HIGH-RESOLUTION RAMAN SPECTROSCOPY CONSTRAINTS ON APATITE HALOGEN COMPOSITION: IMPLICATIONS FOR PLANETARY VOLCANISM AND IGNEOUS PROCESSES.

K. T. Ashley[1], B. E. McKeeby[1], D. E. Harlov[2], R. J. Bodnar[3], and M. S. Ramsey[1], [1]Affiliation Department of Geology and Environmental Science, University of Pittsburgh, 4107 O'Hara Street, Pittsburgh, PA 15260, USA, ktashley@pitt.edu, [2]GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany, [3]Department of Geosciences, Virginia tech, 4044 Derring Hall (0420), Blacksburg, VA 24061, USA

Introduction: Calcium phosphate apatite, $Ca_{10}(PO_4)_6(F,OH,Cl)_2$, is the most abundant phosphate mineral and is nearly ubiquitous in igneous, metamorphic, sedimentary, and hydrothermal systems. The halogen content of apatite may be used as a petrogenetic tracer, with F used as an indicator for magma aluminosity or differentiation index [1]. Inclusions of apatite in rigid hosts can additionally be analyzed to determine the pressure (and therefore depth) of mineral growth [2,3], which is important for tracking magma crystallization and mobility. Despite its utility, accurate determination of the halogen content of apatite is challenging, due to irreversible damage and diffusion of F and Cl during electron microprobe analysis or sample destruction through wet-chemistry and ablation tech-

niques. For rare or irreplacable samples, such as meteorites, destruction and modification should be minimized. In this study, we conduct high-resolution Raman spectroscopy on synthetic apatites to characterize perturbations in peak position, width, and topology that result from the crystallographic accomodations of the substitutions. Additionally, we analyze a sample of Nakla from the University of Pittsburgh meteorite collection with Raman spectroscopy to characterize the halogen content to infer the conditions at the time of magma crystallization.

Methods: Unpolarized Raman spectra were collected using a JY Horiba LabRAM HR (800 mm focallength) micro-Raman spectrometer at Virginia Tech, equipped with a 100 mW 514.57 nm Ar laser. Analyses were collected using a 100x objective, a confocal aperture of 400 µm, a 150 µm slit width, and 1800 lines·mm^{-1} grating. The apatite crystals measured in this study were synthesized along the three binary joins which make up the apatite ternary (Fig. 1) using a high temperature slow-cooled, molten flux method (F-Cl join) [4] and a high temperature anion exchange method (F-OH and Cl-OH joins) [5]. Focus was directed to the $v_1(A_g+E_{2g})$ symmetric $(PO_4)^{-3}$ stretching mode at ~964 cm^{-1} given the intensity and sensitivity of mixing relative to the low-frequncy apatite modes (Fig. 2). Correction for drift was achieved through simultaneous collection of a Ne line (918.66 cm^{-1}).

Spectroscopic Observations and Peak Fitting: For F- and OH-apatites, a single peak fitting is adequate; however, even at low concentrations ($X_{Cl} < 0.1$), the Cl-bearing apatite band contains shoulders, requiring a 4-peak routine using the Pearson VII Area model
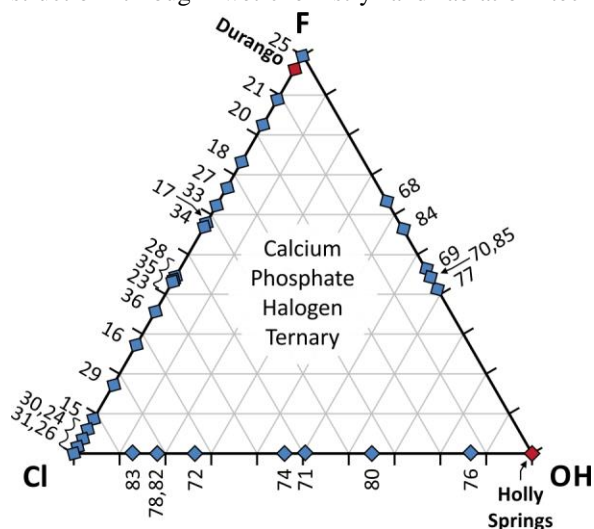

