

Dynamics of zero-valent sulfur species, including polysulfides, in Wadden Sea tidal flat pools

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Zero-valent sulfur (ZVS) species (rhombic elemental sulfur, colloidal elemental sulfur, inorganic polysulfides (S_n^{2-}) and polythionates ($S_nO_6^{2-}$)) play an important role in a variety of environmentally, geochemically and biogeochemically important processes. Polysulfides are known to decompose halogenated pollutants by reductive dehalogenation pathway. They are the important reactants in pyrite formation and sulfurization of sedimentary organic matter during early diagenesis. ZVS compounds are also important bacterial substrates. In natural aquatic systems ZVS species can be produced by microbial as well as by chemical pathways.

ZVS species dynamics in tidal flat pools of Wadden Sea (North Sea) was studied. Concentrations of solid sulfur, colloidal sulfur and distribution of inorganic polysulfide species were detected in different pools as a function of time after detachment of the pool from the sea.

Every sample was analysed by the protocol that consists of 4 procedures: 1) detection of individual inorganic polysulfides by rapid single-phase derivatization with methyl trifluoromethanesulfonate followed by HPLC-UV detection of dimethylpolysulfanes [1]; 2) detection of colloidal elemental sulfur, polysulfide and polythionate ZVS by reaction with hydrogen cyanide followed by HPLC-UV detection of thiocyanate; 3) pre-treatment with zinc chloride solution followed by chloroform extraction and HPLC-UV detection of elemental sulfur; 4) analysis of individual polythionates by HPLC-UV. Detection limit of each procedure was $\leq 2 \mu\text{M}$.

Maximum sulfide concentration detected in the pools was $273 \mu\text{M}$. During the initial 2 hours of pool detachment from the sea the main ZVS pools were colloidal sulfur and polysulfides. Dispersed solid sulfur concentrations reached significant values only 5 hours after pool detachment. Maximum concentration of colloidal sulfur detected in the pools was $73 \mu\text{M}$ and total ZVS $>100 \mu\text{M}$. Polythionates with $n=4-6$ were not observed in any of the analysed samples.

Individual polysulfides with chain lengths of 4-6 sulfur atoms were quantitatively detected for the first time in marine waters. Polysulfides concentrations were found to be lower than the predicted ones by calculations based on thermodynamic values. Maximum detected sum of S_4^{2-} , S_5^{2-} and S_6^{2-} concentrations was $5.9 \mu\text{M}$.

Reference

[1] Kamyshny A., Jr. *et al.* (2006) *Anal. Chem.* **78**, 2631-2639.

A deep mantle reservoir inferred from isotope signatures of kimberlites

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Based on radiogenic isotope systematics, depleted (DM) and enriched (EM1, EM2) mantle reservoirs together with the other one (HIMU) have been generally accepted. However, existence of BSE-like (non- or less fractionated and least degassed) mantle reservoir is a matter of debate.

Although much caution is required to get reliable data of kimberlites, their isotope data bear characteristic features. Based on Sr-Nd isotope systematics, kimberlites have been classified into Group I and II (Smith, 1983). In the Sr-Nd isotope diagram, Group I kimberlites cluster close to the value of BSE, whereas Group II kimberlites in the enriched area. Pb isotope systematics show similar systematics. The latter can be explained by incorporation of recycled materials and their distribution is limited. Hence I concentrate my discussion on Group I kimberlites. Based on Hf isotopes of Greenland kimberlites, Bizzarro *et al.* (2002) suggested the existence of a hidden reservoir, since kimberlite data systematically lie below the Nd-Hf isotope mantle array. While Hf isotope data themselves also cluster close to the BSE value. Sr, Nd and Pb isotope systematics of kimberlites have often been attributed to the mixing of components between the asthenosphere and lithosphere. However, our $^3\text{He}/^4\text{He}$ and Ne isotope studies of Greenland and Russian kimberlites have revealed the occurrence of Loihi-type noble gas isotope signatures in their magmas and suggest their deep mantle origin (Tachibana *et al.*, 2006; Sumino *et al.*, 2006).

Noble gas isotope signatures are similar to those of Loihi-type OIBs. However, solid isotope epsilon data of kimberlites with different time and space cluster much more tightly than those of OIBs and they are close to BSE. To produce such a feature, mixing among two or more multiple components operated with the same degree even in different time and space is unlikely. Accordingly, such a feature would be attributed to the properties of kimberlite magma source itself. Thus, isotope signatures of kimberlites suggest possible existence of a deep mantle reservoir which is close to BSE and less fractionated and less degassed than the other mantle reservoirs. However, Hf isotope signatures might require an additional component to explain the trend of kimberlites.

References

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