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Mn- Fe systematics in major planetary body reservoirs in the Solar System and the positioning of the Angrite Parent body: A crystal chemical perspective

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ABSTRACT

A revised diagram plotting the Fe/ Mn ratio of pyroxene and olivine verses the anorthite content of plagioclase indicates that the angrite parent body originated from a solar system reservoir with a similar Mn-Fe signature to that from which the Earth was derived. The major difference in terrestrial and angritic basalts is the extreme volatile depletion (particularly Na and K) in the latter.

Considerable research and publication has been focused on angrite meteorites which are among the oldest objects in the solar system (~4.56 Ga; Keil 2012). These meteorites include a silica-undersaturated mafic mineral assemblage. The identity and location of their parent body is still unknown and widely debated. Our new work on angrites SAH 99555, LEW 86010, NWA 10463, LEW 87051, and Angra dos Reis focused on olivine and is interpreted in the context of existing pyroxene and plagioclase datasets. This paper improves the "Mn-Fe in olivine and anorthite content of plagioclase tool for planetary parentage" specifically targeted at finding members of the angrite group of meteorites.

INTRODUCTION

In a previous study (Papike et al. 2003), we presented a simple technique using the electron microprobe to determine planetary parentage of basaltic meteorites. This tool is based on Mn-Fe systematics in olivine and pyroxene and the anorthite content of plagioclase. This technique was specific to basalts, and was only to be applied to non-thermally annealed phases (pyroxene, olivine, and plagioclase lacking exsolution). Angrite melts are truly basalts according to the definition adopted by The Basaltic Volcanism in the Solar System Project (BVSP; 1981), the definition we will adhere to in this manuscript. Basalts are melts or near melts with <52% SiO_2, >6% CaO and Al_2O_3, and <12% MgO. Pyroxene, plagioclase, and olivine are the major phases. This technique has been used by many researchers as a quick and easy method to determine planetary parentage best used alongside other metrics of planetary parentage like oxygen isotopes. In a summary diagram in Papike et al. (2003; Fig. 4) based on the Fe/Mn ratio of olivine and pyroxene (y-axis) and anorthite content of plagioclase (x-axis), the position of the angrite parent body was plotted in the wrong location. At that time, only angrite pyroxene was plotted on the diagram. The first author did not realize that angrite pyroxene was not effective on this diagram because the M2 crystallographic site (a 6- to 8-fold coordinated, highly compliant site) was filled with Ca due to the high Ca concentration of the melt. Both the pyroxene M2 site and M1 site (octahedral) must be in play for pyroxene to be used to determine the correct Fe/Mn ratio. If the M2 site is completely filled with Ca, Mn partitioning in pyroxene is severely limited. In this paper we avoid these complications; we present a simple method to identify meteorite members of the angrite suite using the Fe/Mn ratio in angrite olivine and add constraints to the location of the angrite parent body (APB).

ANALYTICAL APPROACH

Thin sections of Sahara 99555, LEW 86010, NWA 10463, LEW 87051 and Angra dos Reis were examined and documented using back-scattered electron (BSE) imaging on the JEOL JXA-8200 electron microprobe (EMP) in the Institute of Meteoritics. Wavelength dispersive X-ray maps were collected for Ca, Mn, and Cr, while energy dispersive (EDS) maps were collected for Mg (note Figure 1). Quantitative point analyses of angrite olivine were conducted at an accelerating voltage of 15 kV, a beam current of 10 nA, and a spot size from 1-3 μm. Elements were standardized using a combination of Taylor Corp. Electron Microprobe mineral standards as well mineral standards that have been developed in-house. Individual olivine microprobe analyses are presented in an electronic appendix. In those figures where the Fe/Mn ratio is used to distinguish planetary bodies (Figs. 3 and 5), only those olivine analyses with <5 mol.% Ca endmember were used. While we acknowledge that this cutoff is somewhat arbitrary, one can readily observe from the olivine quadrilaterals (Fig. 4), that over this range, the relationship between Fe, Mg, and Ca is most linear, and is most likely to represent an igneous fractionation trend, and is therefore the most relevant in the determination of a planetary parentage slope.

