SATURATION STATE OF SEAWATER WITH RESPECT TO THE OTAVITE-CALCITE SOLID SOLUTION

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INTRODUCTION

The concentration of cadmium (Cd) in seawater exhibits a nutrient-type profile (Chester, 2003), i.e. its vertical distribution in the oceans resembles that of the nutrients phosphate and nitrate: it is greatly depleted in the surface waters, with its concentration increasing with depth, until it reaches a maximum value deeper into the water column, at depths around 1000 m. As suggested by this similarity of distributions, the view that currently prevails, in trying to account for the characteristic vertical pattern of Cd, is that its concentration must be regulated by marine biogeochemical processes (Abe, 2001). These processes include the uptake of Cd by phytoplankton in the euphotic zone and, as a consequence of the decay of organic matter, the later remineralization of Cd and the other nutrients at greater depths, with the ensuing increase in their concentrations (Wright, 1995). However, despite this seeming connection to marine organisms, the true biogeochemical role of Cd is still uncertain, as the mechanisms of its uptake by cells are yet to be determined (Kremling and Strew, 2001).

On the other hand, it has also been suggested that the interactions between trace metals in solution and particulate matter could be a major process in regulating the concentrations of these metals in seawater (Sherrell and Boyle, 1992). At near-surface waters, Cd is sorbed onto biogenic particles, including calcitic and aragonitic particles secreted by organisms; these particles later sink towards the bottom, thus depleting the surface waters in Cd. As a result of the change in seawater chemistry with depth (Prothero and Schwab, 1996) - characterized by a decrease in temperature and an increment in pressure and in the total dissolved inorganic carbon - the solubility of calcite and aragonite will increase (Wright, 1995). This increment leads to further dissolution of these carbonates, with the consequent release of Cd²⁺ ions into solution.

Experiments on the sorption of Cd^{2+} to calcite and/or to aragonite surfaces have been carried out by several authors (Tesoriero and Pankow, 1996; Prieto et al., 2003; Cubillas et al., 2005). Tesoriero and Pankow (1996) have measured the distribution coefficients for Cd (D_{Cd}) in freshwater and determined a range of 1000-4500. These high values imply that, if a calcitic and/or aragonitic phase is present, partition of Cd²⁺ to the solid phase will always occur, even if Cd²⁺ is only present at trace concentrations in solution. Also, the extremely low solubility of otavite, compared to that of calcite, further corroborates this strong partition tendency.

When calculating the saturation state of seawater with respect to the possible precipitating phases, solid solutions are not usually considered. Our purpose is, then, to further investigate the mechanisms of Cd sorption onto calcite and aragonite, considering the formation of (Cd,Ca)CO₃ solid solutions in seawater. We expect this study might lead us to a better understanding of the extent, efficiency and importance of this inorganic removal process as a sink for Cd in the oceans, and how it may superimpose on the processes of organic removal, thence influencing the observed distributions of this metal in the ocean.

In this work, prior to any experiments, we have calculated the saturation indices for pure calcite, pure otavite, and $(Cd,Ca)CO_3$ solid solutions, using existing data of seawater composition.

METHODS

The starting data correspond to samples of seawater collected in the equatorial Pacific (lat=0º, long=-140º), at depths ranging from 20 to 175 meters (US Joint Global Ocean Study), and include measurements of temperature, pressure, salinity, total dissolved inorganic carbon, total alkalinity and concentration of Cd. Using the values of salinity, and taking into account that the relative proportions between the major ions are virtually constant in the oceans (Wright, 1995), we have calculated the concentrations of the major elements Na, Cl, Mg, S, K, Ca and Br, with the purpose of modelling the seawater solution. These parameters have been input into the computer code PHREEQC (Parkhurst and Appelo, 2003) in order to calculate the activities of Ca^{2+} , Cd^{2+} and CO_3^{2-} , as well as the saturation indices for calcite and otavite. Moreover, the activities determined with PHREEQC have been used to calculate the saturation index with respect to (Cd,Ca)CO₃ solid solutions.

