

## EVOLUTION OF GEOTHERMAL FLUIDS DEDUCED FROM CHEMISTRY PLOTS: YELLOWSTONE NATIONAL PARK (U.S.A.)

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### ABSTRACT

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Large amounts of chemical data, obtained in geothermal fields, may readily be sorted-out by the aid of a simple set of graphs that provide a clear over-all picture and facilitate the understanding of geochemical processes taking place. As a case study, data from several hundred samples of the thermal springs at the well-known Yellowstone National Park are discussed.

The pattern obtained seems to indicate: (1) geochemical similarity between the spring groups of Heart Lake, Shoshone, Upper, Midway, Lower and Norris Geysir Basins, i.e., a geochemical uniformity of major spring groups located over 40 km apart; (2) these groups may be described as originating from a common fluid, most resembling the composition of Norris waters, accompanied by CO<sub>2</sub> and other volatiles, that react with igneous rocks, forming local variations; (3) the secondary reactions occur at (medium) depth, before the ascent to the surface; (4) extensive concentration–dilution processes occur during the ascent to the surface.

The water of the Mammoth group may be described as originating from the same Norris-like fluid that has been diluted (low Na and Cl contents) and intensively reacted with carbonaceous rocks, thus gaining in Ca, Mg, SO<sub>4</sub> and HCO<sub>3</sub>.

### INTRODUCTION

Chemical analyses of geothermal waters are made to establish mixing patterns, calculate reservoir temperatures, deduce reactions with country rocks, and reconstruct geochemical evolutions. Studies of this nature necessitate data from large numbers of springs and wells and of samples repeatedly collected at different seasons or as production from wells proceeds. As a result huge amounts of chemical data often get accumulated.

The present communication deals with a simple graphical presentation of such data in a mode that is informative for reconnaissance studies (and a mode that allows one to see the forest through the trees).

As a case study the Yellowstone geothermal system has been selected. It is one of the most intensively studied systems (cf. recent papers by White, 1970; Rowe et al., 1973; Truesdell, 1974; White et al., 1975; Truesdell and Fournier, 1976a, b). A report by Thompson et al. (1975) includes hundreds of recent analyses obtained on samples collected between 1965 and 1973. Analyses for which the total ions and total cations (in equivalents) agreed within the limits of  $\pm 10\%$  of each other, have been plotted in Figs. 1 and 2.

The largest number of samples has been collected from seven major spring groups: Heart Lake, Shoshone, Upper, Midway (regarded by many workers as part of Lower Geyser Basin), Lower and Norris Geyser Basins,

