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Liquid–vapor fractionation of B and Br in the H-Na-B-O-Cl-Br system: An experimental study and its application to nature

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The subcritical liquid-vapor fractionation of Boron and Bromine has been studied experimentally in the systems H-Na-B-O-Cl and H-Na-O-Cl-Br between 220 and 420 bar/380 and 450 °C. The experiments were conducted along different isotherms in a large-volume Ti autoclave that enables quasi-isobaric recovering of coexisting liquid-vapor samples. The starting fluids had a neutral pH, an initial B concentration of 200 ppm and an initial Cl/Br ratio of 300, respectively. The initial NaCl concentrations correspond to the composition at the critical point of the respective isotherms (Bischoff and Pitzer[1]). All samples were analysed for Na and B by ICP-AES and for Cl and Br by ion chromatography.

The calculated NaCl concentrations in the coexisting liquid-vapor pairs reproduce the solvi of the respective isotherms[1] within experimental accuracy. We therefore assume that no contamination of liquid and vapor samples occurred during sampling.

With decreasing pressure, i.e. with opening of the solvus, D_B^{lv} ($= c_B^{liquid}/c_B^{vapor}$) increases from 1.0 at the critical points to 2.71 at 400 °C/235 bar and 1.72 at 450 °C/387 bar. Extrapolation of the data to salt saturated conditions gives maxima in B fractionation with $D_B^{lv} = 4.6$ at 400 °C/172 bar and $D_B^{lv} = 3.4$ at 450 °C/250 bar. A linear correlation of D_B^{lv} with D_{NaCl}^{lv} is not observed.

The distribution coefficient D_{Br}^{lv} ($= c_{Br}^{liquid}/c_{Br}^{vapor}$) for the liquid-vapor fractionation of Br correlates linearly with D_{Cl}^{lv} . The calculated K_D ($= D_{Br}^{lv}/D_{Cl}^{lv}$) for the reaction $Br^v + Cl^l = Br^l + Cl^v$ is 1.06 and is independent of pressure and temperature, at least in the investigated P-T range. It indicates that Br has a stronger affinity for the liquid than Cl. Based on the known D_{Cl}^{lv} from [1], the estimated K_D allows to calculate D_{Br}^{lv} as a function of P and T. Maximum Br fractionation occurs at salt saturated conditions with, e.g., $D_{Br}^{lv} = 1.2 \cdot 10^4$ at 380 °C/143 bar and $1.9 \cdot 10^3$ at 450 °C/250 bar.

For natural boiling systems, the K_D indicates that the residual brines are progressively enriched in Br with respect to Cl. This allows for discrimination between boiling, i.e. phase separation, and mixing of fluids from different sources.

Reference

- [1] Bischoff J.L. and Pitzer K.S. (1989) *Am. J. Sci.* **289**, 217-248.

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Geochemical continuity of crustal fluids

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The compositions of crustal brines formed over a wide range of temperatures have been compiled, combining data from oilfield, geothermal and shield brines with fluid inclusions from metamorphic to magmatic settings. The principal controls on the concentrations of the transition metals Fe, Mn, Zn and Pb are salinity and temperature. The relationship between metal and chloride concentrations is constant for each set of data formed at a single temperature, irrespective of whether it is sedimentary or magmatic. For Fe, Fe/Cl remains nearly constant at constant temperature, and the Figure demonstrates that there are almost 6 orders of magnitude variation in Fe/Cl across the temperature range of the data set. About 1 order of magnitude of the scatter at any one T can be ascribed to variations in redox, while the rest is accounted for by pH differences and analytical errors. This continuity in chemistry from sedimentary to metamorphic and magmatic fluids demonstrates the importance of wall rock buffering for the control of fluid composition, and shows that the variation in pH, fS₂ and redox environment between different lithologies is not sufficiently large for variation in these parameters to dominate the variable metal contents of fluids. The importance of temperature in dictating the metal contents of brines that is shown here, implies that there must be effective mechanisms for their extraction from / input to rocks as fluids move up or down temperature.

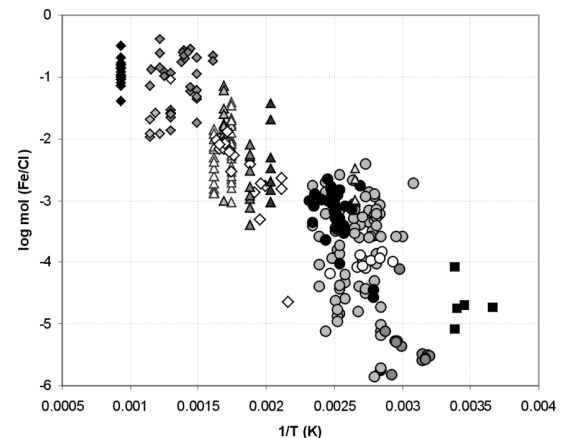


Figure 1: Plot of fluid compositions from a variety of sources. Square symbols, shiled brines; Circles, oilfield brines; Triangles, metamorphic fluid inclusions; Diamonds, geothermal brines and magmatic fluid inclusions.