Sulfur system in anoxic confined aquifers in the northeastern Osaka Basin, Japan

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We used δ^{34}S values and chemical compositions of groundwater to investigate the influence of sulfate reduction and sulfide oxidation processes in a confined aquifer system in the northeastern Osaka Basin (NEOB), central Japan. Shallow confined groundwater (<100 m) in the basin is recharged mainly from mountainous areas to the north, and flows south and southwest through the aquifer system. Anion composition of the groundwater is dominated by HCO_3^- throughout the basin. However, concentrations of redox-sensitive species such as dissolved oxygen, NO_3^-, Fe^{2+}, and Mn^{2+} show that groundwater conditions become increasingly anoxic along the flowpaths. Moreover, $SO_4/(SO_4 + 2HCO_3)$ molar ratios decrease with increasing δ^{34}S along the flowpaths, which demonstrates that sulfate is reduced in the NEOB aquifer system. Groundwater with both high total dissolved solids and high SO_4 content was observed mainly in areas down-flow from faults. Because of the high SO_4 content, the anion composition of this groundwater cannot be adequately explained by a simple sulfate reduction process. A Rayleigh distillation model with $\varepsilon = -20‰$, which allows for sulfide oxidation within marine sediments in proximity to faults, explains the chemistry of all groundwater samples, including those with high SO_4 content. The model demonstrates that 76% of initial sulfate is reduced at maximum, and that reduced SO_4^{2-} content is up to 48.5 mg/L after sulfide oxidation in the NEOB aquifer system.

Adsorption and coprecipitation behaviors of platinum(II) complex ions on and with manganese(IV) dioxide and manganese(II) hydroxide: Model reactions for the concentration mechanism of platinum into oceanic manganese nodule

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In oceanic manganese nodule and crust, platinum (Pt) is more concentrated than sea water and earth's crust. However, the concentration mechanisms of Pt and its chemical state have not been clarified because of its extremely low concentration. From thermodynamic investigation, Pt is considered to be present as Pt(II) complex ion ($[PtCl_{4-n}(OH)_n]^{2-}$) in deep ocean water. Therefore, we investigated the adsorption behavior of Pt complex ions ($[PtCl_{4-n}(OH)_n]^{2-}$) on manganese(IV) dioxide (δ-MnO_2) and the coprecipitation behavior of Pt complex ions with manganese(II) hydroxide ($Mn(OH)_2$) as model reactions for the concentration mechanisms of Pt into manganese nodules and crusts. δ-MnO_2 and $Mn(OH)_2$ that is finally oxidized to manganese(IV) dioxide by dissolved oxygen are regarded as model compounds of manganese nodule and crust.

Pt(II) complex ions were vigorously adsorbed on δ-MnO_2. The XPS and XANES spectra for Pt showed that the Pt(II) complex ions adsorbed on δ-MnO_2 were oxidized to Pt(IV). Based on the analytical result of EXAFS spectrum, the Pt(IV) was present as PtO_6 species, suggesting that the adsorbed Pt(II) may be oxidized and substituted with Mn(IV) in δ-MnO_2. Pt(II)complex ions were also coprecipitated effectively with $Mn(OH)_2$. The Pt(II) may be oxidized to Pt(IV) after the oxidation of $Mn(OH)_2$ to MnO_2.

In conclusion, the concentration mechanism of Pt into manganese nodule and crust can be deduced as oxidative substitution by the redox reaction between Pt(II) in $[PtCl_{4-n}(OH)_n]^{2-}$ and Mn(IV) in manganese(IV) dioxide.