

# Origin of the Chemical Compositions of Some Springs and Lakes

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*The spring waters of the Sierra Nevada result from the attack of high  $\text{CO}_2$  soil waters on typical igneous rocks and hence can be regarded as nearly ideal samples of a major water type. Their compositions are consistent with a model in which the primary rock-forming silicates are altered in a closed system to soil minerals plus a solution in steady-state equilibrium with these minerals. Isolation of Sierra waters from the solid alteration products followed by isothermal evaporation in equilibrium with the earth's atmosphere should produce a highly alkaline  $\text{Na-HCO}_3\text{-CO}_2$  water; a soda lake with calcium carbonate, magnesium hydroxyl-silicate, and amorphous silica as precipitates.*

As natural waters circulate in the water cycle, their compositions change continuously. Evaporation occurs, solid materials react, gases are gained or lost, differential diffusion of components occurs through permeable and semipermeable media, and organisms absorb or lose constituents. Our only hope of gaining some insight into the genesis of various types of water bodies is to study some carefully chosen systems in which relatively few processes are involved and which can be isolated sufficiently from their surroundings to make some approximate mass balances.

We have chosen to study the genesis of the spring waters of the Sierra Nevada because of the availability of a careful set of analyses of the waters plus determinations of the primary igneous rock minerals and of the soil minerals derived from them (3). As we will demonstrate, the Sierra stem emerges as one in which a few primary igneous rock

minerals are being attacked by soil waters high in dissolved  $\text{CO}_2$ , but otherwise nearly pure, to yield soil minerals plus spring water. The system is apparently "closed"; there is little loss or gain of  $\text{H}_2\text{O}$  or  $\text{CO}_2$  during the interaction of soil water and primary silicates. Furthermore, the chemical composition of the igneous rocks of the Sierra is reasonably representative of rocks of the continental crust; consequently, relations in the Sierra system may have widespread application to rock-water systems important in space and time.

## Weathering Relations

Feth *et al.* (3) carefully studied the Sierra Nevada spring waters. We will summarize their results before extending some of their interpretations.

The granitic rocks from which the springs issue range from quartz diorite to quartz microcline gneiss. Feldspars and quartz are the major minerals in the rocks, with accessory hornblende and biotite. The K-feldspar and plagioclase feldspars, although differing widely from place to place, are about equally abundant; the plagioclase ranges in composition from oligoclase ( $\text{An}_{25}$  minimum) to andesine ( $\text{An}_{40}$  maximum). Andesine is the dominant plagioclase. The dissolved content of the springs comes almost entirely from attack of  $\text{CO}_2$ -rich soil water on these silicates, especially on the plagioclase. An aluminosilicate residue, stripped of alkali and alkaline earth metals, is left behind. Traces of gibbsite are found as well as some mica and montmorillonite. Although kaolinite was identified as an important alteration product in almost all instances, the bulk of the residue apparently averages out near the composition of kaolinite. Table I gives the mean values for the compositions of ephemeral and perennial springs.

The ephemeral springs are on the average aggressive waters with a calculated  $\text{CO}_2$  pressure of about  $10^{-1.8}$  atm. (as compared with  $10^{-3.5}$  atm. for ordinary air) and have reacted sufficiently with the rock minerals to use up about half of the original dissolved  $\text{CO}_2$  picked up while the waters pass through the soil zone. The perennial springs apparently average about the same initial  $\text{CO}_2$  pressure, but about three-fourths of the  $\text{CO}_2$  has been changed into  $\text{HCO}_3^-$  by reaction. Figure 1 (1) shows that the sodium content and the pH of the ephemeral springs are consistent with the reaction of  $\text{CO}_2$ -containing water with a plagioclase feldspar to form kaolinite in a closed system.

**Reconstruction of Original Minerals.** To test the conclusions of Feth (3) concerning the weathering reaction, allow an average spring water to back-react with kaolinite, the chief weathering product, and see if the original rock minerals can be formed. The reactions at products

Table I. Mean Values for Compositions of Ephemeral and Perennial Springs of the Sierra Nevada\*

	Ephemeral Springs		Perennial Springs	
	p.p.m.	molality $\times 10^4$	p.p.m.	molality $\times 10^4$
SiO <sub>2</sub>	16.4	2.73	24.6	4.1
Al	0.03	—	0.018	—
Fe	0.03	—	0.031	—
Ca	3.11	0.78	10.4	2.6
Mg	0.70	0.29	1.70	0.71
Na	3.03	1.34	5.95	2.59
K	1.09	0.28	1.57	0.40
HCO <sub>3</sub>	20.0	3.28	54.6	8.95
SO <sub>4</sub>	1.00	0.10	2.38	0.25
Cl	0.50	0.14	1.06	0.30
F	0.07	—	0.09	—
NO <sub>3</sub>	0.02	—	0.28	—
Dissolved solids	36.0	—	75.0	—
pH	6.2*	—	6.8*	—

\* Ref. 3, p. 16.

\* Median Value.

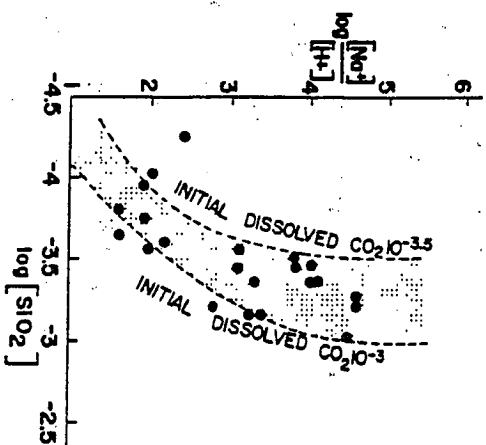


Figure 1. Logarithm of the ratio of Na<sup>+</sup> to H<sup>+</sup> in Sierra spring waters vs. logarithm of silica content. Solid circles are based on water analyses; dashed lines are theoretical compositions that should result from the attack of CO<sub>2</sub>-bearing water on plagioclase to yield solution plus kaolinite.

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are shown in Table II. First the cations and anions in snow water were subtracted from the spring water solutions to determine the materials derived from the rock. Because mean compositions were used, a slight deficiency of anions resulted; this was corrected by giving HCO<sub>3</sub><sup>-</sup> a slightly higher value than that realized by subtracting the mean concentration of HCO<sub>3</sub><sup>-</sup> in snow from that of the springs. Otherwise no corrections were made. Then enough Na<sup>+</sup>, Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, and SiO<sub>2</sub> reacted with kaolinite to make plagioclase, using up all the Na<sup>+</sup> and Ca<sup>2+</sup>. The resultant calculated plagioclase does in fact have a composition similar to that found in the rocks.