RESULTS

The results of the EMP analysis are illustrated in five figures. Figure 1 includes BSE, Mg, Ca, Mn, and Cr maps of SAH 99555, NWA 10463, and LEW 86010. This order also represents the cooling sequence, from fastest to slowest. SAH 99555 represents a near melt composition and shows primary magmatic growth zoning which enables the ^{53}Mn-^{53}Cr chronometer (Papike et al. 2016a). Next is NWA 10463 which has exsolution only in the Fe-enriched rims. Next is LEW 86010, with well developed exsolution in two directions throughout the olivine grains. Last in the sequence (not shown) is Angra dos Reis with almost complete phase separation of

Kirschsteinitic olivine from Fo-Fa olivine. Figure 2 illustrates the major element chemistry of angrite olivines from this study. Figure 2a compares CaO (wt.%) vs. MgO (wt.%), while Figure 2b examines MnO (wt.%) vs. MgO (wt.%). The arrows point in the direction of increasing fractionation. Note that Ca and Mn are enriched toward the grain rims, right to left, in the NWA 10463 olivine (red symbols). However, upon exsolution (the points all the way to the left, Ca increases while Mn decreases. Figure 3 is the new olivine Mn vs. Fe diagram showing Mars, Earth, angrite parent body, and Moon. Figure 3a includes all of the olivine data, including Ca-rich olivines, while Figure 3b only plots olivine with Ca below 5 mol.% on a Ca-Mg-Fe plot. As with pyroxene, the inclusion of Ca in the olivine structure changes the partitioning behavior of Mn relative to Fe. Again, this can be seen in the trend of the exsolution tie-lines in Figure 2. For the purpose of determining planetary parentage, one can still use the Mn/Fe ratio in olivine, provided the olivine does not have a substantial Ca component, hence the 5 mol.% limit. Meteorites LEW 86010 and Angra dos Reis are not plotted here, as they cannot be used effectively on the Mn vs. Fe diagram because they are thermally annealed. Figure 4 illustrates olivine quadrilaterals for five angrite meteorites, unequilibrated angrites SAH 99555, NWA 10463, LEW 87051 and equilibrated LEW 86010 and Angra dos Reis. Figure 4 shows that two meteorites plotted on the left reflect olivine-melt partitioning before exsolution (i.e., SAH 99555 and LEW 87051), the two on the right only reflect subsolidus partitioning between two olivine solid solutions, while NWA 10463 shows aspects of both. Figure 5 is the revised Fe/Mn vs. anorthite content in plagioclase diagram with the new location for the angrite parent body in close proximity to the Earth and Moon. As opposed to Figure 4 in Papike et al. (2003), this figure plots angrite olivine, avoiding the complications inherent to measuring Fe/Mn ratios in high Ca pyroxenes already discussed above.

DISCUSSION

The role of crystal chemistry in the efficacy of olivine as a recorder of planetary parentage

The compositions of the Ca-Fe-Mg olivines can be displayed on an olivine quadrilateral (see Fig. 4). There is complete solid solution between monticellite ($CaMgSiO_4$) and kirschsteinite ($CaFe^{2+}SiO_4$) as well as between forsterite (Mg_2SiO_4) and fayalite ($Fe^{2+}{}_2SiO_4$) at high temperatures. However, at low temperatures there is a large miscibility gap between these two solid solutions. Fittipaldo et al. (2005) studied the thermal histories of Angra dos Reis and LEW 86010. These authors also estimated the dependence of the olivine solvus between high and low Ca olivines as a function of both composition and temperature. Olivine-kirschsteinite pairs in Angra dos Reis record a closure temperature of 600-650 °C, while LEW 86010 has an estimated closure temperature of 700-720 °C. The meteorites studied here have variable cooling histories with SAH 99555 cooling the fastest, therefore representing a good approximation of a melt composition. Second in estimated cooling rate is NWA 10463, with exsolution in olivine only in the Fe-rich rims. Third is LEW 86010 with well developed exsolution in olivine in two directions. Slowest in cooling rate is Angra dos Reis with phase separation of the high-Ca and low-Ca olivines (see Fig. 2a). The M2 site is more compliant than the M1 site and can become 8-coordinated and accommodate Ca. The M1 site is smaller and remains octahedral. Figure 2 tells much of the important site occupancy story. Note that Ca and Mn follow a similar trend (core to rim) with both increasing toward the rim (SAH 99555 and NWA 10463) until the onset of exsolution. This represents a normal igneous zoning trend for two relatively incompatible elements, with Ca being the more incompatible as evidenced by the slopes on the plot. However with exsolution (meteorites LEW 86010 and Angra dos Reis, and to a lesser extent NWA 10463)

Mn and Ca go into separate phases, with Ca in the exsolved kirschsteinitic olivine, and Mn retained in the Fo-Fa olivine. Manganese goes into the M2 site of low-Ca olivine.

