Problems of Trace-Element Ratios and Geothermometry

in a Gravel Geothermal-Aquifer System

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Introduction

The utilization of trace element concentrations and ratios of trace-elements to each other or to chloride in an attempt to understand the chemical evolution of a particular water was first applied to brines, seawater, and mineral springs (Rankama and Sahama, 1950, Chap. 6; Rubey, 1951; White, D. E., 1957). Tonani's (1970) overview paper on geochemical methods applied to geothermal exploration emphasized vapor phase separation of the volatiles hydrogen sulfide, ammonia, and boric acid; figure 1, from a more recent manuscript (Tonani, 1980), shows the fractionation of boron between liquid and vapor phases as a function of temperature. Attempting to utilize B/Cl, Li/Cl, and B/Li ratios, without consideration of total concentration levels can result in misleading interpretations of relatively shallow thermal systems, which undergo a significant amount of dilution.

The system studied is a Tertiary-age, block-faulted basin in which a Pleistocene gravel bed acts as a confined aquifer and permits the lateral dispersion of the geothermal fluids. Vertical movement of the hot water is currently believed to be controlled by faults on the east side of the valley. An aerial magnetic anomaly (Geodata International, 1981, lines 300 and 320) and a Bouguer gravity anomaly (Donovan, et al., 1980) appear to correspond with these eastern faults. Basic data on the geology and trace element halos has been presented previously (Donovan, et al., 1980); figures 3, 4, and 5 from that article are reproduced below, along with the fluoride data (figure 2).

Evaluation of the mixing phenomena in this system was attempted using a dissolved silica-enthalpy graph. Figure 6 differs from most figures of this type in that a chalcedony curve is also plotted. Figure 7, an enthalpy versus chloride plot, suggests that either conductive cooling occurs before mixing or that higher chloride content background waters are available for mixing.

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Ion Ratios from Various Sources

First let us consider the results of short-term leaching of volcanic rocks. The data used to construct Table 1 are from Ellis and Mahon (1977); the temperature was maintained at 250°C for two weeks, a rock/water ratio of 2 was used for all but the rhyolite pumice. For the pumice, a rock/water ratio of 1 was used by the experimenter, and in the absence of a 250°C experimental run, the values from the 200 and 300°C have been averaged. Values for F/Cl, B/Cl, and Li/B for the existing Camp Aqua well were 0.120, 0.020, and 0.136, respectively; these ratios suggested that the thermal potential might be greater than calculated, particularly if the chalcedony curve in figure 6 is used to estimate the reservoir temperature.

Table 2 compares ranges for ion ratios; the first three rows are from White (1957) and the second three rows are from Montana systems. At Ennis, a Na-HCO₃-SO₄ water with 120 mg/kg Cl and a surface temperature of 83°C, yields a 153°C Na-K-Ca-Mg reservoir temperature and a 135°C quartz reservoir temperature, assuming no mixing. A 540 foot well encountered 93°C water. At Warm Springs the surface temperature (77-78°C) agrees with the Na-K-Ca calculated 79.5°C, and chalcedony calculated value of 77.7°C. A 1,500 foot drill hole at Warm Springs encountered 78°C water. The Ennis system is in gneiss, while the Warm Springs system is in Tertiary(?) age valley fill materials and is probably fed by a Paleozoic limestone (high Ca and SO₄ content). The Camp Aqua data generally fit in the same order of magnitude for trace element ratios; however, the total dissolved solids content is less than half as great.

The test well in the Camp Aqua vicinity was drilled with state funds to evaluate a request for funding for a deep, large-diameter production well by a private concern. Table 3 contains chemical data and geothermometer calculations for well 211, (believed to represent the background water in the gravel aquifer), the Camp Aqua well, the test well in the gravel zone, and the test well in the bedrock zone. These data suggest to us that the 124°C source water projected from figure 6 may exist somewhere in the system and that dilution has had a greater effect on the quartz geothermometer than on the Na-K-Ca-Mg geothermometer.

