GRD – Weeks 4, 5 – Exercises

Due October 16, 2024

1a) The dissolution of calcite into water is represented by the reaction:

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO^{3-}$$

The log of the equilibrium constant for this reaction is −0.5838 at 200°C. Write the equilibrium constant expression for this reaction and give the value of the equilibrium constant.

1b) If calcite is dropped into a solution at 200°C with a pH of 2.0 and an HCO_3^- concentration of 0.0001 molal, will it dissolve?

1c) What would be the concentration of $CO_{2(aq)}$ in water at 25°C if the water was in contact with calcite?

1d) In a CO_2-bearing water system, what is the partitioning of CO_2 between the vapor and liquid phases at 100°C? Repeat the analysis at a temperature of 25°C. What possible implications does this have on the chemistry of geothermal systems?

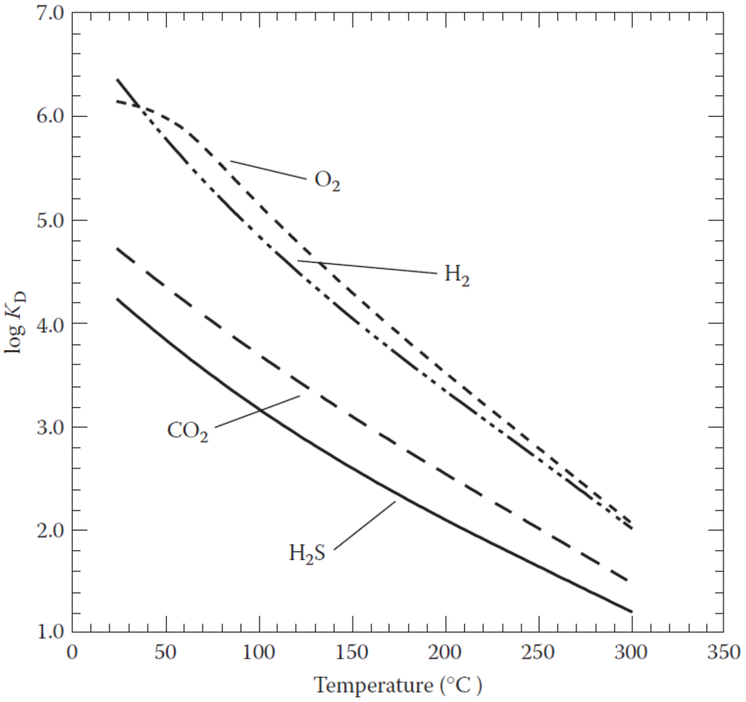

FIGURE 5.8 The variation of the log of the steam: liquid distribution coefficient (K_D) of selected gases with temperature.

2) If a geothermal water at 150°C has an aqueous silica concentration of 0.006 molal, which silica polymorph would be in equilibrium with this geothermal water, which would be supersaturated with respect to the geothermal water, and which would be undersaturated?

