Free Energies of Formation of Illite Solid Solutions and their Compositional Dependence

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Abstract: Electron probe analyses of diagenetic illites in Eocene sandstones from Kettleman North Dome, California, along with analyses of coexisting interstitial waters were used to calculate apparent molal free energies of formation of the illites at the *in situ* conditions of 100° C and 150 bars. Various triangular and rectangular compositional plots, once contoured for free energy, crudely indicate that the free energy decreases as the potassium content increases, decreases as the Al-for-Si substitution increases, and appears to be a minimum along a narrow composition valley having $\sim$3% Fe_2O_3 of octahedral cations. Qualitatively, the shape of the free energy surface suggests only small departures from ideality.

The illites and water samples used in the calculations were chosen as close to each other as possible and are in equilibrium. The waters contain mainly Cl^-, SO_4^{2-}, Na^+, and Ca^{2+} and have a total salinity of $\sim$10,000 ppm. The illites, which coexist in the sandstones with diagenetic quartz, albite, and K-feldspar, are phengitic and contain 5−9% K_2O, 1−3% total FeO, 1% MgO, and minor Na_2O, MnO, and TiO_2. The Fe_2O_3/FeO ratio has been set arbitrarily to 7 by comparison with published analyses.

Log K (100° C) was first calculated for the equilibrium illite $\rightleftharpoons$ ions from the ionic activities obtained through speciation calculations for each water sample. The apparent free energies of formation of illites at 100° C were then calculated. The effect of instrumental uncertainty on the values of ΔG_f was assessed by accepting a 2.5 or 3.5% error in the probe analyses and by using a Monte Carlo method of error propagation. The free energies of formation obtained (on the basis of $O_{10}(OH_2)$) range from −1280 to −1320 kcal/mole at 100° C and 150 bars, and their Monte-Carlo uncertainties are less than $\pm$ 2 kcal/mole. Combining the compositions of natural, coexisting aqueous solutions and mineral solid solutions through thermodynamic equations constitutes a fast method to determine, at least crudely, the free energy-composition surface for the solid solution. This is in contrast to experimental methods such as calorimetry or hydrothermal equilibrium, which are very time-consuming and difficult.