmagorski Ring Complex (Korobeinikov et al., 1998); Talnakh Cu-S deposit (Dmitrieva and Illyukhin 1975); Kimberlites: Frank Smith, Elwin Bay, Udchanaya (Clarke et al., 1977; Clarke et al., 1994; Sharygin et al., 2007); Synthetic (Czamanske et al., 1979); E chondrites, aubrites and iron octahedrite (Fuchs, 1966; El Goresy et al., 1971; El Goresy et al., 1988; Lin and El Goresy, 2002). Please see the online edition for the color version.

**Figure 4** A summary of all djerfisherite on Cu-Fe-Ni and Cu-Fe-Ni, Na-K, S ternary diagrams. (a) Ni-Cu-Fe ternary for terrestrial and extraterrestrial djerfisherite. (b) Close up $Fe_{50}Cu_{50}$ and $Fe_{50}Ni_{50}$ portion of the ternary shown in (a). K-Na, S, Cu-Fe-Ni ternary for djerfisherite (c). All analyses normalized to 100% prior to plotting. See legend for symbols. Refer to text for discussion. Note there is a restricted zone for djerfisherite compositions, regardless of terrestrial or extraterrestrial origin (**c**). The controls on djerfisherite compositional variability in Fe-Ni-Cu space (**a,b**) include a lack of Ni and high exchange between Fe-Cu. The large spread in Fe-Cu contents of djerfisherite from kimberlites compared to those from other igneous complexes, which are restricted in Fe-Cu space is notable. Please see the online edition for the color version.

**Figure 5** Schematic of the FeO-FeS-$SiO_2$ pseudo ternary **(**modified after MacLean, 1969)**)** to illustrate the silicate-sulfide immiscibility field as applicable to the Ilímaussaq djerfisherite.

**Tables**

**Table 1.** Brief sample descriptions.

| **Sample** | **Type/Host** | **Description** | Reference* |
|---|---|---|---|
| Khinbina Massif (Kola Peninsula, Russia) | Alkaline igneous complex | Peralkaline syenites, pegmatitic | Sokolova et al., 1970 |
| Ilímausaq (SW Greenland) | Alkaline igneous complex | Nepheline-bearing peralkaline syenites | Karup-Møller, 1978 |
| ALH 77295 | Enstatite chondrite (EH3) | Unequilibrated mix of enstatite + Fe-metal+ sulfides + chondrules + matrix | Kimura and El Goresy, 1988 |
| SAH 97096 | Enstatite chondrite (EH3) | Unequilbrated mix of enstatite + Fe-metal+ sulfides + chondrules + matrix | Weisberg and Prinz, 1998 |
| Peña Blanca Spring | Enstatite achondrite (aubrite) | Equilibrated enstatite + metal + sulfides | El Goresy et al., 1971 |

