Sulfur in tree rings in Central Europe: A negative $\delta^{34}S$ shift relative to regional pollution sources

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Sulfur isotope composition in tree rings of 50-year old Norway spruce was compared with $\delta^{34}S$ values of local coal and atmospheric deposition in the Black Triangle region of Central Europe. For this purpose we have analyzed soft coal from two East German Basins (Espenheim near Leipzig, and Lausitzer region near the German-Polish border) and two Bohemian basins (Sokolov and Most, northern Czech Republic). In all, 150 soft coal samples from all stratigraphic levels of these Tertiary deposits were analyzed for $\delta^{34}S$. Sulfur isotope composition of air-borne SO_2 was based on 170 monthly samples (Novak *et al*., 2001), $\delta^{34}S$ of rainfall sulfate was based on 200 monthly samples (Novak *et al*., 2000). The studied spruce was one of the few surviving trees in an area affected by pollution-related spruce die-back of the Erzgebirge Mts. The tree was harvested in 2005, while most other trees at the research site died back between 1975 and 1995 due to acidification. Bedrock orthogneiss was S-difficient, and its $\delta^{34}S$ was 5.8 ‰. The $\delta^{34}S$ values systematically decreased in the order Espenheim coal (mean of 12.0 ‰) > Sokolov coal (11.7 ‰) > Lausitzer coal (9.6 ‰) > rainfall sulfate (5.4 ‰) > air-borne SO_2 (2.5 ‰) > Most coal (1.6 ‰) > Ezgebirge tree rings (0.4 ‰). Three of the coal basins had isotopically relatively heavy sulfur, one coal basin (Most, Czech Republic), had isotopically light sulfur. Most of the emissions from the coal-fired power plants were in the form of SO_2, which was partly oxidized to sulfate in the atmosphere before reaching the receptor site. The resulting sulfur became isotopically somewhat heavier than the residual SO_2. The spruce tree rings contained the isotopically lightest S of all studied S reservoirs. Our data indicate that (i) German coal S did not significantly influence trees on the Czech side of the Erzgebirge Mts., and (ii) assimilation of S by Norway spruce is associated with a negative isotope shift relative to ambient S.

References

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Quantification of stable strontium isotope variability in nature by MC-ICP-MS

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There is growing evidence that high-temperature processes, such as diffusion, condensation and evaporation can generate significant stable-isotope fractionation. Recent observations of stable isotope fractionation in elements as heavy as Tl (Z=81) raises the possibility that there may also be natural Sr isotope variation. With conventional $^{87}Sr/^{86}Sr$ measurements, the $^{86}Sr/^{88}Sr$ ratio is used to for correct instrumental fractionation, and although the absolute value used for this correction is unimportant, implicit in its use is the assumption that that $^{86}Sr/^{88}Sr$ ratio remains constant in all analysed materials. This 'internal' correction for instrumental mass fractionation thereby masks the existence of any natural mass dependent fractionation of $^{86}Sr/^{88}Sr$. In this study, we present a new technique that allows simultaneous measurement of both radiogenic Sr isotope variations ($^{87}Sr/^{86}Sr$) and possible small-scale mass dependent isotopic fractionation of the $^{86}Sr/^{88}Sr$ ratio. Radiogenic and stable Sr isotope ratios are measured on a Thermo-Finnigan Neptune MC-ICP-MS and are corrected for mass bias 'externally' using admixed Zr. We present $^{86}Sr/^{88}Sr$ data for NBS 987, a range of natural rock standards and extraterrestrial samples (for which $^{86}Sr/^{88}Sr$ fractionation has already been documented using double spike TIMS). Incomplete recovery of Sr during column separation can significantly fractionate Sr isotopes, which implies that excluding overlapping Rb and Sr tails during column procedures will introduce inaccuracies. We demonstrate that NBS987 is fractionated relative to high-T magmatic rocks (possibly resulting from the manufacturing process), and establish a precise "high-T" reference line. Due to documented variation in low-T and biological samples we suggest that this high-T reference should be adopted for Sr isotope work.