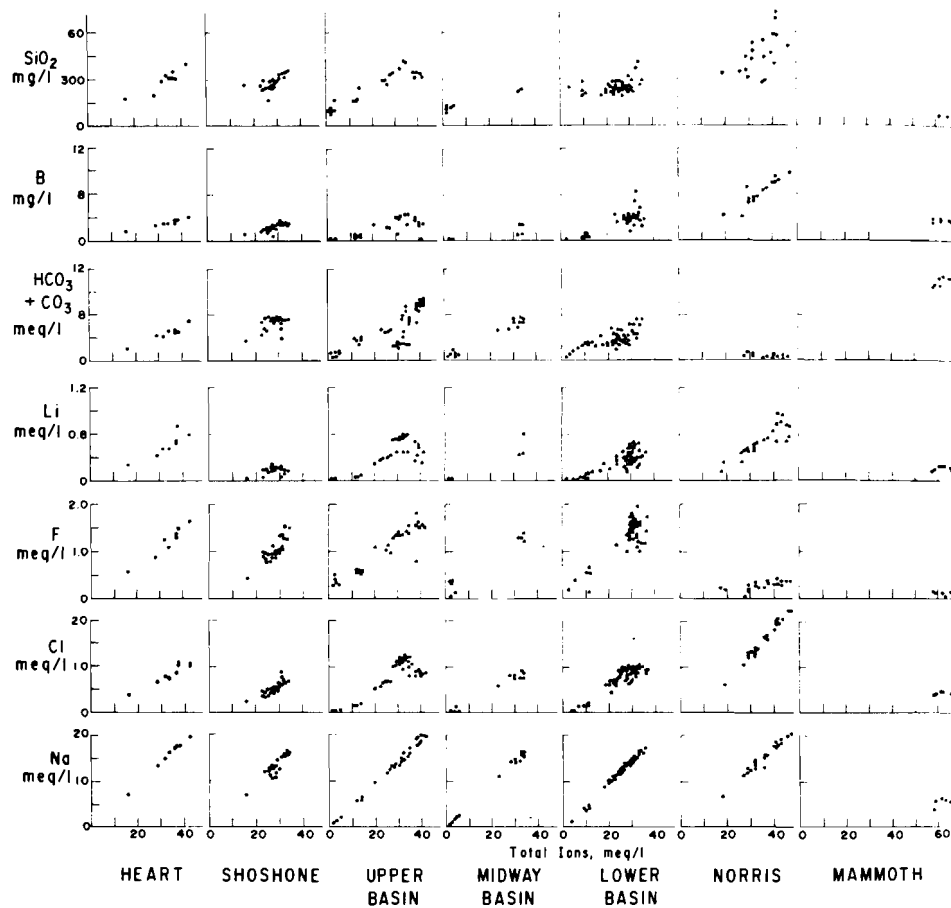


Fig. 1. Chemical compounds positively correlated to the total ion content.

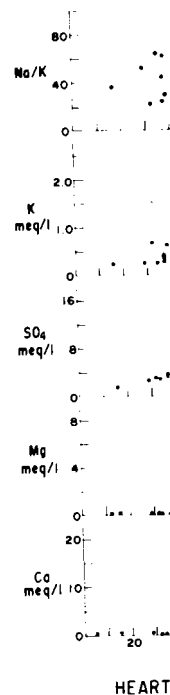


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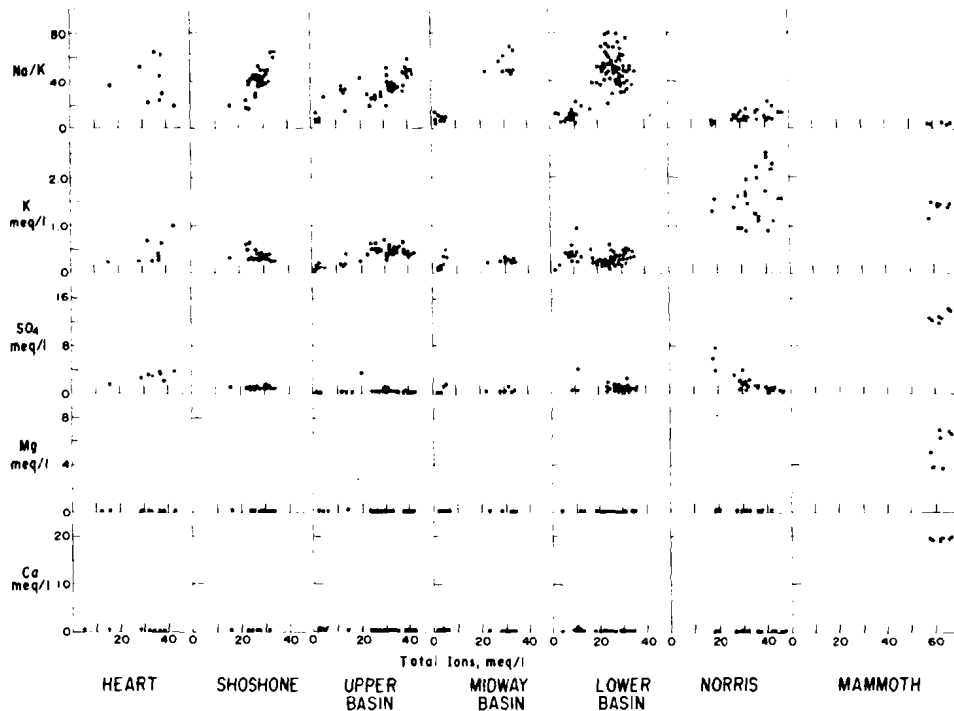


Fig. 2. Chemical compounds not correlated to the *total ion* content.

and Mammoth Hot Springs (Fig. 3). The data of each of these geographical spring groups were plotted separately in Figs. 1 and 2 to facilitate inter-comparisons.

#### CHARACTERISTICS OF YELLOWSTONE HOT SPRING GROUPS

Two major chemical water groups are distinguishable in Figs. 1 and 2:

(1) Heart Lake, Shoshone, Upper, Midway, Lower and Norris Geyser Basins (Fig. 3 and Table I) which have chemical compositions similar to each other and are characterized (in equivalents) by:  $\text{Na} \gg \text{K} \approx \text{Ca} > \text{Mg}$ ;  $\text{Cl} \geq \text{HCO}_3 > \text{SO}_4 \approx \text{F}$ .

