



Department of Energy
Washington, DC 20585

APR 20 1993

Mr. Joseph J. Holonich, Director
Repository Licensing & Quality Assurance
Project Directorate
Division of High-Level Waste Management
Office of Nuclear Material Safety
and Safeguards
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555

Dear Mr. Holonich:

In the U.S. Nuclear Regulatory Commission's (NRC) Phase I review letter of January 4, 1993 (enclosure 1) of the U.S. Department of Energy's (DOE) Study Plan 8.3.1.2.3.2, "Characterization of the Yucca Mountain Saturated-Zone Hydrochemistry," the NRC requested that DOE provide references cited in the study plan that are not readily available in the public domain. Enclosure 2 contains the references requested for Study Plan 8.3.1.2.3.2.

If you have any questions, please contact Ms. Sheila Long at 202-586-1447 or Mr. Chris Einberg of my office at 202-586-8869.

Sincerely,

Dwight E. Shelor
Associate Director for
Systems and Compliance
Office of Civilian Radioactive
Waste Management

Enclosures:

- 1. Ltr, 1/4/93, Holonich to
Roberts w/encl
- 2. References for Study
Plan 8.3.1.2.3.2

see enclosure on shelf

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UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D. C. 20555

JAN 4 1993

I-336001

Mr. John P. Roberts, Acting Associate Director
for Systems and Compliance
Office of Civilian Radioactive Waste Management
U. S. Department of Energy
1000 Independence Avenue, SW
Washington, D. C. 20585

Dear Mr. Roberts:

SUBJECT: PHASE I REVIEW OF U.S. DEPARTMENT OF ENERGY (DOE) STUDY
PLAN "CHARACTERIZATION OF THE YUCCA MOUNTAIN SATURATED
ZONE HYDROCHEMISTRY"

On June 5, 1992, DOE transmitted the study plan, "Characterization of the Yucca Mountain Saturated-Zone Hydrochemistry" (Study Plan 8.3.1.2.3.2) to the U.S. Nuclear Regulatory Commission for review and comment. NRC has completed its Phase I Review of this document using the Review Plan for NRC Staff Review of DOE Study Plans, Revision 1 (December 6, 1990).

The material submitted in the study plan was considered to be consistent, to the extent possible at this time, with the NRC-DOE agreement on content of study plans made at the May 7-8, 1986, meeting on Level of Detail for Site Characterization Plans and Study Plans. The NRC staff recognizes that some of the information required in the agreement, especially information about many of the technical procedures for field and laboratory tests, cannot be provided until the prototype testing described in the study plan is completed. The staff did not consider that absence of such information compromised its ability to conduct its Phase I Review; however, the staff requests that the relevant information be provided to NRC as soon as prototype testing is complete and procedures are written.

Among the references listed for this study plan are several which have not been provided to NRC and are not readily available in the public domain. We therefore request that DOE provide the NRC with copies of those references that are listed in the Enclosure.

A major purpose of the Phase I Review is to identify concerns with studies, tests, or analyses that, if started, could cause significant and irreparable adverse effects on the site, the site characterization program, or the eventual usability of the data for licensing. Such concerns would constitute objections, as that term has been used in earlier NRC staff reviews of DOE's documents related to site characterization (Consultation Draft Site Characterization Plan and the Site Characterization Plan for the Yucca Mountain site). It does not appear that the conduct of the activities described in this study plan will have significant adverse impacts on repository performance and the Phase I Review of this study plan identified no objections with any of the activities proposed.

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ENCLOSURE 1

Mr. John P. Roberts

2

After completion of the Phase I Review, selected study plans are to receive a second level of review, called a Detailed Technical Review, based on the relationship of a given study plan to key site-specific issues or NRC open items, or its reliance on unique, state-of-the-art test or analysis methods. We have decided not to proceed with a Detailed Technical Review of this study plan at this time, in part because all of the technical details required for such a review will not be available until the prototype studies are completed.

If you have any questions concerning this letter, please contact Charlotte Abrams (301) 504-3403 of my staff.

Sincerely,



Joseph J. Holonich, Director
Repository Licensing and Quality
Assurance Project Directorate
Division of High-Level Waste Management
Office of Nuclear Material Safety
and Safeguards

Enclosure: As stated

cc: R. Loux, State of Nevada
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Enclosure

Not-Readily-Available References

Iijima, A., 1975, Effect of pore water to clinoptilolite-analcime-albite reaction series: J. Fac. Sci., Univ. Tokyo, Sec. II, v. 19, p. 133-147.

Jones, B.F., 1966, Geochemical evolution of closed basin water in the western Great Basin, in Rau, J.L., ed., Second symposium on salt, 1, Geology, geochemistry, mining: Cleveland, Ohio, Northern Ohio Geological Society, p. 181-200.

Naff, R.L., 1973, Hydrogeology of the southern part of Amargosa Desert in Nevada [M.S. Thesis]: Reno, Nevada, University of Nevada, 207 p.

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Wikberg, P., 1987, The chemistry of deep groundwaters in crystalline rocks: Stockholm, The Royal Institute of Technology, Department of Inorganic Chemistry, TRITA-00K-1078, 137 p.

Willis, R.D., Thonnard, N., Wright, M.C., Lehmann, B.E., and Rauber, D., 1988, Counting Kr atoms in groundwater using RISTOF (abst.): Fourth International Symposium on Resonance Ionization Spectroscopy and Its Applications, National Bureau of Standards, Gaithersburg, Maryland, 1988.

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Received with letter dated 4/20/93

EFFECT OF PORE WATER TO CLINOPTILOLITE-ANALCIME-ALBITE REACTION SERIES

By

Azuma IJIMA

Abstract

The clinoptilolite-analcime-albite reaction series is commonly recognized in altered silicic tuff interbedded with thick piles of clastic sediments which fill the post-Paleozoic geosynclines. It is also found in altered silicic tuff in the Cainozoic alkaline and saline lake deposits.

Field evidences and experimental data indicate that the reaction series is regarded as essentially dependent on temperature at lower P H₂O below approximately 2 kb. The analcime-albite equilibria exist at 180°~190°C at the lower P H₂O in pure water. However, the clinoptilolite-analcime and the analcime-albite reactions take place at the ordinary temperature and at 55°~65°C, respectively, in the alkaline and saline lake deposits; at 84°~91°C and 120°~125°C, respectively, in the marine geosynclinal deposits. Pore water in the zeolitic rock is characterized by alkaline pH and predominant Na⁺, HCO₃⁻ and CO₃⁻⁻. The concentration of Na⁺ in pore water is estimated as an order of 10⁵ ppm in the saline lake deposits, and an order of 10⁴ ppm in the marine deposits. These facts strongly suggest that the concentration of Na⁺ plays an important role on the lowering of equilibrium temperature of the reaction series. The pH of pore water seems to decrease with the increase of temperature. The concentration of HCO₃⁻ and CO₃⁻⁻ would influence the temperature indirectly by controlling the pH.

INTRODUCTION

Authigenic zeolites and alkali feldspars, one of the main constituents of sediments and sedimentary rocks, are formed under various depositional and physicochemical environments; e.g., in oceanic sediments at low temperature and high pressure, in alkaline and saline lake deposits at the ordinary temperature and pressure, by burial diagenesis in thick piles of marine and fresh-water deposits at somewhat elevated temperature and pressure, and in contact aureoles of intrusive bodies and in geothermal areas at high temperature (HAY, 1966; IJIMA and UTADA, 1966, 1972; MUNSON and SHEPPARD, 1974). Even the same zeolitic reaction occurs at various conditions of different temperature and pressure.

I intend to discuss the effect of chemical composition of pore water in zeolitic rock to the equilibrium temperature of some zeolitic reactions on the basis of field evidences and experimental results. In this paper, the clinoptilolite-analcime-albite reaction series is considered.

This study was financially supported by the Grant for Scientific Researches from the Ministry of Education. Part of this paper was read at the US-Japan

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Encl 2

Joint Seminar on Sedimentary Zeolites at Las Vegas on the 5th July, 1974. Valuable discussions with the members of the Joint Seminar, above all, with Dr. R. A. SHEPPARD of the U.S. Geological Survey at Denver have supported the progress of the manuscript. Most part of this paper was also read at the IXth International Congress of Sedimentology at Nice on the 7th July, 1975. My thanks go to Miss Yuki KOMOTO who typed the manuscript.

EXPERIMENTS ON ANALCIME-ALBITE EQUILIBRIA

The equilibria of the reaction, analcime+quartz=albite+H₂O, were calculated thermodynamically by CAMPBELL and FYFE (1965), and refined by THOMPSON (1971) based on an experiment by the reaction-rate method. The equilibrium point exists at 190°C at nil P H₂O. It is significant for the temperature to be regarded as constant at lower P H₂O below 2 kb (Fig. 1). In other words, the reaction is essentially controlled by temperature at the lower P H₂O which is usual during the zeolitic burial diagenesis. The stability fields of albite and analcime determined by hydrothermal syntheses (FYFE *et al.*, 1958; COOMBS *et al.*, 1959; NAKAJIMA, 1973) also indicate that the reaction is almost dependent on temperature at the lower P H₂O, though they show much higher temperature than the above-stated equilibria (Fig. 1). In any case, sodium ions are not contained in the liquid phase.

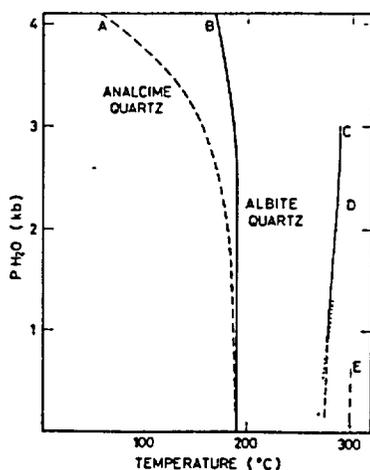


Fig. 1. Diagram showing the analcime-albite equilibria after CAMPBELL and FYFE, 1965 (A), and THOMPSON, 1971 (B). Results of hydrothermal syntheses are also illustrated after NAKAJIMA, 1973 (C), COOMBS *et al.*, 1959 (D), and FYFE *et al.*, 1958 (E).

CLINOPTILOLITE-ANALCIME-ALBITE REACTION SERIES IN NATURE

The clinoptilolite-analcime-albite reaction series has been found in thick piles of marine and fresh-water deposits filling the post-Paleozoic geosynclines and in the Cainozoic alkaline and saline lake deposits. In deep-sea pelagic sediments, clinoptilolite is commonly found associated with or without phillipsite (REX and FAN, 1974 MS; KOSOVSKAYA, 1975); however, analcime occurs very sparsely and no evidence proves the formation of analcime from clinoptilolite. In geothermal areas and the contact aureoles of intrusive bodies, calcic zeolites, such as mordenite, laumontite and wairakite, predominate over clinoptilolite and analcime (UTADA, 1971; IJIMA and UTADA, 1972).

I. Zeolitic Reactio

A. Vertical Distri

In thick piles authigenic zeolites morphism (COOMBS; UTADA, 1966; HAYASHI, 1966) in tuffaceous rock and silicates, for they deposits.

IJIMA and UTADA (1972) from three MITI 1 deep which were marine Neogene at coast of Sea of Japan in Miocene time, so that interbedded with tuffaceous rocks. As a result, the authigenic zeolites show zonal arrangement.

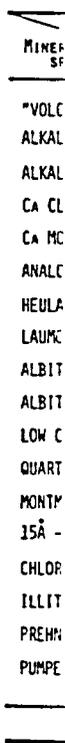


Fig. 2. Scheme of mineral zones in siliceous Cretaceous geosynclines.

I. Zeolitic Reactions in Geosynclinal Deposits

A. Vertical Distribution of Authigenic Zeolites

In thick piles of marine and freshwater deposits filling geosynclines, authigenic zeolites and the related silicates are formed by the burial metamorphism (COOMBS, 1954), or preferably, by the burial diagenesis (IIJIMA and UTADA, 1966; HAY, 1966). Fragments of silicic glass consisting tuff and tuffaceous rock are much important as the original material of the authigenic silicates, for they are reactive and widely distributed in the geosynclinal deposits.

IIJIMA and UTADA (1971) reported the present-day zeolitic burial diagenesis from three MITI Holes, Obuchi, Shimoigarashi, and Masugata, of about 5 km deep which were drilled into gently-dipping and undisturbed strata of the marine Neogene and Pleistocene clastic sediments beneath Niigata Plain on the coast of Sea of Japan. This area has been the site of deposition since the Miocene time, so that zeolitic reactions should be in progress as tuff layers interbedded with the clastic sediments are buried to the critical depths. As a result, the authigenic minerals are progressively distributed in a vertically zonal arrangement. Such vertical distribution of authigenic minerals has been

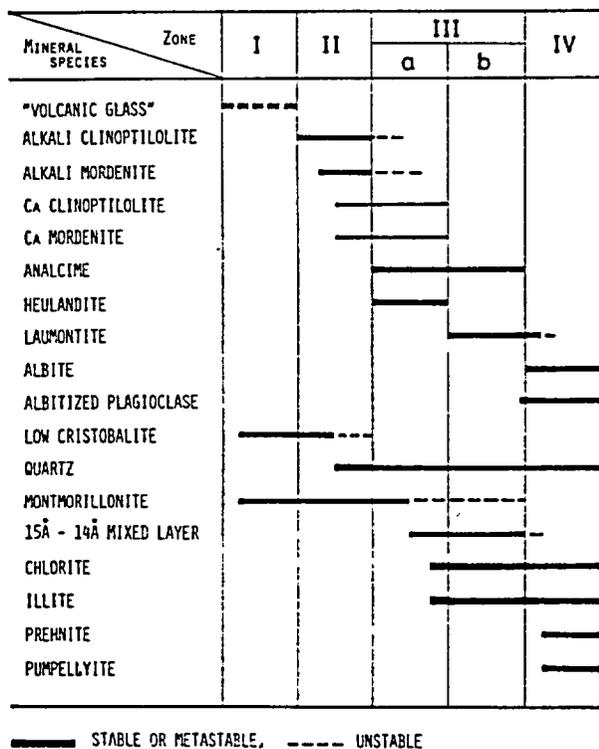


Fig. 2. Schematic diagram showing the zonal distribution of authigenic minerals in silicic tuff due to the burial diagenesis of the Tertiary and Cretaceous geosynclinal deposits in Japan.

recognized not only in the subsurface undisturbed strata but also on exposures of deformed strata of volcanic sediments in the Tertiary and Cretaceous geosynclines throughout the Japanese Islands (UTADA, 1971; IJIMA and UTADA, 1972; IJIMA *et al.*, 1974; SHIMOYAMA and IJIMA, 1974).

