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Fluorite solubility equilibria in selected geothermal waters

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Abstract—Calculation of chemical equilibria in 351 hot springs and surface waters from selected geothermal areas in the western United States indicate that the solubility of the mineral fluorite, CaF_2, provides an equilibrium control on dissolved fluoride activity. Waters that are undersaturated have undergone dilution by non-thermal waters as shown by decreased conductivity and temperature values, and only 2% of the samples are supersaturated by more than the expected error. Calculations also demonstrate that simultaneous chemical equilibria between the thermal waters and calcite as well as fluorite minerals exist under a variety of conditions.

Testing for fluorite solubility required a critical review of the thermodynamic data for fluorite. By applying multiple regression of a mathematical model to selected published data we have obtained revised estimates of the pK (10,96), ΔG_f^0 (−280.08 kcal/mole), ΔH_f^0 (−292.59 kcal/mole), S° (16.39 cal/deg/mole) and C_P^0 (16.16 cal/deg/mole) for CaF_2 at 25°C and 1 atm. Association constants and reaction enthalpies for fluoride complexes with boron, calcium and iron are included in this review. The excellent agreement between the computer-based activity products and the revised pK suggests that the chemistry of geothermal waters may also be a guide to evaluating mineral solubility data where major discrepancies are evident.

INTRODUCTION

THE INCREASED development of geothermal resources to help meet energy demands requires a better understanding of the chemistry of geothermal waters. It is necessary to know not only what the composition of a particular water is, but what processes determine that composition. This knowledge is useful in the design and operation of power plants, in the exploration for new fields and in the evaluation of the potential effects of wastewater disposal. In order to adequately model the chemical processes within a geothermal region, field measurements, experimental laboratory investigations and theoretical considerations must be carefully synthesized. If a model is proved successful, it can then be used to assess the environmental impact of geothermal development.

One of the elements which occurs in relatively high concentrations (commonly greater than 1 mg/l) in many geothermal waters is fluorine. The purpose of this paper is to test the hypothesis that fluoride concentrations are governed by the solubility of the mineral fluorite, CaF_2, in several geothermal regions of the western United States. With the use of high-speed computers, it is now possible to make a quantitative analysis of a possible solubility-controlled reaction without laborious and time-consuming manual calculations. The success of this approach is very encouraging and should provide useful information for other geochemical surveys.

A preliminary assessment of several geothermal waters for fluorite saturation supported our suspicion that there were errors in the published thermodynamic data for fluorite. This finding provided the impetus for a critical review of the literature on the thermodynamic properties of fluorite from which we have calculated a set of revised values.

FLUORIDE IN GEOTHERMAL WATERS

The fluoride content of surface waters rarely surpasses 1.6 mg/l, the maximum recommended concentration for domestic water supplies when maximum daily air temperatures are 22–26°C (ENVIRONMENTAL PROTECTION AGENCY, 1972). Geothermal waters, however, commonly exceed recommended water quality criteria for dissolved fluoride. Although fluoride concentrations are generally below 20 mg/l in thermal springs and in solutions from rock-leaching experiments (ELLIS, 1967), they have been reported as high as hundreds and even thousands of milligrams per litre in acid (pH < 2) hot springs by ELLIS (1973) and OZAWA *et al.* (1973). Under these acid conditions fluorine would be present largely as aqueous HF, HF_2^- and SiF_6^{2-}, which would partially escape into the air as HF and SiF_4 gases at atmospheric pressures. Low and stable levels (0.5–1.7 mg/l) of dissolved fluoride are required to maintain dental health, prevent teeth mottling and prevent fluorosis in livestock (UNDERWOOD, 1971). Thus, geothermal waters constitute a source of potential fluoride contamination to natural water systems.

In this study a total of 351 water analyses from selected springs, wells and streams in Yellowstone

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National Park (COX, 1973), hot springs in Yellowstone (ROWE *et al.*, 1973), as well as hot springs in Nevada (MARINER *et al.*, 1974a), Oregon (MARINER *et al.*, 1974b) and California (WILLEY *et al.*, 1974) were used as input data for our computations. Only water analyses reporting: (1) *in situ* temperatures and pH values, (2) pH values greater than 4.0, (3) all major constituents, (4) fluoride and calcium, and (5) specific conductance were tested. Acid hot springs with pH values less than 4.0 were avoided because compilation and evaluation of the appropriate complexes has not yet been completed.

TESTING FOR FLUORITE SATURATION

MAHON (1964) and ELLIS and MAHON (1964, 1967) have argued that the concentration of fluoride in geothermal waters is controlled by the solubility of fluorite. They base their arguments on rock-leaching experiments and fluorite solubility determinations carried out at 100–350°C and a constant pressure of 345 bars. The rock-leaching experiments demonstrated that fluoride concentrations tended toward limiting values which could be related to the solubility of pure fluorite under similar pressure and temperature conditions. Unfortunately, non-equilibrium conditions were present in some of these experiments, as indicated by increasing and decreasing concentrations of fluoride with time. In addition, they did not account for ionic strength and complexing effects. Their conclusions were based on concentration products rather than activity products. Comparison of their solubility data with thermal water analyses can only be considered a qualitative indication that an equilibrium solubility control exists.

The solubility of fluorite as shown by the following reaction:

$$\mathrm{CaF}_{2(\alpha)} \rightleftarrows \mathrm{Ca}^{2+}_{(aq)} + 2\,\mathrm{F}^{-}_{(aq)} \tag{1}$$

can be affected by temperature, pressure, ionic strength, particle size, polymorphism, complexing capacity of the solution, and kinetic barriers. In order to simplify the problem, we have assumed equilibrium conditions with no particle size effects. The negative log of the equilibrium constant, K, for reaction (1) is:

$$\mathrm{p}K = -\log K = -\log(a_{\mathrm{Ca}^{2+}})(a_{\mathrm{F}^-})^2, \tag{2}$$

which expresses the equilibrium concentrations in terms of the activities of dissolved calcium ($a_{\mathrm{Ca}^{2+}}$) and dissolved fluoride (a_{F^-}). Since activities are used instead of concentrations, ionic strength effects are taken into account.

Polymorphism is not a major difficulty because the crystalline alpha phase (α) of fluorite is stable up to 1424°K (NAYLOR, 1945). Temperature effects are calculated from the van t'Hoff equation:

$$\frac{\mathrm{d}\log K}{\mathrm{d}(1/T)} = -\frac{\Delta H_r}{2.303\,R}, \tag{3}$$

where ΔH_r is the partial molal reaction enthalpy, R is the gas constant, and T is the Kelvin temperature. Pressure effects are determined from the relationship:

$$\frac{\mathrm{d}\log K}{\mathrm{d}P} = -\frac{\Delta V_r}{2.303\,RT}, \tag{4}$$

where ΔV_r is the partial molal volume change for the reaction.

Complexing can often be the single most important factor which determines the total concentration of fluorite which dissolves. Upon dissolution of fluorite, the ions may associate with themselves to form a monofluoride complex:

$$\mathrm{Ca}^{2+}_{(aq)} + \mathrm{F}^{-}_{(aq)} \rightleftarrows \mathrm{CaF}^{+}_{(aq)}. \tag{5}$$

Fluoride ion, being a strong ligand, will also complex with several cations, such as magnesium, iron and aluminum:

$$\mathrm{Mg}^{2+}_{(aq)} + \mathrm{F}^{-}_{(aq)} \rightleftarrows \mathrm{MgF}^{+}_{(aq)} \tag{6}$$

$$\mathrm{Fe}^{3+}_{(aq)} + n\mathrm{F}^{-}_{(aq)} \rightleftarrows \mathrm{FeF}^{(3-n)}_{n(aq)};\ n = 1,2,3 \tag{7}$$

$$\mathrm{Al}^{3+}_{(aq)} + n\mathrm{F}^{-}_{(aq)} \rightleftarrows \mathrm{AlF}^{(3-n)}_{n(aq)};\ n = 1,2,3,4,5,6. \tag{8}$$

Due to the low concentrations of iron (usually less than 1 mg/l) and aluminum (less than 0.1 mg/l) in neutral thermal waters, fluoride would not be bound to these cations to any significant extent. Magnesium may be an important complexing cation because its concentration ranges up to 62 mg/l in our samples.