A note of warning should be stressed at this point. Secondary calcite, and possibly dolomite, have been noted in the cuttings, both from the gravel and bedrock zones. Thus the correlation between the Na-K-Ca-Mg

Table 2. Approximate ranges of ion ratios from chloride dominated waters
(From White, 1957) and data from the Camp Aqua well and two springs

	F/Cl	B/Cl	Li/Na	As (ppm)	H ₂ S (ppm)	Li/B
Ocean	7×10^{-5}	2.4×10^{-4}	10^{-5}	2×10^{-3} - 1.7×10^{-2}	0-60	N.L.
Oil-field Brines	10^{-5} - 10^{-3}	10^{-5} - 2×10^{-2}	10^{-4} - 3×10^{-3}	?	0-3,000	N.L.
Volcanic Hot Springs	5×10^{-4} - 10^{-1}	10^{-2} - 10^{-1}	3×10^{-3} - 3×10^{-2}	10^{-1} - 10^{-1}	0-10	N.L.
Camp Aqua	1.2×10^{-1}	2×10^{-2}	5.7×10^{-4}	---	---	0.136
Ennis	9.2×10^{-2}	5×10^{-3}	7.6×10^{-4}	2.5×10^{-2}	---	0.426
Warm Springs	7.8×10^{-1}	2×10^{-2}	3×10^{-3}	---	0.7	3.60

* halo from lower temperature wells up to 0.1 ppm

N.L. - Not Listed

--- - Data not available

Table 1. Ratios by weight of leach solutions

	F/Cl	B/Cl	Li/B
Basalt	0.024	0.006	0.214
Andesite	0.192	0.048	0.200
Dacite	0.375	0.048	0.368
Rhyolite Pumice	0.438	0.006	---

--- insufficient data, value @ 200°C is 3.33

Table 3. Chemical data from Camas area wells

	Ca	Mg	Na	K	SiO ₂	Field Alka.	Cl	SO ₄
Well LB-211	29.4	6.6	24.0	0.8	20.8	125	1.4	23.8
Well LB-32	3.2	0.3	152.	4.0	42.2	293	32.5	4.1
Test Well 264'	3.4	0.3	159.	3.2	45.9	297*	35.8	0.4
Test Well 324'	10.7	2.1	139.	2.9	38.8	328	35.9	<.1
	F	Li	B	As	H ₂ S	Temp °C	TDS	Field pH
Well LB-211	0.4	<.008	<.09	0.009	<.1	10	179	8.26
Well LB-32	3.9	0.087	0.64	<.0001	--	52	437	8.71*
Test Well 264'	5.2	0.083	0.64	0.0005	--	49	432	8.72*
Test Well 324'	4.6	0.050	0.63	<.0001	--	47	406	7.82
	Chalcedony	Quartz	Na-K-Ca-Mg					
Well LB-211	33°	65°	-58°					
Well LB-32	66°	94°	117°					
Test Well 264'	68°	98°	119°					
Test Well 324'	60°	90°	79°					

* Laboratory value

temperatures and the 124°C projection from figure 6 may be wholly fortuitous. It is our belief, at this time, that only the chalcedony curve in figure 6 can be used with any confidence, and that the 77°C source water is the more probable of the two. The trace element data ratios are probably, in part, controlled by fines (clays) within the gravel due mainly to ion exchange. At least one zeolite (either heulandite or clinoptilolite) has been detected in the bedrock cuttings (along with pyrite and chalcopyrite(?)). We are definitely looking at an old hydrothermal system. What is uncertain at the present time is whether the hydrothermal alteration and mineralization are related synoptically to the current hot water system, or whether the modern geothermal circulation systems simply following the same flow pathway followed by older (possibly Tertiary) hydrothermal fluids and intrusives.

