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Comment on “An experimental study of oxygen isotope fractionation between inorganically precipitated aragonite and water at low temperatures” by G.-T. Zhou and Y.-F. Zheng

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1. INTRODUCTION

Zhou and Zheng (2002, 2003) synthesized aragonite at low temperatures by two methods of precipitation from various solutions of $\text{Ca}(\text{HCO}_3)_2$ that contained seed crystals or Mg^{2+} . From the isotopic data obtained, these authors proposed a new relation for the equilibrium oxygen isotope fractionation between synthetic aragonite and water. In combination with previous determinations of the calcite-water fractionation, this new relation implies that the fractionation between aragonite and calcite is negative at low temperatures. Both the magnitude and the direction of the fractionation between these two polymorphs of CaCO_3 are highly controversial and bear importantly on our understanding of the oxygen isotope geochemistry of carbonates and carbonate-water systems, arguably among the most important geochemical systems examined in earth science. The authors suggested that certain calcite preparations judged by Kim and O’Neil (1997) to have formed in equilibrium with their parent solutions were instead precipitated initially as aragonite that subsequently transformed into calcite. The implication of this suggestion is that the fractionations we reported are not calcite-water fractionations but rather aragonite-water fractionations that are, in their view, significantly smaller than the equilibrium fractionations between calcite and water.

Zhou and Zheng (2003) present new experimental data and discuss some of the complexities in the oxygen isotope geochemistry of the calcite-aragonite-water system. We strongly disagree with them on a number of critical points that concern their experimental protocols and interpretations of analytical results obtained both by them and by us. In this comment we explain the bases of our disagreements and reaffirm our contention that the equilibrium calcite-water expression of Kim and O’Neil (1997) derived from experiments performed with dilute solutions of Na-Ca- HCO_3 is reliable.

The oxygen isotope fractionations between aragonite and water reported by Zhou and Zheng (2003) are significantly smaller than those obtained by most others (Tarutani et al., 1969; Grossman and Ku, 1986; Patterson et al., 1993; Thorrold et al., 1997; Böhm et al., 2000) and thus support their concept that the aragonite-calcite fractionation is negative. To the best of our knowledge, ^{18}O enrichment in calcite relative to aragonite has been suggested only twice (Tarutani et al., 1969; Horibe and Oba, 1972). In the first case, the authors examined the data set of Epstein et al. (1953) which contained analyses of

both polymorphs grown under relatively well known conditions. They concluded that there is no definitive direction of the fractionation between the two polymorphs, but there is a slight tendency for ^{18}O to be concentrated in calcite relative to aragonite. In the second case, analyses were made of aragonite and calcite from shells cultured in the wild. It has not been determined if the aragonite-bearing organism used in this study (*Andara broughtoni*) precipitates carbonate with a vital effect. A negative aragonite-calcite fractionation is predicted from calculations made by Zheng (1999).

Arguing that certain selected carbonates they synthesized were precipitated in isotopic equilibrium with water in the solutions employed, Zhou and Zheng (2003) conclude that (1) aragonite studied previously by others was precipitated out of isotopic equilibrium because of kinetic or metabolic effects, and (2) calcite synthesized by Kim and O’Neil (1997) inherited the isotopic properties of aragonite from which it was supposedly transformed in solution. On the contrary, relatively large (10–15 μm) rhombs of calcite precipitated in all our calcite experiments, and no transitions between CaCO_3 polymorphs were observed. We believe that solution chemical effects not considered by Zhou and Zheng (2003) provide more reasonable explanations for the results they obtained.

2. EFFECTS OF SOLUTION CHEMISTRY

The new aragonite-water relation (Eqn. 1 of Zhou and Zheng, 2003) was formulated by combining two independent sets of data from (1) precipitations at 50°C and 70°C by a two-step overgrowth method in solutions of Na_2CO_3 (Zhou and Zheng, 2002) and (2) slow precipitations at 0°C and 25°C from solutions of $\text{Ca}(\text{HCO}_3)_2$ variously containing relatively high concentrations of Na^+ , Mg^{2+} , and Cl^- (Zhou and Zheng, 2003). Major differences in the chemical compositions of the solutions employed in the two methods explain the differences in oxygen isotope compositions observed for aragonite synthesized by those methods.

2.1. The Two-Step Overgrowth Method

Important factors to consider when evaluating the two methods of aragonite synthesis employed by Zhou and Zheng (2002, 2003) are (1) rate of CaCO_3 precipitation and (2) pH of the solutions. The dilute solutions of Na_2CO_3 used in the two-step overgrowth method had a much higher pH (9.9 to 11.2) than the solutions used in the slow precipitation method (~7.0) where either NaHCO_3 or CaCO_3 was brought into solution by addition of CO_2 gas. Thus, in the two-step overgrowth method,

