

**THE VOLATILE CHEMISTRY OF APATITE IN PLANETARY MATERIALS: IMPLICATIONS FOR THE BEHAVIOR OF VOLATILES DURING PLANETARY DIFFERENTIATION?** F. M. McCubbin<sup>1,2</sup>, R. H. Jones<sup>2</sup>, C.K. Shearer<sup>1,2</sup>, S. M. Elardo<sup>1,2</sup>, C. B. Agee<sup>1,2</sup>, A. R. Santos<sup>1,2</sup>, P. V. Burger<sup>1</sup>, A. S. Bell<sup>1</sup>, and J.J. Papike<sup>1</sup>. <sup>1</sup>Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131, <sup>2</sup>Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131 (fmccubbi@unm.edu).

**Introduction:** Planetary differentiation, defined here as primary metal-silicate separation and the development of primary geochemical reservoirs in the silicate portion of a planetary body, is a difficult process to study because it is largely based on inference instead of observation. Planet-scale magma oceans are commonly called upon to explain how the terrestrial planets and large asteroids (like 4-Vesta) differentiated, but substantial geochemical evidence for such a process seems to be unique to the Earth-Moon system [1-2], although evidence for Earth seems to have been partially erased due to plate tectonics. Although support is mounting for the presence of magma oceans on Mars, Mercury, and 4-Vesta, geochemical evidence for these magma oceans is somewhat limited [1, 3]. Importantly, it is uncertain how applicable the lunar magma ocean is to magma ocean differentiation on bodies smaller and large than the Moon.

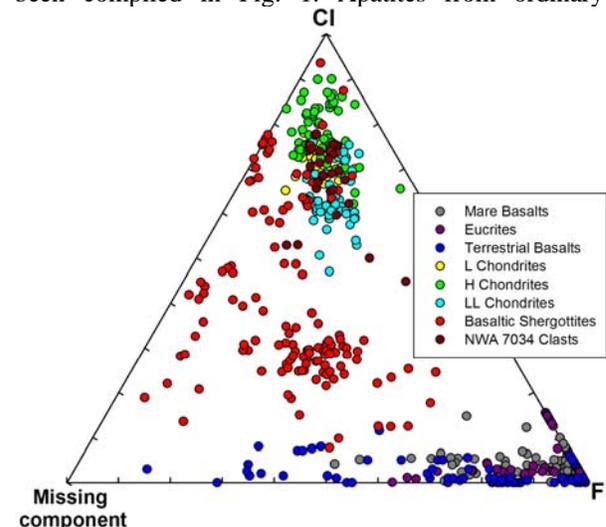
The largescale homogenization that occurs with planet-wide melting has important implications for the kinds of geochemical reservoirs that are likely to form in planetary mantles. In particular, comparisons among incompatible elements could be informative about the differentiation processes that have taken place, given the limited mantle mineralogy that supposedly results from magma ocean crystallization [1, 3-5]. In the present study, we attempt to construct a new window through which to look for evidence of planet wide magma ocean processes by comparing the volatile chemistry of the mineral apatite in a number of basaltic rocks from various differentiated bodies, and by comparing these with apatite compositions from ordinary chondrites in which no differentiation has occurred. This comparison could provide insight into how volatile are incorporated and stored in planetary mantles.

**Apatite Crystal Chemistry:** The mineral apatite  $[\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})]$  is a common volatile-bearing phosphate phase found in a wide variety of planetary basalts and primitive solar system materials. The crystallographic site that typically hosts fluorine, chlorine, and hydroxyl is referred to as the X-site. The primary goal of our study is to compare the occupancy of this site among a number of planetary materials from both differentiated and undifferentiated bodies.

