

Analcime and K-Feldspar in Tuffs of the Green River Formation, Wyoming

JONATHAN H. GOODWIN, *Department of Geological and Geophysical Sciences, University of Utah, Salt Lake City, Utah 84112*

Abstract

Tuffs in the Green River Formation (Eocene) of Wyoming have been altered by contact with the hypersaline brines of an ancient lake. Authigenic minerals formed in the tuffs include clay minerals, clinoptilolite, modernite, analcime, potassium feldspar, quartz and possibly albite. Si/Al ratios of analcime in the tuffs determined by X-ray diffraction range from 1.95 to 2.58. Authigenic potassium feldspar formed from analcime in the tuffs. Si/Al ratios of analcime associated with potassium feldspar range from 2.0 to 2.44 and statistical tests on these data suggest that there is no relationship between the Si/Al ratio of analcime and the presence or absence of potassium feldspar. The reaction mechanism for the formation of potassium feldspar from analcime did not cause desilication of the analcime. The major parameters of the brines controlling the formation of the authigenic silicate minerals appear to have been the activity of water, the pH, the Si/Al activity ratio, the Na⁺/K⁺ activity ratio, and the partial pressure of CO₂.

Introduction

The Green River Formation of southwestern Wyoming consists of about 620 meters of thin-bedded, argillaceous, lacustrine, limestone, siltstone and shale, and minor interbedded sandstone, crystalline limestone, dolostone and tuff. Extensive beds of trona are a major portion of the subsurface stratigraphy, and shortite and other saline minerals are present as disseminated crystals throughout almost one-half of the section. In outcrop, the saline minerals have dissolved, leaving empty molds or calcite-filled pseudomorphs. The upper part of the formation contains abundant fish and plant fossils, and both the upper and lower parts of the formation are moderately rich in hydrocarbon mineraloids.

Tuffaceous rocks constitute as much as two percent of the total thickness of the Green River Formation. Most tuffs were deposited as vitric tuffs and contain no more than 15 to 20 percent of crystal or lithic fragments. All of the tuffs are altered, some more than others. Hay (1966, p. 65-70) found in modern, alkaline, saline lakes that tuff beds exposed to the lake brines are commonly altered to zeolites, analcime or feldspar in zones related to varying chemistry of the lake water.

The peculiar mineral assemblages of the Green River Formation have long been an enigma to petrologists. The rocks were never subjected to pressures or temperatures much in excess of normal,

near-surface conditions. However, some secondary minerals found in the formation are not found elsewhere except under hydrothermal, igneous or metamorphic conditions. The unique mineral assemblages of the Green River Formation suggest that the rocks were subjected to unusual chemical conditions. This study outlines what some of those conditions were.

Methods of Study

The Green River Formation occurs in three intermontane basins in Wyoming. The study area is in a small part of the westernmost of these three basins, the Green River or Bridger Basin (Fig. 1).

An area of 1100 km² within townships 15 N through 18 N, and ranges 106 W through 108 W, of Sweetwater County, Wyoming, was selected for detailed investigation. This area was chosen because of the easy accessibility of surface outcrops and the good subsurface stratigraphic control that could be obtained from drill cores stored at the University of Wyoming, the United States Geological Survey in Denver, Colorado, and the United States Bureau of Mines, Laramie Petroleum Research Center.

Detailed sampling of tuff beds of the Green River Formation exposed in surface outcrop was conducted during the summers of 1967 through 1969. During field sampling, general rock types were noted and stratigraphic positions were measured with Brunton compass and tape. Where possible, sections were

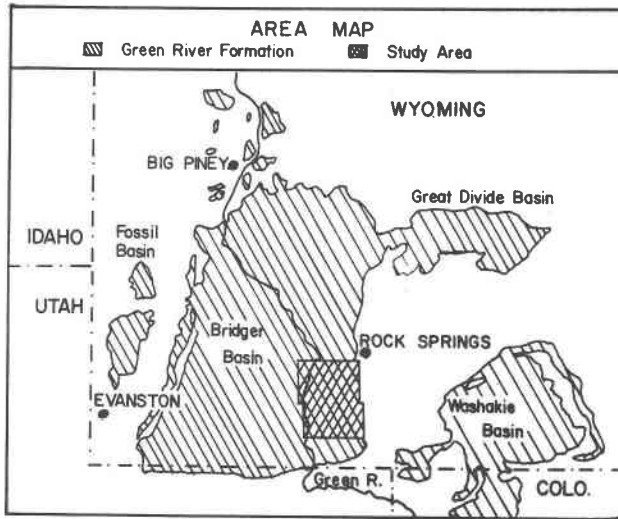


FIG. 1. Regional map showing areas in Wyoming where the Green River Formation crops out, and the location of the study area.