**Complete description of djerfisherite for particular locality or sample*

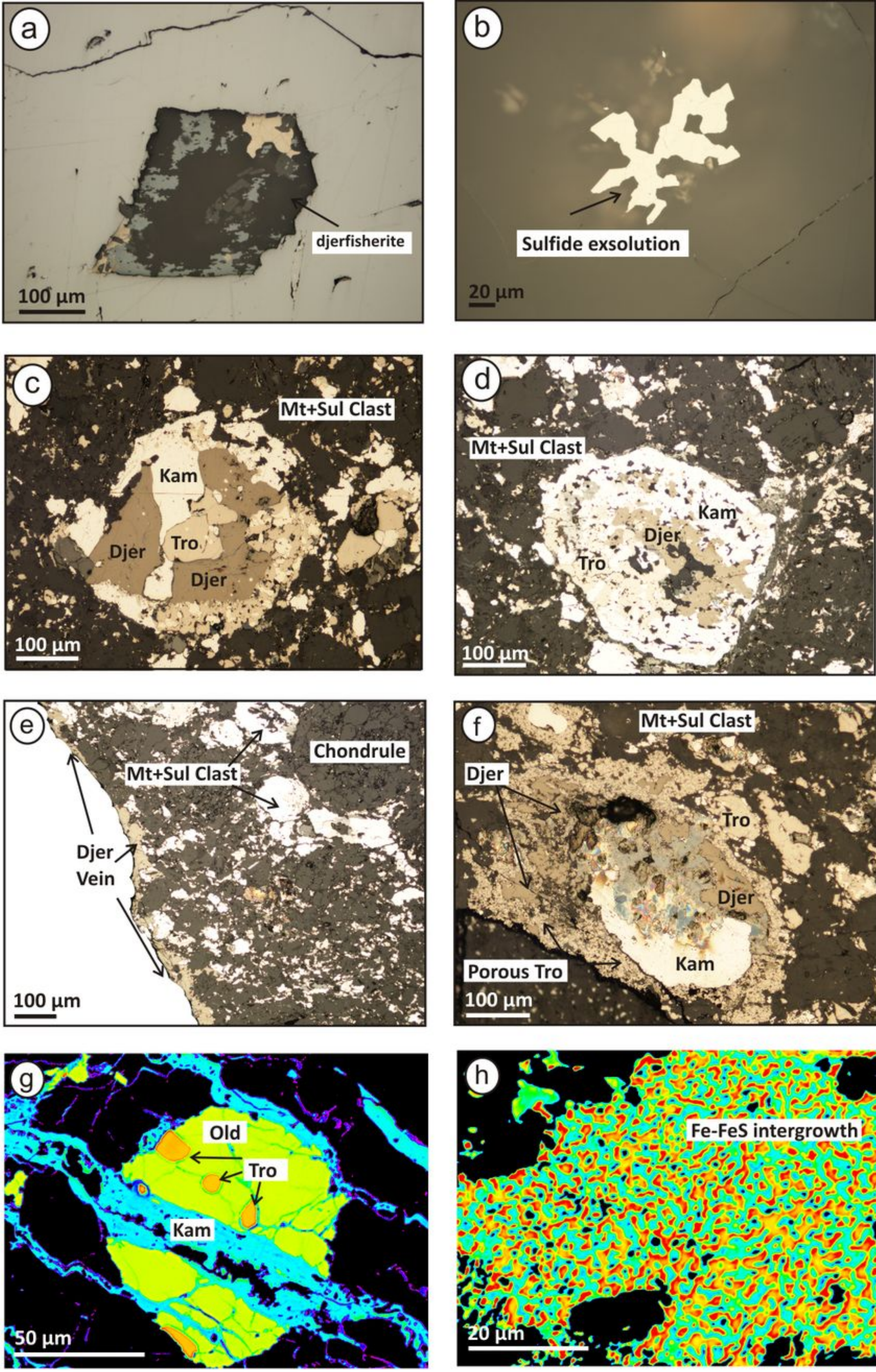
