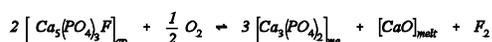


FLUORINE, CHLORINE AND WATER FUGACITIES IN PLANETARY BASALTS RECORDED BY PHOSPHATE EQUILIBRIA. A.E. Patiño-Douce¹ and M.F. Roden¹, ¹Department of Geology, University of Georgia, Athens GA 30602, USA (alpatino@uga.edu)

Water and halogens influence a wide range of planetary properties and processes, such as magma compositions and densities, mantle melting temperatures, the composition of oceans and atmospheres and the occurrence of life, to an extent that is generally disproportionate to their low bulk abundances in the terrestrial planets. Apatite is a widely distributed high-temperature rock-forming mineral that also preserves a record of the halogen and water fugacities that existed during the waning stages of crystallization of planetary magmas, when they became saturated in phosphates. We [1] have developed a thermodynamic formalism based on apatite-merrillite equilibria that makes it possible to compare the relative values of halogen (F, Cl) and water fugacities in Martian, lunar, eucritic and terrestrial basalts. We show that, even though it is not possible to use results obtained from basaltic rocks to estimate absolute volatile fugacities in planetary mantles, it is feasible to infer the *ratios* between the fugacities of these three volatiles in the mantles of Mars, the Earth, Moon and the eucrite parent body.

The thermodynamic formalism is based upon the equilibrium between apatite and merrillite, exemplified here with the fluorine end-member:



We define the variable $\Delta \log f(F_2)_{QFM}$ (log relative fluorine fugacity) as follows:

$$\Delta \log f(F_2)_{QFM} = \frac{1}{2} \Delta \log f(O_2)_{QFM} - \log K_{F-phosphates}$$

The variable $\Delta \log f(F_2)_{QFM}$ records the fluorine fugacity under which a given apatite-merrillite assemblage crystallized, measured relative to the fluorine fugacity that would exist at equilibrium between pure end-member fluorapatite and merrillite at the same pressure, temperature and lime activity as the assemblage of interest, and at the oxygen fugacity of the QFM buffer for that pressure and temperature (choice of this or any other oxygen fugacity reference is purely

arbitrary and does not affect the conclusions). Log relative chlorine and water fugacities are defined in an identical manner, except that log relative water fugacity is independent of oxygen fugacity. We find that log relative fluorine fugacities in lunar and Martian basalts are nearly constant, which suggests that $\Delta \log f(F_2)_{QFM}$ can be used as a reference to compare volatile fugacity ratios among the terrestrial planets. We accomplish by defining two additional variables, which are applicable to merrillite-absent assemblages (such as terrestrial basalts):

$$\Delta \log f(Cl_2)_{F_2} = \Delta \log f(Cl_2)_{QFM} - \Delta \log f(F_2)_{QFM}$$

$$\Delta \log f(H_2O)_{F_2} = \Delta \log f(H_2O)_{QFM} - \Delta \log f(F_2)_{QFM}$$

We find that the ratio of $f(Cl_2)$ to $f(H_2O)$ is broadly the same in the mantles of the Earth and Mars, but the Earth's mantle has lower H_2O/F_2 and Cl_2/F_2 fugacity ratios than the Martian mantle. The Cl_2/H_2O relationship is important because it implies that, if the mantle of one of the two planets is drier than the other, then it is also more strongly depleted in Cl_2 . Our analysis thus shows that *the Martian mantle parental to SNC meteorites was both dry and poor in Cl compared to the terrestrial mantle*. We argue that the high Cl contents measured in some SNC's must arise from the presence of chlorine-bearing phases of secondary (surficial) origin and do not reflect high mantle Cl contents. The limited data available also show remarkably little variability in halogen and water fugacities throughout almost 4 billion years of the planet's history, from ALH84001, through Lafayette to the basaltic shergottites, thus supporting Lodders and Fegley's [2] contention that the volatile inventory of the Martian mantle was "frozen in" early on, most probably prior to 4 billion years ago. The high Cl and Br contents of the Martian surface [3,4], together with the planet's surficial water, have most likely resided in the planet's surficial systems since at least 4 Ga, and may have been degassed from the planet's interior during a primordial crust-forming event.

In comparison to the Earth and Mars, the Moon, and possibly the eucrite parent body too, are strongly depleted in chlorine, not only in absolute terms [5] but also with respect to water. We

speculate that the relative volatile depletions observed in the Moon ($\text{Cl}_2 > \text{H}_2\text{O} > \text{F}_2$) are a signature of catastrophic volatile loss, perhaps associated with the Moon-forming collision. The absence of this chlorine loss signature in Earth and Mars attests to the relatively less violent early histories of the two planets.

References: [1] Patiño-Douce, A.E. and Roden, M.F., in review, *Geochim. Cosmochim. Acta*. [2] Lodders, K. and Fegley Jr., B. (1997) *Icarus* 127, 373-394. [3] Gellert, R. et al. (2004) *Science* 305, 829-832. [4] Rieder, R. et al. (2004) *Science* 306, 1746-1749. [5] Ringwood, A.E. and Kesson, S.E. (1977) *The Moon* 16, 425-469.