

Redox chemistry profiling in the Kara sea sediments (from the Ob-river to the Saint Anna trench)

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Submeridional redox profile across the bottom sediments of the Kara sea from the Ob' river (71 N) to the St. Anna trench (77 N) was studied in the course of the Russian expedition on the R / V «Akademik Mstislav Keldysh» in September 2007. Redox profile is formed under the influence of diagenetic reactions in sediments with organic matter (OM), produced into the sea and brought from the shore. The main oxidants involving microorganisms consistently are oxygen, nitrates, oxyhydroxides of manganese and iron, sulphates and carbon dioxide, while in the pore water accumulate NH_3 , Mn^{2+} , Fe^{2+} , H_2S and CH_4 . The content of the OM, which is a fundamental characteristic of sediments, is more than 1.5% (dw) Corg in the Ob' delta (71 N), close to 1% in the estuary (72 N), 0.5-0.75% in the sediments of inner and outer shelf (72-75 N), as well as in the slope (75-76 N), 2% in the sediments of the of the St. Anna trench (77 N). OM in the deltaic part is mainly terrigenous, in the northern part of the profile the cause of increased OM content is the primary production of plankton. On the border of the estuary and the shelf there is a sharp decrease of suspended matter in the surface waters (from 7 to 1 mg/l), the Corg and many metals of the river runoff in the sediments reach maximum values (Mn 0.3%, Fe 7% dw). The growth of OM stimulates the reduction processes, as reflected in higher concentrations of the dissolved components in the pore water (Mn^{2+} up to 260, Fe^{2+} to 100 μM) and derivatives of H_2S (up to 0.3 %) in the sediments. Dissolved Mn remove from the sediments to the bottom water, dissolved Fe is oxidized by oxygen of the bottom water and forms a thin oxidized layer on the surface. Recycling of Mn and Fe is accompanied by formation of ferromanganese nodules. Sedimentation in central and northern part of the profile, adjacent to the St. Anna trench are characterized by lower content of Mn due to both long distance from the river outflow and diagenetic removal of Mn from the sediments of higher Corg content. In this part of the profile derivatives of H_2S are mainly represented by organic forms, which are very typical for Arctic sediments in contrast to the bottom sediments of the temperate and tropical zones, in which among H_2S -forms prevails diagenetic pyrite.

Effects of lead and strontium on radium uptake by barite: Atomistic simulations and thermodynamic assessment

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Experimental studies related to safety issues of the long-term disposal of spent nuclear fuel in deep geologic formations suggest that Ra released from the fuel can be efficiently immobilized as a constituent of a barite-rich solid solution (SS) [1,2]. Here the uptake of Ra by barite is investigated using the Gibbs free energy minimization method [3] at variable fractions of PbSO_4 and SrSO_4 in the SS. The SSs were modelled as ternary $(\text{Ba}, \text{Sr}/\text{Pb}, \text{Ra})\text{SO}_4$ regular mixtures. The mixing parameters ($W_{\text{BaPb}} = 5.4$, $W_{\text{PbRa}} = 1.5$, $W_{\text{BaRa}} = 2.5$, $W_{\text{BaSr}} = 8.9$, $W_{\text{SrRa}} = 19.6$, $W_{\text{SrPb}} = -0.3$ kJ/mol) were computed from first principles with the aid of the single defect method [4]. The system contained 0.00214 moles of $\text{Ba}_{1-x}(\text{Sr}/\text{Pb})_x\text{SO}_4$, 0.1 m of NaCl, $5.0 \cdot 10^{-6}$ m of RaCl_2 and 1 kg of H_2O . The concentration of $\text{Ra}(\text{aq})$ decreases with the $(\text{Sr}/\text{Pb})\text{SO}_4$ fraction in the system due to the common anion effect. However, in the SrSO_4 case, after the fraction of SrSO_4 exceeds ~ 0.01 , the concentration of $\text{Ra}(\text{aq})$ starts to grow due to the corresponding increase in the mole fraction of RaSO_4 in barite. This effect is suppressed by the decomposition of the SS in Ba- and Sr-rich phases; the concentration of $\text{Ra}(\text{aq})$ remains less than that in the Sr-free system up to the Sr/Ba ratio of ~ 10 . Therefore, at certain conditions, an admixture of PbSO_4 or SrSO_4 in barite would lead to a more efficient immobilization of Ra. The study is funded by BMBF-IMMORAD project through the grant 02NUK019E.

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