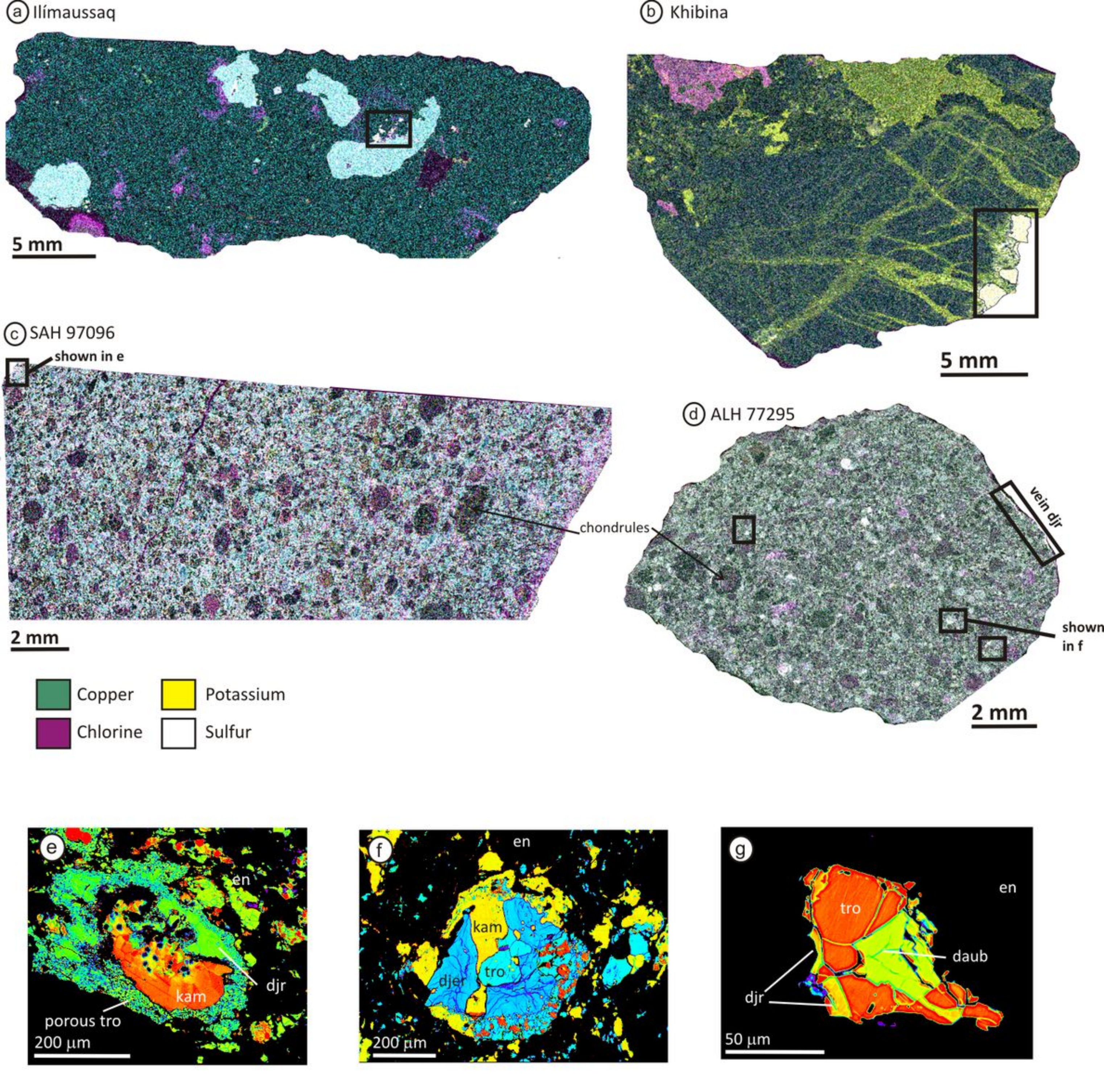
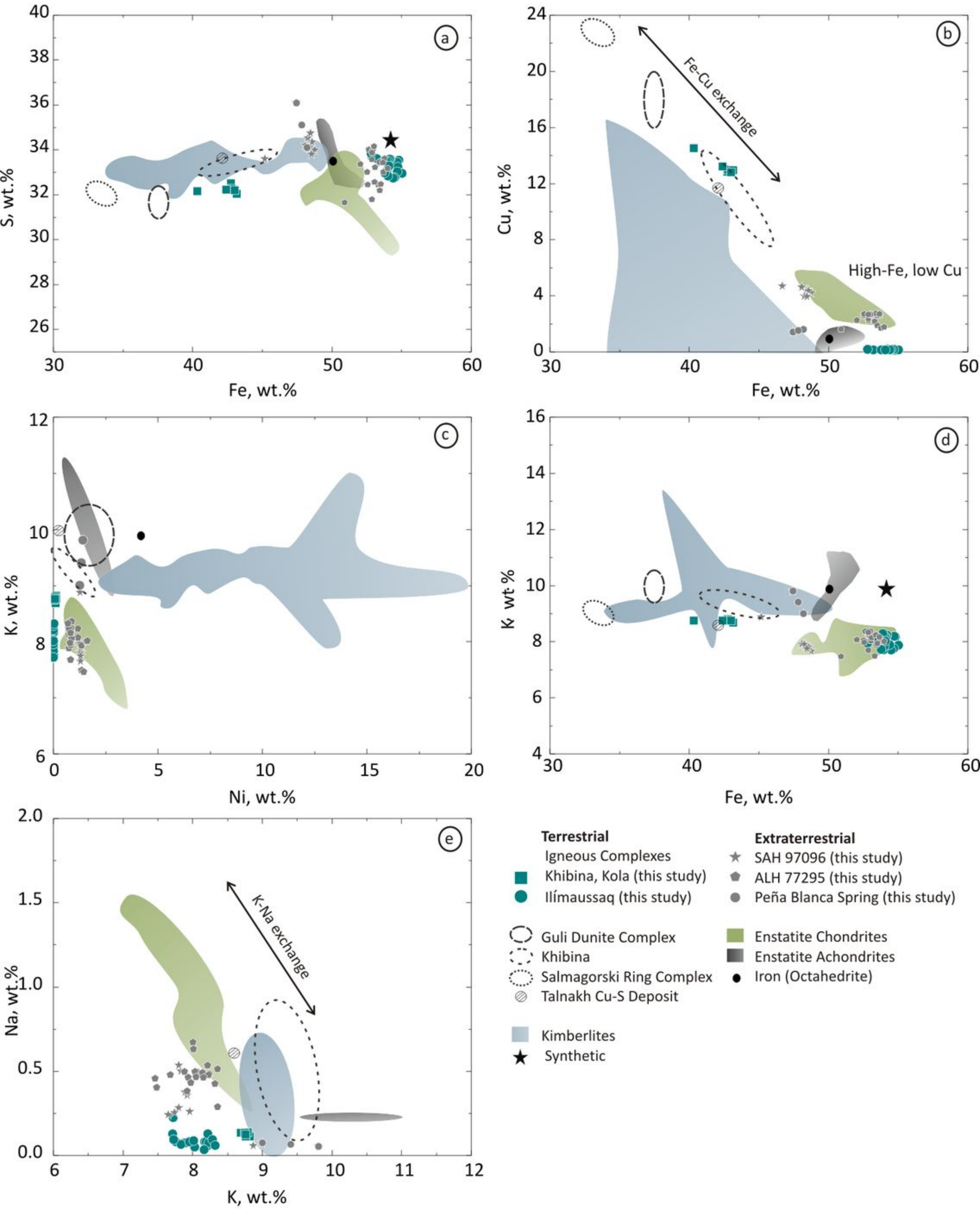