Papike (1981) recognized that in any one planetary body there were a number of Mn/Fe slopes for different basaltic environments. For example for Earth, seven different environments were compared and differences were noted (Papike, 1981). Also for the moon, significant differences were observed between high- and low- Ti basalts (Papike et al., 1976). The Fe/Mn ratio of a given mineral phase in a planetary body results from several different factors, but can be broadly categorized into differences in the initial bulk silicate composition or differences resulting from changes to the partitioning behavior of Fe relative to Mn. With respect to the former, the initial Fe/Mn ratio results from the initial bulk composition of a planetary body and early processes which may alter this ratio such as differentiation and core formation. For example, sequestering metallic Fe into a planetary core will lower the initial Fe/Mn of its derivative mantle. On the other hand, changes in the partitioning behavior of Fe relative to Mn can result from differences in bulk melt chemistry (NBO/T), or differences in mineral chemistries Mn (i.e., "QUAD" pyroxene vs. fassaite, Al, Ti-rich calcic- pyroxene). Finally dynamic changes in the fO_2 of the crystallizing melt can also significantly alter the crystal/melt partitioning behavior of Fe. When we refer to the partitioning behavior of Fe vs. Mn into a silicate phase, whether it is olivine or pyroxene, we are really referring to the partitioning of Fe^{2+} vs. Mn^{2+}. Consider two olivines crystallizing from equivalent melts (same chemistry and bulk Fe/Mn), different only in the fO_2 of crystallization, one may measure different Fe/Mn ratios. In the more oxidizing environment, the Fe^{3+}/ Fe^{Total} in the liquid will be higher, resulting in a lower apparent Fe/Mn in the olivine, as the compatibility of $Fe^{3+} << Fe^{2+}$. This is not likely a concern with the angrites presented in this study. The inclusion of Fe^{3+} in the olivine structure requires a

coupled substitution, for example, Al^{3+} in the in tetrahedral site, for Si^{4+}. The molar concentration of Al^{3+} in olivine can therefore be seen as an upper limit to the Fe^{3+} concentration, and a quick look at the electronic appendices for all of the angrite olivines demonstrates that Al, and hence Fe^{3+}, is very limited. All of these factors can affect Fe/Mn trends for a given mineral phase in a planetary body. This explains the spread observed in the planetary trends for olivine and pyroxene in Papike et al. (2003). Despite this, the fact remains that each planetary body has a distinct, over-arching trend that is the fingerprint of the planetary source or planetary parentage. This paper improves the "tool" for planetary parentage. It does not explain why it works, the planetary dispersion of Mn/Fe ratio, or the apparent correlation between Mn/Fe slope and heliocentric distance.

Intra- and Inter- planetary differences in Mn-Fe systematics

In a book by Stuart Ross Taylor "Solar System Evolution," Taylor (1992) discusses the systematic differences in planets with heliocentric distance from the Sun. One noteworthy observation was increasing iron-rich core size with increasing proximity to the Sun. Taylor also notes the increased volatile element concentration in planets with increasing distance from the Sun. With respect to Mn, one would expect the bulk silicate Mn/Fe ratio of a planet to increase with increasing heliocentric distance because Mn is more volatile than iron and would be lost relative to iron near the Sun. Core formation serves to sequester Fe into a planet's core, so that one would expect planets with larger cores (i.e., those closer to the Sun) to have proportionally less Fe in their silicate mantles than those with smaller cores. The cumulative effects suggest that the silicate mantles of planets closer to the Sun should have both less Mn and Fe than those further from the Sun. Perhaps it is somewhat surprising, then, that the Mn/Fe ratios still seem to show an overarching correlation with heliocentric distance (Fig. 1, Papike et al. 2003; Fig. 3, this

paper). We believe that the Earth, Moon, and Angrite Parent Body (APB) came from a similar planetary reservoir.

IMPLICATIONS

Many of our past studies have explored how the chemical systematics of important rock-forming minerals including pyroxene, olivine and feldspar, can provide important clues to their planetary parentage and subsequent thermal and oxygen fugacity histories. The major implications of the present study indicate is that a very important solar system reservoir for the angrite meteorites is very similar to the terrestrial solar system reservoir. The major difference between angrite basaltic melts and terrestrial basaltic melts is the severe volatile and alkali element depletion leading to the presence of almost pure anorthite plagioclase in angrite basalts. We suggest that one way of getting this volatile depletion is that an asteroid sized parent body for angrites condensed from a hot vapor cloud, resulting in volatile depletion. Keil (2012), in his excellent review of angrites, discusses this topic and concludes that the angrite parent body (APB) must have been >100 km in radius. Keil (2012) also points out that some angrites, for example D'Orbigny, contain vesicles indicating vapor lost and suggested the vapor is dominated by CO_2. He also observes that angrites do not contain obvious features of a shock or brecciation history. Our earlier paper (Papike et al. 2003) indicated that the Mn/Fe slope might suggest that the location of the angrite parent body was close to the Sun and perhaps might even be Mercury. We think many more recent studies can rule out Mercury as the source.

