

Sr isotope ratios determination by LA-MC-ICPMS in Rb rich samples: Online separation of Rb by electrothermal aerosol heating

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Rb/Sr geochronology using LA-ICPMS has successfully been demonstrated for solid samples where the Rb/Sr concentration ratio is lower than 0.02 [1] and 0.14 [2]. For samples with higher Rb content, the determination of Sr isotope ratios remains challenging because mathematical correction of the isobaric interference from ^{87}Rb leads to increased uncertainties in the results. Using electrothermal vaporization (ETV)-ICPMS, a method has been conceived by Rowland *et al.* [3] in order to selectively pre-vaporize Rb from a reference potassium feldspar sample (NIST SRM607) making the measurement of Sr isotope ratios possible for samples where the Rb/Sr ratio can be as high as 8.

In an earlier study we could demonstrate that heating laser generated aerosols from a silicate glass reference material (NIST SRM610, Rb/Sr ~ 1) with a commercially available ETV unit (Perkin Elmer, HGA 600MS) to about 2000 °C, enables the reduction of the signal intensity of Rb by 99%, while the signal intensities for Sr remain practically unaffected [4]. The approach has now been used for Sr isotope ratios measurements in NIST SRM 610 (Rb/Sr = 1), USGS BCR2G (Rb/Sr = 0.14) and $\text{Li}_2\text{B}_4\text{O}_7$ fused disks of NIST SRM607 (Rb/Sr = 8) using multicollector ICPMS coupled to the LA-ETV setup. The combination of electrothermal vaporization for interferences suppression and laser ablation for spatially resolved sampling of solids is expected to broaden the range of applications for Rb/Sr –geochronology since both, isotope ratios and elemental concentrations, can principally be determined under highly similar conditions when using either sequential LA-ICPMS approaches or a split-flow prior to ETV configuration with MC-ICPMS and single collector ICPMS operating in parallel [5].

- [1] Ramos *et al.* (2004) *Chem. Geol.* **211**, 135-158.
[2] Jackson *et al.* (2006) *Earth Planet. SC Lett.* **245**, 260-277.
[3] Rowlan *et al.* (2008) *J. Anal. Atom. Spectrom.* **23**, 167-172.
[4] Brogioli *et al.* (2011) *Anal. Bioanal. Chem.* **399**, 2201-2209, [5] Yuan *et al.* (2008) *Chem. Geol.* **247**, 100-118.

Bioreduction of biotite and chlorite: Effects on mineral reactivity

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Interactions with mineral phases can dictate the mobility of contaminants in the subsurface. Electron transfer processes in particular have the potential to reduce redox-sensitive metals (including radionuclides) so as to form much less soluble and less mobile phases. This work concerns investigating the role that microorganisms can play in such electron-transfer processes, examining interactions involving two key phyllosilicates found in the sub-surface.

Biotite and chlorite are sheet silicate minerals containing both ferric and ferrous iron in their octahedral layers. The redox reactivity of these minerals when fresh, and after undergoing bioreduction, was studied. The model Fe(III)-reducing microorganism *Shewanella oneidensis* MR-1 was used in anaerobic batch experiments where reduction of structural iron was stimulated by addition of an electron donor. The bioreduced mineral was collected and washed before use in redox reactivity experiments.

Ferrous iron assays using the ferrozine method show that *S. oneidensis* MR-1 is able to reduce the bioavailable Fe(III) in both minerals, both in the presence and absence of an artificial electron shuttle and humic analogue (AQDS). Chromate (Cr(VI)) was used as a redox probe to explore mineral reactivity. Unaltered biotite and chlorite reduced up to $\sim 15\%$ of 1mM Cr(VI), compared to 82.8% for the bioreduced biotite, and 91.6% for the bioreduced chlorite. This demonstrates the importance of bioreduction in metal cycling, with the mineral surfaces conditioned to reduce the metals in solution. The amount of reduction suggests that the processes involve more than just the available Fe(II) surface atoms. Surface analysis (XPS) combined with XAS are being used to determine the biologically induced mineralogical changes that are driving the reduction process.

The work is being extended to radionuclides, and the reduction of technetium (^{99}Tc). It is anticipated that the amount of reduction will be similar to that of Cr(VI) as Tc reduction is also a three-electron transformation (Tc(VII) to Tc(IV)).