Hydrogen Isotope Fractionation in the System Brucite-Water at 3 GPa

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Introduction

Upper mantle rocks are depleted in D by 80‰ relative to the oceans. As water is recycled through the upper mantle-hydrosphere system over geologic time, the offset between mantle and ocean is likely created by fractionation of isotopes during the processes of hydration and subsequent partial dehydration of subducted material. To understand how hydrogen isotope fractionation occurs during subduction, we need to know fractionation factors for hydrous mantle minerals at pressures and temperatures relevant to subduction.

As a pilot study to develop experimental and analytical techniques which will allow us to extend measurements to temperatures and pressures attainable in solid media high pressure apparatus, we have made measurements in the chemically simple brucite-water system, which has been the subject of previous high pressure experimental (up to 0.8 GPa, 600 ˚C) and theoretical work [1,2].

Experiments and Analysis

Piston cylinder experiments at 3 GPa, 500-700 ˚C
Thick walled Au capsules in NaCl pressure medium

Experiments quenched at >200 ˚C/s
Starting material: fine grained brucite (δD = -100 ‰) + water (δD = -190 to +117 ‰)

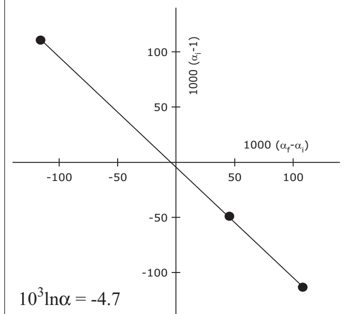
Partial exchange experiments consist of groups of 3 piston cylinder experiments:
> Same pressure, temperature, duration
> Same fluid/solid ratio
> Different starting water δD

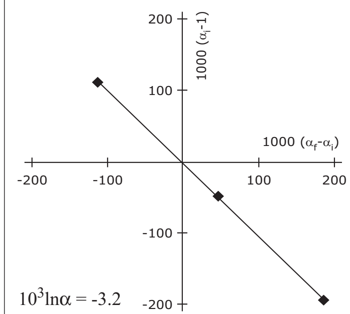
Water analysis
> Capsules recovered without weight loss
> Dried under vacuum for 12h
> Pierced and placed under Ar
> Non-condensed gases extracted at -90 ˚C
> Water extracted at 175 ˚C, under vacuum, for 1h
> Trapped water flooded with Ar, divided into 3 µl charges
> Analysed using standard Zn reduction [3]

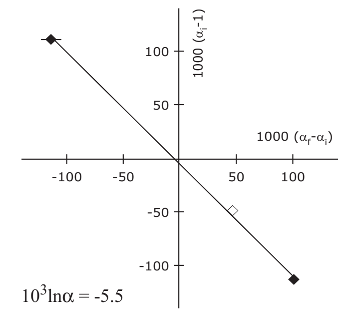
Brucite analysis
> Dried under vacuum for 12 h at 150 ˚C.
> Dehydrated at >900 ˚C (gas torch)
> Non-condensed gases passed over hot CuO
> Collected water analysed using standard Zn reduction
> NBS 30, VSMOW, VSLAP and GISP used as standards

Results

	3GPa, 500°C, 48h			3GPa, 700°C, 12h			3GPa, 700°C, 48h			700°C, 144h
Initial water δD (σ)	-190.1 (1.9), n=7	14.5 (1.1), n=3	-54.1 (1.7), n=12	-190.1 (1.9), n=7	117.1 (2.8), n=7	-54.1 (1.7), n=12	14.5 (1.1), n=3	-54.1 (1.7), n=12	-190.1 (1.9), n=7	-190.1 (1.9), n=7
Initial brucite δD (σ)	-100.4 (1.5), n=13	-100.4 (1.5), n=13	-100.4 (1.5), n=13	-100.4 (1.5), n=13	-100.4 (1.5), n=13	-100.4 (1.5), n=13	-100.4 (1.5), n=13	-100.4 (1.5), n=13	-100.4 (1.5), n=13	-100.4 (1.5), n=13
Final water δD (σ)	-153.2 (2.1), n=4	-43.6 (0.8), n=2	-66.6 (0.7), n=4	-155.9 (3.5), n=3	42.0 (3.5), n=5	-66.3 (0.5), n=4	-20.1 (1.3), n=3	*-68.3*	-153.0 (1.0), n=4	-158.6 (2.5), n=4
Final brucite δD (σ)	-157.7, n=1	-48.5, n=1	-69.9 (1.1), n=2	-157.7 (0.1), n=2	33.0 (0.1), n=2	-68.6 (3.1), n=2	-32.1 (1.4), n=2	-70.1 (0.1), n=2	-155.6 (7.1), n=2	-166.4 , n=1
Apparent 1000 ln(α)	-5.4	-5.2	-3.5 (1.4)	-2.1 (4.2)	-8.7 (3.4)	-2.4 (3.4)	-12.3(1.9)	*-1.9 (2.1)*	-3.0 (8.5)	9.3
Change in bulk δD (‰)	+6.5	-23.5	+1.1	+8.8	-8.1	+1.6	-1.3		+7.4	+6.6





