Monitoring beam-induced radiolysis effects on transition metal complexes in hydrothermal fluids

A.J. ANDERSON[1], R.A. MAYANOVIC[2], M.R. FRANK[3] AND S. PASCARELLI[4]

[1]Department of Earth Sciences, St. Francis Xavier University, Antigonish, Nova Scotia, Canada (aanderso@stfx.ca)
[2]Department of Physics, Astronomy & Material Science, Missouri State University, Springfield, Missouri, USA (RobertMayanovic@missouristate.edu)
[3]Department of Geology and Environmental Geosciences, Northern Illinois University, DeKalb, Illinois, USA (mfrank@niu.edu)
[4]European Synchrotron Radiation Facility, Grenoble, France (sakura@esrf.fr)

The irradiation of aqueous solutions with high brilliance synchrotron x-rays causes the decomposition of water molecules and the formation of transient species such as $H^{\bullet}$, $^{\bullet}OH$, H^{+}, OH^{-} and hydrated electrons, e_{aq}^{-}. These radiolysis products may react rapidly with solutes to modify aqueous speciation. In order to study the effects of beam-induced radiolysis on transition metal-bearing hydrothermal fluids, the structure of Cu and Fe chlorocomplexes was monitored using time-resolved x-ray absorption spectra.

XANES data were obtained at beamline ID-20-C at the Advanced Photon Source, Argonne National Laboratory, from synthetic fluid inclusions of known composition, and from solutions in hydrothermal diamond anvil cells (HDAC) up to 600 ºC. *In situ* energy-dispersive x-ray absorption spectroscopic (ED-XAS) measurements were also made on Fe^{2+} chloride solutions at beam line ID24 at the European Synchrotron Radiation Facility. The ED-XAS spectra were measured at 100 intervals with 1 s time resolution followed by 30 or 60 intervals with 60 s time resolution. Our results indicate that Fe^{2+} ions are oxidized or reduced, depending upon the pressure – temperature conditions of the aqueous fluid. Extended irradiation at 500 ºC resulted in the formation of Fe and Cu nanoparticles.

A single x-ray absorption spectrum acquired over a period of several minutes using a scanning monochromator may measure beam-induced modifications produced during the scan. Such artefacts of radiolysis may be minimized or eliminated by analyzing hydrothermal fluids in a flow-through system or by using ED-XAS to reduce the exposure time to synchrotron x-rays.

Portable Rb-Sr geochronology

F.S. ANDERSON*, K. NOWICKI AND T. WHITAKER

Southwest Research Institute, 1050 Walnut, Suite 300, Boulder, CO 80302 (anderson@boulder.swri.edu, knowicki@ boulder.swri.edu, whitaker@boulder.swri.edu)

We have produced a preliminary, low precision, 12-point Rubidium-Strontium (Rb-Sr) geochronology measurement of the Boulder Creek Granite using a laser desorption resonance ionization mass spectrometer (LDRIMS) capable of being miniaturized into a portable unit. Our current prototype can measure the isotope ratio of lab standards with 10 ppm net Sr or Rb to a precision of ±0.1% (1σ), with a sensitivity of $1{:}10^{10}$ in <15 minutes/point. Using the 1) known Rb-Sr ratios and modal mineralogy from Martian and lunar samples, and 2) LDRIMS precision & accuracy, we have numerically modeled the age error for 100-1000 points and determined that uncertainties <±50 Ma are possible [1]. The ability to make in-situ lunar and Martian radiometric measurements with uncertainties <±50 Ma would significantly improve geologic interpretation of these complex surfaces and potentially constrain impactor flux throughout the solar system.

Preliminary results from the Elephant Butte Boulder Creek Granite (BCG_EB) are compared with TIMS Rb-Sr dates of 1700±40 m.y. from 19 whole rock samples [2]. With careful choice of the statistical binning technique, an identifiable isochron, with an MSWD of 2, can be produced (Fig. 1). The age error of ±870 m.y. is consistent with our analytical models for 12 measurements at ±0.4% precision. If expanded to 100-1000 measurements, our statistical models show that this will improve to <50-100 m.y. values [1]. We have also identified and corrected a resonance effect causing the ~15% fractionation offset of $^{87}Sr/^{86}Sr$ observed in Fig. 1.

Ongoing work will improve precision, increase the number of spot measurements, and produce a portable demonstration instrument.

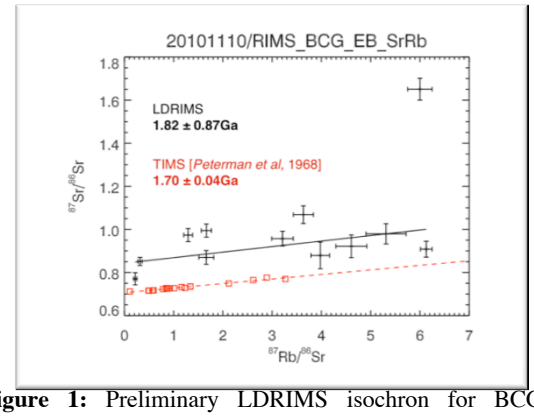

Figure 1: Preliminary LDRIMS isochron for BCG_EB (MSWD 2) is consistent with TIMS results. The age error can be reduced further by making hundreds to thousands of measurements.

[1] *Anderson and Nowicki*, LPSC, abs# 1979, 2010. [2] *Peterman et al*, JGR, 73, 2277, 1968.