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STABLE ISOTOPE PARTITIONING IN BRINE-GAS-MINERAL SYSTEMS RELEVANT TO GEOTHERMAL RESOURCES

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ABSTRACT

We present an overview of our experimental program investigating the kinetics and equilibrium of isotope partitioning in the systems: liquid-vapor, C-O-H gases, and mineral-water, conducted at Oak Ridge National Laboratory. Our research demonstrates that not only temperature, but also pressure and fluid composition, are key variables in determining equilibrium isotope partitioning between water and other materials at elevated temperatures. The kinetics of isotopic exchange in C-O-H gases and mineral-water is controlled by many other factors (grain size, mineral catalysts, fracturing in rocks). Our new, precise data on isotope fractionation, both kinetic and equilibrium, are useful for the interpretation and modeling of isotopic data from various geothermal systems.

1. INTRODUCTION

The distribution of the stable isotopes of oxygen, hydrogen, carbon, and other light elements (D/H, $^{18}O/^{16}O$, $^{13}C/^{12}C$, *etc*.), which partition as a function of temperature and the bonding characteristics of individual phases, has been widely studied in geothermal systems in order to constrain their time-temperature history, the sources and fluxes of fluids, the extent of boiling and mineral deposition from the fluids, and the temporal relationship among alteration minerals. Despite the wide use of the isotopic techniques for the exploration and development of geothermal energy resources, fundamental information on how stable isotopes partition at conditions encountered in geothermal systems is still limited. Furthermore, it has recently been recognized that pressure and fluid composition also significantly affect equilibrium fractionation between aqueous fluids and other phases. These two variables are particularly relevant to geothermal systems.

The objectives of our research are twofold:

(1) Provide a set of internally consistent, precise experimental results on the partitioning of oxygen and hydrogen isotopes among geothermal materials (water, brines, steam, gases, and minerals) as a function, not only of temperature, but also of pressure and fluid composition, that can be directly used to better characterize geothermal reservoirs (temperature, origin and residence time of fluids, phase separation, and water-rock interaction) and to trace injected fluids to production sites, in order to monitor injectate breakthrough and assess their contribution to steam production.

(2) Develop general isotopic models of geothermal systems at various physical and chemical conditions, which can be used to interpret isotopic data of geothermal fluids and rocks (boiling, degassing, mineral precipitation, *etc*.).

2. METHODS AND TECHNIQUES

To achieve the above goals, we have been conducting detailed, systematic experimental isotope studies for different systems: (a) liquid-vapor system of pure water and brines, (b) C-O-H gas system, and (c) mineral-water system, utilizing the unique, state-of-the-art experimental-analytical facilities and expertise available at Oak Ridge National Laboratory.

3. RESULTS

3.1 Liquid-Vapor System

The phase separation of water (boiling and condensation) is a fundamental physical process in geothermal systems, affecting the transport of energy and material. The salinity of geothermal waters varies widely depending on the source of water (fresh meteoric waters to hypersaline magmatic brines) and the stage of the phase separation.

Pure-water system

Liquid-vapor partitioning of oxygen and hydrogen isotopes was precisely determined over a wide range of temperature from 25° to 350°C. All experimental data on the fractionation factor $\alpha_{liquid\text{-}vapor}$, including those from the literature, were fitted to simple equations as a function of temperature (Figs. 1 and 2, Horita and Wesolowski, 1994). Both the oxygen and hydrogen isotope fractionation factors are very sensitive to the temperature of the phase separation. The vapor phase is enriched in deuterium compared to the liquid phase above 229°C ("cross-over"), while the liquid phase is always enriched in ^{18}O.

Salt-solution system

It is of great importance to understand the liquid-vapor isotope partitioning of salt solutions at elevated temperatures, because deep-seated, high-temperature (magmatic?) fluids in geothermal systems are often hypersaline. Our results show that naturally occurring salts (NaCl, KCl, $CaCl_2$, *etc*.) change measurably the liquid-vapor isotope partitioning compared to the pure water system (the isotope salt effect) (Horita *et al*., 1993a, b, 1995). Our results for NaCl brine-steam to 350°C show that the value of $10^3\ln\alpha_{brine\text{-}vapor}(D/H)$ is always smaller than that of pure water, while the value of $10^3\ln\alpha_{brine\text{-}vapor}(^{18}O/^{16}O)$ starts to deviate to more positive values with increasing temperature (Figs. 1 and 2). The deviations from pure water are indeed large at elevated temperatures. Recent studies in the literature (Berndt *et al.*, 1996; Shmulovich *et al.*, 1999; Driesner and Seward, 2000) also support our results that there exists substantial liquid-vapor isotope fractionation at temperatures up to 600°C.

