An experimental study of hydrogen isotope fractionations between brucite and water at low temperatures

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Chemical synthesis techniques have been utilized to determine oxygen isotope fractionation factors between minerals and water at low temperatures. It appears that the formation of minerals in solutions is accompanied by a large change in free energy, which normally drives the achievement of complete isotope equilibrium between the minerals and water. If different reaction pathways are applied to synthesize the same minerals, the mechanism of mineral reactions can be explained in addition to testing for isotopic equilibrium. This can overcome the problem of incomplete equilibrium in partial exchange techniques due to the very low rates of isotopic exchange at low temperatures. In this study, chemical synthesis methods are used to produce brucite in aqeous solutions and to determine hydrogen isotope fractionations between brucite and water at low temperatures.

Methods

By using $MgCl_2$ and Mg_3N_2 as reactants, respectively, two different pathways of reaction are employed to synthesize $Mg(OH)_2$ in aqeous solutions at 25 to 90°C. It is based on the following equations of chemical reaction:

$$MgCl_2 + 2NaOH = Mg(OH)_2\downarrow + 2NaCl$$
$$g_3N_2 + H_2O = Mg(OH)_2\downarrow + NH_3\uparrow$$
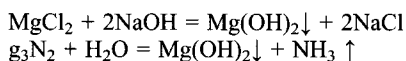
After all of the $Mg(OH)_2$ solutions produced by the different synthesis reactions were aged for enough time, precipitates were filtered out and the filtrated solutions were used for isotopic analyses. The precipitates were dried in oven at 100~120°C for 24 hours. Powder XRD technique was used for examining crystal structure and SEM for morphology.

Hydrogen isotope analysis of both brucite and water was following the conventional Zn-reduction method. Producibility of the hydrogen isotope analyses is generally better than $\pm 2‰$.

Results

With respect to the pathways of the two synthesis reactions there are different origins for hydrogen in the synthesized brucites. Hydrogen in the brucite synthesized by the $MgCl_2$ method was originated from both NaOH and water. The hydroxyl hydrogen in the NaOH would have attained hydrogen isotope equilibrium with the water in preparing the NaOH solution, thus the δD values of the brucite synthesized reflect those of the hydroxyls in isotopic equilibrium with the aqeous solution. Hydrogen in the brucite synthesized by the Mg_3N_2 method is originated only from water, so that complete isotope exchange is required to achieve hydrogen isotope equilibrium between the precipitated brucite and the water.

Figure 1 plots the hydrogen isotope fractionations between brucite and water derived from the synthesis experiments. The results show that the fractionations uniformly decrease in a linear fashion with decreasing temperatures from 90 to 25 and that there is a high degree of consistency between the results from the two different methods of synthesis within the limits of the analytical uncertainties. This demonstrates that hydrogen isotope equilibrium has been achieved between the synthesized brucite and water at the given temperatures. A linear regression of the data yields the following fractionation equation:

$$10^3 \ln\alpha = -4.88 \times 10^6/T^2 - 22.54$$

Apparently, brucite is depleted in D relative to coexisting water at low temperatures, and the degree of D-depletion becomes larger with decreasing temperatures.

There were dissolved salts ($MgCl_2$ and NaCl) in the reaction solution of the $MgCl_2$ method (the total concentration is 1.08 to 2.4 wt.%), while there was no dissolved salt in the reaction solution of the Mg_3N_2 method. However, inspection of the data shows that
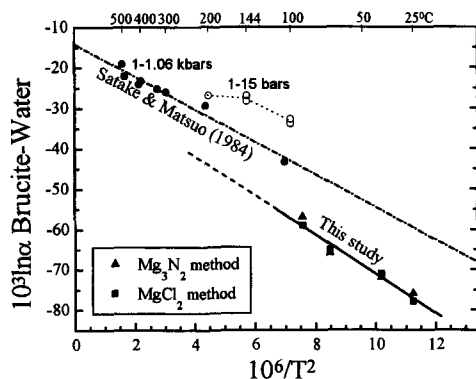
FIG. 1. Experimentally determined hydrogen isotope fractionations between brucite and water.

there is no significant effect of salt contents on the hydrogen isotope fractionations between brucite and water at the low temperatures.

There was a by-product of gaseous ammonia (NH_3) from the Mg_3N_2 method. Although a major part of the NH_3 gas has been escaped from the $Mg(OH)_2$ solution, there is still a little dissolved NH_3 as ammonia water (NH_4OH) which may exchange hydrogen isotopes with the solution. Since the hydrogen content of the dissolved NH_4OH is negligible relative to that of water in the solution (especially in the alkaline solution), no effect is expected on the hydrogen isotope fractionation between brucite and water. However, the δD values of water in the filtrated solution are -34 to $-45‰$, which are slightly different from the δD value of $-36‰$ for pure water used in the synthesis experiments. This may imply considerable influence of NH_3 outgassing on the hydrogen isotope composition of the solution.

Using partial exchange techniques Satake and Matsuo (1984) investigated hydrogen isotope fractionations between brucite and water under the hydrothermal conditions of high pressures (1000 to 1060 bar) and low pressures (1 to 15 bar), respectively. The temperature range for the high pressure experiments was from 510 to 100°C, whereas that for the low pressure runs was from 200 to 100°C. There were lower percentages of isotopic exchange in their low-pressures experiments

than those in the high-pressure runs. As shown in Fig. 1, the fractionations extrapolated from the low-pressure experiments are unreasonably greater than those from the high-pressure runs, suggesting isotopic disequilibrium for the low-pressure data.

It is known that pressure has significant effect on hydrogen isotope fractionations between hydroxyl-bearing minerals and water (Mineev and Grinenko, 1996; Driesner, 1997). In this regard, it may be appreciate to regress the experimental data of Satake and Matsuo (1984) only at the high pressures of 1000 to 1060 bars, which yields the following equation:

$$10^3 \ln\alpha = -4.04 \times 10^6/T^2 - 14.1$$

As depicted in Fig. 1, when the high-pressure fractionation data at the high temperatures above 100°C are extrapolated to the low temperatures below 100°C, they are systematically greater than those obtained from the synthesis experiments in this study. Numerically, the difference in fractionation is about 6.0‰ at 100°C and about 17.5‰ at 25°C.

The pressure effect can be also applied to explain the apparent discrepancies in the fractionation curves for the brucite-water system between the present synthesis experiments at the low pressures (1 bar) and the hydrothermal exchange experiments of Satake and Matsuo (1984) at the high pressures (1000 to 1060 bar). It is the difference in pressure that results in the high-pressure fractionations are apparently greater than the low-pressure ones.

By comparing the present results with existing calibrations involving the other low-temperature minerals, it suggests the following sequence of D-enrichment in hydroxyl-bearing minerals: Al^{3+}-OH > Mg^{2+}-OH > Fe^{3+}-OH.

Acknowledgements

References

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