The primary analytical tool used to analyze apatite in this study is the electron microprobe, and hydroxyl cannot be measured directly by this instrument; however, a missing component in the X-site of the apatite

can be calculated on the basis of stoichiometry. If both F and Cl are analyzed with sufficient accuracy, this missing component can be attributed to some combination of the anions  $\text{OH}^-$ ,  $\text{O}^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{Br}^-$ , and  $\text{I}^-$  and/or structural vacancies [6] and/or structural  $\text{H}_2\text{O}$  [7]. The most likely culprit for this missing component in terrestrial igneous systems is  $\text{OH}^-$  [8], and recent analyses of lunar and martian apatite indicate the same [9-13]. However, assumptions that the X-site is fully occupied by F, Cl, and OH can be erroneous as a possible  $\text{O}^{2-}$  + vacancy substitution has been suggested for some synthetic and naturally occurring Cl-rich apatites [14-15]. Consequently, we refer to this missing constituent in the X-site as a missing component unless otherwise noted through the direct analysis of OH by secondary ion mass spectrometry techniques. The EPMA methods used for analyzing apatite are the same as those reported in [13, 16].

**Results:** Apatites were analyzed in basaltic shergottites, gabbroic clasts in NWA 7034, mare basalts, eucrites, and ordinary chondrites [12-13, 15-18], and literature data on terrestrial basalts were compiled from a number of sources [8, 19-20]. All analyses have been compiled in Fig. 1. Apatites from ordinary

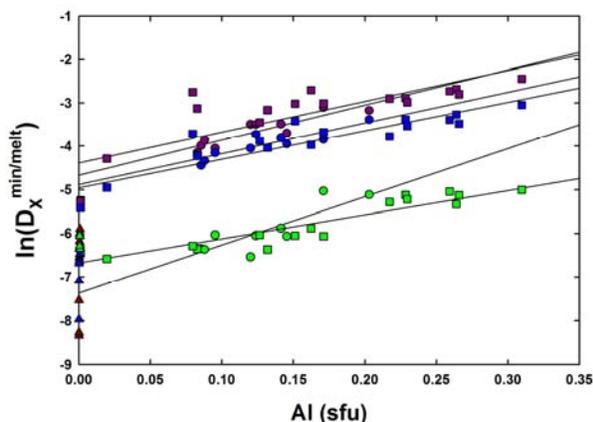


**Fig. 1.** Ternary plot of Apatite X-site occupancy. Apatite from various planetary materials. All extraterrestrial apatite analyses conducted by or previously published by authors of the present study [12-13, 15-16, 17, 32, 18]. Terrestrial apatites are from [8, 19-20] and represent basalts that have not seen secondary metasomatism.

chondrites (OC) are consistently Cl-rich. Although the apatites in OCs appear to have substantial missing components in the X-site, attempts to quantify OH

have indicated they are very dry [15]. Apatite from mare basalts, eucrites, and terrestrial basalts all plot in generally the same portion of the X-site ternary, indicating F-OH rich compositions that have a much more limited amount of Cl. Apatite from basaltic shergottites and gabbroic clasts from the new martian meteorite NWA 7034 have apatite that are anomalously Cl-rich compared to the apatite from other planetary basalts. The missing components in martian, lunar, and eucrite apatites are likely to be OH, as examples of each have been previously analyzed by SIMS and shown to have a nearly full X-site when F, Cl, and OH are summed [9, 11-12, 16, 21].

**Discussion:** Based on the volatile contents of the lunar picritic fire-fountain glasses as well as volatile contents of apatite from mare basalts, KREEP basalts, and KREEP-rich highland rocks, [22] pointed out that partial melts from the lunar mantle are extremely low in chlorine. Furthermore [22] showed that the crustal rocks with a KREEP-component have apatite that indicate they formed from an environment with more Cl than F or H<sub>2</sub>O. Next, [22] discussed these observations in the context of a global magma ocean, showing that these observations could be the result of the partitioning behavior of F, Cl, and OH between nominally anhydrous magma ocean minerals (pyroxene and olivine) and the magma ocean liquid. Because F and OH are preferred in pyroxene more than an order of magnitude more than Cl (Fig. 2), the resulting lunar mantle would be enriched in F and OH relative to Cl. Furthermore, this should hold true for any planet that experienced a magma ocean and had olivine, pyroxene, garnet, and



**Fig. 2.** Mineral/melt partitioning behavior of F, Cl, and H<sub>2</sub>O for cpx, opx, and olivine from [23-24]. Cl was below detection for all mineral phases, so D was computed assuming the concentration was equal to the detection limit. Green = Cl, Purple = F, Blue = H<sub>2</sub>O. Circle = opx, Square = cpx, Triangle = olivine.

oxides as the primary crystallizing phases. In fact, the observed relative volatile abundances in lunar basalts inferred from apatite are fairly consistent with those inferred from vestan and terrestrial basaltic apatites (Fig. 1).