In silicic volcanic sediments interbedded with clastic rocks in the geosynclines, the mineral phase is generally classified into four zones, on the basis of the reaction series of silicic glass-alkali zeolites-albite, as shown in Fig. 2. The depth of burial increases from Zone I to Zone IV in the same area.

Zone I: characterized by lacking of zeolites and presence of silicic glass which is partly altered to montmorillonite and low cristobalite.

Zone II: characterized by reaction of silicic glass to form alkali clinoptilolite, alkali mordenite, low cristobalite and montmorillonite.

Zone III: characterized by transformation of the clinoptilolite and the mordenite into analcime. Clinoptilolite sometimes changes to heulandite in the upper part (IIIa), while the latter to laumontite in the lower part (IIIb) of this zone. Within this zone, the cristobalite is recrystallized to quartz, while the montmorillonite to chlorite and/or illite and their mixed layers.

Zone IV: characterized by transformation of the analcime into albite. Clastic plagioclase also undergoes albitization.

Heulandite and laumontite, varieties of calcian zeolites, occur far less and local than varieties of alkali zeolites including clinoptilolite, mordenite, and analcime during the burial diagenesis of silicic tuff in Japan (IJIMA, 1974 MS).

A geopetal structure in altered pumice tuff of the folded Hakobuchi Group of Late Cretaceous age evidently shows that the diagenetic alteration took place before folding (Plate 8). The tuff was collected from a depth of 1505.55~.65 m of the MITI-Enbetsu Hole in the Tenpoku Oilfield in northern Hokkaido (Fig. 3b). It belongs to the Zone IIIa characterized by analcime and heulandite. Rhyolitic glass of pumice grains is replaced by an aggregate of microcrystalline montmorillonite and quartz which was formed simultaneously with analcime. Vesicles within the altered pumice grains are partially filled with the same aggregate. The top surface of the filling is tilted at about 12° which is equivalent with the dip of the tuff bed. This proves that the alteration occurred when the tuff bed was horizontal.

Within deformed strata, the zones are usually tilted, folded and faulted by tectonic movements. In the MITI-Sorachi Hole, they appear repeatedly by the Ponbetsu thrust, as illustrated in Fig. 3a. This fact suggests that the burial diagenesis essentially progressed prior to the tectonic deformation of strata, and that retrogressive alteration is insignificant. It seems to be true that the zonal distribution of authigenic zeolites in the deformed strata was formed in the same way as the present-day diagenesis in the undisturbed strata beneath Niigata Plain.

B. Factors to Control Vertical Zoning in Burial Diagenesis

What is the main factor to control the vertical zoning of authigenic alkali zeolites and albite which has been described in the preceding paragraph?

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UTADA, 1971)

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III~IV

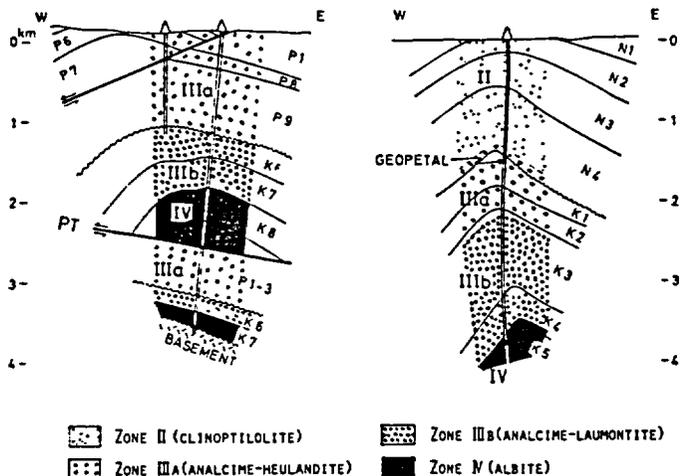


Fig. 3a (Left). Cross-section showing the repetition of the diagenetic zones as well as the stratigraphic sequences of the Paleogene (P1~9) and Cretaceous (K6~8) strata in the MITI-Sorachi Hole in central Hokkaido. The repetition results in the Ponbetsu thrust (PT) which dislocates the Pliocene strata. The P1 above P8 should be corrected as P7.

Fig. 3b (Right). Cross-section showing the normal diagenetic zones in the Neogene (N1~4) and Upper Cretaceous (K1~5) strata in the MITI-Enbetsu Hole in northern Hokkaido. Note that the unconformity at the base of N4 seems not to affect the zoning. The depth from which the tuff with a geopetal structure was collected is also shown.

IJIMA and UTADA (1971) studied the zeolitic burial diagenesis of the MITI Holes which is presently in progress beneath Niigata Plain, and discovered that the zone boundaries of the mineral phase are not correlated with the depth of burial and the stratigraphic boundaries, but well with temperature which is estimated from the bottom-hole temperature, as shown in Table 1.

Petrological analyses of the Tertiary and Cretaceous deposits of four MITI Holes of 4~4.5 km deep in the central-meridional part of Hokkaido (IJIMA, 1975) support the above discovery (Fig. 4). Geothermal gradient in this region is at present 20°~25°C/km. In the MITI-Hamayuchi Hole, the Zone II changes to the Zone III at about 85°C; the Zone III, in turn, to Zone IV at about 120°C. In other three holes, the transitions occur at lower temperature than in the Hamayuchi. This probably results from the recent uplift and erosion of about 1~1.5 km columns in the areas of those three holes.

Table 1. The temperature and the depth of burial at boundaries of the diagenetic zones in the MITI Holes beneath Niigata Plain and in the Yabase Oilfield. Temperature is estimated from the measured bottom-hole temperature. (After IJIMA and UTADA, 1971)

Boundary of zones	Temperature	Depth of burial
II~III	84°~ 91°C	1700~3500 m
III~IV	120°~125°C	2500~4500 m

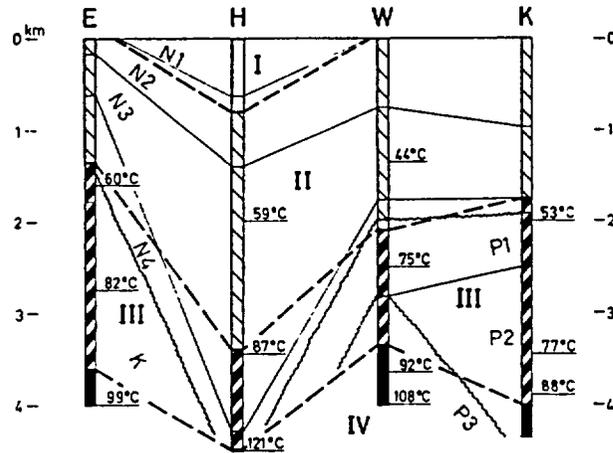


Fig. 4. Schematic cross-section showing the diagenetic zones (I~IV) in the Neogene (N1~4), Paleogene (P1~3), and Upper Cretaceous (K) strata in the MITI-Enbetsu (E), -Hamayuchi (H), -Wakkanai (W), and -Karumai (K) Holes in the central-meridional part of Hokkaido.

Temperature indicated is the measured bottom-hole temperature. The transitional temperature at zone boundaries in the Hamayuchi Hole is well correlated with that in the MITI Holes beneath Niigata Plain. In the other three holes, all the temperature at zone boundaries is considerably lower. This is probably caused by the recent uplift and erosion in the areas of those holes.

In the Japanese Tertiary coal measures, a clear relationship has been found between the zeolite zoning and the degree of coalification which is defined by the O/C and the H/C ratios and by the mean values of reflectance of vitrinite; that is, lignite and subbituminous coal belong to the Zone II, and bituminous coking coal to the Zone III (SHIMOYAMA and IJIMA, 1974). It is well known that coal is most sensitive for metamorphism, and that coalification is primarily a function of temperature and reaction time.

Thermodynamical and synthetic studies on the analcime-albite equilibria, as already stated, indicate that the reaction is essentially dependent on temperature at the lower P H₂O.

These evidences probably allow to lead to the conclusion that the main factor to control the zeolite zoning in the burial diagenesis is not the total pressure and P H₂O but temperature, i. e., geothermal gradient.

II. Zeolitic Reactions in Alkaline and Saline Lake Deposits

A. Horizontal Distribution of Authigenic Zeolites

Alkaline and saline lake deposits including authigenic zeolites are distributed in the present and past, arid to semiarid regions in the USA and Africa. (HAY, 1966; SHEPPARD, 1971). Fragments of silicic glass in tuff beds are one of the principal raw materials for the zeolites including clinoptilolite, mordenite and analcime which are common in the geosynclinal deposits. The authigenic

silicates in the ally zonal arrangement of the burial diagenesis of the lake basins. The authigenic zeolites, analcime, phillipsite, chabasite, and K-feldspar, are common in the authigenic zeolite lakes under the alteration pattern seen in the Platteau (1968).

B. Factors to

It is evident that the authigenic minerals that form in the lakes are a function of temperature and pressure. The authigenic zeolites, analcime, phillipsite, and K-feldspar, are common in the authigenic zeolite lakes under the alteration pattern seen in the Platteau (1968).

C. Authigenic

The authigenic zeolites, analcime, phillipsite, and K-feldspar, are common in the authigenic zeolite lakes under the alteration pattern seen in the Platteau (1968). The authigenic zeolites, analcime, phillipsite, and K-feldspar, are common in the authigenic zeolite lakes under the alteration pattern seen in the Platteau (1968).

III. Chemical

A. Clinoptilolite

Clinoptilolite is a zeolite mineral with a ratio of cation to silicon of 1.5. It is common in the authigenic zeolite lakes under the alteration pattern seen in the Platteau (1968; 1969). The authigenic zeolites, analcime, phillipsite, and K-feldspar, are common in the authigenic zeolite lakes under the alteration pattern seen in the Platteau (1968).

B. Analcime

Sodium is a common cation in the authigenic zeolites, analcime, phillipsite, and K-feldspar, are common in the authigenic zeolite lakes under the alteration pattern seen in the Platteau (1968).

silicates in the alkaline and saline lake deposits are distributed in a horizontally zonal arrangement, which is contrasted with the vertical distribution of the burial diagenesis. Silicic glass, remaining unaltered in the peripheral part of the lake basin, reacts to form alkali zeolites, such as clinoptilolite, mordenite, phillipsite, chabazite and erionite. These zeolites, in turn, change to analcime and K-feldspar in the central part of the basin where saline minerals, including trona and nahcolite, are precipitated. These reactions occur in sediments of playa lakes under highly alkaline and saline to hypersaline environments. This alteration pattern is common to the younger Cainozoic deposits as is typically seen in the Pleistocene Tecopa Lake Beds of California (SHEPPARD and GUDE, 1968).

B. Factors to Control Horizontal Zoning in Alkaline and Saline Lake Deposits

It is evident from the alteration pattern and the association of saline minerals that the above-stated horizontal zoning is not controlled by temperature and pressure, but essentially by chemical gradient in lake water and pore water, such as pH, $[Na^+]$, $[K^+]$, $[SiO_2]$, and etc. (HAY, 1966; SHEPPARD and GUDE, 1968; SURDAM and PARKER, 1972).

C. Authigenic Albite in the Green River Formation of Wyoming

The Eocene Green River Formation of Wyoming is so far only the alkaline and saline lake deposits that yield authigenic albite which is transformed from analcime (IIJIMA and HAY, 1968), despite of having the common horizontal zoning of mordenite, analcime, and K-feldspar (HAY, 1966; GOODWIN and SURDAM, 1967). Consequently, it is impossible to consider that the alkaline and hypersaline pore water gave rise to the analcime-albite reaction at the ordinary temperature. The albitized tuff beds were buried to a depth of approximately 2,000 m, so that the reaction took place at a condition of as high as $55^{\circ}\sim 65^{\circ}C$ in temperature if the geothermal gradient would be $20^{\circ}\sim 25^{\circ}C/km$ and the surface temperature $15^{\circ}C$ (IIJIMA and HAY, 1968).

III. Chemical Composition of Clinoptilolite, Analcime and Albite

A. Clinoptilolite

Clinoptilolite has a wide range of chemical composition not only in the ratio of cations but also in the Si:Al ratio (MINATO and UTADA, 1971; BOLES, 1971). Sodium is the dominant cation of the clinoptilolite formed from silicic glass in the alkaline and saline lake deposits (SHEPPARD and GUDE, 1968; 1969). Sodium and potassium usually predominate over calcium in the clinoptilolite formed from silicic glass in the geosynclinal deposits belonging to the Zone II (IIJIMA, 1971, 1974; MINATO and UTADA, 1971).

B. Analcime

Sodium is nearly exclusive cation of the analcime which are transformed from clinoptilolite and mordenite in altered silicic tuff of the Tertiary and Cretaceous geosynclinal deposits in Japan (Table 2). There is no tendency for

MINATO
UTADA
1971

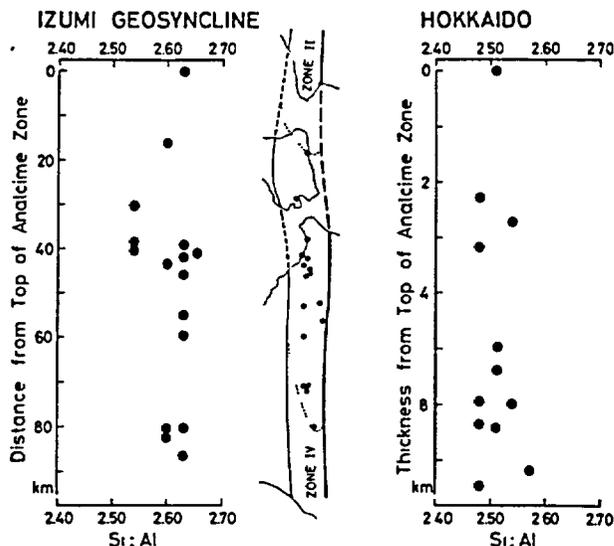


Fig. 5. Variation diagrams of the Si: Al ratio in analcime with respect to the position within the Zone III in the Upper Cretaceous sediments in the Izumi geosyncline, and in the Tertiary and Cretaceous in central Hokkaido. The Si: Al ratio was obtained after the SAHA's method (SAHA, 1959).

the content of calcium in the analcime to increase toward the bottom of the Zone III. Furthermore, the Si: Al ratio of the analcime, ranging from 2.48 to 2.70, seems not to be correlated with the depth of burial, as illustrated in Fig. 5. This fact suggests that the Si: Al ratio would be not essentially controlled by temperature and pressure, but principally by chemical composition of the precursor zeolites, clinoptilolite and mordenite, like analcime in the Barstow Formation of California (SHEPPARD and GUDE, 1969).

