

## Siderite in Archaean banded iron formations - A sensor for CO<sub>2</sub> partial pressures of ancient atmospheres?

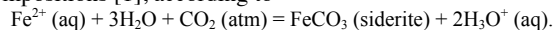
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It has been around for some time that siderite in Archaean BIFs can serve as a CO<sub>2</sub> sensor for Archaean atmospheric compositions [1], according to



This equilibrium is seemingly shifted to the right as the CO<sub>2</sub> partial pressure (pCO<sub>2</sub>) of the atmosphere rises, triggering the precipitation of marine carbonates including siderite if there is sufficient Fe<sup>2+</sup>(aq) dissolved in seawater. In reality, rising pCO<sub>2</sub> causes the H<sub>3</sub>O<sup>+</sup> activity to increase (ocean acidification), lowering the CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup> activity ratio in water until carbonate minerals become unstable. Hence, the above equilibrium is metastable and unviable to describe natural atmosphere-seawater interactions, contrary to assertions by Ohmoto *et al.* [1]. We are equilibrating natural and artificial seawater at 25°C with oxidized N<sub>2</sub>-O<sub>2</sub>-CO<sub>2</sub> and reduced N<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>-CO<sub>2</sub> atmospheres with variable pCO<sub>2</sub> ranging from < 10<sup>-5</sup> to 1 atm. Up to a pCO<sub>2</sub> of ~ 0.05 atm, the carbonate alkalinity of seawater is independent of pCO<sub>2</sub> as predicted by thermodynamics, however, when pCO<sub>2</sub> increases above 0.07 atm (pH < 6.5) carbonate alkalinities gradually decline and carbonate minerals become unstable. Carbonate minerals find ideal conditions when the pCO<sub>2</sub> of the atmosphere is at its minimum and the CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup> activity ratio in seawater at its maximum (i.e. high weathering rates, low atmospheric pCO<sub>2</sub>). When the pCO<sub>2</sub> < 2\*10<sup>-4</sup> atm (< 200 ppm CO<sub>2</sub> in the gas phase), natural seawater at 25°C spontaneously precipitates aragonite in the form of micro-ooids. The precipitation of siderite in Fe<sup>2+</sup>-doped seawater equilibrated with a reduced atmosphere is impossible, so long as the water contains the current marine Ca<sup>2+</sup> concentrations. In an artificial, NaCl-NaHCO<sub>3</sub>-FeCl<sub>2</sub>-bearing, Ca<sup>2+</sup>-free seawater proxy (100 ppm Fe<sup>2+</sup>, carbonate alkalinity 4000 μmol kg<sup>-1</sup>), falling pCO<sub>2</sub> causes the precipitation of an amorphous blue-green phase that we tentatively identify as ferrous-ferric carbonate hydrate. Precipitation of that phases lowers the carbonate alkalinity by around 40 percent. That phase may qualify as precursor to siderite and could be an important primary inorganic precipitate from an Fe<sup>2+</sup>-bearing, sulfate-poor, reduced Archaean ocean in exchange equilibrium with a reduced CH<sub>4</sub>-bearing, CO<sub>2</sub>-poor atmosphere. We conclude that siderite is not likely to be a primary precipitate from Archaean seawater. We further conclude that potential precursor phases to siderite (i.e. amorphous Fe-carbonate-hydrates) are most stable at maximum CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup> activity ratios in the water, hence are favoured at atmospheric compositions poor in CO<sub>2</sub>.

[1] Ohmoto H., Wanatabe Y, Kumazawa K. (2004) *Nature* **429**, 395-399.

## Growth rate effect on oxygen isotope fractionation between calcite and fluid: *In situ* data

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The oxygen-18 content of carbonates (expressed as δ<sup>18</sup>O) is widely used in paleoclimatology, yet it is clear from comparison between experimental and natural carbonates that isotopic equilibrium is not always achieved. This observation underscores the importance of exploring possible effects of growth rate on isotopic fractionation, which is the focus of this study.

*In situ* Secondary Ion Mass Spectrometry (SIMS) analyses of δ<sup>18</sup>O were performed on single crystals of experimentally grown calcite at an external reproducibility of 0.25 ‰ (1σ). Growth rate (V) variations within crystals grown isothermally (at 15, 20, 22, and 25°C) were monitored by sequentially spiking calcite-precipitating fluids with rare earth element (REE) dopants. The REE were analyzed with SIMS at spots matching those where δ<sup>18</sup>O was determined. REE patterns reveal concentric domains of calcite growth. The growth rate of calcite generally decreases with time - i.e., crystal rims advanced at slower rates than cores. The compositions of δ<sup>18</sup>O in bulk calcites and experimental fluids were measured by Fisons Optima and Finnigan MAT 251 mass spectrometers, respectively. The average of SIMS δ<sup>18</sup>O values agrees with bulk δ<sup>18</sup>O determined by conventional mass spectrometry within analytical uncertainty. The fractionation factor (α<sup>18</sup>O) decreases by 0.8±0.08 ‰ with increasing V (0.12–16 μm/day) at 25°C. If the core is included at an estimated V>30 μm/day, a total range of 1.7 ‰ is observed at 25°C. A maximum difference of 3 ‰ was observed between the rim and core of the calcite crystal grown at 15°C.

Our results provide the first *in situ* evidence that <sup>18</sup>O may be depleted in the near-surface region of calcite relative to the bulk crystal lattice, consistent with the surface entrapment model [1]. As predicted, this effect increases with decreasing temperature. Therefore, knowledge of crystal growth rates needs to be accounted for when using δ<sup>18</sup>O in natural carbonates as a proxy for sea-water temperature.

[1] Watson (2004) *Geochim. Cosmochim. Acta*, **68**, 1473–1488.