

Quadruple sulfur isotope determination by SIMS: Limitations, progress and prospects

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The discovery of mass independent fractionation effects in sulfur isotopes leading to what is commonly referred to as “anomalous” or “MIF” sulfur has revolutionised our understanding of the evolution and interaction of sulfur reservoirs. Of the four naturally occurring sulfur isotopes, variations in the abundance of ^{33}S and ^{36}S may be produced by upper atmosphere photo-catalysed reactions acting on SO_2 . The distinctive and irreversible signatures preserved in sulfides or sulfates in the geological record are key to understanding the evolution of Earth’s atmosphere [1], and provide important tracers in geobiological [2] and ore-forming processes [3]. Recent studies have also investigated ^{36}S abundance as a potential tracer of the MIF process [4].

Among the various methods available to measure sulfur isotopes, secondary ion mass spectrometry (SIMS) combines high-spatial and -volume resolution with a precision adequate for many studies, as well as the ability to efficiently analyse a large number of *in situ* targets. To date, SIMS studies have been limited to the three most abundant isotopes, ^{32}S , ^{33}S and ^{34}S , all of which may be measured simultaneously using Faraday cups (FC’s) with typical precision on $\delta^{33}\text{S}$ (and $\Delta^{33}\text{S}$) and $\delta^{34}\text{S}$ of $<0.2\text{‰}$ (1σ). The low abundance of ^{36}S (ca. 0.02%) however presents a significant analytical challenge to SIMS. Under typical analytical conditions used for triple-sulfur isotope analysis, a ca. 10^9 cps ^{32}S will be accompanied by only 2×10^5 cps ^{36}S which is too low to yield acceptable precision using FC’s. Furthermore, the ~ 5 - 10 -fold signal increase needed to reach such precision can only be achieved with a considerable loss of spatial resolution. An alternative approach is to measure ^{36}S in a pulse-counting electron multiplier (EM) but the small Hamamatsu EM’s on the IMS1270/80 experience significant gain drift at high count rates. Nonetheless, with appropriate within and between run drift correction, usable internal precision on $\Delta^{36}\text{S}$ of $\sim 0.5\text{‰}$ (1σ) can be achieved with spatial resolution $<10 \mu\text{m}$, as will be demonstrated with case studies from both early- and late-Archean sulfides. Lower noise FC amplifiers or substitution of a more robust EM can eventually improve precision.

[1] Farquhar & Wing (2003) *EPSL* **213**, 1-13. [2] Kamber & Whitehouse (2007) *Geobiology* **5**, 5-17. [3] Bekker *et al* (2009) *Science* **326**, 1086-1089. [4] Shen *et al.* (2009) *EPSL* **279**, 383-391

Geomicrobiology of hyperalkaline Cr(VI) contaminated land

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Chromium in the form of its carcinogenic anion, chromate, has been entering the soils beneath a chromite ore processing residue (COPR) disposal site in the north of England for over 100 years, as a hyper alkaline (pH 13.5) liquor. This study reports the findings of a multi-disciplinary investigation into the biogeochemical processes occurring within the subsurface that influence contaminant fate.

The soil immediately beneath the waste was found to have a pH of 11→12.5, and contain 0.3→0.5% w/w chromium, and 45→75% of the microbially available iron is Fe(II). The soil pH and Cr concentrations were found to decrease with distance from the waste. XAS and (S)TEM analysis indicated that Cr is present throughout the soils as a mixed Cr(III)-Fe(III) oxy-hydroxide phase, resistant to air oxidation. This suggests that the elevated soil Cr content is due to reductive precipitation of Cr(VI) by Fe(II), producing a stable long term host for Cr(III). 16s rRNA community analysis of the soil immediately beneath the waste found a microbial population dominated by *Proteobacteria*, *Firmicutes* and *Bacteroidetes* species. Addition of this soil to alkaline Fe(III) containing growth media (pH=9.2) produced a consortium of iron reducing microorganisms dominated by the *Firmicutes* species, particularly *Anaerobranca*, *Anaerovirgula* and *Tissierella*.

Microcosm experiments demonstrated the capacity of COPR affected soil to abiotically remove all Cr(VI) from COPR leachate within 40 days. Amendment of the pH (\sim pH 9) resulted in the development of a cascade of microbially mediated terminal electron accepting processes, reaching Fe(III) reduction after complete Cr(VI) removal. A *Firmicutes* dominated population (73%) was identified in the pH amended microcosm systems during Fe(III) reduction, with *Dethiobacter sp* dominant, but *Anaerobranca sp* also present.

This work suggests that abiotic reductive precipitation of Cr(VI) by microbially produced Fe(II) can be effective at preventing the spread of chromium from COPR waste sites.