Another species which complexes with $\mathrm{F}^{-}_{(aq)}$ is boric acid and since the boron content of geothermal waters occasionally reaches concentrations of 150 mg/l (ELLIS, 1967), these complexing reactions need to be considered:

$$\mathrm{B(OH)}_{3(aq)} + n\mathrm{F}^{-}_{(aq)} \rightleftarrows \mathrm{BF}_n(\mathrm{OH})^{-}_{4-n(aq)} + (n-1)\,\mathrm{OH}^{-}_{(aq)};\quad n = 1,2,3,4. \tag{9}$$

Calcium ion also complexes significantly with carbonate and sulfate ions which can increase the solubility of fluorite. Complexing has the effect of reducing free calcium and fluoride activities, thereby increasing the tendency for fluorite to dissolve. The dissociation constants for some of the above reactions as well as enthalpy and heat capacity considerations are given below in the discussion on thermodynamic data.

When complexing is accounted for, the activity product, $AP = (a_{\mathrm{Ca}^{2+}})\,(a_{\mathrm{F}^-})^2$, can be calculated from a water analysis containing all of the major constituents. The ratio of the AP and the equilibrium constant, K, gives the degree of saturation of a water with respect to fluorite. To express this in terms of a free energy difference, ΔG_r, we have:

$$\Delta G_r = \Delta G_r^0 + 2.303\,RT\log(a_{\mathrm{Ca}^{2+}})(a_{\mathrm{F}^-})^2 \tag{10}$$

$$= -2.303\,RT\log K + 2.303\,RT\log AP \tag{11}$$

$$= 2.303\,RT\log(AP/K). \tag{12}$$

When a water is undersaturated, $AP < K$ and $\Delta G_r < 0$; when supersaturated, $AP > K$ and $\Delta G_r > 0$; and at equilibrium (saturation), $AP = K$ and $\Delta G_r = 0$.

The computations involving activity corrections, temperature dependence, effect of complexing, and degree of saturation can be easily made with available computer programs. We employed the PL/I programs WATEQ (Truesdell and Jones, 1974) for our computations and EQPRINT and EQPLOT (J. W. Ball, U.S. Geological Survey, unpublished programs) to evaluate our results graphically. In brief, WATEQ uses the chemical analysis and on-site measurements of temperature, pH and Eh and distributes the total concentrations of species among all of the known associated and unassociated species according to their equilibrium constants. Distribution of species is accomplished by iteration and correction of the free anion concentration for each successive cycle. The ionic strength and activity coefficients are also corrected on each iteration. Iteration is stopped when the sum of the weak acids, free anions and their complexes is within 0.5% of the analytical values for each major anion.

Calculated log AP values for fluorite were plotted as a function of on-site temperature with EQPLOT using letter symbols to indicate the basin from which the samples came. These results are shown in Fig. 1. All of the letters plot significantly below the fluorite solubility curve of Helgeson (1969), which suggests two possible explanations. These thermal waters may be undersaturated with respect to fluorite because some other mineral phase is controlling the calcium and fluoride activities at undersaturated values or else kinetic or hydrodynamic factors are preventing saturation. Alternatively, the thermodynamic values used by WATEQ or by Helgeson (1969) or by both are in error. The most striking observation that appears in Fig. 1 is the well-defined upper boundary to the log AP values. This defines a limit proportional to log $(a_{Ca^{2+}})(a_{F^-})^2$ over a wide temperature and compositional range, thereby making the suggestion of consistent undersatuaration unlikely. Furthermore, 90% of the values for hot springs with temperatures greater than 30°C agree to within 2 log AP units (2.7 kcal of energy). Thus, a critical evaluation of the thermodynamic data was mandated.

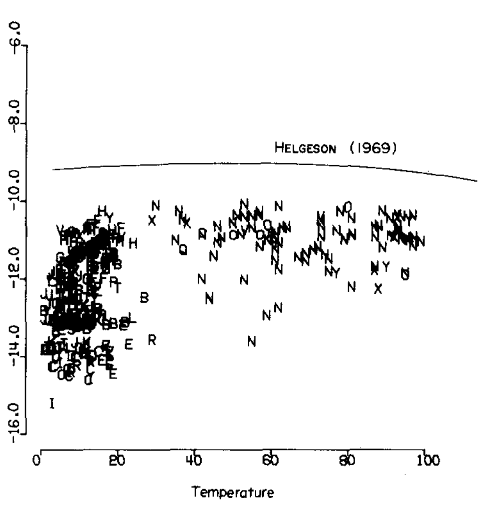

Fig. 1. Log of the activity product for fluorite plotted as a function of on-site temperatures for geothermal waters of the western U.S. Letter symbols (see Appendix 2) represent different basins or regions. The solid line represents the equilibrium solubility of fluorite from Helgeson (1969).

THERMODYNAMIC DATA

Proper evaluation of the accuracy of published thermodynamic data needed for chemical equilibria computations of natural waters is a tedious and time-consuming task. We have reviewed the literature for data on: (1) aqueous fluoride complexes, (2) free energies, enthalpies and entropies of fluorite, and (3) the heat capacities of fluorite, $Ca^{2+}_{(aq)}$ and $F^-_{(aq)}$ in order to test the equilibrium control by fluorite solubility. Final revised estimates of these values were obtained by regression of a mathematical model to the data (Haas, 1974).

Dissolved complexes

Association constants and enthalpy values (or temperature-dependent power functions) are used in WATEQ to calculate species distribution. Included in WATEQ are the values for the association of MgF^+, AlF^{2+}, AlF_2^+, AlF_3^0 and AlF_4^- to which we have added the values for $BF(OH)_3^-$, $BF_2(OH)_2^-$, $BF_3(OH)^-$, BF_4^-, FeF^{2+}, FeF_2^+, FeF_3^0 and CaF^+. The association constants for reactions (9) were determined by Grassino and Hume (1971) and their value for $n = 4$ agrees with previous work. Although they measured these constants at two temperatures (25 and 35°C), the lack of precision and the lack of sufficient difference in the association constants makes it impossible to obtain any enthalpy information except for $n = 4$. We have estimated the reaction enthalpies in the following manner, Wagman *et al.* (1968) give free energies of formation for $BF_2(OH)_2^-$, $BF_3(OH)^-$ and BF_4^- which give log K values for the association reactions within 10% of the values from Grassino and Hume (1971). Unfortunately, standard enthalpies of formation are only listed for $BF_3(OH)^-$ and BF_4^-. A linear free energy relationship holds between the free energies of $BF_2(OH)_2^-$, $BF_3(OH)^-$ and BF_4^- as a function of the number of complexed fluoride ions. Since the entropy difference between BF_4^- and $BF_3(OH)^-$ is quite small, it should be safe to assume that a linear relationship holds for the enthalpies as well. By extrapolation, $\Delta G_f^0\ [BF(OH)_3^-] = -303.05$ kcal/mole, $\Delta H_f^0\ [BF(OH)_3^-] = -342.20$ kcal/mole, and $\Delta H_f^0\ [BF_2(OH)_2^-] = -353.60$ kcal/mole. Reaction enthalpies were then computed using the $\Delta H_f^0\ [F^-]$ from this study and $\Delta H_f^0\ [OH^-]$ from Wagman *et al.* (1968). In order to incorporate the distribution of boron species among these fluoride complexes into WATEQ, we found it necessary to modify the program so that iterative calculations for boron were included.

Association constants for the iron fluoride complexes [reaction (7)] were taken from unpublished selected values.* Although enthalpies for reaction (7) calculated from WAGMAN *et al.* (1969) agree with those listed in ASHCROFT and MORTIMER (1970) for $n = 1$ and $n = 2$, a serious discrepancy was found for $n = 3$. The same discrepancy occurs in the free energy calculations for $n = 3$ using WAGMAN *et al.* (1969). Therefore, we have preferred to use the reported enthalpy value from ASHCROFT and MORTIMER (1970) for $n = 3$.

A review of the literature revealed four different investigations of reaction (5) both as a function of temperature (up to 40°C) and ionic strength (TANNER *et al.*, 1968; AZIZ and LYLE, 1969; ELQUIST, 1970; BOND and HEFTER, 1971). All of the pK values at 25°C were plotted as a function of $\sqrt{I}$ and extrapolated to zero ionic strength to obtain a corrected pK. Then the pK values for the same ionic strength were plotted as a function of $1/T$ to obtain the reaction enthalpy. Agreement between investigators was quite good (the variance is less than 0.1 of a pK unit).

These additional values for association constants and reaction enthalpies have been added to WATEQ and are listed here in Table 1. ELLIS (1967) has suggested that fluorosilicate complexing may be important in geothermal waters. CADEK and MALKOVSKY (1966) have shown that silicon fluoride complexes can form in acid solutions, but under the neutral conditions we have selected, fluoride is not affected by silica complexing.