a
djerfisherite
100 µm
b
Sulfide exsolution
20 µm
c
Mt+Sul Clast
Kam
Djer
Tro
Djer
100 µm
d
Mt+Sul Clast
Kam
Djer
Tro
100 µm
e
Chondrule
Mt+Sul Clast
Djer
Vein
100 µm
f
Mt+Sul Clast
Djer
Tro
Djer
Porous Tro
Kam
100 µm
g
Old
Tro
Kam
50 µm
h
Fe-FeS intergrowth
20 µm

Figure 1



a Ilímaussaq
5 mm
b Khibina
5 mm
c SAH 97096
shown in e
chondrules
2 mm
d ALH 77295
vein djr
shown in f
2 mm
Copper
Chlorine
Potassium
Sulfur
e
en
djr
kam
porous tro
200 µm
f
en
kam
tro
djer
200 µm
g
en
tro
daub
djr
50 µm


Figure 2



a
S, wt.%
Fe, wt.%
b
Cu, wt.%
Fe, wt.%
Fe-Cu exchange
High-Fe, low Cu
c
K, wt.%
Ni, wt.%
d
K, wt.%
Fe, wt.%
e
Na, wt.%
K, wt.%
K-Na exchange
Terrestrial
Igneous Complexes
Khibina, Kola (this study)
Ilímaussaq (this study)
Guli Dunite Complex
Khibina
Salmagorski Ring Complex
Talnakh Cu-S Deposit
Kimberlites
Synthetic
Extraterrestrial
SAH 97096 (this study)
ALH 77295 (this study)
Peña Blanca Spring (this study)
Enstatite Chondrites
Enstatite Achondrites
Iron (Octahedrite)