Fig. 1 Anion ternary diagram showing composition of synthetic apatites analyzed in this study.
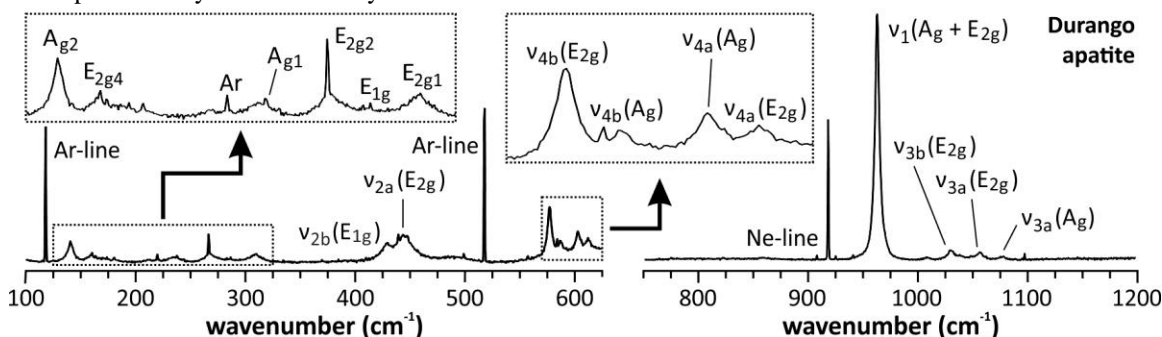

Fig. 2 Low- and high-frequency Raman modes for Durango fluorapatite along [001]. Calibration lines are shown for reference.
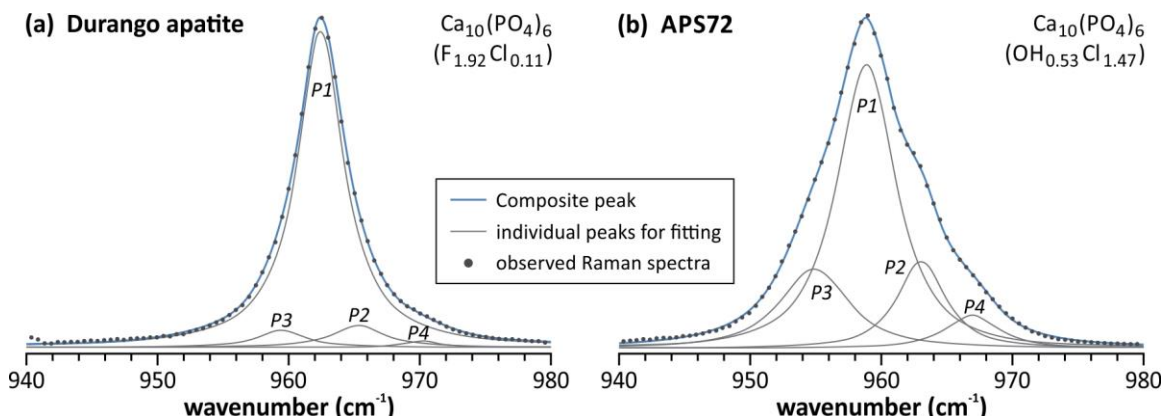
Fig. 3 Peak deconvolution for (a) Durango fluorapatite and (b) synthetic sample APS72. Significant mixing along the binaries results in peak broadening and the development of shoulders on the band at ~964 cm^{-1}.
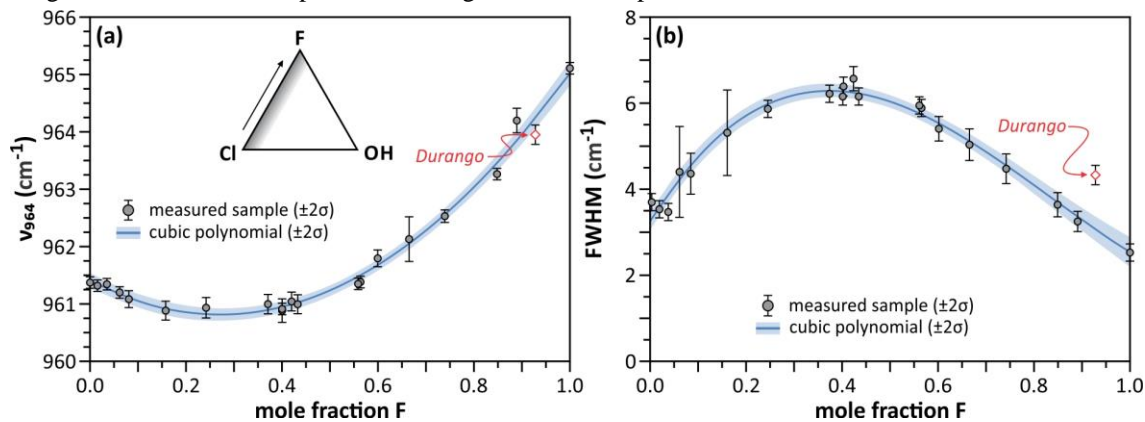