We are not suggesting that angrites are early Solar System condensates (e.g., CAIs). Their parent body may reflect condensation but they are true basalts that experienced melt evolution. The accreting material was likely CI chondrites, as for Earth. In summary, this paper

improves an important tool for determining planetary parentage. It is observed, but not yet completely understood, that the mantle source that gave rise to planetary basalts on the bodies 4 Vesta, Mars, Earth, angrite parent body, and Moon have differing Mn/Fe slopes that show a correlation with heliocentric distance with the exception for APB and Moon which may show signs of volatile loss of Mn. Volatility of Mn and core formation both affect the Mn/Fe ratio in planetary basalts. Despite this, each planetary body is characterized by a unique trend.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1. BSE, Mg, Ca, Mn, Cr maps of SAH 99555, NWA 10463, and LEW 86010. This is also the cooling sequence, with SAH 99555 representing a melt composition and showing primary growth zoning which enables the ^{53}Mn-^{53}Cr chronometer. NWA 10463 represents the next step in cooling history with exsolution lamellae appearing in the Fe-rich outer zones of olivine. LEW 86010 has well developed exsolution throughout the olivine grains. Phases are labeled as follows: ol = olivine, pyx = pyroxene, an = anorthite. Bright white areas in the NWA 10463 Ca map are thought to be terrestrial alteration (carbonate?), but have not been identified.

Figure 2. Major element chemistry of angrite olivines from this study. (a) CaO (wt.%) vs. MgO (wt.%). (b) MnO (wt.%) vs. MgO (wt.%). Tie lines connect the exsolved olivine phases.

Figure 3. Mn vs. Fe systematics for angrite olivine for 5 angrite meteorites. (a) All angrite olivine analyses meeting stoichiometric requirements. (b) Angrite olivine analyses meeting

stoichiometric requirements and with <5 mol.% of the Ca-olivine end member. The asterisk here, and in Fig. 5, is used to denote this subset of angrite olivines. These are the olivines that should be used to determine the Mn/Fe ratio.

Figure 4. Olivine quadrilaterals for 5 angrite meteorites, unequilibrated SAH 99555, NWA 10463, LEW 87051 and equilibrated LEW 86010 and Angra dos Reis. Olivine endmembers include forsterite (Fo; Mg_2SiO_4), fayalite (Fa; Fe_2SiO_4) monticellite (Mo; $CaMgSiO_4$) and kirschsteinite (Ki; $CaFeSiO_4$). The trends represent well documented fractionation trends of olivine crystallizing from melt followed by exsolution near the Fe-rich portion of the QUAD.

Figure 5. Diagram plotting Fe/Mn ratio in angrite pyroxene and olivine (X-axis) vs. anorthite content of angrite plagioclase (Y-axis). The asterisk here indicates only those angrite olivines with <5 mol.% of the Ca-olivine end member were used to define the angrite field. This diagram was revised after Papike et al. (2003; Fig. 4), and was constructed using the same methodology. The solid vs. hashed outlines serve to distinguish pyroxene from olivine, respectively.

