On the application of jarosite and hematite thermochronology to assess aqueous environments on Mars

J. KULA* AND S.L. BALDWIN

Department of Earth Sciences, Syracuse University, Syracuse, NY 13244, USA (*correspondence: jkula@syr.edu)

Hematite and jarosite, identified in the Burns Formation by the Opportunity Mars Exploration Rover (MER), have been interpreted as *in situ* evidence for past aqueous conditions on the Martian surface. Hematite has been demonstrated as a useful (U-Th)/He chronometer, although it is not a commonly analyzed mineral. Likewise, jarosite has been used as a $^{40}Ar/^{39}Ar$ chronometer, although prior to this study, argon diffusion kinetics in jarosite were unknown. Using long-duration, low-temperature, furnace step heating, jarosite argon diffusion parameters (E, log D_o/a^2) have been determined. Incremental fractional loss measurements from three size fractions (75-125, 125-150, 150-200 μm) yield an average activation energy (E) of 38.80 ± 1.58 kcal/mol and a log D_o/a^2 of 6.09 ± 0.67 s^{-1} corresponding to a closure temperature (cooling rate 100°C/Ma) of 146 ± 30°C. Using published morphologic constraints and He diffusion kinetics on hematite spherules, and newly determined argon diffusion parameters for jarosite, we use the forward modeling program DECOMP to assess if these minerals will retain original (U-Th)/He and $^{40}Ar/^{39}Ar$ ages during long residence times (4.0 Ga) at Martian surface conditions (22°, 0°C). Model results indicate that for hematite spherules ($\geq$1.0 mm in diameter), (U-Th)/He ages will record the timing of formation within analytical certainty. Jarosite (75-200 μm in diameter) is also expected to retain radiogenic ^{40}Ar, with predicted ages falling within 0.5% of the true age. We infer that in the absence of post-crystallization diffusive He or $^{40}Ar^*$ loss, (U-Th)/He and $^{40}Ar/^{39}Ar$ ages measured from Martian hematite spherules and jarosite respectively, can be used to constrain the time since water was present on Mars. Application of model results to the 'wetting-upwards' Burns Formation at Meridiani Planum, indicates that post depositional hematite from the lower eolian dune subunit would provide a minimum age of deposition, while possibly syndepositional hematite from the upper interdune/playa unit may yield the age of the unit. Jarosite ages throughout the section should record a downward migrating aridification front as the water table retreated. A vertical profile of hematite and jarosite ages may constrain the timing and rates of the transition from wet to dry conditions at Meridiani Planum. Application of hematite and jarosite thermochronology to samples returned from Mars may be key to determining if water was available for sufficient durations required for the development of life.

Rhine River: First case of anthropogenic lanthanum as a dissolved microcontaminant in the hydrosphere

SERKAN KULAKSIZ* AND MICHAEL BAU

Jacobs University Bremen, Earth and Space Sciences, Campus Ring 8, 28759, Bremen (*correspondence: s.kulaksiz@jacobs-university.de)

The rare earth elements (REE) are a group of elements that behave coherently in natural systems, usually plotted with concentrations normalized to a known reference (e.g. shale). This style of representation makes the presence of anomalies easier to distinguish.

The first report of anthropogenic contamination of the natural REE distribution in river water appeared in the mid-1990s (Bau & Dulski, 1996). Gadolinium (Gd) concentrations in the Havel River downstream of the city of Berlin were up to 3 orders of magnitude higher than natural background concentrations. This study also reported on the Rhine River showing a similar excess of Gd concentration. Gadolinium is used in magnetic resonance imaging as a contrast agent, causing positive anthropogenic Gd anomalies in sewage effluent, rivers, estuaries and groundwater via several pathways in its highly-stable form (e.g. Gd-DTPA).

More recently, excess lanthanum (La) was also measured in the River Rhine, up to an order of magnitude higher than background values. The anomaly is introduced into the Rhine River north of the city of Worms at Rhine river-km 447.4. Samples taken a few hundred meters upstream/downstream of an effluent at this location show strong differences in La and light REE concentrations. The effluent itself shows 49 mg/kg La, well-above levels that are ecotoxicologically effective. Excess La is present 400 km downstream at the German-Dutch border where >93% of total La and Gd are of anthropogenic origin.

Since River Rhine water is used for artificial groundwater recharge and bank infiltration, anthropogenic La (and Gd) are both to be expected in tap water of those cities that rely on the Rhine River as a drinking water source. Indeed, several cities along the Rhine River carry positive anthropogenic Gd anomalies (e.g. Leverkusen, Koblenz, Düsseldorf, Duisburg, and Essen) and positive anthropogenic La anomalies (e.g. Leverkusen, Worms, and Kleve).

While several adverse health effects of Lanthanum are known, information on the potential health risks to the ecosystem inhabiting the river is lacking. Further research and monitoring is essential in order to avoid potential negative environmental consequences.