Liquid-vapor isotope fractionation of complex mixed brines such as Salton Sea brines is also significantly different from that of a pure water system. The magnitude of these deviations (salt effects) can be easily calculated as a summation of the effects caused by each single salt solution (Horita *et al.*, 1993b).

3.2 C-O-H Gas System

Geothermal fluids are composed of water and various proportions of other C-O-H fluids (CO_2, CO, CH_4, H_2, *etc.*). The composition of these C-O-H fluids, which is determined by many thermodynamic variables (P, T, fO_2, C/O/H ratios, *etc.*), has been used for evaluating reservoir temperatures (chemical geothermometry). The isotopic composition (D/H, $^{13}C/^{12}C$, $^{18}O/^{16}O$) of these gases has also been used for estimating the temperature of reservoirs (isotope geothermometry), but there are conflicting results in the literature as to the practical utility of these isotopes. The behavior of carbon isotopes between CO_2 and CH_4, the two most dominant C-bearing gases, is particularly problematic, and there is even a doubt whether the $^{13}C/^{12}C$ equilibrium can be achieved under geothermal conditions. We have conducted a series of experiments to investigate kinetic and equilibrium partitioning of $^{13}C/^{12}C$ between CO_2 and CH_4 at elevated temperatures.

Equilibrium isotope fractionation in the system CO_2-CH_4

In the presence of a Ni-catalyst, CO_2 and CH_4 approached equilibrium $^{13}C/^{12}C$ values from opposite directions (isotopic reversal) over a wide range of temperatures from 200° to 600°C within a few days to a few weeks (Fig. 3). The isotopic exchange was promoted by net chemical reactions involving many C-O-H gases (CO_2, CH_4, H_2O, and H_2) as the gas composition approached the expected equilibrium compositions. Our experimental values of $10^3\ln\alpha(CO_2\text{-}CH_4)$ are slightly, but systematically greater than theoretical calculations (Richet *et al.*, 1977). Our experiments demonstrate that the $^{13}C/^{12}C$ equilibrium between CO_2 and CH_4 can be readily attained in the presence of suitable catalysts, possibly including naturally-occurring minerals with high transition metal contents.

Kinetic isotope fractionation during CO_2 reduction to CH_4

The partitioning of $^{13}C/^{12}C$ ratios was investigated during the hydrothermal formation of CH_4 from CO_2 dissolved in water under reducing conditions at 200°-400°C and 500 bars, similar to those of mid-ocean ridge systems and ophiolite zones (Horita and Berndt, 1999).

$$HCO_3^- + 4H_2 \ \Psi \ CH_4 + 2H_2O + OH^- \qquad (1)$$

No CH_4 was formed in the presence of magnetite. However, hydrothermally formed Ni-Fe alloy catalyzed the above reaction significantly. Carbon mass-balance shows that an intermediate product(s) formed during the reduction of CO_2 to CH_4, and it is most likely formate ion ($HCOO^-$) rather than carbon deposits. The CH_4 formed was very depleted in ^{13}C (35 to 60‰) compared to the starting CO_2 and isotopically indistinguishable from typical biogenic CH_4 (Fig. 4). $\delta^{13}C$ values of the intermediate product, calculated based on a $^{13}C/^{12}C$ balance, were between those of the CO_2 and CH_4, but eventually became greater than the CO_2.

3.3 Mineral-Water System

The isotopic exchange in mineral-water systems can be accomplished by many different processes: (a) transformation of host rocks to secondary minerals, (b) recrystallization of existing minerals via dissolution-precipitation cycles, and (c) diffusion. Temperature, pressure, solution composition, and grain size are major factors controlling the kinetics of isotope exchange. Equilibrium isotope fractionation between mineral and water has been considered to be independent of pressure and fluid composition. However, our recent results demonstrate that these two variables can change mineral-water isotope partitioning. Here, we briefly summarize results of our laboratory experiments on the kinetic and equilibrium isotope partitioning of several mineral-water systems (carbonates, hydrous minerals) at temperatures from 200° to 700°C.