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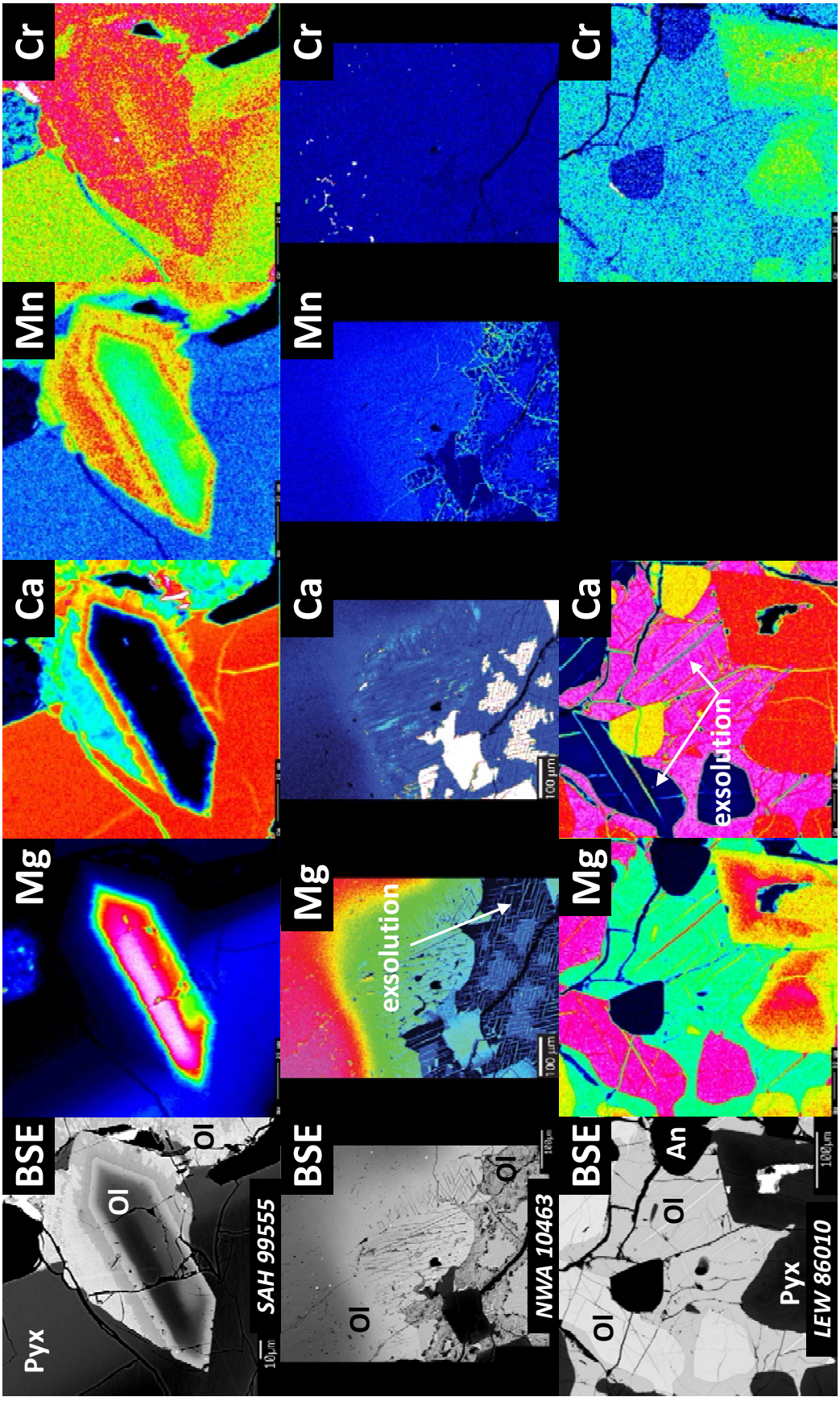

Figure 1.

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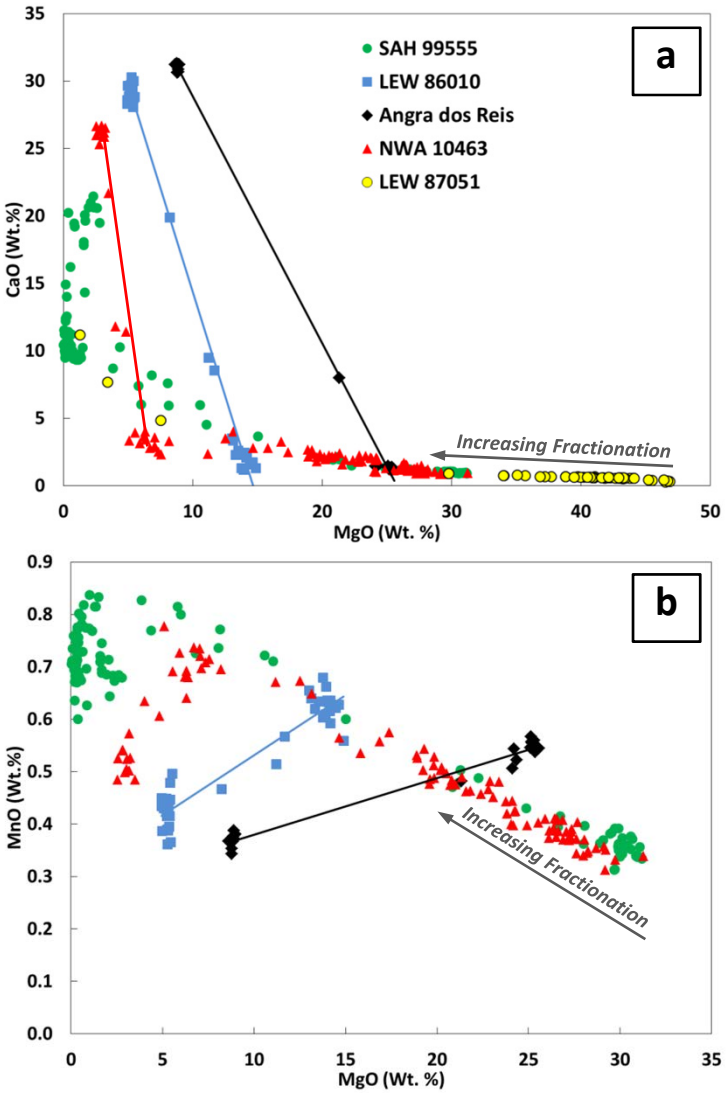

Figure 2.

