Tracing the source of oxygen during pyrite oxidation with $\Delta^{17}O_{SO_4}$

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We show how the three isotopes of oxygen ($\Delta^{17}O = \delta^{17}O - 0.528 \times \delta^{18}O$) 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].

$\Delta^{18}O_{SO_4}$ signatures are determined both by the $\delta^{18}O$ value of the reactants (O$_2$ vs. H$_2$O), and by the isotopic fractionation factors associated with the reaction mechanisms. Two studies [2, 3] have recently attempted to use $\delta^{18}O_{SO_4}$ values to quantitatively determine 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, $\Delta^{17}O_{SO_4}$ values indicate a switch to water as the dominant source of oxygen (>$95\%$). A biotic fractionation factor $\epsilon_{SO_4}^{18}O$ of +9.86‰ is deduced, and extrapolation of the biotic $\epsilon_{SO_4}^{18}O$ value gives a span of ~28.64 to ~34.44‰. An abiotic $\epsilon_{SO_4}^{18}O$ value of +8.75‰ is inferred from a S-oxidation experiment with 100% air-oxygen followed by precipitation as BaSO$_4$ in spiked water.

$\Delta^{17}O_{SO_4}$ 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.


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 reproducibility 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 $^{188}$Os spikes with alkaline fusion equilibration. Subsequent new separate replicates using single $^{185}$Re and $^{188}$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 spikes and aqua regia-Carius tube digestion gave 41.2 ± 0.2 and 41.3 ± 0.3 Ma, confirming the prior aqua regia digests. 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 evaporation during alkaline fusion, or spike calibrations. Alternatively, the difficulty in producing and quantifying an Os standard may also play a role as the single $^{188}$Os spike was calibrated against the so called “B-Standard” whereas the mixed spike was calibrated against a new standard (subsequently 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.