measured near previously measured sections. In general, however, published descriptions did not locate specific tuff beds accurately enough for purposes of this study. General stratigraphy of the formation was taken from published descriptions, but all stratigraphic locations of tuff beds were obtained by direct measurement. Measured thicknesses of major units generally agreed with published thicknesses of nearby measured sections within ± 3 meters.

Cores from 11 drill holes that penetrate all or part of the formation were examined in detail and all tuff beds were sampled. Because of the ease of

measurement and the availability of descriptions of all the cores, stratigraphic control was much more precise in the cores and measurements of stratigraphic positions are believed correct to within ± 25 cm. The absence of weathering in the cores made the tuff beds much easier to locate than in surface sections.

Figure 2 is a diagrammatic sketch of the stratigraphic section of the Green River Formation in the Green River (Bridger) and Washakie Basins, showing the intertonguing relationships and the approximate stratigraphic positions from which most of the sampling for this study was done.

Samples were analyzed by X-ray diffraction techniques to determine the mineral assemblages. Those samples that showed unusual mineral assemblages, or unusual peak positions or intensities in their X-ray diffraction patterns were selected for thin section analysis. The use of petrographic thin sections with cover glasses was later abandoned in favor of polished thin sections which could be examined with the electron microprobe as well as with an ordinary petrographic microscope. The exceedingly fine grain size of most of the rocks made normal petrographic examination extremely difficult.

X-ray fluorescence analyses for SiO_2 , Al_2O_3 , K_2O and CaO were made on 137 samples of tuff to determine the horizontal and vertical variations in compositions. Nineteen of these samples were selected for analysis of Na_2O and MgO . X-ray diffraction techniques were used to determine the Si/Al ratio in 67 samples of analcime.

Description of Tuffs

Within the study area, the tuffs of the Green River Formation rarely exceed 20 cm in thickness and most are less than 5 cm thick. Contacts of the tuffs with overlying and underlying beds are sharp and generally conformable. Depositional features, such as ripple marks, cross-bedding and graded bedding are rare, although a few of the tuffs locally have mud-shrinkage cracks on their upper contact surface. The tuffs rarely show any admixture of the underlying or overlying beds.

Colors of the tuffs range from very light gray (N8) to light brown (5YR5/6) depending on the degree of iron oxide staining and content of organic matter (Goddard *et al.*, 1948).

Although most tuffs are well cemented, the degree of induration is variable. Some of the tuffs occur as loose powders in outcrop, whereas others have

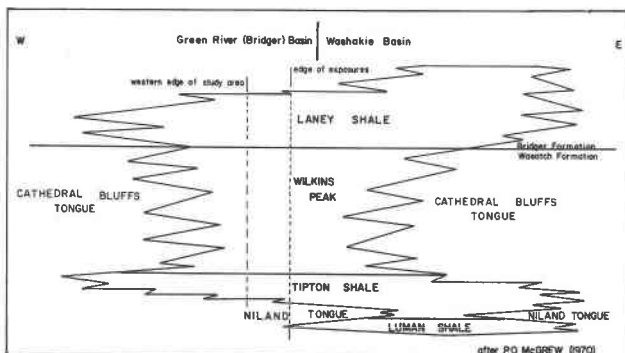


FIG. 2. Diagram of regional stratigraphic relationships of the Green River Formation in Wyoming. Dashed vertical lines indicate eastern and western boundaries of the study area. Nomenclature of the tongues of the Wasatch Formation on the western side of the Bridger Basin in this diagram is not strictly correct.

cementation strong enough to cause breakage across mineral grains. Both powdery and well-cemented tuffs may contain the same mineral suites, but tuffs containing K-feldspar tend to be better cemented than tuffs containing other authigenic minerals. The tuffs form both resistant ledges and deep undercuts in outcrop.

