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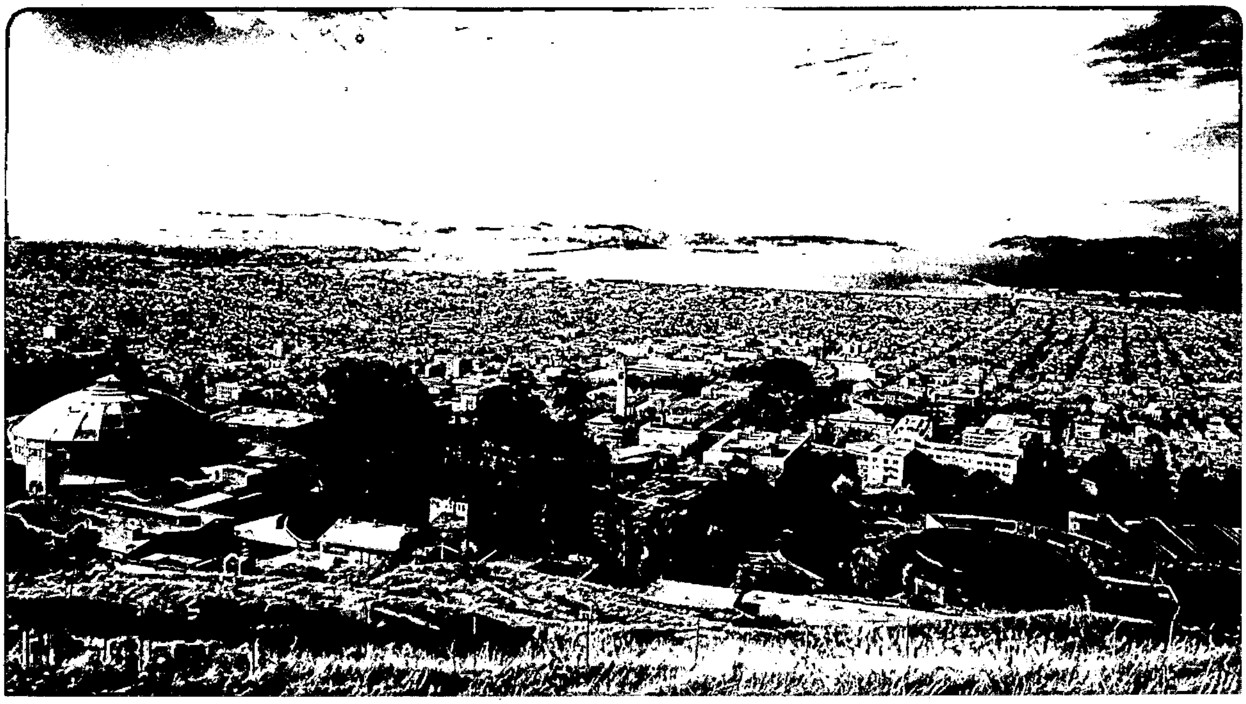

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Correlation of the Na/K ratio in geothermal well waters with the thermodynamic properties of low albite and potash feldspar

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ABSTRACT: The Na/K ratio in geothermal well waters provides a better estimate of the relative stability of low albite and potash feldspar than do predictions from calorimetry and high temperature phase equilibria. The calculated saturation indices from field data for low albite, potash feldspar suggest that $\Delta G^{o}_{f,298}$ for the latter should be revised to -3748.6 ± 3.7 kJ.mol^{-1}.

INTRODUCTION

For many years, the element concentration ratio, Na/K, in the liquid aqueous phase has been used to estimate the source region temperature of hot springs and geothermal effluents. As a concentration ratio, it possesses the advantage that it is unaffected by transient boiling or condensation, and is affected only slowly by conductive cooling, although Fournier and Truesdell (1973) recommended its use only where source region temperatures are greater than 150°C.

The thermochemical basis for the Na/K geothermometer is not well defined. Usually, discussion centers on the "exchange" reaction between plagioclase (low albite) and potash feldspar (adularia or microcline);

$$NaAlSi_3O_8 + K+ = KAlSi_3O_8 + Na^+ \tag{1}$$

where

$$\log K(T) = \frac{[Na^+]}{[K^+]} \tag{2}$$

Attempts to reconcile field observations with calculations using published thermodynamic properties of the participating species, have not been particularly successful.