Kinetics of isotopic exchange in the system calcite-water

Variations in the extent of oxygen isotope exchange, $F=(\alpha_i-\alpha_f)/(\alpha_i-\alpha_{eq})$, have been measured in the system calcite-water as a function of temperature (300°-600°C), pressure (0.25-2 kbars), and NaCl concentration (0-4 molal) at a water-solid ratio of 4 for run durations of 211-1956 hr. There is a pronounced increase in the F-values with increasing temperature, salinity, pressure, and degree of grain coarsening (Fig. 5). The rate of change in F is initially steep, but tends to flatten out with increasing NaCl above 1 molal. These data were used to estimate the rate of isotopic exchange in the calcite-H_2O-NaCl system (Cole, 1992).

Effect of pressure and solution composition on equilibrium isotope fractionation

We have been investigating the effect of pressure and fluid composition on equilibrium oxygen and hydrogen isotope fractionation between minerals (calcite, brucite) and water at 200°-500°C and 150-8000 bars with 0-5 molal NaCl solutions (Horita *et al.*, 1995; 1999). The isotope pressure and salt effects (Γ_P and Γ_X) at a given temperature can be determined as,

$$10^3\ln\Gamma_{P\text{ or }X} = 10^3\ln\alpha_{\text{mineral-brine, }P} - 10^3\ln\alpha_{\text{mineral-pure water, }P(\text{ref})} \qquad (2)$$

Equilibrium D/H fractionation factor between brucite, $Mg(OH)_2$, and pure water systematically increased 12.4‰ with pressure increase from 0.15 to 8 kbars at 380°C (Fig. 6). A good linear relationship was observed between the measured D/H fractionation factor and the density of water (0.070 to 1.035 g/cm^3). The trend of the isotope pressure effect observed is the same as that of recent theoretical studies (Polyakov and Kharlashina, 1994; Driesner, 1997), but the magnitude is smaller. These are the first unambiguous experimental results that demonstrate the effect of pressure on equilibrium isotope fractionation. A 5 molal NaCl solution also increased the brucite-water D/H fractionation factor 4 to 8‰ at 380°C, and at 200 and 250 bars.

We also conducted experiments to determine the effect of dissolved NaCl on calcite-water $^{18}O/^{16}O$ fractionation at 300°-400°C and 1 kbars. Despite large errors resulting from low F-values (7-25%), a systematic decrease in the $10^3\ln\alpha_{calcite\text{-}water}$ was observed with increasing NaCl concentration at 300°C (Fig. 7). This result is consistent with those obtained from the liquid-vapor equilibration method (Fig. 2).

4. DISCUSSION

The mechanisms and rates of isotopic exchange among different chemical systems within a geothermal system varies significantly, and a time scale for achieving chemical and isotopic equilibria would range from near instantaneous (liquid-vapor system) to hundreds to thousands of years (mineral-water system).

The phase separation of volatiles (exolution from melts, boiling and condensation of water, degassing from water, *etc.*) are rapid and (near) equilibrium processes. High-salinity (magmatic?) brines likely exist at great depths in many geothermal systems. The trajectory of isotopic evolution during adiabatic decompression and phase separation of ascending water depends on the salinity. The contrasting liquid-vapor behavior of hydrogen and oxygen isotopes at elevated temperatures (the vapor phase is depleted in ^{18}O, but enriched in deuterium compared to the liquid phase) may contribute to observed large variations in D/H ratios of waters associated with magmatic environments.

When both steam and water are sampled, their isotopic compositions, particularly the $\Delta D/\Delta^{18}O=(\delta D_{liquid}-\delta D_{vapor})/(\delta^{18}O_{liquid}-\delta^{18}O_{vapor})$, can be used as an isotope geothermometer (Horita and Wesolowski, 1994). From the isotopic composition of water and steam from the Otake Geothermal field in Japan (Mizutani, 1972), an isotopic temperature of 140°-150°C was calculated, which is slightly higher than the measured steam temperature (136°C). The $\Delta D/\Delta^{18}O$ is of better use than the values of ΔD or $\Delta^{18}O$, because the latter are strongly affected by the contamination and condensation of steam. The isotopic composition of water can also be used as a tracer for evaluating the extent of recovery of reinjected water from power plant steam condensate, because steam condensate is significantly enriched in both deuterium and ^{18}O, due to evaporation at the surface.