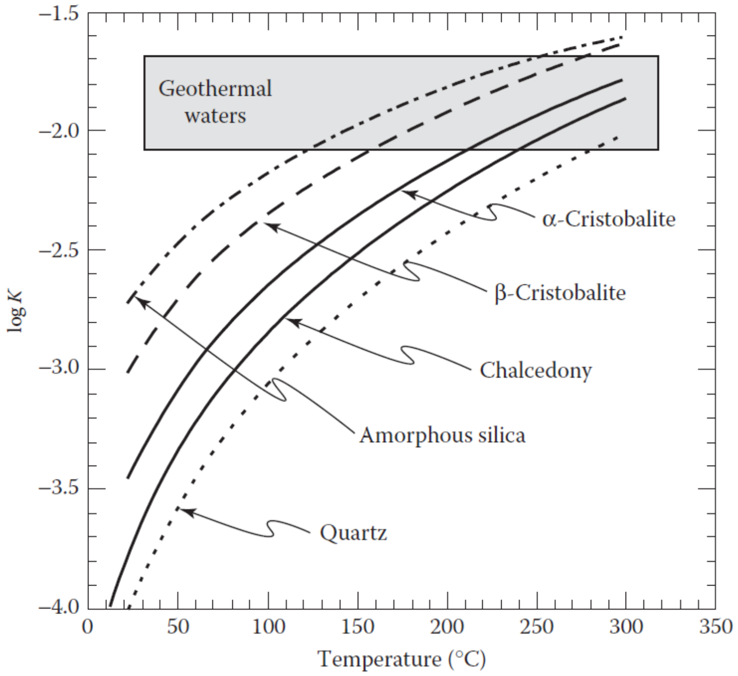

FIGURE 5.10 Log of the equilibrium constant as a function of temperature for the indicated silica polymorphs. The shaded region near the top of the figure encloses the compositions of the waters in Table 5.2.

3) List three surface features that are important indicators of near-surface geothermal resources and discuss what they indicate

4a) Listed below are three geothermometers (Henlet et al., 1984). All concentrations are in mg/kg:

SiO_2: T (°C) = [1032/(4.69−log SiO_2)]−273.15

Na/K: T (°C) = [855.6/(log (Na/K)+0.8573)]−273.15

Na-K-Ca: T (°C) = [1647/(log (Na/K)+{0.33*[log(sqrt(Ca)/Na)+2.06]}+2.47)]−273.15

Compute the temperatures for the waters listed in Table 5.2. Which samples have the best agreement among the geothermometers?