The coexistence of secondary low albite and potash feldspar in geothermal systems is frequently mentioned in the literature. Tomasson and Kristmannsdottir (1972), in discussing mineral alteration in the geothermal area of Reykjanes, Iceland, refer to the occasional presence of albitized plagioclase as well as the sporadic occurrence of newly formed potash feldspar in all geothermal holes. Mehegan and Robinson (1982) and Viereck et al. (1982) describe secondary hydrothermal alteration in the Reydarfjordur drill core from Eastern Iceland. Low albite and adularia coexist in most of the intersected volcaniclastic rocks, whereas authigenic albite replaces primary plagioclase crystals in some of the interdigitated basaltic flows. Browne and Ellis (1970) noted the presence of adularia and secondary albite in hydrothermally altered intermediate and acid lavas and volcaniclastic rocks intersected by boreholes in the Ohaki-Broadlands hydrothermal area in New Zealand. On the Kamchatka Peninsula, Naboko, et al. (1965) refer to secondary adularia and albite in dacitic and andestic volcaniclastics of the Pauzhetka geothermal field, whereas Trukhin and Petrova (1974) describe alteration zones containing secondary albite and adularia in andesitic lavas and andesitic and dacitic tuffs of the Bolshe-Bann geothermal field. In contrast, mineralogical studies of cores penetrating sea floor basalts, between ~4°C and 70°C, never mention the coexistence of low albite with potash feldspar, although frequent reference is made to the presence of the latter, sometimes replacing plagioclase. Plagioclase is usually replaced by secondary clays instead of low albite. Analcime is commonly observed as an authigenic phase, although it is rarely observed in basalts saturated with meteoric waters at similar temperatures.

Because of extensive mineralogical observations confirming the coexistence of secondary low albite and potash feldspar in geothermal fields, it is reasonable to assume that the

Na/K ratio in the aqueous phase reflects a close approach to chemical equilibrium between these two minerals, particularly at temperatures greater than 150°C, where the Na/K geothermometer has proven to be most reliable.

COMPARISON OF Na/K, PREDICTED FROM THERMODYNAMIC DATA, WITH FIELD DATA

Several comprehensive internally consistent compilations of thermodynamic data of minerals have been published in which $\Delta H^{o}_{f,298}$ or $\Delta G^{o}_{f,298}$, of both low albite and potash feldspar (adularia or microcline) are included (Helgeson et al., 1978, Robie et al., 1979; Berman, 1988; Holland and Powell, 1990). Their properties are based on calorimetry and high temperature, i.e. > 400°C, phase equilibria with coexisting minerals. Helgeson et al. also used the Na/K ratio from gas field brines to correlate the properties of the two feldspars. Recently, Kiseleva et al. (1990) redetermined $\Delta H^{o}_{f,298}$ for microline using high temperature lead borate melt calorimetry.

In Figure 1, the calculated values of log K(T) for Eqn. (1) from all five sources are compared with the analytical determinations of the Na/K ratio in well waters from geothermal fields and deep water-saturated formations from around the world. Field temperatures were measured down hole or computed from well discharge data. The log K(T) values are calculated along the water saturation curve, employing the entropies cited by Robie et al. (1979) and Maier-Kelley heat capacity functions, cited by Helgeson et al. (1978), for low albite and potash feldspar. The thermodynamic properties for the ionic species, Na^{+} and K^{+}, are those given by Shock and Helgeson (1988). The uncertainty is estimated from those given in the cited references.

Although mineralogical studies from most sites selected for the correlation describe the presence of authigenic low albite and potash feldspar, there is no assurance that the recovered groundwaters originated where low albite and potash feldspar coexisted. Some sampled well waters may have been mixtures from several producing zones. In spite of these uncertainties the field data are generally consistent and can be fitted by a univariant curve, positioned as indicated on Figure 1 to within ± 0.2 $\log(Na^+)/(K^+)$, or 1 kJ in ΔG^o_r for reaction (1) at 25° and 2 kJ at 300°C. This contrasts with an uncertainty of nearly 3.5 kJ for the log K(T) predicted from calorimetry or phase equilibrium measurements. The fitted curve follows closely the equation proposed by Fournier (1981) for the Na/K geothermometer and the data reported by Il'in et al. (1979), for the Pauzhetka geothermal field, but it does not fit their data from the lower temperature Paratunka field in the same region.

The precision of Na/K predictions using either calorimetric and/or high temperature phase equilibrium data do not do justice to the quality of routinely obtainable field measurements. Groundwater analyses may therefore have the potential for calibrating thermodynamic data, provided that rigorous control is maintained over sampling and analysis procedures.