D/H and $^{18}O/^{16}O$ isotope geothermometers of geothermal gases (H_2O-H_2, CH_4-H_2, and H_2O-CO_2) generally yield results consistent with measured temperatures or those calculated with cation/solubility geothermometers. However, results of $^{13}C/^{12}C$ (CO_2-CH_4) are largely discordant with other techniques. A similar result was obtained from fluids venting from sediment-free mid-ocean ridges. The discrepancies among the different isotope geothermometers of C-O-H gases are due to the difference in isotope exchange rates of different gaseous species in the order H_2O-CO_2(oxygen) > H_2O-H_2(hydrogen) > CH_4-H_2(hydrogen) > CO_2-CH_4(carbon) (Hulston, 1977). There is an increasing number of studies which suggest that heterogeneous reactions catalyzed by the surface of minerals with high contents of transition metals (Ni, Fe, Co, *etc.*) play a key role in chemical and isotopic reactions among C-O-H gases. Our experimental results clearly demonstrate that even small amounts of naturally occurring material can catalyze chemical reactions involving CO_2 and CH_4, and thus carbon isotope exchange between the two gases. The exact role of such mineral catalysts in nature is still not well understood.

Isotope exchange between minerals and fluids are the slowest among many chemical systems. A dominant process whereby isotopic exchange is accomplished under typical geothermal conditions is the alteration of host rocks to secondary minerals. Temperature, pressure, the mineralogy, grain size, and isotopic composition of host rocks, the chemical and isotopic compositions of fluids, redox conditions, and water-rock ratios are main variables in controlling the rate and equilibrium isotopic composition of minerals. Alteration minerals in geothermal systems appear to be in oxygen isotope equilibrium with prevailing fluids (Cole, 1994). The degree of oxygen isotopic equilibration between whole rocks and aqueous fluids is also controlled by the above variables, and increases with increasing temperature, salinity, and intensity of fracturing (Fig. 8, Cole, 1994). The ability for fractures to remain open or to propagate, allowing continued fluid flow, may be the deciding factor in the attainment of isotopic equilibration in geothermal systems as a whole. Hydrogen isotope composition of hydrous minerals is, on the other hand, a better indicator of the source (magmatic, meteoric), evolution (exolution, phase separation), and hydrodynamic flow (mixing) of geothermal fluids.

Our experimental results demonstrate that in addition to temperature, pressure and dissolved salts can modify substantially an isotope fractionation factor between water and coexisting phase (mineral, steam, gas);

$$\alpha_{A\text{-water}} = f(T, P, X_{fluid}) \qquad (3)$$

In geothermal systems where pressure is relatively low (#1 kbars) and salinity of deep-seated brines could be high (∃10 wt%), pressure and fluid composition may be at least as important as temperature in determining isotopic fractionation between fluids and other phases. Many mineral-water D/H fractionation factors reported in the literature are rather insensitive to temperature. Thus, if not taken into account, pressure variations alone could lead to large errors (∃100°C) in calculated formation temperatures. It is of great interest to understand whether C-O-H-N-S gases, which can be major components of geothermal fluids, affect mineral-water isotope fractionation.

5. CONCLUSIONS

During the last few decades, the application of stable isotope techniques has matured and become one of the standard geochemical methods in the study of geothermal systems. The recognition of pressure and fluid composition as important variables in isotope partitioning could provide a new opportunity for the use of stable isotopes (isotope geobarometry). A basic knowledge of isotope partitioning is becoming increasingly important in an era when micro-analytical techniques (ion-probe, laser-probe, and compound-specific isotope analyses) and computer-based modeling techniques are developing rapidly.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

Berndt, M.E., Seal, R.R. II, Shanks, W.C. III, and Seyfried, W.E., Jr. (1996) Hydrogen isotope systematics of phase separation in submarine hydrothermal systems: Experimental calibration and theoretical model. *Geochim. Cosmochim. Acta* Vol.60, pp1595-1604.

Bottinga, Y. (1969) Calculated fractionation factors for carbon and hydrogen isotope exchange in the system calcite-carbon dioxide-graphite-methane-hydrogen-water vapor. *Geochim. Cosmochim. Acta* Vol.33, pp49-64.