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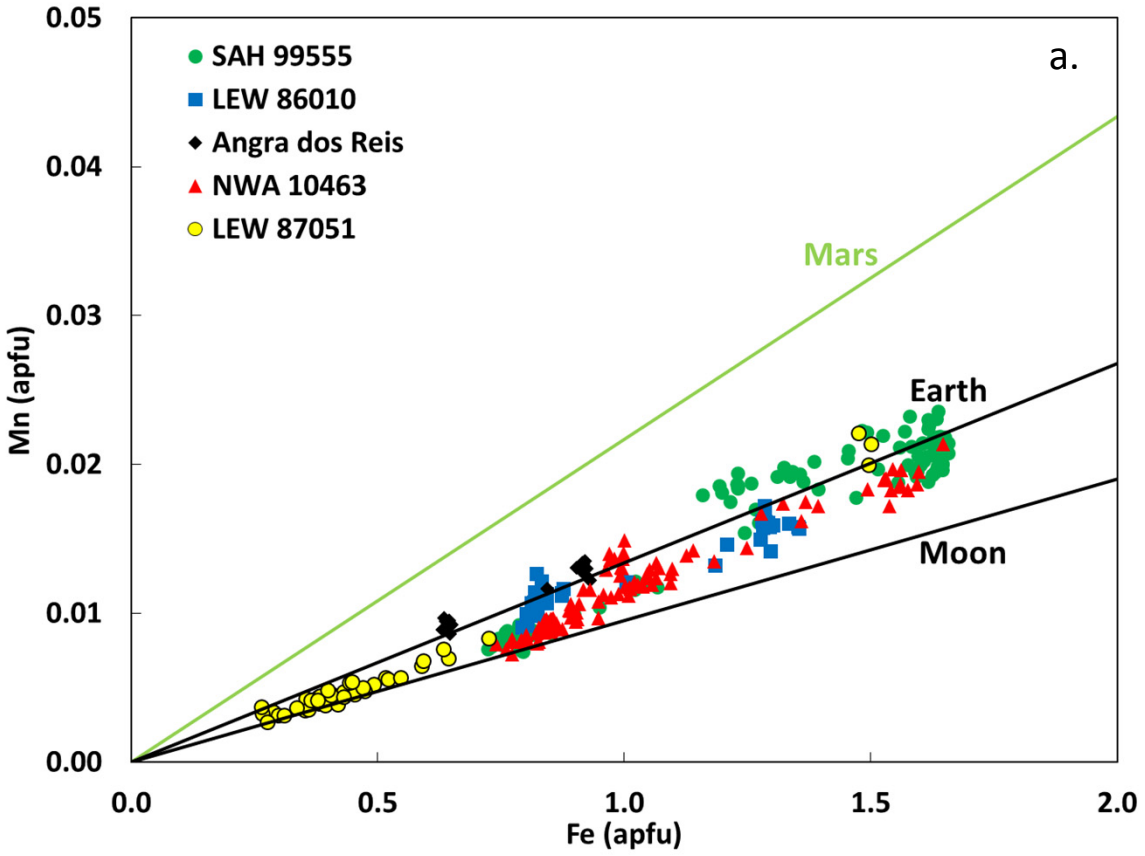

