

HALOGEN (Cl, Br, I) SYSTEMATICS OF LUNAR FERROAN ANORTHOSITES: EVIDENCE FOR SUB-CHONDRITIC LUNAR VOLATILES J. F. Pernet-Fisher¹, P. L. Clay¹, R. Burgess¹, K. H. Joy¹, ¹School of Earth and Environmental Sciences, University of Manchester, M13 9PL, UK (john.pernet-fisher@manchester.ac.uk).

Introduction: We report halogen (Cl, Br, I) abundances for a suite of 10 lunar Ferroan Anorthosites (FANs). The volatile elements, including the halogens, are crucial components in planetary differentiation and evolution as they influence melting temperatures, magma viscosity, and magmatic eruptions [1,2]. As crystallization products of the earliest phases of the Moon's history, anorthosites have the potential to shed light on the volatile systematics of the lunar magma ocean (LMO). Additionally, any such estimates will be important for evaluating existing apatite-derived volatile abundance estimates of the Moon, derived from partial melts of the lunar mantle (formed from mafic LMO cumulates). Apatite contains relatively high abundances of halogens (F+Cl) and water relative to other rock forming minerals (i.e., ol, pyx, plag). Thus, many studies have routinely used apatite to calculate magmatic water and halogen abundances, ultimately deriving water and halogen abundances for the lunar mantle [e.g., 2]. However, apatites are among the final phases to crystallize from a magma (~95% solidification). Processes such as crustal assimilation or magmatic degassing over the lifetime of a magma can result in large uncertainty in any resulting apatite-derived volatile back-calculations.

Methods : We were allocated 10 FAN Apollo 16 samples from a range of different sampling stations, and one Apollo 15 sample. All these samples are thought to be 'pristine' and do not contain any impactor HSE component. Chips ~ 50 mg in mass were analyzed using the neutron irradiation noble gas method [4] on a Thermo-Fisher Argus VI multi-collector mass spectrometer at the University of Manchester. This method enables the precise determination of low abundance (sub-ppm) halogens such as Br and I.

Results: The Apollo 15 sample is within range of the Apollo 16. Ratios of Br/Cl and I/Cl for this suite of anorthosites generally overlap values reported for lunar volcanic glass beads, extending from chondritic compositions to sub-chondritic values (**Fig. 1**).

Discussion: Due to the volatile nature of the halogens, they can be easily modified by secondary processes such as impact modification and magmatic degasses/metamorphism. Therefore, before the FAN halogen systematics can be assessed in the context of a crystallizing LMO, the effects of secondary processes need to be considered first.

Role of Impact: Impacts have the potential to fractionate relative halogen abundances [5]. Pernet-Fisher

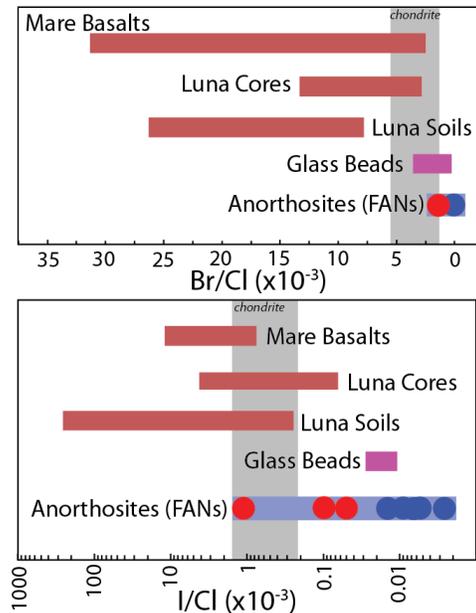


Figure 1: Plots of Br/Cl and I/Cl of lunar FANs in context with other lunar materials. Figure modified from [1]. Red symbols represent samples that display enrichments in halogens. Blue symbols represent samples that likely reflect LMO halogen ratios. Gray bar represents the reported range of carbonaceous and ordinary chondrites.

et al. [6] characterized the extent of shock damages for a number of anorthosites investigated here. Samples display a range of shock states, ranging from near-pristine (< 3 GPa) displaying clear igneous cumulate textures to high shock states (~20 GPa; e.g., sample 60015) displaying cataclastic brecciated textures. No systematic relationships are observed between plagioclase shock state and halogen abundances, indicating that impact shock processing have had a minimal effect on modifying halogen systematics.

Role of metamorphism within the crust: Due to the water restricted nature of the Moon relative to the Earth, magmatic degassing can be dominated the volatilization of phases such as HCl and metal halides [7,8]. This will result in the gases/fluids that are enriched in Cl relative to Br and I. Such degassing has been linked to $\delta^{37}\text{Cl}$ enrichments in lunar samples [e.g., 3,7], and in extreme cases has resulted in low-T alterations around the rims of phases such as FeNi metal sulfides [9]. The best example of this is from Apollo 16 sample 66095 'rusty rock' which contains Fe-oxide alteration phases such as lawrencite (FeCl_2) [9]. No such alteration has