Sodium is almost exclusive cation of the analcime in altered silicic tuff in the alkaline and saline lake deposits (SHEPPARD, 1971). Analcime of the Green River Formation contains negligible or only trace amounts of potassium and calcium; the Si: Al ratio ranges from 1.95 to 2.90, and the analcime associated with authigenic albite is less siliceous (IJIMA and HAY, 1968).

C. Albite

Within the Zone IV of the geosynclinal deposits, authigenic albite is formed not only from analcime but also by albitization of plagioclase. The XMA analyses indicate that both types of albite has chemical composition of nearly pure sodium plagioclase (Table 2). The Green River albite replacing analcime is also pure sodium plagioclase (IJIMA and HAY, 1968).

Effect

Table
by

SiO ₂	61.2
Al ₂ O ₃	19.1
Fe ₂ O ₃	0.1
MgO	—
CaO	0.4
Na ₂ O	10.5
K ₂ O	0.4
	91.2

Analyst:

- (1) Analcime, 4006.63 m of
- (2) Analcime group, Paleocene
- (3) Analcime, Ehime, Neogene
- (4) Analcime, Cretaceous;
- (5) Analcime, Cretaceous;
- (6) Albitization formation, M
- (7) Albitization, 4188.6 m of t
- (8) Albitization, Upper Cretaceous

It is quite difficult to determine in which atmosphere of the water table it occurs on some

I. Pore Water

Pore water is nearly pure sodium as the same

WEAVER mudstone or site of sedimentation by dominant pH 8~9. It is constant at the concentrations

Table 2. The XMA analyses of authigenic analcime and albite formed by the burial diagenesis of silicic volcanic sediments in Japan.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
SiO ₂	61.2 %	57.3 %	59.1 %	60.1 %	58.4 %	70.6 %	68.6 %	68.6 %
Al ₂ O ₃	19.1	20.3	20.5	19.8	20.3	20.2	19.7	19.7
Fe ₂ O ₃	0.02	0.04	0.07	0.00	0.00	0.00	0.00	0.04
MgO	—	0.00	—	—	0.00	0.00	—	—
CaO	0.04	0.00	0.00	0.04	0.01	0.11	0.00	0.04
Na ₂ O	10.8	11.9	11.9	11.5	11.9	11.7	11.4	10.7
K ₂ O	0.06	0.02	0.15	0.02	0.01	0.08	0.04	0.03
	91.22	89.56	91.72	91.46	90.62	102.69	99.74	99.11

Analyst: R. MATSUMOTO. 15 KV, 0.018 mA on MgO, Beam diameter 20 microns.

(1) Analcime in altered silicic vitric tuff of the Shiya formation, Miocene; 4006-63 m of the MITI-Masugata Hole, Nigata.

(2) Analcime in altered silicic vitric tuff of the Takisawa formation, Setogawa group, Paleogene; Shimada, Shizuoka. Near the bottom of Zone III.

(3) Analcime in altered silicic vitric tuff of the Izumi group, Upper Cretaceous; Ehime. Near the bottom of Zone III.

(4) Analcime in altered silicic vitric tuff of the Upper Yezo group, Upper Cretaceous; 3766 m of the MITI-Enbetsu Hole, Hokkaido; near the bottom of Zone III.

(5) Analcime in altered silicic vitric tuff of the Lower Yezo group, Lower Cretaceous; Teshio, Hokkaido; near the bottom of Zone III.

(6) Albite replacing analcime in altered rhyolitic vitric tuff of the Fukuyama formation, Miocene; Fukushima, Hokkaido. The same sample as Lower Right of Plate 8.

(7) Albite replacing plagioclase in dacitic tuff breccia of the Nanatani formation; 4188.6 m of the MITI-Obuchi Hole; Niigata.

(8) Albite replacing plagioclase in volcanic sandstone of the Upper Yezo group, Upper Cretaceous; 3746 m of the MITI-Enbetsu Hole, Hokkaido.

CHEMICAL COMPOSITION OF PORE WATER

It is quite difficult to know the true chemical composition of pore water in which authigenic zeolites are formed, because of the difficulty of extraction of the water without any changes. However, we are probably able to estimate it on some assumptions.

I. Pore Water in Marine Geosynclinal Deposits

Pore water in marine geosynclinal deposits has been often presumed to be nearly pure water by some metamorphic petrologists, or sometimes regarded as the same as brine oilfield water.

WEAVER and BECK (1971) studied pore water in the marine Neogene mudstone of the Chevron cores beneath Mississippi Delta where has been the site of sedimentation since Miocene time. The pore water is characterized by dominant Na⁺ and HCO₃⁻ (including CO₃⁻ and CO₂), and moderately high pH 8~9. It is remarkable that the concentration of sodium seems to be nearly constant at the range 1.5~2.5×10⁴ ppm over the whole depth observed, while the concentration of chlorine declines toward the bottom (Fig. 6). The concentrations of Mg, Ca, and K change rather systematically along with the

depth of burial.

The concentration of chlorine* in pore water of the marine Neogene mudstone and interbedded zeolitized silicic tuff of the MITI cores beneath Niigata Plain is much less than that of the normal sea water. The chlorine values decrease gradually with the increase of the depth of burial (IJIMA and UTADA, 1971), excepting for shallower depths less than approximately 1000 m where it is probably diluted by meteoric water (Fig. 6). The behavior of chlorine as well as the geological situations of the MITI cores are quite similar to those of the Chevron cores beneath Mississippi Delta. Furthermore, the chlorine values fall into the same range both in mudstone and in zeolitized silicic tuff. Consequently, we may consider that the pore water in zeolitized tuff of the MITI cores would have chemical composition like that in mudstone of the Chevron cores.

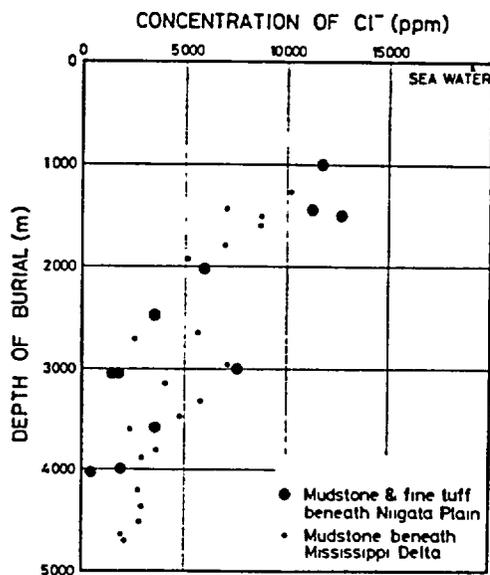


Fig. 6. Variation diagram of the concentration of chlorine in pore water versus the depth of burial in the Neogene marine mudstone and fine-grained silicic tuff. The data are collected from the MITI-Obuchi, -Masugata, and -Shimoigarashi cores beneath Niigata Plain (IJIMA and UTADA, 1971), and from the Chevron cores beneath Mississippi Delta (WEAVER and BECK, 1971). The concentration of chlorine gradually decreases toward the bottom.

* The concentration of chlorine was analysed at the Technical Research Laboratory of the Japan Petroleum Exploration Company (JPDC, 1968). 50 g of dried core sample was dispersed in 100 ml of distilled water with a roller mill. After centrifuging at 10,000 rpm, the content of extracted chlorine (C) was determined by the Mohr's method. The concentration of chlorine in pore water was calculated from the equation, $C_{1+} = (50 S / 100 W)$, where S is the bulk density of core sample, and W is the volume ratio of pore water in the core sample. The content of water was measured by using toluene vapor.

Effect

II. Pore Water

Alkaline scattered in pore water high pH 9~10 during authigenic water and and saline (1972) estimated filled the E saline stage ly represent

Both figures are essentially (Fig. 1 and principally by the field temperature of chemical discussed here

I. Analcime

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Chemical lowering of alkaline and Na⁺, HCO₃⁻ saturated with albite. to be the concentration is n

II. Pore Water in Alkaline and Saline Lake Deposits

Alkaline and saline lakes in which authigenic zeolites are forming are scattered in the West of the USA and East Africa. The lake water and the pore water in sediments are predominant in Na^+ , HCO_3^- , CO_3^{--} and SiO_2 with high pH 9~10 (HAY, 1966). The past alkaline and saline lake deposits containing authigenic zeolites and alkali feldspars would have the same type of lake water and pore water, because they are commonly associated with alkaline and saline minerals such as trona, nahcolite and etc. SURDAM and PARKER (1972) estimated the concentration of sodium in the Gosiute lake water, which filled the Eocene Green River basin, as 10^5 ppm during the most alkaline and saline stage. Pore water in albitized tuff of the Green River Formation probably represents the same order of the sodium values.

EFFECT OF PORE WATER TO CLINOPTILOLITE-ANALCIME-ALBITE REACTION SERIES

Both field and synthetic data have proved that the analcime-albite equilibria are essentially affected by temperature at $P_{\text{H}_2\text{O}}$ less than approximately 2 kb (Fig. 1 and Table 1). The alkali clinoptilolite-analcime equilibria would be also principally influenced by temperature at the lower $P_{\text{H}_2\text{O}}$ as being suggested by the field data (Table 1). Nevertheless, these reactions take place at different temperature under various chemical environments as stated before. The effect of chemical composition of pore water to the equilibrium temperature is discussed here.

I. Analcime-Albite Equilibria

The analcime-albite equilibria exist at $180^\circ\sim 190^\circ\text{C}$ at $P_{\text{H}_2\text{O}}$ below 2 kb (CAMPBELL and FYFE, 1965; THOMPSON, 1971). In nature, the reaction of analcime with quartz to form albite occurs in the marine geosynclinal deposits at $120^\circ\sim 125^\circ\text{C}$ at the depth of burial ranging from 2.5 km to 4.5 km (IJIMA and UTADA, 1971; SHIMOYAMA and IJIMA, 1974). The same reaction takes place in the Green River Formation, the Eocene alkaline and saline lake deposits, at $55^\circ\sim 65^\circ\text{C}$ at a depth of approximately 2 km. The discrepancy in the equilibrium temperature would not result from the difference between the total pressure and the partial pressure of water, because the reaction is essentially independent on the lower $P_{\text{H}_2\text{O}}$.

Chemical composition of pore water probably plays a decisive role on the lowering of the temperature. The pore water in the marine deposits and in the alkaline and saline lake ones is characterized by alkaline pH and predominant Na^+ , HCO_3^- , and CO_3^{--} , as stated in the preceding chapter. Silica is oversaturated with respect to quartz, because authigenic quartz is always associated with albite. One of the essential factors to lower the temperature is considered to be the concentration of sodium ions in the pore water, because the concentration is nil to trace in the hydrothermal experiments, $1.5\sim 2.5\times 10^4$ ppm in

the marine geosynclinal deposits, and 10^5 ppm in the alkaline and saline lake deposits.

The relation of the concentration of sodium ions in pore water to the equilibrium temperature is illustrated on a schematic diagram in Fig. 7. On the diagram, three points, i. e., the alkaline and saline lake deposits, the marine deposits, and the thermodynamical equilibria, are connected with a smooth curve which probably shows the analcime-albite equilibria at the lower P H_2O in respect of the temperature and the concentration of sodium ions in pore water. The width of curve reflects the range of observations. The data of hydrothermal syntheses are also shown on the diagram, though they are much higher in temperature than the equilibria.

In the Otake geothermal area in Kyushu, albite is formed by reaction of plagioclase with weakly alkaline hot water of 800~1,500 ppm Na^+ at $150^\circ \sim 240^\circ C$ (HAYASHI, 1973). These figures are not inconsistent with the equilibrium curve (Fig. 7), reflecting the fact that albitization of plagioclase progresses in

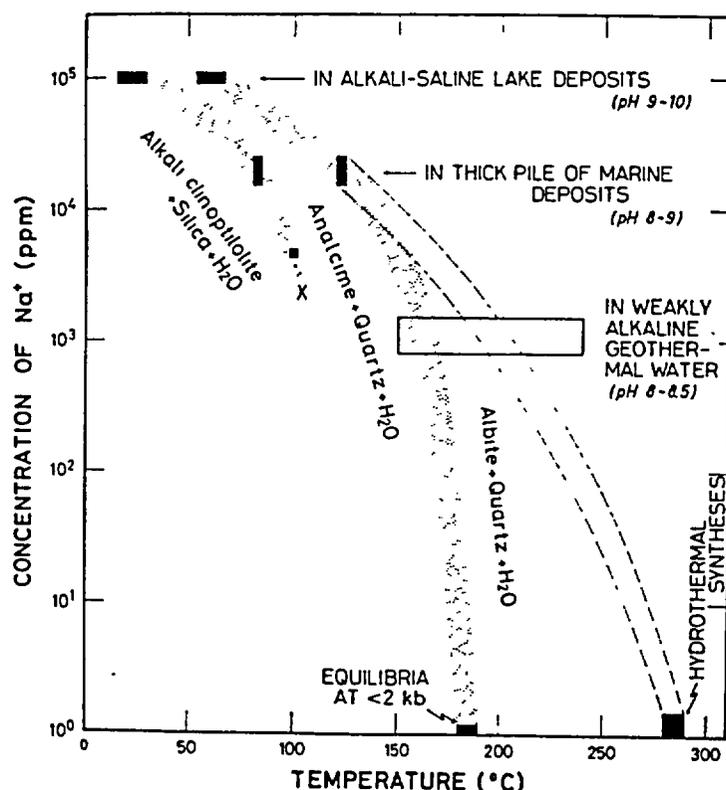


Fig. 7. Stability fields of the alkali clinoptilolite-analcime-albite reaction series with respect to temperature and the concentration of sodium ions in pore water. Silica is always oversaturated with respect to quartz. The point x is after the hydrothermal experiment by BOLES (1971). The open rectangle represents the occurrence of albitized plagioclase in hot water in the Otake geothermal area according to HAYASHI (1973).

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II. Alkali Clu

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subparallel to the analcime-albite reaction (Fig. 2).