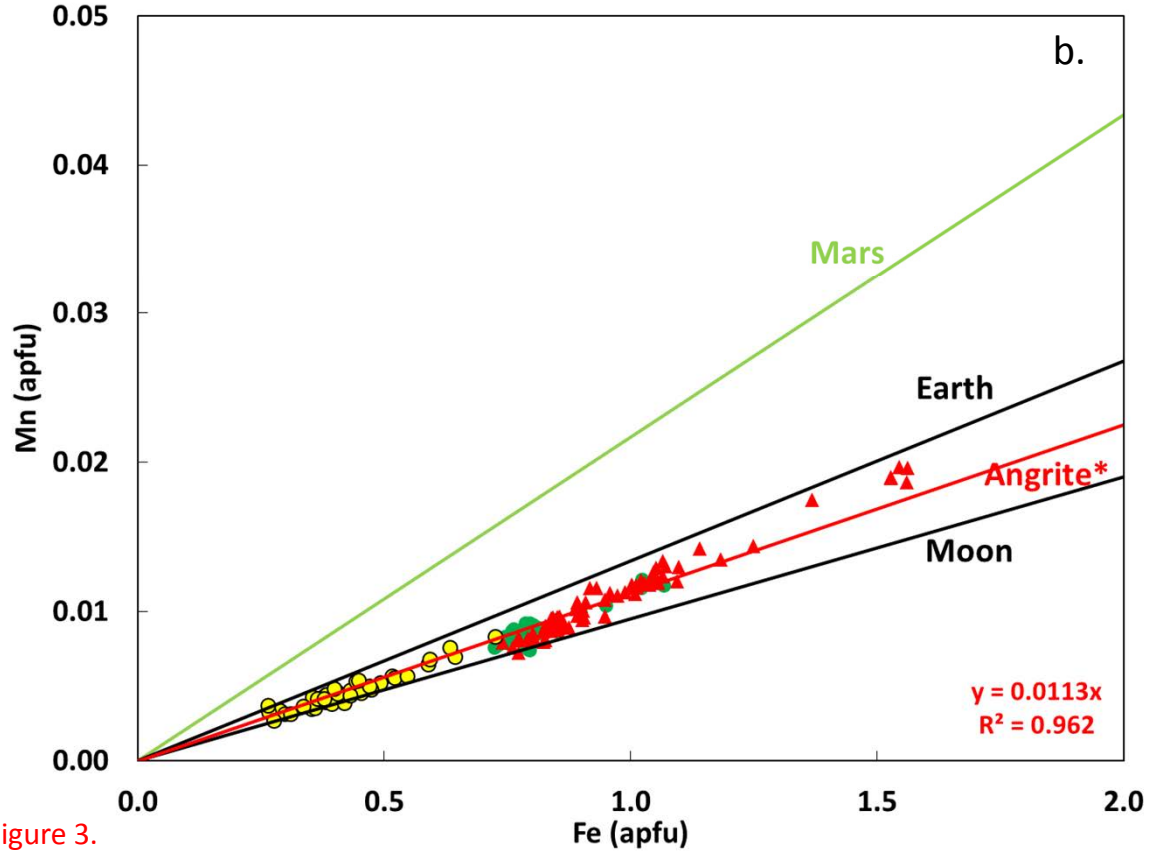

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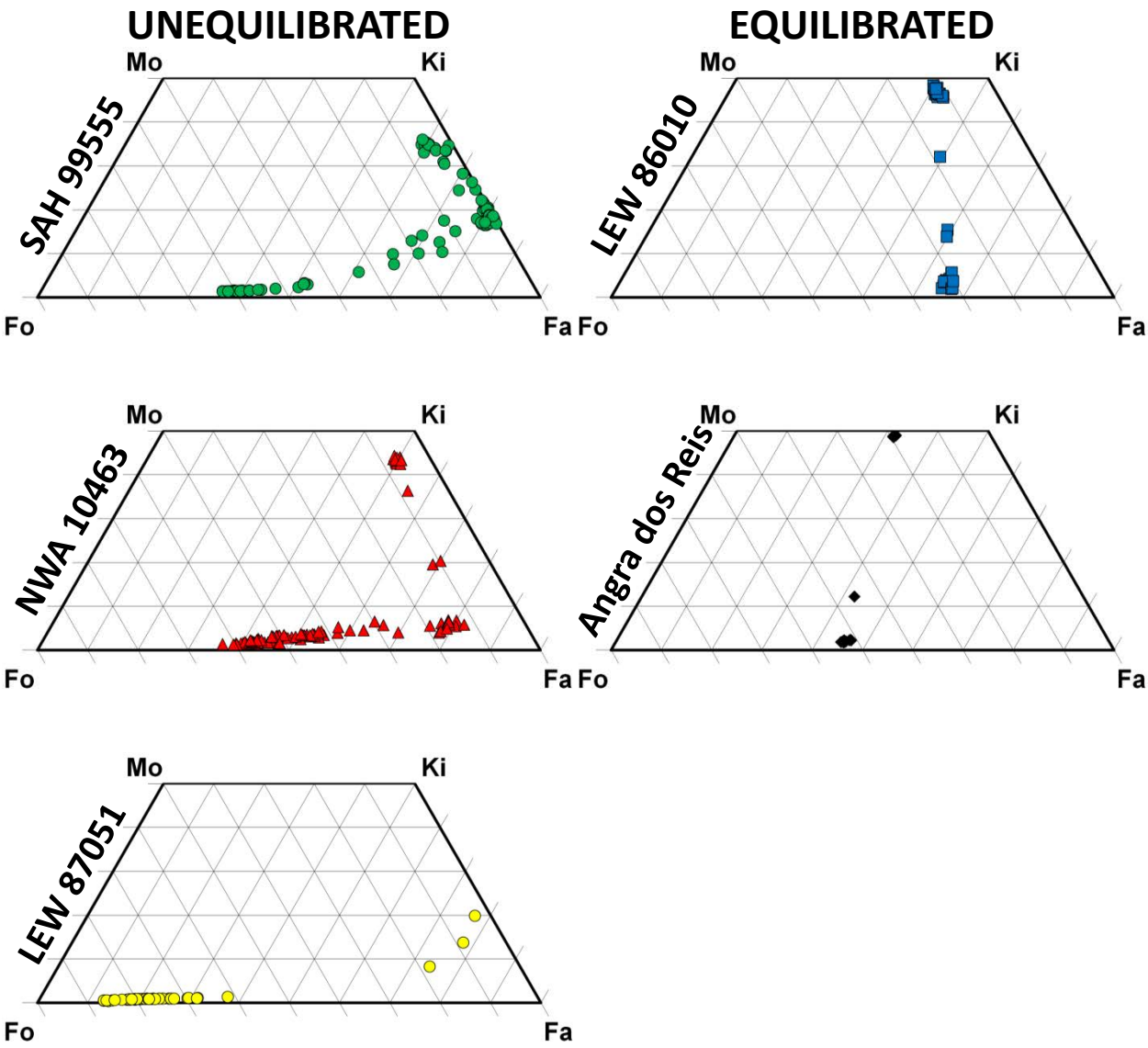

