THERMOCHEMISTRY OF APATITE AND ITS SOLID SOLUTIONS, APATITE-MELT PARTITIONING, AND IMPLICATIONS FOR THE MOON.

A. H. Treiman[1] and J. W. Boyce[2], [1]Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston TX 77058 <treiman#lpi.usra.edu>. [2]Division of Geological and Planetary Sciences, Caltech, 1200 E. California Blvd. Pasadena, CA 91125 <jwboyce$caltech.edu>.

Introduction: Following the observation of H in lunar basaltic glasses [1], most of subsequent evidence has comes from analyses and interpretation of apatite grains in lunar igneous rocks [2-4]. Compositions of these apatites have been used to infer water contents of their parental magmas. To do this calculation properly requires knowing thermochemistry of volatile partitioning between apatite and melts, solid solution properties of apatites, and the effects of physical and chemical conditions on that partitioning.

Thermochemistry: To constrain the volatile compositions of phases associated with lunar apatite, one needs precise and accurate thermochemical data on apatite and its solid solutions. Literature data for end-member Ca-apatites are sufficient and mostly self-consistent (fluorapatite: [5-8]; chlorapatite: [5,9-12]; hydroxylapatite: [5,10,11,l3,14]). The thermochemistry of solid solutions in $Ca_5(PO_4)_3(F,Cl,OH)$ are not entirely clear. They may be ideal at the temperatures expected for lunar magmas and fluids [5,8,9], may also be non-ideal [15-17] consistent with evidence for anion ordering [18,19]. These apparent non-idealities have also been ascribed to solid solution of O^{2-} in place of OH & Cl [8,20].

Apatite-Melt Partitioning: Partition coefficients (as normally defined) like $D^F_{apat/basalt}$ are strongly dependent on compositions of both apatite and basalt. This dependency arises first because of closure: apatite must contain a fixed proportion of F+Cl+OH, while melts and fluids are not so constrained. Consider an OH-free, Cl-free, melt just saturated in F-apatite giving $D^F_{apat/basalt} = D_0$. The melt can accept more F, but the apatite cannot; thus $D^F_{apat/basalt}$ can vary, and be smaller than D_0! Thus, use of an experimental value for $D^F_{apat/basalt}$ can lead to an overestimate of the magma's proportion of F (or OH).

More proper is to consider exchange equilibria like $Ca_5(PO_4)_3Cl + F^-(melt) = Ca_5(PO_4)_3F + Cl^-(melt)$. For this, one can calculate an equilibrium constant K

$$\frac{x_{F-Ap}}{x_{Cl-Ap}} \cdot \frac{x_{Cl^-}}{x_{F^-}} = \exp\left(\frac{-\Delta G^0_{rxn}}{RT}\right) = K$$

(here assuming ideal solid and melt solutions). Experimental data on anion partitioning are accommodated (to zero order) by this simple model: Fig. 1. Scatter in those fits can be ascribed to analytical undertainties [23], and to other compositional dependencies (e.g., F-Cl and F-OH partitionings are not identical [21,22], though they plot together in the Figure). Most of the literature data on apatite/basalt partitioning are for OH-rich systems, which may not be relevant for lunar magmas.
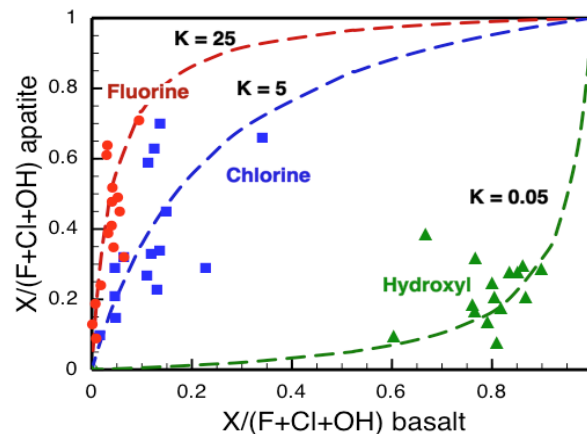

Fig. 1. Anion partitioning between apatite and basalt melt [21,22], and model fits with K values as in the equation.

Conclusions: Although the thermochemistry of Ca apatites is fairly certain, more data are needed on their solid solutions at magmatic temperatures. There is a critical need for apatite/melt partitioning experiments with lunar-relevant compositions. Use of single-element partition coefficients (e.g., $D^F_{apat/basalt}$) can lead to erroneous inferences. Apatite compositions can provide crucial clues to volatile abundances and proportions in lunar magmas, but must be interpreted with care.

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