Experimental investigation of K incorporation into tourmaline at high temperature and pressure

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Tourmaline's extensive stability in pressure-temperature space and ability to incorporate a multitude of elements in its structure have motivated investigation into its potential as a recorder of its formation conditions, especially in terms of temperature and composition [1]. However, the discovery of microdiamond-bearing K-dominant dravitic tourmaline, with up to 0.576 apfu K (2.76 wt.% K_2O), in the Kokchetav Massif, Kazakhstan, [2] has increased interest in the relationship between formation pressure and tourmaline's composition, particularly with respect to the incorporation of K. Indeed, a comparison of tourmaline's composition with its inclusion mineralogy has revealed a correlation between K incorporation and increasing pressure [3]. However, whether or not the presence of microdiamond inclusions is sufficient evidence for high pressure formation of K-dominant tourmaline has been questioned [4].

A series of piston-cylinder and hydrothermal synthesis experiments was conducted to begin addressing the absence of experimental data on K-bearing tourmaline and to investigate the effect of pressure and fluid composition on the Na/K ratio of hydrothermal dravitic tourmaline ($NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_3OH$). Approximate unit cell dimensions were determined by Rietveld refinement of X-ray diffraction patterns and chemical formulae were calculated from electron microprobe analyses. To date, the highest pressure and temperature conditions investigated (40 kbar, 700°C) have yielded dravitic tourmaline with up to 0.7 apfu K when exposed to a pure KCl fluid. This is the first time Na-absent "potassium dravite" has been synthesized experimentally.

[1] van Hinsberg *et al*. (2011) *The Canadian Mineralogist* **49**, 1-16. [2] Shimizu & Ogasawara (2005) *ÖMG* **150**, 141. [3] Shimizu &Ogasawara (2013) *Journal of Asian Earth Sciences* **63**, 39-55. [4] Marschall *et al*. (2009) *Journal of the Geological Society, London* **166**, 811-823.

Deconstructing the dissimilatory sulfate reduction pathway: Isotope fractionation of a mutant unable to grow on sulfate

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Dissimilatory sulfate reduction plays a significant role in shaping the sulfur isotope composition of sedimentary sulfides, which are, in turn, a record of Earth's surface redox history. The fractionation produced by this microbial metabolism is controlled by the flux of sulfur through the respiratory reaction network and the isotopic effect associated with each reaction. Although the net isotope fractionations of this metabolism have been well studied, unravelling the isotopic influence of each component of its pathway is still a challenge. The sulfite to sulfide reduction step is a particularly complicated one. Its full biochemistry is not fully understood and the associated isotope effect is inferred from fractionations associated with the entire metabolic pathway. Here, we investigated a mutant strain of *Desulfovibrio vulgaris* Hildenborough in batch and continous culture to address these issues. This deletion mutant is missing its QmoABC complex, a principal enzyme in the reduction of adenosine phosphosulfate (APS) to sulfite. Thus, this strain is incapable of using sulfate as a terminal electron acceptor. By hindering APS reduction, this mutation also eliminates sulfite disproportionation. In all experiments, lactate and sulfite consumption are concomitant with sulfide and thiosulfate production. Rates of thiosulfate production were one order of magnitude larger in batch than continuous culture experiments. Results from batch culture show a $\delta^{34}S$ between sulfite and sulfide of ≈ -9 ‰. The two components of the thiosulfate pool (sulfonate and sulfane moieties) present a large $^{34}S/^{32}S$ fractionation, with sulfonate more ^{34}S enriched than sulfane by 30 ‰. However, the net fractionation between thiosulfate and sulfite is ≈ +1 ‰. This is inconsistent with isotopic observations of abiotic thiosulfate formation. Steady-state models are presented to understand the mechanism of fractionation during sulfite reduction and incorporate this step into the overall metabolism of sulfate reduction.

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