

Isotopic evidence of possible Cr(III) oxidation in an early contaminated site from NE Italy

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Trivalent chromium [Cr (III)] is an essential human and animal nutrient at the proper amount of ingestion; hexavalent chromium [Cr (VI)] is toxic and causes a wide range of health effects. Under the redox and pH conditions usually found in nature, Cr (VI) has the tendency to be reduced to Cr (III), e.g. in the presence of aqueous Fe (II), and is scavenged from solution by adsorption, in particular onto clay mineral surfaces. Only few oxidants are present in natural systems which can oxidize Cr (III) to Cr (VI). It has been demonstrated that Cr isotopes fractionate during the Cr (VI) to Cr (III) conversion under reducing conditions [1]. In the present study, preliminary $\delta^{53}\text{Cr}$ data were obtained on groundwaters draining a phreatic aquifer in the High Friuli Plain (NE Italy), an area which underwent extensive Cr (VI) contamination from manufacturing during 1985, creating a plume of Cr (VI)-contaminated groundwaters. Later, the industrial activity was made environmentally protective and a natural reduction of contamination occurred over the years. Recently, new spikes in the Cr (VI) content, reaching 1600 $\mu\text{g/L}$, have been observed in a number of wells, with concentration generally decreasing downgradient from the original site of contamination. The measured $\delta^{53}\text{Cr}$ on the Cr (VI) contaminated waters ranges between -0.50 and -2.96. These data are tentatively interpreted, within a Rayleigh distillation model, as possible evidence of the oxidation of the trivalent chromium originated by reduction of the anthropogenic Cr (VI), released during the '80s, which accumulated onto alluvial sediments.

[1] Berna *et al.* (2010) *Environ. Sci. Technol.* **44**, 1043-1048

LA-(MC-)ICP-MS element and isotope ratio analysis of fluid inclusions in minerals

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Element concentration and isotope ratio data for individual fluid inclusions revolutionize our understanding of fluid-mediated element transfer and enrichments in geologic systems down to subarc depths. Here, we focus on LA-ICP-MS analytical strategies and progress.

Average fluid solute concentrations can be determined down to 0.0X $\mu\text{g/g}$ for a given fluid inclusion assemblage. Uncertainties can be as good as $\pm 5\%$ 1 SD, while counting statistics uncertainties raise to $\pm X0\%$ 1 SD for elements nearing their LOD. Accuracy is limited by internal standardization for quantification and, for metals heavily enriched in micronuggets, by representative recording of short transient signals. A jump routine in which the metal of interest is recorded every other time in a sweep (recording cycle) mitigates the latter problem [1] as will be illustrated by simple modeling. But quadrupole instruments measure strictly with increasing mass in a sweep, even if at least one instrument suggests the opposite; thus rendering it impossible so far to benefit from using the jump routine.

Precise and accurate isotope ratio measurements for Pb and Sr on an individual inclusion are possible using LA-MC-ICP-MS and within-run mass bias correction. Limitations are the small dynamic range of detectors and uncertainties in faraday - multiplier cross-calibration, and settling time issues for faraday amplifiers. The latter require either complete, controlled ablation of the entire inclusion and bulk signal integration, or implementation of Tau correction schemes, which we have adapted for fast transient signal analysis. Inclusion-to-inclusion accuracy can be as good as $\pm 0.8\%$ (± 1 SD) for $^{208}\text{Pb}/^{206}\text{Pb}$ for as little as 0.01 ng Pb present in an individual inclusion. Ratios normalized to ^{204}Pb are less precise due to limitations in ^{202}Hg and ^{204}Hg (Pb) recording using Faraday detectors.

The analysis of Sr isotope ratios is currently explored using synthetic fluid inclusions with known Sr isotope and Rb/Sr ratios. Proper interference correction (Kr, Ca-argides, ^{87}Rb) is essential and shows that the limiting parameter for accuracy is a high Rb/Sr ratio in the fluid, thus suggesting that potential applications of the Sr isotope tracing approach may be limited to fluids with low Rb/Sr ratios.

[1] Pettke T. (2008), *MAC SC* **V40**, 189-218