

Oxygen isotope fractionation in the precipitation of calcite and aragonite

When carbonate minerals are precipitated from aqueous solution, ^{18}O is preferentially incorporated in the mineral, so that the $^{18}\text{O}/^{16}\text{O}$ ratio in the mineral is greater than that in the H_2O of the solution. The extent of this fractionation is temperature-dependent, in that the extent of the preferential incorporation of ^{18}O is greater at lower temperatures. Thus one expects plots like the diagram at right, in which fractionation factors increase with decreasing temperature.

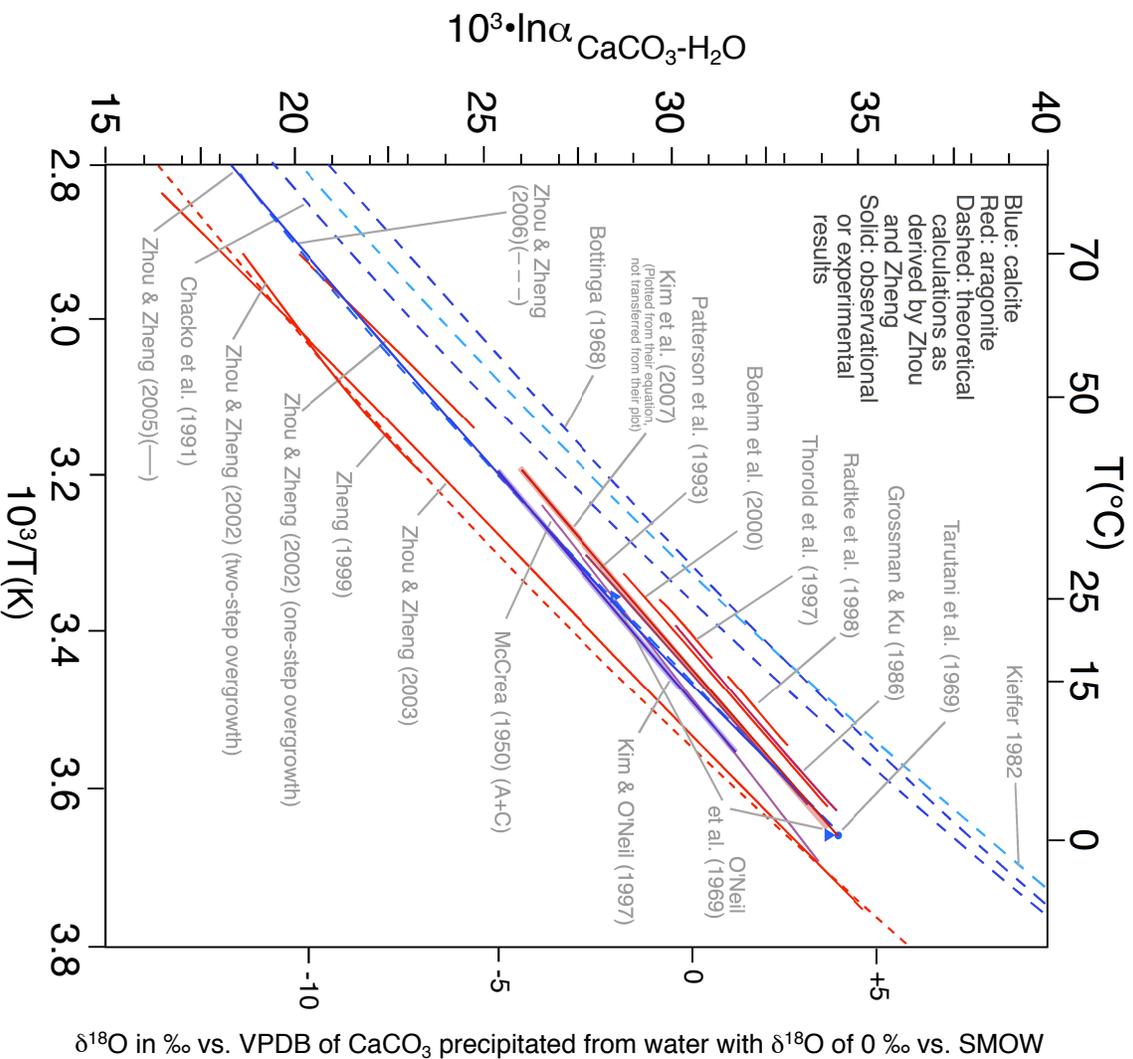
Though most of the late twentieth century, carbonate geochemists had assumed that the extent of this fractionation was greater in aragonite than in calcite, so that if the two minerals were precipitated from solutions of the same $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ at the same temperature, the aragonite would have a $\delta^{18}\text{O}_{\text{CaCO}_3}$ about 1 ‰ greater than that of the calcite. Researchers analyzing sequences of CaCO_3 with both aragonite and calcite therefore commonly "corrected" their aragonite data by subtracting 1 ‰ to allow comparison between data from the two polymorphs (a dubious practice at best).

