

Mineral-Solution Equilibria in Groundwater Systems

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Introduction

The essence of this contribution is to demonstrate the state of mineral-solution equilibria in groundwater systems without consideration of which minerals are involved and, therefore, without knowledge on their thermodynamic properties. The data base used includes about 400 samples; of surface waters from Iceland and, in particular, thermal and non-thermal groundwater associated with volcanic rocks from different geological environments worldwide and ranging from basaltic to silicic in composition. The aquifer temperature of the groundwater range from ambient to over 300°C and salinity varies from very low levels (<10 ppm Cl) to that of seawater. Equilibrium is generally closely approached with respect to major components (Si, Na, K, Ca, Mg, Fe, Al, carbonate-C, sulphide-S, sulphate-S and F, in addition to pH), except Cl and sometimes SO₄, when temperature exceeds 100°C and in extreme cases at temperatures as low as 10°C.

Theoretical Considerations

The number of independent variables that must be specified to completely specify a chemical system at equilibrium is defined by the Gibbs Phase Rule. According to Durhem's Theorem, which considers closed systems at equilibrium, the number of independent variables is equal to 2, i.e. the intensive variables temperature and pressure. If partial equilibrium prevails (equilibrium is attained for some components but not for others) the number of independent variables required to define a closed system is equal to temperature + pressure + the number of non-equilibrated components.

For the groundwater systems considered here, pressure ranges from 1 to about 200 bars. In this range, it has relatively small effect on the values taken by equilibrium constants, both for species-species and mineral-solution reactions, at least compared to temperature. It is, therefore, a reasonable approximation to omit pressure when defining the system. Thus, in order to approximately specify fully a groundwater system, including the aqueous phase, at partial equilibrium it suffices to specify temperature and all the non-equilibrium components. The assessment of the data given below centres around this theoretical result.

Results

Cation/proton activity ratios vary linearly with 1/T Kelvin for groundwaters with aquifer temperatures >40°C as exemplified for Ca (Figure 1A). Al displays this kind of relationship for all waters and Fe and Mg for all groundwaters. This is also the case for Na, K and Ca for some groundwaters to temperatures as low as 10°C. By contrast cation/proton activity ratios in surface waters, except those for Al, show variable and lower ratios than slightly thermal groundwaters.

Some high-temperature geothermal systems in Iceland with temperature of 240–250 C host dilute water (source water meteoric) but others saline water (source water seawater). The dilute and saline waters possess about the same cation/proton activity ratios although these ratios differ in their source waters. Thus, during heating-up and reaction with the minerals of the host rock (basalt) these different kinds of water have attained the same cation/proton activity ratios. These changes should be regarded as equivalent to changes in mineral-solution experiments when equilibrium is demonstrated by approaching it from super- and undersaturation.

Values taken by equilibrium constants for mineral-solution reactions vary about linearly with 1/T from 0 to 250–300°C. Thus, the results for the cation/proton activity ratios indicate that these ratios represent equilibrium values, often down to 40°C and in some cases to temperatures as low as 10°C. They must correspond with equilibrium constants for unspecified hydrolysis reactions. The ratios are practically the same for waters associated with basaltic to silicic volcanics. Yet, the same mineral buffers are not always involved, neither over the whole temperature range, nor for the different rock types. The results indicate that the value of the equilibrium constant for a specific cation/proton ratio taken by different mineral buffers is very similar.

The activities of the weak acids H₄SiO₄, H₂CO₃, H₂S and HF, the conjugate anions of which constitute the major aquatic anions, vary linearly with 1/T for groundwaters above 40°C as exemplified for H₂CO₃ in Figure 1B. For silica this is a consequence of equilibration with quartz/chalcedony but for the other acids it is due to equilibration with minerals containing a conjugate anion of these acids and hydrolysis reactions which control the respective cation/proton activity ratio. This is sometimes also the case with SO₄.

Slight, yet systematic discrepancy in individual acid activities at a particular temperature are observed which can be related to rock type and water salinity. The reason is probably that different minerals are involved.

Conclusions

To specify activities of acids and cation/proton ratios of major components in groundwaters above 100°C it generally suffices to specify temperature and Cl concentrations. At lower temperatures SO₄ may also need to be specified. In line with this observation, the linear variation of the respective activities and activity ratios with 1/T and the chemical evolution of dilute and saline geothermal waters in Iceland, it is concluded that chemical equilibrium is generally closely approached for all major

components in groundwater systems hosted in basaltic to silicic volcanics when temperatures exceed 100°C and in extreme cases to temperatures as low as 10°C.

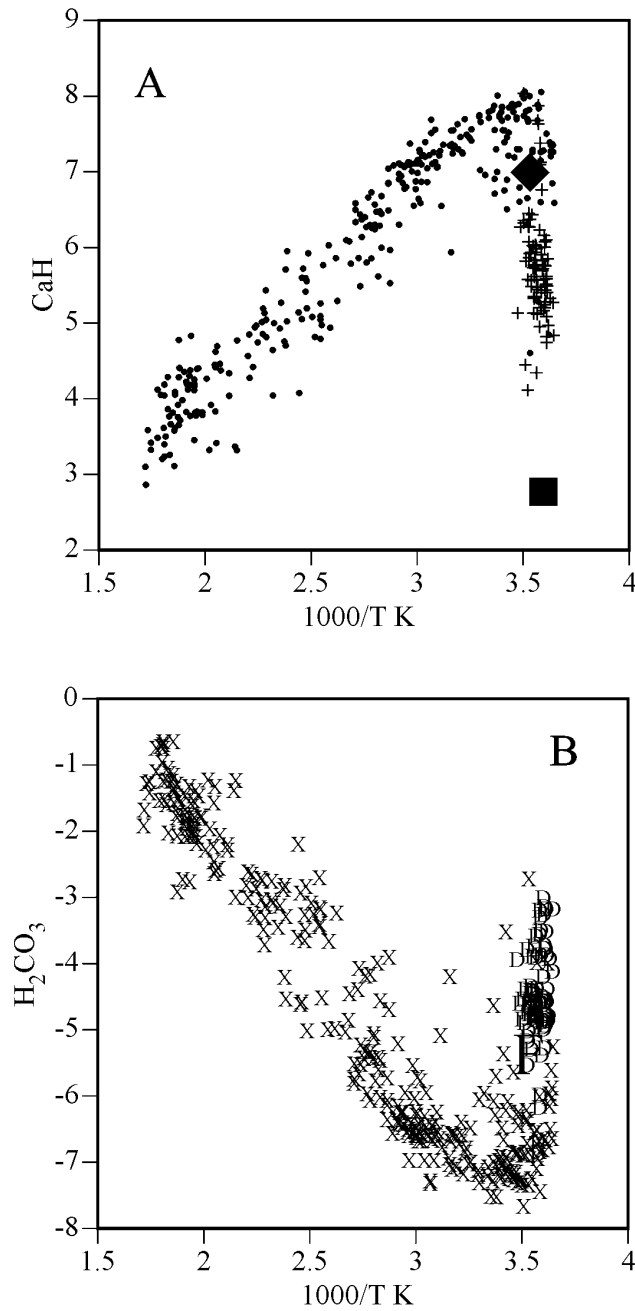


Figure 1: The logarithms of (A) aqueous Ca/H ion activity ratios (CaH) and (B) carbonic acid activity (H_2CO_3) versus the reciprocal of the absolute temperature ($1/T$) in selected natural waters. Dots: groundwater, crosses: surface waters.