THE CHLORINE ISOTOPE COMPOSITION OF LUNAR FERROAN ANORTHOSITES.

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Introduction: The Moon has an uniquely large range of chlorine isotope compositions ranging from -0.7‰ to > +35‰ [1-7]. The mechanism for producing such heavy chlorine isotope enrichments on the Moon is commonly accepted to be a result of the degassing of metal-chloride species such as $FeCl_2$ and loss of the light chlorine isotope to space [5]. Degassing may be a local feature during eruption [5], a global feature during degassing of the KREEP parent magma [2, 3] or vapor phase metasomatism [8]. In fact, it is likely that some combination of these processes may be occurring. It has been suggested that the anomalous chlorine isotope values are sourced from urKREEP (the hypothetical incompatible element enriched residuum reservoir following LMO crystallization and differentiation) with a $\delta^{37}Cl$ value of approximately +30‰ as a general trend exists between incompatible trace elements and $\delta^{37}Cl$; however, large intra-sample variability >10‰ occurs from apatite within single thin sections and suggests that a localized process produces significant changes in $\delta^{37}Cl$ values [2, 3]. In order to address the source of high $\delta^{37}Cl$ values and the mechanism by which heavy chlorine isotope enrichments are produced on the Moon, we measured the chlorine isotope composition of the ferroanorthosites (FANs). The FANs are chemically primitive rocks thought to represent an early floatation crust formed by an accumulation of positively buoyant plagioclase [9, 10]. The standard model of LMO crystallization and chronology of lunar rocks suggest that FANs are the oldest samples in the present lunar suite and have likely escaped incorporation of the urKREEP component. Here, we present preliminary data of the chlorine isotope compositions of FANs in order to better constrain the volatile history of the Moon.

Samples & Methods: The following samples were measured: 60015, 60025, and 62255. Chlorine isotope measurements were made following the same procedure used for the first chlorine isotope measurements of lunar materials by Sharp et al. 2010. Measurements were made of water-soluble (WSC) and structurally bound chloride (SBC) fractions of each sample. The WSC fraction was obtained by leaching powders in 18MΩ DI water. The SBC fraction was obtained by pyrohydrolysis where powders were melted in a stream of water vapor. Measurements were made by gas source mass spectrometry on a Delta^PLUS^XL. Cl concentration [Cl] are given in ppm (wt fraction) and $\delta^{37}Cl$ values are reported in standard per mil notation relative to Standard Mean Ocean Chloride (SMOC) ($\delta^{37}Cl_{SMOC} = 0‰$).

Results: The chlorine isotope compositions and Cl concentrations are shown in Fig. 1. Cl concentrations range from <1 to 9 ppm Cl. The Cl isotope values are all heavy, ranging from 10 to 30‰. There is a positive correlation between Cl concentration and $\delta^{37}Cl$ values. This is the opposite of what is seen for a similarly volatile elements such as Zn and Ga, in which the [Zn]-$\delta^{66}Zn$ are negatively correlated (Fig. 1)[11, 12]. Two samples, 60015 and 62255 have been measured for both Zn and Cl: The Zn concentrations and isotope ratios of these two samples are similar, but are very different for Cl, suggesting that these two chemical systems are not directly correlated.
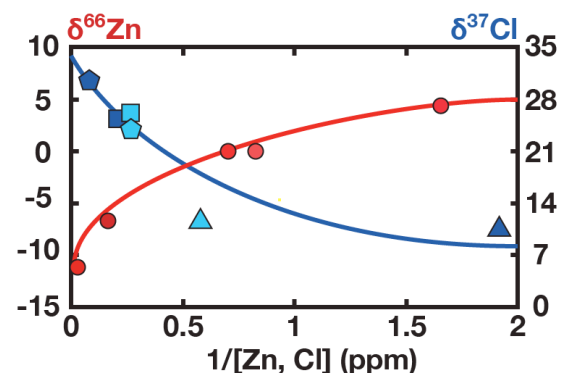

Fig. 1. Cl and Zn isotope composition and concentration. The two isotope systems have an opposite trend. Dark blue: structurally-bound Cl; pale blue: water-soluble Cl; pentagons: 60025, squares: 62255; triangles: 60015. Samples 62255 and 60015 have high and low $\delta^{37}Cl$ values, respectively, but almost identical $\delta^{66}Zn$ values of 0‰. Zn data from [11].

Discussion: A number of conclusions can be made from the new Cl isotope data. First, given the high Cl concentrations in the FANs and the fact that there are no Cl-bearing phases in these lithologies, the Cl was likely introduced post-crystallization as a vapor phase. The source of the introduced Cl is not metal chlorides, or we would expect a similar trend in the Zn and Cl isotope data. Instead, the Cl source was probably HCl. If the data are explained as a two-component mixing trend, then the negative [Cl]-$\delta^{37}Cl$ relationship corresponds to an introduced (exogenous) Cl component with a $\delta^{37}Cl$ value greater than 30‰. This interpretation has several important implications. First, it means that the HCl vapor phase was exsolved from the under-

lying crystallizing magma and permeated through the ferroananorthosite 'lid'. If this process did occur, then the FANs are permeable to vapor loss from below. Second, it requires that only the very latest stages of vapor loss are retained in the FANs. If the initial $\delta^{37}Cl$ value of the source magma was Earth-like (near 0‰) and became heavy by the process of degassing, then the degassed component, now trapped in the FANs, should reflect the complimentary light component. The fact that the Cl in the FANs is heavy may be explained if only the last remnants of vapor loss were trapped in the FANs. Cl retention may have only occurred below a critical temperature threshold in the latter stages of degassing. Third, if the Cl is sourced from below, it requires a surpringly large fractionation between a melt and exsolving HCl phase at modest pressures. Most studies consider the high Cl isotope fractionation to occur across a melt-vacuum interface. Fractionation between the melt and overlying anorthosite lid is problematic.

A second possibility is that the Cl is introduced during later impact processes. If there is a heavy surficial Cl component in the regolith, then impacts may introduce the Cl as a metasomatic vapor phase. Partial evaporation and loss would raise the $\delta^{37}Cl$ values further. We were careful to select samples that had no visible signs of impact-related melt to minimize this effect.

A third possibility is that the high Cl isotope compositions are related to degassing from a primary Cl-rich anorthosite. This scenario is not likely because anorthosites should not inherently incorporate Cl, and if degassing was the cause of the high $\delta^{37}Cl$ values, then the [Cl]-$\delta^{37}Cl$ values should show a negative correlation, as is seen for Zn.

A hybrid model may best explain the data. Of the three samples analyzed, there is a large range of [Cl] and $\delta^{37}Cl$ values, suggesting heterogeneous introduction and/or loss of Cl between the different samples. It is possible that samples which had larger initial Cl inputs also lost a larger amount of Cl during degassing. This would result in the positive [Cl]-$\delta^{37}Cl$ trends that we observe. It is also possible that variable amounts of surficial Cl were introduced during impacts to the different samples. Additional measurements of FANs and related samples (highland rocks) are planned.

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