

## ANALCIME COMPOSITION IN TUFFS OF THE GREEN RIVER FORMATION OF WYOMING

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### ABSTRACT

The composition of analcime samples from the Green River Formation of Wyoming was determined by optical, X-ray, and electron-microprobe methods. The analcime ranges from 1.95 to 2.90 in Si/Al ratio; Ca<sup>2+</sup> and K<sup>+</sup> are present in only trace amounts. On the basis of silica content, most analcime falls into two groups, one generally having Si/Al ratios between 2.00 and 2.30, and the other generally ranging from 2.60 to 2.80. High-silica analcime predominates in silicic tuffs of the Laney Shale and Tipton Shale members and in that part of the Wilkins Peak Member nearest the margin of the basin.

Low-silica analcime is nearly always associated with authigenic alkali feldspars, and it is most abundant in the transitional zone between the tuffs with siliceous analcime and those lacking analcime and consisting largely of authigenic alkali feldspars. Within the transitional zone, the Si/Al ratio is inversely proportional to the amount of authigenic alkali feldspars. The Si/Al ratio in analcime also corresponds to the probable salinity of the intrastatal solutions, with the high-silica analcimes associated with low salinities and the low-silica analcimes with high salinities. Both low- and high-silica analcimes are commonly associated with authigenic quartz.

Analcime has extensively reacted to form alkali feldspars in the Green River Formation, and new data show that siliceous analcime crystals become partly desilicated in their reaction to form feldspars. Stratigraphic position of most of the altered analcime in and near the margin of the saline facies suggests that salinity has played a major role in the reaction of analcime to form alkali feldspars. Petrographic relationships show that at least some of the widespread shortite crystallized after the analcime had formed but before it had been replaced by alkali feldspars.

### INTRODUCTION

In the 38 years since Bradley (1928, 1929) first reported the occurrence of analcime in tuffs of the Green River Formation, at least seventeen authigenic species of silicate minerals have been recognized in this formation, forming one of the most remarkable mineral assemblages in the world (see especially Milton and Fahey, 1960, Milton and others, 1960). Analcime, albite, and K-feldspar are probably the most abundant and widespread of the authigenic silicates, and their pattern of occurrence closely correlates with the occurrence of saline minerals and with the probable salinity of the depositional environment in the Green River Formation of Wyoming (Hay, 1966). Petrographic relationships show that much of the authigenic feldspar has formed by reaction of analcime.

Coombs and Whetten (1967) found a wide range of Si/Al ratio in the six samples of analcimic tuff from the Green River Formation that they examined, explaining the compositional differences by different chemical

compositions of the lake waters during diagenesis. The present study is a systematic attempt to determine the Si/Al ratio of enough samples to show more precisely the pattern of analcime composition in tuffs and its relationship to that of saline minerals and authigenic alkali feldspars and quartz. Reaction of analcime to form alkali feldspars was studied using several laboratory techniques.

#### METHODS OF STUDY

*Sampling of Tuffs.* Approximately 100 individual tuffs more than 5 mm thick and aggregating 8 to 10 feet in thickness were logged and sampled in drill cores of Butler #1, and McKenna #1 (Hay, 1966, p. 44-51). The sampled intervals include the most tuffaceous parts of the stratigraphic column: the upper part of the Wilkins Peak Member, the upper part of

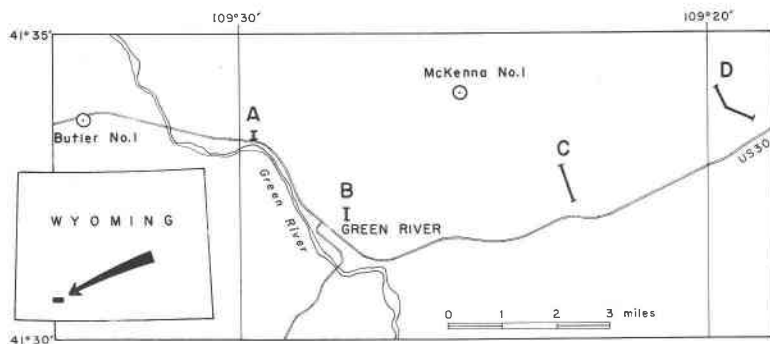


FIG. 1. Map showing localities from which were obtained samples of analcimic tuffs of the Green River Formation.

the Tipton Shale Member, and throughout the Laney Shale Member. Several individual tuff layers were sampled in more than one core.

Several dozen individual tuff layers were also examined and sampled in the field over an east-west distance of 10 miles from a point two miles west of the town of Green River to the eastern limit of exposures, near the margin of the basin (Fig. 1). Several tuffs were sampled in different stratigraphic columns (Hay, 1966, p. 49, Fig. 7).

Forty-one analcimic tuff samples were selected for careful examination, and different parts of many samples were studied in order to show the variation in texture and mineralogy within individual hand samples. A total of 69 analcime samples from the 41 tuff samples were examined.

*Laboratory Examination. Petrographic microscope.* Thin-sections of most samples were studied, and immersion oils were used to determine refractive indices of the analcime.

