

## Adsorption behavior of gold (I and III) complexes on manganese dioxide

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It is essential in geochemistry to elucidate the uptake mechanism of trace elements into manganese nodules. It is well known that transition metals such as Co, Cu and Zn are concentrated in manganese nodules. However, only a few investigations have conducted on the uptake of noble metals such as Au, Pd and Pt. It is recognized that adsorption of metal ions on manganese dioxide was investigated to explore their uptake mechanism into marine manganese nodules.

In this study, a model compound of manganese nodule was manganese dioxide. As model compounds of gold,  $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$  and  $[\text{AuCl}_{4-n}(\text{OH})_n]^-$  complexes were selected for convenience because gold(I) and gold(III) ions are present in hydrosphere.

The adsorption behavior of  $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$  and  $[\text{AuCl}_{4-n}(\text{OH})_n]^-$  complexes on the surface of manganese dioxide was investigated with pH. The adsorption behaviors were quite different. The percentage of  $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$  adsorbed increased with decreasing pH (from 8 to 4). Above pH 8, which is the same pH of ocean water, no  $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$  was adsorbed on manganese dioxide. Since the isoelectric point of the manganese dioxide was around pH 4-5, the surface negative charges increase with increasing pH above pH 4-5. This opposite correlation between the surface charge and percentage of  $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$  adsorbed suggests that the adsorption of  $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$  may be controlled by electrostatic force. On the other hand, the percentage of  $[\text{AuCl}_{4-n}(\text{OH})_n]^-$  adsorbed increased from pH 4 to 6 and showed a maximum at pH 6-8. This result indicates that the adsorption of  $[\text{AuCl}_{4-n}(\text{OH})_n]^-$  occurred by overcoming the electrostatic repulsion.

In addition, the chemical state of gold adsorbed on manganese dioxide was examined by XPS. The results showed that  $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$  and  $[\text{AuCl}_{4-n}(\text{OH})_n]^-$  complexes adsorbed on manganese dioxide were spontaneously reduced to elemental gold.  $[\text{AuCl}_{4-n}(\text{OH})_n]^-$  may be specifically adsorbed by condensation reaction (the formation of Au-O-Mn bond) between two OH groups in the  $[\text{AuCl}_{4-n}(\text{OH})_n]^-$  and two OH groups on manganese dioxide. The adsorbed  $[\text{AuCl}_{4-n}(\text{OH})_n]^-$  may be distorted due to the regulation by the two OH groups on the manganese dioxide, and then its redox potential may be changed and reduced by water molecules. In contrast, the adsorbed  $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$  may disproportionate to form Au(0) and Au(III) species. The resulting Au(III) may be reduced to Au(0) by the above same mechanism.

Based on the results of this study, the chemical state of gold in marine manganese nodules should be investigated spectroscopically.

## Dissolution and precipitation kinetics of magnesite at conditions relevant for CO<sub>2</sub> geologic sequestration

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Understanding carbonate mineral reactivity is of critical importance to assessing and optimizing potential CO<sub>2</sub> storage sites (c.f. Oelkers and Schott, 2005). In particular, carbonate dissolution and precipitation rates play a fundamental role in CO<sub>2</sub> mineral fixation. To address this need, the dissolution and precipitation rates of magnesite (MgCO<sub>3</sub>) have been studied as a function of pH (2 < pH < 10), solution composition and P<sub>CO<sub>2</sub></sub>. Experiments have been performed using both open and closed-system reactors at temperatures from 100°C to 200°C and reactive fluid concentrations having ionic strengths varying from 0.01 to 1 M.

Measured dissolution rates decrease strongly with decreasing chemical affinity and increasing HCO<sub>3</sub><sup>-</sup> concentration. The last observation is in agreement with the magnesite surface speciation model of Pokrovsky *et al.* (1999). Within this model all aqueous species able to form complexes with Mg surface hydrated sites, and thus decreasing >MgOH<sub>2</sub><sup>+</sup> concentration, inhibits magnesite dissolution. In addition, a significant increase in dissolution rates is observed with increasing reactive solution ionic strength: rates measured in 1 mol/kg NaCl solutions are on average 5 times faster than those observed in < 0.1 mol/kg NaCl solutions at a pH of ~ 7.

Magnesite is observed to precipitate at 150°C only at relatively high degrees of supersaturation. For example measured magnesite precipitation rates are found to be 2x10<sup>-12</sup> only at a saturation index  $\Delta$  of ~ 30, when the CO<sub>2</sub> pressure is at atmospheric or lower values. Moreover, the degree of supersaturation required for magnesite precipitation is observed to decrease with increasing temperature.

### References

- Oelkers E.H. and Schott, J. (2005) *Chem. Geol.* **217**, 183-186.  
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