

## Preliminary results on the behaviour of Ni(II) in the calcite-water system

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The input of heavy metals into the environment from anthropogenic sources is often much higher than natural input. In one particular case in Denmark however, it is the aquifer material that serves as a source for high nickel concentrations in the groundwater. Because the majority of Danish drinking water comes directly from aquifers, with no more treatment than filtration, aquifers contaminated in this way are unusable for most water supply needs. There was considerable interest in understanding where the nickel came from, and which geochemical processes controlled its concentration in the groundwater. Studies with classical geochemical methods demonstrated that Ni was released from pyrite during oxidation as a result of lowering of the water table (Larsen and Postma, 1996). Calcite is an abundant mineral both in the chalk and in the clayey-till horizons that most commonly serve as aquifers in Denmark, and calcite is known to be effective at adsorbing and incorporating divalent trace metals. Therefore, our studies were planned to focus on the behaviour of Ni<sup>2+</sup> in the calcite-water system.

In addition to the expected uptake processes of adsorption and coprecipitation for the divalent cations, some previous studies have shown that Cd<sup>2+</sup> and Zn<sup>2+</sup> may also be incorporated into calcite by solid-state diffusion (Stipp *et al.*, 1992; Stipp, 1994). Cadmium and zinc both have 10 electrons in their outermost d-orbital, hence, as with calcium, they lose two 2 s-electrons to form their cation. Furthermore, their sizes are compatible: Cd<sup>2+</sup> is only about 2% smaller than Ca<sup>2+</sup> and Zn<sup>2+</sup> is about 25% smaller, so these three ions behave similarly. This is evident in their ability to form solid-solutions. The series is continuous between otavite (CdCO<sub>3</sub>) and calcite (T = 25C) and Zn can substitute into at least 15% of calcite's metal sites (T = 650C) before the separate formation of smithsonite (ZnCO<sub>3</sub>) is favoured (Goldsmith and Northrop, 1965). Although nickel is only about 5% smaller than Zn and it also loses its outermost s-electrons to form the cation, it has only 8 electrons in its outermost d-orbital. This difference in electron

configuration leads to a different behaviour so calcite can tolerate less than 5% Ni in the atomic lattice (T=750C) before gaspeite (NiCO<sub>3</sub>) forms as a separate phase (Goldsmith and Northrop, 1965). A contrast is also observable in the hydrolysis behaviour of these four ions and in their formation of ion-pairs with CO<sub>3</sub>. Therefore, from the perspective of understanding fundamental geochemical relationships, it was interesting to compare the uptake behaviour of Ni<sup>2+</sup> on calcite, with that observed previously for Cd<sup>2+</sup> and Zn<sup>2+</sup>.

The application of surface analytical methods to studies of geochemical processes that control interface composition has proven successful in the past; this study uses surface techniques to monitor changes in surface concentration and morphology, in order to test if adsorbed Ni<sup>2+</sup> also moves into the calcite lattice structure.

### Methods

There are many surface-sensitive techniques, but the two most applicable to the goals of this study are X-ray photoelectron spectroscopy (XPS) and Atomic force microscopy (AFM). XPS uses an X-ray beam to energise a sample. The binding energy of the emitted photoelectrons provides information about the atom of origin, telling its identity and the character of the bonds that hold it within the sample. With XPS we were able to determine the relative concentrations of Ni, Ca, O and C within about the top 10 nanometers of the calcite surface, as a function of time. XPS gives direct information about atomic bonding structure, but cannot provide information about surface morphology. AFM uses a sharp tip to probe the physical features of a surface and it can produce images that resemble topography with resolution of fractions of a nanometer. With this technique, we could observe changes in physical appearance with time of exposure to air, in situ, without a coating of gold or graphite, or vacuum, as are required for Scanning Electron Microscopy (SEM). Fig. 1 is an example of an AFM image.