Next all Mg<sup>2+</sup> and enough K<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, and SiO<sub>2</sub> reacted with kaolinite to make biotite, leaving a small residue of K<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, and SiO<sub>2</sub> to form K-feldspar. Some silica remained—about 4% of the original concentration. Thus, the mass balance is probably within the limits of error of the original values of concentration used for the median composition of spring waters.

The reactions work out too well to leave much doubt that we are indeed dealing with a closed system reacting with CO<sub>2</sub> and that the weathering product is kaolinite or a material with a composition close to kaolinite in terms of the Al to Si ratio and the balance of alkali or alkaline earth cations.

**Some Quantitative Aspects of the Weathering Process.** The success of reconstructing the original rock minerals leads to several important conclusions.

First, there is at most a slight excess of silica over that needed to form the original silicates. Thus, the conclusion of Feth *et al.* (3) is re-emphasized—*i.e.*, the silica in the water came from the breakdown of the silicates and an insignificant amount from direct solution of quartz. The silica represents CO<sub>2</sub> changed into HCO<sub>3</sub><sup>-</sup> by the weathering process.

Second, Feth *et al.* (3) observe that the waters gain much of their silica in a few feet of travel, showing that it is the action of the high CO<sub>2</sub> water that produces "kaolinite." The rock minerals react, forming "kaolinite" continuously in the system, and the "kaolinite" controls the water composition by its presence. If the aluminum analyses were not so low, and hence analytically suspect, an attempt could be made to calculate an equilibrium constant for the substance formed. All that can be said at the moment is that the values of SiO<sub>2</sub> and Al concentrations and of pH are reasonable for those controlled by an aluminosilicate of the approximate stability of kaolinite.

Third, Table II illustrates that about 80% of the rock-derived dissolved constituents in the ephemeral springs can be accounted for by the breakdown of plagioclase alone. Even though K-feldspar is abundant in the rocks, little breakdown occurs; the high Na to K ratio in these

waters apparently is related to the differential rate of weathering of the feldspars rather than to  $K^+$  adsorption after release upon clay minerals, as is often assumed. In the Sierra, the residual material left after initial attack of the aggressive waters on the rock minerals should be chiefly a mixture of quartz, K-feldspar, and kaolinite, and perhaps small amounts of aluminum oxide hydrates.

Some insight into what happens after the original strong attack on the silicates can be gained by subtracting the ephemeral spring analyses from those of the perennial springs. The perennial springs circulate deeper and have higher pH values when they encounter the rocks. Table III shows the "pick up" of constituents by continued circulation.

It is immediately apparent that the constituents added by deeper circulation are different from those derived by initial attack in some important ways. The ratio of  $SiO_2$  to  $Na^+$  in the increment is nearly 1 to 1. Because weathering of plagioclase to kaolinite releases dissolved  $SiO_2$  and  $Na^+$  in a ratio of 2 to 1 (see Table II) and plagioclase is the only reasonable source of  $Na^+$ , a solid other than kaolinite is being produced. Table IV is an attempt to deduce the reactions that occur during deeper

Table II. Source Minerals

Reaction (coefficients $\times 10^4$ )	Ephemeral Springs	
	$Na^+$	$Ca^{2+}$
Initial concentrations in spring water	1.34	0.78
Minus concentrations in snow water	1.10	0.68
Change kaolinite back into plagioclase		
Kaolinite		
$1.23 Al_2Si_2O_5(OH)_4 + 1.10 Na^+ + 0.68 Ca^{2+}$		
$+ 2.44 HCO_3^- + 2.20 SiO_2 =$	0.00	0.00
Plagioclase		
$1.77 Na_{0.02}Ca_{0.38}Al_{1.38}Si_{2.02}O_8 + 2.44 CO_2 +$		
$3.67 H_2O$		
Change kaolinite back into biotite		
Kaolinite		
$0.037 Al_2Si_2O_5(OH)_4 + 0.073 K^+ + 0.22 Mg^{2+}$		
$+ 0.15 SiO_2 + 0.51 HCO_3^- = 0.073$	0.00	0.00
Biotite		
$KMg_3AlSi_3O_{10}(OH)_2 + 0.51 CO_2 + 0.26 H_2O$		
Change kaolinite back into K-feldspar		
$0.065 Al_2Si_2O_5(OH)_4 + 0.13 K^+ + 0.13 HCO_3^-$	0.00	0.00
$+ 0.26 SiO_2 =$		
K-feldspar		
$0.13 KAlSi_3O_8 + 0.13 CO_2 + 0.195 H_2O$		

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circulation. With the thought that  $Cl^-$  is derived from NaCl, and  $SO_4^{2-}$  from  $CaSO_4$ , enough  $Na^+$  and  $Ca^{2+}$  are removed to balance these anions. This assumption is weak, but fortunately the concentrations of  $SO_4^{2-}$  and  $Cl^-$  are so low that this step is not important.

Next it seems reasonable to use up  $Mg^{2+}$  and  $K^+$  along with kaolinite to make biotite, inasmuch as the ratio of  $K^+$  to  $Mg^{2+}$  in the waters is nearly that of a K-Mg biotite. This leaves  $Na^+$  equal to  $SiO_2$ , so the remaining  $SiO_2$  was apportioned between the reconstruction of kaolinite to plagioclase and that of montmorillonite to plagioclase. The montmorillonite composition chosen was that of a calcium beidellite of average cation exchange capacity. Beidellites seem to be prevalent under weathering conditions, and at such low concentrations of  $Na^+$  and  $K^+$  it is almost certain that the exchange positions are primarily occupied by  $Ca^{2+}$ .

After these steps, a considerable amount of  $Ca^{2+}$  and  $HCO_3^-$  remain, and we believe that with deep circulation, the waters which have lost much of their original aggressiveness, pick up  $Ca^{2+}$  (and perhaps some  $Mg^{2+}$ ) from minor amounts of carbonates encountered en route.

## for Sierra Nevada Springs

(concentrations moles/liter $\times 10^4$ )					
$Mg^{2+}$	$K^+$	$HCO_3^-$	$SO_4^{2-}$	$Cl^-$	$SiO_2$
					Products moles/liter $\times 10^4$
0.29	0.28	3.28	0.10	0.14	2.73
0.22	0.20	3.10	—	—	2.70
Derived from rock					
minus plagioclase					
0.22	0.20	0.64	0.00	0.00	0.50
					1.77 $Na_{0.02}Ca_{0.38}$ feldspar
minus biotite					
0.00	0.13	0.13	0.00	0.00	0.35
					0.073 biotite
minus K-feldspar					
0.00	0.00	0.00	0.00	0.00	0.12
					0.13 K-feldspar

Table III. Effects of Deeper Circulation on Spring Waters\*

	SiO <sub>2</sub>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>
Perennial Spring	4.10	2.60	0.71	2.59	0.40	8.95	0.25	0.30
Ephemeral Springs	2.73	0.78	0.29	1.34	0.28	3.28	0.10	0.14
Increment	1.37	1.82	0.42	1.25	0.12	5.67	0.15	0.16

\* Analyses are mean values in moles/liter  $\times 10^4$ .