Conclusions

The valley fill aquifer system in the vicinity of Camp Aqua is still poorly understood with respect to the temperature of source waters. For a low TDS (420 mg/kg) Na-HCO₃ water in valley fill materials it is advised that trace element ratios be used with great caution, and the absolute values of the trace elements and chloride must be considered. The role of cation (Li) and base (B) exchange by clays in a system affected by waning or prior hydrothermal alteration is not presently clear, and needs further study.

References Cited

- Donovan, J. J., Wideman, C. J., and Sonderegger, J. L., 1980, Geochemical evaluation of shallow dilution of geothermal water in the Little Bitterroot Valley, Montana: Geothermal Resources Council Trans., v. 4, p. 157-160.
- Fournier, R. O., 1980, Application of water geochemistry to geothermal exploration and reservoir engineering: in, Ryback, L., and Muffler, L. P. J., eds, Geothermal Systems: Principles and Case Histories, Wiley, New York, p. 109-143.
- Geodata International, 1981, Aerial radiometric and magnetic survey, Wallace national topographic map, Idaho/Montana: U. S. Dept. Energy, Grand Junction Office, Nat. Uranium Resource Evaluation Publication GJBX-111(81).
- Rankama, Kalervo, and Sahama, T. G., 1950, Geochemistry: Chicago, Univ. Chicago Press, 912 p.
- Rubey, W. W., 1951, Geologic history of sea water. An attempt to state the problem: Geol. Soc. America Bull., v. 62, p. 1111-1148.

- Tonani, Franco, 1970, Geochemical methods of exploration for geothermal energy: *Geothermics*, v. 2, pt. 1, p. 492-515.
- Tonani, Franco, 1980, Overview of the specific contribution of geochemistry to geothermal exploration: Invited lecture to the Seminar on European Geothermal Research, Strabourg, March 4-6, 1980, 26 p.
- White, D. E., 1957, Magmatic, connate, and metamorphic waters: *Geol. Soc. America Bull.*, v. 68, p. 1659-1682.

Figure 1. Plot of boron fractionation between the liquid and vapor phases as a function of temperature (from Tonani, 1980).

Figure 2. F^- concentrations (mg/kg) in well waters.

Figure 4. B concentrations ($\mu\text{g/kg}$) in well waters.

Figure 5. Cl^- concentrations (mg/kg) in well waters.

Figure 6. Enthalpy - SiO₂ plot of data from a typical background well (211) and the Camp Aqua well. The chalcedony curve has been added using data from Fournier (1980).

Figure 7. An enthalpy-chloride plot for waters from the gravel aquifer in the Camp Aqua vicinity.

Addendum

The first issue of Geothermics for 1981 (v. 10, no. 1) arrived after submission of this manuscript. This issue includes an article entitled "Sodium/Lithium Ratio in Water Applied to Geothermometry of Geothermal Reservoirs" by Christian Fouillac and Gil Michard (p. 55-70). They present the following two empirical equations for reservoir temperature calculation:

$$(1) \log_{10}(m_{\text{Na}}/m_{\text{Li}}) = 1000/T - 0.38, \text{ for } \text{Cl}^- < 0.2\text{M, and}$$

$$(2) \log_{10}(m_{\text{Li}}) = -2258/T + 1.44, \text{ for } \text{Cl}^- < 0.2\text{M;}$$

the reader is referred to Fouillac and Michard for details on the ~~derivation~~ ^{derivation} deviation of the equations.

Using these equations with the Camp Aqua well data results in the highest calculated reservoir temperatures. Equation (1) yields a reservoir temperature of 49°C, slightly below the observed temperature at the wellhead. Equation (2) yields a reservoir temperature of 83°C, slightly greater than our source temperature using the chalcedony curve on the SiO₂ - Enthalpy plot (figure 6). While these calculations are subject to the concerns about dilution and ion-exchange processes, these data provide additional support for use of the chalcedony curve on SiO₂ - Enthalpy plots for low-temperature geothermal systems.

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