Fig. 4 (a) Peak position and (b) FWHM for synthetic apatites along teh F-Cl join. Incorporation of Cl into apatite results in a negative frequency shift and peak broadening.

to deconvolve the spectra with acceptable fit statistics (R^2 > 0.999; Fig. 3). For the composite peaks derived from Cl-bearing apatite, we measured peak position and full width half maximum (FWHM) for the most intense peak ("P1").

Spectroscopic Results: Spectroscopic fitting results show significant frequency shifts (> 4 cm^{-1}) of the main peak with mixing along the F-Cl and Cl-OH joins, with only nominal adjustments along the F-OH join (Fig. 4). A significant increase in the FWHM of this primary band is also observed with mixing along the F-Cl and Cl-OH binaries, increasing from ~3 cm^{-1} for the pure endmembers to >6 cm^{-1} with ~50:50 F-Cl or Cl-OH mixing along either join. These trends are the result of the significantly larger ionic radius of Cl relative to F (+32.31%), which results in O shifting and Ca repulsion [4], whereas the size of OH is much more similar (+2.31%) with a direct substitution for F occurring. The development of shoulders on the phosphate mode at ~964 cm^{-1} is likely the result of strain of the phosphate tetrahedra and/or degradation to a lower crystallographic symmetry. Whereas other studies show similar negative frequency shifts and broadening of the 964 cm^{-1} band with F-reduction, the trends have

been presented as linear [6] and do not account for peak shoulder development. We show the trends are best described by a 3rd-order (asymmetric) polynomial function (Fig. 4).

Implications for Understanding Planetary Igneous Processes: Nakhlites are believed to originate from a localized flow sequence derived from the same magma source and alteration fluid [7]. Based on the halogen species of apatite-bearing melt inclusions in olivine, we are able to constrain the fluid environment at the time of olivine crystallization within the cumulate and develop models for magma evolution in and on the Martian crust. If present in sufficient abundance, Raman measurements on current/future rovers would help with petrologic assessments on *in-situ* samples.

References: [1] Chu M. et al. (2009) *J. Pet., 50, 1829-1855*. [2] Ashley K. T. et al. (2017) *Amer. Min., 102, 743-749*. [3] Barkoff et al. (2017) *Geology, 45, 947-950*. [4] Schettler G. et al. (2011) *Amer. Min., 96, 138-152*. [5] Hughes J. M. et al. (2016) *Amer. Min., 101, 1783-1791*. [6] Kollegger P. et al. (2011) *CORALS II Conference, Abstract #4018*. [7] Filiberto et al. (2014*) EPSL, 401, 110-115*.