The over-all picture of what happens to the soil waters, as illustrated by Tables II and IV, is that initially they rapidly attack the rocks, kaolinitizing chiefly plagioclase plus biotite and K-spar. As they penetrate more deeply, the reaction rate slows down, and both kaolinite and montmorillonite are weathering products. Also, an important part of the Ca<sup>2+</sup> comes from solution of small amounts of carbonate minerals.

Before attempting to document the formation of montmorillonite, a few remarks on weathering rates are of interest. Roughly one-half the initial CO<sub>2</sub> seems to be expended in the soil zone, and most of the rest alters rock minerals at deeper levels. The total reacting capacity is about

Table IV. Source Minerals and Concentrations in

Reaction (coefficients $\times 10^4$ )	Na <sup>+</sup>	Ca <sup>2+</sup>
Initial concentrations (perennial minus ephemeral)	1.25	1.82
Remove Ca <sup>2+</sup> = SO <sub>4</sub> <sup>2-</sup> , and Na <sup>+</sup> = Cl <sup>-</sup>	1.09	1.67
Adjust HCO <sub>3</sub> <sup>-</sup> = total electrical charge of cations	1.09	1.67
Change kaolinite back into biotite		
0.07 Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> + 0.42 Mg <sup>2+</sup> + 0.14 K <sup>+</sup> + 0.28 SiO <sub>2</sub> + 0.98 HCO <sub>3</sub> <sup>-</sup> = 0.14 KMg <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub> + 0.98 CO <sub>2</sub> + 0.49 H <sub>2</sub> O	1.09	1.67
Change kaolinite back into plagioclase		
0.26 Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> + 0.235 Na <sup>+</sup> + 0.144 Ca <sup>2+</sup> + 0.47 SiO <sub>2</sub> + 0.52 HCO <sub>3</sub> <sup>-</sup> = 0.38 Na <sub>0.02</sub> Ca <sub>0.38</sub> Al <sub>1.38</sub> Si <sub>2.02</sub> O <sub>8</sub> + 0.52 CO <sub>2</sub> + 0.78 H <sub>2</sub> O	0.85	1.53
Change montmorillonite back into plagioclase		
0.81 Ca <sub>0.17</sub> Al <sub>0.33</sub> Si <sub>2.87</sub> O <sub>10</sub> (OH) <sub>2</sub> + 0.85 Na <sup>+</sup> + 0.38 Ca <sup>2+</sup> + 0.61 SiO <sub>2</sub> + 1.62 HCO <sub>3</sub> <sup>-</sup> = 1.37 Na <sub>0.02</sub> Ca <sub>0.38</sub> Al <sub>1.38</sub> Si <sub>2.02</sub> O <sub>8</sub> + 1.62 CO <sub>2</sub> + 1.62 H <sub>2</sub> O	0.00	1.15
Precipitate CaCO <sub>3</sub>		
1.15 Ca <sup>2+</sup> + 2.30 HCO <sub>3</sub> <sup>-</sup> = 1.15 CaCO <sub>3</sub> + 1.15 CO <sub>2</sub> + 1.15 H <sub>2</sub> O	0.00	0.00

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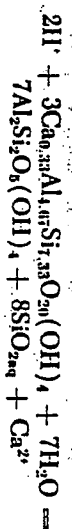
$9 \times 10^{-4}$  equivalents per liter and corresponds to the destruction of about  $3.5 \times 10^{-4}$  moles of plagioclase,  $0.2 \times 10^{-4}$  moles of biotite, and about  $0.2 \times 10^{-4}$  moles of K-spar. The annual precipitation in this part of the Sierra averages about 100 cm./year. Therefore, the rate of chemical weathering is about  $3.6 \times 10^{-3}$  moles/year/sq. cm. If the rock consists of one-third plagioclase by volume, the rock should be disintegrated to an average depth of one meter in about 9000 years, and the residue would be chiefly a rubble of quartz, K-feldspar, and kaolinite.

**Phase Control of Water Composition.** The conclusion that kaolinite forms quickly and continuously during weathering, plus the strong suggestion that the deeper circulating waters are forming montmorillonite as well, can be tested qualitatively by predicting the compositional genesis of the waters, especially in terms of Ca<sup>2+</sup> and Na<sup>+</sup>. If one assumes that the CO<sub>2</sub>-bearing waters continuously react with plagioclase to form first "kaolinite" and then "montmorillonite" and that these phases maintain equilibrium with the waters as they are continuously fed from the feldspar, then observed compositions can be compared with those based on these assumptions.

## Weathering Products of Deeper Circulation

moles/liter $\times 10^4$	Na <sup>+</sup>	Ca <sup>2+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	SiO <sub>2</sub>	Mineral altered and product (moles/liter $\times 10^4$ )
0.42	0.12	5.67	0.15	0.16	1.37			
0.42	0.12	5.67	0.00	0.00	1.37			
0.42	0.12	5.39	0.00	0.00	1.37			
0.00	0.02	4.41	0.00	0.00	1.09			0.14 biotite 0.07 kaolinite
0.00	0.00	3.89	0.00	0.00	0.62			0.38 plagioclase 0.26 kaolinite
0.00	0.00	2.27	0.00	0.00	0.01			1.37 plagioclase 0.81 montmorillonite
0.00	0.00	0.03	0.00	0.00	0.01			1.15 calcite

For the reaction of montmorillonite to kaolinite,



the equilibrium constant is

$$K = \frac{[\text{Ca}^{2+}][\text{SiO}_2]^8}{[\text{H}^+]^2}$$

Thus, for a montmorillonite of the average composition shown and neglecting changes in the activity of water, a water undersaturated with respect to montmorillonite but saturated with respect to kaolinite should have a value for the quotient less than  $K$ , and all waters saturated with respect to both phases should have a constant value of the quotient. Figure 2 shows a plot of the compositions of Sierra springs, in which the

