

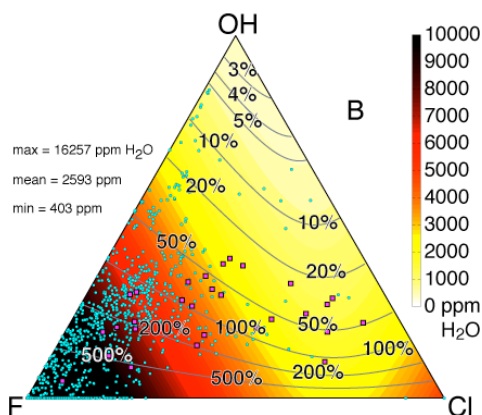
## ANALYSIS OF VOLATILES IN APATITE: IMPLICATIONS FOR QUANTITATIVE HYGROMETRY.

J.W. Boyce<sup>1,2</sup>, <sup>1</sup>Division of Geological and Planetary Sciences, Caltech (1200 E. California Blvd. Pasadena, CA 91125. jwboyce@caltech.edu), <sup>2</sup>Department of Earth and Space Sciences, UCLA (Los Angeles, CA 90095-1567).

**Introduction:** In order to begin quantifying H in a host melt, rock, or planetary body based on measurements of H in apatite ( $H_{AP}$ ), one must be able to make precise and accurate measurements of  $H_{AP}$  at a spatial scale of a few to tens of  $\mu\text{m}$ .

**Quantitative Analysis by Electron Microprobe:**

The practice of estimating  $H_{AP}$  by measuring F and Cl using the electron probe (EPMA) is still employed. A recent study of best practices for measuring F and Cl in apatite by EPMA [1] indicates that the most reliable data result from the combination of defocused beams ( $10 \times 10 \mu\text{m}$ ) with large rastered areas ( $30 \times 30 \mu\text{m}$ ), on crystals with their c-axis perpendicular to the electron beam. Such analyses require large crystals and still result in significant uncertainties ( $\sigma$ ) in F and Cl, and thus  $H_{AP}$ . Even these best protocols yield large  $\sigma(F)$  and  $\sigma(Cl)$  for crystals not oriented with the electron beam perpendicular to the c-axis of the crystal (Fig. 1). The  $\sigma(F)$  and  $\sigma(Cl)$  must then be propagated into  $\sigma H_{AP}$ , resulting in  $\sigma(H_{AP})$  of  $10^2$ - $10^4$  ppm (Fig. 1). For melt-apatite partitioning of H [2,3], where small grains were analyzed,  $\sigma(H_{AP})$  could easily exceed 100%, leading to a non-trivial  $\sigma$  in partitioning.



**Fig.1:** Uncertainties in hydrogen estimates shown in absolute ppm (color scale, as  $\text{H}_2\text{O}$ ) and % (contours) for best EPMA protocols of [1], but worst orientation (c-axis parallel to electron beam). All calculated as two standard deviations of the mean. Cyan circles are natural apatite data from GEOROC, squares are synthetics from [2,3] used to define partitioning relationships.

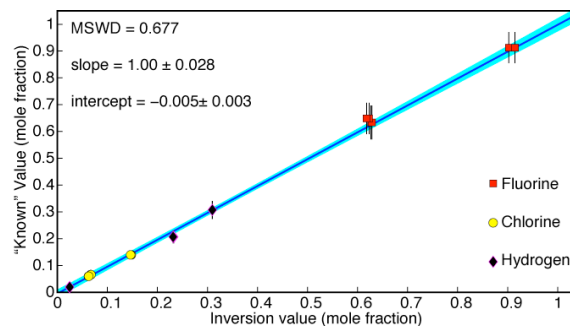
**Quantitative Analysis by SIMS:** SIMS is a better method for determining  $H_{AP}$ , as it requires less than  $\sim 20 \times 20 \mu\text{m}$  areas for quantitative analysis of volatiles. However, such efforts are limited by the paucity of adequate standards: the  $\sigma$  of the standards and calibra-

tion are largely responsible for  $\sigma(H_{AP}) > 15\%$  [4,5] derived from “conventional” calibrations (CC).

I report an advance in the measurement of H, F, and Cl in apatite that eliminates the need for homogeneous, well-characterized standards by using measured ratios to solve an inverse problem that yields calibration slopes for each element. This “inverse calibration” (IC) model assumes that measured intensities are linearly correlated with concentrations for all elements in all measured samples ( $m$  in Eq. 1), and that  $F+Cl+OH=100\%$  occupancy (right hand side of Eq. 1). These assumptions appear to be justified at the resolution of SIMS measurements. The slopes ( $m$ ) are the only unknowns, with the measured ratios ( $R$ ) and masses ( $M$ ) held constant. For  $N \geq 3$  linearly independent analyses we can solve the system of equations.

$$\frac{m_{OH}R_{OH}}{M_{OH}} + \frac{m_F R_F}{M_F} + \frac{m_{Cl}R_{Cl}}{M_{Cl}} = 1 \quad \text{Equation 1}$$

IC has been tested on a well-characterized apatites (F. McCubbin and colleagues), and reproduces their H, F, and Cl to within the typical 6-12%  $\sigma$  (Fig. 2). IC is further improved by adding additional apatites of different H, F, and Cl, even “unknown” apatites: In doing so, IC reproduces CC-derived H concentrations on Durango apatite to within  $<1\%$ , F within 3%, and Cl within 1%. In all cases, IC yields individual  $\sigma$  that are smaller than those of CC by a factor of 2-18. Eliminating the need for homogeneous, well-characterized standards will allow more labs to generate more accurate and precise  $H_{AP}$ .



**Fig.2:** Comparison of H, F, and Cl values (as mole fractions) derived from CC and IC methods. Slope = 1 and small intercept indicates good agreement for all elements.

**References:** [1] Goldoff, B. et al., *AGU* (2010). [2] Mathez, E. & J. Webster, *GCA* (2005). [3] Webster, J.D. et al., *GCA* (2009). [4] McCubbin et al. *PNAS* (2010). [5] Greenwood et al., *Nature Geosci.* (2011).