*X-ray*: The atomic ratio of Si to Al was determined for all samples by Saha's  $\Delta 2\theta$  method (Saha, 1959; 1961), using the calibration curve of Coombs and Whetten (1967). Samples of powdered analcime tuff were mounted in an aluminum sample holder and run at a speed of  $0.25^\circ 2\theta$  per minute on a Phillips Norelco diffractometer. Three measurements were obtained for each sample. The Si/Al ratio thus obtained represents the average composition of analcime crystals in each sample.

Amounts of the different minerals were estimated semi-quantitatively on the diffractograms by comparing peak intensities with those of prepared mixtures of analcime, authigenic feldspars,<sup>1</sup> dolomite, calcite, quartz, etc. Pyrogenic feldspars characteristically give higher diffractometer peaks than equal amounts of authigenic feldspar, hence the total mineral content of samples rich in primary plagioclase commonly exceeded 100 percent by

TABLE 1. ELECTRON MICROPROBE AND X-RAY ANALYSES OF ANALCIME SAMPLES OF THE GREEN RIVER FORMATION<sup>a</sup>

Sample No.	(1)		(2)	(3)	(4)	(5)		(6)
	(a)	(b)				(a)	(b)	
SiO <sub>2</sub>	57.2	59.8	60.2	58.5	59.5	52.0	54.3	58.2
Al <sub>2</sub> O <sub>3</sub>	19.6	19.1	18.3	19.5	19.1	19.0	20.7	18.9
K <sub>2</sub> O	—	—	tr	—	—	—	—	—
CaO	tr	tr	tr	tr	tr	tr	tr	tr
Si/Al ratio	2.56	2.77	2.90	2.64	2.74	2.42	2.32	2.72
Si/Al ratio by x-ray	2.11	2.75	2.81	2.60	2.71	2.16	2.13	2.71
Deviation	-0.45	-0.02	-0.09	-0.04	-0.03	-0.26	-0.19	-0.01
Refractive index ( $\pm 0.002$ )	1.488	1.483	1.484	1.484	1.484	1.488	1.488	1.484

<sup>a</sup> Analcimes were analyzed in two different parts of samples (1) and (5). In all samples, X-ray analyses required larger sample volumes than did microprobe analyses.

using authigenic-feldspar mixtures as standards. In these cases, igneous feldspars were used as standards. Percentages obtained by X-ray diffraction generally compared closely with amounts estimated in thin sections.

*Electron microprobe*: The chemical composition of six samples was determined by the electron microprobe (Table 1). These samples were analyzed for the elements K, Ca, Si, and Al. Chemically analyzed analcimes from Golden, Colorado, and alkali feldspars were used as standards in microprobe analysis of the analcimes of the Green River Formation. Analyses of standards are unpublished.

<sup>1</sup> The standards used were authigenic albite from the Franciscan Formation and authigenic feldspar from the Barstow Formation (Sheppard and Gude, 1967). Their intensities are nearly the same as those of authigenic feldspars in the Green River Formation. All of the K-feldspars associated with analcime in the Green River Formation are monoclinic—that is, the triclinicity  $\Delta = 0$  (Goldsmith and Laves, 1954).

## CHEMICAL COMPOSITION OF ANALCIME

The atomic ratio of Si to Al obtained by X-ray diffraction ranges from 1.95 to 2.81 in analcime crystals of the Green River Formation. These results generally agree with those measured by the microprobe (Table 1). Most of the analcime samples give a single sharp ( $\bar{6}39$ ) diffraction peak, indicating a uniform composition. However, the analcime associated with authigenic alkali feldspars commonly gives either a broad ( $\bar{6}39$ ) peak or two separate peaks, suggesting analcime of variable composition within a single sample. The microprobe also shows that analcime crystals of differing composition are present in the same sample, and the Si/Al ratio may vary even within single crystals. Calcium and potassium occur in only trace amounts in samples analyzed by the microprobe.

Analcime crystals in rocks containing authigenic feldspars are generally altered to various degrees, making them unsuitable for microprobe analysis. Slightly altered crystals are penetrated by anastomosing channels that give them a spongy appearance in thin section; crystals in late stages of alteration are represented by delicate lacelike relicts of analcime embedded in authigenic feldspars and quartz (Fig. 7b). Because of the narrow width of analcime relicts exposed in the highly altered crystals, only the least-altered crystals, having the higher Si/Al ratios, could be satisfactorily analyzed with the microprobe. This explains why the Si/Al ratio calculated from microprobe measurements in samples No. 1a and 5a of Table 1 is higher than the average ratio obtained by X-ray diffraction of the same samples, which include both fresh and altered analcime.

## DESCRIPTION OF THE TUFFS AND THEIR PATTERN OF ALTERATION

Tuffs constitute perhaps as much as one percent of the Green River Formation in the Green River Basin (Hay, 1966, p. 46). Few tuffs are as much as a foot thick, and most of them are less than an inch thick. The tuffs were dominantly vitric, and crystals rarely form more than 10 percent of any single tuff. Most of the tuffs were originally rhyodacite or dacite, judging from the content of primary quartz, biotite, hornblende, and rare augite and sanidine. These tuffs may have originated from vents in the Yellowstone Park-Absaroka volcanic province to the north, judging from the similar pyrogenic minerals and coarser texture of tuffs of late early Eocene Age (late Wasatchian, Lost Cabin) in the Wind River Basin, which lies to the northeast of the Green River Basin. The tuffs of the Wind River Basin were transported and deposited by southerly winds from vents in the southern part of the Absaroka Range (Hay, 1956).

