Controls on isotopic fractionation in volatiles from icy ocean world brines

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Flight instruments for upcoming and proposed missions to icy ocean worlds are designed to evalauate not only the chemical composition of the surface and exosphere, but also isotope ratios of volatiles evolved from the surface. We synthesized Europa- and Enceladus-analog brines and analyzed volatile isotopologues of CO_2 to characterize the relationship between brine water chemistry and volatiles. Our experiments demonstrate isotopic disequilibrium between the liquid and gas phases of Europa-analog brines that is not constrained by current models of isotopic fractionation in brines, yet equilibrium for Enceladus-analog brines. Our data suggest isotopic equilibrium and deviation from current models is controlled by the concentration and speciation of CO_2 in the brines and the pH of the brines.

Isotopologues of volatile CO_2 from $MgCl_2$ and KCl solutions are within error of established models. Measured $\delta^{18}O$ for NaCl, $MgSO_4$, and Na_2SO_4 solutions demonstrate large deviations (up to –4‰) from established isotope fractionation models that vary with the concentration of gaseous CO_2 in the system. The magnitude of divergence from established fractionation models of multiple salt solutions increases for binary and multiple salt solutions. These results imply that the concentration of CO_2 interacting with a brine could have demonstrable effects on the observed $\delta^{18}O$ of volatile CO_2.

$NaHCO_3$-bearing Enceladus-analog brines promote $\delta^{13}C$ fractionations up to –26‰. The effect of CO_2 concentration on the isotope fractionation of Enceladus-analog brines is less pronounced than the addition of $NaHCO_3$, yet may promote further fractionation by up to –4.5‰. Mass balance calculations of binary composition brines indicate that all sulfate- and chloride-brines are in isotopic disequilibrium, while $NaHCO_3$-bearing brines are typically in isotopic equilibrium. It is unclear if this observation is due to the higher pH of $NaHCO_3$-bearing Enceladus analog brines over Europa-analog brines, or if equilibrium is promoted by CO_2 speciation as HCO_3^- and CO_3^{2-}. These results suggest that volatiles from alkaline brines, such as those theorized on Enceladus, may be in equilibrium and may directly reflect brine chemistry. However, volatiles from a more acidic system such as Europa may be out of equilibrium and therefore more difficult to directly relate to brine chemistry.