Fluorite, $CaF_2(\alpha)$

Thermodynamic parameters for the heat content, heat capacity, entropy, enthalpy and free energy of fluorite are available from calorimetric, solubility, and electrochemical measurements. Unfortunately, there are major discrepancies between the results from different investigators. It became necessary to make a full compilation of values, to review the methods of measurement, and to select data sets which were expected to be more accurate on the basis of the precision of the results and the reliability of the method used. This task was greatly facilitated by the use of the computer program made available by HAAS (1974). This program, PHAS20, carries out a simultaneous multiple regression of a mathematical model to any group of measurements of thermochemical data for a single species, a reaction or group of chemically related species. The mathematical model is based on an empirically-derived power function of temperature which is a modified version of the Maier–Kelly equation. The heat capacity power function used is:

$$Cp_i = a_i + 2b_i T + c_i T^{-2} + f_i T^2 + g_i \sqrt{T} \quad (13)$$

for a solid species, i, and

$$Cp_i = a_i + 2b_i T + c_i T^{-2} + f_i T^2 - \frac{g_i T f(T)}{\epsilon} \quad (14)$$

for an aqueous species, i, where

$$f(T) = \alpha^2 \exp^2(\beta + \alpha T) + \alpha^2 \exp(\beta + \alpha T) \quad (15)$$
$$+ \frac{2\alpha}{\theta} \exp(\beta + \alpha T) + \frac{1}{\theta^2}.$$

a_i, b_i, c_i, f_i and g_i are power series coefficients for the heat capacity function, Cp_i, T is the Kelvin temperature, ϵ is the dielectric constant of the solution and α, β and θ are fitted constants. Equation (15) was adopted from HELGESON (1967) by HAAS (1974). PHAS20 provides the user with deviation plots which permit easy evaluation of discordant data.

The thermochemical data inputed to PHAS20 is compiled in Table 2 along with the values obtained from the regression analysis. NAUMOV *et al.* (1974) obtained their values by least squares fit of a mathematical model using a linear heat capacity power function ($Cp_i = bT$) to only one set of data; therefore, we have not used their data. Their methods are outlined in KHODAKOVSKIY *et al.* (1968). The enthalpy value of VECHER and VECHER (1967) was not used because they give no experimental measurements, only a final ΔH_f^0 for $CaF_{2(\alpha)}$ which assumes that the entropy change for their solid-state reaction:

$$CaO + MgF_2 \rightleftarrows CaF_2 + MgO \quad (16)$$

is zero at 1200°K and which utilizes unevaluated enthalpies for the other species. The high free energy value reported by SKELTON and PATTERSON (1973) was not used because of an internal inconsistency as pointed out by CHATTOPADHYAY *et al.* (1975). Furthermore, the latter authors report a ΔG_f^0 for NiF_2 at 298°K of 1.4 kcal/mole more positive than the value reported by SKELTON and PATTERSON (1973).

Table 1. Log K and standard enthalpies of reaction (298°K, 1 atm) for dissolved fluorine complexes†

Reaction	log K	ΔH_r^0 (kcal/mole)
$B(OH)_3^0 + F^- \rightleftarrows BF(OH)_3^-$	-0.30	-6.11
$BF(OH)_3^- + F^- \rightleftarrows BF_2(OH)_2^- + OH^-$	-5.97	13.43
$BF_2(OH)_2^- + F^- \rightleftarrows BF_3(OH)^- + OH^-$	-7.96	13.43
$BF_3(OH)^- + F^- \rightleftarrows BF_4^- + OH^-$	-7.39	13.43
$Fe^{3+} + F^- \rightleftarrows FeF^{2+}$	6.20	2.70
$FeF^{2+} + F^- \rightleftarrows FeF_2^+$	4.60	2.10
$FeF_2^+ + F^- \rightleftarrows FeF_3^0$	3.20	0.60
$Ca^{2+} + F^- \rightleftarrows CaF^+$	0.94	4.12

† See text for sources of data.

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* These values were obtained from an unpublished manuscript by E. Hogfeldt and L. G. Sillén (1966) which was made available to us by the courtesy of Dr. J. J. Morgan. The values in the Hogfeldt and Sillén compilation were selected from SILLÉN and MARTELL (1964).

Table 2. Thermodynamic data compilation

Species	G°_f (kcal mole^{-1})	H°_f (kcal mole^{-1})	S° (cal deg^{-1} mole^{-1})	Method	Source
$F_{2(g)}$	0	0	48.44	revised data	Wagman, et al. (1968)
	0	0	48.61	spectroscopy	Moore (1972)
	0	0	48.45	calorimetric	Naumov, et al. (1974)
	0	0	48.438	calorimetric	Hultgren (1973); this study
$Ca_{(\alpha)}$	0	0	9.97	calorimetric	Naumov, et al. (1974)
	0	0	9.902	calorimetric	Hultgren (1973);this study
$Ca^{++}_{(aq)}$	-132.3	--	--	analytic fit	Stull and Prophet (1971)
	-132.1	-129.7	-13.2	calorimetric	Naumov, et al. (1974)
	-132.30	-129.74	-12.7	revised data	Parker, et al. (1971)
	-132.30	-129.72	-12.7	regression anal.	This study
$F^-_{(aq)}$	-66.64	-79.50	-3.3	revised data	Wagman, et al. (1968)
	-66.95	--	--	analytic fit to $HF_{(g)}$	Stull and Prophet (1971)
	-66.92	-79.79	-3.35	calorimetric	Naumov, et al. (1974)
$F^-_{(aq)}$ (cont'd)	--	-80.2	--	calorimetric and estimate	Finch, et al. (1968)
	-66.42	-79.08	-2.7	regression anal.	This study
$CaF_{2(\alpha)}$	--	--	16.46	calorimetric	Todd (1949)
	-280.48	-293	16.389	analytic fit	Stull and Prophet (1971)
	-281.07	-293.58	16.46	analytic fit	Naumov, et al. (1974)
	--	-291.9	--	calorimetric	Finch, et al. (1968)
	-280.35	-292.6(calc.)	17.36(calc.)	emf at high T	Rezukhina, et al. (1974)
	-279.00	-291.50	16.46	revised data	Parker, et al. (1971)
	--	-294.3	--	emf at high T	Vecher and Vecher (1967)
	-278.85	--	--	emf at high T	Skelton and Patterson (1973)
	-280.08	-292.59	16.39	regression anal.	This study

Since NiF_2 is used as a reference electrode, it is clear that its thermodynamic properties need to be more accurately known before free energy calculations can be made from these electrochemical studies. The remainder of the data in Table 2 was weighted in the regression analysis according to the precision reported by the investigator except: (1) TODD (1949), where the reported absolute error of ±0.3% was used, (2) NAYLOR (1945), whose absolute error was estimated at ±1% (reported precision = ±0.3%), (3) standard state (298°K, 1 atm) values, which are subject to the greatest variation and are weighted to cover the range of reported values (e.g. ±1.5 kcal for the free energy and enthalpy of formation of fluorite), and (4) the solubility data of STRÜBEL (1965) which was weighted at ±0.1 of a p*K* unit.

Numerous solubility determinations on fluorite have been carried out on both synthetic and natural samples. A literature search revealed p*K* values for fluorite dissolution at 25°C ranging from 8.27 to 11.19 as shown in Table 3. Many of these values are based on total dissolved solids and do not account for ionic strength or complexing, but with calcium and fluoride concentrations of about 4×10^{-4} M there should be no significant changes in solubility from these effects. Furthermore, it can be shown that the CaF^+ complex is weak and carbonate complexing in these dilute solutions should have little effect on the solubility. The values for p*K* listed in Table 3 were $\gamma_{Ca^{2+}} = \gamma_{F^-} = 1$ except for the measurements of STRÜBEL (1965) for which activity coefficients were interpolated from the data of KIELLAND (1937) and the values of ROBERSON and SCHOEN (1973) which were obtained from ion-selective electrodes. By assuming stoichiometric dissolution and given the solubility of fluorite as x mg/l of dissolved CaF_2, then $x = x_{Ca^{2+}} + x_{F^-}$. Since 2 moles of fluoride ion are produced for every mole of calcium ion, then

$$
\begin{aligned}
x &= (40)(M_{Ca^{2+}})(10^{-3}) + (2)(19)(M_{Ca^{2+}})(10^{-3}) \\
&= (78)(M_{Ca^{2+}})(10^{-3})
\end{aligned}
$$

and

$$
\begin{aligned}
M_{Ca^{2+}} &= x/[(78)(10^{-3})] \quad \text{and} \\
M_{F^-} &= 2x/[(78)(10^{-3})]. \qquad (17)
\end{aligned}
$$