Figure 3

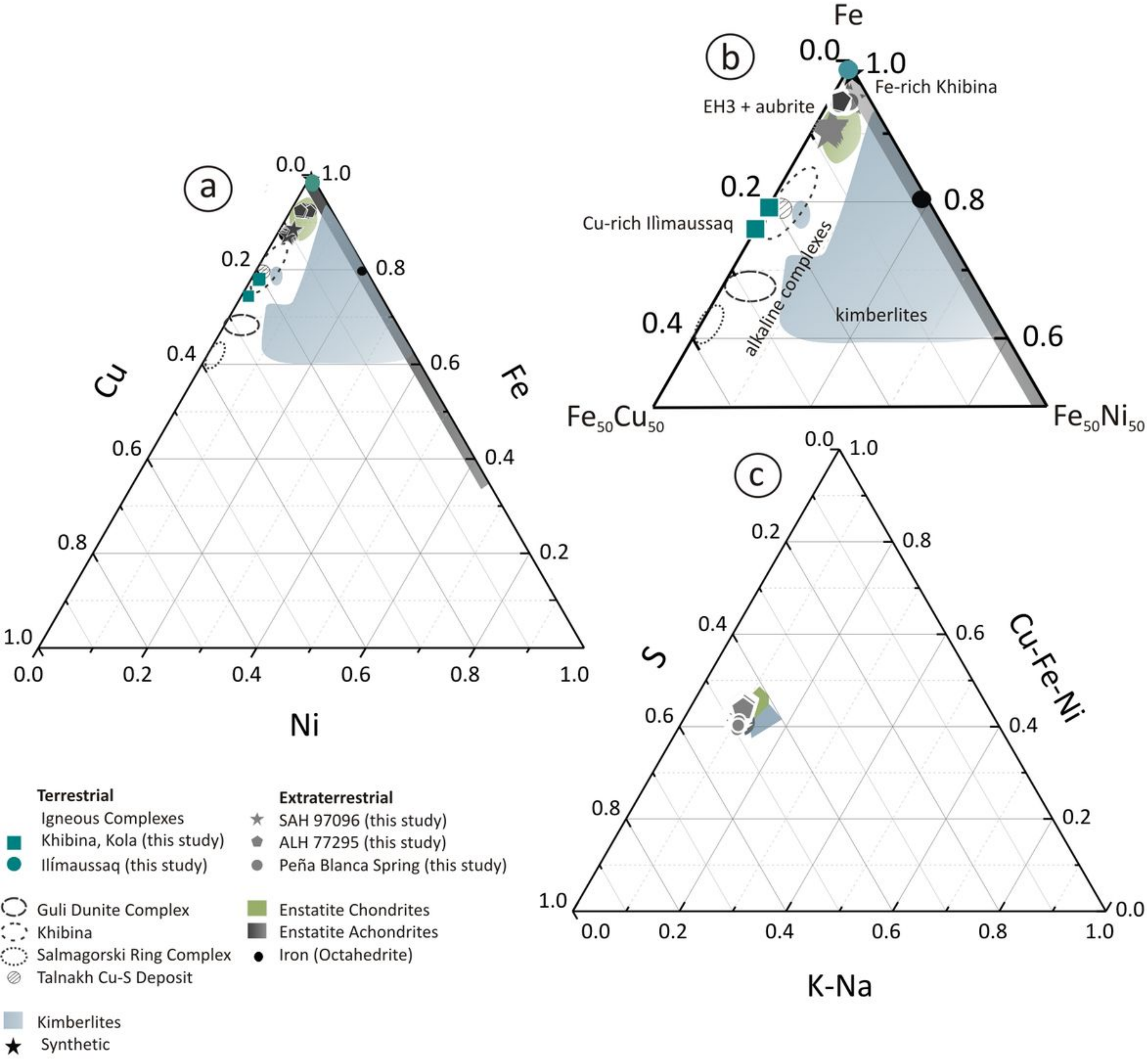

a
b
c
Fe
0.0
1.0
Fe-rich Khibina
EH3 + aubrite
0.2
0.8
Cu-rich Ilìmaussaq
alkaline complexes
kimberlites
0.4
0.6
$Fe_{50}Cu_{50}$
$Fe_{50}Ni_{50}$
Cu
Fe
Ni
S
Cu-Fe-Ni
K-Na
Terrestrial
Igneous Complexes
Khibina, Kola (this study)
Ilímaussaq (this study)
Guli Dunite Complex
Khibina
Salmagorski Ring Complex
Talnakh Cu-S Deposit
Kimberlites
Synthetic
Extraterrestrial
SAH 97096 (this study)
ALH 77295 (this study)
Peña Blanca Spring (this study)
Enstatite Chondrites
Enstatite Achondrites
Iron (Octahedrite)