The largest primary mineral grains in the tuffs are no more than 0.3 to 0.4 mm across the maximum dimension. Authigenic mineral grains rarely reach 0.4 mm in maximum dimension and most grains are much smaller, usually less than 0.05 mm across. The mesostasis of most tuffs, which usually makes up at least 80 percent of the rock, consists commonly of a very fine grained, felted mass of crystallites less than 0.01 mm in maximum dimension.

Primary Minerals

Primary minerals constitute no more than 15 to 20 percent of most tuffs of the Green River Formation. All the tuffs contain minor amounts of resorbed and embayed, clear, anhedral quartz grains, and most contain minor amounts of green hornblende or biotite and rare sanidine and augite. On the basis of this primary mineral assemblage, Iijima and Hay (1968, p. 187) concluded that the tuffs of the Green River Formation were originally rhyodacitic to dacitic in composition. Bradley (1964, p. A2) reports that on the basis of the primary mineral suites, the tuffs range from andesitic to rhyolitic.

Authigenic Minerals

Authigenic minerals constitute more than 80 percent of most tuffs in the Green River Formation. The mineral suites are simple, rarely consisting of more than four minerals, and commonly only one or two. The suites are made up of various mixtures of clay minerals, especially montmorillonite and illite (Tank, 1969, p. 1593–1595), clinoptilolite, mordenite, analcime, K-feldspar and perhaps albite. A list of the mineral assemblages and their frequency of occurrence is given in Table 1.

Analcime. Analcime is present as anhedral microcrystals in the mesostasis of tuffs, and as chains of interlocked and intergrown euhedral crystals up to 0.1 mm in maximum dimension (see Fig. 3B). Most of the analcime in the Green River Formation is completely isotropic, except in tuffs in which the analcime is associated with large amounts of K-feldspar. In these tuffs, the analcime in reaction relation

Table 1.
Major Authigenic Mineral Assemblages in Tuffs of the Green River Formation

Assemblage	Frequency of Occurrence	Percent Frequency
Mordenite, analcime	1	0.2
Mordenite, clinoptilolite, clay	1	0.2
Mordenite	2	0.5
Clinoptilolite	2	0.5
Analcime, clay	5	1.2
K-feldspar, analcime	6	1.5
Clay	8	2.0
Analcime, albite, quartz, K-feldspar	12	2.9
Analcime	14	3.4
Analcime, albite	14	3.4
Analcime, K-feldspar, quartz	21	5.1
Albite, quartz	21	5.1
K-feldspar, quartz	30	7.3
K-feldspar, albite, quartz	32	7.8
Quartz, analcime, feldspar	35	8.6
Analcime, quartz	43	10.5
K-feldspar	46	11.3
Analcime, albite, quartz	116	28.5
	409	100.0

All assemblages are of authigenic alteration minerals, although some of the quartz and perhaps all of the albite is primary, clastic grains.

Mineral contents determined by X-ray diffraction. Samples containing large amounts of calcite or dolomite, or large amounts of quartz as a primary mineral as in sandstones, have been deleted from the table. Biotite and amphibole contents are not included in the tabulation because the contents of these minerals are independent of stratigraphic position.

to the authigenic K-feldspar shows a slight birefringence. Most of the analcime has so many fine inclusions that it appears brownish in color. The nature of these inclusions is unknown, but they are presumed to be quartz or opal as in the tuffs of the Barstow Formation of California (Sheppard and Gude, 1969, p. 10). Original shard fabric was not observed in any of the tuffs containing large amounts of analcime, although Bradley (1929, Plate 2A) has pictured a thin section of an analcimic tuff in which at least some shard fabric is preserved.

Three of the thin sections contain mordenite associated with small amounts of analcime. Mordenite forms the nearly isotropic, extremely fine-grained mesostasis of these rocks. Shard fabric is preserved in varying degrees in all of these samples (Fig. 3C). Shard shapes appear as curved alignments of mordenite crystallites and are frequently hollow or partially filled with mordenite and analcime. In one of the samples, the mordenite-rich matrix of the tuff is composed of very fine crystallites of mordenite in nearly opaque aggregates whose shape and fabric are suggestive of the later-formed analcime fabric. In this sample the interstices between the blobs are filled with analcime (Fig. 3D).