Cole, D.R. (1992) Influence of solution composition and pressure on the rates of oxygen isotope exchange in the system: calcite-H_2O-NaCl at elevated temperatures. *Chem. Geol.*, Vol.102, pp199-216.

Cole, D.R., (1994) Evidence for oxygen isotope disequilibrium in selected geothermal and hydrothermal ore deposits systems. *Chem. Geol.*, Vol.111, pp283-296.

Craig, H. (1953) The geochemistry of the stable carbon isotopes. *Geochim. Cosmochim. Acta* Vol.3, pp53-92.

Driesner, T. (1997) The effect of pressure on deuterium-hydrogen fractionation in high-temperature water. *Science* Vol.277, pp791-794.

Driesner, T. and Seward, T.M. (2000) Experimental and simulation study of salt effects and pressure/density effects on oxygen and hydrogen stable isotope liquid-vapor fractionation for 4 molal NaCl and KCl aqueous solutions to >400°C. *Geochim. Cosmochim. Acta* (in press).

Horita J., Wesolowski D.J., and Cole D.R. (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* Vol.57, pp2797-2817.

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* Vol. 57, pp4703-4711.

Horita, J. and Wesolowski, D.J. (1994) Liquid-vapor fractionation of oxygen and hydrogen isotopes of water from the freezing to the critical temperature. *Geochim. Cosmochim. Acta* Vol.58, pp3425-3437.

Horita, J., Cole, D.R., and Wesolowski, D.J. (1995) The activity-composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions. III: Vapor-liquid water equilibration of NaCl solutions to 350°C. *Geochim. Cosmochim. Acta* Vol.59, pp1139-1151.

Horita, J. and Berndt, M.E. (1999) Abiotic methane formation and isotopic fractionation under hydrothermal conditions. *Science*, Vol.285 pp1055-1057.

Horita, J., Driesner, T., and Cole, D.R. (1999) Pressure effect on hydrogen isotope fractionation between hydrous minerals and water at elevated temperatures. *Science* Vol.286, pp1545-1547.

Hulston, J.R. (1977) Isotope work applied to geothermal systems at the Institute of Nuclear Sciences, New Zealand. *Geothermics* Vol.5, pp89-96.

Mizutani, Y. (1972) Isotopic composition and underground temperature of the Otake geothermal water, Kyushu, Japan. *Geochem. J.* Vol.6, pp67-73.

O'Neil, J.R., Clayton, R.N., and Mayeda, T.K. (1969) Oxygen isotope fractionation in divalent metal carbonates. *J. Chem. Phys*. Vol.51, pp5547-5558.

Polyakov, V.B. and Kharlashina, N.N. (1994) Effect of pressure on equilibrium isotopic fractionation. *Geochim. Cosmochim. Acta* Vol.58, pp4739-4750.

Richet, P., Bottinga, Y., and Javoy, M. (1977) A review of hydrogen, carbon, nitrogen, oxygen, sulfur, and chlorine stable isotope fractionation among gaseous molecules. *Ann. Rev., Earth Planet. Sci*. Vol.5, pp65-110.

Shmulovich, K.I., Landwehr, D., Simon, K., and Heinrich, W. (1999) Stable isotope fractionation between liquid and vapor in water-salt systems. *Chem. Geol*. Vol.157, pp343-354.

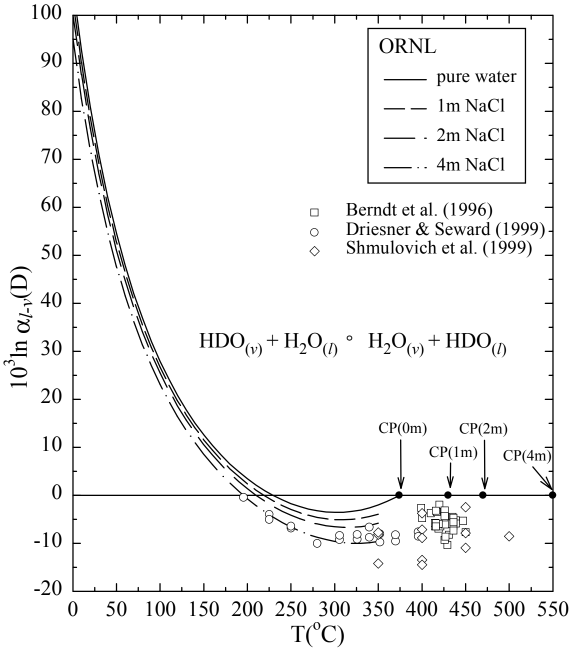

Fig. 1 Water liquid-vapor D/H partitioning (Horita *et al.*, 1995)

