

A new Cenozoic Record of Sulfur Isotopes from Foraminiferal Calcite.

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The sulfur isotope composition of marine sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$) reflects the balance between the weathering and burial fluxes of both evaporite minerals and pyrite, and their isotopic composition. These are the dominant fluxes into and out of the marine sulfur cycle, and thus a change in the seawater $\delta^{34}\text{S}_{\text{SO}_4}$ would reflect a change in the global sulfur cycle. The importance of the sulfur cycle lies in its potential to help elucidate the subsurface remineralization of organic carbon and, indirectly, the oxidation state of Earth's surface environment.

Reconstructions of seawater $\delta^{34}\text{S}_{\text{SO}_4}$ have previously been made using marine barite (limited to the past 130Ma) and discontinuous evaporite deposits. However, carbonate-associated sulfate (CAS), sulfate that has been incorporated into the carbonate lattice, has potential to act as an alternative archive for seawater S-isotope history and can provide information on regional and global variations in the S-cycle over geological time.

We present CAS $\delta^{34}\text{S}_{\text{SO}_4}$ results from single species foraminifera, using a new sulfur isotope analytical technique optimised for mass limited samples [1]. We report an interspecies variability of up to 1‰ in planktonic forams and a large decrease in $\delta^{34}\text{S}_{\text{SO}_4}$ variability upon the choice of shell cleaning. This method also allows us to identify contaminant phases with greater ease than in bulk studies. Our $\delta^{34}\text{S}_{\text{SO}_4}$ record for the Cenozoic, using a species-specific approach, is in agreement with the coeval barite $\delta^{34}\text{S}_{\text{SO}_4}$ record, engendering confidence in CAS as a proxy for $\delta^{34}\text{S}_{\text{SO}_4}$.

[1] Paris *et al.* (2013) *Chemical Geology*, **345**, 50-61.

Past and present impact of mining activity on metal and metalloid contamination in sediments of the Gardon River watershed (France)

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Contamination of river sediments by metal(loid)s originating from mining activity is a worldwide problem. Because the transport of metals associated with sediments can represent more than 90% of the total flow of metals in rivers, identify their sources and evaluate their potential mobility are particularly important.

The purpose of this work was to assess past and present influence of mining activity on metal(loid) enrichment in sediments of a former mining watershed now industrialized and urbanized, the Gardon River watershed (France).

Samples of a sedimentary archive and current sediments of the Gardon River and its tributaries were characterized combining geochemical analyses, zinc isotopic analyses and sequential extractions.

Considering metal(loid) concentrations in sediments upstream from the mining sites and in bottom sediments of the archive, natural background values were proposed. Based on these values, enrichment factors (EF) were calculated. Several tributaries were highly impacted by old mining sites (EF values up to 250 for Pb, 160 for Cd, 60 for Zn, 70 for As and 1850 for Sb) and by industrial activity. These polluted tributaries impacted metal(loid) content of the main stream sediments. EF values increased in Gardon River sediments downstream from old Pb/Zn mines about 3-fold for Pb, Cd and 2-fold for Zn, As and downstream from old Sb mines about 5-fold for Sb. Interelement relationships were used to distinguish the main contaminant sources. Although Zn isotopic signatures differed significantly for mining impacted tributaries ($\delta^{66}\text{Zn} \sim 0.08\text{‰}$) and for industrial impacted tributary ($\delta^{66}\text{Zn} \sim 0.31\text{‰}$), Zn isotopic composition remained homogeneous in the main stream sediments of the Gardon River watershed ($\delta^{66}\text{Zn}$ values around 0.20‰). Finally, the percentage of metal(loid)s present in the "mobile" pool, as estimated by sequential extraction, was: Sb (1-5%) < As (1-22%) < Zn (10-65%) = Pb (15-68%).