The concentrations in each group vary over wide ranges, the most concentrated members ranging from 34 to 47 meq/l total dissolved ions.

(2) In contrast, the Mammoth group on the northern edge of the Park reveals a different pattern of:  $\text{Ca} \gg \text{Mg} > \text{Na} > \text{K}$ ;  $\text{HCO}_3 \geq \text{SO}_4 \gg \text{Cl} > \text{F}$ .

The distribution of concentrations at Mammoth differs greatly from the other Yellowstone groups as no dilute springs occur (cf. Rowe et al., 1973). The observed values cluster in the range of 58–67 meq/l, i.e., higher than in the other Yellowstone groups.

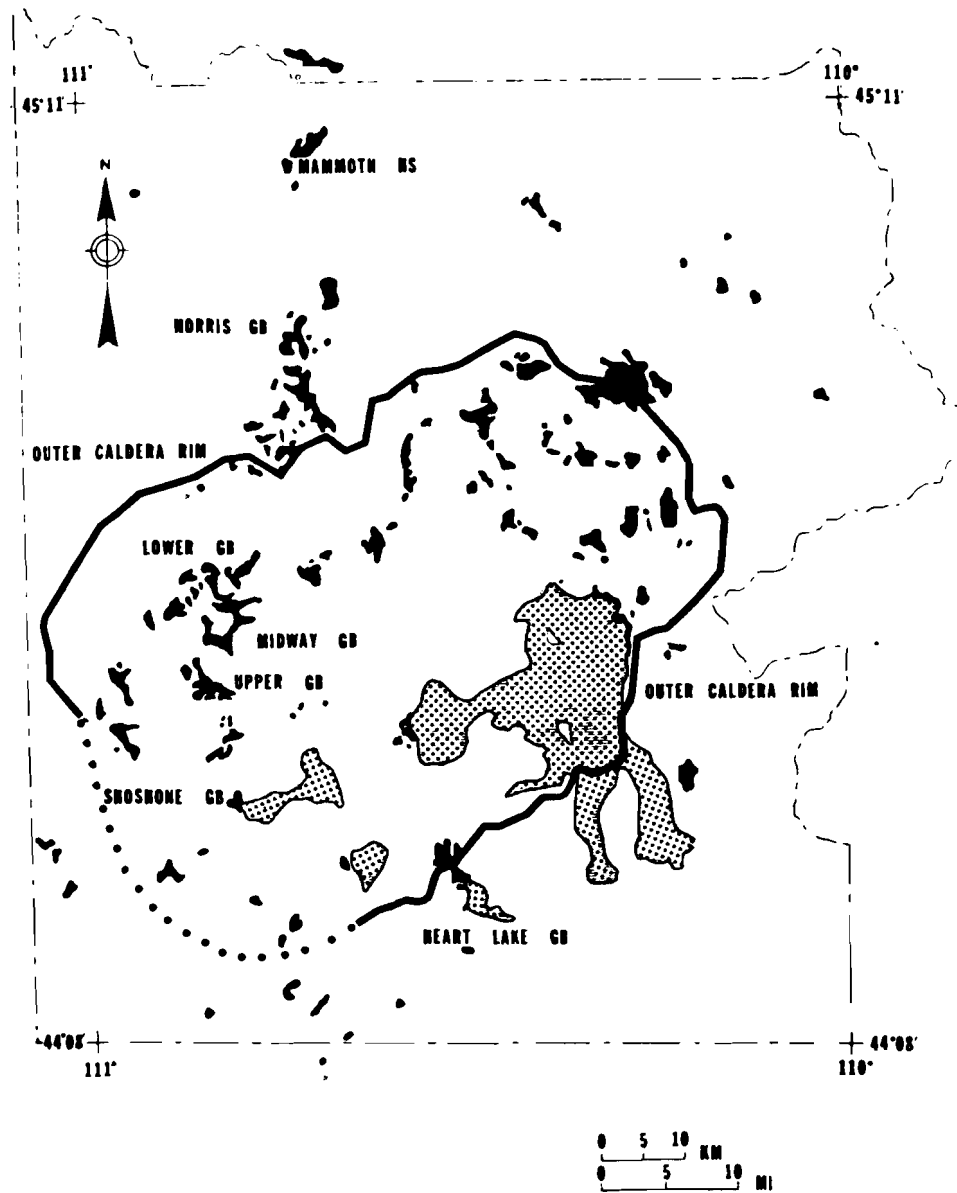


Fig. 3. Location of major spring groups at Yellowstone-proper and Mammoth. Rim of caldera and regions of intense heat flow (black areas) were adopted from Christiansen and Blank (1972).