Figure 4.

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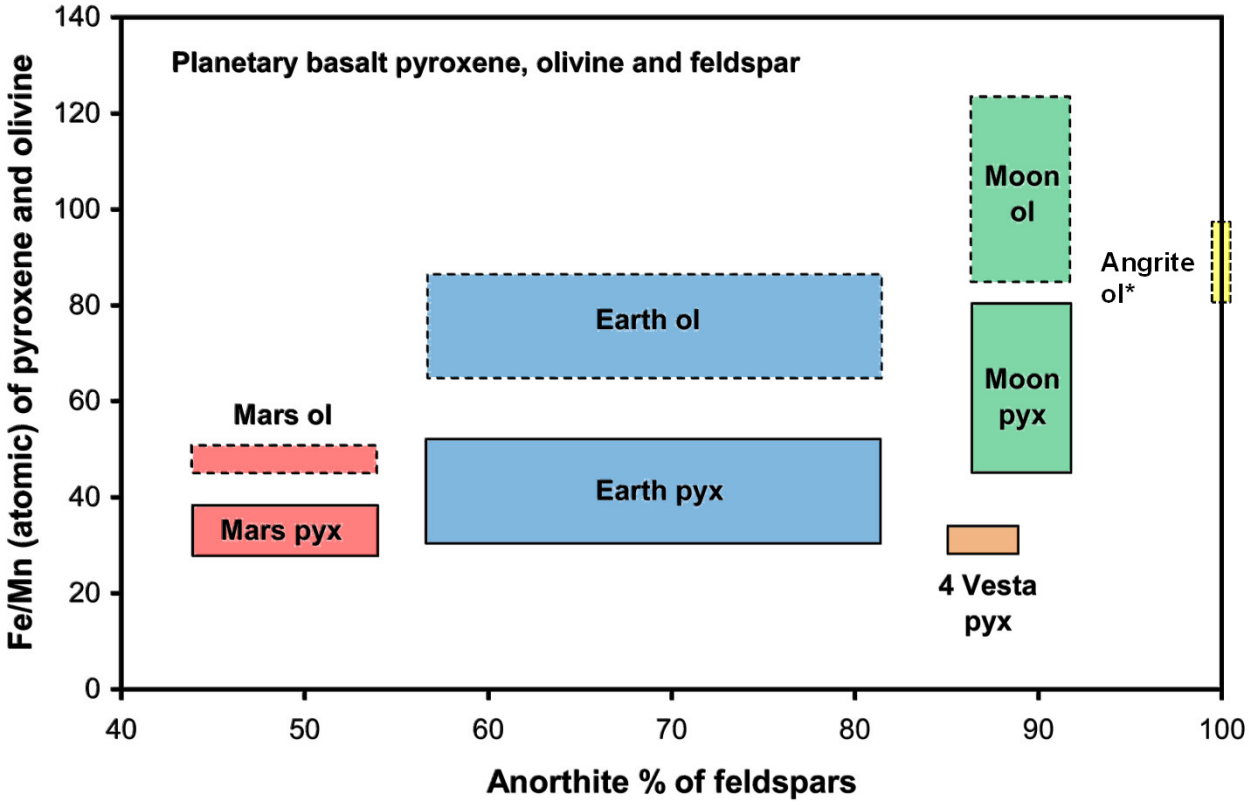

Figure 5.