Solid - Liquid Equilibria for the ternary Na$_2$B$_4$O$_7$ - NaBr - H$_2$O System at 348 K

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Introduction

Many salt lake brines on the Qinghai - Tibet plateau in China are well known for high concentrations of Li, K and B. Furthermore, a huge amount of underground gasfield brine was also discovered in China,such as Sichuan western basin. Sodium chloride, potassium, boron , bromine and sulfates are the major chemical component of the oilfield brine, which often accompanies Li, Sr and I. The ternary system Na$_2$B$_4$O$_7$ - NaBr - H$_2$O is a subsystem of the underground gasfield brines.

Results

The solid - liquid equilibria for the ternary system Na$_2$B$_4$O$_7$ - NaBr - H$_2$O at 348 K were measured experimentally using the method of isothermal solution saturation. On the basis of experimental data, the phase diagram of the ternary system was constructed. In the phase diagram of the ternary system Na$_2$B$_4$O$_7$ - NaBr - H$_2$O at 348 K(Figure 1), there are one invariant point E and two univariant curves E1E and E2E. The points E1 and E2 represent the solubility of the binary systems of Na$_2$B$_4$O$_7$- H$_2$O and NaBr - H$_2$O at 348K with mass fraction (100w_b) of 19.30 and 54.35, respectively. Curve E1E and E2E are the solubility isotherms of Na$_2$B$_4$O$_7$·5H$_2$O and NaBr, respectively. The invariant point E corresponds to the solution saturated with both NaBr and Na$_2$B$_4$O$_7$ · 5H$_2$O. Phase equilibrium solids were NaBr and Na$_2$B$_4$O$_7$·5H$_2$O in the studied ternary system. The crystallization area of Na$_2$B$_4$O$_7$ · 5H$_2$O (E1ED field) in the phase diagram is obviously bigger than that of NaBr (E2EA field).
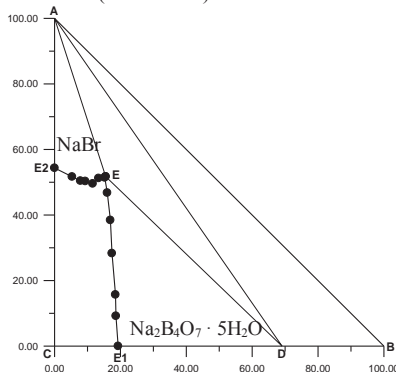
Figure 1 Phase diagram of the ternary system Na$_2$B$_4$O$_7$ - NaBr - H$_2$O at 348 K

Use of two new Na/Li thermometric relationships for geothermal fluids in volcanic environments

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Thermometers such as Silica, Na/K, Na/K/Ca, Na/K/Ca/Mg or δ^{18}O (H$_2$O-SO$_4$), based on empirical or semi-empirical laws derived from chemical equilibrium reactions between water and minerals in the deep reservoirs, are commonly used in geothermal exploration in order to estimate the reservoir temperatures. Unfortunately, these estimations are not always concordant because of processes which can perturb the chemical composition of the fluids during their ascent up to the surface (water mixing, fluid cooling, etc.). Given these discordances, auxiliary thermometers such as Na/Li, based on statistical relationships, were also developed. As Li is rather lowly reactive, the use of this thermometer can give more reliable temperature estimations. Presently, three different Na/Li relationships ([1], [2]) are mainly available according to the fluid salinity and the geological environment (volcanic/granitic and sedimentary rocks).

This study carried out in the framework of the European HITI project (HIgh Temperature Instruments for supercritical geothermal reservoir characterization and exploitation) with the collaboration of ISOR Iceland Geosurvey proposes two new Na/Li thermometric relationships. The first concerns the fluids derived from high-temperature seawater-basalt interaction processes existing in the oceanic ridges and rises as well as in the emerged rifts such as those of Iceland (Reykjanes, Svartsengi and Seltjarnarnes geothermal fields) and Djibouti (Asal-Ghoubbet and Obock geothermal areas). It can be expressed as follows:

Log (Na/Li in mol/l) = 920/(T°K) + 1.105 (r^2 = 0.994).

The second relationship, developed using dilute fluids collected only from Icelandic geothermal wells in the 100-325°C range, surprisingly close to that determined by Fouillac and Michard (1981) for volcanic saline fluids at temperatures ≥ 200°C, is:

Log (Na/Li in mol/l) = 1786/(T°K) - 0.936 (r^2 = 0.976).

The uncertainty on temperature estimation is ± 25°C for both relationships. These results confirm that the Na/Li ratios not only depend on temperature but also on other parameters. The nature of the reservoir rocks and fluid seems to be the most influent one. Some literature case studies and thermodynamic considerations suggest that the Na/Li ratios could be controlled by chemical equilibrium reactions involving different mineral assemblages where illite and micas would be, however, always present.

[1] Fouillac Ch. and Michard G. (1981) *Geothermics,* **10**, n°1, 55-70. [2] Kharaka and Mariner (1989) *Naeser and McCulloch Eds, Springer-Verlad, New York,* 99-117.