# Towards a resolution of the timing of Martian magmatism: Diffusion study of Hf in clinopyroxene and geochronological implications

#### E. BLOCH AND J. GANGULY\*

Dept. of Geoscience, Univ. of Arizona, Tucson, AZ, 85721, USA (\*correspondence: ganguly@email.arizona.edu)

The igneous crystallization age of the Shergottite suite of Martian meteorites has been a subject of considerable debate. While <sup>147</sup>Sm-<sup>143</sup>Nd and <sup>176</sup>Lu-<sup>176</sup>Hf mineral isochrons yield relatively young ages of ~150-225 Ma, <sup>206</sup>Pb-<sup>207</sup>Pb ages from the same samples exceed 4.0 Ga. It has been proposed that the <sup>206</sup>Pb-<sup>207</sup>Pb dates reflect the true crystallization age of the Shergottites and that the <sup>147</sup>Sm-<sup>143</sup>Nd and <sup>176</sup>Lu-<sup>176</sup>Hf "isochrons" represent either a mixing line with phosphate-hosted material or reflect the effect of thermal resetting at ~200 Ma [1,2]. Alternatively, it has been argued that the <sup>206</sup>Pb-<sup>207</sup>Pb array is simply a mixing line arising from contamination by modern terrestrial Pb [3].

Lapen et al. [4] argued against the "mixing hypothesis" for younger Lu-Hf age on the basis of lack of correlation between  $\epsilon$ (Hf) and 1/[Hf] of the samples defining Lu-Hf "isochron". In order to test the alternative hypothesis of thermal resetting via diffusion of Hf, we have determined the diffusion kinetic properties of Hf4+ in clinopyroxene, which is the primary host mineral of Hf. To evaluate thermal resetting due to a shock event, we assume a maximum estimate of post-shock temperature of ~1000°C. Using the average clinopyroxene radius (r) in the Shergottite RBT-04262 (0.5 mm), our diffusion data yield ~210 kyr as the time required for diffusive re-equilibration of Hf isotopes, which precludes resetting within a shock-heated and -ejected material. We have also addressed the problem of extended heating during a nonejection impact event (or other thermal perturbation) by measuring and modeling Cr diffusion profiles in olivine in RBT-04262. Using Cr diffusion from [6], we obtain a time scale of ~1 year at the peak temperature of 1150 °C [7]. This leads to a vlue of  $Dt/r^2$  of  $\sim 3x10^{-5}$  for Hf in clinopryoxene, which precludes any significant diffusive resetting of Lu-Hf chronometer for the sample [8].

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Stöffler *et al.* (1991) *GCA* **55**, 3845-3867. [6] Ito and Ganguly {2006) *GCA* **70**, 709-809 [7] Mikouchi *et al.* (2008) LPSC XXXIX [8] Crank (1975) Mathematics of Diffusion

# What defines a saline aquifer for CO<sub>2</sub> injection?

## MADALYN S. BLONDES\* AND MARGO D. CORUM

### U.S. Geological Survey, 12201 Sunrise Valley Dr., Reston, VA 20192, USA (\*correspondence: mblondes@usgs.gov, mcorum@usgs.gov)

The U.S. Geological Survey is currently assessing potential CO<sub>2</sub> subsurface storage formations in the United States. The U.S. Environmental Protection Agency requires that any U.S. CO<sub>2</sub> sequestration assessment or project avoid subsurface formations containing potential drinking water. The Underground Injection Control Program (UIC) for Class VI (CO<sub>2</sub> storage) wells protects fresh water, defined as water with a total dissolved solids (TDS) concentration < 10,000mg/L. However, the UIC does not define how the limit must be interpreted statisically or spatially to determine potential storage formations. For example, if one analysis has a TDS concentration > 10,000 mg/L, is the entire formation considered a saline aquifer? Could a saline water analysis from a previous injection well in the same reservoir then be cited as evidence of a saline formation available for CO<sub>2</sub> injection? Other possibilities include using a median or mean within uncertainty for a water chemistry dataset. Though sitespecific hydrogeological studies would be required before injection to predict CO<sub>2</sub> migration to aquifers, the concern is whether fresh water aquifers could be defined as saline based on existing subsurace water quality data.

For example, the Mesaverde Formation in the Southwestern Wyoming Province is a known aquifer with fresh water near the surface and saline water at depth. Using multiple water quality databases that cover the Rocky Mountain region, we find n = 789 independent analyses with non-null reported TDS concentrations between 72 and 249,838 mg/L at depths > 1 km. Whereas the mean TDS concentration is "saline" (13,240 ± 17,191 (1 $\sigma$ ) mg/L), the median concentration is "fresh" (9,482 mg/L).

Since the scale of a sequestration project is not across an entire basin, we can also provide a spatial definition of salinity. If we see a region with suitably saline data, how far from those wells can we assume the formation is saline? Though this is a complex hydrogeologic problem, our interest is simply to define whether a potential storage region is "saline" or "fresh." Using 1-D Darcy flow (neglecting convection and dispersion) for a range of applicable reservoir properties and time-scales, we model length scales of saline water flux. These results then define the radial distance from a saline data region that could be considered saline at the time-scales relevant to long-term  $CO_2$  storage.

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