The chemical analyses of geothermal wells below 200°C reported by Arnorsson et al. (1983) include Al^{+++}. The saturation indices of low albite and potash feldspar can therefore be computed for those well waters, and their solubility products compared with those predicted from calorimetry and high temperature phase equilibria. The results, illustrated in Figure 2, show the saturation indices referenced to the data by Berman (1988), who used the thermodynamic properties of low albite taken from Hemingway and Robie (1977). The saturation indices of both feldspars show trends towards supersaturation below 100°C. This trend might be indicative of the sampled waters originating at temperatures higher than those measured and that they were not in equilibrium with the local environment, a condition reflecting the uncertain validity of Na/K ratio in the low temperature domain. In spite of the scatter, the saturation indices suggest that $\Delta G^o_{f,298}$ of low albite might be more nearly correct than that of potash feldspar in Berman's database.

ADJUSTMENT OF $\Delta G^{o}_{f,298}$ FOR POTASH FELDSPAR

A correction to $\Delta G^{o}_{f,298}$ for potash feldspar alone using the field correlation of Na/K yields a revised value of –3748.6 ± 3.7 kJ.mol^{-1}, which is more negative than that of Robie et al. (1979), –3742.3 ± 3.4 kJ.mol^{-1}, or that of Berman (1988), –3745.4 kJ.mol^{-1}, but is much less negative than –3754.2 ± 3.7 kJ.mol^{-1} calculated from $\Delta H^{o}_{f,298}$ of microcline determined by Kiseleva et al. (1990).

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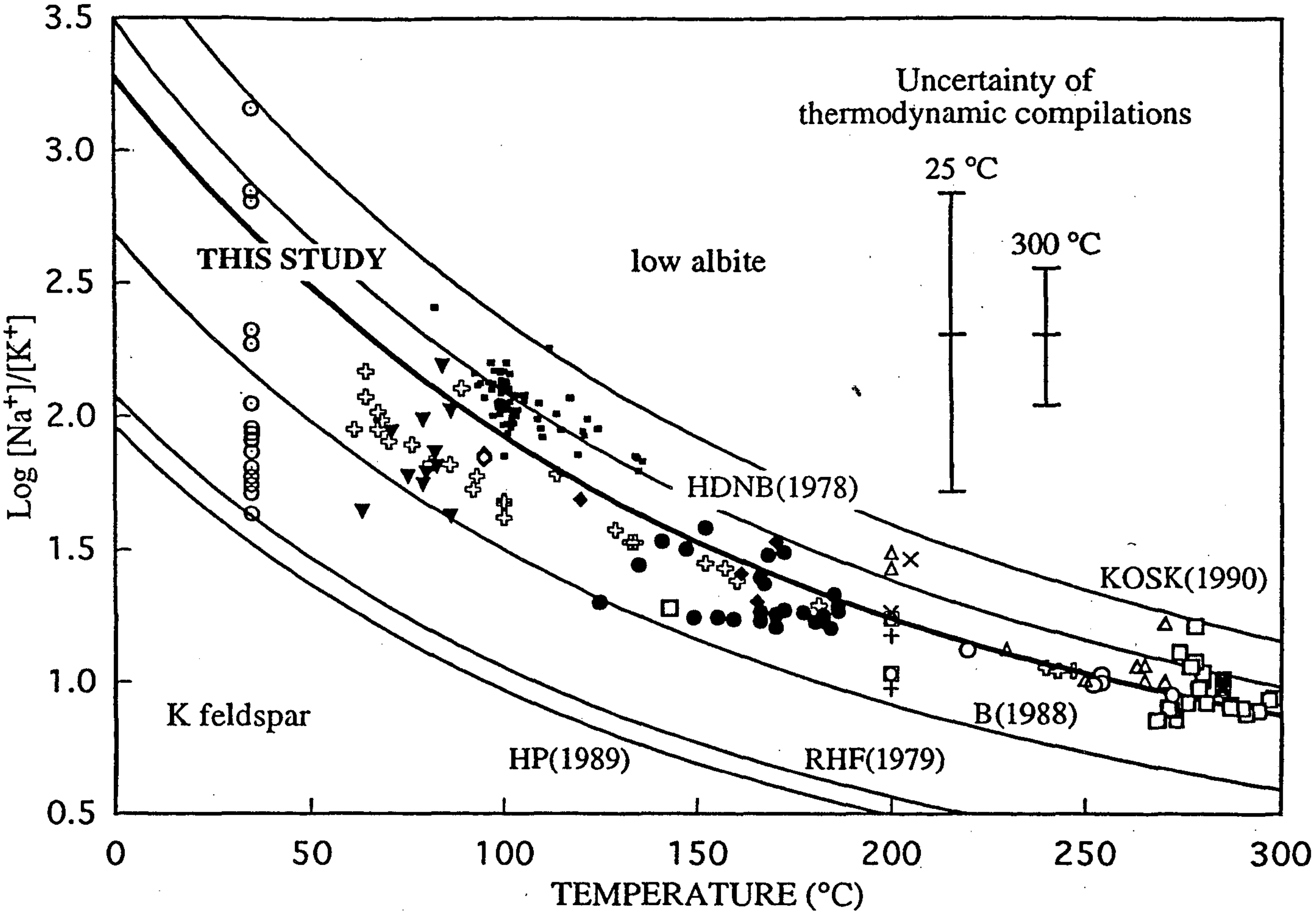

