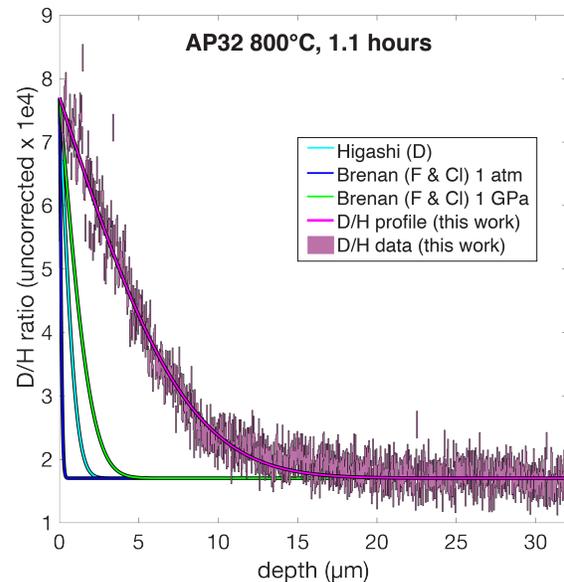


**HYDROGEN DIFFUSION IN APATITE.** J. W. Boyce<sup>1</sup>, M. B. Baker<sup>2</sup>, Y. Guan<sup>2</sup>, & C. A. Macris<sup>3</sup>, <sup>1</sup>NASA-JSC, 2101 E NASA Pkwy, Houston, TX 77058, jeremy.w.boyce@nasa.gov; <sup>2</sup>California Institute of Technology, 1200 E California Blvd, Pasadena, CA 91125; <sup>3</sup>Indiana University-Purdue University Indianapolis, 723 W. Michigan Street, SL118, Indianapolis, IN 46202.

**Introduction:** The mineral apatite is one of the principle reservoirs of H in rocks from the Earth, Moon, & Mars. Apatite therefore has the potential to provide a record of water abundance or source. However, the ability of apatite to retain any record of water depends in part on the rate at which H is exchanged within apatite. The diffusivity of H in apatite has been the subject of one study [1], wherein H diffusion was found to be faster than previously determined rates for F & Cl in apatite at 1 atm [2]. This led [1] to conclude that H transport was occurring by proton/deuteron ( $H^+$  &  $D^+$ ) diffusion as opposed to hydroxyl ( $OH^-$  &  $OD^-$ ) diffusion, as the latter would be expected to have a diffusivity similar to that of F.

In order to test the proposed mechanism of [1], we can compare diffusion of D & H. If D is observed to diffuse much more slowly than H, then a model where H transport is accomplished by  $H^+$  &  $D^+$  would be favored, as they have very different masses. If not, this would favor a hydroxyl mechanism. It is also possible that both mechanisms operate in apatite, as multiple mechanisms have been proposed for Li diffusion in olivine [3, 4]. Here we report the preliminary results of experiments designed to determine both the rate & mechanism of hydrogen diffusion in apatite.

**Experimental Design:** Polished, oriented 1–1.5mm dia. cubes of apatite were cut from euhedral crystals. Experiments were conducted by loading a cube into a 0.15" OD Pt capsule along with 38–49 mL of  $D_2O$ -enriched water ( $\delta D \sim +5000\%$  VSMOW). Welded capsules were  $\sim 0.33$ " in length & were weighed & then tested for leaks by placing them in a 110°C drying oven for  $\sim 30$  min. Each capsule was placed in a  $\sim 0.4$ " long, pressed NaCl cylinder & positioned at the mid-point of a 0.75" piston cylinder assembly consisting of an outer sleeve of NaCl, a "stepped" graphite furnace ( $\sim 1.70$ " in total length), & inner end pieces of crushable MgO. Temperature was monitored & controlled using a type-D thermocouple and, at the start of each run, temperature & pressure were ramped up along an approximate isochor with a ramp rate of 100°C/min. All experiments were run at 10 kbar & temperatures of 600, 700, or 800°C & were quenched by turning off the power. At the end of a run, the capsule was extracted from the NaCl plug, washed in warm water to remove any remaining salt, dried, & then weighed. Post-run capsules all contained water & were 0.02–0.05% heavier than their pre-run weights.



**Figure 1. D/H ratio as a function of depth for experiment AP32 (800°C, 1.1 hours). Magenta solid line represents best fit diffusion curve, cyan, blue, & green lines represent theoretical curves assuming the diffusion coefficients of [1] & [2].**

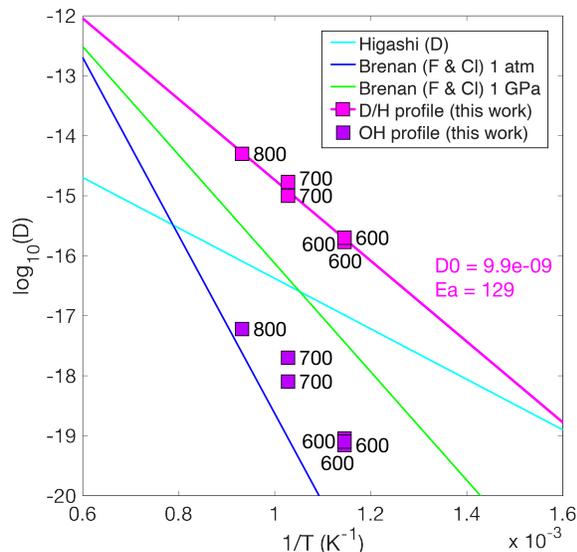
Post-run apatite cubes have no quench crystals and decreased in weight by no more than 0.03%, implying negligible dissolution ( $< 0.02 \mu m$  of surface loss).