II. Alkali Clinoptilolite-Analcime Equilibria

The petrological study of the MITI cores beneath Niigata Plain (IJIMA and UTADA, 1971) strongly suggests that the alkali clinoptilolite-analcime reaction is also essentially affected by temperature at the lower P H_2O . The reaction takes place in the marine deposits at $84^{\circ}\sim 91^{\circ}C$ at the depth of burial ranging from 1.7 km to 3.5 km. It occurs in the alkaline and saline lake deposits at the ordinary temperature. In the laboratory, BOLES (1971) succeeded to transform clinoptilolite into analcime in the Na_2CO_3 - $NaOH$ solution of 4,600 ppm Na^+ at $100^{\circ}C$.

The chemical composition of pore water, above all, the concentration of sodium ions, seems to be the main factor to lower the reaction temperature. The clinoptilolite-analcime equilibria are also illustrated on the diagram of temperature versus concentration of sodium ions (Fig. 7).

Clinoptilolite as well as phillipsite are commonly found in pelagic sediments of the DSDP cores (REX and FAN, 1974 MS), while analcime occurs rarely at the contact with basaltic rock (KASTNER, Oral communication at the US-Japan Joint Seminar on Sedimentary Zeolites in July 1974). It is probable to consider that the mode of occurrence of deep-sea zeolites would result in insufficient temperature which is not high enough to promote the clinoptilolite-analcime reaction in pore water of the pelagic sediments with the concentration of sodium ions of an order of 10^4 ppm.

III. Remarks

Besides sodium ions, other components of pore water undoubtedly influence the equilibrium temperature of the clinoptilolite-analcime-albite reaction series. The values of pH seem to lower with the increase of temperature (Fig. 7). The pH of pore water may affect the equilibrium temperature of the zeolitic reactions. The concentration of HCO_3^- and CO_3^{--} may indirectly affect the temperature as the buffer of pH.

The clinoptilolite-analcime and the analcime-albite reactions probably take place in pore water in the microdissolution-precipitation process, because the original vitroclastic texture is commonly well-preserved and even the pseudomorphs of precursor zeolites are sometimes observed under the microscope. The sodium and probably hydrogen ions in pore water may play a role of the catalyzers which accelerate the activation of the surfaces of the reacting crystals. It is not obvious whether the sodium ions are fixed to the neoforming crystals.

In final, the alkali clinoptilolite-analcime and the analcime-albite equilibria, in respect of temperature, P H_2O , and the concentration of sodium ions in pore water, are illustrated in Fig. 8. The diagram is, of course, tentative. It needs much more data on the chemistry of pore water and on the physicochemical conditions at which the zeolitic reactions take place.

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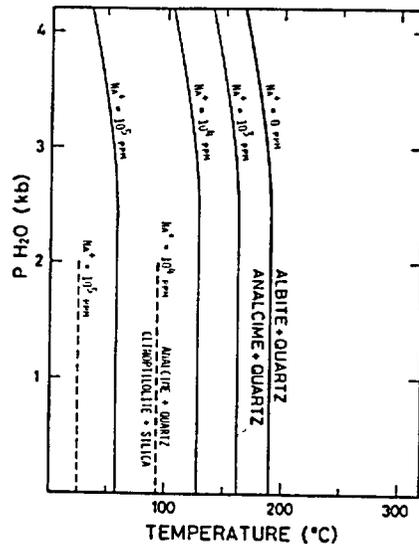


Fig. 8. Tentative diagram showing the clinoptilolite-analcime and the analcime-albite equilibria with respect to temperature, P_{H_2O} , and the concentration of sodium ions in pore water.

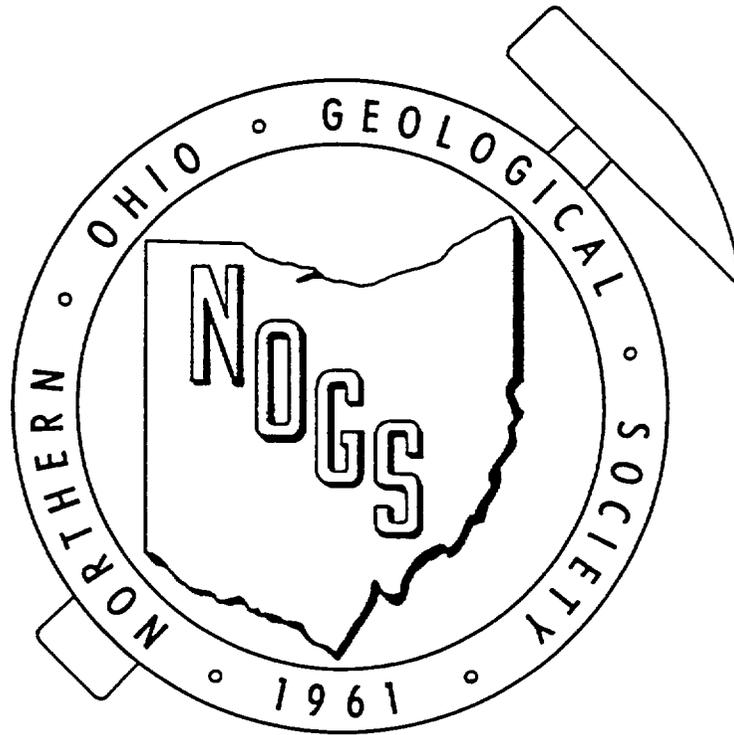
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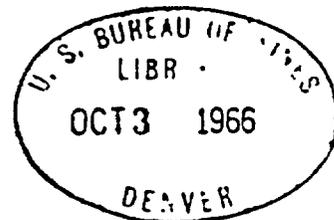


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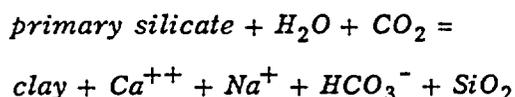
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Geochemical Evolution of Closed Basin Water in the Western Great Basin

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ABSTRACT

The composition of saline waters in inland basins is largely the result of weathering processes accompanied by simple evaporative concentration and selective mineral [solid] precipitation. In the absence of older chemogenic deposits in the drainage basin to provide solutes by simple solution, water compositions are related primarily to three major types of inorganic reactions: (1) silicate hydrolysis, (2) uptake of CO₂ from the atmosphere and/or of sulfate from oxidation of sulfides, and (3) precipitation of alkaline earth compounds. Silicate hydrolysis reactions are typically combined with aqueous CO₂ uptake schematically as follows:



With increasing solution concentration, calcium is precipitated first as calcite and then, with rising salinity and sulfate content, as gypsum. However, if silicate hydrolysis proceeds more rapidly than CO₂ uptake, either because of highly reactive phases or the limited access of ground water to atmospheric or soil CO₂, the pH of the solution rises. This pH rise is accompanied by decreased calcite solubility, and further concentration provides more complete precipitation of calcium as CaCO₃. These processes ultimately lead to sodium carbonate or (with extensive mineralization in the area) sulfocarbonate waters. The rate of silicate hydrolysis is dependent on the original silica-bearing phase and the grain size. Glasses or fine-grained silicates formed at high temperatures are much more soluble in water than are quartz or clay minerals, and they are more reactive than coarse-grained silicates; indeed, the silica content of many alkaline waters is apparently related to the solubility of cristobalite or silica gel. Thus waters containing the highest carbonate or sulfocarbonate concentrations are found in basins where the major drainage areas are underlain by volcanics, fine-grained intrusives, or sedimentary materials derived from such rocks. Secondary modification of lacustrine saline water composition is brought about by CO₂ release and sulfate reduction accompanying organic decay.

The occurrence and interaction of all the aforementioned processes are well illustrated by data from several intermontane areas of the western Great Basin.

INTRODUCTION

The development of saline waters in interior basins is essentially a simple function of solute supply and subsequent concentration by evaporation. The geochemical evolution of closed basin waters can thus be described in terms of solution, transport, and mineral precipitation reactions arranged in a sequence controlled by the basin hydrology. Primary solute composition is set for the most part by the reaction of natural waters with the basic lithologies underlying each drainage basin. Secondary modifications are closely tied to hydrologic setting and process.

Because of the normal heavy dominance of sodium among the cations of continental saline waters (Truesdell, Jones, and Van Denburgh, 1965), classification or trends in compositional evolution are most succinctly described in terms of the major anions. The Great Basin waters have been subdivided on the basis of the most characteristic anion in the saline lake or playas of the major intermontane drainages. Thus, chloride is by far the most dominant dissolved species in the Bonneville Basin, whereas relatively high carbonate concentrations distinguish saline waters of the Lahontan and adjacent territories. Sulfate is characteristic of some of the smaller individual basins, as in parts of the Mojave Desert and areas immediately north. Outside the Great Basin, sulfate is the predominant anion in the saline lakes of the glaciated regions of North Dakota and Washington State.

OBSERVED TRENDS

Hutchinson (1957, p. 565) has utilized a triangular plot of anions in waters from the Lahontan Basin and adjacent areas to illustrate a general compositional trend from inflow to lake or playa waters, as shown in Fig. 1. He has suggested that the nature of such a trend may be distinctive

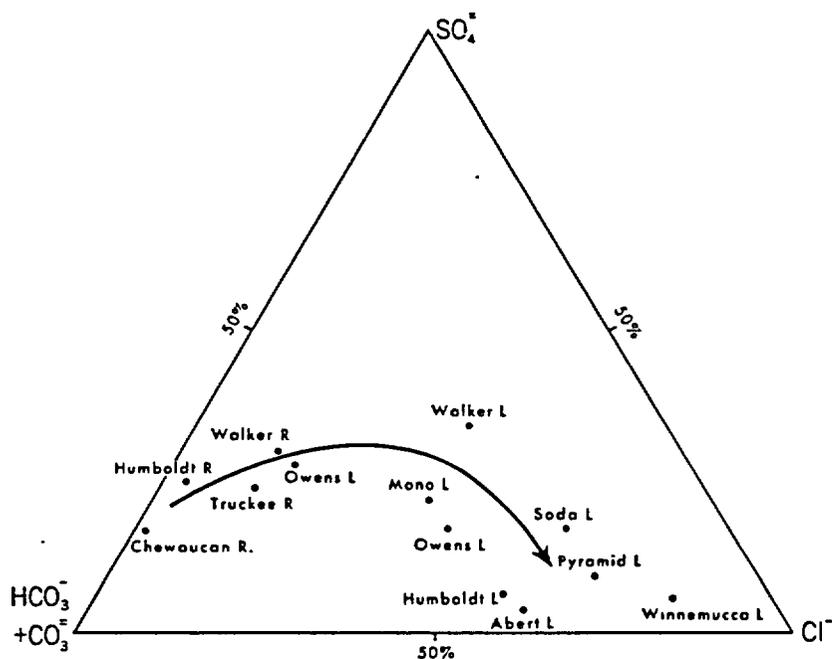


Figure 1. Anionic compositions of rivers and lakes in the Lahontan Basin and in closed basins to the north and west, after Hutchinson (1957, p. 566). Data are from Clarke (1924, pp. 156-166). All locations but Soda Lake are further discussed herein.

for particular regions, but that "the great variation in composition of the individual waters... makes it impossible to follow... a process in the data." Though Hutchinson was certainly correct in detail when pointing to "the complexity of processes occurring even in the simplest cases," it appears possible to make some generalizations based on a few fundamental processes and basic types of solute source.

In the evaporation and concentration of sea water, the trend in anionic composition is severely restricted by the high proportion of chloride and small quantity of carbonate species, because of concentration processes that have already occurred. Precipitation of calcium sulfate enriches the brine in chloride until saturation with halite is achieved and a marked reversal toward higher proportions of sulfate takes place. However, for the first tenfold increase in total salinity, the anionic proportions change less than 10 per cent. In contrast, plots of the major anion distribution in both inflow and lake or playa waters from the major closed basins in the western Great Basin reveal the large-scale changes and distinctive trends which accompany an entire course of concentration. There is significant overlap in the anion composition of initial inflow, but definite differences may characterize the waters of intermediate areas as well as the end products of interior drainage. These differences are illustrated not only for basins where one specie (carbonate, sulfate, or chloride) is heavily predominant, but they can also be distinctive for waters of intermediate anionic type.

In the trilinear plots utilized herein to illustrate major anion composition, total dissolved solids content generally increases in the direction of the chloride apex for each individual drainage basin, but this certainly is not always the case. The location of the major drainage units of the western Great Basin to be discussed is given in Fig. 3. Previously unpublished analytical data from the area are given in Table 1. Methods of analysis were generally those given by Rainwater and Thatcher (1960). Reference to analyses available in other publications is given in the explanation of the figure where the data is utilized. It must be borne in mind that the diversity of sources and of methods employed even by the same laboratories or investigators over the course of time has produced results of variable quality. The very generalized trilinear method of presentation utilized herein serves to minimize the influence of such analytical inconsistencies.

Chloride type.

The Great Salt Lake may be taken as the best example of an interior basin of the chloride type. Hahl and Langford (1964) have compiled estimates of dissolved solids contributions by surficial inflow to the lake for the water years 1960 and 61 and have calculated the percentage contributed by each major source to the total dissolved constituents. Taken in conjunction with the few special analyses presented for the area by Whitehead and Feth (1961), the trend in anionic composition for the bulk of the inflow (> 76 per cent) is directly from the dilute carbonate waters of the Weber River and east shore mountain streams, through the chlorocarbonate Bear River composition, to the very low carbonate, 5-10 per cent sulfate, waters of the lake itself (Fig. 2). The end point of this trend in solution composition is represented by the pure chloride interstitial brines of the Bonneville Desert. The Jordan River and, to a lesser extent, the artificial drains and canals which discharge to the lake have a notably higher sulfate content than other Great Salt Lake inflow as a consequence of human influences. Thus, consideration of the anionic proportions in "average inflow" would offset the general trend toward that presented by Hutchinson for the major drainages of the western Great Basin; there is considerable justification, however, for regarding this offset as artificial. In either case, the course and final result of compositional change is distinctive when compared to that for other Great Basin areas.

Carbonate type.

Though many writers have taken waters of the Lahontan Basin as typical of the carbonate type, the most extreme example of the type actually lies in the Alkali Valley of central Oregon, which is some distance north of the farthest extension of pluvial Lake Lahontan (Fig. 3). Here, in a playa of approximately 5 square miles total area, numerous circular depressions known as potholes (Allison and Mason, 1947) contain carbonate brines which vary considerably in total dissolved solids concentration, but much less in anionic proportions. The potholes are apparently fed by artesian waters evaporating at a rate roughly equivalent to discharge. The anionic composition of dilute water from a nearby well, which is probably representative of inflow to the potholes themselves (Fig. 4). Waters from this area afford the minimum change in anion composition with increased concentration.

