Thermodynamic description of aqueous non-electrolytes at infinite dilution over a wide range of state parameters

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An approach for describing the thermodynamic properties of aqueous non-electrolytes at infinite dilution is proposed. It is based on the accurate equation of state for the solvent (H_2O) given by Hill (1990) and requires only three empirical parameters that are independent of temperature and pressure. The master equation for chemical potential of the dissolved component μ_2 is:

$$\mu_2(P,T) = \mu_{2,g}(T) - RT\ln N_w + (1-\xi)RT\ln f_1 + RT\xi\ln\left(\frac{R_V T}{M_1}\rho_1\right) + RT\rho_1\cdot\left(a + b\cdot\left(\frac{10^3}{T}\right)^{0.5}\right)$$

Here $\mu_{2,g}(T)$ stands for chemical potential of the pure gaseous component at temperature T and standard pressure P = 1 bar, R = 1.987 cal·mol^{-1}·K^{-1} and R_V = 83.14 cm^3·bar·K^{-1}·mol^{-1} are gas constants, $N_w \approx 55.51$ mol/kg, M_1, f_1 and ρ_1 denote molar mass (g/mol), fugacity (bar) and density (g/cm^3) of the pure solvent (H_2O) at P-T conditions of interest, respectively, and ξ, a and b are empirical parameters that have definite physical meaning: ξ is introduced to describe the difference between intrinsic volumes of H_2O and the dissolved molecule (Plyasunov et al. 2000), and a and b characterise the difference in the short-range interaction energy between solute and solvent molecules. Thus, knowledge of the pure gas thermodynamic properties, together with these three parameters, enables prediction of the whole set thermodynamic properties of the solute at infinite dilution (chemical potential, entropy, molar volume, and apparent molar heat capacity) over a wide range of temperatures (0 - 500°C) and pressures (1 - 2000 bar), including the near-critical region. In the cases where experimental thermodynamic data are lacking, the empirical parameters could be estimated from the known standard-state properties of the solute only. The proposed approach has been tested for non-polar (Ar, Ne, H_2, N_2, O_2, CO_2) and polar (H_2S, NH_3, H_3BO_3, $SiO_{2,aq}$) dissolved molecules, ion pairs (HCl), and aqueous carbohydrates (CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_6H_6).

References

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SHRIMP dating of lower crust xenoliths from Bering Sea region

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The Late Cenozoic Bering Sea basalt province represents the most significant volume of alkali basalts erupted in the Arc tic region within the last 10 Ma. Most of the volcanic fields are dominated by relatively LREE-enriched basalts with intraplate geochemical characteristics. Pb, Sr and Nd isotopic compositions of the basalts are diverse, indicating sources similar to those from MORB to OIB.

Trapped crustal xenolith suites in basalts include mostly undeformed, mafic Pl-Opx-Cpx cumulate rocks and pyroxene gneisses which equilibrated between 3 to 9 kb. Zircons were found in eleven plagioclase-bearing xenoliths from the Enmelen volcanoes (Chukchi Peninsula), and in one sample from the Imuruk volcanic field (Seward Peninsula) and were dated by the U-Pb method with the SHRIMP RG at Stanford University. Two types of zircons were observed - zoned prismatic ones (magmatic) and non-zoned rounded ones (metamorphic) with lower Th/U ratio. These data are combined with more limited results of a similar study of xenoliths from St.Lawrence Island basalts (Fig.1).

Zircons from Enmelen mafic xenoliths indicate that 80-110 Ma magmatic rocks were involved in a younger thermal event between 60 and 75 Ma (peak at 70 Ma) that affected a large region of the deeper crust beneath the Bering Sea.

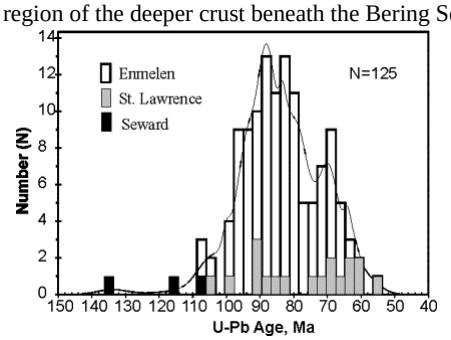

Figure 1. Histogram of U-Pb zircon ages from lower crust xenoliths of the Bering Sea basalt province.

The results suggest that the lower crust was significantly modified in the Cretaceous by magmatic underplating and heated again in the early Tertiary. These ages coincide with two major pulses of magmatism dated as 115-80 and 75-55 Ma which occurred together with and post-dated extensional collapse of previously thickened crust. Xenoliths ages thus reflect widespread signature of these events in the deep crust beneath the region.

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