Figure 4

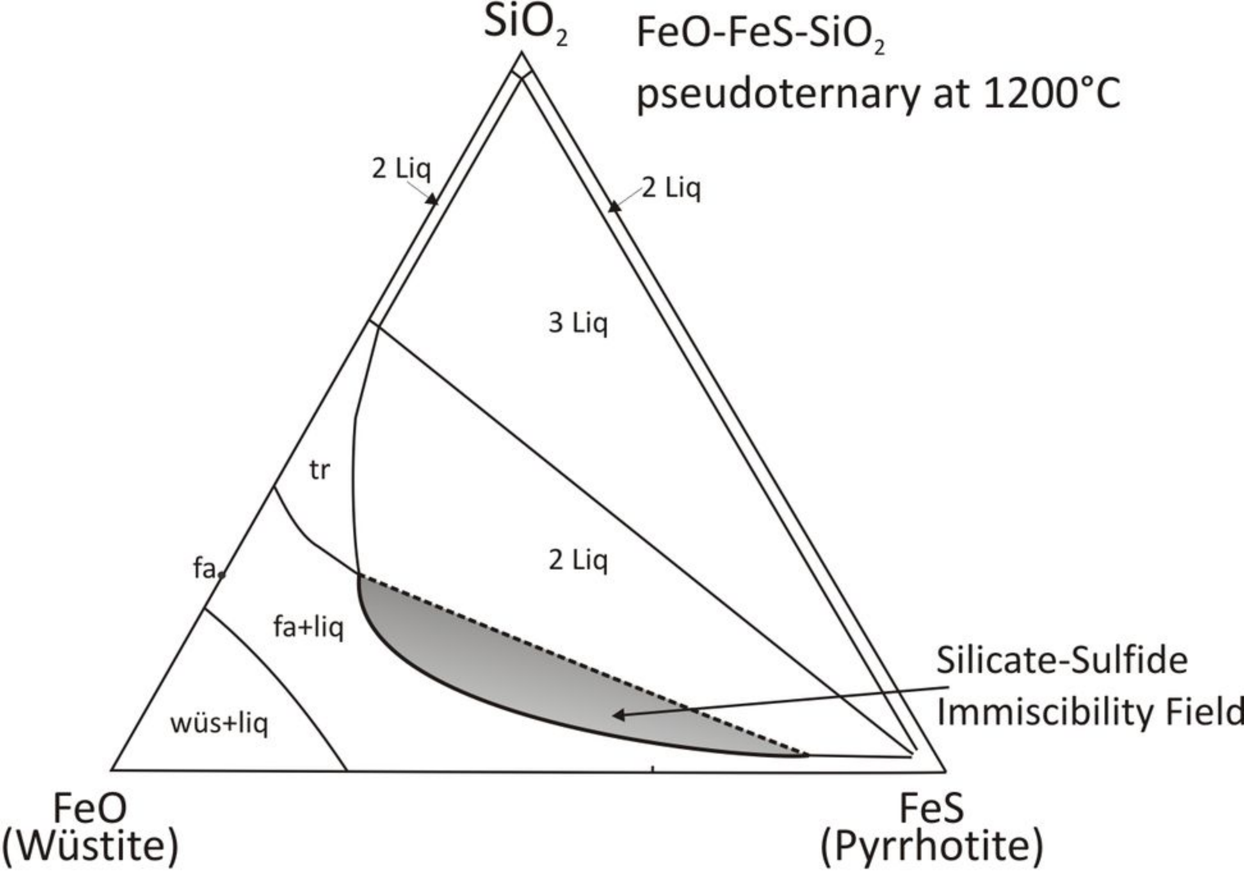

SiO2
FeO-FeS-SiO2
pseudoternary at 1200°C
2 Liq
2 Liq
3 Liq
tr
2 Liq
fa
fa+liq
Silicate-Sulfide
Immiscibility Field
wüs+liq
FeO
(Wüstite)
FeS
(Pyrrhotite)

Figure 5