Four lines of evidence suggest that analcime in tuffs of the Green River Formation formed from

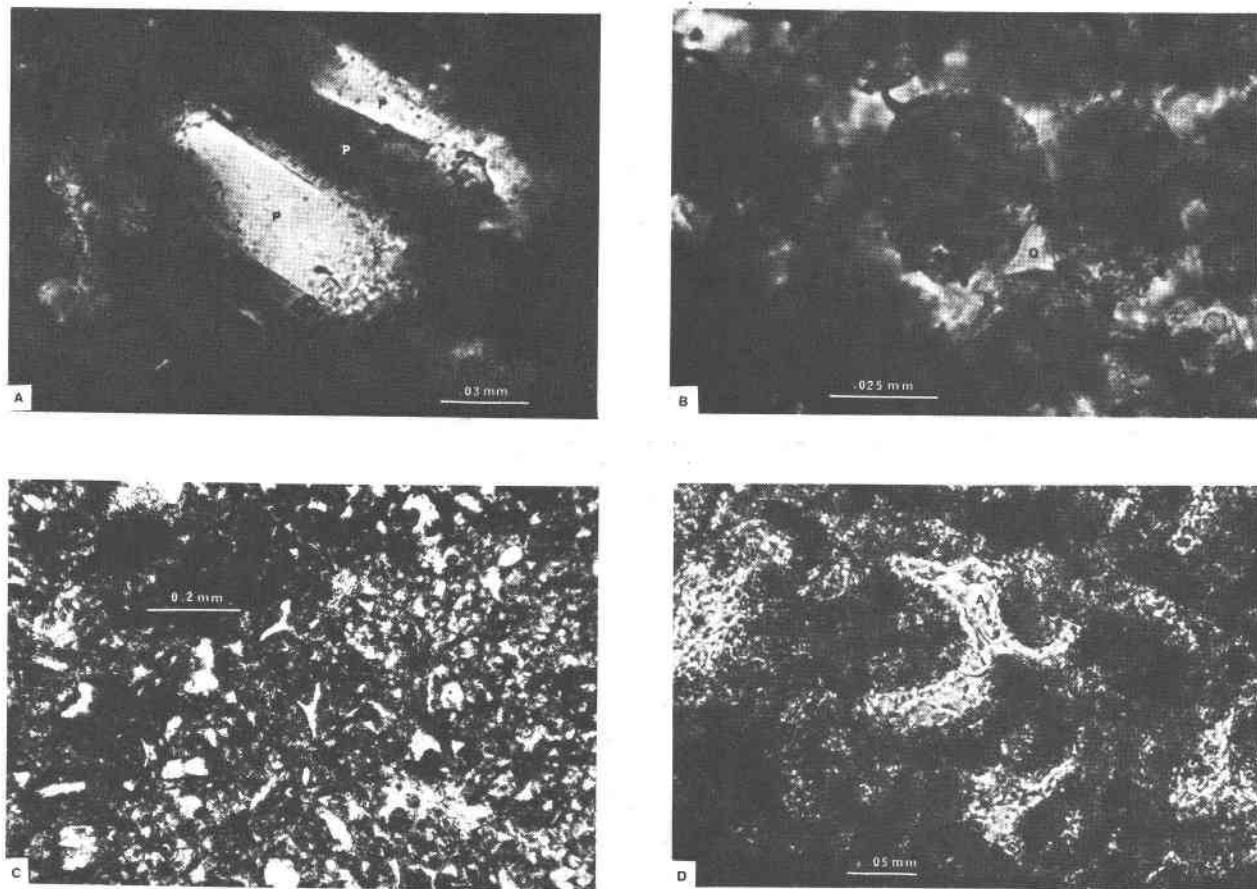


FIG. 3. Photomicrographs of altered tuffs from the Green River Formation, Wyoming.