Table 1. - Chemical analyses of waters from the western Great Basin

[Chemical analyses in parts per million]

No. on figure	Source	Location ¹	Date of collection	Water Temperature (°F)	Silica (SiO ₂)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO ₃)	Carbonate (CO ₃)	Sulfate (SO ₄)	Chloride (Cl)	Boron (B)	Dissolved solids	pH
1.	Alkali Valley, Oreg. ² Pothole nr. log roadway on SW side of Alkali Lake playa.	30/23-18dd	8-13-61	87	542	--	--	117,000	8,850	2,510	91,400	46,300	45,700	185	314,000	10.1
2.do.....do.....	8-13-63	96	1130	--	--	105,000	5,420	15,400	113,000	18,600	18,600	274	271,000	9.9
AW	Flowing 8" well at log roadway, SW side of Alkali Lake playa.		8-13-63	55	65	--	--	163	16	148	94	34	38	.77	484	9.7
Abert-Summer Lakes basin, Oreg.																
1.	NE end Abert Lake, 0.3 mi. from east shore. ³	33/22-db	8-7-63	75	--	--	--	14,600	522	3,640	6,880	744	12,900	33	37,600	9.7
2.	Abert Lake at gage ³	34/21-24dca	1-12-62	33	144	1.4	.6	22,000	752	5,930	9,460	990	19,300	--	55,900	9.6
C2.	Chewaucan R. at mouth ³	35/21-21cbd	6-12-62	69	26	20	5.3	36	5.5	162	0	12	7.0	--	193	7.6
C3.do.....do.....	8-7-63	77	30	11	3.7	10	3.2	76	0	5.0	1.5	--	102	7.5
E1.	2.7 mi. NE of Valley Falls, Oreg. Chewaucan R. estuary. ³	35/21-21cd	8-8-63	75	30	10	4.0	45	4.6	115	0	5.0	34	--	190	8.1
E2.	2.8 mi. NE of Valley Falls, Oreg. Chewaucan R. estuary. ³do.....	8-8-63	75	32	10	4.0	253	12	188	79	15	215	--	715	9.6
11.	Seepage into pit dug in muds at edge of Brine pool. ³	33/21-35bd	8-12-63	77	698	--	--	38,000	1,480	9,680	16,100	3,240	33,400	56	97,800	9.4
12.	Brine pool, west part of salt flat north of Abert lake. ³do.....	8-12-63	93	645	--	--	119,000	3,890	0	60,300	9,230	115,000	469	309,000	9.8
13.	Seepage from pit dug in playa muds of east part of salt flats north of Abert Lake. ³	Sec. 7, T33B, R22E	7-22-64	93	93	--	--	31,800	1,450	4,090	6,830	2,250	39,300	53	84,000	9.45
S1.	Abert Lake, north shore; center Bog spring feeding brine pond. ³	33/21-35bd	8-12-63	59	52	8.0	4.9	104	14	196	16	28	45	.52	369	8.5
S2.	Spr. SW of Abert Lake ³	35/21-21bba	6-9-62	66	65	9.5	7.5	290	14	282	0	47	295	--	867	8.1
P1.	Poison Creek just above Hey bridge, Lake Co. ³	35/22-1ba	7-26-64	66	30	7.5	4.7	5.9	2.5	59	0	1.6	2.0	0.19	84	7.15
P2.	Spr. at corral on toe of Poison Creek fan, Lake Co.	35/22-1bb	7-26-64	53.5	34	14	8.5	18	3.1	77	0	15	24	.01	156	6.65
S3.	Summer Lake Hot Spring ³	33/17-12aac	10-8-48	116	96	1.4	.4	399	6.8	374	30	111	285	--	1,120	8.5
2.	Summer lake ³	32/16-2abd	4-25-61	68	110	2.5	13	2,830	115	1,880	1,230	348	1,600	--	7,200	9.6
1.	Ana River ³	30/17-6dd	4-25-61	58	36	5.0	2.3	39	3.6	91	9	5.8	12	--	158	8.8
Surprise Valley																
1.	Middle Alkali Lake, Modoc Co. ⁴	42/16-2N	9-17-53	55	37	17	6.2	2,330	9.0	1,010	325	510	2,380	31	6,150	9.2
2.do.....	42/16-3R	5-5-54	75	28	17	8.9	3,180	7.5	1,300	363	576	3,330	38	8,200	9.1
6.	Rt. 8A middle of levee Middle Alkali Lake. ⁴	42/16-2ca	3-25-59	--	36	11	31	4,090	11	1,410	664	900	4,110	35	10,600	9.2
8.	Middle Alkali Lake, at causeway nr. center of north end of Lake. ²do.....	8-15-63	87	39	14	.7	1,340	5.3	830	148	134	1,280	17	3,400	9.0
	Liskey Hot Spr., Modoc Co. ⁴	42/16-6c	3-25-59	90	103	22	3.2	269	5.5	46	17	293	187	4.1	932	8.7
	Rt. 8A E. side of lake, hot spring inflow to Middle Alkali Lake. ⁴	42/16-12bd	3-25-59	--	79	50	6.1	562	18	151	0	597	432	7.5	1,840	7.5

See footnotes at end of table

Table 1. - Chemical analyses of waters from the western Great Basin--Continued

No. on figure	Source	Location ¹	Date of collection	Water Temperature (°F)	Silica (SiO ₂)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO ₃)	Carbonate (CO ₃)	Sulfate (SO ₄)	Chloride (Cl)	Boron (B)	Dissolved solids	pH
1.	Honey Lake															
	Honey Lake, 1.5 mi. WSW of Wendel ⁴ ...	29/15-26d	3-23-59	--	54	28	14	62	5.2	189	11	50	23	.40	342	8.6
2.	Honey Lake, east side at northern boundary of Herlong Ordnance Depot, 100 from shore. ²	28/16-17cc	8- 2-63	77	69	12	1.9	450	26	648	20	138	224	1.0	1,270	8.3
11.	Honey Lake bed interstitial brine from 2 ft. pit on east side at northern boundary of Herlong Ordnance Depot 12' from edge of water. ²do.....	8- 3-63	77	98	--	--	9,320	191	2,830	5,320	4,350	2,810	190	23,900	9.8
Honey Lake--Continued																
12.	Dug pit, Honey Lake, bottom of hole ca. 30' from lake shore. ²		8- 3-63	77	85	--	--	11,900	249	3,840	6,190	6,480	4,870	44	31,700	9.7
13.	Honey Lake bed, interstitial brine from 2' pit 30' from edge of water nr. inflow area of Amedee Hot Spring. ²		8- 2-63	82	55	--	--	18,300	1,630	5,490	8,020	12,100	9,680	44	52,900	9.7
1.	Amedee Hot Sprs, outflow downstream from central orifice on east side Honey Lake. ²	28/16-8ac	8- -63	87	--	18	--	249	5.6	52	0	309	188	--	780	7.8
2.	Honey Lake bed, interstitial brine from 2.5 ft. pit at limit of vegetation nr. inflow area of Amedee Hot Sprs. ²	28/16-7dd	8- 4-63	77	5.7	32	270	9,930	372	1,690	426	11,300	6,570	43	29,800	8.7
Pyramid Lake ⁴																
	Pyramid Lake beach, west shore at Sutcliffe, Nev.		3-26-59	--	13	7.2	117	1,630	120	939	214	274	1,980	--	4,820	8.9
Winnemucca Lake basin ⁵																
1.	Winnemucca Lake Valley, spring.....	27/23-27a	6-18-59	--	69	14	2.3		31.2	97	--	12	9	.42	189	7.8
2.do.....	27/23-26c	6-22-59	--	38	23	3.3		849	744	--	149	775	3.4	2,220	7.5
3.	Winnemucca Lake Valley, well, 2' deep.	26/23-11	6-24-59	--	14	28	3.3	1,695		708	159	305	1,790	5.3	4,340	9.3
4.	Winnemucca Lake Valley, well, 12' deep.	25/23-23c	6-17-59	--	11	4.2	4.5	4,350		744	128	918	5,290	8.8	11,100	8.7
Humboldt Sink																
4.	Humboldt Sink, Toulon Lake.....	25/29-24dd	3-27-59	--	21	28	134	3,880	169	1,040	120	1,740	4,530	17	11,200	8.6
5.	Humboldt R. at gage about 3 mi. above Humboldt Sink.	25/31-11bd	3-27-59	--	64	83	36	2,940	52	377	38	570	4,150	--	8,100	8.5
Carson Sink ⁴																
2.	Carson R. Flats, 5 mi. N of Fallon, Nev.	19/29-5b	3-27-59	--	.0	3.2	4.0	15,900	135	3,310	9,720	8,730	4,570	63	41,000	9.9
3.	Slough, E side of Carson sink, N of Stillwater, Nev.	21/31-20	3-26-59	--	17	36	118	1,220	68	666	57	695	1,380	5.7	3,930	8.6
4.	Carson sink, 2 mi. SE of Parran, Nev.	22/29-17b	3-27-59	--	19	261	129	56,800	3,240	322	0	786	88,900	123	152,000	7.8
Mono Lake ⁴																
1.	Shoreline sample, Mono Lake at Tioga Lodge.		3-30-59	53	14	4.5	34	21,500	1,170	5,410	10,300	7,380	13,500	--	56,600	9.6
Rhodes Marsh ⁴																
1.	Well at Old Plant.....	5/35-16	3-27-59	48	49	8.6	2.1	874	30	260	90	850	494	--	2,540	8.8
2.	Rhodes Marsh nr. Mina, pond in center of marsh.	5/35-15	3-27-59	--	142	17	.5	3,680	102	23	648	2,590	3,070	81	10,400	9.5
3.	Spring in center of marsh.....do.....	3-27-59	60	121	15	2.2	2,550	70	115	384	1,830	2,110	55	7,210	9.3
Owens Lake Basin ⁴																
	Owens Lake, first centrifugal pump, Columbia Southern Line.		5-19-61	71	853	--	--	122,000	9,120	--	--	37,900	101,000	1,200	310,000	10.3

See footnotes at end of table

Table 1. - Chemical analyses of waters from the western Great Basin--Continued

No. on figure	Source	Location ¹	Date of collection	Water Temperature (°F)	Silica (SiO ₂)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO ₃)	Carbonate (CO ₃)	Sulfate (SO ₄)	Chloride (Cl)	Boron (B)	Dissolved solids	pH
1.	Saline Valley ²	14/38-10ab	1-21-63	--	30	34	22	86	8.1	141	0	193	36	--	980	7.5
	Artesian well, 0.33 mi. W of Palm Springs.															
2.	Tumco Mine Camp Spr.....	14/38-28	1-31-64	71	28	90	35	21	4.9	144	6	264	11	--	525	8.4
3.	Beveridge Canyon water.....	14/38-17c	2- 1-64	49	36	83	10	15	3.7	128	0	153	14	--	378	7.6
4.	Hunter Canyon Stream.....	14/38-28b	1-31-64	51	33	72	8.9	12	2.5	122	2	122	11	--	323	8.3
5.	Brine from just under crust of Saline V. salt pan, 0.5 mi. N of end of old tramway.	14/38-23cc	1-22-63	--	74	538	438	101,000	1,610	534	0	8,410	155,000	156	267,000	7.5
6.	Brine from 3' depth, NW edge of Saline V. playa, 1 mi. from road intersection, N side.	14/38-15ac	2- 2-64	49	1.8	477	1,670	33,000	4,560	211	133	39,200	31,500	27	111,000	8.2
7.	Brine from 3' depth, 3 mi. N of road along southern edge of playa.	14/39-20bb	1-23-63	--	--	--	--	103,000	5,190	6,200	(*)	31,400	144,000	701	287,000	8.25
8.	Surface brine from spr. area 3 mi. N of road along southern edge of playa.	14/39-18da	2- 1-64	67	12	9.4	3.5	28,800	1,650	1,510	1,300	10,100	37,400	90	80,900	8.55
9.	Brine from 5' depth, NW corner of Saline Valley playa, 1.5 mi. S of road to Palm Sprs.	14/38-12bc	2- 7-64	57	--	352	134	9,430	914	156	0	5,590	12,300	2.2	28,800	7.75
10.	Surface pool in ephemeral channel, 0.75 mi. E of sta. 38 Saline V. playa.	14/38-12ad	2- 7-64	--	12	378	1,210	23,900	2,960	166	0	7,390	38,900	8.1	74,500	7.65
11.	Brine from 4' depth on old tramway rd, 0.25 mi. N of main valley rd.	14/38-26ac	2- 9-64	57	51	692	107	4,300	57	123	0	3,900	5,600	10	14,800	7.5

¹ Location system the same as that used by Cohen and Loeltz (1964).

² Shirley L. Retting, analyst.

³ A. S. Van Denburgh, Solute balance of saline Abert and Summer Lakes, Oreg. (in preparation).

⁴ J. Barnhart and R. K. Reeves, analysts.

⁵ U. S. Geological Survey, Quality of Water laboratory, Salt Lake City, Utah.

⁶ U. S. Geological Survey, Quality of Water laboratory, Portland, Oreg.

⁷ Carbonate endpoint not discernible when graphed; assumed to be all bicarbonate.

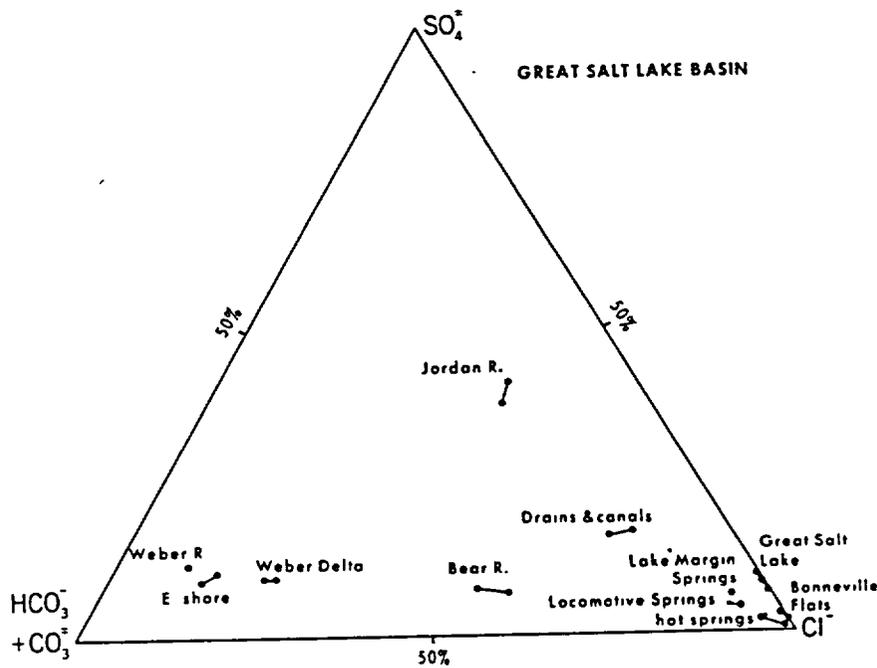


Figure 2. Major anion composition of waters from the Great Salt Lake area, Utah. Most of the points are taken from the analyses of Hahl and Langford (1964, Table 3), with additions from the data of Whitehead and Feth (1961).