Glass is entirely altered in all of the tuffs of the Green River Forma-

tion that were sampled. Tuffs of the upper (Laney Shale) and lower (Tipton Shale) members of the formation are represented chiefly by medium- to coarse-grained analcime. Authigenic albite and less commonly K-feldspar are major constituents in some tuffs of the lower 60 feet of the Laney Shale Member and the upper 40 feet of the Tipton Shale Member in cores of Butler #1 and McKenna #1. Two tuffs nearest the base of the Tipton Shale Member are bentonites in which glass has altered to montmorillonite (Hay, 1966, Fig. 6).

Tuffs of the Wilkins Peak Member are largely altered to alkali feldspar and quartz in the central part of the basin, where saline minerals are abundant. Analcime is a major constituent in tuffs nearer the margin of the basin, where saline minerals are rare or absent (Fig. 2). Analcimic tuffs show all stages of replacement by alkali feldspars and quartz in the transitional zone between dominantly analcimic and dominantly feldspathic tuffs.

Analcimic tuffs are medium- to coarse-grained, and commonly exhibit "crystal sandstone" textures; where fresh, they are commonly pale gray or bluish-gray. Tuffs consisting largely of authigenic K-feldspar are characteristically very fine-grained, white, and chalklike in appearance. Feldspar-rich tuffs containing major proportions of albite or quartz, or both, are commonly pale brown, relatively coarsely crystalline, and appear aphanitic or "stony." Many of these coarser-grained tuffs exhibit relict analcime textures.

#### FREQUENCY DISTRIBUTION OF ANALCIME COMPOSITION AND CORRELATION WITH OTHER VARIABLES

*Frequency distribution of analcime composition.* The frequency distribution of Si/Al ratio is bimodal, showing a paucity of samples having Si/Al ratios between 2.30 and 2.50, thus separating the analcimes into more siliceous and less siliceous groups (Fig. 3). The modal Si/Al ratio for the more siliceous group is 2.70–2.80, and samples of this composition constitute 20.3 percent of the total samples analyzed and 39.0 percent of the high-silica group. The modal Si/Al value for the low-silica group is 2.10–2.20, and represents 46.5 percent of the low-silica group.

The distribution pattern of Si/Al ratio in analcime correlates rather closely with the associated authigenic minerals. Authigenic alkali feldspar is nearly always present in tuffs containing low-silica analcime. Only one tuff sample with low-silica analcime lacks authigenic feldspars, and this sample contains shortite ( $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ ), a common authigenic mineral in the Wilkins Peak Member. Two other samples, consisting largely of authigenic feldspar and quartz, include small feldspar-free areas of low-silica analcime.

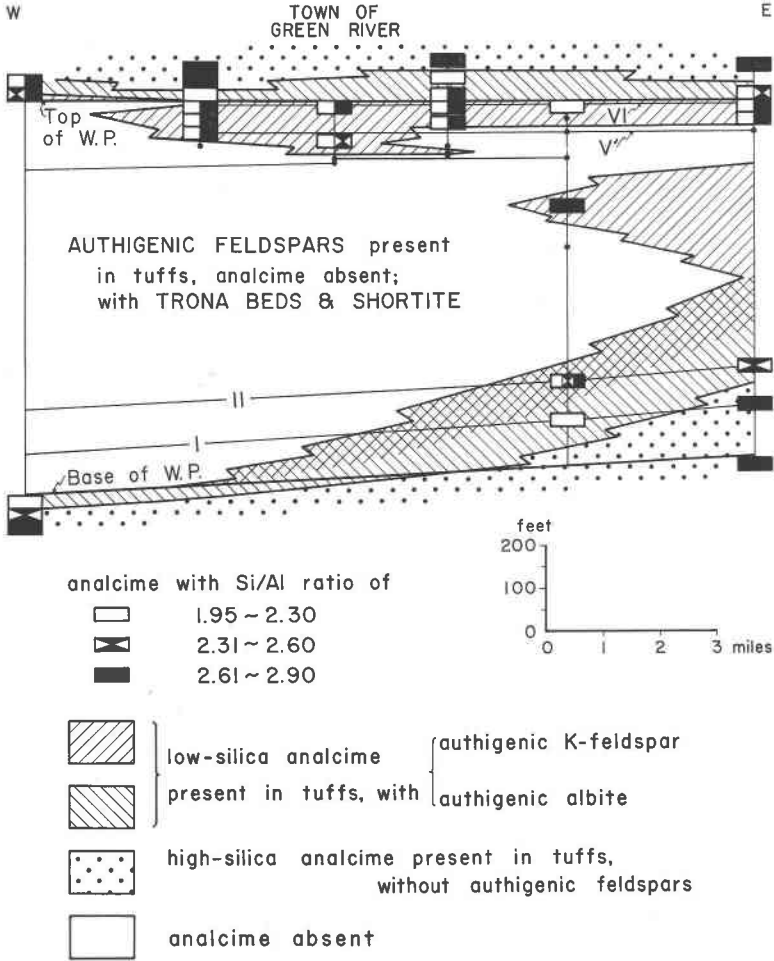


FIG. 2. Schematic east-west cross section through the eastern half of the Green River Basin, showing the pattern of alteration of tuffs in the Wilkins Peak Member (abbreviated as W. P.) and the beds which overlie and underlie the Wilkins Peak Member. Roman numerals refer to numbered tuffs of Culbertson (1961).