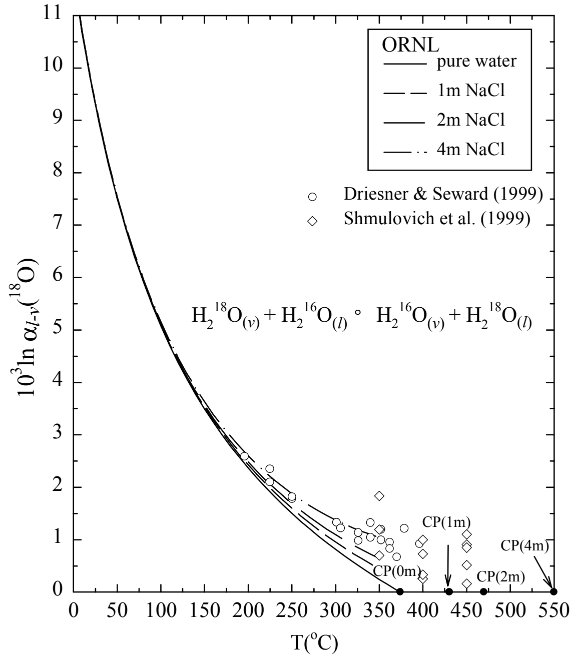

Fig. 2 Water liquid-vapor $^{18}O/^{16}O$ partitioning (Horita *et al.*, 1995)

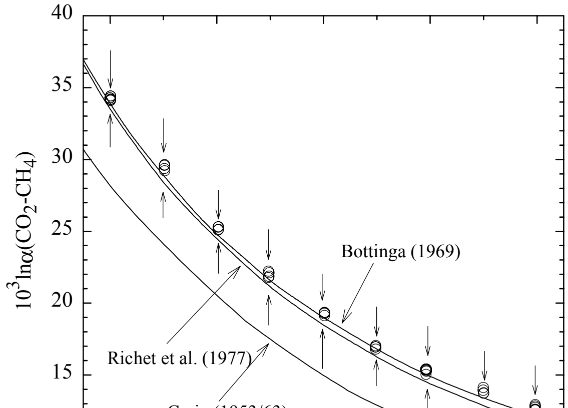

Fig. 3 Equilibrium CO_2-CH_4 $^{13}C/^{12}C$ partitioning

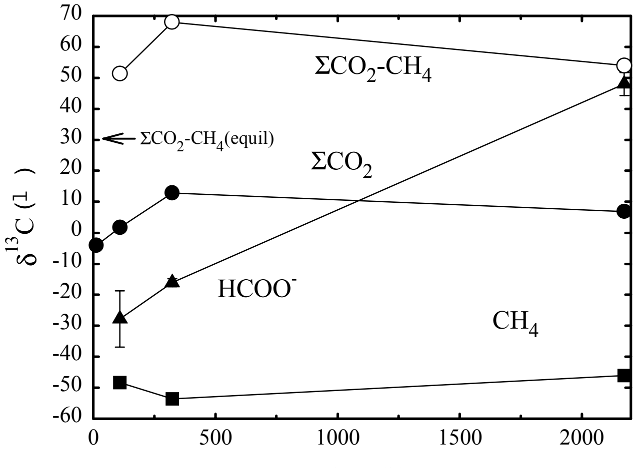

Fig. 4 $^{13}C/^{12}C$ partitioning during hydrothermal CO_2 reduction to CH_4 at 200°C and 500 bars. ΣCO_2: total dissolved CO_2. $HCOO^-$ forms as intermediate (Horita and Berndt, 1999)