Mixed waters.

Drainages included in Hutchinson's plot of anionic composition in the Lahontan adjacent basins (Fig. 3) that show some similarity in hydrochemical evolution are of mixed type, but for most of the basins compositional trends are separate and distinct. South of the Alkali Valley in Oregon, for example, the Abert-Summer Lake area contains "end-point" waters best classified as chlorocarbonate in type. These two bodies of water, both remnants of pluvial Lake Chewaucan, present a distinct contrast in the chemical nature of inflow and lake water (Van Denburgh, 1964). In total dissolved solids concentration and anionic proportions, Summer Lake and its principal inflow, the Ana Springs, are bracketed by the Chewaucan River and Abert Lake (Fig. 4). Some spring inflow suggests slight sulfate enrichment prior to reaching the lakes, but the anion trend for waters of the two adjacent basins is toward increased chloride with nearly constant sulfate content.

The effects of addition of sulfate to basin waters by hot spring systems are shown in the Surprise Valley and Honey Lake Basins of northeast California. Both drainage areas contain playa lakes occupying the downthrown parts of fault block basins. The principal inflow is from

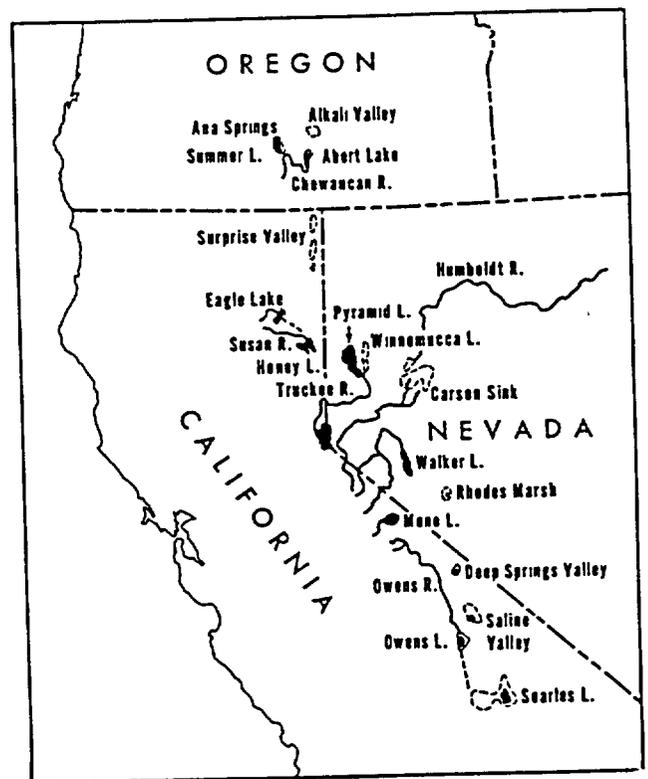


Figure 3. Index map showing the location of some of the principal closed drainage systems of the western Great Basin north of the Mojave Desert.

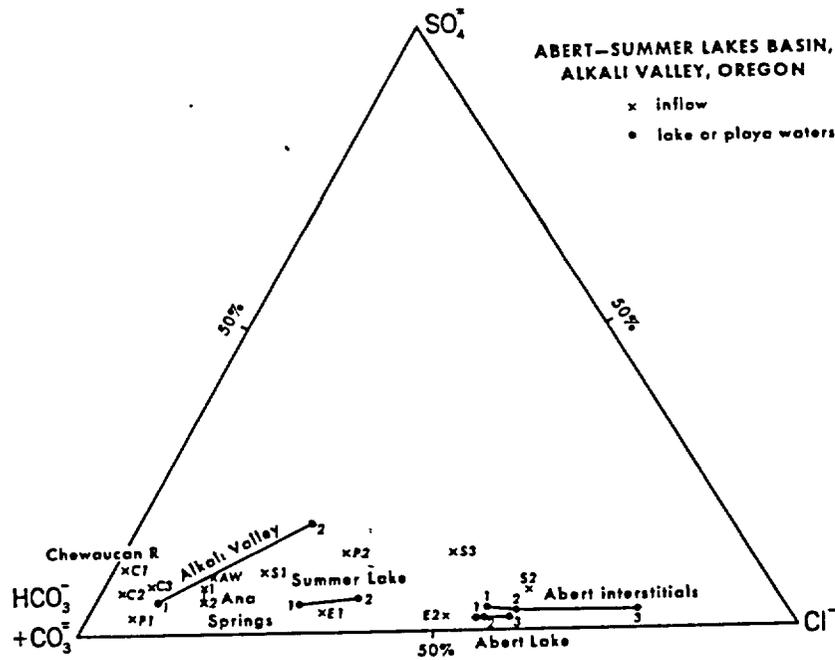


Figure 4. Major anion composition of waters from the Abert-Summer Lakes Basin and the Alkali Valley, south-central Oregon. Analysis number 1 of the Chewaucan River, Ana Springs, Summer Lake, and Abert Lake analysis number 3 all taken from Clarke (1924, p. 163). All other analyses given in Table 1. Most data for the Abert-Summer Lakes Basin is taken from a report in preparation by A. S. Van Denburgh, "Solute balance of the saline Abert and Summer Lakes, south-central Oregon."

mountain streams, which are nearly pure bicarbonate in anionic composition. Typical are the waters of the Susan River, and of Eagle Lake, which loses water to Honey Lake by seepage outflow. The result of addition of hot spring inflow varies from the nearly equivalent anionic proportions of sulfate and carbonate in the interstitial brines from the eastern side of the Honey Lake playa, to compositions only slightly higher in sulfate than Abert Lake (Fig. 5). Compared with any of the individual basins herein considered, this trend is the closest to Hutchinson's "average," represented by the arrow in his diagram (Fig. 1) for the western Great Basin.

A significant proportion of sulfate characterizes the only other drainage of the western Great Basin which rivals the Lahontan in area -- the Owens River system. Hutchinson considered only the changes in composition from Owens River to Owens Lake; but as has been discussed by Gale (1915) and Smith (1962), the pluvial Owens River drainage overflowed Owens Lake and carried southward to China Lake, Searles Lake, and at highest stages, onward to the Panamint Basin and probably Death Valley; the Searles Lake Basin with its abundant lacustrine salt deposits (Smith and Haines, 1964) no doubt represented the end point of the Owens River system through most of pluvial times. This relation is further seen in the anion plots for analyses of Owens Lake and the Searles brines (Fig. 6). Older analyses of Owens Lake (Clarke, 1924, p. 162), taken at a time when an extensive body of saline water still covered the basin, plot intermediately between analysis of Owens Lake as it is today, a very shallow body of saturated brine resulting from continued evaporation following nearly complete diversion of the Owens River into the southern California water-supply system, plots very close to recent analyses of the interstitial Searles Lake brines. The closest modern equivalents to the waters of the former Owens Lake are those of Mono Lake. Mono Lake occupies the basin of a larger pluvial ancestor and is fed primarily by Sierra Nevada runoff, which is very similar in composition to tributary streams of the Owens River. Mono Lake and representative surface inflow compositions (Fig. 6) show an anionic trend which is relatively constant in proportions of sulfate.

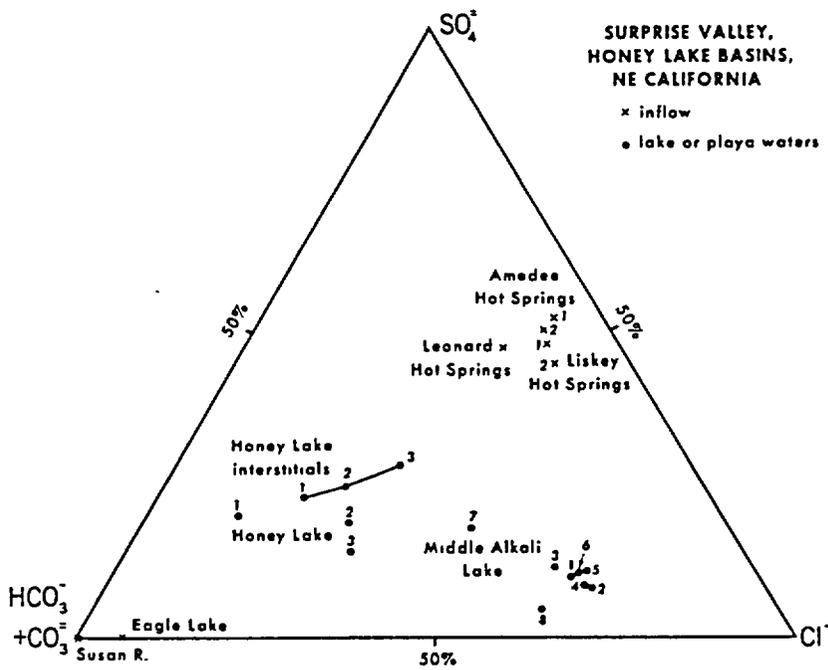


Figure 5. Major anion composition of closed basin waters of northeast California. Susan River analysis from unpublished data, U. S. Geological Survey, 1955. Eagle Lake analysis from Livingstone (1963, p. 617). Honey Lake analysis number 2, Middle Alkali Lake analyses numbers 3 and 4, and data for the Leonard Hot Spring from California Department of Water Resources (1960). All other analyses are given in Table 1.

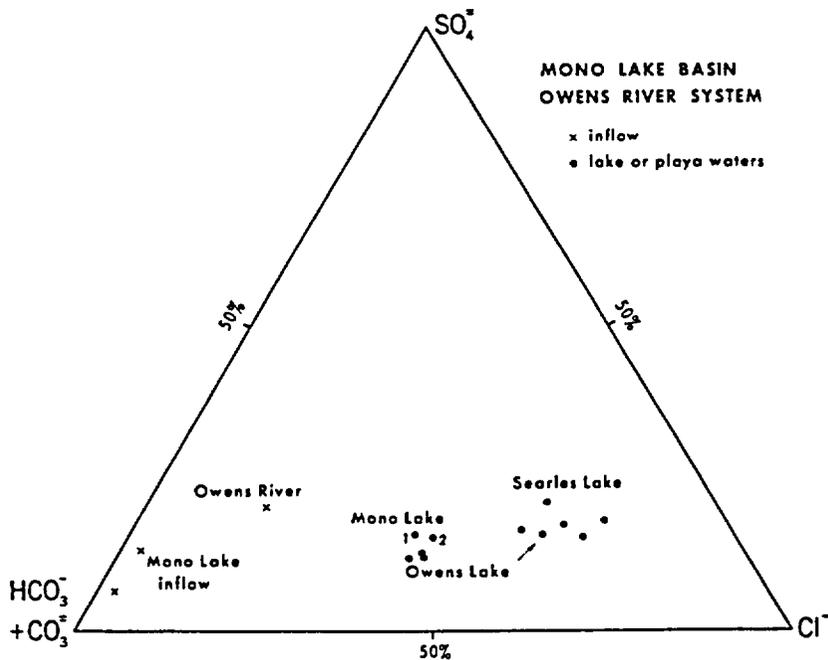


Figure 6. Major anion composition of waters from the Mono Lake Basin and Owens River system of eastern California. Data for Owens Lake and the Owens River prior to diversion are from Clarke (1924, p. 162). Mono Lake analysis number 2 and data for Mono Lake inflow from Whitehead and Feth (1961). Analyses of Searles Lake brines from White, Hem, and Waring (1963, p. F56) and unpublished records. Analyses of present-day Owens Lake and Mono Lake are given in Table 1.

D. E. White (personal communication, 1965) has suggested that the Owens River analysis may be higher in sulfate than the general trend because of the influence of hot springs in its upstream drainage, which can account for 80 per cent of the boron carried by the Owens River system. During the Pleistocene, when much of the salt load was actually carried into Owens Lake, the Owens River probably received a greater proportion of its flow from surface waters similar to present Mono Lake inflow. An analysis of the Owens River of Pleistocene time might well plot near a straight line between Mono Lake and its principal inflow.

The most variable and complete range in anionic proportions among the closed basin waters considered by Hutchinson occurs within the central part of the Lahontan area (Fig. 7), although the significance of recent analyses is reduced by complications arising from extensive irrigation. Recent analyses of Pyramid Lake and interstitial waters from the sediments of presently dry Winnemucca Lake contain distinctly lower proportions of chloride than the older analyses of Clarke (1924, p. 160). More recent analyses also make apparent a considerable range in the composition of the Truckee River at successive downstream sites. Modern waters from the Humboldt and Carson Sink areas apparently contain higher quantities of sulfate than previously indicated in Clarke's data. The combined data show that the central Lahontan Basin drainage today exhibits anionic trends not far from the average suggested by the arrow in Hutchinson's diagram for the western Great Basin (Fig. 1).

Sulfate type.