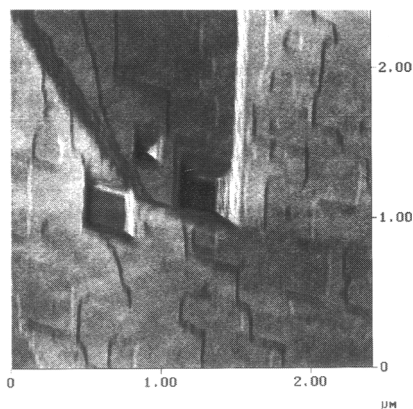


FIG. 1. AFM image of freshly cleaved calcite surface exposed to  $\text{Ni}(\text{ClO}_4)_2$  for 1 min. Height difference is 20 nm. Light parts of the image are closest to the viewer. One monolayer is approximately 3 Å.

Samples were prepared by dipping freshly cleaved calcite crystals into aqueous solutions containing  $10^{-2}$  M  $\text{Ni}(\text{ClO}_4)_2$ . After 1 minute, they were removed and excess solution was blown off with a jet of  $\text{N}_2$ . This method was shown to favour adsorption and result in minimal precipitation of the components of the solution. Samples were analysed immediately (Fig.1) and some were stored in a container in contact with air but free of dust and reanalysed periodically.

### Results and discussion

XPS spectra show that nickel is present on the surface of the freshly dipped samples. Over many months, the Ni:Ca ratio does not change significantly, with respect to sample preparation and analysis reproducibility, suggesting that if  $\text{Ni}^{2+}$  is taken up from the surface into bulk calcite, the change in surface concentration is lower than our detection limit, and its diffusion coefficient must be many orders of magnitude smaller than that of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ .

One question that arose from the previous studies of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  uptake concerned the mechanism for a process with a rate that seemed very high for non-diagenetic conditions. Studies with AFM investigated surface morphology and its change with time at high resolution. Immediately following cleavage, calcite surfaces always have broad flat terraces separated by steps that range in height from one atomic layer (0.3 nm) to several micrometers. As a result of exposure to solution, etch pits form (fig.1), but with exposure only to air, surfaces spontaneously rearrange themselves. Samples exposed to solutions of  $\text{Ni}(\text{ClO}_4)_2$  behaved in exactly the same way as

samples exposed to pure water, and as freshly cleaved surfaces that had only been exposed to air. Such a rearrangement of surficial material would surely bury ions adsorbed at the surface if they were capable of forming solid solution. If only this process were responsible for loss of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  from calcite surfaces, then one would also expect  $\text{Ni}^{2+}$  to disappear, at least to some extent.

The behaviour we observe confirms that some additional mechanism must control the incorporation of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  and suggests that  $\text{Ni}^{2+}$  is minimally affected by solid-state diffusion. This is compatible with what one might expect from theory. Because of its different electronic configuration, Ni hydrates and hydrolyses to a higher degree than  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , or  $\text{Ca}^{2+}$  (Baes and Mesmer, 1976); (Casey, 1995), so  $\text{Ni}^{2+}$  adsorbed at the calcite surface has a higher activation barrier to dehydration before it could be incorporated during precipitation or move through the lattice by diffusion. Moreover, the different electronic configuration of  $\text{Ni}^{2+}$  makes its molar fraction in a  $\text{Ni}_x\text{Ca}_{(1-x)}\text{CO}_3$  solid-solution considerably lower than the molar fraction of Zn or Cd in calcite. Therefore, less Ni is likely to be taken up into the calcite atomic lattice by either process, by surface mixing or by solid-state diffusion.

### Conclusions and implications

Based on the data that we have collected until now, we can conclude that  $\text{Ni}^{2+}$  does not appear to be taken up into the calcite atomic lattice in the same way that is observed for  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ .  $\text{Ni}^{2+}$  loss from solution in a pure  $\text{CaCO}_3\text{-H}_2\text{O-CO}_2$  system appears to be controlled only by the precipitation of  $\text{NiCO}_3$  when solution concentrations are excessive, or by adsorption and coprecipitation with calcite at lower concentrations. Therefore, models to adequately describe uptake behaviour of  $\text{Ni}^{2+}$  by calcite, at pH conditions in the range of slightly acidic to slightly basic, need not include a parameter to describe solid-state diffusion, as should be used for  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ .

### References

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