Neither authigenic crystals of alkali feldspar nor of shortite are found in tuffs containing analcime with a Si/Al ratio exceeding 2.60. However, partly albitized plagioclase is present in some samples containing siliceous analcime.

Dolomite and calcite correlate to some extent with the Si/Al ratio in analcime. Although calcite occurs with analcime of all compositions, it generally forms more than 10 percent of the tuffs that contain siliceous

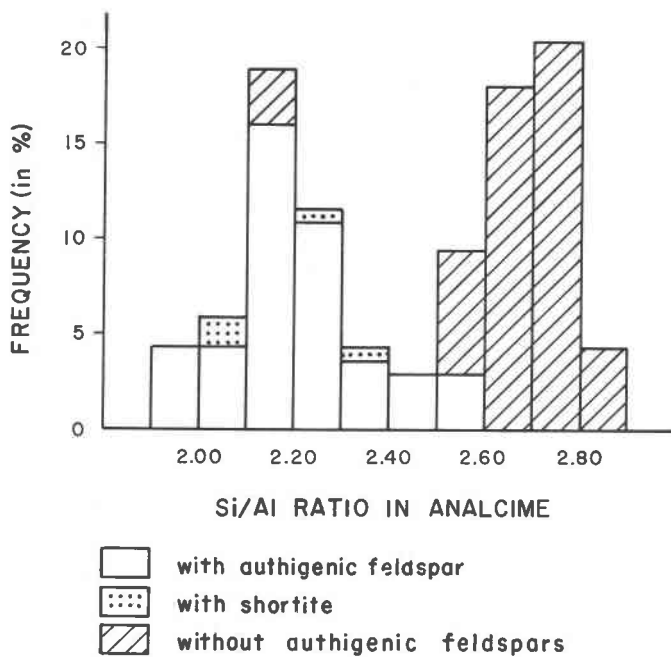


FIG. 3. Histogram showing the frequency distribution of the Si/Al ratio of analcime in 69 samples from the Green River Formation.

analcime. By contrast, dolomite is generally associated with low-silica analcime.

*Correlation Between Si/Al Ratio and Quantity of Analcime.* There is a slight correlation between the Si/Al ratio and the total amount of analcime. High-silica analcime commonly occurs in highly analcemic rocks (analcimolites), whereas low-silica analcime is characteristic of less-analcemic tuffs usually containing abundant authigenic feldspar.

*Correlation between Si/Al ratio and quantity of authigenic feldspars.* The Si/Al ratio in analcime generally varies inversely with the content of authigenic feldspar (Fig. 4). Nearly all of the samples lacking authigenic crystals of feldspar are siliceous. The Si/Al ratio seems to decrease more rapidly as a function of the content of albite than of K-feldspar (Fig. 4). The upper and lower limits of distribution are confined by straight lines as represented in Figure 4. The four exceptions that appear below the lower limiting line are analcimes either associated with shortite or small unreplaced patches of analcime in samples that elsewhere contain abundant authigenic feldspar.

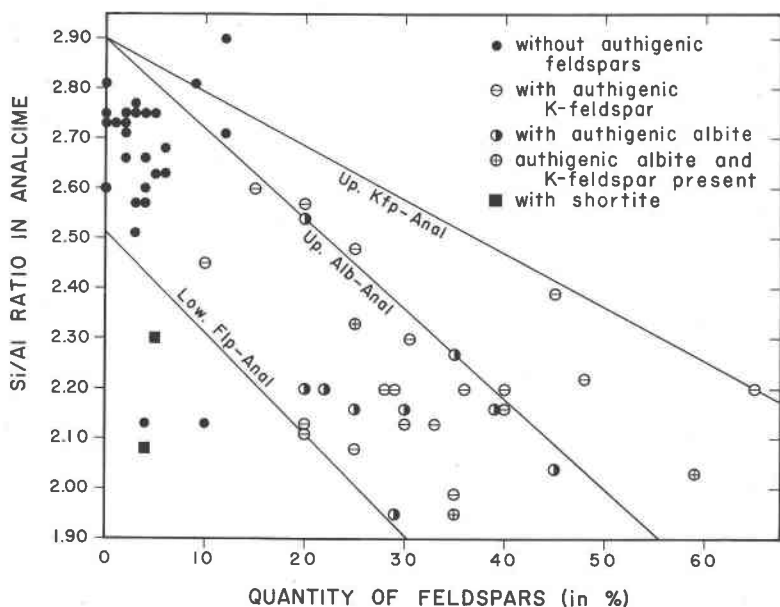


FIG. 4. Scatter diagram showing the relationship between Si/Al ratio in analcime and the quantity of feldspar, most of which is authigenic. Indicated by straight lines are the upper limits of K-feldspar—analcime and albite—analcime and the lower limit of all authigenic feldspar—analcime.