Closed drainage systems of the western Great Basin north of the Mojave region that can be considered of the sulfate type are Rhodes Marsh of western Nevada and the Saline Valley of eastern

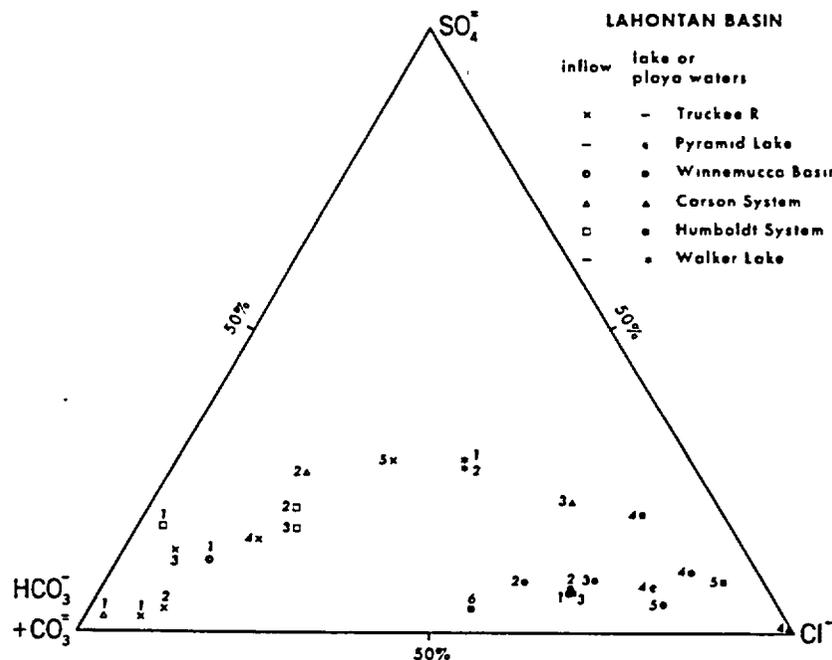


Figure 7. Major anion composition of waters from the Lahontan Basin. Analyses number 1 from the Humboldt River, number 4 from the Truckee River, number 6 from Humboldt sink, number 4 from Pyramid Lake, and number 5 from Winnemucca Lake, all from Clarke (1924, pp. 159-161). Analyses of Walker Lake, Pyramid Lake (number 2), plus the Truckee River at Wadsworth (number 3) and Nixon (number 5), Nevada, from Whitehead and Feth (1961). Other analyses of Pyramid Lake (number 1) and the Truckee River (Lake Tahoe, number 1, and at Farad, number 2) from Livingstone (1963, p. 617). Discharge weighted mean data for the Humboldt River at Rye Patch Dam, Nevada, from U. S. Geol. Survey (1952, 1957). All other analyses given in Table 1.

California. Both these basins contain extensive salt-encrusted playas fed primarily by ground waters. Spring waters collected around the Saline Valley (Lombardi, 1963, Table 3; Hardie, 1965) exhibit a wide range in anionic composition, including high proportions of carbonate, but the bulk of such waters is characterized by high concentrations of sulfate (Fig. 8). Samples of inflow

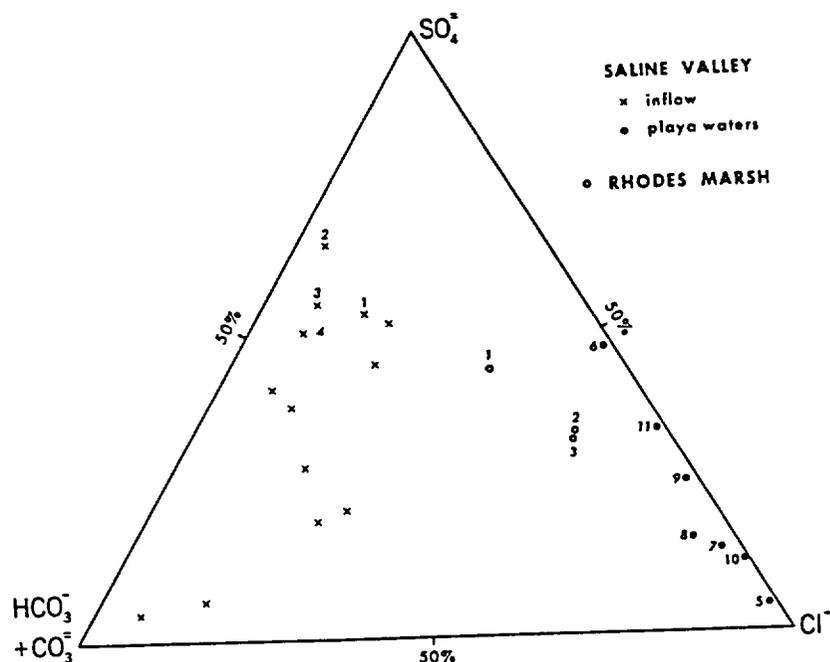


Figure 8. Major anion composition of waters from the Saline Valley, California, with a few points representing inflow in the immediate area of the Rhodes Marsh playa, Nevada. Data for inflow to the Saline Valley from Lombardi (1963, Table 3). Data for Saline Valley brines, selected to give a representative range of anionic composition, from analyses assembled (1965, Table 31).

waters collected in the immediate area of the Rhodes Marsh playa illustrate anionic compositions intermediate between the Saline Valley inflow springs and interstitial brines of the Saline Valley playa. The overall anionic trend accompanying concentration increase from the average Saline Valley spring composition through the Rhodes Marsh solutions to Saline Valley interstitial brines shows the most marked decrease in proportions of sulfate only after the sulfate-chloride edge is approached. Further enrichment in chloride takes place in brines which are nearly carbonate free.

Close to an average trend in anion composition for closed basin waters is provided by analyses of inflow and playa waters from the Deep Springs Valley of eastern California (Fig. 9). In this small intermontane basin, which lies just north of the Saline Valley and east of the Owens River system, salt deposits occur in both a small playa and a nearby fault-trough pond. The area combines an extensive range in lithology with all the natural processes at work elsewhere to give a representative example of compositional evolution in waters of the entire western Great Basin.

PROCESSES RESPONSIBLE FOR THE TRENDS

The primary influence on the initial anion composition of any closed basin water is the gross lithology of the materials with which the water has been in contact. This influence is exerted by two basic mineral-water reactions, solution and hydrolysis. Secondary anionic changes in closed basin waters result principally from the interaction of evaporative concentration with reactions related to organic processes or mineral precipitation. Despite limitations, the trilinear plotting of major anion compositions does reflect these processes, though suggestions made from the

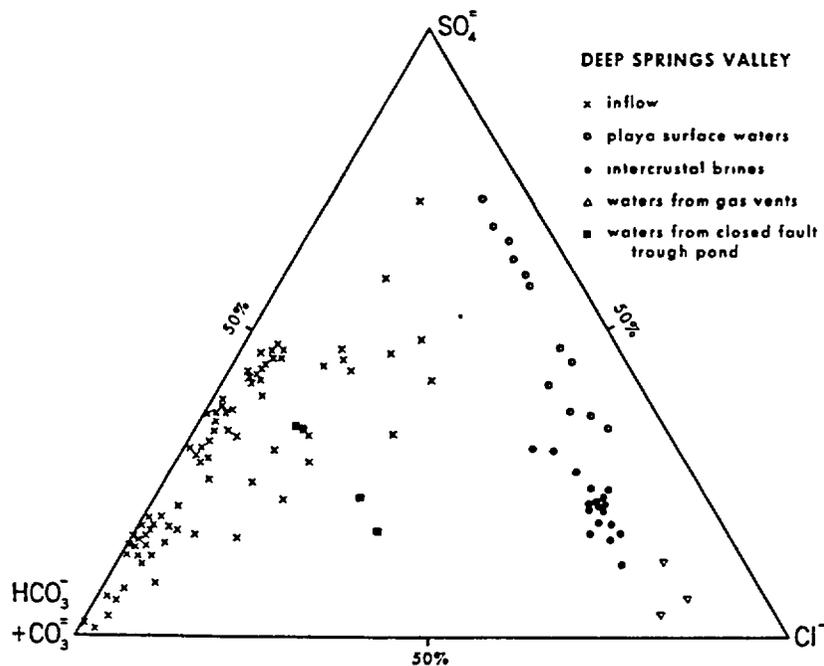


Figure 9. Major anion composition of waters from the Deep Springs Valley, California. Data from Jones (1965, Table 7).

relationships shown must be verified by further evidence (Hem, 1959, p. 183). The primary reactions control the position of points representing basin inflow while secondary processes dictate the anionic trend through the course of evaporative concentration. In general, concentration increase is accompanied by an increase in chloride; and solid precipitation, by a decrease in the appropriate anion. The direction of compositional trends may be similar, but distinct differences in actual path for each of the major drainage areas are established and, to some degree at least, are maintained by the lithologic environment.

Simple solution.

The most straightforward reaction providing solutes to closed basin waters is that of complete solution of readily soluble, simple ionic mineral compounds. Whenever evaporites are present in the drainage area, this process dominates the geochemical evolution of the basin waters. As pointed out by Hutchinson (1957, p. 568), drainage from pre-existing salt beds appears to account for most nearly pure chloride waters. The purest chloride waters discussed herein are the interstitial brines of the Bonneville salt flats. Indeed, it has been postulated that bedded evaporites, primarily halite, have contributed most of the salt load of the Bonneville Basin and the Great Salt Lake (Feth, 1959). Much of the salts in modern inflow to the lake, however, may be simply recycled from older Bonneville sediments.

Another obvious source of the solutes in water is the solution of calcite from limestones. This process exerts a major control on the composition of inflow draining areas underlain by Paleozoic marine strata, as in the immediate area of the Great Salt Lake or parts of the Deep Springs and Saline Valleys.

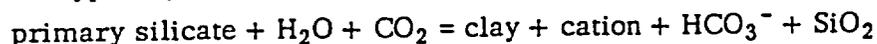
The leaching of ions absorbed or trapped in interstitial fluids in clastic sediments is another solution mechanism providing dissolved components in water. In this way, for example, chloride incorporated in clayey strata by membrane filtration during compaction (White, 1965) might be obtained. The chloride that makes up such a high proportion of the most concentrated brines of the Saline Valley playa may have had such a source. The term leaching may also be used to describe the removal by solutions of the products of oxidation of sedimentary sulfur compounds, largely pyrite. In the western Great Basin it is difficult to differentiate sulfate of sedimentary origin from that associated with areas of hydrothermal alteration without detailed study of each

contributive drainage system (barring possible isotopic differences). Outside the Great Basin sulfate becomes the major constituent of closed basin waters in the glaciated areas of Washington State and the northern Great Plains.

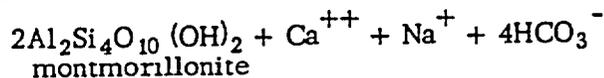
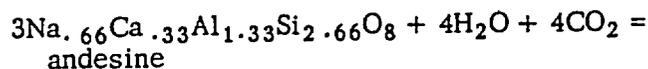
Silicate hydrolysis.

The initial compositions, subsequent evolution, and the importance of carbonate in the major drainages of the western Great Basin are chiefly related to the hydrolysis of primary silicates. The gross effect of such reactions is dependent not only on the quantitative proportions of igneous vs. sedimentary material in contact with basin waters but also on the relative stability of the individual silicate mineral species composing these rocks. In the weathering sequence of clay sized minerals established by Jackson and others (1948) the relative stability of the primary silicates, with the exception of feldspar, increases roughly with decreasing ratios of silica to alumina. This reflects the higher solubility of silica over alumina in natural water, as well as considerations of crystal structure. Preferential attack on mafic mineral phases with high Si/Al ratio further increases the quantity of silica leached by solutions penetrating primary igneous materials. Examination of the detritus in the recent lacustrine deposits of the western Great Basin indicates that feldspars from a wide variety of sources are left intact, while the mafic components of igneous rocks have been extensively altered or completely broken down. The original grain size is an additional factor affecting primary silicate stability; smaller grain size provides additional surface area for solution attack on minerals. An optimum combination for silicate hydrolysis is in pyroclastic deposits. These materials combine metastable molecular structure with maximum granular surface area and, typically, relatively high Si/Al ratios. The highest initial concentrations of silica in natural water can usually be traced to association with such deposits.

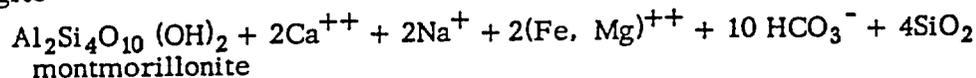
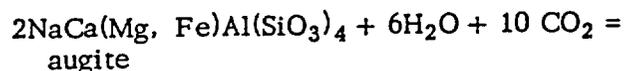
The most common impetus behind the hydrolysis of primary silicates is the reactions of carbon dioxide with water to form carbonic acid. The resulting reactions provide bicarbonate ions in proportion to the release of metallic cations and the solution of silica. Silicate hydrolysis reactions are typically combined with aqueous CO₂ uptake schematically as follows:



Alkali feldspar is most frequently cited as the primary silicate and kaolinite as the clay product in weathering reactions (e.g., Garrels, 1965), but for the more common igneous rocks of the western Great Basin:



This reaction yields no silica, but abundant amounts of SiO₂ can be obtained by mafic mineral alteration, such as¹:

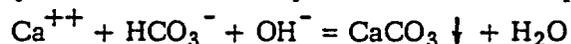


Lesser amounts of silica may be expected from silicic intrusive rocks which bear mafic phases with low Si/Al ratios than from extrusives.

The carbon dioxide for the hydrolysis reactions is derived primarily within soils which support a P_{CO₂} significantly above that of the atmosphere because of biotic activity. Some carbon dioxide may be derived from other sources, as indicated by the high CO₂ content of waters of deep circulation from some fault zones or thermal areas. After steam, carbon dioxide is the next most abundant component of volcanic emanations (White and Waring, 1963). However, the brines of

¹In both equations, the formula for montmorillonite has been idealized to that of pyrophyllite for ease in balancing. In actual fact, divalent cations are in part retained by the clay, thus further enhancing the proportions of alkalis in the solution.

the western United States with the highest carbonate content apparently result from the in situ evaporative concentration of alkaline waters which derive their carbonate content from silicate hydrolysis at the normal temperatures of weathering. The "potholes" of the Alkali Valley in Oregon are fed by seepage which appears to be made alkaline by reaction with lacustrine deposits of reworked pyroclastics. Similarly, the carbonate brines of the fault trough pond in Deep Springs Valley result from the concentration of dilute, but highly alkaline, seepage inflow. This mechanism apparently operates at points in the Abert, Mono, and Searles Lake Basins also. In any case, silicate hydrolysis in the subsurface has proceeded more rapidly than CO₂ uptake by weathering solutions. This may be because of highly reactive phases (pyroclastic deposits) or restricted contact with the atmosphere or both. Under such circumstances, the participation of CO₂ in silicate hydrolysis reactions such as presented earlier is restricted and OH⁻ substitutes for HCO₃⁻ as a reaction product. Hydroxyl thus released to a normal calcium bicarbonate water by rapid silicate hydrolysis is neutralized by increased calcite precipitation as follows:



This process effectively removes all but traces of the alkaline earths from solution. The amount of silica in solution increases with rising pH, and in the "potholes" and fault trough pond, at least, silica values are above saturation with respect to amorphous silica. With additional concentration the trend of increasing pH and carbonate content continues until the solution becomes saturated with a sodium carbonate phase, as suggested by Garrels (1965). The nature of this phase is related to how high organic matter has maintained the P_{CO₂} in the system (Milton and Eugster, 1959; Jones, 1965; Eugster and Smith, in press).