Apatites from martian basalts are anomalous in that compositions cover a wide range and are more Cl-rich than apatites from basalts on Earth, Moon, or 4-Vesta (Fig. 1). Some martian apatite compositions overlap with Cl-rich compositions from ordinary chondrites. However, this observation alone does not necessarily imply anything about Mars' differentiation history. There are a number of scenarios that could cause a global-scale difference between apatite compositions among planetary basalts. One possibility is that Mars has a ubiquitous Cl-rich phase in its mantle that formed during magma ocean crystallization. In fact, [25] recently speculated that scapolite may be present within the martian mantle, as long as the bulk Cl content of Mars was sufficiently elevated. Another possibility is that all martian basalts that have been analyzed to date have been substantially modified or contaminated by Cl-rich fluids. Metasomatized terrestrial settings are a common host for Cl-rich apatites [8, 14], and this process has already been shown to have operated on Mars through studies of the chassignites, nakhlites, and ordinary chondrites [15, 17, 26-27]. However, contamination by Cl-rich fluids may be difficult to justify given that all the martian basalts have Cl-rich apatite, but the basalts have preserved their properties of geochemical enrichment/depletion and variability in  $fO_2$  [28-29]. A third possible explanation for martian apatite compositions is that Mars could be highly depleted in fluorine, although a process for such a depletion is presently unknown. A final possible explanation for the chlorine-rich apatite compositions in martian basalts is that there was no magma ocean on Mars, and the Cl from chondritic precursor materials remained sequestered in the mantle. This model has several problems, the largest of which include the rapid time constraints for core formation on Mars and the antiquity of the geochemically enriched and depleted silicate reservoirs based on isotopic studies [30-31]. Regardless, Mars is a clear outlier when relative volatile abundances of basaltic apatite are compared with Earth, Moon, and 4-Vesta, and it is going to take more work to determine the reason(s) behind the differences.

**References:** [1] Elkins-Tanton (2012) *Ann. Rev. E&PS*. [2] Tonks and Melosh (1993) *JGR- planets* [3] Righter and Drake (1997) *MAPS* [4] Brown and Elkins-Tanton (2009) *EPSL* [5] Elardo et al. (2011) *GCA* [6] Pand and Fleet (2002) *RiMG Phosphates* [7] Mason et al. (2009) *Am Min* [8] Piccoli and Candela (2002) *RiMG Phosphates* [9] Boyce et al. (2010) *Nature* [10] Greenwood et al. (2011) *Nature Geosci* [11] McCubbin et al. (2010) *PNAS* [12] McCubbin et al. (2012) *Geology* [13] McCubbin et al. (2010) *Am Min* [14] Hovis and Harlov (2010) *Am Min* [15] Jones et al. (2011a) *LPSC* [16] McCubbin et al. (2011) *GCA* [17] Jones et al. (2011b) *LPSC* [18] Santos et al. (2013a) *LPSC* [19] Filiberton and Treiman (2009) *Geology* [20] Rossi et al. (2011) *Am Min* [21] Sarafian et al. (2012) *LPSC* [22] McCubbin et al. (2012) *Lunar Highlands workshop* [23] Hauri et al. (2006) *EPSL* [24] O'Leary et al. (2010) *EPSL* [25] McCubbin and Elardo (2012) *Mars mantle workshop* [26] McCubbin and Nekvasil (2008) *Am Min* [27] McCubbin et al. (2009) *GCA*. [28] Borg and Draper (2003) *MAPS* [29] Herd et al. (2002) *GCA*. [30] Borg et al. (1997) *GCA*. [31] Brandon et al. (2000) *GCA*. [32] Lewis et al. (2013) *LPSC*