*Correlation of Si/Al ratio and quantity of quartz.* No general relationship exists between the Si/Al ratio of analcime and the quantity of quartz, both pyrogenic and authigenic in tuffs containing low-silica analcime. However, there seems to be a slight tendency for the Si/Al ratio of analcime to increase in direct proportion to the amount of quartz. In tuffs containing siliceous analcime, there is no apparent relationship between the Si/Al ratio and the quantity of quartz, which may form as much as half of individual samples. Thin-section study indicates that most of the quartz in nearly all of the tuffs is authigenic.

#### CORRELATION BETWEEN AUTHIGENIC FELDSPARS AND QUARTZ

Tuffs containing authigenic quartz may or may not contain authigenic feldspar. Where authigenic quartz and feldspars occur together, the quantity of quartz generally varies inversely with the amount of authigenic feldspar (Fig. 5). This relationship is similar to the inverse rela-

<sup>1</sup> Authigenic quartz may occur either as small, perfectly formed euhedra or as a mosaic of small irregular crystals in the cement of tuffs. Pyrogenic quartz generally forms angular fragments, some of which are broken euhedra.



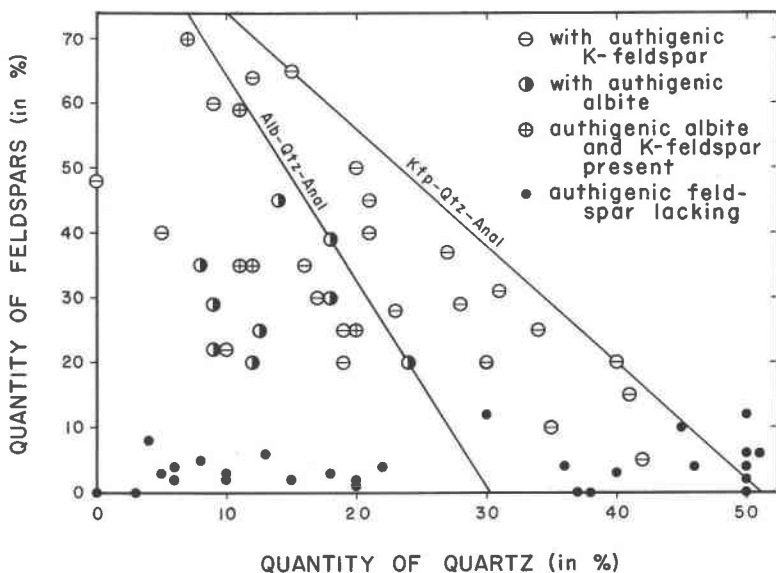


FIG. 5. Scatter diagram showing the relationship between the quantity of feldspar and the quantity of quartz in analcime-bearing samples of the Green River Formation.

tionship of Si/Al ratio in analcime and the quantity of authigenic feldspar (Fig. 4). The amount of quartz is commonly greater in rocks containing K-feldspar than in those containing albite, as indicated by the upper distribution limits for the assemblages albite-quartz-analcime and K-feldspar-quartz-analcime (Fig. 5).

The group of quartz-bearing samples lacking authigenic crystals of feldspar lies near the bottom of the diagram. The quantity of quartz, most of which is authigenic, ranges from 0 to 50 percent, whereas the content of pyrogenic feldspars is usually less than 10 percent.

#### GLASS-ZEOLITE-FELDSPAR REACTIONS IN THE GREEN RIVER FORMATION

*Reaction of glass to form alkali-rich zeolites.* Silicic glass probably altered initially to alkali-rich zeolites such as phillipsite, clinoptilolite, and erionite. This initial reaction is inferred from studies of Quaternary saline lake deposits, where these zeolites are the most abundant primary reaction products of glass (Hay, 1964, 1966). In no example was analcime found to form directly from glass. Glass may react in a hypersaline, alkaline environment to form alkali-rich zeolites within a few thousand years after burial and at depths of less than 20 feet.

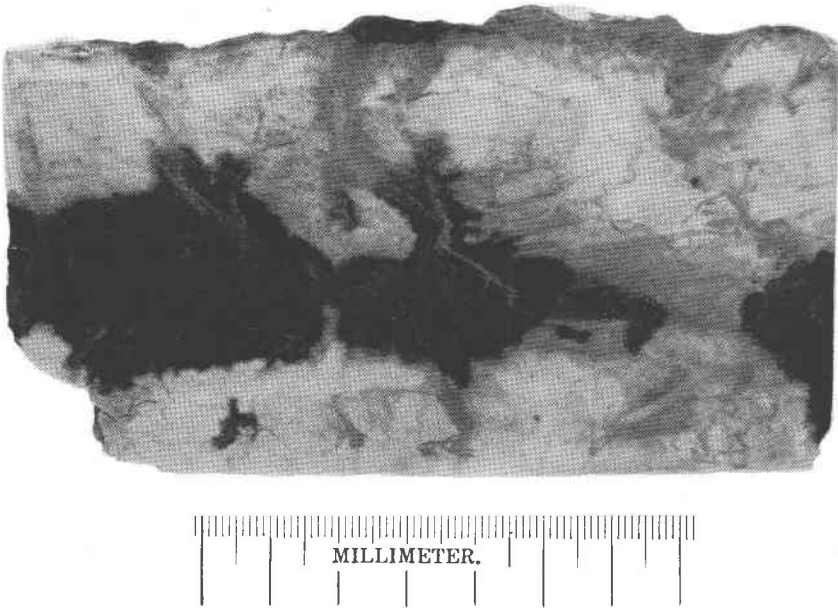


FIG. 6. Photograph of a hand sample showing unreplaced patches of dark-colored analcime-rich tuff in a matrix of white tuff consisting largely of authigenic K-feldspar and quartz and containing partly altered analcime crystals (see Fig. 7b). Analcime of the unreplaced patches has a Si/Al ratio of 2.73; relict analcime in the feldspar-rich matrix has an Si/Al ratio of 2.20. Sample of Wilkins Peak Member.