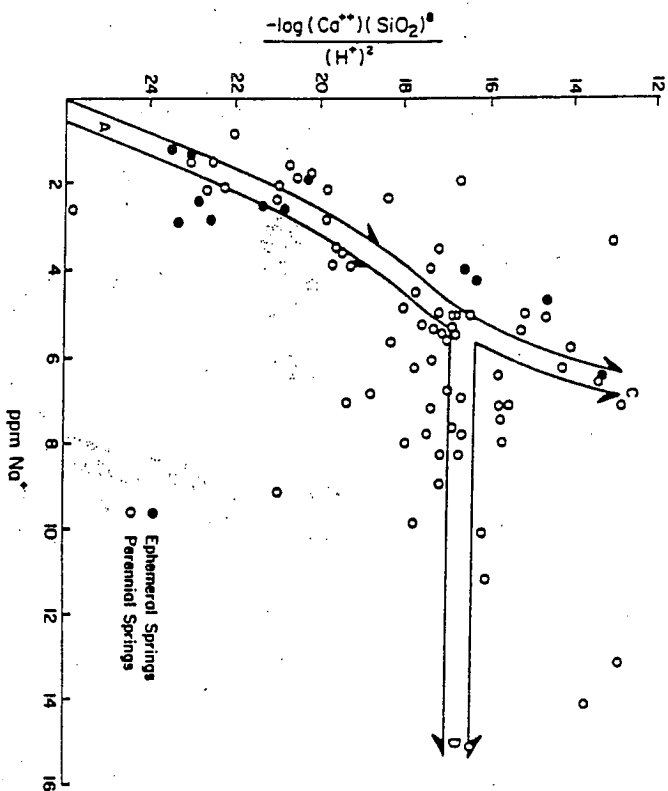


Figure 2.  $pK'$  for equilibrium between Ca-bedeilite and kaolinite plotted as a function of Na content of Sierra Nevada spring waters. Arrow ABC is the path of water evolution calculated for the reaction from  $\text{Na}_{0.68}\text{Ca}_{0.32}\text{Si}_{1.32}\text{Al}_{1.68}\text{O}_{20}(\text{OH})_4$  to kaolinite in a closed system with an initial dissolved  $\text{CO}_2$  of 0.0006 moles per liter. ABD is the expected path if evolution is also controlled by the two-phase equilibrium kaolinite-montmorillonite.

logarithm of the quotient  $\frac{m_{\text{Ca}^{2+}} \cdot m_{\text{SiO}_2}^8}{m_{\text{H}^+}^2} (pK')$  is plotted against p.p.m.  $\text{Na}^+$ .

The arrow ABC is calculated assuming that only kaolinite results from decomposition of plagioclase, whereas the arrow ABD is the predicted evolution if kaolinite is formed first, but that montmorillonite also forms when the waters gain sufficient  $\text{SiO}_2$ ,  $\text{Ca}^{2+}$ , and a high enough pH. The position of the arrow for kaolinite-montmorillonite equilibrium has been estimated from the boundary on Figure 3 and the exchange constants for Na-Ca montmorillonites. Despite the scatter, it is clear that the ephemeral springs alter feldspar chiefly to kaolinite and that many of the perennial springs, although their evolution is to kaolinite, have compositions that suggest a halt in that path of evolution and possible control by equilibrium with both phases.

If this is true, and it must, be regarded as a highly tentative conclusion, then the upper limits of silica content of many natural waters, which are far less than saturation with amorphous silica ( $\approx 115$  p.p.m.), may well be controlled by equilibrium between the waters and various silicate phases. This does not mean that the controlling solids are well-crystallized, clearly distinguishable substances, but there is definitely an interplay between the waters and solid aluminosilicates. Furthermore, the aluminosilicates apparently differ from each other in important compositional steps, and are not simply continuous gradations resulting from progressive adsorption and alteration as water compositions change. This generalization from the Sierra studies is more strikingly shown by Bricker and Garrels (1). Figure 3 is adapted from their work and shows that the compositions of dilute ground and surface waters in silicate-bearing rocks are contained within a set of phase boundaries derived from equilibrium relations among silicate phases.

An idealized water, derived from the attack of  $\text{CO}_2$ -bearing water on a typical felsic rock to produce only kaolinite, should have the following characteristics, expressed in terms of molar concentrations:

- (1)  $\text{HCO}_3^-$  should be the only anion, except for small concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  from fluid inclusions in the minerals, oxidation of pyrite, and other minor sources.
- (2)  $\text{Na}^+$  and  $\text{Ca}^{2+}$  should be the chief cations, and the ratio of  $\text{Na}^+$  to  $\text{Ca}^{2+}$  should be the same as that in the plagioclase of the rock.
- (3) The total of  $\text{Mg}^{2+}$  and  $\text{K}^+$  should be less than about 20% of the total of  $\text{Na}^+$  and  $\text{Ca}^{2+}$ . The ratio of  $\text{Mg}^{2+}$  to  $\text{K}^+$  should range around 1 to 1, with higher values related to higher percentages of mafic minerals, and lower values to higher ratios of K-feldspar to mafic minerals.
- (4) The ratio of  $\text{SiO}_2$  to  $\text{Na}^+$  should be about 2 to 1, with somewhat higher ratios from rocks unusually high in K-feldspar and/or mafic minerals.
- (5) The ratio of  $\text{Na}^+$  to  $\text{K}^+$  should be 5 to 1 or higher, because of the abundance and high weathering rate of plagioclase, as compared to the

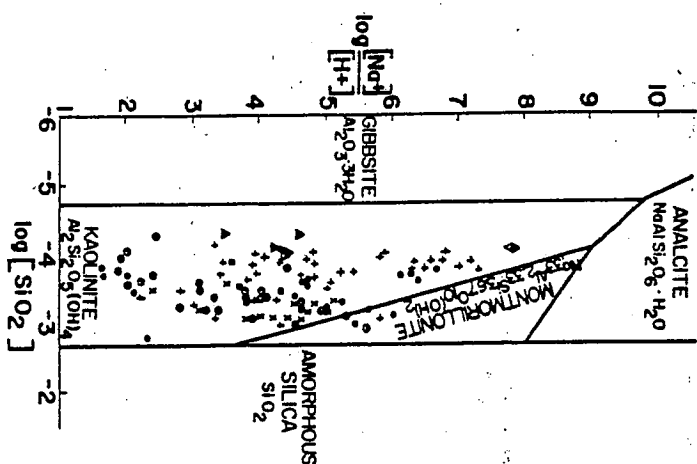


Figure 3. Stability fields of some minerals in the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  system at  $25^\circ\text{C}$ , as a function of  $\text{Na}^+$ ,  $\text{H}^+$ , and dissolved silica. Points are from ground water analyses of siliceous rocks

○ = granite, rhyolite    ■ = andesite, diorite  
 △ = lamprocarbautes    × = basalt, gabbro  
 ◇ = sea water    ● = sandstone, clay, shale  
 + = sandstone, arkose, graywacke

low weathering rate of K-feldspar and the generally low abundance of micas or other K-bearing phases.

