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## Crystallization of calcite, aragonite, vaterite, otavite, strontianite, and witherite by CO<sub>2</sub> diffusion technique between 10 and 30°C

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In the present study carbon dioxide  $(CO_2)$  diffusion through a polyethylene membrane induces a CO<sub>2</sub>flux into an alkaline metal bearing solution to crystallize calcite, aragonite, vaterite, otavite, strontianite, and witherite between 10° and 30°C. The applied  $CO_2$ -diffusion-technique is used as a simple mixed flow reactor, where the  $CO_2$  flux may be varied by changing the thickness or type of the membrane, or by adjusting the chemical composition of the solution (e.g. pH,  $CO_{2(aq)}$  or metal concentration). For this purpose 0.5 L of a solution containing 0.83 mol  $L^{-1}$  of NaHCO<sub>3</sub> adjusted to pH 7.5 by the addition of diluted HCl is prepared ( $[CO_{2(aq)}]_{in} = 10^{-4.2} \text{ mol cm}^{-3}$ ). This inner solution is stored in a closed polyethylene bottle which is placed in a vessel containing 51 of the outer solution. The outer solution consists of  $[Ca^{2+}]$ ,  $[Sr^{2+}]$ ,  $[Ba^{2+}] = 0.01 \text{ mol } L^{-1} \text{ or } [Cd^{2+}] = 0.001 \text{ mol } L^{-1} \text{ and respective concentrations of}$ chloride. The outer solution is adjusted to pH of 9.0 with an ammonia buffer, and the temperature was kept constant with a climate chamber ( $\pm 0.2$  °C). As the experiments proceeds, CO<sub>2</sub> diffuses from the inner solution through the polyethylene membrane into the outer solution. Consequently the different carbonates crystallize in the continously stirred outer solution. The precipitation rate can be followed by decrease of metal ions over time or amount of precipitation. In general, elevated temperatures induce higher precipitation rates and larger crystals. Crystallization of aragonite instead of calcite occurs by maintaining a  $[Mg^{2+}]/[Ca^{2+}]$  ratio of 2 in the fluid, whereas additional amounts of vaterite are crystallized at elevated precipitation rates. The CO<sub>2</sub>diffusion-technique can be used as a mixed flow reactor for the co-precipitation of trace elements with the above carbonate minerals for natural and applied systems. Preliminary results with respect to the incorporation of trace elements e.g. Sr, Mg, Ca,

and Co are presented.