*Reaction of alkali-rich zeolites to form siliceous analcime.* Analcime in saline-lake deposits characteristically forms from earlier-formed alkali-rich zeolites, judging from the increasing ratio of analcime to potassic zeolites as a function of age in these deposits (Hay, 1966, p. 72-74). This reaction has been demonstrated for the Barstow Formation, where analcime has formed from clinoptilolite and phillipsite (Gude and Sheppard, 1967). Clinoptilolite and mordenite have been recently discovered in tuffs of the Tipton Shale Member, suggesting that these zeolites were precursors for siliceous analcime in the Green River Formation (Goodwin and Surdam, 1967).

*Reaction of siliceous analcime to form low-silica analcime and alkali feldspars.* Analcime has extensively reacted to form K-feldspar and albite in the Green River Formation. This fact is indicated by both macroscopic and microscopic evidence in the zone transitional between the part of the Wilkins Peak Member where tuffs are replaced by feldspars and quartz and the adjacent beds where tuffs are replaced by analcime and quartz

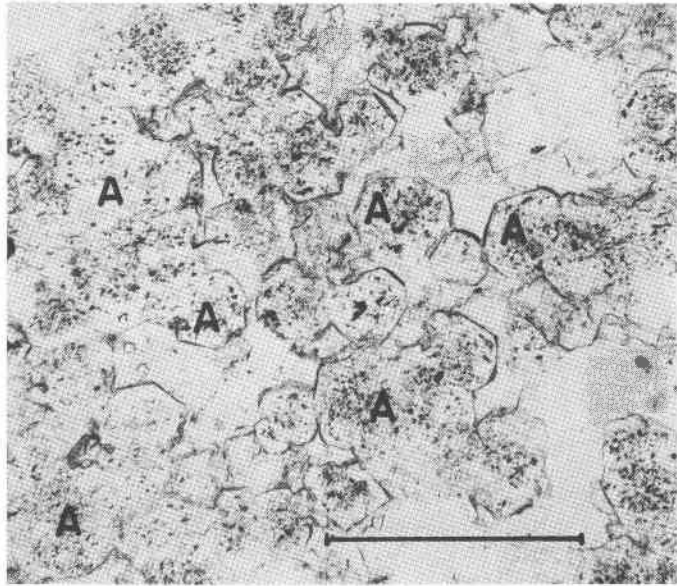


FIG. 7a. Photomicrograph of analcime-rich tuff from the hand sample shown in Figure 6. Some of the analcime crystals are designated by A. Length of bar is 0.2 mm. Photographed with plain light.

(Fig. 2). All stages of replacement of analcime tuffs by K-feldspar, quartz, and albite can be observed. Unreplaced patches of siliceous analcime (Figs. 6, 7a) are embedded in a matrix of authigenic feldspars and quartz containing partly altered analcime crystals (Figs. 6, 7b). Partly altered analcime crystals have been observed in many tuffs consisting of authigenic feldspars and quartz in the upper and lower parts of the Wilkins Peak Member, in the upper part of the Tipton Shale Member, and in the lower part of the Laney Shale Member.

Analcime crystals in tuffs with authigenic feldspars are commonly altered to varying degrees. Slightly altered crystals are penetrated by anastomosing channels which give the crystals a spongy appearance in thin section (Fig. 7b). Crystals in late stages of alteration are represented by delicate lacelike relicts of analcime embedded in finely crystalline feldspar and quartz. Partly altered analcime crystals are characteristically less siliceous than unaltered crystals nearby, as indicated by x-ray and microprobe data. Indeed, the electron microprobe shows that single, partly altered crystals can vary in composition. Clearly siliceous analcime crystals become desilicated in their reaction to form feldspars.