Table V compares the Sierra waters with some waters from other felsic rocks. The fundamental similarities are clearly apparent as well as the minor variations that show the imprint of the details of rock mineralogy and small additions of constituents from various other sources.

#### Evaporative Concentration of Sierra Waters

The alteration of the igneous rocks of the Sierra was treated as an example of the genesis of waters in an essentially closed system. There

Table V. Compositions of Waters from Various Igneous Rocks (mole %)

	Sierra Epithermal Springs*	Sierra Perennial Springs*	Springs from Sierra Volcanic Rocks*	Ground Water from Granite, R.I.*	Ground Water from Rhyolite, N.M.*
$\text{SiO}_2$	33.8	21.0	19.5	19.9	38.6
$\text{Ca}^{2+}$	8.5	13.0	10.3	9.6	4.6
$\text{Na}^+$	13.8	13.0	10.3	12.5	20.0
$\text{Mg}^{2+}$	2.8	3.5	8.0	6.6	2.5
$\text{K}^+$	2.5	2.0	1.4	1.2	1.3
$\text{HCO}_3^-$	38.7	45.0	48.5	38.0	28.0
$\text{Cl}^-$	—	1.5	1.4	8.4	2.5
$\text{SO}_4^{2-}$	—	1.5	0.2	0.6	0.8
pH	6.2	6.8	7.0	7.6	7.2

\* Data from Ref. 3.

\* Data from Ref. 8.

was no indication from an analysis of the processes involved that a "final" equilibrium had been attained. Although the rates of altering the primary silicates diminished as  $\text{CO}_2$  was used up and the concentration of dissolved solids increased, primary rock-forming silicates definitely are unstable in any waters produced. It would be interesting to attempt to deduce the final composition of waters and solids if a given quantity of  $\text{CO}_2$ -charged water were permitted to react indefinitely with a felsic rock, but the real situation seems to be that the waters emerge from the closed system when they have reached compositions similar to those of the Sierra and begin to lose and gain constituents from other sources.

Perhaps the next step in trying to understand the complexities of the genesis of natural waters is to see what might happen if the Sierra springs were isolated from the parent rock and solid alteration products and permitted to evaporate isothermally in equilibrium with the  $\text{CO}_2$  of the earth's present atmosphere. In terms of a natural situation, this process might resemble the fate of waters discharged to the east of the Sierra and evaporated in a playa of the California desert. It is, of course, impossible to have a real situation without adding reactive solids from some source, but such interference could be treated afterwards in terms of additional variables. Also, this particular situation might shed some light on the effects of the "igneous rock component" of natural waters during the evaporative processes that change stream waters into oceans.

Table VI gives the mean composition of the perennial springs of the Sierras. We have chosen to ignore Fe, Al,  $\text{NO}_3$ , and F and restricted ourselves to the following analysis (Table VI).

Calculations and Procedures. The general procedure we have used is to calculate the effects of concentrating the waters by various factors

Table VI. Composition of Sierra Spring Water  
Used in Evaporation Study (3)

	p.p.m.	moles/liter $\times 10^3$
SiO <sub>2</sub>	24.6	4.10
Ca <sup>2+</sup>	10.4	2.60
Mg <sup>2+</sup>	1.70	0.71
Na <sup>+</sup>	5.95	2.59
K <sup>+</sup>	1.57	0.40
HCO <sub>3</sub> <sup>-</sup>	54.6	8.95
SO <sub>4</sub> <sup>2-</sup>	2.38	0.25
Cl <sup>-</sup>	1.06	0.16*

\* Cl<sup>-</sup> has been diminished by 0.14 from the calculated 0.30 derived from 1.06 p.p.m. given in the analysis to correct initial electrical imbalance between anions and cations. This change is important in the compositions calculated but not in the general pattern of change to be presented.

pH (median) = 6.8; ionic strength = 0.0013

up to 1000-fold, determining the stages at which various solids should precipitate from the system, and determining the effects of removing solids on composition and pH.

The conditions imposed are that the water remains in equilibrium with a CO<sub>2</sub> pressure of 10<sup>-3.5</sup> atm., that the temperature remains constant at 25°C., and that pure water (except for a little CO<sub>2</sub>) is continuously removed from the system. It is further assumed that any solids formed remain in equilibrium. As it turns out, the question as to whether precipitated solids are isolated after formation or continue to react is not important here, although it is important in many comparable systems.

To keep track of the minerals that might form, we tried to assess the possible combinations of dissolved species to form solids. Table VII

Table VII. Solids Considered as Possible Precipitates  
in Concentrated Spring Water

Species	Solid	Equilibrium Constant
Na <sup>2+</sup>	None	None
K <sup>+</sup>	None	None
Ca <sup>2+</sup>	None	None
gypsum calcite	CaSO <sub>4</sub> · 2H <sub>2</sub> O CaCO <sub>3</sub>	$a_{\text{Ca}^{2+}}a_{\text{SO}_4^{2-}} = 10^{-4.02}$ $a_{\text{Ca}^{2+}}a_{\text{CO}_3^{2-}} = 10^{-8.35}$
Mg <sup>2+</sup>		
brucite	Mg(OH) <sub>2</sub>	$a_{\text{Mg}^{2+}}a_{\text{OH}^-}^2 = 10^{-11.15}$
magnesian hydromagnesite	MgCO <sub>3</sub> Mg <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	$a_{\text{Mg}^{2+}}a_{\text{CO}_3^{2-}} = 10^{-8}$ $a_{\text{Mg}^{2+}}a_{\text{CO}_3^{2-}}a_{\text{OH}^-}^2 = 10^{-34.10}$
sepiolite	Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	$a_{\text{Mg}^{2+}}a_{\text{SiO}_2}^3a_{\text{OH}^-}^2 = 10^{-24}$
SiO <sub>2</sub>		
amorph <sup>1</sup> silica	SiO <sub>2</sub> · 2H <sub>2</sub> O	$a_{\text{SiO}_2} = 10^{-2.7}$

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shows the species we considered and some data concerning them. The values for the equilibrium constants, except for sepiolite, have been calculated from the free energy values given by Garrels and Christ (4). The value for sepiolite is discussed in the text.