- A) *RS-1*—Altered tuff from the Tipton Shale Member showing relict igneous plagioclase twins (P) partially replaced by K-feldspar (K). Altered twin plate in center of picture is 0.03 mm across. Both illuminated plates are part of the same twin set in one crystal. Note that the extinguished twin set is more altered than the illuminated set, suggesting compositional variation among twins. (Crossed nicols)
- B) *SC68-7*—Altered tuff from the Wilkins Peak Member showing euhedral grains of inclusion-filled analcime. Note the interpenetration of euhedral grains forming characteristic chains of crystals. Interstitial material is anhedral quartz (Q). Central analcime grain is 0.05 mm across. (Uncrossed nicols)
- C) *RS-2T*—Altered tuff from the Tipton Shale Member showing relict shard fabric. Shards are partially filled with mordenite and analcime. The matrix of the tuff is predominantly anhedral to subhedral microcrystals of mordenite. The “Y” shaped shard in center of the picture is 0.10 mm long. (Uncrossed nicols)
- D) *GL-2*—Altered tuff from the Tipton Shale Member showing incipient development of analcime fabric. Round, nearly opaque blobs consist of fine crystallites of mordenite. Interstices surrounding blobs are partially filled with analcime (A). (Uncrossed nicols)

alkali-rich zeolite precursors, and not directly from the original glass of the tuffs.

1) The original shard fabric is rarely preserved in tuffs that contain large amounts of analcime. The absence of glass-shard pseudomorphs in tuffs that are predominately of analcime suggests that the rock has been recrystallized and that the original fabric of the rock was destroyed as the analcime crystallized.

2) Tuffs that contain alkali-rich zeolites such as

clinoptilolite or mordenite show obvious preservation of the original shard fabric. Analcime, when present in minor amounts in association with other zeolites, is present both as partial fillings of open shards, and as patchy replacements of the zeolites. Where analcime replaces other zeolites, the shard fabric is indistinct. Analcime occurs as patchy replacements of alkali-rich zeolites within a single hand specimen, appearing as isolated nodules in a zeolitic matrix.