Analcime is replaced both by alkali feldspars and by quartz. The

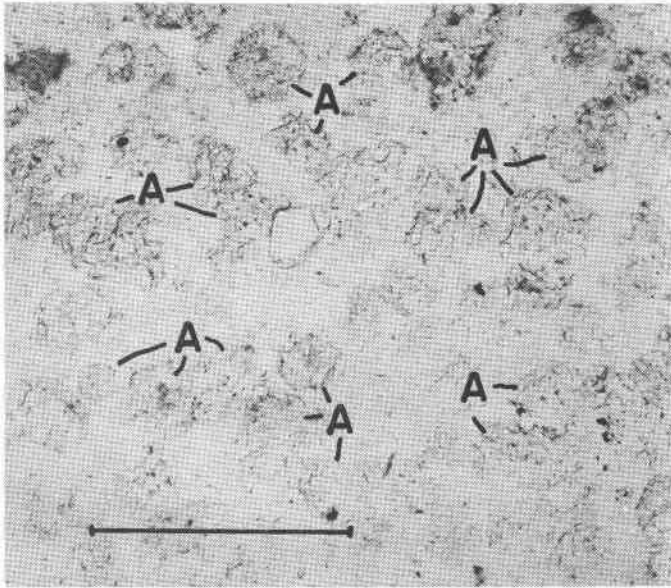


FIG. 7b. Photomicrograph of partly altered analcime crystals in the quartzo-feldspathic part of the sample shown in Figure 6. Analcime crystals, designated by A, are porous and commonly have ragged outlines. They lie in a matrix of finely crystalline authigenic K-feldspar and quartz. Length of bar is 0.2 mm. Photographed in plain light.

quantity of quartz and the Si/Al ratio of analcime in the analcime tuffs generally decreases as the quantity of authigenic feldspars increases (Figs. 4 and 5).

Shortite replaces analcime in a few of the samples studied microscopically. The analcime associated with shortite has relatively low Si/Al ratios, regardless of whether the analcime appears fresh or partly altered. Shortite can be shown to have crystallized after analcime but prior to alkali feldspars in a few samples. Shortite replaces medium- to coarse-grained analcime in several thin sections, showing that it crystallized after the analcime had grown to its full size. A few tuffs consisting largely of authigenic feldspars and quartz with analcime textures contain large shortite crystals containing unaltered analcime. Thus the shortite must have enclosed the analcime crystals before the feldspars and quartz had crystallized. These few tuffs are invariably relatively coarse-grained and "stony" or aphanitic in appearance; the fine-grained white chalklike tuffs do not contain shortite crystals with fresh analcime. Unaltered plagioclase crystals lacking albite overgrowths are present within coarse shortite crystals in one tuff where the plagioclase elsewhere is extensively

albitized and contains albite overgrowths. Here the albite was formed after the shortite had been deposited.

Albite was deposited later than K-feldspar in one sample, which contains pyrogenic plagioclase crystals with authigenic overgrowths of K-feldspar upon which albite overgrowths have formed.

#### PHYSICO-CHEMICAL ENVIRONMENT OF ANALCIME REACTION

The pressure and temperature of the analcime reactions are unknown, although 4,000 feet is the probable maximum burial depth of the Green River Formation in the Green River Basin (J. D. Love, personal communication, 1964). A normal geothermal gradient probably prevailed in the basin, for contemporaneous igneous intrusions and lava flows have not been recognized in the basin. Hence, temperatures of the Green River Formation at depths of 4000–5800 feet would have been about 40–70°C. The alteration of analcime is unrelated to its depth within the Green River Formation, as analcime has reacted to form alkali feldspars both near the base and top of the Wilkins Peak Member, which is about 900 feet thick, and unaltered siliceous analcime characterizes the tuffs both near the base and the top of the Green River Formation (Fig. 2).

The distribution of authigenic montmorillonite, analcime, and feldspars in the Green River Formation corresponds closely to the probable salinities of the depositional and post-depositional environments. Montmorillonitic tuffs near the base of the formation (Hay, 1966, p. 46) may have been deposited in essentially fresh water during the initial growth of the lake. Analcime is the principal authigenic silicate mineral in beds probably deposited in slightly to moderately saline lake water; and albite and K-feldspar are largely restricted to the saline facies, deposited in a sodium carbonate-bicarbonate-chloride brine, from which trona and halite precipitated.

Salinities were probably increased by de-watering and compaction (see especially Smith and Haines, 1964, p. 39). The widespread shortite may have formed at least partly as a result of increasing salinity during and possibly after burial as well as a result of elevated temperatures and possibly a lowered partial pressure of CO<sub>2</sub> (Milton and Eugster, 1959). It is nowhere known to be a primary precipitate in a saline lake, and it occurs widely in beds of the Green River Formation lacking trona, halite, and other minerals precipitated directly on the floor of the lake. Compaction may have been particularly effective in elevating salinities in the oil shales, for which Bradley (1964, p. 47) has locally shown a minimum 5:1 ratio of unconsolidated mud to present-day shale.

Stratigraphic position of most of the altered analcimes in and near the margin of the saline facies suggests that salinity has played a major role in the reaction of analcime to form alkali feldspars.

The Si/Al ratio in analcime also corresponds to the probable salinity of the intrastratal solutions. The high-silica analcime, having an Si/Al ratio of 2.60–2.90, occurs in the part of the formation that lacks saline minerals and was evidently deposited in water too dilute for compaction to produce shortite or other saline minerals. The low-silica analcime, usually having Si/Al ratios between 2.10 and 2.30, is generally found either in beds containing shortite or in beds immediately underlying or overlying the shortite-bearing saline facies of the formation.

The distribution of albite and K-feldspar may reflect the  $K^+/Na^+$  ratio of the intrastratal solutions. K-feldspar predominates in most beds containing sodium-bearing saline minerals, whereas albite is most abundant in the outer part of the transition zone, where saline minerals are absent or rare. Probably the  $K^+/Na^+$  ratio was elevated in the more saline facies by crystallization of sodium-bearing salts, thus favoring K-feldspar. Albite would be favored over K-feldspar by low  $K^+/Na^+$  ratios.

