

MN-FE SYSTEMATICS IN MARTIAN OLIVINE: EFFECT OF MANTLE SOURCE, OXYGEN FUGACITY, AND TEMPERATURE OF CRYSTALLIZATION. James J. Papike¹, Paul V. Burger¹, Aaron S. Bell¹, and Charles K. Shearer¹,¹Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131, U.S.A

INTRODUCTION. Recently, our research group has renewed activities concerning the Mn-Fe systematics in the solar system. Our most recent effort [1] concerned the angrite parent body [APB]. Now we focus on martian basalts and use our manuscript “Silicate mineralogy of martian meteorites [2] as a guide. We start by considering the Mn/Fe (apfu) trend lines of olivine and pyroxene (= Mn^{2+}/Fe^{2+} slope) compared to other planetary bodies. Each body has an over-arching trend line. On an olivine Mn vs. Fe diagram for Mars, Earth, Moon, and angrites [1]; the sequence is Mars, Earth, angrite parent body (APB), and Moon. We do not plot 4 Vesta on the olivine diagram because basalts from 4 Vesta (eucrites) have little or no olivine. For pyroxene, the Mn vs. Fe sequence is 4 Vesta, Mars, Earth, angrite parent body (APB) and Moon. However despite the existence of a Mn-Fe fingerprint of for each planetary body, several factors cause dispersion or variations from the mean Mn/Fe ratio. Potential variables causing this variation in a single planetary body include the temperature of olivine and pyroxene crystallization and oxygen fugacity. We consider these factors in the following text and in addition conduct modeling calculations and add some new experimental data on martian melt composition Y980459.

In a recent paper entitled (Mn- Fe systematics in major planetary body reservoirs in the Solar System and the positioning of the Angrite Parent body: A crystal chemical perspective) we refined a technique introduced by [3] where the Mn/Fe ratio for olivine or pyroxene and the anorthite content of plagioclase provided a tool to identify the planetary parentage of newly discovered meteorites. The focus of this new paper was the angrite meteorites and a new, robust determinative curve was provided. However, in that short paper we did not discuss in any detail why we can compare complex parental bodies (example Earth and Mars) that have undergone complex evolutionary histories including core formation, magma oceans, serial magmatism, a range of basalt compositions and a large dynamic range of oxygen fugacity (~IW-3 to FMQ + 2) to much simpler, smaller bodies like Moon, 4 Vesta, and the angrite parent body or APD. Despite the fact that with enough high quality microprobe data, for olivine, pyroxene, and plagioclase we find an over-arching fingerprint of planetary parentage, in any individual suite there is significant scatter or dispersion along the average trend line. The purpose

of this paper is to explore this scatter for the martian, basaltic meteorites and try to access several factors including oxygen fugacity and the temperature of crystallization of olivine and pyroxene crystallization. The major focus is on olivine-phyric basalt Y98 where we have new experimental data. The shergottites have a range of REE patterns from LREE-depleted to LREE-enriched. These REE pattern shapes may represent mantle source characteristics.

EXPERIMENTS: We have conducted a series of 1 bar gas mixing experiments to examine how changes in fO_2 and temperature influence the Fe-Mn systematics in martian olivines. These experiments were conducted using the synthetic bulk composition modeled on the olivine-phyric shergottite Y98.

RESULTS: The results of these experiments are displayed in 2 figures. Figure 1 illustrates the effect of temperature of crystallization of olivine between 1200 and 1400 degrees C. Figure 2 illustrates the effect of oxygen fugacity between IW and FMQ+5.4 on the slope of the trend line.

DISCUSSION:

The effect of mantle source on the Mn/Fe ratio in martian olivine and pyroxene

In our review manuscript “Silicate mineralogy of martian meteorites” [2] we discussed the origin of two important martian mantle reservoirs for shergottite magmas “Enriched” and “Depleted”. There are a number of differences between basalts from these two reservoirs. Basalts from the martian enriched reservoir display ~ flat REE patterns ~ 10 X chondrites while basalts from the depleted reservoir display LREE depleted REE patterns. Our first question is whether these two mantle reservoirs results in basalts with significantly differences in the Mn/Fe ratio of bulk basalts, individual olivines, or individual pyroxenes. The answer appears to be no. The bulk rock ratios of MnO/ FeO (wt. %) for basalts from both mantle sources is 0.27. Also, if we look at the Mn vs Fe (apfu) trend line for olivine we see the depleted martian basalts, example Y98, and enriched martian basalts, example NWA 1110, fall on the same trend line (note Figure 10 in [2]. This is also true for martian pyroxene, displayed in Figure 17 of Papike et al. 2009 [2]. Pyroxene from both Y98 and NWA 1110 fall on the same trend

The relative effect of increasing oxygen fugacity on olivine and pyroxene Fe-Mn systematics. We modeled Fe_2O_3 (wt. %) versus fO_2 (relative to IW, 1200 degrees C) for a melt of Y980459 composition