TABLE 1

Composition of weighed most concentrated samples\*

Region	Number of samples	Na	K	Li	Ca	Mg	Cl	HCO <sub>3</sub> +CO <sub>3</sub>	SO <sub>4</sub>	F	B	SiO <sub>2</sub>	Total ions
<i>I. mg/l</i>													
Heart	10	450	40	5.5	10	1.2	355	300	187	30	3.9	390	
Shoshone	35	380	27	1.4	4	0.5	250	430	48	13	0.6	350	
Upper Basin	46	460	~20	4.9	12	3.6	~370	630	24	28	4.3	180	
Midway Basin	19	370	~16	4.9	12	0.7	320	460	24	25	2.8	220	
Lower Basin	46	390	~16	3.5	14	0.1	355	~300	34	30	4.5	350	
Norris	28	470	59	7.0	6	1.2	760	30	24	8	11.4	650	
Mammoth	7	125	55	1.4	400	79.0	160	880	650	3	3.8	58	
<i>II. meq/l:</i>													
Heart	10	19.7	1.0	0.8	0.5	0.1	10.0	5.0	3.9	1.6	0.36	43	
Shoshone	35	16.5	0.7	0.2	0.2	0.04	7.0	7.0	1.0	0.7	0.06	34	
Upper Basin	46	20.0	~ 0.5	0.7	0.6	0.3	~ 10.5	10.4	0.5	1.5	0.40	42	
Midway Basin	19	16.0	~ 0.4	0.7	0.6	0.06	9.0	7.5	0.5	1.3	0.26	34	
Lower Basin	46	17.0	~ 0.4	0.5	0.7	0.01	10.0	~ 5.0	0.7	1.6	0.42	36	
Norris	28	20.5	1.5	1.0	0.3	0.1	21.5	0.5	0.5	0.4	1.06	47	
Mammoth	7	5.4	1.4	0.2	20.0	6.5	4.5	14.5	13.5	0.14	0.35	67	

\*Calculated for the highest total ion observed in each region, reading the relevant ion content from the bestfit lines in Fig. 1 (i.e., for ions revealing a positive correlation to total ion content) or an estimated average for cases of Fig. 2 (i.e., for components not correlated to the total ion content).

### *Concentration variations and their possible meaning*

The springs in the first six groups of Figs. 1 and 2 reveal three general features:

(a) The total dissolved ion concentrations vary over a range of almost two orders of magnitude.

(b) Na, Cl, F, Li, B, SiO<sub>2</sub>, and HCO<sub>3</sub>+CO<sub>3</sub> show positive correlations to the total dissolved ion contents. The best correlations are observed for Na in all six groups, and the best lines for all the elements are seen at Heart Lake and Norris.

(c) The better defined lines seen in Fig. 1 extrapolate to the origins of the plots, a trend best observed on the Na plots.

These patterns indicate (in a simplified mode) that at each of the six spring groups there is essentially one local fluid which becomes either concentrated or diluted. A concentration process might be steam loss (cf. also Truesdell, 1974), whereas dilution may be either by condensed steam or by dilute (fresh) groundwater (Truesdell and Fournier, 1976a). These processes seem to be of minor importance at Mammoth as the variations in ion contents are small.

### *Compounds not correlated to total ion contents*

SO<sub>4</sub> and K are seen in Fig. 2 to reveal no correlation to the total ion content (and similarly reveal no correlation to the Na, Cl, F, B, Li and SiO<sub>2</sub> concentrations). It seems that the concentrations of these two compounds are controlled by secondary reactions acting on the local primary fluid, presumably during ascent to the surface.

The SO<sub>4</sub> content is remarkably constant in five spring groups, namely Shoshone, Upper Basin, Midway Basin, and, with some scatter, also in Lower Basin, and in the higher total dissolved ion cases of Norris (Fig. 2). The contents of SO<sub>4</sub> in these spring groups fluctuate in the range of 0.5–1.0 meq/l, with no correlation to the total salinity. Truesdell (1974) and Truesdell and Fournier (1976a, b) explained the origin of the SO<sub>4</sub> by oxidation of H<sub>2</sub>S present in the primary fluid by free atmospheric oxygen dissolved in the recharging water. These authors calculated that the oxygen dissolved in water entering the ground at 5°C will suffice to form the commonly observed SO<sub>4</sub> contents. Hot-spring waters with high SO<sub>4</sub> contents are observed in all spring groups. These waters invariably are relatively acid and may be attributed to intensified oxidation near the surface (White, 1957). Examples of such waters are not included in Fig. 2 because the highly acid waters have been only partially analyzed, and do not allow calculation of the total ion content. A second type of SO<sub>4</sub> enrichment may occur where a deep-seated brine dissolves sulfate from sediments. Such a case may be seen at Heart Lake where SO<sub>4</sub> values are too high (>1 meq/l) to be explained by H<sub>2</sub>S oxidation by dissolved oxygen.

