Thermodynamic models of aqueous systems to high temperature and concentration

N. MOLLER* AND J.H. WEARE

Chemistry and Biochemistry, UCSD, San Diego, CA, 92093
(*correspondence: nweare@ucsd.edu)

We have developed thermodynamic models, using the Pitzer specific interaction equations, that describe interactions as well as solid-liquid-gas equilibria to high temperature and concentration within the H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$ Cl^-, OH^-, HSO_4^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, $Si(OH)_4$, $SiO(OH)_3^-$, SiO_2 (aq), CO_2 (aq/g), H_2S (aq/g), CH_3 (aq/g), H_2O system. In this presentation, the construction of two models that produce predictions with accuracy near the uncertainty of the experiments is discussed. One, correctly calculates solute/solvent activities and solid-liquid equilibria in the H-Na-K-OH-Cl-HSO$_4$-SO$_4$-H$_2$O system from dilute to high solution concentration and from low to high pH within the $0°$ to $250°C$ temperature range. The other correctly predicts solvent/solute activities and monomeric aluminum hydrolysis speciation as well as solid-liquid equilibria in the H^+, Na^+, Al^{3+}, Cl^-, $Si(OH)_4$, $SiO(OH)_3^-$, OH^-, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$ system as a function of pH to high salt concentrations ($I \leq 5$ m NaCl), for temperatures up to $300°C$ and for saturation pressures. The latter model accurately predicts the fluid compositions for the low Al ($\leq 10^{-5}$ m) and Si(OH)$_4$ ($\leq 10^{-4}$ m) concentrations commonly encountered in the intermediate pH ranges typical of most natural fluids. For high and low pH regions where the formation of polymeric Al hydrolysis species is low, the model will apply to higher total aluminum concentrations. The successful prediction of the solubility of aluminiosilicate solid phases falling within this system is also described.

REE in groundwater as indicators of catchment lithology in semi-arid regions

P. MÖLLER[1], C. SIEBERT[2] AND S. GEYER[2]

[1]Helmholtz Zentrum Potsdam, Deutsches GeoForschungsZentrum, D-14473 Potsdam
[2]Helmholtz Center for Environmental Research-UFZ, Halle/Saale 06120, Germany

REE in groundwater (GW) in regions with little soil coverage characterize the lithology of its recharge area because interaction of precipitation with soil coverage is short to absent. Under such conditions the dissolution of minerals in the catchment area becomes an important tool in particular in regions with dominant transboundary GW flow in politically unstable regions.

REE patterns in GW recharged over limestones resemble those of the limestones. GW recharged over olivine bearing basalts yield REE patterns that are controlled by dissolution of the least stable minerals such as olivine and by scavenging during weathering by ferric hydroxides and calcite. Bowl-shaped REE patterns are typical. REE in GW from sandstones are controlled by leachable minerals of their cements. In the presences of gypsum and phosphates the intermediate REE are enriched in GW.

REE in GW from aquifers of the same lithology of fthe recharge area are controlled by strong sorption of REE onto mineral surfaces. In case of limestones overlaying basalts the GW from basalts shows nearly the same pattern as in GW from the limestone above because the high REE abundance in GW is adsorbed by minerals of the basalt and thus with time GW passes the basalt without significant changes. In case of basalts overlaying limestones the REE abundance in the final GW is lower than expected from interaction with limestones. Due to high Ca and Mg concentration from weathering of plagioclase and olivine in basalts dissolution of calcite from limestones is limited and thus the REE patterns achieved from the basalt is not significantly altered during the passage of limestone.