Tracing the source of oxygen during pyrite oxidation with $\Delta^{17}O_{SO4}$

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We show how the three isotopes of oxygen ($\Delta^{17}O=\delta^{17}O-0.528*\delta^{18}O$) can be used to trace the sources of oxygen in sulfate produced during sulfide oxidation, an important biogeochemical process on Earth's surface and possibly also on Mars [1].

$\delta^{18}O_{SO4}$ signatures are determined both by the $\delta^{18}O$ value of the reactants (O_2 vs. H_2O), and by the isotopic fractionation factors associated with the reaction mechanisms. Two studies [2, 3] have recently attempted to use $\delta^{18}O_{SO4}$ values to quantify the different oxygen contributions to sulfate. When tracing oxidation using $^{18}O/^{16}O$ alone, the relative contributions of fractionation mechanisms and reactant $\delta^{18}O$ values are difficult to deconvolve; a two-isotope approach is not sufficient to identify sources of oxygen uniquely in this process.

We are investigating the use of $\Delta^{17}O$ as a quantitative and qualitative tracer for processes and oxygen sources involved in sulfate production. We conducted controlled abiotic and biotic (*A. ferrooxidans*) laboratory experiments, in which the use of water spiked to obtain an extreme $\Delta^{17}O$ value has allowed us to clearly distinguish and quantify the processes and sources of sulfate-oxygen.

Results show that during the initial phase of microbial pyrite oxidation, 80-90% of the oxygen derives from air. After the microbes' exponential growth stage, $\Delta^{17}O_{SO4}$ values indicate a switch to water as the dominant source of oxygen (>95%). A biotic fractionation factor $\varepsilon^{18}O_{(SO4-H2O)}$ of +9.86‰ is deduced, and extrapolation of the biotic $\varepsilon^{18}O_{(SO4-O2)}$ value gives a span of –28.64 to –34.44‰. An abiotic $\varepsilon^{18}O_{(SO4-H2O)}$ value of +8.75‰ is inferred from a S-oxidation experiment with 100% air-oxygen followed by precipitation as $BaSO_4$ in spiked water.

$\Delta^{17}O_{SO4}$ signatures specify the source of oxygen, and possibly reveal biotic processes. Our results hold promise for using $\Delta^{17}O$ as a tracer in natural as well as experimental systems.

[1] Brunner & Coleman (2005) *LPSC* **XXXVI**, abstr. 1932. [2] Balci *et al.* (2007) *GCA* **71**, 3796-3811. [3] Pisapia *et al.* (2007) *GCA* **71**, 2474-2490.

The El Salvador Cu Deposit, Chile: Insight from a decade of Re-Os data

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Sulfide samples from the El Salvador Cu porphyry deposit, Indio Muerto area, Chile, have been analyzed over the past decade using improving Re-Os techniques. New molybdenite ages suggest a slightly older bias to the early ages, due to issues with either the Os spike or Os standard, or more likely sample-spike isotopic equilibration using alkaline fusion. Nonetheless, the entire data suite suggests formation of a major Cu deposit over a short time period of ~0.5 m.y.

Molybdenite sample DD-1140-20 is used to compare the accuracy and reproduciblity of incrementally improved Re-Os procedures. As previously reported [1], an age of 42.2 ± 0.2 Ma was determined using single ^{185}Re and ^{190}Os spikes with alkaline fusion equilibration. Subsequent new separate replicates using single ^{185}Re and ^{190}Os spikes and an *aqua regia*-Carius tube digestion resulted in ages of 41.2 ± 0.2 and 41.3 ± 0.2 Ma. Given the disparity in ages, two more new separate replicates utilizing mixed ^{185}Re-^{188}Os-^{190}Os spike and *aqua regia*-Carius tube digestion gave 41.2 ± 0.2 and 41.3 ± 0.3 Ma, confirming the prior *aqua regia* digestions. Additional samples from the deposit also fell within the range of 41.6 to 41.0 Ma, verifying the Carius tube results.

The disparity between Re-Os ages obtained by alkaline fusion digestion in an open Zr crucible and *aqua regia* digestion in a sealed Carius tube is likely attributable to incomplete spike-sample isotopic equilibration, spike loss by evaportaion during alkaline fusion, or spike calibrations. Alternatively, the difficulty in producing and quantifying an Os standard may also play a role as the single ^{190}Os spike was calibrated against the so called "B-Standard" whereas the mixed spike was calibrated against a new standard (subseqently used to characterize the Henderson molybdenite Reference Material [2]). Furthermore, Re-Os data from early alkaline fusion analyses of molybdenite sample DD-1104-14 suggested spike loss from evaporation or spike-sample disequilibration when two replicates resulted in ages of 42.0 ± 0.2 and 41.4 ± 0.2 Ma.

[1] Watanabe *et al.* (1999) *GSA Abstracts with Programs* **31/7**, A-30. [2] Markey *et al.* (2007) *Chem. Geol.* **244**, 74-87.