Table 3. Fluorite solubility data at 0–350°C

T (°C)	-log K (pK)	Method	Reference
0	10.72	conductivity	Kohlrausch (1908)
0	10.01	colorimetric (F^-)	Kazakov and Sokolova (1950)
10	9.78	colorimetric (F^-)	Kazakov and Sokolova (1950)
10	10.40	colorimetric	Ikrami, et.al. (1971)
16	10.56	conductivity	Kohlrausch (1908)
17	10.55	conductivity	Kohlrausch (1908)
17.5	10.44	conductivity	Kohlrausch (1908)
18	10.46	conductivity	Kohlrausch (1904)
18	10.55		Mougnard (1931)
20	9.60	colorimetric (F^-)	Kazakov and Sokolova (1950)
20	10.31	colorimetric	Ikrami, et.al. (1971)
25	10.57		Smyshlyaev and Edeleva (1962)
25	8.27	titration	Lingane (1967)
25	9.77	ion-selective electrodes	Roberson and Schoen (1973)
26	10.37	conductivity	Kohlrausch (1908)
26.6	10.46	conductivity	Kohlrausch (1908)
30	10.31	colorimetric	Ikrami, et.al. (1971)
40	10.41	conductivity	Kohlrausch (1908)
100	8.70	colorimetric (F^-)	Kazakov and Sokolova (1950)
23	11.28	weight loss	Strubel (1965)
25	11.23	weight loss	Strubel (1965)
26.5	11.21	weight loss	Strubel (1965)
39	10.94	weight loss	Strubel (1965)
50	10.70	weight loss	Strubel (1965)
61	10.54	weight loss	Strubel (1965)
76.5	10.44	weight loss	Strubel (1965)
86.5	10.43	weight loss	Strubel (1965)
98.5	10.44	weight loss	Strubel (1965)
150	10.56	weight loss	Strubel (1965)
200	10.75	weight loss	Strubel (1965)
250	10.95	weight loss	Strubel (1965)
300	11.43	weight loss	Strubel (1965)
350	11.67	weight loss	Strubel (1965)

Thus

$$
\begin{aligned}
K &= (M_{\mathrm{Ca}^{2+}})(M_{\mathrm{F}^-})^2(\gamma_{\mathrm{Ca}^{2+}})(\gamma_{\mathrm{F}^-})^2 \\
&= \frac{(4)(x)^3(10^{-3})^3(0.905)(0.975)^2}{(78)^3} \\
&= (x)^3(0.72)(10^{-14}),
\end{aligned}
$$

where M = molal concentration, and pK values were calculated from:

$$\mathrm{p}K = 14.14 - 3\log(x). \qquad (18)$$

The ionic strength has been assumed to be 0.0005.

These calculations are in agreement with the pK values which KHODAKOVSKIY *et al.* (1968) calculated from Strübel's data without explanation of their mode of calculation.

The only determination of fluorite solubility as a function of temperature and pressure has been the work of STRÜBEL (1965) who approached equilibria from undersaturation. These data were used in the regression analysis and found to be consistent with the other experimental measurements mentioned above for the vapor-saturated curve for water. When an attempt was made to include the temperature-dependent data of KOHLRAUSCH (1904, 1908) and the value from SMYSHLYAEV and EDELEVA (1962), a poorer fit was obtained and the added pK values were all significantly discordant with the new fit. The other published solubility determinations were approached from undersaturation and are not very reliable for various reasons. KAZAKOV and SOKOLOVA (1950) analyzed colorimetrically only for fluorine and did not properly characterize their solid phase, and IKRAMI *et al.* (1971) titrated for calcium complexometrically and titrated for HF in the CaF_2–HF mixtures, but it is not clear how they analyzed for fluorine when HF was absent, and there is no indication that more than one measurement might have been taken at each temperature. Furthermore, unpublished data on fluorite solubility (from undersaturation) by the senior author are in closer agreement with those of STRÜBEL (1965).

The only available determination of fluorite solubility determined by titration or by supersaturation are those of LINGANE (1967) and ROBERSON and SCHOEN (1973), respectively. These values are among the highest recorded and are not in agreement. Particle size effects or metastable equilibrium may have been a problem in these determinations. LINGANE (1967) states that his potentiometric measurements of the equilibrium constants for Th, La and Ca fluorides were most difficult for Ca and that true equilibrium had not been reached. Lingane's solutions probably became supersaturated during the titration. This same problem was encountered by EVERSON and RAMIREZ (1967) during their thermometric titrations of calcium and fluoride solutions. ROBERSON and SCHOEN (1973) found precipitates of fluorite (by X-ray diffraction) when they supersaturated four natural thermal waters with excess fluoride, but the precipitation rate was slow. Although only small differences in the log *AP* for fluorite were noticeable between 10 and 30 days after supersaturation, 3 of the 4 solutions showed a decreasing trend in fluoride activity with time which may indicate that final equilibrium had not yet been reached. The discrepancies in pK determinations by approaching equilibrium from supersaturation have not been adequately explained and it may require some long-term rate studies to clarify this problem.

Heat capacities

Accurate heat capacity data on crystalline, homogenous, pure solids are usually available over a wide temperature range. Ionic heat capacities are not well known, if at all. Values for the heat capacity of $\mathrm{Ca}^{2+}_{(aq)}$, $\mathrm{F}^-_{(aq)}$, and $\mathrm{CaF}_{2(\alpha)}$ at 25°C are compiled in Table 4 based on the following conventions (see CRISS and COBBLE, 1964):

$$\bar{C}^0_{p,H^+} = 0 \qquad (19)$$

$$\bar{C}^0_{p,i}(\mathrm{conv}) = \bar{C}^0_{p,i}(\mathrm{abs}) - z_i\bar{C}^0_{p,H^+}(\mathrm{abs}) \qquad (20)$$

$$\bar{C}^0_{p,m_jx_k} = j\bar{C}^0_{p,m}v^+ + k\bar{C}^0_{p,x}v^- \text{ at infinite dilution,} \qquad (21)$$

where $\bar{C}^0_{p,i}$ is the standard partial molal heat capacity for species i, (conv) and (abs) denote conventional and absolute values, H^+ denotes the aqueous hydrogen

Table 4. Heat capacity data (298°K, 1 atm)

Species	$\bar{C}^{o}_{p,i}$(conv) (cal deg^{-1} $mole^{-1}$)	Source
$Ca^{++}_{(aq)}$	-9	Lewis and Randall (1961)
	-6	Gregory, et. al. (1970)
	-2	Criss and Cobble (1964)
	(+9.1)[1/]	Mishchenko and Ponomarev (1952)
	(+0.2)	Khodakovskiy, et.al. (1968); Naumov, et. al. (1974)
$F^{-}_{(aq)}$	-29.5	Lewis and Randall (1961)
	-25.5	Parker (1965); Wagman, et al.(1968)
	-29	Criss and Cobble (1964)
	(+4.8)	Mishchenko and Ponomarev (1952)
	(-25.1)	Khodakovskiy, et. al. (1968); Naumov, et. al. (1974)
$CaF_{2(\alpha)}$	16.02	Todd (1949)
	16.393	Stull and Prophet (1971)
	17.0	Naylor (1945)
	16.16	This Study

[1] Values in parentheses are discounted for reasons given in the text.

ion, $m_j x_k$ is an electrolyte with v^+ and v^- denoting the valence states of the dissociated ions, z_i is the absolute value of the charge on i, and j as well as k are stoichiometric coefficients.

Certain published heat capacity values may be discounted. MISCHENKO and PONOMAREV (1952) based all of their values on the erroneous assumption that $\bar{C}^0_{p,NH_4^+} = \bar{C}^0_{p,Cl^-} = \frac{1}{2}\bar{C}^0_{p,NH_4Cl}$. Heat capacities for anions and cations are usually of opposite sign (LEWIS and RANDALL, 1961) and more recent information on ionic heat capacities show better agreement with the early values listed in LEWIS and RANDALL (1961) than with those of MISCHENKO and PONOMAREV (1952). KHODAKOVSKIY *et al.* (1968) have used Mischenko and Ponamarev's values for their reference state. At present, we prefer to use the values of GREGORY *et al.* (1970) for calcium and PARKER (1965) for fluoride.