Cubes were pressed into indium with the c-axis normal to the plane of the mount, & gold-coated for secondary ion mass spectrometry (SIMS) analysis on the Cameca 7f-GEO using a  $Cs^+$  primary beam. To increase the sputtering rate and reduce possible sample charging, small sizes of beam-rastering (25-50  $\mu m$ ) and field aperture ( $\sim 12 \mu m$  of projection) were used for depth profiling of the samples. Depths of the SIMS pits were measured using a Zscope Zegage optical profilometer with nanometer precision. Diffusion profiles were generated by converting SIMS analysis times to depths assuming a constant sputtering rate. Three replicate profiles were measured for the experiment at 600°C, two for the experiment at 700°C, & one for the experiment at 800°C.

**Results & Discussion:** Depth profiles of D/H define curves that are reasonably well-fit by simple volume diffusion (Figure 1), though there is a consistent misfit downhill from the point of greatest curvature. Regardless, the observed variations in D/H are incon-

sistent with any previously measured diffusivity (blue & green curves in Figure 1).

Depth profiles of  $\text{OH}^-/\text{P}^-$  and  $\text{OD}^-/\text{P}^-$  are an order of magnitude shorter, & only barely resolved at the sputtering rate & integration period used to measure these deep D/H profiles. The shallow  $\text{OH}^-$  and  $\text{OD}^-$  profiles indicate that the diffusive transport is affecting abundances over a shorter length scale than it is isotope ratios. These new data are consistent with multiple mechanisms of diffusive transport, as discussed above.

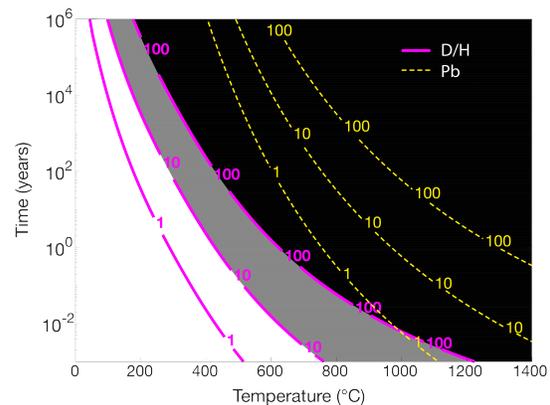


**Figure 2.** Arrhenius diagram with older diffusion data plotted as cyan, blue, & green lines from [1] & [2]. New experiments plotted as magenta & purple squares with best fit lines & corresponding diffusion parameters  $D_0$  &  $E_a$ .

Our data is shown on an Arrhenius diagram (Figure 2), along with curves derived from previous studies. We find that hydrogen isotope exchange is orders of magnitude faster than previous studies (except at very low temperatures outside the study range), but abundances are modified at rates that are intermediate between 1 atm (dry) & 1 GPa (hydrous) experiments of [2]. Given the large uncertainties on the very short profiles of H abundance, we cannot definitively evaluate the extent to which the purple curve in Figure 2 is different from the blue curve of [2]. However, the isotope exchange rate derived from our data is clearly different from any previous work.

**Implications.** We interpret our faster rate as representative of diffusion of protons & deuterons. This is the same assertion made by [1] based on their own data. The two assertions are not obviously compatible. One possibility is that [1] has actually constrained diffusion of  $\text{OH}^-$  (or  $\text{OD}^-$ ). They dismiss this on the basis

that their 1 atm diffusivities are much different than the 1 atm data of [2]. However, the apparent pressure effect observed by [2] implies a negative activation volume (uncommon & poorly justified by theory), & may instead be the effect of the water content of the experiments, as postulated by [2]. That the hydrous 1 atm data of [1] & the hydrous data 1 GPa data of [2] are more similar in the range of 600-800°C is consistent with this hypothesis. But this hypothesis cannot account for our observations of slow transport of OH into apatite (purple). Regardless of mechanism, the D/H of apatite can be modified quite rapidly even at sub-magmatic temperatures.



**Figure 3.** Contours of diffusive length scale ( $\mu\text{m}$ ) for D/H exchange (calculated using parameters from magenta Arrhenius line in Figure 2) & Pb exchange (based on [5]) in apatite for various isothermal holdings. Length scale calculated by dimensional analysis:  $x = \sqrt{Dt}$ .

If boundary conditions change, D/H ratios can be decoupled from hydrogen abundances, as well as other isotope ratios. Figure 3 shows the diffusive length scale for isothermal holding of Pb [5] in yellow & D/H in magenta. Large portions of temperature-time space result in diffusive length scales for D/H that are 100 times longer than those of Pb, scenarios that completely reset hydrogen isotopes without changing Pb ages in large apatite crystals. The model space where Pb & D/H are decoupled includes  $< 1$  m.y. timescales for  $T \geq 225$  °C. This—and a similar relationship between OH content & age—implies that surface processes can modify the relationships between D/H, H abundance, & age, a potential problem for studies such as [6].

**References:** [1] Higashi et al., *Geochem. J.*, 2017, 51:115–122. [2] Brenan, *Chem. Geol.*, 1993, 110:195–210. [3] Dohmen et al., *GCA*, 2010, 74:274–292. [4] Richter et al., *GCA*, 2017, 219(Supplement C):124–142. [5] Cherniak, et al., *GCA*, 1991, 55:1663–1673. [6] Sarafian, et al., *Science*, 2014, 346:623–626.