Fig.1. Log[Na+]/[K+], as a function of temperature, calculated from thermodynamic compilations (labeled by authors' first letters and date) and well waters (symbols).

◆ Bolshe Bann, Ru.

● Pauzhetka, Ru.

✣ Iceland

□ Ohaki-Broadlands, N.Z.

○ Tauhara, N.Z.

△ Wairakei, N.Z.

◇ Cajon Pass, Ca.

▼ Paratunka, Ru.

⊠ Kawerau, N.Z.

⊙ Savannah River, U.S.

▪ Kettleman Dome, U.S.

⧈ Orakeikorako, N.Z.

× Rotorua, N.Z.

\+ Waiotapu, N.Z.

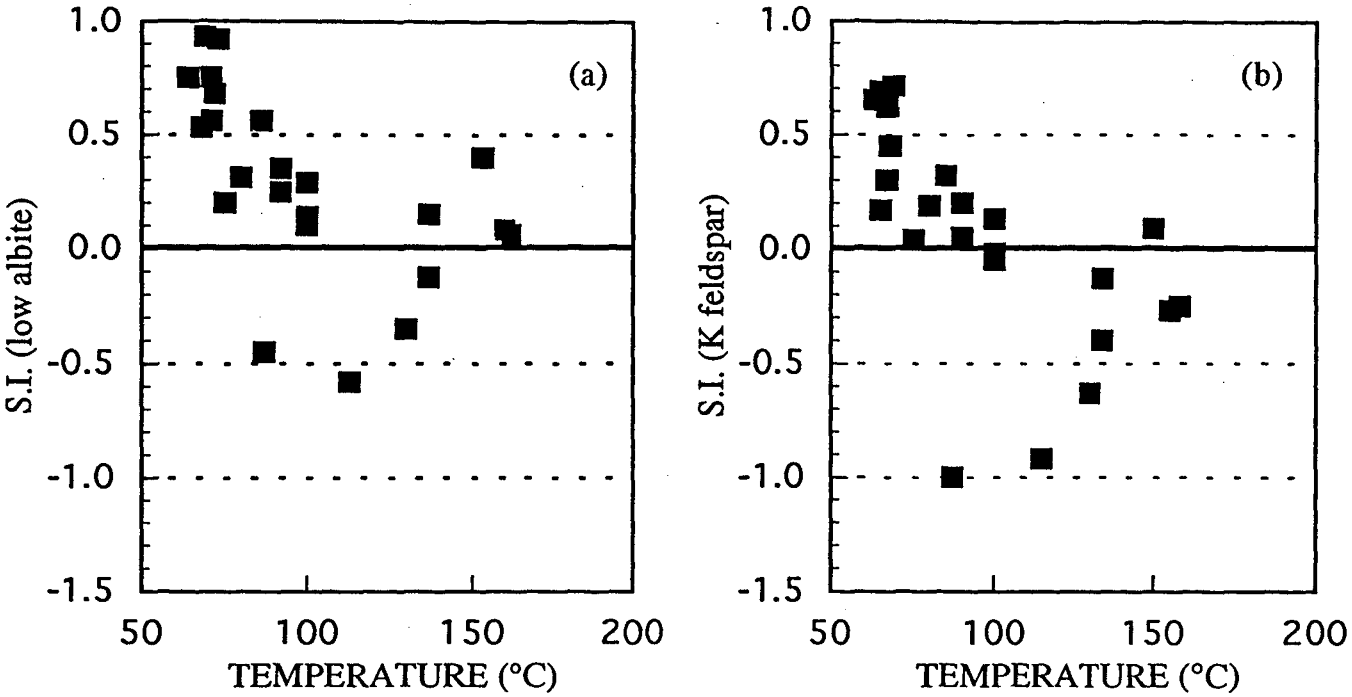

Fig.2. Saturation indices for (a) low albite and (b) potash feldspar as a function of temperature, calculated from well waters in Iceland from data by Arnorsson et al. (1983)