The heat capacity values for fluorite are used in the regression analyses by PHAS20. The heat capacity values for the ions as a function of temperature have not been measured so that this information was not available for the regression. Regression analysis may be performed with enthalpy of dilution measurements and the temperature-dependent $HF_{(aq)}$ ionization measurements as well as consideration of the theoretical values obtained by CRISS and COBBLE (1964). This study will be published elsewhere. We feel that further revision will not make any significant differences in the conclusions stated in this paper, but we acknowledge that further refinement of the data will improve its reliability and needs to be done.

EVIDENCE FOR EQUILIBRIUM SOLUBILITY

Comparison of log *AP* values for fluorite from selected geothermal waters with available calorimetric data (Fig. 1) has suggested a re-evaluation of the thermodynamic properties of fluorite. A compilation of calorimetric solubility and electrochemical measurements for fluorite has been examined and a revised set of free energy, enthalpy, entropy, and heat capacity values has been obtained by regression with the computer program PHAS20. An equation for log *K* as a function of temperature may be derived from equations (13) and (14) (HAAS and FISHER, 1976) and substituting coefficients from PHAS20 output, we have:

$$\log K = 109.25 + 0.0024\,T - 3120.98\,T^{-1} - 37.63\log T - 2088.47\,T^{-2} - 4.9 \times 10^{-7}\,T^{2} - 298.4\,T^{-1/2}$$

for fluorite dissolution over the temperature range 0–350°C. This equation is internally consistent with the other thermodynamic functions listed in Table 2. For temperatures above 100°C, the mathematical model assumes the pressure conditions along the vapor-saturated curve for water.* Other thermodynamic values calculated from the regression analysis have been included in Table 2 for comparison.

The revised p*K* calculated from equation (22) has been used to compute log (*AP*/*K*) for the thermal waters. The log (*AP*/*K*) values or the 'disequilibrium indices' (PAČES, 1972) are plotted in Fig. 2 as a function of temperature to show the variation from saturation. If we make an allowance of ±0.5 of a log (*AP*/*K*) unit to account for inaccuracies due to sampling technique, analytical procedures, complexes not considered, and errors in the thermodynamic data,

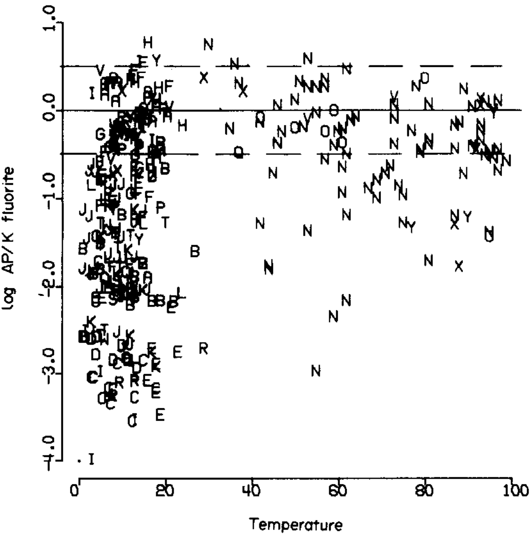

Fig. 2. Variance in the disequilibrium indices as a function of on-site temperature. The equilibrium state is shown by the solid horizontal line at log (*AP*/*K*) = 0 calculated from equation (22) with a total error of ±0.5 as designated by the dashed horizontal lines.

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* It should be noted, however, that from the data of ELLIS and MAHON (1964) fluorite solubility is only valid to 230°C. Above this temperature non-stoichiometric dissolution takes place.

then we can represent the equilibrium state by 0.00 ± 0.5 as suggested by PAČES (1972). The dashed lines in Fig. 2 show these boundaries for equilibrium. It should be noted that the suggested limits on the equilibrium state must vary for different mineral reactions according to their stoichiometry, with much larger limits placed on those reactions containing larger numbers for the stoichiometric coefficients since they become exponents in the activity product expression.

In Fig. 2, only 2% of the values exceed +0.5, demonstrating good agreement between the upper limit of the calculated activity products from geothermal waters and our revised estimate of fluorite solubility. Most of the values which fall below saturation are from creeks, rivers and other surface waters in geothermal areas. It appears that although hot springs are close to saturation with respect to fluorite, when these waters are diluted by surface or near-surface waters, they become undersaturated. Using conductivity as an indication of dilution by non-thermal ground and surface waters, we have plotted the disequilibrium index as a function of log conductivity in Fig. 3. This plot shows a distinct convergence toward equilibrium (accentuated by the arrow) as the conductance increases, and illustrates a regular departure from mineral equilibria by dilution.

Several water analyses from the same drainage area reflect the dilution pattern and one of the best examples is provided by the Firehole River in Yellowstone National Park (Fig. 4). The log (AP/K) values for the Firehole show a linearly decreasing trend with decreasing conductance. The low conductivity values are representative of that part of the river just upstream from the Upper Geyser Basin before any significant influence from hot spring activity. As hot springs enter the river, log conductivity and the disequilibrium index increase until the maximum values are reached which represent water taken from the Firehole downstream from all major hot spring inputs.

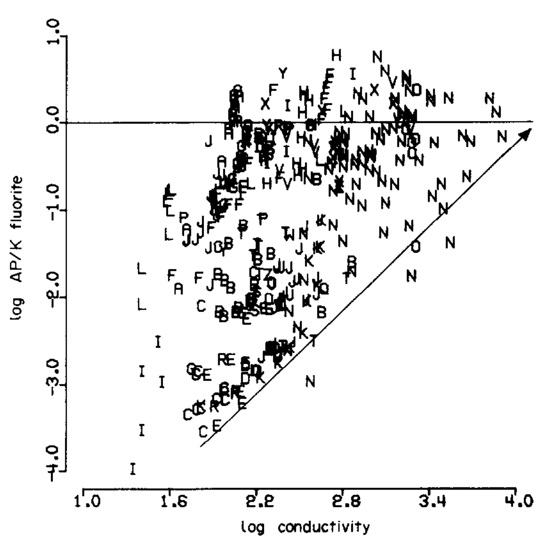

Fig. 3. Variation in the disequilibrium index with the log of the conductivity. The arrow emphasizes the tendency of the disequilibrium indices to approach saturation with increased conductance.

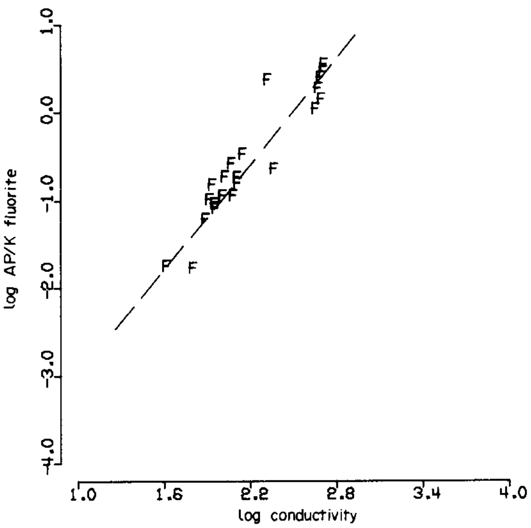

Fig. 4. Variation in the disequilibrium index for the Firehole River in Yellowstone National Park as a function of the log conductivity. The dashed line emphasizes the dilution pattern. The dilution results from a change in discharge or from proceeding upstream away from the thermal basins.

Figure 4 shows a vertical cluster of maximum log (AP/K) values (from Madison Junction where the Firehole joins the Gibbon River) separated from a sloping cluster of lower values (above diversion near Old Faithful). Since the cluster of lower values symbolize waters that are at the edge of Upper Geyser Basin, one would expect changes in the disequilibrium index and log conductivity to change proportionally with the discharge of the Firehole River. As the Firehole decreases in flow seasonally, there should be more contribution from hot springs and consequently higher log (AP/K) and conductance readings. In fact, the lowest two 'F' symbols have the highest discharge of that group and the discharge decreases fairly consistently as one moves up the dashed line. The dilution pattern is remarkably clear from this type of plot and the approach should be applicable in many other types of water chemistry investigations.