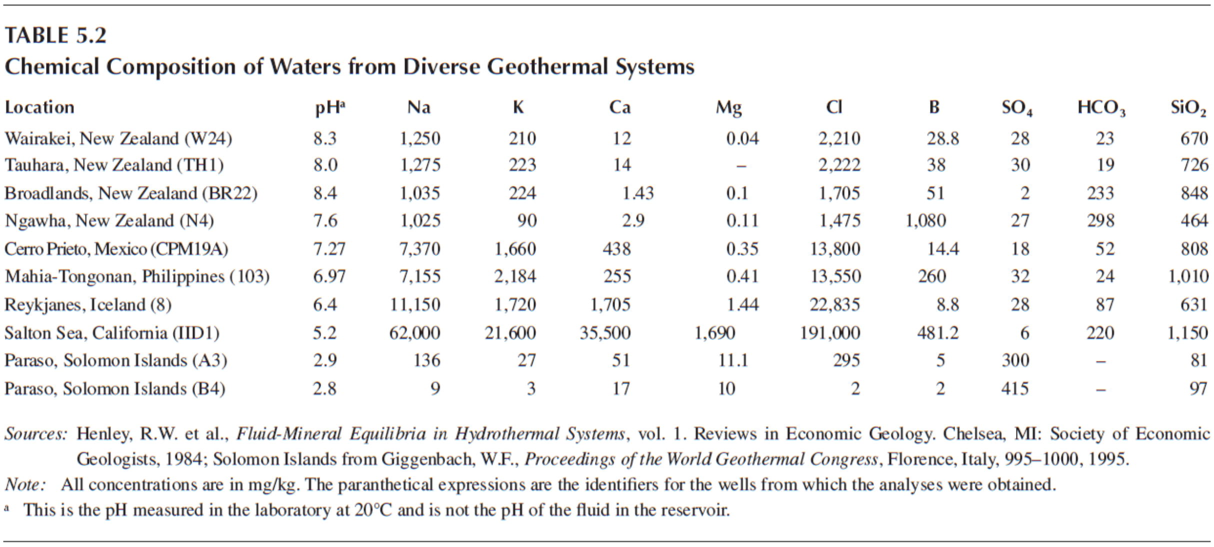

TABLE 5.2
Chemical Composition of Waters from Diverse Geothermal Systems

Location	pH[a]	Na	K	Ca	Mg	Cl	B	SO_4	HCO_3	SiO_2
Wairakei, New Zealand (W24)	8.3	1,250	210	12	0.04	2,210	28.8	28	23	670
Tauhara, New Zealand (TH1)	8.0	1,275	223	14	–	2,222	38	30	19	726
Broadlands, New Zealand (BR22)	8.4	1,035	224	1.43	0.1	1,705	51	2	233	848
Ngawha, New Zealand (N4)	7.6	1,025	90	2.9	0.11	1,475	1,080	27	298	464
Cerro Prieto, Mexico (CPM19A)	7.27	7,370	1,660	438	0.35	13,800	14.4	18	52	808
Mahia-Tongonan, Philippines (103)	6.97	7,155	2,184	255	0.41	13,550	260	32	24	1,010
Reykjanes, Iceland (8)	6.4	11,150	1,720	1,705	1.44	22,835	8.8	28	87	631
Salton Sea, California (IID1)	5.2	62,000	21,600	35,500	1,690	191,000	481.2	6	220	1,150
Paraso, Solomon Islands (A3)	2.9	136	27	51	11.1	295	5	300	–	81
Paraso, Solomon Islands (B4)	2.8	9	3	17	10	2	2	415	–	97

Sources: Henley, R.W. et al., *Fluid-Mineral Equilibria in Hydrothermal Systems*, vol. 1. Reviews in Economic Geology. Chelsea, MI: Society of Economic Geologists, 1984; Solomon Islands from Giggenbach, W.F., *Proceedings of the World Geothermal Congress*, Florence, Italy, 995–1000, 1995.

Note: All concentrations are in mg/kg. The paranthetical expressions are the identifiers for the wells from which the analyses were obtained.

[a] This is the pH measured in the laboratory at 20°C and is not the pH of the fluid in the reservoir.

4b) Explain the disagreement among the samples. Is there anything systematic about the results?

4c) Using the quartz and chalcedony geothermometers in Table 6.5, compute the temperatures for the waters in Table 5.2. What would explain the discrepancies? Provide an argument, for which geothermometer you think is the most accurate.