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Potassium does with postulated terrigenous country rock silica. These reactions produce waters.

### *Geochemical patterns*

The dissolved S (Fournier and Roy et al., 1974). The observations:

(1) The values concentrations at lesser extent, also SiO<sub>2</sub> in these same fluid at each local during ascent seen lines that do not

(2) The values of SiO<sub>2</sub>/total ions brine at Norris as with temperature

(3) The SiO<sub>2</sub> c or Cl) at Mammoth brine or a high d

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Potassium revealed (Fig. 2):

(1) Highest values (ions), in agreement with temperatures measured by thermometers.

(2) The values before, a phenomenon at the surface.

Thus, in contrast to Upper, Midway

The higher  $\text{SO}_4\text{--Cl}$  cases at Heart Lake may, however, also be caused by near-surface boiling that enhances steam loss and  $\text{H}_2\text{S}$  oxidation (D.E. White, pers. commun.).

Potassium does not correlate to the total ion content, in agreement with postulated temperature-dependent re-equilibration reactions with country rock silicates (cf. White, 1970; Truesdell and Fournier, 1976a). These reactions presumably reflect the cooling history of the ascending waters.

#### *Geochemical patterns relevant to ion-geothermometry*

The dissolved  $\text{SiO}_2$  content is used to deduce reservoir temperatures (Fournier and Rowe, 1966; Fournier and Truesdell, 1974; and Fournier et al., 1974). The  $\text{SiO}_2$  patterns in Fig. 1 reveal the following relevant observations:

(1) The values generally show a positive correlation with the total ion concentrations at Heart Lake, Shoshone, Upper and Midway, and, to a lesser extent, also at Lower Geyser Basins. This seems to indicate that  $\text{SiO}_2$  in these samples is basically brought up by the local deep-seated fluid at each location, but dilution and secondary precipitation or solution during ascent seems to be superimposed (causing scatter of points and best-fit lines that do not extrapolate to the origin of the axis).

(2) The values at Norris are highest (in the absolute values and in terms of  $\text{SiO}_2/\text{total ions}$ ), indicating highest temperature of the deep-seated brine at Norris as well as rapid ascent. This is also in good agreement with temperatures observed in drill-holes (White et al., 1975).

(3) The  $\text{SiO}_2$  contents are lowest (absolute and relative to total ions or Cl) at Mammoth, probably indicating lower temperature of the local brine or a high dilution rate.

The  $\text{SiO}_2$  content in the Yellowstone springs except Mammoth seems, thus, to be brought up by the deep-seated fluids and as such may be applied to geothermometric calculations, provided, however, that corrections for concentrations and dilution are made. Such corrections have been discussed by Fournier and Truesdell (1974) and Fournier (1977).

Potassium reveals the following pattern related to geothermometry (Fig. 2):

(1) Highest values are observed at Norris (absolute and relative to total ions), in agreement with observed higher  $\text{SiO}_2$  values and higher temperatures measured in the research drillholes and reflected by chemical geothermometers.

(2) The values do not correlate with the total ion content, as stated before, a phenomenon attributed to secondary reactions during ascent to the surface.

Thus, in contrast to  $\text{SiO}_2$ , the K content in Heart Lake, Shoshone, Upper, Midway and Lower Geyser Basins does not reflect directly the

deep-brine temperature in each location but is more likely to indicate re-equilibration temperatures attained during ascent. In contrast, the high K values at Norris seem to reflect a combination of high initial temperature and rapid rise to the surface, leaving little time for K losses.