It should be emphasized that the processes outlined above can be expected to dominate in any area where the drainage is underlain principally by silicic igneous rocks or alluvial deposits derived from such material. Higher dissolved solids content of inflow preceding the onset of evaporative concentration can be expected in areas of pyroclastics or glassy lavas than in normal plutonic terrain, but the prevailing solution compositions are similar in either case.

Silicate hydrolysis proceeds by the same sort of reaction, but even more readily, where oxidation and hydration of sulfides gives sulfuric acid. In areas of extensive mineralization, this process becomes a major factor in determining water composition. Of the basins considered here, the most extensive mineralization in proportion to the total drainage area is within the Saline Valley area, where the famous Cerro Gordo district straddles the southwest drainage divide, and ore deposits occur to the north and east also. It is apparent that mineralized areas contribute much to the drainage around Rhodes Marsh, and, to a lesser degree, the Deep Springs Valley and Owens River system as well. Cohen (1962) has demonstrated the effects of hydrothermal alteration zones on waters of the Truckee Meadows area, and similar conditions locally influence the Carson system.

Silicate hydrolysis processes, whether including either CO₂ as carbonic acid or hydrolyzed sulfides as sulfuric acid, can also be looked upon as a form of low temperature hydrothermal alteration, or "hydrogen metasomatism," as discussed by Hemley and Jones (1964), involving primarily the substitution of H⁺ in silicate phases unstable in the weathering environment.

Hydrologic effects.

The disposition of solutes derived from simple solution or hydrolysis reactions is controlled in large part by hydrologic factors. Of initial importance in any drainage basin is the total and seasonal distribution of rainfall, as reflected in the relative amounts of infiltration versus runoff. Higher infiltration rate and deeper circulation favor more complete reaction of sparingly soluble materials, and enhance the role of hydrolysis reactions. This factor may account in part for compositional differences even within individual spring systems of the Deep Springs and Saline Valleys (Figs. 8 and 9).

The nature and quantity of solutes in spring waters of closed basins often reflect flow patterns which are physically obscure, but these hydrologic routes in large measure dictate the major lithologic influence on compositional trends. A shift in source area with seasonal change in storm patterns may also affect water compositions significantly. Such influences are illustrated at the Buckhorn Springs of the Deep Springs Valley where marked compositional changes reflect

variation in the amounts contributed from areas underlain by igneous as compared to sedimentary rocks (Jones, 1965).

Secondary effects.

Secondary modifications of the anion distribution originally established by primary solution and hydrolysis may not be related solely to evaporative concentration. The most obvious example is the mixing of inflow waters of different composition. This generally is a simple quantitative addition, as illustrated by the Chewaucan River "estuary," where the inflow passes through a straight line transition from the anion composition of the river to that of the lake. Similarly, the composition of some interstitial brines in the Honey Lake Basin appears to be a 1:1 anionic mixture of stream and hot spring waters, and two compositionally distinct spring orifices which supply inflow to Deep Springs Lake provide a compositional intermediate by simple surface mixing proportional to discharge (Fig. 10).

A most important secondary mechanism for modification of closed basin water compositions is the addition of CO_2 to the system by organic respiration and decay. In the Deep Springs Valley, Barnes (1965, p. 100) has suggested that respiration may account for P_{CO_2} levels in Birch Creek well in excess of those in the atmosphere, though more recently Slack (personal communication, 1965) has attributed these levels largely to decay processes. Similarly, significantly higher alkali carbonate content at one orifice of the Corral Springs than at another in the Deep Springs Valley can be attributed to evapotranspiration, respiration, and decay by marsh vegetation flourishing around a spring outlet of very low discharge. The effects of combined biotic activity and evaporative processes on water compositions in the immediate area of low discharge springs is also shown by the increased total dissolved solids (from 257 to 447 ppm) and alkali concentration (from 22 to 37 ppm) in waters from spring orifice as compared to those at the marsh edge in the central Bog Mound spring of the Deep Springs Lake area (Jones, 1965).

The largest contribution of CO_2 to closed basin waters from organic activity is probably the result of anaerobic decay at lake bottoms or interstitially in lacustrine sediments. This is indicated by the higher CO_2 content of interstitial brines obtained from Abert Lake bottom sediments as compared to the immediately overlying lake waters. It is also recorded by nahcolite (NaHCO_3) which occurs in traces in the bottom muds of the closed fault trough pond at Deep Springs and which is abundant in the parting muds of the Searles saline deposits; nahcolite has been shown (Milton and Eugster, 1959; Jones, 1962, 1965; Eugster and Smith, in press) to require a high P_{CO_2} environment for formation.

Anaerobic decay of organic materials in closed basin waters also gives rise to significant loss of sulfate by bacterial reduction to H_2S , particularly in open bodies of saline waters. The effect of this process is clearly suggested in the trends of anionic composition at Abert, Summer, Honey, Pyramid, and Owens Lakes. The tendency for inflow to increase in sulfate percentage with increasing total dissolved-solids content apparently is abruptly halted upon entry into the lakes proper. In the Abert-Summer and Honey Basins, the sharp shift in trend is more apparent than real because of the effects of diverse sources and large differences in amounts of inflow; but

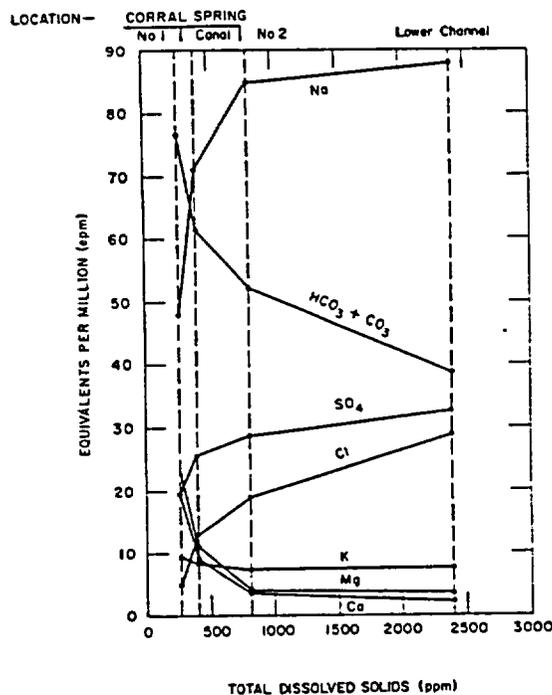


Figure 10. Relation of major ion concentration to total dissolved solids for Corral Springs waters inflow to Deep Springs Lake. The waters of the canal represent a simple mixture, proportional to discharge, of waters from Corral Springs Numbers 1 and 2 (from Jones, 1965, p. 38).

the contrast in trend paths between the Pyramid Lake or Mono Lake-Owens River Systems, and the relatively ephemeral Carson or Humboldt sink areas reflects the increased sulfate reduction possible within the permanent lacustrine regime. Further, the proportion of sulfate consistently decreases northward in the permanent lacustrine features of the western Great Basin. This situation conforms well with Jenny's (1941) observation of increased organic matter accumulation with decrease in temperature in soils within belts of uniform moisture conditions and comparable vegetation, although changes in geologic setting suggest that the coincidence is most likely fortuitous.

Mineral precipitation.

The final major reactive process which modifies the anionic composition of closed basin waters is precipitation of solids. As an ordinary fresh water increases in concentration, alkaline earth carbonate is the first material deposited. The extent of calcium removal from solution and the point of initial precipitation in the drainage basin are related to the relative importance of limestone solution vs. silicate hydrolysis in primary solute derivation. The combination of abundant calcite supply with the pH rise and CO₂ uptake accompanying hydrolysis results in the initiation of deposition within drainage lines, such as in the tributaries of the Deep Springs Valley. Quantitatively, carbonate deposition reaches a maximum in the marginal areas of the saline lake or playa, as indicated by the carbonate saturation levels in the springs adjacent to Deep Springs Lake (Table 2). The carbonate chemistry of these springs is suggestive of the favorable inorganic conditions which have permitted the formation of the algal tufa mounds of the Searles (Scholl, 1960), Mono (Scholl and Taft, 1964), and Lahontan Basins.

Table 2. Ion activity products (IAP) of alkaline earth carbonate for inflow from springs to Deep Springs Lake, August, 1961

Locality	Water temperature (°F)	pH	Calcite Keq ¹ x 10 ⁻⁹	Calcite IAP x 10 ⁻⁹	Dolomite ² IAP x 10 ⁻¹⁷
Buckhorn Springs, main channel	68	7.97	5.281	7.906	7.534
Corral Springs, combined flow	72	8.29	4.992	7.212	6.176
Bog Mound Springs, central orifice	55	8.26	6.447	13.50	14.38
central marsh	68	7.95	6.281	36.64	90.06

¹Keq = equilibrium constant.

²Keq for dolomite is probably about 2 x 10⁻¹⁷ (Hsu, 1963).

Compared to basins where solutes are apparently derived in similar amounts by limestone solution and silicate hydrolysis, carbonate deposition is more restricted areally in basins where one or the other process predominates. In the Abert-Summer (pluvial Lake Chewaucan) Basin where inflow is in almost exclusive contact with volcanics and there is a relative paucity of Ca in the water, carbonate deposition is confined to the lake basin. In the Bonneville Basin, where calcite saturation is brought about more by rising salinity than excess alkalinity, carbonate deposits are also confined to the lake or playa areas, but they are very abundant and in the

immediate Great Salt Lake area form widespread oolitic sands (Eardley, 1938). With the near neutral pH and relatively low bicarbonate content of Great Salt Lake and brines from the Bonneville Flats, significant amounts of calcium still remain in solution even after saturation with respect to gypsum has been exceeded.

In contrast to the Bonneville Basin evaporating waters of the Lahontan Basin and adjacent territories continue to deposit carbonate until the alkaline earths in solution are nearly exhausted. Total alkaline-earth content is below detection by titrametric methods in brines from the Alkali Valley, interstitial brines of the Abert Lake and Honey Lake areas, and in Owens Lake, Deep Springs, and Searles Lake brines. These basins all contain alkaline-earth carbonates in lacustrine muds, and at Deep Springs and Searles Lakes varved muds may contain in excess of 75 per cent carbonate in alternating layers composed primarily of aragonite and dolomite (Jones, 1965; Smith and Haines, 1964).

In heavily mineralized regions sulfate substitutes in large measure for bicarbonate as the resultant anion in hydrolysis reactions. Coupled with a predominant solution of alkaline earth from limestone, and P_{CO_2} values restricted to atmospheric levels, carbonate precipitation is overshadowed by gypsum deposition. The "normal" precipitation sequence of calcite and gypsum on evaporation of an "ordinary" fresh water should result, as pointed out by Hutchinson (1957, p. 374), in a water containing chloride as its main anion. Indeed, such is the case with the nearly pure sodium chloride brine in the playa pond of the Saline Valley, but only after considerable precipitation of sodium sulfate (Hardie, 1965). The sodium chloride brines of the Columbus and Silver Peak playas of western Nevada may represent a similar residuum.

Because of the great disparity in solubility between the alkaline earth carbonates or gypsum and the alkali salts, changes in anion proportion of closed basin waters intermediate in concentration can only be attributed to hydrologic or organic effects. Langbein (1961, p. 14) has shown that variation in total concentration of many closed lakes can be related to strictly hydrographic variables including net evaporation, depth, total lake area, and areal variation with time. Such a treatment implies measurable depths, lack of stratification, generally stable anionic proportions, and a solute gain or loss that affects all constituents alike and avoids fractional precipitation. About the only suitable processes are marginal precipitation or insulation through sedimentation. Accordingly, preliminary data indicate significant incorporation of salts in interstitial solutions of closed lake sediments in a number of areas. Although the above criteria appear to hold for many examples treated by Langbein, the shift in anionic proportions brought about by alkali sulfate precipitation at Deep Springs Lake has been demonstrated by Jones (1965), and more subtle changes in anionic proportions at Summer Lake resulting from selective aerosol movement have been shown by Van Denburgh (Written communication, 1964).

Usually the last process to affect the composition of closed basin waters is the precipitation of the alkali salines. In the Great Basin this process takes place both in open bodies of saline water and interstitially in playa sediments. Quantitatively, the most significant saline deposit presently forming is the halite which is precipitating in the northwest arm of the Great Salt Lake. Sodium carbonate (trona and/or natron) is deposited from the open waters of the Alkali Valley "potholes" and playa pond. Further desiccation of Owens Lake will undoubtedly lead to further growth of sulfocarbonate crusts composed primarily of trona and burkeite ($2Na_2SO_4 \cdot Na_2CO_3$). Sodium sulfate is the major precipitate of Deep Springs Lake at low stage, whereas trona is a major constituent of crusts which form at low stage in the closed fault trough pond. Saline deposits from perennial open waters are characterized by crustal layering where more than one salt phase has precipitated. The layering follows the sequence of precipitation expected according to solubility, except where secondary reaction of the saline phase with solution has taken place (Jones, 1965).

Within a "dry lake" or playa environment saline deposition takes place according to the "evaporating dish" principle illustrated by Hunt (1960) for the Death Valley salt pan. In this process, areal shrinkage of a shallow body of water by evaporation results in continuous precipitation of salts in concentric zones from edge inward according to their relative solubilities; alkaline-earth carbonates precipitate in the outermost areas, sulfates in the intermediate zones, and chlorides at the center. Similar salt pan zoning involving somewhat different phases has been recorded at Deep Springs Lake (Jones, 1961), and in the Saline Valley (Hardie, 1965).

Available data are insufficient to illustrate well the effects of precipitation of the alkali salines on trends in anionic composition. Distinct shifts in trend away from the sulfate apex in the central Lahontan Basins and the Saline Valley are correlative with the precipitation of sulfates, but the initiation of this process cannot be definitely pinpointed in most places. This fact is related to the inclusion within the trend sequence of anomalously dilute waters which have picked up salts in proportions which reflect relative position in the whole drainage system. In this way it appears that trends in anionic composition may be as meaningful in ephemeral as in perennial systems.

SUMMARY

In summary, the major drainage units of the Great Basin may be classified according to the major anion in their most saline waters, and each basin is characterized by a distinctive compositional trend from dilute inflow to most concentrated brine. Each of the three major anions in highly concentrated lake or playa waters points to distinctive association of lithology and weathering process within the contributive drainage areas. High percentages of chloride indicate sedimentary rocks or marine origin and solution processes; carbonate reflects igneous lithologies and the hydrolysis of primary silicates; predominance of sulfate suggests ore mineralization and acid alteration. Secondary hydrologic, organic, and mineral precipitation processes can severely alter but do not completely obliterate the initial lithologic control of water composition.

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