We would like to emphasize the agreement between the log AP for hot springs with high conductivity values and the revised log K for fluorite solubility. Using conductivity as a guide to separate dilute surface waters from hot springs we examined a plot of log (AP/K) vs conductivity and found that at 800 μ℧/cm a break occurs which conveniently divides the waters into two major groups. We then replotted all of the log AP values with conductivities greater than 800 μ℧ vs temperature in Fig. 5a along with the revised log K which is shown by a solid line. By plotting these same values in terms of the disequilibrium index (Fig. 5b) we find that 70% of the geothermal water samples analyzed fall within the equilibrium boundaries (dashed lines). Most of the remaining 30% lie in the undersaturated region and may indicate hot springs which have mixed with dilute ground waters while still maintaining their high temperatures due to heating by rising steam. They may also indicate a low availability of fluorine or of calcium. If saturation with respect to calcite is

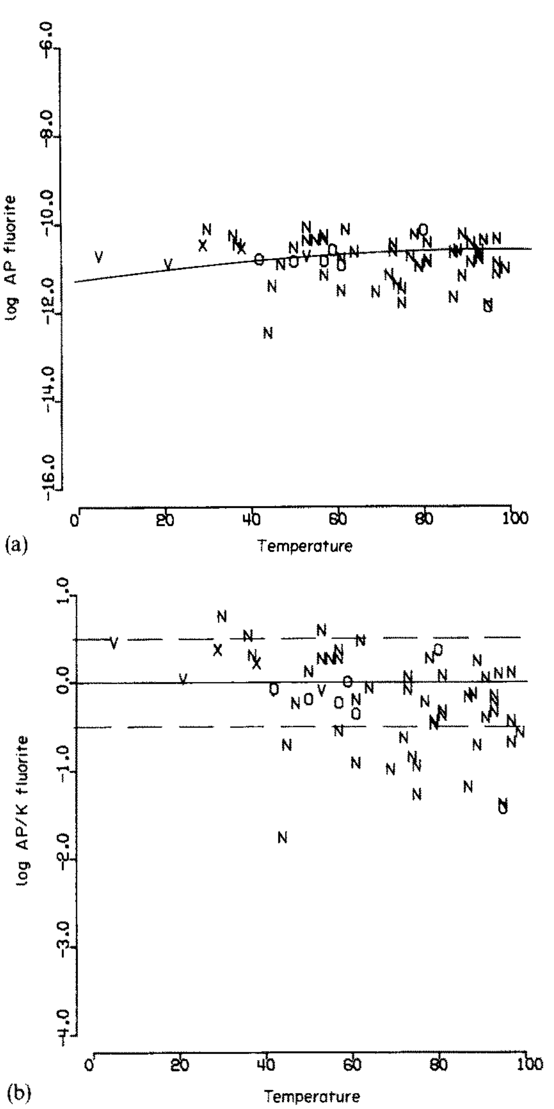

Fig. 5. (a) Log *AP* values for waters with conductivities greater than 800 $\mu℧$ plotted as a function of on-site temperature. The solid line represents the revised log *K* calculated from equation (22). (b) Disequilibrium indices plotted as a function of on-site temperature. The chemical analyses for these samples are given in Appendix 1.

reached as a result of high dissolved carbonate concentrations then calcium concentrations would be suppressed and fluorite undersaturation could result. Unfortunately, the temperature effect on the fluorite solubility curve is less than the variation among log *AP* values and therefore, it is not possible at the present time to distinguish between values which may represent near-surface equilibrium and those which may represent deep, subsurface equilibrium. Direct mineralogic analysis of core samples is perhaps the best available method of determining the spatial distribution of fluorite which will affect its saturation in associated water.

One of the implications from the log *AP* data presented here is that fluorite must be present in the subsurface in these geothermal regions. Unfortunately, only very limited drill core information is available. BARGAR *et al.* (1973) have described several hydrothermal minerals including fluorite from a drill core located near Ojo Caliente hot spring in the Lower Geyser Basin, Yellowstone National Park. A water analysis of Ojo Caliente was given from which a disequilibrium index was calculated to be about +0.05, well within the saturation boundaries of ±0.5. Further drill core mineralogy should show fluorite to be a widespread hydrothermal mineral in many geothermal regions of the western United States.

ELLIS (1967) points out the common occurrence of calcite at depth in hydrothermal regions and the importance of this mineral in controlling calcium concentrations. By plotting log (AP/K) for fluorite vs log (AP/K) for calcite as shown in Fig. 6a we are able to simultaneously test the effect of solubility by both of these minerals on the chemical composition of these thermal waters. This shows that the solubility limits for fluorite and calcite provide a natural control on water composition, such that calcium, fluoride and carbonate activities are interdependent. In Fig. 6b we removed all of the low conductivity values (<800 μmhos/cm) from Fig. 6a and the remaining waters plot in a group which clusters close to the intersection of fluorite and calcite solubility. The importance of the chemical control of water composition stands out very clearly in this diagram. In addition, it can be seen that all but one of the waters which plotted in the fluorite undersaturated region in Fig. 5b plot within the calcite saturation zone of Fig. 6b. This lends credence to the suggestion that either some of the locations may have low availability of fluorine, or that calcite saturation is preventing fluorite saturation by reducing the calcium activity. Low availability could mean that fluorine occurs in less abundance in the source reservoir at some geothermal areas, or it may indicate other mineral reactions are selectively removing fluorine from the water during its movement to the surface to give an undersaturated *AP* for fluorite.

SUMMARY AND CONCLUSIONS

The concentration of fluorine and calcium of geothermal waters in the western United States is influenced by the equilibrium solubility of calcite and fluorite. Fluorite solubility control on fluoride concentrations is indicated by the near absence of log (AP/K) values greater than 0.5. Convergence of the fluorite activity product to the equilibrium value occurs more systematically with increasing conductivity than with increasing temperatures. This trend suggests that geothermal waters are at equilibrium with fluorite at depth but are diluted to varying degrees upon mixing with low-fluoride surface waters and non-thermal ground waters. Since some of the mixed waters are reheated with rising steam, temperature is a poor indicator of the relative portion of the spring water which is of deep origin. The significant number of samples (70%) which are in equilibrium [for example, log $(AP/K)_{\mathrm{fluorite}} = 0.00 \pm 0.5$] suggests that either: (1) some of the waters rise to the surface without dilution by near surface water; or (2) steam loss is balanced by dilution (which seems unlikely);

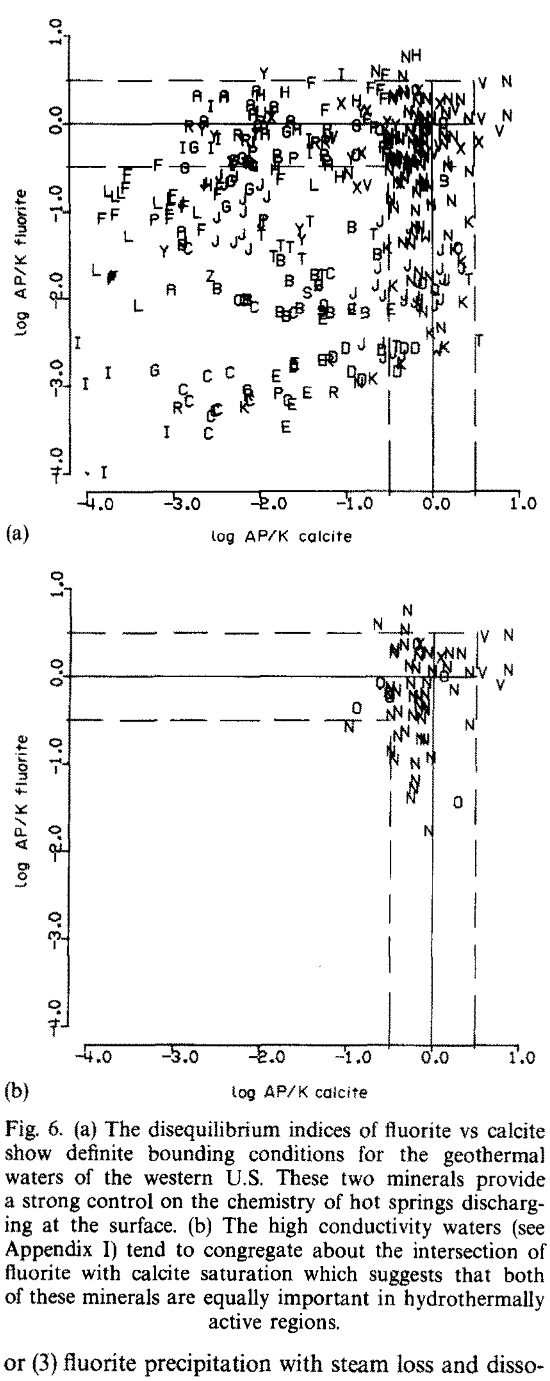

Fig. 6. (a) The disequilibrium indices of fluorite vs calcite show definite bounding conditions for the geothermal waters of the western U.S. These two minerals provide a strong control on the chemistry of hot springs discharging at the surface. (b) The high conductivity waters (see Appendix I) tend to congregate about the intersection of fluorite with calcite saturation which suggests that both of these minerals are equally important in hydrothermally active regions.

or (3) fluorite precipitation with steam loss and dissolution with dilution from ground waters are equilibrium processes as long as the temperature remains sufficiently high for the reaction to proceed rapidly enough.