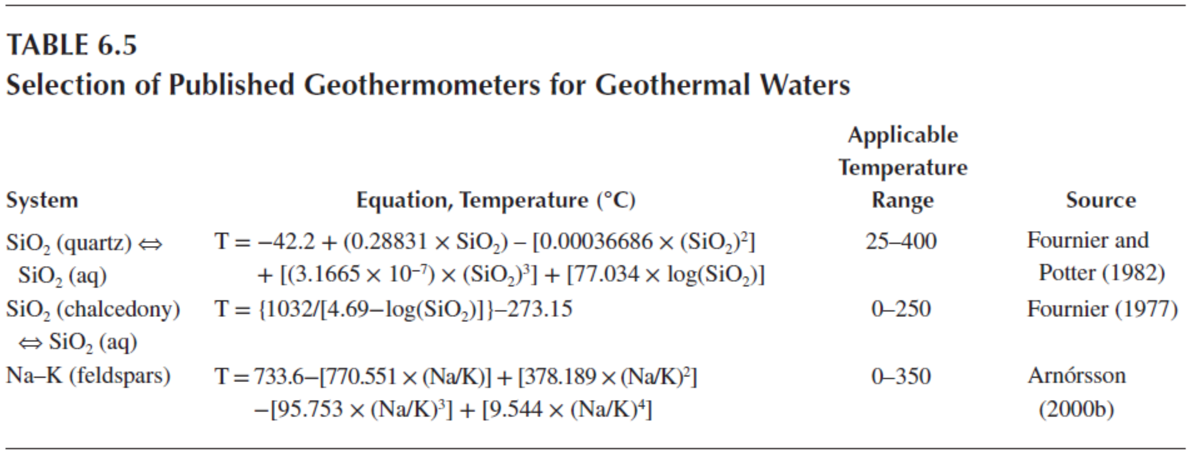

TABLE 6.5
Selection of Published Geothermometers for Geothermal Waters

System	Equation, Temperature (°C)	Applicable Temperature Range	Source
SiO_2 (quartz) ⇔ SiO_2 (aq)	$T = -42.2 + (0.28831 \times SiO_2) - [0.00036686 \times (SiO_2)^2] + [(3.1665 \times 10^{-7}) \times (SiO_2)^3] + [77.034 \times \log(SiO_2)]$	25–400	Fournier and Potter (1982)
SiO_2 (chalcedony) ⇔ SiO_2 (aq)	$T = \{1032/[4.69 - \log(SiO_2)]\} - 273.15$	0–250	Fournier (1977)
Na–K (feldspars)	$T = 733.6 - [770.551 \times (Na/K)] + [378.189 \times (Na/K)^2] - [95.753 \times (Na/K)^3] + [9.544 \times (Na/K)^4]$	0–350	Arnórsson (2000b)

5) Assuming that the water at The Geysers is mixing with Primitive Magmatic Water, what proportion of magmatic water is in The Geysers sample with the highest oxygen isotope ratio?

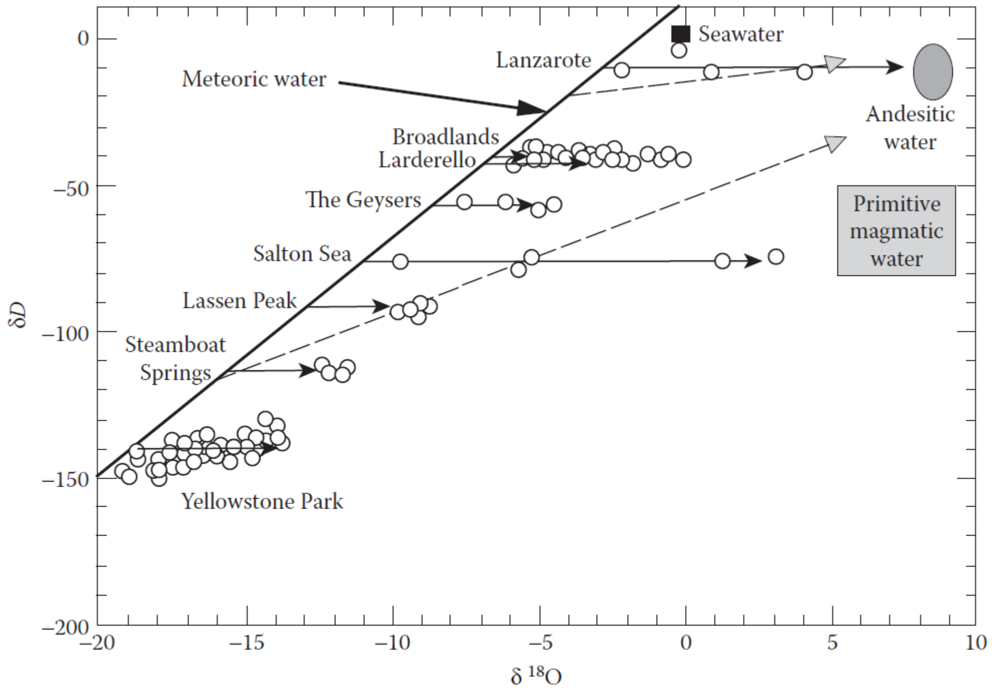

FIGURE 6.18 δ*D* and δ^{18}O values for waters from geothermal areas. (Modified from Craig, H., The isotopic geochemistry of water and carbon in geothermal areas. In *Nuclear Geology on Geothermal Areas: Spoleto, 1963*, ed. E. Tongiorgi, Consiglio Nazionale delle Ricerche, Laboratorio di Geologia Nucleare, Pisa, Italy, 17–53, 1963; Craig, H., Science, 154, 1544–1548, 1966; Truesdell, A.H. and Hulston, J.R., Isotopic evidence on environments of geothermal systems. In *Handbook of Environmental Isotope Geochemistry*, vol. I. The Terrestrial Environment, eds. P. Fritz and J.Ch. Fontes. Elsevier, Amsterdam, the Netherlands, 179–226, 1980)