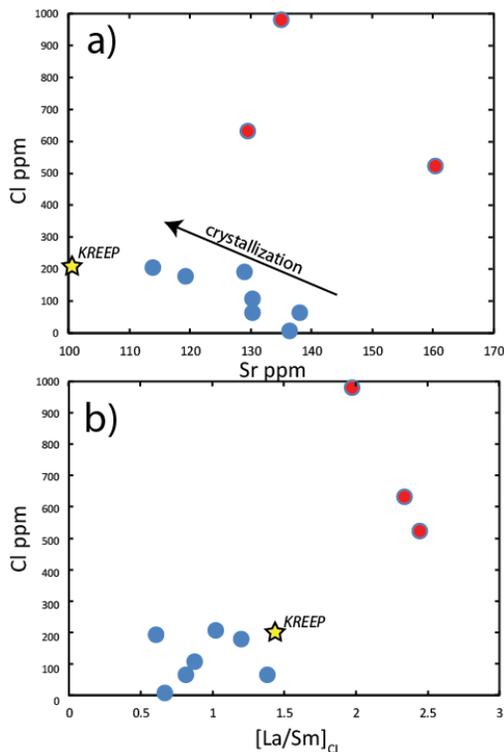


Figure 2: a) Cl vs. Sr ppm. Blue symbols display a negative correlation expected for a crystallizing LMO trending towards KREEP. b) Cl vs. $[La/Sm]_{Cl}$. For blue symbols Cl abundance does not vary with La/Sm as is expected during fractional crystallization. Red symbols in a) and b) display enrichments in Cl and LREE relative to trends expected in a fractional crystallization sequence. Sr and REE data from [10], KREEP from [14].

been reported for any lunar anorthosites, however, to date no Cl-isotope ratios have been reported for lunar anorthosites making it hard to assess the extent to which these samples have been affected by degassing.

Halogens in the LMO: It is anticipated that halogens should become progressively concentrated in residual LMO melts given the incompatibility of these elements in earlier crystallized olivine, pyroxene, and plagioclase [2]. Thus, within this suite of anorthosites, negative correlations are expected between indices of fractional crystallization (i.e., elements like Sr that are strongly affected by plagioclase fractionation) and halogen abundance. With the exception of 3 samples (red symbols in **Fig. 1** and **2**; 67635, 60135, 60515), such correlations are generally observed, indicating that fractional crystallization of a solidifying LMO is largely controlling FAN halogen abundance (**Fig. 2a**). The 3 noted samples above display both high halogen abundances and high Sr abundances, inconsistent with the trend expected for fractional crystallization. Indeed, these 3 samples also display large LREE enrichments ($La/Sm_{Cl} > 2$; **Fig. 2b**). The observation of LREE en-

richments within lunar anorthosites are not accounted for by the fractional crystallization of a single evolving LMO melt [10, 11].

Several mechanisms have been proposed to account for the observation of LREE enrichments (and enrichments of KREEPy elements such as Th) in lunar anorthosites. These range from partial melts induced by mantle-overturn mixing with plagioclase-saturated LMO melts [10] to serial magmatism intruding plagioclase-saturated melts into the lunar crust [12]. In either case, it is clear that the mechanism that is introducing LREE enriched/KREEPy signatures to some FANs are also introducing enrichments in halogens.

Disregarding these three halogen-enriched samples, no to weak correlations are observed between halogen abundances (and ratios) and La/Sm (**Fig. 2b**), consistent with a simple crystallizing LMO melt. As such, these samples are the best available for constraining the volatile systematics of the LMO. As incompatible elements do not fractionate during fractional crystallization, the observed sub-chondritic Br/Cl and I/Cl ratios for these samples likely represent the halogen ratios of the LMO during solidification.

This interpretation is supported by the halogen systematics of lunar volcanic glass beads (**Fig. 1**). Due to the primitive nature of the glass beads, these samples are thought to have erupted through the lunar crust rapidly, having undergone minimal degassing relative to other eruptive volcanic products such as mare basalts [13]. Thus, the halogen ratios reported for these samples should represent a close approximation to the mantle signatures at the source of the glass beads. The observations that the FANs overlap these ratios, therefore, support our interpretation that the lunar mantle has sub-chondritic halogen signature.

In conclusion, we suggest that the Moon had an initial sub-chondritic halogen composition. This is consistent with the fact that Br and I are more volatile than Cl. Any volatile loss during the Moon-forming impact event is likely to have preferentially lost Br and I relative to Cl, driving down Br/Cl and I/Cl values.

References: [1] Clay et al. (2017). *Nature*, 551, 614; [2] McCubbin et al. (2015) *Am. Min.*, 100, 1668-1707; [3] Barnes et al. (2016). *EPSL*, 447, 84-94; [4] Ruzié-Hamilton et al. (2016) *Chem. Geol.*, 437, 77-87; [5] Treiman et al. (2014) *Am. Min.* 99, 1860-1870; [6] Pernet-Fisher et al. (2017) *Sci. Rep.*, 7, 5888; [7] Sharp et al. (2010). *Science*, 329, 1050-1053; [8] Tartese et al. (2013) *GCA*, 122, 58-74; [9] Shearer et al. (2014) *GCA*, 139, 411-433; [10] Pernet-Fisher et al. (2017) *LPSC 48 #1931*; [11] Floss (1998) *GCA*, 62, 1255-1283; [12] Gross et al. (2014) *EPSL*, 388, 318-328; [13] Saal et al. (2008) *Nature*, 454, 192. [14] Warren (1988) *Workshop on Moon in Transition*.