(3) The Na/K ratios are seen in Fig. 2 to vary along with the total ion contents. This seems to be a direct result of Na occurring as the major cation and hence Na/K shows some correlation to total ion contents although K itself reveals no correlations. (The diluting meteoric waters have low Na and K contents and are of little importance in this respect.) This behavior of the Na/K ratio makes it useless for estimating temperatures. This is brought out by the fact that the Na/K ratios seem to reach extremely high values of 80 and more. In contrast, certain other systems show constant Na/K values regardless of the total ion content and the Na/K values are much lower. A good example for such a "well behaving" system is the Cerro Prieto geothermal field at Mexico (Mañon et al., 1977; Mazor and Mañon, 1978).

#### *Possible origin from one type of fluid*

The chemical patterns of Heart Lake, Shoshone, Upper, Midway, Lower and Norris Geyser Basins are seen in Figs. 1 and 2 to be similar to each other — a remarkable feature, considering that these spring groups are over 40 km apart. It seems that these waters may be described as originating from one type of fluid, which most resembles Norris brine and is accompanied by volatiles, mainly CO<sub>2</sub>. Truesdell and Fournier (1976b) have postulated that Yellowstone-waters originate from one brine, with little modification by secondary reactions at Norris, but with more modification in the other spring groups. The addition of HCO<sub>3</sub>+CO<sub>3</sub>, Na, and F, (Fig. 1), and the lower reservoir temperatures deduced above, may be explained by CO<sub>2</sub> reacting with silicates, the process being more effective at moderate temperatures. Such reactions cause additions of several meq/l of HCO<sub>3</sub> and Na at Heart, Shoshone and the three Basins.

The Mammoth Springs may be formed by dilution of the original (Norris-resembling) brine, and by addition of HCO<sub>3</sub>, Ca, Mg and SO<sub>4</sub> as a result of the reaction of CO<sub>2</sub> and carbonates.

It would be of interest to know whether these reactions occur at depth or during ascent to the surface. The positive correlation noticed for HCO<sub>3</sub>+CO<sub>3</sub>, Na, and F to total dissolved ions, and the extrapolation to the origin of the axis (Fig. 1), indicate that these reactions take place at (probably medium) depth, prior to fluid ascent (and its accompanied concentration-dilution effects).

#### **SUMMARY OF THE TYPES OF GEOCHEMICAL PROCESSES DEDUCIBLE FROM THE CHEMISTRY PLOTS**

The processing of a large number of chemical data obtained from many

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springs at Yellowstone leads to identification of the following processes:

(1) *Geographical grouping.* Three major geographical-geochemical spring groups emerge: (a) Norris, (b) Heart Lake, Shoshone, Upper, Midway, and Lower Geyser Basins — which are of similar composition though they are located over 40 km apart, and (c) Mammoth.

(2) *An evolutionary trend* is observable. At Norris Geyser Basin a least modified deep-seated brine is recognized. At the other five spring groups this brine has gained  $\text{HCO}_3+\text{CO}_3$  and Na, due to CO-involving reactions with igneous rocks. At Mammoth a diluted Norris-type brine interacted intensively with carbonaceous sedimentary rocks, gaining in Ca, Mg,  $\text{HCO}_3+\text{CO}_3$ , and  $\text{SO}_4$ .

(3) *Modes of fluid cooling* are suggestive from the variations observed in ion contents. In five spring groups the ion concentrations vary over two orders of magnitude but the relative abundances of Cl, Na, F, B, Li, and  $\text{SiO}_2$  are constant in each area. This is shown by positive correlations to the total ions, and the observed covariance lines in Fig. 1 (extrapolating to the origins of the axis). Hence, cooling occurred (a) by steam loss, causing ion concentration, and (b) by dilution with fresh (cold) water. In contrast, these processes seem to be of small importance at Mammoth where little variations in ion contents are seen. There, cooling by conduction may play a major role, along with dilution at depth (as revealed by the low, yet constant, Cl concentrations).

(4) *Geothermometric indications.* The plots of Figs. 1 and 2 lend themselves to a study of the basic premises that have to be valid before ion geothermometric calculations may be applied to a studied region. The intensive concentration—dilution processes observed at Yellowstone springs have to be taken into account, applying the mixing-model approach of Fournier and Truesdell (1974) and Truesdell and Fournier (1976b). In contrast, Na/K ratios (Fig. 2) are shown to be of no use at Yellowstone (varying with total ion contents, over a range of about 3-100!). The Na—K—Ca geothermometer reveals better results in these waters.

Some features of evolution of geothermal fluids of the Yellowstone National Park can be deduced from plots of the large numbers of chemical data available. This mode of data presentation seems useful as a general approach in geochemical work, especially in newly studied geothermal regions.

#### ACKNOWLEDGEMENTS

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