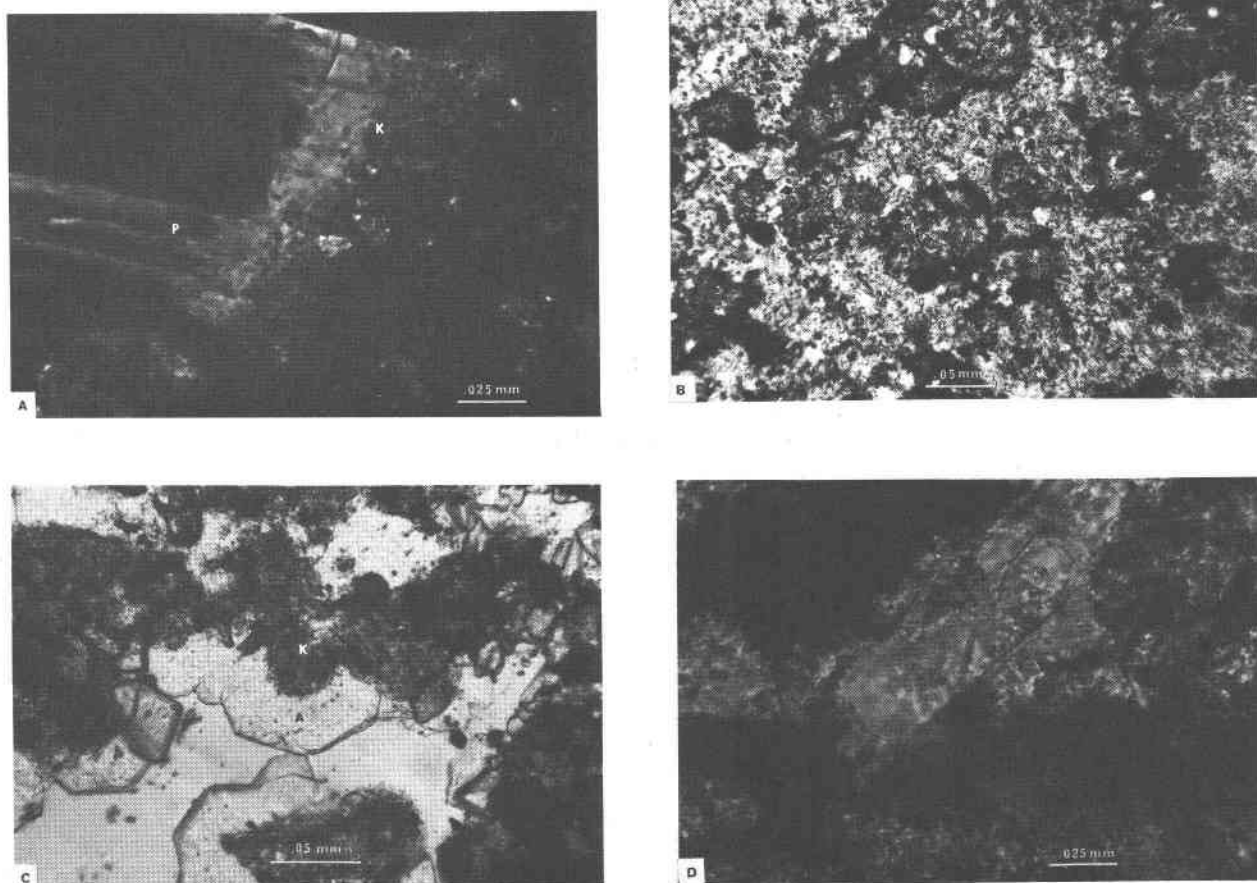


FIG. 4. Photomicrographs of tuffs from the Green River Formation, Wyoming.

- A) *RS-1*—Altered tuff from the Tipton Shale Member showing twinned plagioclase crystal (P) partially replaced by K-feldspar (K). Note the absence of twinning in the region replaced by K-feldspar. Width of K-feldspar replacement zone is 0.025 mm. (Crossed nicols)
- B) *MF68-3*—Altered tuff from the Wilkins Peak Member showing almost total destruction of analcime fabric. Although relict fabric by alteration of the analcime to K-feldspar is preserved, analcime is no longer present in the X-ray diffraction pattern of this sample. Analcime ghost in center of picture is 0.10 mm in diameter. (Uncrossed nicols)
- C) *K-10*—Altered tuff from the Tipton Shale showing clear, euhedral analcime grains (A) encroached upon and embayed by K-feldspar (K). Reaction zone in center of picture marked by (K) is 0.1 mm across. Grains showing high relief are calcite rhombohedra (C). (Uncrossed nicols)
- D) *MF68-3*—Altered tuff from the Wilkins Peak Member showing analcime (A) overgrown and replaced by K-feldspar (K). Analcime core is slightly birefringent, but has an index of refraction distinctly lower than the surrounding K-feldspar. Grain shown is 0.15 mm long. (Uncrossed nicols) Analyses of this grain with the electron microprobe show a sudden increase in K_2O and decrease in Na_2O as the boundary is crossed from analcime into K-feldspar. No gradient in Si/Al ratio was found.

3) Analcime almost never occurs with fresh glass in altered, silicic tuffs in modern and Pleistocene saline lakes. Alkali-rich zeolites and clay minerals, especially montmorillonite, are the minerals most commonly associated with fresh glass in such environments (Hay, 1966, p. 91; Sheppard and Gude, 1969, p. 10).

4) The increased amount of analcime with increased age in unmetamorphosed, saline, alkaline lake deposits suggests that initially formed alkali-

rich zeolites commonly tend to react to form analcime (Hay, 1966, p. 72–76, 91).

K-feldspar. Except for 11 scattered occurrences within the uppermost Tipton Shale Member, authigenic K-feldspar occurrences are confined to the Wilkins Peak Member and some zones in the Laney Shale. K-feldspar is present as fine-grained, felted masses of crystallites in the mesostasis of tuffs, and as overgrowths on detrital plagioclase and authigenic analcime. Tuffs whose X-ray patterns show only

K-feldspar contain relict plagioclase grains both partially and completely altered to K-feldspar. Highly altered plagioclase grains form either lacy, boxwork relicts enclosed in overgrowths of K-feldspar, or coherent grains with twinning barely discernible (Figs. 3A and 4A).

Sheppard and Gude (1970, written communication) determined the unit cell parameters of an authigenic K-feldspar collected from outcrops of the Wilkins Peak Member exposed near the town of Green River. Refinement of X-ray powder diffraction data for this K-feldspar gave the following unit cell parameters: $a = 8.609 \pm 0.014\text{\AA}$, $b = 12.997 \pm 0.012\text{\AA}$, $c = 7.181 \pm 0.004\text{\AA}$, Volume = $721.45 \pm 0.99\text{\AA}^3$, $\beta = 116.11 \pm .058$ degrees.

Most authigenic K-feldspar in the Green River Formation was formed from the alteration of analcime precursors. The evidence for this hypothesis is as follows:

1) Tuffs whose X-ray diffraction patterns indicate that they contain pure K-feldspar show patches of relict fabric characteristic of that formed by euhedral analcime grains. Analcime can be seen in all stages of replacement by K-feldspar.

