

UV induced mass-independent sulfur composition in stratospheric volcanic eruptions

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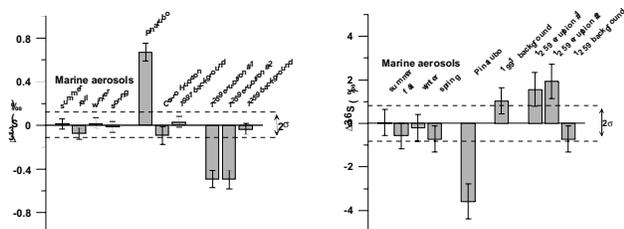
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Introduction

The discovery of mass-independently fractionated sulfur isotopic compositions (Farquhar, 2002) in Archean crustal and sedimentary rocks changed our vision of the Earth's early sulfur cycle. It has been hypothesized that atmospheric photochemistry involving sulfur dioxide in a primitive atmosphere with reduced oxygen and ozone levels produced the sulfur isotopic anomaly (Farquhar, 2001). We tested this hypothesis by extracting sulfates of different origins (tropospheric from marine and volcanic sources, and stratospheric from volcanic sources) from Antarctic ice.

Results and discussion

The sulfur isotopic anomalies, reported in $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ notations, are displayed in figure 1. Only sulfates produced in the stratosphere, following the massive volcanic eruptions of Pinatubo (1991) and the Unknown event (1259 AD) possess significant mass-independent sulfur isotope compositions. Comparison with laboratory results shows that these sulfur isotopic anomalies are consistent with UV dissociation of SO_2 at 248 nm, and not below 220 nm as it is the case for the Archean samples. This further confirms that the sulfur anomaly is associated with UV photochemistry. In the present, or more recent atmosphere, the anomaly is sensitive to the O_3 column density.



References

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Experimental estimation of sorption removal influence on the transformation of dissolved fluorine runoff in river mouth areas

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Fluorine behavior in river mouths formally corresponds to the conservative behavior type (Savenko, 2001). Nevertheless the results of field observations are not always the ground to judge on the actual significance of physical-chemical and biological processes. It was experimentally established in particular (Savenko, 2000) that in spite of conservative behavior the transformation of dissolved boron runoff in river mouths is controlled by sorption proceeded while river suspended matter interact with seawater. Sorption provides for more than 60 % of removal in geochemical balance of boron in the Ocean.

This paper presents the results of experimental study of fluorine sorption from river water and seawater at major clay minerals of suspended matter of the continental runoff.

The experiments have been provided on the examples of kaolinite, montmorillonite, and poliminerall gzhel clays. The first series of the experiments has simulated the interaction between clays and the filtered water from the Moscow River. The second series has simulated fluorine sorption at the clays from the artificial seawater with salinity of 35 ‰.

The results for sorption equilibrium parameters allow to calculate the amount of fluorine, which is removed at river suspended matter during their interaction with seawater. The difference between the values of specific sorption of fluorine from river water and seawater at kaolinite, montmorillonite, and gzhel clays is equal to 30.6, 664, and 14.2 mg F/kg, respectively.

The mineral composition of gzhel clay matches closely the mineral composition of world river suspended matter with the exception of montmorillonite. According to the data of experiments with gzhel clay 280–330 thousand tons of fluorine is removed annually from seawater due to sorption at river suspended matter. If river suspended matter contain 3 ‰ of fluorine annually. In this case the actual annual values of fluorine sorption at river suspended matter will approach 600–700 thousand tons.

Thus, the annual amount of dissolved fluorine, which is removed from the Ocean due to interaction between seawater and river suspended matter, ranges 280–330 to 600–700 thousand tons that corresponds to 7–18 ‰ from the annual fluorine entry with river runoff. This fact is the ground to assert that the conservative type of dissolved fluorine behavior observed in river mouths is not the evidence for geochemical inertness of this element.

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