A few notes on our selections and on some of the other mineral possibilities may help to clarify the use of these particular species. Gypsum seems to be the most likely sulfate phase. It is stable with respect to anhydrite, is a common precipitate from low temperature natural waters, and except in highly concentrated brines, double sulfates would not be expected. Calcite was chosen in preference to aragonite or possibly a whole variety of magnesian calcites because it is the stable phase and commonly precipitates directly from dilute solution. Also, the difference in solubility between calcite and aragonite is not great enough to influence the general picture. Dolomite is certainly a possibility in the system, as is the metastable mineral huntite (CaMg<sub>2</sub>(CO<sub>3</sub>)<sub>4</sub>), but even at 1000X concentration of these waters the conditions apparently necessary in nature to precipitate dolomite (evaporation of sea water to a dense brine, gypsum precipitation, and  $\frac{\text{Mg}^{2+}}{\text{Ca}^{2+}}$  ratio  $\geq 30$  (2) are not approached). The low Al (Table I) precludes more than traces of aluminosilicates, and Mg is the only cation likely to make a silicate species. Hostetler (5), after reviewing the occurrence of the Mg-silicates, concluded that sepiolite tends to form in most natural solutions at room temperature in preference to serpentine or talc, especially in a high silica environment, and he cites many occurrences of sepiolite plus magnesite and amorphous silica. Furthermore, Siffert (7) synthesized sepiolite within a day at room temperature at pH values of about 8.8 in high SiO<sub>2</sub>/MgO solutions. Our greatest difficulty was in assigning an equilibrium constant for sepiolite. From Siffert's work and using the formula in Table VII, we get a K value of about 10<sup>-22</sup> for the reaction:



On the other hand, we precipitated a magnesium silicate from sea water by adding sodium metasilicate that gave an approximate K of 10<sup>-24</sup> after aging. Siffert's material was freshly precipitated and could be expected to age significantly, like other poorly crystalline silicates. Consequently, the value chosen is open to considerable doubt.

Some other phases considered were nesquehonite (MgCO<sub>3</sub> · 3H<sub>2</sub>O), arinite (Mg<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub> · 2H<sub>2</sub>O), and lansfordite (MgCO<sub>3</sub> · 5H<sub>2</sub>O), but all are rare and according to Hostetler (5) are not stable.

Our procedure was to follow the changes in concentrations and ionic strength as the water is evaporated, and by correcting for volatilities by activity coefficients, keep track of the ion activity product — the various

Table VIII. Calculated Ion Activity Products of Various Concentration

	<i>Calcite</i> $\text{CaCO}_3$	<i>Gypsum</i> $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	<i>Brucite</i> $\text{Mg(OH)}_2$
Initial water in equilibrium with atmosphere	8.8	8.3	15.7
Concentrated by a factor of			
1.25	Saturated	8.1	15.5
2.0	Saturated	8.0	15.1
5.0	Saturated	7.7	15.9
10.0	Saturated	7.9	15.9
100.0	Saturated	8.3	15.9
1000.0	Saturated	8.8	15.4
Equilibrium Constant	8.35	4.62	11.15

\* Products are expressed as negative logarithms (pK').

solids as shown in Table VIII. If an ion activity product reached the equilibrium constant value, we then maintained equilibrium with that solid during continuing concentration. Sample calculations show the procedure used.

**Sample Calculations.** The first step was to determine if the water analysis represents a solution in equilibrium with the atmosphere. For the reaction



the equilibrium constant is

$$\frac{a_{\text{HCO}_3^-} a_{\text{H}^+}}{a_{\text{CO}_2} a_{\text{H}_2\text{O}}} = K_{\text{CO}_2} = 10^{-7.32} \quad (1)$$

Rearranging, and writing in terms of activity coefficients and molalities and assuming the pH is a measure of  $a_{\text{H}^+}$

$$a_{\text{CO}_2} = \frac{\gamma_{\text{HCO}_3^-} m_{\text{HCO}_3^-} a_{\text{H}^+}}{K_{\text{CO}_2} a_{\text{H}_2\text{O}}} \quad (2)$$

In all solutions considered, the activity of water is greater than 0.99 and was considered unity throughout. The ionic strength (I) of the original water is only 0.0013 and that of the final water 0.408, so that individual ion activity coefficients calculated from Debye-Hückel equations (4) were used throughout to estimate ion activities. The calculated  $a_{\text{CO}_2}$ , using the median pH of 6.8 is shown in Equation 3.

Possible Solid Compounds in Sierra Water as a Function of by Evaporation\*

<i>Magnesite</i> $\text{MgCO}_3$	<i>Hydromagnesite</i> $\text{Mg}_3(\text{CO}_3)_4(\text{OH})_2$	<i>Sepiolite</i> $\text{Mg}(\text{SiO}_3)_2(\text{OH})_2$	<i>Silica Gel</i> $\text{SiO}_2$
9.4	43.6	25.9	3.4
8.8	42.5	25.3	3.3
8.7	40.2	24.3	3.1
9.6	44.6	Saturated	3.0
9.6	48.9	Saturated	Saturated
9.6	44.0	Saturated	Saturated
9.0	42.5	Saturated	Saturated
8.0	34.9	24.0	2.7

$$P_{\text{CO}_2} = \frac{0.97 \times 10^{-3.5} 10^{-1.5}}{10^{-7.32}} = 10^{-3.2} \text{ atm.} \quad (3)$$

The  $\text{CO}_2$  pressure of the water is considerably above the atmospheric value of  $10^{-3.5}$  and therefore the initial water is not in equilibrium with the atmosphere.

The next step, which is representative of all pH calculations, is to find the pH and the accompanying changes in dissolved carbonate species when the water comes to equilibrium with the atmosphere with respect to  $P_{\text{CO}_2}$ . As  $\text{CO}_2$  is lost, the pH will rise.