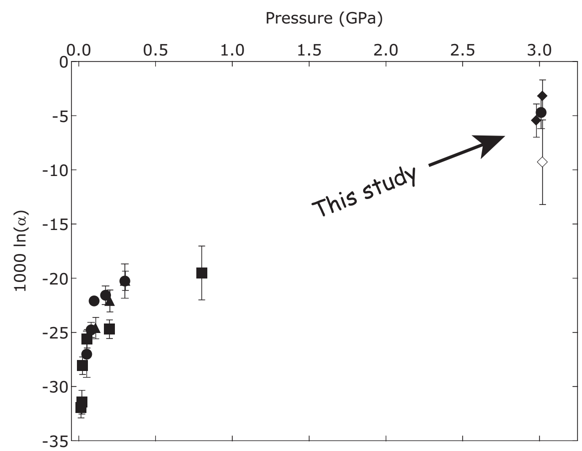


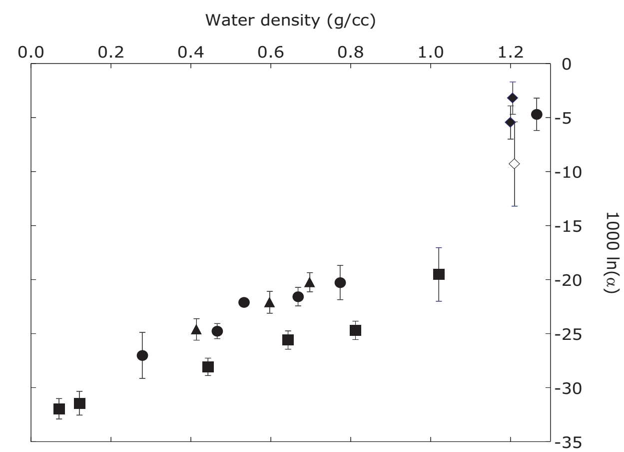
italicised figures and open symbol determined by mass balance calculations

$$\alpha_{brucite-water} = \frac{(D/H)_{brucite}}{(D/H)_{water}}$$

α_i = α at start of experiment
α_f = α at end of experiment

δD reported relative to SMOW





Key for graphs:
■ 380°C, Horita et al.
● 500°C, Horita et al., Satake & Matsuo, This Study
▲ 600°C, Horita et al.
◆ 700°C, This Study (open symbol represents single experiment)
3 GPa data are offset for clarity

Conclusions

Bulk δD measured at the end of an experiment is different to calculated bulk δD, indicating either diffusive exchange with pressure medium or significant absorbed water in the starting material

Brucite-water fractionation factors ($10^3\ln\alpha$) are smaller than -10 at 3 GPa and 500-700 ˚C

Pressure has a significant effect on D/H fractionation, even at elevated pressures and temperatures

Measurements of hydrous and nominally anhydrous mantle phases are required to understand D/H systematics of the Earth

References

[1] Horita J., Cole D.R., Polyakov, V.B. and Dreisner, T. (2002) Experimental and theoretical study of pressure effects on hydrogen isotope fractionation in the system brucite-water at elevated temperatures. *Geochimica et Cosmochimica Acta* 66: 3769-3788

[2] Satake H. and Matsuo S. (1984) Hydrogen isotopic fractionation factor between brucite and water in the temperature range from 100 to 510 ˚C. *Contributions to Mineralogy and Petrology* 86: 19-24

[3] Vennemann T.W. and O'Neil J.R. (1993) A simple and inexpensive method of hydrogen isotope and water analyses of minerals and rocks based on zinc reagent. *Chemical Geology* 103: 227-234