D/H fractionation during phase separation of seawater in subseafloor hydrothermal systems: Isobaric heating and adiabatic decompression

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Introduction

Large Cl variations in mid-ocean ridge vent fluids suggest that phase separation processes are occuring in many sub-seafloor hydrothermal systems. However, relatively little is known about whether the actual process that occurs is induced by heating or decompression and whether the hydrothermal systems are best characterized as either open or closed with respect to mass. One way to distinguish between possible styles of phase separation may be to use δD and Cl measurements in vent fluids. Vent fluids reveal distinct differences in isotopic systematics at different sites (Shanks *et al.*, 1994). However, data on hydrogen isotope fractionation related to phase separation at temperatures and pressures in the vicinity of the critical point of seawater are lacking. Here we present new experimental measurements of hydrogen isotope fractionation factors (α) for coexisting brines and vapours in the two-phase region of seawater which can be used to model the effect of phase-separation on hydrogen isotopes in mid-ocean ridge hydrothermal systems.

Methods

Phase separated $NaCl$–H_2O fluids were generated using flexible-cell hydrothermal techniques similar to those described by Berndt and Seyfried (1991). Following equilibration times ranging from 3 to 14 days, vapours and brines were sampled through a capillary line extending from the top of the reaction cell to a sampling valve outside the furnace. The reaction cell, which was held within a water-filled autoclave, could be rocked through a 180° angle to permit sequential sampling of coexisting brines and vapours. Samples for isotopic analysis were reduced to H_2 by reaction with zinc reagent at 500°C for 30 minutes.

Results

All vapour samples were enriched in D relative to their coexisting brines. These data suggest a statistical preference for ion-hydration processes to exclude D relative to H. We note, for example, that the larger difference there is in the Cl concentrations in brine/vapour pairs, the greater the isotopic fractionation. Thus, the amount of fractionation in the two phase region of seawater increases with increasing temperature or decreasing pressure owing to temperature and pressure dependent changes in the compositions of coexisting vapours and brines. This fractionation obeys the following relationship:

$$1000 \ln\alpha_{vap-br} = 3.0 + 2.53 \log (P_{cr} - P) \qquad (1)$$

where P_{cr} is the maximum pressure of two-phase coexistence at the temperature of interest (defined by the critical curve) and P is the pressure for which α corresponds (Fig. 1).
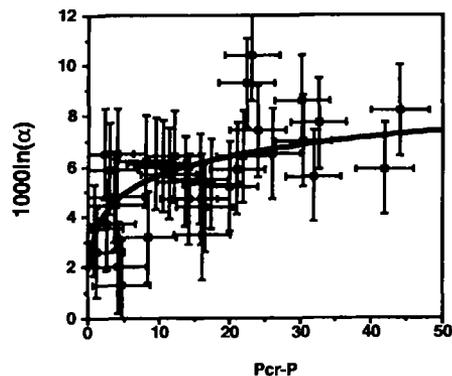

FIG. 1. 1000 $\ln\alpha_{vap-brine}$ as a function of P_{cr} – P for fluids samples from hydrothermal experiments. Curve corresponds to equation (1) in text.
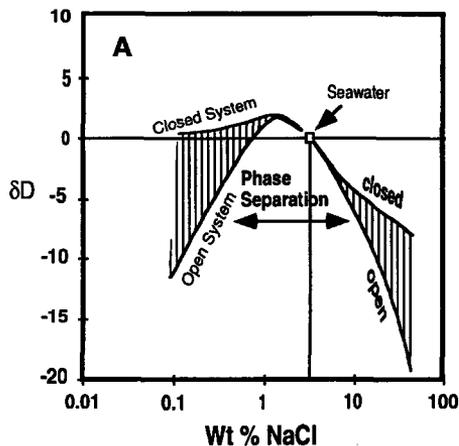
FIG. 2. δD vs. wt% NaCl of hydrothermal fluids derived during phase separation of seawater by isobaric heating at 300 bar.
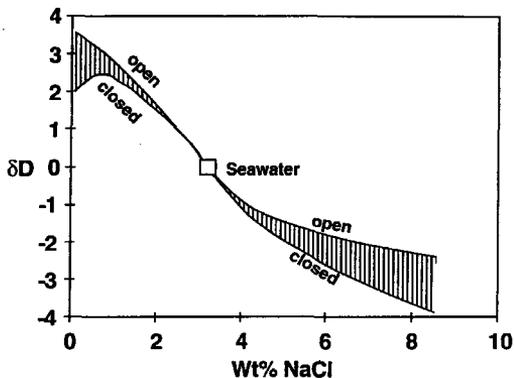

FIG. 3. δD and wt% NaCl of fluids produced during phase separation by adiabatic decompression where ascending fluid intersect the two phase surface at 409°C and 304 bar and follow an adiabat to the seafloor (250 bar).

Application

Equation (1) can be used along with composition data for the NaCl–H$_2$O system (Bischoff and Pitzer, 1989) to model the effect of phase separation on the hydrogen isotopic composition of mid-ocean ridge hydrothermal fluids. Closed-system isobaric phase separation, for example, results in δD values which are only slightly elevated with respect to initial seawater while the brines have greatly reduced δD values (Fig. 2). The mass of vapour evolved during this process is generally much larger than the mass of the brine, thereby eliminating the possibility for large fluctuations in δD of vapours by closed-system isobaric heating in subseafloor environments. The maximum δD for vapours produced by this mechanism decreases with increasing pressure, due to the increasing salinity and decreasing mass of coexisting brines.

Much larger fluctuations in the isotopic compositions of vapours and brines are obtained during isobaric heating in an open system. This type of model permits the relatively buoyant vapour phases to escape continuously during heating but retains the brine phase for further heating and phase separation. In this case, δD of the vapour phase decreases rapidly with decreasing Cl concentration (Fig 2). Shanks et al. (1994) have suggested the possibility of direct magmatic water contribution from a crystallizing dike to account for low negative δD values in low salinity vents at 9–10°N, but open-system isobaric phase separation may help produce the negative δD fluids.

Boiling during adiabatic decompression can also be modeled as an open or a closed process, however, in this case, the open system is represented by incremental loss of brine from an ascending vapour phase. This type of model applies to fluids which intersect the two phase surface during ascent to the seafloor rather than by heating on approach to a magma chamber. Our results indicate that fluids evolving in this type of system will reveal a negative correlation between δD and Cl for both the brine and vapour phases, regardless of whether the system is open or closed (Fig. 3). Some of the isotopically heavy and low salinity vent fluids sampled at Endeavor and Axial may have been affected by this type of process.

In contrast, high salinity vent fluids at most localities tend to have positive δD values which cannot be accounted for by simple phase separation processes (Shanks, 1994). This suggests that high salinity vent fluids have relatively long residence times in the oceanic crust at conditions conducive to formation of hydrous alteration phases.

References

Berndt, M. E. and Seyfried, W. E., Jr. (1990) Geochim. Cosmochim. Acta, 54, 2235–45.

Bischoff, J. L. and Pitzer, K. S. (1989) Amer. J. Sci., 289, 217–48.

Shanks, W. C. III, J. K. Bohlke and R. R. Seal II (1994) In Physical, Chemical, Biological, and Geological Interactions within Hydrothermal Systems, (J. Lupton, L. Mullineaux and R. A. Zierenberg, eds.), American Geophysical Union, AGU Monograph, in press.