In the case of solid solution – aqueous solution systems, the saturation index of the aqueous solution with respect to the solid solution is not a single value but a function that depends on the composition of the solid solution that is considered (Prieto et al., 1993). Therefore, starting from the concept of «stoichiometric saturation» (Glynn and Reardon, 1990), Prieto et al. (1993) defined a «stoichiometric supersaturation function», which describes the saturation state of any given fluid composition with respect to any solid solution composition. This function has a maximum that corresponds to the composition of the solid solution for which the aqueous solution is most supersaturated. Here this concept has been used to calculate the saturation state of seawater with respect to $(Cd,Ca)CO_3$ solid solutions, according to:

$$\Omega(x) = \frac{a(Cd^{2+}) \cdot a(Ca^{2+})^{(1-x)} \cdot a(CO_3^{2-})}{\left(x \cdot K_{CdCO_3} \cdot \gamma_{CdCO_3}\right) \cdot \left((1-x) \cdot K_{CaCO_3} \cdot \gamma_{CaCO_3}\right)^{(1-x)}}$$
(1)

where, $a(Cd^2)$, $u(Cu^{2*})$ and $u(CO_3^{2*})$ correspond to the activities of the ions in the aqueous phase, K_{CdCO_3} and K_{CaCO_3} refer to the equilibrium solubility products of otavite and calcite, respectively, and γ_{CaCO_3} and γ_{CaCO_3} to the activity coefficients of these endmembers in the solid phase. The composition of the solid solution is given by $x = X_{CdCO_3}$, where X_{CdCO_3} is the mole fraction of otavite in the solid solution.

RESULTS

As can be observed in Fig. 1, the calculated saturation indices indicate that, for this range of depths, seawater is always supersaturated with respect to calcite (SI>0). This degree of supersaturation diminishes with depth. In contrast, seawater is always rather subsaturated with respect to otavite (SI<0), though the degree of subsaturation decreases with depth, as the activity of Cd^{2+} in solution rises.

Computing the «stoichiometric supersaturation function» for the whole range of solid solution compositions, with x varying from 0 (pure calcite) to 1 (pure otavite), one can observe that the values of maximum supersaturation obtained do not correspond exactly to pure calcite, as shown in Fig. 2(b). Instead, these values coincide with solid solution compositions that, despite their proximity to the calcite endmember, would comprise a very small fraction of Cd^{2+} ions substituting for Ca^{2+} in the calcite structure. Also, one can observe a decrease in the values of maximum supersaturation with depth, which agrees with the known



Figura 1: Comparison between the saturation index of seawater with respect to calcite (SI Calcite) and to otavite (SI Otavite), for different depths.



Figura 2: (a) Variation, with depth, of the compositional range of the $(Cd-Ca)CO_3$ solid solution for which the seawater is supersaturated. (b) Variation, with depth, of the solid solution composition for which seawater is most supersaturated.

increment of solubility of the carbonates deeper into the water column.

The values of D_{Cd} , corresponding to the maximum supersaturations, varied from 3981, at 20 m, to 4677, at 175 m, testifying that, for these seawater solutions, the Cd²⁺ ions would preferentially partition to the solid phase, despite their low concentration in solution.

CONCLUSIONS

From our calculations we have observed that, for this range of depths, seawater is always supersaturated with respect to pure calcite and subsaturated for pure otavite. Moreover, the value of the maximum supersaturation decreases with depth. The solid solution composition for which the aqueous solution is most supersaturated corresponds to a value of $X_{\mbox{\tiny CdCO}_3}$ higher than zero, and this value increases as the activity of Cd2+ in solution is enhanced with depth (Fig. 2(b)). Thence, a very low fraction of otavite component will continually be present in the precipitating solid phase. In addition, the compositional range of the solid solution corresponding to supersaturation of the aqueous solution (Ω >1) tends to widen with depth (Fig. 2(a)), i.e. seawater will not only be supersaturated for pure calcite, but also for a whole range of $(Cd_{2}Co_{3})$ solid solution compositions.

All these findings could account for the depletion of Cd in the surface waters on an inorganic basis, by sorption or co-precipitation on/in carbonate particles.

Finally, the high values obtained for D_{Cd} (in the range of 3900-4700) confirm that Cd^{2+} will always partition to the solid phase, even when present at trace concentrations in solution. The increase of these values with depth reflects a growing partitioning of Cd^{2+} towards the solid phase, as the activity of this ion is intensified in solution.

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