

Requiem for a RAMSAR site, a bird sanctuary in Southern Chile, as evidenced by stable isotopes, radiotracers and benthic ecology

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In January 2004, a strong smell invaded a nearby city, Valdivia. Soon after, thousands of black-necked swans died and emigrate from Carlos Anwandter Sanctuary located on the Cruces River Estuary. I participated actively for 3 years, trying to pinpoint the sources of the changes that originated that tragedy. Water column concentration of cations, anions, metals, oxygen, sulfur stable isotopes, as well as an exhaustive sampling of benthos (animals, SPI, biogeochemistry, radiotracers, X-Ray, sedimentology) were measured. Historical record on fluxes and concentration profiles of metals, dissolved cations-anions and S isotopes as well as oxygen, pH, Eh link this ecological disaster to the activities of a pulp mill located few kilometers upstream of the RAMSAR Site Carlos Anwandter Sanctuary that begun working on January 2004.

I discuss my findings in view of the political, social and international laws and regulations dealing with the use of natural capitals and their lack of concern and protection for the sake of an economical trend.

Solubility of monohydrocalcite between 5 to 40°C

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Monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$; MHC) is rare mineral in geological settings. It is metastable with respect to calcite and aragonite. MHC formation is favour at low temperature [1]. There have been two reports of the solubility of MHC. One was given by Hull and Turnbull (1973), who determined the solubility at 25°C. Another was measured by Kralj and Brecevic (1995), who determined the solubility between 15 to 50°C. The latter showed that the solubility decreases with the temperature same as anhydrous calcium carbonate such as calcite and aragonite. However, the temperature dependency is opposite to ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) which is hydrous calcium carbonate [4]. In order to understand the reliable stability relationships of calcium carbonate minerals under low temperature, we determined MHC solubility between 5 to 40°C.

Synthesized MHC was added to pre-heated or cooled electrolyte solutions containing trace amounts of phosphate that is inhibitor for the MHC transformation. The suspensions were stirred and bubbled with high purity CO_2 gas at constant temperatures. The pH of suspensions were monitored during the experiments. After the attainments of the equilibrium, the suspensions were filtered through the membrane. Calcium concentrations of filterates were measured by ion-chromatography. Solubility product of MHC were calculated by Visual MINTEQ based on CO_2 partial pressure, calcium concentrations, and pH.

The solubility of MHC increases with the temperature. MHC is stable at lower temperature. The temperature dependence of MHC solubility was opposite in sign to that of earlier study [3] which becomes increasingly soluble at lower temperatures. In addition, the solubility of MHC becomes lower than vaterite at the temperatures lower than 10°C. It indicates that MHC is possibly third stable calcium carbonate at lower temperature.

[1] Dahl, K and Buchardt, B. (2006) *J. Sedimentary Research* **76**, 460-471. [2] Hull, H. and Turnbull, H.D., (1973) *Geochim. Cosmochim. Acta* **37**, 685-694. [3] Kralj, D. and Brecevic, L., (1995). *Colloid Surf. A* **96**, 287-293. [4] Bischoff J.L., Fitzpatrick J.A., and Rosenberg R.J., (1993) *J. Geology* **101**, 21-33