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CO_3^{2-} is by far the dominant species in solution compared to HCO_3^- , H_2CO_3 , and $\text{CO}_2(\text{aq})$. Most importantly, the $^{18}\text{O}/^{16}\text{O}$ ratio of CO_3^{2-} is much lower than that of HCO_3^- in carbonate solutions that are in internal equilibrium (Uzdowski et al., 1991; Uzdowski and Hoefs, 1993; Zeebe, 1999). As a consequence, aragonite precipitated quickly from high-pH solutions in which CO_3^{2-} is dominant will have a lower $\delta^{18}\text{O}$ value than aragonite precipitated at the same rate and temperature from solutions with lower pH. This effect arises simply because crystals growing relatively quickly, as they do in the two-step overgrowth method, have more chances to incorporate the more abundant and isotopically lighter CO_3^{2-} ions. In addition, surface carbonate has little opportunity to undergo subsequent equilibrium oxygen isotope exchange with water in such a solution. In effect, carbonate-water fractionations derived from aragonite quickly precipitated from a high pH solution *must* be smaller than fractionations derived from either abiogenic or biogenic aragonite that crystallized slowly from solutions with a circum-neutral pH. These facts explain why all aragonite synthesized in Na_2CO_3 solutions has a lower $^{18}\text{O}/^{16}\text{O}$ ratio than aragonite synthesized by other methods (Fig. 3 of Zhou and Zheng, 2003). As a consequence of these chemical and kinetic effects, the two-step overgrowth method of Zhou and Zheng (2002) is simply not a suitable protocol for synthesizing aragonite in isotopic equilibrium with water and dissolved carbonate species.

2.2. The Slow Precipitation Method

Aragonite-only precipitation in low-temperature aqueous solutions can be promoted by adding seed crystals and/or magnesium to the solution (Morse et al., 1997). Accordingly, Zhou and Zheng (2002, 2003) precipitated aragonite by adding SrCO_3 as a seed material in the two-step overgrowth method, and $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ in the slow precipitation method.

In the slow precipitation method employed at 0°C and 25°C by Zhou and Zheng (2003), 15–60 mM solutions of NaHCO_3 containing relatively high concentrations (32–1000 mM) of Mg^{2+} and Cl^- were used as starting solutions for aragonite synthesis. Because the ionic strengths of these solutions were relatively high, dissolved salts in the solution changed the isotopic properties of the free water molecules (O'Neil and Truesdell, 1991; Horita et al., 1993a, 1993b) and important ion pairs were formed. On the basis of speciation calculated using PhreeqcI v. 2.8 (Charlton and Parkhurst, 2002) and Geochemist's Workbench (Bethke, 1996, 1998) at $\text{pH} = 6.7\text{--}7.0$, MgHCO_3^+ is the dominant dissolved carbonate species in 4 out of the 6 solutions used by Zhou and Zheng (2003) in their slow precipitation method. Using the same method of calculation, HCO_3^- comprises more than 90% of the carbonate species in the dilute solutions used by Kim and O'Neil (1997). Despite a lack of evidence, it would seem likely that the oxygen isotope properties of MgHCO_3^+ would be quite different from those of HCO_3^- in a solution. In addition, these ion pairs influence aragonite solubility and possibly the precipitation mechanism as well. It is suggested, therefore, that oxygen isotope compositions of aragonite precipitated from concentrated solutions must be differentiated from those of aragonite synthesized from dilute solutions and those of biogenic aragonites precipitated from seawater (e.g., corals and foraminifera). In other words,

salt effects must be systematically evaluated, if possible, when investigating oxygen isotope fractionations between minerals and highly concentrated solutions at low temperatures.

3. THEORETICAL CALCULATION OF THE ARAGONITE-CALCITE FRACTIONATION

Zheng (1999) calculated oxygen isotope fractionations among carbonate and sulfate minerals using the modified increment method (Zheng, 1993). His calculated oxygen isotope fractionation between aragonite and calcite is -4.47‰ at 25°C . Regardless of sign, we consider the magnitude of this calculated fractionation to be unrealistic because it is much larger than the measured fractionation of -2.51‰ between witherite (BaCO_3) and calcite (CaCO_3) at the same temperature (Kim and O'Neil, 1997). These two carbonates have very different crystal structures and cations of very different size and mass. Given that the radius and mass of the cation are the dominant controls on oxygen isotope fractionations between carbonate minerals (O'Neil et al., 1969), the witherite-calcite fractionation should be larger than the aragonite-calcite fractionation. We conclude that one or more assumptions used in the aragonite calculation are invalid.

4. CONCLUSIONS

The nature and concentration of solutes as well as the pH of parent solutions strongly affect speciation of dissolved carbonate and influence the isotopic compositions of carbonates precipitated in both laboratory and natural environments. Failure to take into account these effects in the interpretation of data from laboratory experiments and the possible use of invalid assumptions in calculating partition function ratios of carbonate minerals may explain the conclusion of Zhou and Zheng (2003) that the aragonite-calcite fractionation is large and negative. Evidence presented by others and ourselves leads us to conclude that this fractionation is small and positive. If we are in doubt about merely the direction of this fractionation, our confidence level in the one oxygen isotope system we thought we understood fairly well (carbonate-water) must remain low.