The equation for electrical neutrality is:

$$2m_{\text{Ca}^{2+}} + 2m_{\text{Mg}^{2+}} + m_{\text{Na}^+} + m_{\text{K}^+} + m_{\text{H}^+} = 2m_{\text{HCO}_3^-} + m_{\text{Cl}^-} + m_{\text{NO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-} \quad (4)$$

Rewriting to put pH-dependent species on the right

$$2m_{\text{Ca}^{2+}} + 2m_{\text{Mg}^{2+}} + m_{\text{Na}^+} + m_{\text{K}^+} - 2m_{\text{HCO}_3^-} - m_{\text{Cl}^-} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-} - m_{\text{H}^+} \quad (5)$$

The terms on the right of Equation 5 can be expressed in terms of pH, equilibrium constants,  $P_{\text{CO}_2}$ , and ionic activity coefficients; the terms on the left are known from the water analysis (Table VI). Rearranging Equation 2 gives Equation 6.



$$m_{\text{HCO}_3^-} = \frac{K_{\text{CO}_2} P_{\text{CO}_2}}{\gamma_{\text{HCO}_3^-} a_{\text{H}^+}} = \frac{10^{-1.42} 10^{-3.5}}{\gamma_{\text{HCO}_3^-} a_{\text{H}^+}} = \frac{10^{-4.92}}{\gamma_{\text{HCO}_3^-} a_{\text{H}^+}} \quad (6)$$

The parallel equation for  $\text{CO}_3^{2-}$  is

$$m_{\text{CO}_3^{2-}} = \frac{K_{\text{HCO}_3^-} K_{\text{CO}_3^{2-}} P_{\text{CO}_2}}{\gamma_{\text{CO}_3^{2-}} a_{\text{H}^+}^2} = \frac{10^{-10.23} 10^{-7.82} 10^{-3.50}}{\gamma_{\text{CO}_3^{2-}} a_{\text{H}^+}^2} = \frac{10^{-21.55}}{\gamma_{\text{CO}_3^{2-}} a_{\text{H}^+}^2} \quad (7)$$

and for  $\text{OH}^-$

$$m_{\text{OH}^-} = \frac{K_{\text{H}_2\text{O}}}{\gamma_{\text{OH}^-} a_{\text{H}^+}} = \frac{10^{-14}}{\gamma_{\text{OH}^-} a_{\text{H}^+}} \quad (8)$$

Substituting analytical values of molality for the terms on the left of Equation 5, Debye-Hückel activity coefficients in the right-hand terms, and neglecting  $m_{\text{H}^+}$

$$0.00052 + 0.000142 + 0.00026 + 0.00004 - 0.000050 - 0.000016 =$$

collecting terms,

$$\frac{10^{-11.22}}{0.97 a_{\text{H}^+}} + \frac{2(10^{-21.49})}{0.86 a_{\text{H}^+}^2} + \frac{10^{-14}}{0.97 a_{\text{H}^+}}$$

$$0.000896 = \frac{10^{-11.22}}{a_{\text{H}^+}} + \frac{10^{-21.28}}{a_{\text{H}^+}^2} + \frac{10^{-14.0}}{a_{\text{H}^+}}$$

solving for  $a_{\text{H}^+}$ ,

$$a_{\text{H}^+} = 10^{-8.26}, \text{ pH} = 8.26.$$

From this value of pH, the values for  $m_{\text{HCO}_3^-}$ ,  $m_{\text{CO}_3^{2-}}$ , and  $m_{\text{OH}^-}$  are obtained from Equations 6, 7, and 8, and the total water analysis can be determined. The only important change is in pH, which rises from 6.8 to 8.26; the change is accompanied by a loss in dissolved  $\text{CO}_2$  and a slight increase in  $\text{CO}_3^{2-}$ —actually not enough to be worth showing in the analysis.

The next step is to determine whether or not the water as a result of the pH change has become saturated with respect to any of the solid phases considered (Table VII). For this, ion activity products are computed for each phase and compared with the equilibrium value (Table VIII). The calculation for calcite is given to illustrate the procedure. The ion activity product is

$$\gamma_{\text{Ca}^{2+}} m_{\text{Ca}^{2+}} \gamma_{\text{CO}_3^{2-}} m_{\text{CO}_3^{2-}} = K'$$

The value of  $\gamma_{\text{Ca}^{2+}} m_{\text{Ca}^{2+}}$  is obtained from the pH and Equation 7:

$$\gamma_{\text{Ca}^{2+}} m_{\text{Ca}^{2+}} = \frac{10^{-21.68}}{(10^{-8.26})^2} = 10^{-5.15}$$

The Debye-Hückel equation yields 0.88 for  $\gamma_{\text{Ca}^{2+}}$ , and  $m_{\text{Ca}^{2+}}$  is  $2.60 \times 10^{-4}$  or  $10^{-3.59}$  (Table VI). Thus  $K$  is  $(0.88)(10^{-3.59})(10^{-5.15}) = 10^{-8.78}$ .

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Consequently, because the equilibrium value of the ion activity product is  $10^{-8.78}$ , the water is slightly undersaturated with respect to calcite, its  $\text{Ca}^{2+}$  content is fixed by  $\text{CO}_2$  pressure and pH; in other words, because the product of  $a_{\text{Ca}^{2+}}$  and  $a_{\text{CO}_3^{2-}}$  is a constant,  $a_{\text{Ca}^{2+}}$  and hence  $m_{\text{Ca}^{2+}}$  can be expressed as a negative term on the right side of the electrical balance equation. After sepiolite precipitates, it can be handled similarly. The

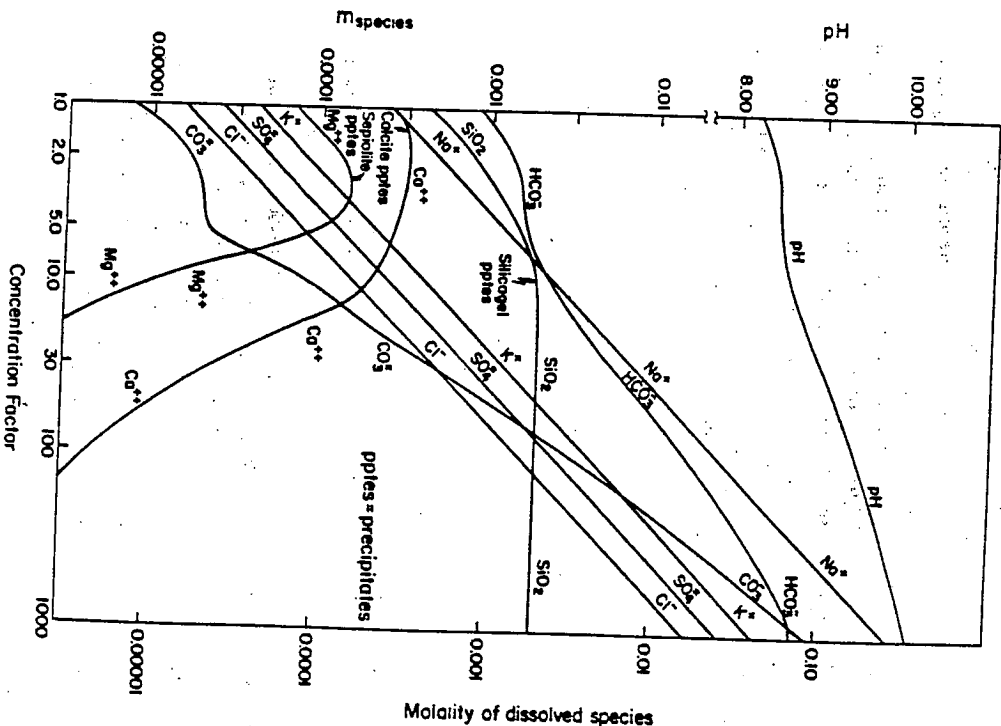


Figure 4. Calculated results of evaporation of typical Sierra Nevada spring water at constant temperature in equilibrium with atmospheric  $\text{CO}_2$ .