(Y 98). The change in Mn/ Fe slope for olivine and pyroxene is different with increasing oxygen fugacity when one plots Mn/ Fe (apfu) or if one plots Mn^{2+}/Fe^{2+} . This is because ferric iron is very incompatible in in olivine but not in pyroxene. Many coupled substitution involving ferric iron are possible and observed in pyroxene. These are discussed and illustrated in Table 6 in [4]. They all involve Fe^{3+} in the M1 site of pyroxene which causes a charge excess that must be compensated by either a monovalent element in the M2 site (example Na) or a trivalent element in the tetrahedral site (example Al). See Papike et al. [3] for more possible coupled substitutions. Thus plots of Mn/Fe (apfu) or Mn^{2+}/Fe^{2+} verses fO_2 make a significant difference. For example, in a plot of Mn/Fe in olivine verses increasing oxygen fugacity there is a pronounced increase in Mn/Fe in olivine in oxygen fugacities above FMQ. This is a result of higher ferric iron in the melt and it is not accommodated in the olivine structure and thus the Mn/Fe ratio increase dramatically. On the other hand, in a plots of Mn/Fe in pyroxene with increasing oxygen fugacity the trajectory of Mn/Fe is less pronounced because of coupled substitutions involving ferric iron. If one corrects the pyroxene microprobe data for ferric iron and then plots Mn^{2+}/Fe^{2+} then the olivine and pyroxene will be more similar but not the same. Olivine will still have a higher Fe/ Mn upward trajectory at high oxygen fugacities because in olivine both the M2 and M1 sites are octahedral and not easily expandable while the M2 site in pyroxene can vary between 6- and 8- fold coordination.

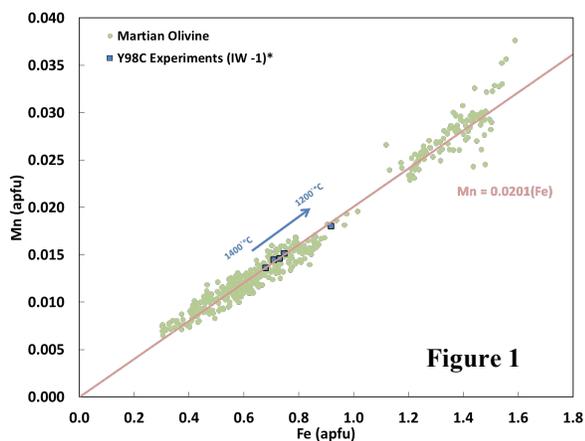


Figure 1

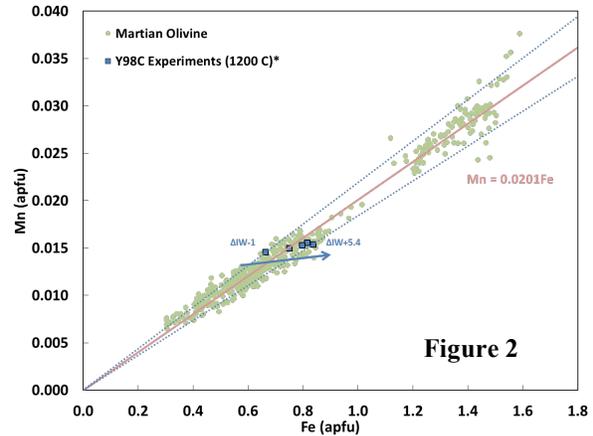


Figure 2

Comparison to other volatile element ratios.

B/Be and K/Th have been used to examine the volatile characteristics of planetary bodies [6 and references within]. Based upon boron abundances and B/Be for Earth, Moon, 4 Vesta, and Mars, it appears that the B/Be values correlate with the estimated K/Th [6]. Extending this correlation to Venus and Mercury allows approximations of the relative bulk boron and B/Be of these planetary bodies. These comparisons suggest that the volatile characteristics as represented by the B/Be is C1 chondrite >> Mercury = Mars > Venus = Earth >> Moon > 4 Vesta and the extent of boron depletion relative to C1 chondrites is 4 Vesta > Moon > Earth = Venus > Mars = Mercury.

IMPLICATIONS. Basalts are considered by many planetary petrologists as windows into the nature of planetary mantles (BVSP, 1981)[5]. However not all basalts are equal in this regard. Primary basalts (derived from a planetary mantle without gain or loss of material) are the most valuable. These basalts are Mg-rich and usually olivine phyrlic and this is why we concentrate in martian olivine in this short paper. In terms of using Mn/Fe ratios for determining planetary parentage and the reasons for dispersion in this trend for each body, variation in oxygen fugacity appears to be the most important factor.

REFERENCES. [1] Papike et al. (2017) American Mineralogist, 102, 1759-1762. [2] Papike et al. (2009) G.C.A 73, 7443-7485. [3] Papike et al. (2003) American Mineralogist (2003). 88, 469-472 [4] Papike et al (2005) American Mineralogist 90,277-290. {5} BVSP (1981) Pergamon, 1286 p. [6] Shearer and Simon (2017) Elements, 13, 231-236.