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REFERENCES

- Bethke C. M. (1996) *Geochemical Reaction Modeling: Concept and Applications*. Oxford University Press.
- Bethke C. M. (1998) *The Geochemist's Workbench, Version 3.0: A Users Guide to Rxn, Act2, Tact, React and Gtplot*. Hydrogeology Program, University of Illinois, Urbana.
- Böhm F., Joachimski M. M., Dullo W.-C., Eisenhauer A., Lehnert H., Reitner J., and Wörheide G. (2000) Oxygen isotope fractionation in marine aragonite of coralline sponges. *Geochim. Cosmochim. Acta* **64**, 1695–1703.
- Charlton S. R. and Parkhurst D. L. (2002) PhreeqcI: A graphical user interface to the geochemical model PHREEQC: U.S. Geological Survey Fact Sheet FS-031-02, April 2002.
- Epstein S., Buchsbaum R., Lowenstam H., and Urey H. C. (1953) Revised carbonate-water isotopic temperature scale. *Bull. Geol. Soc. Am.* **64**, 1315–1326.

- Grossman E. L. and Ku T.-L. (1986) Oxygen and carbon isotope fractionation in biogenic aragonite: temperature effects. *Chem. Geol.* **59**, 59–74.
- Horibe Y. and Oba T. (1972) Temperature scales of aragonite-water and calcite-water systems. *Fossils* **23/24**, 69–79.
- Horita J., Cole D. R., and Wesolowski D. J. (1993a) The activity-composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions: I. Vapor-liquid water equilibration of single salt solutions from 50 to 100°C. *Geochim. Cosmochim. Acta* **57**, 2797–2817.
- Horita J., Cole D. R., and Wesolowski D. J. (1993b) The activity-composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions: II. Vapor-liquid water equilibration of mixed salt solutions from 50 to 100°C and geochemical implications. *Geochim. Cosmochim. Acta* **57**, 4703–4711.
- Kim S.-T. and O'Neil J. R. (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochim. Cosmochim. Acta* **61**, 3461–3475.
- Morse J. W., Wang Q., and Tsio M. Y. (1997) Influences of temperature and Mg:Ca ratio on CaCO₃ precipitates from seawater. *Geology* **25**, 85–87.
- O'Neil J. R. and Truesdell A. H. (1991) Oxygen isotope fractionation studies of solute-water interactions. In *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*. The Geochemical Society, Special Publication No. 3 (eds. H.P. Taylor, Jr., J.R. O'Neil, and I.R. Kaplan), pp. 17–25.
- O'Neil J. R., Clayton R. N., and Mayeda T. K. (1969) Oxygen isotope fractionation in divalent metal carbonates. *J. Chem. Phys.*, **51**, 5547–5558.
- Patterson W. P., Smith G. R. and Lohmann K. C. (1993) Continental Paleothermometry and seasonality using the isotopic composition of aragonitic otoliths of freshwater fishes. In *Climate Change in Continental Isotopic Records* (eds. P. K. Swart, K. C. Lohmann, J. McKenzie and S. Savin), Geophysics Monograph Series 78, pp. 191–202. American Geophysical Union.
- Tarutani T., Clayton R. N., and Mayeda T. K. (1969) The effect of polymorphism and magnesium substitution on oxygen isotope fractionation between calcium carbonate and water. *Geochim. Cosmochim. Acta* **33**, 987–996.
- Thorrold S. R., Campana S. E., Jones C. M., and Swart P. K. (1997) Factors determining $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ fractionation in aragonitic otoliths of marine fish. *Geochim. Cosmochim. Acta* **61**, 2909–2919.
- Uzdowski E. and Hoefs J. (1993) Oxygen isotope exchange between carbonic acid, bicarbonate, carbonate and water: A re-examination of the data of McCrea (1950) and an expression for the overall partitioning of oxygen isotope between the carbonate species and water. *Geochim. Cosmochim. Acta* **57**, 3815–3818.
- Uzdowski E., Michaelis J., Böttcher M. B., and Hoefs J. (1991) Factors for the oxygen isotope equilibrium fractionation between aqueous CO₂, carbonic acid, bicarbonate, carbonate and water (19°C). *Z. Phys. Chem.* **170**, 237–249.
- Zeebe R. E. (1999) An explanation of the effect of seawater carbonate concentration on foraminiferal oxygen isotopes. *Geochim. Cosmochim. Acta* **63**, 2001–2007.
- Zheng Y. F. (1993) Calculation of oxygen isotope fractionation in anhydrous silicate minerals. *Geochim. Cosmochim. Acta* **57**, 1079–1091.
- Zheng Y. F. (1999) Oxygen isotope fractionation in carbonate and sulfate minerals. *Geochim. J.* **33**, 109–126.
- Zhou G.-T. and Zheng Y. F. (2002) Kinetic mechanism of oxygen isotope disequilibrium in precipitated witherite and aragonite at low temperatures: An experimental study. *Geochim. Cosmochim. Acta* **66**, 63–71.
- Zhou G.-T. and Zheng Y. F. (2003) An experimental study of oxygen isotope fractionation between inorganically precipitated aragonite and water at low temperatures. *Geochim. Cosmochim. Acta* **67**, 387–399.