These tests for equilibrium required revision of the thermodynamic data on fluorite. Critical evaluation of the available data followed by computer refinement gave a p*K* for fluorite dissolution of 10.96 at 25°C and 1 atm. The agreement of the log *AP* from higher conductivity waters with this p*K* provides the major evidence for solubility control by fluorite. It also indicates that careful studies of the chemistry of geothermal waters may provide an indication of the reliability of existing thermodynamic data.

In this study techniques are presented for (1) evaluating thermodynamic data, (2) determining solubility controls on the composition of geothermal waters, and (3) determining the effects of mixing geothermal water with cool dilute waters. The results of this study imply that fluorite should be widely distributed in geothermal areas of the western United States.

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APPENDIX 1. PHYSICAL AND CHEMICAL CHARACTERISTICS OF

DATA SET#	PLOT CHAR	DATE	DISCHG CU M/S	TEMP DEG C	PH	SPEC COND	TOT DISS SOLIDS	CA	MG
1124	O	5/18/72	0.0	79.0	6.5	1950	1260.0	50.00	0.60
854	N	5/1/74	0.0	88.0	7.4	2430	0.0	44.00	0.60
855	N	5/1/74	0.0	72.0	8.6	914	0.0	3.60	0.02
856	N	5/1/74	0.0	96.0	7.6	6910	0.0	108.00	1.70
858	N	5/1/74	0.0	56.0	7.2	908	0.0	60.00	15.50
864	N	5/1/74	0.0	61.0	7.3	1650	0.0	75.00	37.00
865	N	5/1/74	0.0	54.0	7.2	818	0.0	48.00	12.00
867	N	5/1/74	0.0	90.0	7.0	1760	0.0	49.00	13.00
869	N	5/1/74	0.0	56.0	6.3	1730	0.0	53.00	35.00
870	N	5/1/74	0.0	98.0	9.0	1020	0.0	1.00	
1125	O	5/19/72	0.0	94.0	9.2	1920	1420.0	0.90	0.10
1126	O	5/24/72	0.0	60.0	7.2	1800	1300.0	3.30	0.10
1128	O	5/22/72	0.0	56.0	6.5	1790	1260.0	25.00	0.60
1129	O	5/22/72	0.0	49.0	6.6	1900	1340.0	22.00	0.60
1163	N	5/1/74	0.0	52.0	6.8	1168	0.0	18.00	0.80
1164	N	5/1/74	0.0	36.0	7.3	2410	0.0	16.00	0.30
1165	N	5/1/74	0.0	96.0	7.3	2020	0.0	14.00	0.30
1166	N	5/1/74	0.0	76.0	6.7	4590	0.0	13.00	2.20
1167	N	5/1/74	0.0	73.0	8.0	2490	0.0	0.90	0.10
1168	N	5/1/74	0.0	68.0	7.3	2970	0.0	12.00	1.80
1169	N	5/1/74	0.0	78.0	8.1	810	0.0	3.70	0.10
1206	V	5/23/68	0.0	20.0	7.8	1430	985.0	139.00	48.00
1207	V	5/11/67	0.5	52.0	7.7	1740	1240.0	156.00	59.00
1233	X	9/13/68	0.0	28.0	7.3	988	699.0	21.00	2.80
1132	N	5/1/74	0.0	74.0	6.5	810	0.0	33.00	6.80
1133	N	5/1/74	0.0	80.0	7.9	902	0.0	4.80	0.10
1135	N	5/1/74	0.0	92.0	7.6	1520	0.0	4.60	0.10
1136	N	5/1/74	0.0	93.0	7.1	1560	0.0	14.00	0.40
1138	N	5/1/74	0.0	90.0	7.5	934	0.0	10.00	0.10
1139	N	5/1/74	0.0	80.0	8.0	947	0.0	8.40	
1141	N	5/1/74	0.0	72.0	6.5	1180	0.0	43.00	9.40
1143	N	5/1/74	0.0	49.0	6.5	1530	0.0	45.00	4.90
1145	N	5/1/74	0.0	35.0	7.6	1640	0.0	40.00	3.30
1151	N	5/1/74	0.0	29.0	7.1	1040	0.0	36.00	4.40
1152	N	5/1/74	0.0	77.0	6.5	3220	0.0	95.00	25.50
1153	N	5/1/74	0.0	92.0	7.4	811	0.0	8.80	0.50
1154	N	5/1/74	0.0	56.0	8.4	6200	0.0	260.00	0.10
1155	N	5/1/74	0.0	86.0	7.1	7610	0.0	68.00	1.20
1156	N	5/1/74	0.0	80.0	7.9	1800	0.0	31.00	4.20
1157	N	5/1/74	0.0	94.0	7.2	3340	0.0	16.00	0.70
1159	N	5/1/74	0.0	86.0	7.6	1720	0.0	35.00	0.10
1160	N	5/1/74	0.0	46.0	6.5	2570	0.0	38.00	7.80
1170	N	5/1/74	0.0	74.0	7.7	1140	0.0	40.00	0.20
1172	N	5/1/74	0.0	78.0	7.3	1490	0.0	16.00	0.20
1173	N	5/1/74	0.0	88.0	7.8	1370	0.0	8.80	0.10
1174	N	5/1/74	0.0	96.0	7.8	1120	0.0	13.00	
1175	N	5/1/74	0.0	43.0	8.4	1790	0.0	2.10	0.10
1176	N	5/1/74	0.0	71.0	7.6	4300	0.0	210.00	0.20
1177	N	5/1/74	0.0	44.0	7.8	2890	0.0	225.00	0.10
1180	N	5/1/74	0.0	63.0	7.4	1330	0.0	34.00	0.50
1181	N	5/1/74	0.0	60.0	7.6	1090	0.0	24.00	0.20
1182	N	5/1/74	0.0	87.0	7.3	1010	0.0	8.80	0.20
1185	N	5/1/74	0.0	92.0	7.3	4030	0.0	100.00	1.30
1187	N	5/1/74	0.0	60.0	8.2	1173	0.0	72.00	0.20
1189	N	5/1/74	0.0	52.0	8.3	1370	0.0	3.20	
850	X	9/17/68	0.0	37.0	7.4	1330	949.0	18.00	1.90
851	V	5/26/67	0.0	4.0	8.0	1320	933.0	133.00	62.00
1130	O	5/20/72	0.0	58.0	7.5	1500	1000.0	15.00	0.40
1131	O	5/23/72	0.0	41.0	6.6	1630	1130.0	23.00	1.20