analytical expression, after the water becomes saturated with calcite, sepiolite, and silica, is

$$m_{Na^+} + m_{K^+} + 2m_{H_2SiO_4^{2-}} - m_{Cl^-} = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-} - 2m_{Ca^{2+}} - 2m_{Mg^{2+}},$$

or

$$m_{Na^+} + m_{K^+} - 2m_{H_2SiO_4^{2-}} - m_{Cl^-} = \frac{10^{-11.2}}{\gamma_{HCO_3^-} a_{H^+}} + \frac{2(10^{-12.0})}{\gamma_{CO_3^{2-}} a_{H^+}^2} + \frac{10^{-14}}{\gamma_{OH^-} a_{H^+}} - \frac{2(10^{13.2} a_{H^+}^2)}{\gamma_{Ca^{2+}}} - \frac{2(10^{12.1} a_{H^+}^2)}{\gamma_{Mg^{2+}}}$$

In calculating for a given degree of water concentration, the ionic strength is estimated, and tentative activity coefficients for the ions are obtained. After an approximate pH is obtained and values can be assigned for the molalities of the pH-dependent species, new values for the ionic strength and activity coefficients are obtained, and the electrical balance equation is solved again. One such iteration usually suffices to provide satisfactory results. Using the Debye-Hückel activity coefficients obviously leads to an increasing uncertainty in  $\gamma$  values with increasing ionic strength, and the values calculated for 1000X concentration should be regarded as rough approximations.

**Discussion.** A summary of the calculated changes in water composition during evaporation is shown in Figure 4. In essence, evaporation changes the water from a nearly neutral Na-Ca-HCO<sub>3</sub> water to a highly alkaline Na-HCO<sub>3</sub>-CO<sub>3</sub> water. Calcium and magnesium are removed by early precipitation of calcite and sepiolite, and their concentrations diminish to small values as the values of CO<sub>3</sub><sup>2-</sup> and OH<sup>-</sup> rise. Because of the initial high silica, there is enough silica to permit the water to precipitate silica gel at about 10X concentration. Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> concentrate without forming solids.

Table IX. Analyses of Various

	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>
Sierra 100 X	595	159	0.2
Lower Alkali Lake, Eagleville, Calif.*	370	11	6.9
Amargosa River, Nev.*	423	17	2.0
Kurusch Col, Iran*	730	29	11
Keene Wonder Spring, Calif.*	1040	25	23
Sierra 1000 X	5950	1590	0
Soap Lake, Wash.*	12,500	12,500	3.9
Lenore Lake, Wash.*	5360	5360	3.0

\* Analyses from Ref. 6, Chapter G.  
\* Analyses from Ref. 8, Chapter F.

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Buffering of pH during the early heavier precipitation of calcite and sepiolite is clear and is reflected in a near constancy of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. However, after Ca<sup>2+</sup> and Mg<sup>2+</sup> are substantially reduced, the pH again rises with further concentration. Because the Sierra waters are so low in sulfate, gypsum does not precipitate; abstraction of Ca<sup>2+</sup> as calcite never permits the solubility product of gypsum to be exceeded.

The 100X and 1000X waters resemble some natural waters. Table IX compares, in p.p.m., the hypothetical Sierra waters with several natural water bodies.

## *Summary of Genesis and Evaporation of Sierra Waters*

The preceding study of the origin of the composition of spring waters in felsic rocks and the results of evaporating the waters in the absence of the solid weathering residues show that the processes are highly asymmetric. The weathering study showed that dissolved silica comes chiefly from the incongruent solution of silicate minerals rather than from congruent solution of quartz, and as a result the univalent and bivalent cations in solution derived from these silicate minerals are balanced by HCO<sub>3</sub><sup>-</sup>. During evaporation in equilibrium with the atmosphere, the bivalent ions tend to form insoluble carbonates or hydroxysilicates, and the pH of the evaporating solution remains relatively constant until the silicates have been largely removed. The univalent ions, on the other hand, do not form similar compounds of low solubility, and concentrate continuously with a concomitant increase in HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and pH. Therefore, waters maintained in equilibrium with the atmosphere and separated from decomposition products, with univalent ions originally derived from incongruent solution of silicates will inevitably become highly alkaline if concentrated greatly.

## *Saline Waters, p.p.m.*

Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	SiO <sub>2</sub>	pH
0	990	212	240	56	120	9.45
0.9	1200	1200	307	1160	63	p
0.2	639	639	257	109	70	p
25	1200	1200	306	342	p	p
38	1070	29	796	567	57	8.4
0	4250	4500	2400	560	120	10.02
23	11,270	5130	6020	4680	101	p
20	6090	3020	2180	1360	22	p

It is obvious that the silica present in these waters, if denied the opportunity to react with aluminous minerals, must precipitate as amorphous silica or as silicates of the bivalent cations, as illustrated by sepiolite in the example chosen. In nature the silica may be removed by organisms, such as diatoms, but they do not change the gross chemistry.

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#### Literature Cited

- (1) Bricker, O. P., Garrels, R. M., *Proc. Ann. Rudolphs Conf.*, 4th, 1965, Rutgers Univ., New Brunswick, 1967.
- (2) Delleyer, D. K., Laethi, F. J., Weyl, P. K., *Science* 143, 678 (1963).
- (3) Felt, J. H., Roberson, C. E., Polzer, W. L., *U.S. Geol. Surv. Water Supply Paper* 1535-I, 170 (1964).
- (4) Garrels, R. M., Christ, G. L., "Solutions, Minerals, and Equilibria," Appendix 2, p. 430, Harper and Row, New York, 1965.
- (5) Hostetler, P. H., Ph.D. thesis, Harvard University, 1960.
- (6) Livingstone, D. A., *U.S. Geol. Surv. Profess. Paper* 440-G, 61 (1963a).
- (7) Siffert, B., *Geol. Assoc. Lorraine* 21, 32 (1962).
- (8) White, D. E., Hem, J. D., Waring, G. A., *U.S. Geol. Surv. Profess. Paper* 440-F, 14 (1963).

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