

Proof of biogenic origin of marine aerosol by ^{13}C and ^{14}C analysis

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A contribution of various sources to aerosol organic matter has been notoriously difficult to discern due to the poorly resolved organic matter speciation, but is of paramount importance to global carbon budget. Carbon isotope analysis can offer a powerful tool, because different sources have unique isotopic signatures [1]. Carbon isotope measurements of marine aerosols have been very rare [2] mainly due to technical and analytical challenges. By combining stable carbon isotope (^{13}C) and radiocarbon (^{14}C) analytical methods we were able to prove biogenic origin of marine aerosol over the North Atlantic. During MAP project submicron aerosol was sampled during 2006 and analysed for ^{13}C and ^{14}C . ^{13}C ratio of marine aerosol was between -21 and -23‰, while polluted aerosol exhibited much lower ratios between -25 and -27‰ with significant seasonal pattern. By using isotope mixing equation it was possible to discern marine and continental organic matter using ^{13}C data only. ^{14}C analysis enabled to discern continental natural and anthropogenic sources by separating 'modern' and 'fossil' carbon [3]. ^{14}C analysis revealed the dominant fraction of non-fossil carbon in marine aerosols and still substantial fraction of non-fossil carbon in polluted (continental) aerosol. An even more detailed picture is emerging if organic and black carbon fractions can be separated for isotope analysis. By combining ^{13}C and ^{14}C data one can calculate regional aerosol carbon budget.

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[1] Raymond (2005) *GRL* **32**, L14402. [2] Chesselet *et al.* (1981) *GRL* **8**(4) 345-348. [3] Szidat (2009) *Science* **323**, 470-471.

Influence of sulfide mineralogy on oxygen and sulfur isotope ratios of sulfate generated via oxidation

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An important source of terrestrial sulfate is oxidative weathering of sulfide minerals. Mineralogical data indicate that the structure of pyrite (FeS_2) is unique and that this mineral is oxidized by different mechanisms compared to sphalerite (ZnS), galena (PbS) and S^0 [1]. In order to test if the oxidation of distinct sulfide minerals produces sulfate having different $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ values, we carried out metal sulfide oxidation experiments (biological vs. abiotic) at pH 3.0 and 2.7 under aerobic and anaerobic conditions, with water having different $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values. Pyrite, sphalerite, galena and S^0 were used in the experiments. Biological experiments were conducted in the presence of Fe(II)-sulfur oxidizing bacterium, *Acidithiobacillus ferrooxidans*. The $\delta^{18}\text{O}_{\text{SO}_4}$ values from aerobic biological S^0 & ZnS and anaerobic ZnS experiments indicated that H_2O was the sole source of O_2 for sulfate with an oxygen isotope enrichment factor ($\epsilon_{(\text{SO}_4\text{-H}_2\text{O})}$) of ~ 9 ‰. $\epsilon_{(\text{SO}_4\text{-H}_2\text{O})}$ for the aerobic/anaerobic biological FeS_2 experiments was ~ 4 ‰. These results suggest that $\delta^{18}\text{O}_{\text{SO}_4}$ values from aerobic and anaerobic sphalerite and the aerobic S^0 experiments were ~5‰ higher compared to those from FeS_2 experiments. The $\delta^{34}\text{S}_{\text{SO}_4}$ from aerobic & anaerobic FeS_2 experiments closely reflected the parent $\delta^{34}\text{S}_{\text{FeS}_2}$ value (<1 ‰) whereas the $\delta^{34}\text{S}_{\text{SO}_4}$ values from anaerobic ZnS experiments were ~3 ‰ lower than the $\delta^{34}\text{S}_{\text{ZnS}}$ value. Our experimental results compared well with the $\delta^{18}\text{O}_{\text{SO}_4}$ values observed at different acid mine drainage sites, suggesting that $\delta^{18}\text{O}_{\text{SO}_4}$ values may be used to elucidate the mineralogy of the oxidized minerals.

[1] Crundwell (1988) *Hydrometallurgy* **21** 155-190.