THE SAMPLES PLOTTED IN FIGS. 5 AND 6b

- - - - - - MG/L - - - - - - - - - - - - - - - -							
K	NA	HCO3	CL	SO4	SIO2	F	B
30.00	410.00	735.00	200.00	96.00	110.00	8.40	10.60
26.00	450.00	114.00	380.00	470.00	180.00	7.90	2.40
6.50	190.00	111.00	126.00	111.00	115.00	16.30	0.89
42.00	1480.00	90.00	2200.00	190.00	170.00	5.00	15.00
39.00	120.00	488.00	16.00	72.00	65.00	1.90	0.70
31.00	300.00	1135.00	27.00	32.00	105.00	7.20	0.89
22.00	130.00	482.00	14.00	40.00	40.00	5.20	0.67
41.00	390.00	1180.00	40.00	18.00	84.00	7.20	0.77
58.00	230.00	913.00	1.00	7.00	67.00	6.60	2.10
16.00	230.00	321.00	69.00	130.00	320.00	17.00	2.10
45.00	390.00	450.00	280.00	130.00	340.00	12.00	15.00
25.00	380.00	466.00	250.00	120.00	300.00	11.00	13.00
37.00	310.00	828.00	150.00	68.00	250.00	4.60	7.70
43.00	400.00	845.00	170.00	69.00	240.00	4.80	8.80
10.80	270.00	439.00	24.00	204.00	105.00	12.80	0.89
31.00	500.00	420.00	300.00	350.00	190.00	9.00	16.60
28.00	450.00	374.00	250.00	434.00	160.00	7.20	15.00
69.00	960.00	1196.00	780.00	220.00	120.00	10.20	30.00
35.00	550.00	774.00	240.00	230.00	200.00	16.00	10.50
13.00	630.00	566.00	590.00	140.00	92.00	3.30	11.30
3.90	170.00	202.00	79.00	86.00	83.00	9.00	7.90
34.00	82.00	243.00	107.00	411.00	40.00	1.80	2.10
51.00	117.00	208.00	149.00	547.00	48.00	2.40	3.20
22.00	201.00	528.00	57.00	15.00	113.00	6.20	0.90
22.00	130.00	429.00	18.00	56.00	66.00	1.80	1.10
4.50	180.00	261.00	59.00	120.00	105.00	10.00	1.80
25.00	320.00	436.00	160.00	130.00	160.00	14.00	6.90
23.00	330.00	495.00	160.00	120.00	150.00	12.00	7.50
8.20	180.00	156.00	47.00	230.00	150.00	6.80	2.10
8.70	180.00	139.00	48.00	220.00	160.00	7.10	2.90
36.00	200.00	672.00	22.00	51.00	77.00	4.70	2.60
34.00	250.00	813.00	29.00	110.00	80.00	4.80	2.30
16.00	305.00	112.00	87.00	597.00	46.00	7.40	2.30
20.00	180.00	374.00	40.00	150.00	110.00	7.80	1.90
80.00	540.00	544.00	770.00	51.00	150.00	5.70	3.80
13.00	160.00	366.00	29.00	53.00	135.00	7.80	1.20
160.00	1100.00	24.00	1900.00	340.00	110.00	3.00	6.10
130.00	1400.00	83.00	2200.00	400.00	165.00	4.50	9.90
17.00	340.00	458.00	240.00	46.00	82.00	7.00	1.90
66.00	680.00	364.00	837.00	73.00	270.00	2.10	47.00
7.10	300.00	56.00	430.00	140.00	81.00	1.40	2.60
36.00	610.00	1710.00	50.00	13.00	82.00	3.90	15.00
7.20	190.00	53.00	59.00	400.00	98.00	1.20	1.00
11.00	280.00	153.00	240.00	200.00	180.00	4.90	13.60
9.00	280.00	232.00	170.00	240.00	130.00	5.40	11.20
8.50	210.00	79.00	120.00	260.00	140.00	4.40	6.90
4.60	39.00	406.00	280.00	120.00	94.00	2.20	6.90
15.00	690.00	17.00	1300.00	170.00	96.00	1.20	6.40
6.30	392.00	19.00	788.00	260.00	50.00	0.80	5.10
9.70	240.00	160.00	140.00	290.00	110.00	4.80	6.60
6.00	200.00	161.00	55.00	290.00	170.00	4.70	4.70
16.00	190.00	198.00	120.00	120.00	180.00	9.40	4.10
31.00	720.00	142.00	1300.00	140.00	83.00	3.40	4.10
7.00	190.00	26.00	77.00	400.00	80.00	1.20	2.20
3.40	325.00	493.00	155.00	34.00	104.00	21.00	2.60
31.00	293.00	748.00	67.00	14.00	148.00	6.80	1.00
29.00	58.00	333.00	60.00	393.00	31.00	2.20	0.87
22.00	310.00	516.00	170.00	81.00	150.00	7.50	7.90
28.00	320.00	695.00	150.00	59.00	205.00	4.60	8.10

APPENDIX 2. DESCRIPTION AND SOURCE OF SAMPLES PLOTTED IN FIGS. 5 AND 6b

DATA SET	PLOT CHAR	SAMPLE SOURCE	REFERENCE
1124	O	CA, Long Valley, Hot Spring, Little Hot Creek, 3S/28E-13ES3	Willey, et al., 1974
854	N	NV, Churchill Co., Lee Hot Springs	Mariner, et al.,1974a
855	N	NV, Churchill Co., Dixie Valley Hot Springs	"
856	N	NV, Churchill Co., Flowing well in Stillwater	"
858	N	NV, Elko Co., Hot Hole	"
864	N	NV, Elko Co., Unnamed hot spring near Wells	"
865	N	NV, Elko Co., Unnamed hot spring (Wild Horse Reservoir)	"
867	N	NV, Elko Co., Hot Sulfur Springs	"
869	N	NV, Eureka Co., Hot Springs Point	"
870	N	NV, Eureka Co., Beowawe Hot Spring	"
1125	O	CA, Long Valley, Geothermal Well Magma-Richie 5, 3S/28E-32E95	Willey, et al., 1974
1126	O	CA, Long Valley, Hot Bubbling Pool, 3S/28E-35ES1	"
1128	O	CA, Long Valley, Hot Spring, 3S/29E-21NS1	"
1129	O	CA, Long Valley, Hot Spring, 3S/29E-28HS1	"
1163	N	OR, Harney Co., Unnamed hot spring (Trout Creek)	Mariner, et al.,1974b
1164	N	OR, Harney Co., Hot Lake	"
1165	N	OR, Harney Co., Unnamed hot spring (near Hot Lake)	"
1166	N	OR, Harney Co., Alvord Spring (Indian Spr)	"
1167	N	OR, Harney Co., Mickey Springs	"
1168	N	OR, Harney Co., Unnamed hot spring (near Harney Lake)	"
1169	N	OR, Harney Co., Crane Hot Springs	"
1206	V	WY, Yellowstone Nat'l Park, discharge from Jupiter Terrace, Mammoth Hot Springs	Cox, 1973
1207	V	WY, Yellowstone Nat'l Park, Hot River, near Mammoth	"
1233	X	WY, Yellowstone Nat'l Park, Madison Junction 1	"
1132	N	NV, Humboldt Co., Unnamed hot spring, near Golconda	Mariner, et al.,1974a
1133	N	NV, Humboldt Co., Double Hot Springs	"
1135	N	NV, Humboldt Co., West Pinto Hot Spring (well)	"
1136	N	NV, Humboldt Co., East Pinto Hot Spring	"
1138	N	NV, Humboldt Co., Flowing well near Baltazar Hot Spring	"
1139	N	NV, Humboldt Co., Baltazar Hot Spring	"
1141	N	NV, Lander Co., Spencer Hot Springs	"
1143	N	NV, Lander Co., Buffalo Valley Hot Springs	"
1145	N	NV, Mineral Co., Soda Springs	"
1151	N	NV, Pershing Co., Unnamed hot spring (Jersey Valley)	"
1152	N	NV, Pershing Co., Kyle Hot Springs	"
1153	N	NV, Pershing Co., Leach Hot Springs	"
1154	N	NV, Washoe Co., Steam Geyser (Needle Rocks)	"
1155	N	NV, Washoe Co., Great Boiling Spring	"
1156	N	NV, Washoe Co., Flowing well near Gerlach	"
1157	N	NV, Washoe Co., Steamboat Springs	"
1159	N	OR, Clackamas Co., Austin Hot Springs	Mariner, et al.,1974b
1160	N	OR, Grant Co., Weberg Hot Spring	"
1170	N	OR, Klamath Co., Olene Gap Hot Springs	"
1172	N	OR, Lake Co., Crump (Charles Crump's Spring)	"
1173	N	OR, Lake Co,, Berry Ranch Hot Springs	"
1174	N	OR, Lake Co., Hunters Hot Springs	"
1175	N	OR, Lake Co., Summer Lake Hot Spring	"
1176	N	OR, Lane Co., Belkap Hot Springs	"
1177	N	OR, Lane Co., Cougar Reservoir Hot Spring	"
1180	N	OR, Malheur Co., Unnamed hot spring (near Riverside)	Mariner, et al.,1974b
1181	N	OR, Malheur Co., Beulah Hot Springs	"
1182	N	OR, Malheur Co., Neal Hot Springs	"
1185	N	OR, Marion Co., Breitenbush Hot Spring	"
1187	N	OR, Union Co., Medical Hot Springs	"
1189	N	OR, Wasco Co., Kahneeta Hot Springs (Kah-Ne-Tah)	"
850	X	WY, Yellowstone Nat'l Park, Madison Junction 3	Cox, 1973
851	V	WY, Yellowstone Nat'l Park, Mammoth 1	"
1130	O	CA, Long Valley, Hot Spring, 3S/29E-31AS1	Willey, et al., 1974
1131	O	CA, Long Valley, Hot Spring, 3S/29E-34KS1	"