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Effect of magnesium ions on the stable oxygen isotope equilibrium between dissolved inorganic carbon species and water.

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Stable oxygen isotope (δ^{18}O) values of foraminiferal calcites, which represent one of the most fundamental paleoceanographic tools to reconstruct ancient seawater temperatures, are influenced by seawater pH variations. Understanding the driving mechanism for such phenomenon requires precise knowledge of the equilibrium ^{18}O fractionation factors between dissolved inorganic carbon (DIC) species and water. An experimental study by Beck et al. (2005) successfully refined the ^{18}O fractionation factors between DIC components and water. Based on these results, the overall ^{18}O fractionation between total DIC and water as a function of pH can be readily calculated (e.g., Zeebe, 2007). However, these calculations may not be applicable to seawater because the fractionation factors were measured in freshwater. Natural seawater contains numerous ionic species and other dissolved constituents, which may affect the fractionation factors. For example, it has been experimentally demonstrated that the presence of magnesium ions (Mg^{2+}) in solutions affect equilibrium carbon isotope (^{13}C) fractionation between aqueous CO_2 and carbonate ions presumably due to the enrichment of ^{13}C isotopes in Mg-CO_3^0 complexes (Thode et al., 1965). This suggests that the presence of Mg^{2+} in solutions similarly affects the ^{18}O fractionation factors between DIC species and water. On the other hand, Beck et al. (2005) concluded that the effect of ion pairs on the δ^{18}O equilibrium appears to be negligible. However, this conclusion may not apply to ion paring in general, because experiments were not conducted for metal ions other than Na^+. Given that Mg^{2+} has a marked effect on the equilibrium δ^{13}C fractionation factors and Mg-CO_3^0 is the most abundant form of metal-CO_3-complexes in natural seawater, the potential effect of Mg^{2+} on the ^{18}O fractionation factors between DIC components and water needs to be examined. Here, we will present preliminary results from quantitative carbonate precipitation experiments to evaluate the influence of Mg^{2+} on the δ^{18}O equilibrium in the DIC-water system.

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