

## Biological cycling of sulphate in small mountain lakes determined from natural $^{35}\text{S}$

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The biological cycling of sulphate in watersheds is an important issue and will more so with a possible switch to the use of more coal and oil shale. One approach to studying this problem is the use of naturally-occurring  $^{35}\text{S}$ , produced by cosmic-ray spallation of argon in the atmosphere. In this study,  $^{35}\text{S}$  is used to investigate the cycling of sulphate in two small lakes in the Flattops Wilderness Area, Colorado. The two lakes are Ned Wilson Lake and Upper Ned Wilson Lake, with areas of about 10000 m<sup>2</sup> and 2500 m<sup>2</sup> respectively. The main source of water for these lakes is snow melt and there is no observable surface flow into or out of them in the summer. During the summer of 1995 and 1996, concentrations of snow-melt derived  $^{35}\text{S}$  decreased much more rapidly than can be accounted for by decay alone. The drop in  $^{35}\text{S}$  concentrations can not be explained by changes in sulphate concentrations and there was no accompanying change in sulphate stable isotope ratios. Influx of "dead" sulphate from groundwater is ruled out by other chemical data. The most likely cause for  $^{35}\text{S}$  concentrations to decrease faster than decay is biological exchange with the biota in the lake. Sulphate containing  $^{35}\text{S}$  is incorporated into the biota and sulphate containing non-radioactive sulphate is returned to the system, with little or no net change in sulphate concentration. This process entails no fractionation. Using the specific concentrations of  $^{35}\text{S}$  ( $^{35}\text{S}/\text{SO}_4$ ) we were able to estimate biological exchange rates from 2-10 microgms/L per day with the higher rates being found in Upper Ned Wilson Lake each year.

## The stability of Zr in F-bearing hydrothermal solutions

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Although zirconium is widely believed to be one of the most immobile of elements during the interaction of rocks with crustal fluids, this view has been challenged by discoveries of hydrothermally altered zircon [1] and zircon containing fluid inclusions [2]. However, there is no reliable information on the behaviour of zirconium in crustal fluids, i.e., its speciation, and therefore no basis for evaluating these observations in the context of zircon solubility. Information on the stability of zirconium species in hydrothermal solutions is limited to a single theoretical extrapolation of low-temperature data [3] that predicts insignificant stability of fluoride complexes of zirconium at  $T > 100^\circ\text{C}$ . The goal of our study was therefore to check this prediction and to derive experimentally determined stability constants for fluoride complexes of zirconium at temperatures up to  $250^\circ\text{C}$ . Our experiments investigated the solubility of synthetic  $\text{ZrO}_2$  in HF-bearing solutions. The experimental method is identical to that reported by us for determining the stability of REE fluoride species [4]. Experiments involved equilibrating solid  $\text{ZrO}_2$  with solutions containing a range of HF concentrations. After equilibrium was attained, the autoclaves were quenched,  $\text{ZrO}_2$  was removed, and any Zr precipitated was dissolved by adding hydrofluoric acid to the experimental solutions. The concentrations of Zr and F in the solutions were analysed using NAA. The preliminary data obtained in this study are in extraordinary disagreement with the earlier theoretical study [4] and suggest that Zr fluoride species are many orders of magnitude more stable than predicted. For example, whereas the recommended value of the logarithm of the formation constant for  $\text{ZrF}_2^{2+}$  at  $200^\circ\text{C}$  is 4.44 [3], the corresponding preliminary value derived in our study is 21.6. Indeed, the latter value is actually much closer to values reported for low temperatures (e.g., 16.93 at  $60^\circ\text{C}$  [5]). The very high preliminary information constants obtained for zirconium fluoride species in this study help explain reports of zirconium mobility in natural systems.

[1] Schaltegger (2007) *Elements*, **3**, 51,79 [2] Dubinska *et al.* (2004) *Chem. Geol.*, **203**, 183-203 [3] Aja *et al.* (1995) *Appl. Geochem.*, **10**, 603-20 [4] Migdisov and Williams-Jones (2007) *Geochim. Cosmochim. Acta*, **71**, 3056-69 [5] Hammer (1979) ENICO-1004.