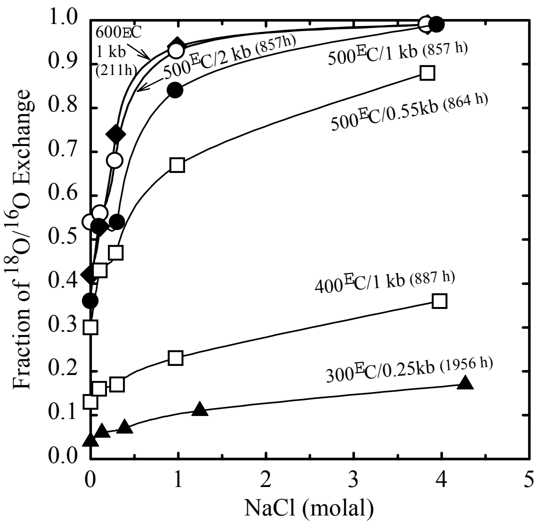

Fig. 5 Kinetics of $^{18}O/^{16}O$ exchange between calcite and water as function of temperature, pressure, and salinity (Cole, 1992)

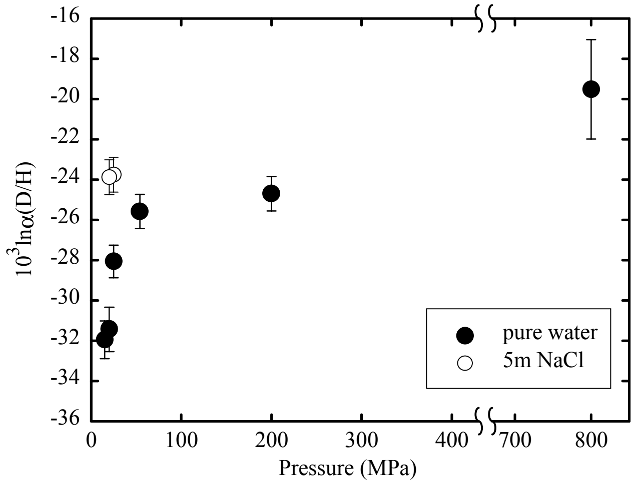

Fig. 6 Pressure and salt effect on brucite-water D/H fractionation at 380°C (Horita *et al.*, 1999)

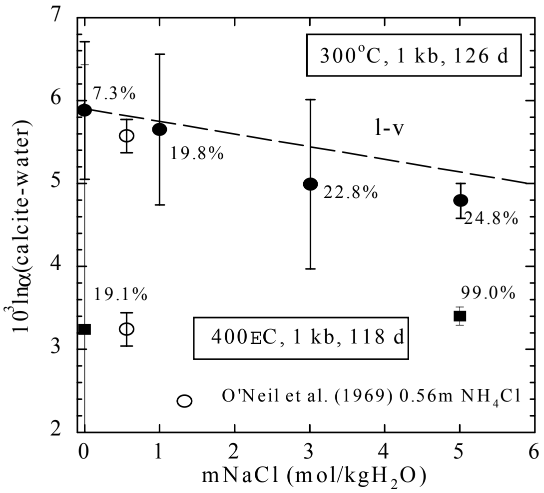

Fig. 7 Salt effect on calcite-water $^{18}O/^{16}O$ fractionation
●: 300ºC/1kb. ■: 400ºC/1kb. Dashed line: result of water liquid-vapor experiments.

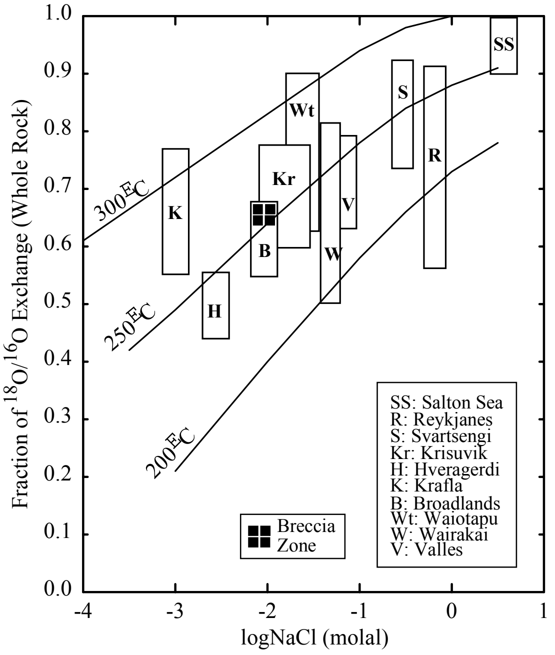

Fig. 8 Degree of oxygen isotope equilibrium vs. NaCl concentration for selected geothermal and ore deposit systems. Solid lines: calculations of a simple, closed system model (Cole, 1994).