Vapor-liquid fractionation of B, Li, and Cl stable isotopes: Experimental constraints at 400 and 450°C, 20 to 42 MPa

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We experimentally determined the vapor-liquid fractionation of the B, Li, and Cl stable isotopes in the systems H_2O-NaCl-B_2O_3 and H_2O-LiCl. Experiments were performed at 400 and 450°C / 20 to 42 MPa. Vapor and liquid samples were analyzed for Na, B, and Li by inductively coupled plasma emission spectrometry. Isotopic ratios were determined by positive thermal ionization mass spectrometry ($^{11}B/^{10}B$), inductively coupled plasma mass spectrometry ($^{7}Li/^{6}Li$), and gas source mass spectrometry ($^{37}Cl/^{35}Cl$).

No coherent vapor-liquid fractionation of the different stable isotope systems is apparent. ^{11}B has a preference for the vapor and fractionation increases along the individual isotherms towards lower pressure. The data have been fitted with a logarithmic function of the form $1000\ \ln\alpha_{v\text{-}l} = a + b\ \ln[(P - P_{crit.}) + e^{(-a/b)}]$ and extrapolated to salt saturated conditions: maximum stable isotope fractionation is $1000\ \ln\alpha_{v\text{-}l}(^{11}B) = 0.94$ ‰ at 400°C and = 1.43 ‰ at 450°C. Mass balance calculations show that for high degrees of fractionation fluid phase separation in an open system significantly alters the boron isotope signature of low-salinity fluids in hydrothermal systems. Comparing the results with natural oceanic hydrothermal fluids, however, indicates that other processes than fluid phase separation dominate the boron geochemistry in oceanic hydrothermal fluids.

Contrary to the boron system, the lithium system indicates a slight preference of the heavy ^{7}Li for the liquid. Measured fractionation is, however, very small and the data do not allow extrapolation of $1000\ \ln\alpha_{v\text{-}l}(^{7}Li)$ to salt saturated conditions. The data nevertheless suggest $1000\ \ln\alpha_{v\text{-}l}(^{7}Li) \leq -0.5$ ‰ at all studied conditions. The very small isotope fractionation indicates that even for fractionation in an open system the Li isotopic signature of vapor, liquid, and bulk system will not be altered by more than 1 ‰. The lithium stable isotopes are conservative tracer during aqueous fluid phase separation and any lithium stable isotope fractionation in natural hydrothermal systems reflect the combined effects of source reservoir and fluid-mineral interactions.

For the chlorine system, no trend is apparent: At all studied conditions $1000\ \ln\alpha_{v\text{-}l}(^{37}Cl)$ is < 0.2 ‰ and switch between positive and negative values. Our data suggest a lack of notable stable isotope fractionation between vapor and liquid in the H_2O-NaCl system. This is at variance to the H_2O-HCl system, where recent data indicate significant vapor-liquid fractionation of up to 9 ‰.

Can millennial-scale geomagnetic field models improve time-integrated predictions of cosmogenic nuclide production rate scaling models? Preliminary results using *in situ* cosmogenic ^{14}C

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In situ cosmogenic nuclide (CN) production rates are typically determined by measuring CN concentrations in surficial rocks with well-constrained exposure histories. Scaling these time-integrated production rates to other locations with different exposure durations, though, requires knowledge or assumptions of how temporal and spatial geomagnetic field variations have affected instantaneous production rates. Previous attempts to quantify geomagnetic effects on CN production rate scaling have relied on various geocentric dipolar approximations to the effective vertical cutoff rigidity (R_C), driven by separate records of geomagnetic pole position and paleointensity (e.g., Lifton *et al*., 2005). However, the CN production rate scaling models in those studies are parameterized using detailed modern geomagnetic field representations. Applying dipolar paleomagnetic records spanning millennial time scales to scaling models derived using the modern geomagnetic field may lead to systematic errors in any calculated results.

A new continuous geomagnetic model covering the last 7 kyr (CALS7K.2) (Korte and Constable, 2005) may allow reduction of such errors by bridging the gap between detailed modern geomagnetic and simplified paleomagnetic models. I have developed a new model describing temporal and spatial variation in R_C for 0-7 ka and earlier, based on CALS7K.2, which explicitly accounts for non-dipole field effects while attempting to mitigate systematic scaling biases.

Scaling factors derived using the new R_C model predict significant longitudinal variability in time-integrated CN production, while predictions using dipolar geomagnetic approximations do not. One can test these predictions using *in situ* cosmogenic ^{14}C (*in situ* ^{14}C) in quartz. Due to its short half-life, ^{14}C attains secular equilibrium between production and decay after approximately 25 ky of exposure, at which point its measured concentration is only a function of its integrated average production rate. Preliminary *in situ* ^{14}C results from samples at secular equilibrium from 38°N and 3.5 km in Tibet and eastern California are consistent with the longitudinal variability predicted by the new model.

References

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