Stratigraphic position of most of the altered analcime crystals in and near the margin of the saline facies suggests that salinity has played a major role in the reaction of analcime to form alkali feldspar. Increasing salinities during burial may have favored the dehydration of analcime to form alkali feldspars by lowering the chemical activity of water (Campbell and Fyfe, 1965; Hay, 1966, p. 94).

The activity of silica in solution must also be considered a possible factor in the low-temperature reaction of analcime. Solutions in the Green River Formation must have been supersaturated with respect to quartz, as crystalline quartz was deposited together with albite and K-feldspar in beds containing altered low-silica analcimes. Nevertheless, there is no obvious evidence of high silica supersaturation such as opal or chalcedony in these beds, and much of the authigenic quartz displays crystal faces showing that it crystallized as quartz.

Why siliceous analcime should desilicate in reacting to form feldspars is not clear, inasmuch as siliceous analcime requires additional silica to form albite. Perhaps increased salinity and the consequent lowered chemical activity of  $H_2O$  have favored the formation of low-silica analcime because it is less hydrous than siliceous analcime (Saha, 1961). Alternatively, the less siliceous analcime may be thermodynamically more stable than siliceous analcime, and the more stable (less siliceous) form of analcime is formed as the initial step in the alteration of siliceous analcime in the Green River Formation. Finally, siliceous analcime may dis-

solve incongruently in forming feldspar, and silica is removed more rapidly than alumina from the altering analcime crystals, so that the last analcime to alter has a relatively low content of silica.

#### GENERAL RELATIONSHIP BETWEEN Si/Al RATIO AND ORIGIN OF ANALCIME

In their study of analcime in sedimentary rocks, Coombs and Whetten (1967) made the following generalizations on the relationship between Si/Al (Na, K,  $\frac{1}{2}$ (Ca) ratio and the mode of origin of analcime.

(1) The most siliceous analcime was formed by reaction of silicic glass with saline water. However, they noted that low-silica analcime may occur in silicic tuffs exposed to highly saline alkaline solutions.

(2) Most analcime of "burial metamorphic" origin is intermediate in composition.

(3) "Analcime formed either by direct precipitation from highly saline waters or by reaction of these waters with clay minerals and possibly volcanic glass tend to have compositions near the soda-rich, silica-poor extreme of the sedimentary analcime series . . ."

These generalizations can now be modified and supplemented by additional data. Regarding (1) above, analcime forms from a zeolite precursor such as phillipsite or clinoptilolite, rather than as a primary reaction product of silicic glass in saline lakes (Hay, 1966, p. 90-93). Data presented in this report substantiate the suggestion that low-silica analcime may form in silicic tuffs exposed to highly saline, alkaline water. Our new data indicate, however, that this low-silica analcime is generally formed as an intermediate stage in the reaction of siliceous analcime to form alkali feldspars.

Regarding analcime of "burial metamorphic" origin, Coombs and Whetten (1967) described only intermediate composition through a great thickness of the Murihiku Supergroup rocks of New Zealand in which albite has formed. However, altered silicic tuffs of the Green Tuff region of Japan contain analcime ranging from 2.00 to 2.93 as recalculated from *a*-spacings given by Utada (1966). These analcimic tuffs were deposited in both marine and fresh-water environments, and they occur within one zone of a vertically zoned zeolitic sequence that was formed in response to increasing burial depth and temperature (Iijima and Utada, 1966; Utada, 1966). The range in Si/Al ratio is nearly the same as that in analcime of the Green River Formation. Whether or not the low-silica analcime represents a stage in the reaction of silicic analcime to form feldspars is not known.

Analcime of silica-poor (melillite nephelinite to alkali basalt) palagonite tuffs of the Honolulu Series of middle and late Pleistocene age on

Oahu (Winchell, 1947) represent an additional type of occurrence not considered by Coombs and Whetten (1967). Our laboratory study of these tuffs shows that analcime is locally common, and it is commonly associated with low-silica phillipsite, chabazite, members of the natrolite-thomsonite series, montmorillonite, and calcite. An authigenic silica phase is lacking in samples containing analcime. These zeolites, montmorillonite, and calcite were formed at low temperatures by reaction of glass with percolating ground water of meteoric origin (Hay, 1966, p. 82, 83). A little of the analcime replaces earlier-formed zeolites, but most of it was precipitated as a cement and in vesicles within pyroclasts. The Si/Al ratio of analcime ranges from 1.68 to 2.30, and most of it is between 1.80 and 2.10 in Si/Al ratio. The low silica content of analcime is to be expected from the silica-poor nature of the glass and the associated zeolite species.

## ACKNOWLEDGMENTS

We are indebted to R. S. Houston and D. L. Blackstone for the opportunity to sample drill cores of the Green River Formation. The National Science Foundation (Grant G-22094) supported this study. The manuscript was reviewed by D. S. Coombs, W. S. Fyfe, W. D. Keller, Charles Meyer, Charles Milton, and R. A. Sheppard.

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- Manuscript received, August 8, 1966; accepted for publication, October 27, 1967.*