All this was thrown into question in the early 2000s when Gen-Tao Zhou and Yong-Fei Zheng published a series of papers with data and calculations that called the assumption above into question. The diagram at right superposes curves shown in figures in their 2003, 2005, and 2006 papers. Comparison of curves representing theoretical calculations (the dashed lines at right) consistently suggest greater fractionation in calcite (blue) than aragonite (red). However, Horita and Clayton (2007) published a discussion questioning Zhou and Zheng's calculations in deriving the curves for calcite, a suggestion to which Zhou and Zheng (2007) replied in disagreement.

When one includes the results of Zhou and Zheng, experimental and observational data (solid lines) yield overlapping curves for aragonite and calcite. With regard to previous experimental work, and especially that of Kim and O'Neil (1997), Zhou and Zheng (2003 p. 397) reminded readers that experiments commonly result in precipitation of aragonite that in short times (hours) inverts to calcite, so that experiments seemingly reporting results from calcite may in fact actually report isotopic compositions and fractionations partly derived from original precipitation of aragonite. If that has happened, it would mean that experimental curves for calcite should be shifted away from the corresponding aragonite curves on the plot at right. However, Kim and O'Neil (2005) published a comment in which they argued that their 1997 results were derived solely from calcite, and in which they argued that the methods in the experiments of Zhou and Zheng may account for the difference between their results and those of virtually all previous researchers. Zhou and Zheng did not respond with a reply.

In 2007, Kim et al. (including O'Neil) published an equation for aragonite fractionation based on further experimental work. The resulting curve, shown at right in solid red with a wider background curve, lies above the curve from their 1997 equation for calcite, which is shown in solid blue with a broader background curve. Thus the combination of their work supported the conventional previous understanding: greater fractionation in aragonite would leave it about 0.8 ‰ enriched in ^{18}O relative to calcite precipitated at the same temperature out of a solution of the same $\delta^{18}\text{O}_{\text{H}_2\text{O}}$.

It's not clear where all this leaves us – it may leave us exactly where we were before. However, one should at least be aware that Zhou and Zheng (2003, 2005, and 2006) published equations that are counter to the work of others, and that unsuspecting use of equations from both groups will likely result in "apples and oranges" comparisons.



Kim and O'Neil 1997 *Geochimica et Cosmochimica Acta* 61: 3461-3475.
 Zhou and Zheng 2003 *Geochimica et Cosmochimica Acta* 67: 387-399.
 Zhou and Zheng 2005 *American Mineralogist* 90: 1121-1130.
 Kim and O'Neil 2005 *Geochimica et Cosmochimica Acta* 69: 3195-3197.
 Zhou and Zheng 2006 *Aquatic Geochemistry* 12: 239-268.
 Horita and Clayton 2007 *Geochimica et Cosmochimica Acta* 71: 3131-3135.
 Zhou and Zheng 2007 *Geochimica et Cosmochimica Acta* 71: 3136-3143.
 Kim et al 2007 *Geochimica et Cosmochimica Acta* 71: 4704-4715.