2) Several samples that contain K-feldspar in one part of the sample contain analcime in the immediately adjacent portion.

3) Within single crystals, slightly anisotropic analcime is overgrown and replaced by K-feldspar (Fig. 4D).

4) Analcime tuffs near the eastern margin of the exposures of the Green River Formation in the Green River (Bridger) Basin contain K-feldspar when traced westward toward the saline facies. The same relationship was observed by Iijima and Hay (1968, p. 193).

5) Authigenic K-feldspar has formed from the alteration of relict plagioclase and analcime in the Barstow Formation of California (Sheppard and Gude, 1969, p. 20).

Sheppard and Gude (1969, p. 30) report that they formed K-feldspar from clinoptilolite by heating to 80°C . for 44 hours in concentrated KOH. Although these conditions are not likely to represent the actual conditions of authigenesis, the extreme rapidity of the reaction from zeolites to K-feldspar is amply demonstrated.

Quartz. Authigenic quartz is present in almost all samples as overgrowths on primary quartz grains, as inclusions in analcime grains and probably as microcrystalline grains in the mesostasis of tuffs. The

source of the quartz is uncertain, and it may be of multiple origins. Much of the quartz is in very small, euhedral grains in oil shale, tuff, argillaceous limestone, and dolostone (Milton *et al.*, 1960, p. 181). This suggests crystallization of the quartz from silica-saturated pore solutions in the rocks. According to Iijima and Hay (1968, p. 195), shortite encloses some grains of euhedral analcime in tuffs that also contain authigenic feldspar and quartz outside the shortite. Thus, the quartz and feldspar formed later than the shortite, after the analcime was well formed, and probably in the later stages of authigenic alteration. Some of the silica lost by the glass in reacting to form zeolites, and in the reacting of zeolites to form analcime in the Green River Formation, may have precipitated from solution as quartz, as it did in the John Day Formation of Oregon (Hay, 1963, p. 224).

Calcite and Dolomite. In the tuffs studied in thin section, samples rarely contained more than 20 percent of calcite and dolomite. Bradley (1964, p. A33) found that a number of tuffs in the Green River Formation contain as much as 80 percent carbonate minerals. In this study, samples containing large amounts of carbonate minerals and only minor amounts of authigenic silicates, judged on the basis of X-ray diffraction peak heights, were considered to be limestone or dolostone and not tuffs. Such samples were therefore not studied in detail.

Albite. Albite is present in major or minor amounts in 195 of the 409 samples studied by X-ray diffraction, but its validity as an authigenic mineral is in question. Albite is a major constituent of most sandstones in the Green River Formation. Although thin sections show K-feldspar forming from analcime, no clear genetic relationships between analcime and albite have been observed, in spite of the common association of these two minerals. The Green River Formation is the only reported occurrence of authigenic albite formed in altered tuffs in saline lake deposits that have not been deeply buried (Hay, 1966, p. 16ff). Much, if not all, of the albite in the Green River Formation probably was deposited either directly as clastic material, or formed by albitization of more calcic clastic plagioclase. The refractive index, determined with immersion oils, of all optic axes of the plagioclase ranges from 1.530 to 1.540, indicating nearly pure albite composition (Kerr, 1959, p. 272). The autochthonous nature of the oil shales of the Green River Formation explains the general absence of

albite in the oil shales and its concentration in the allochthonous tuffs.

Geochemistry of Alteration

Si/Al ratio of Analcime

Iijima and Hay (1968, pp. 184–189), in their study of the composition of analcime in the Green River Formation, reported that the Si/Al ratio of the analcime ranged from 1.95 to 2.81 and suggested that this variation might be caused by the reaction of analcime to authigenic feldspar. They noted that analcime associated with authigenic feldspar had a lower Si/Al ratio than analcime not associated with feldspar (Iijima and Hay, 1968, p. 190). They also noted a general decrease in Si/Al ratio of analcime from east to west in the Green River Formation and suggested that this trend might be caused by increased alteration of analcime to authigenic feldspar as the primary saline mineral facies was approached (Iijima and Hay, 1968, p. 197).

A similar study of Si/Al ratios of analcime was undertaken for this paper. The method of analysis was that of Saha (1959). Si/Al ratios ranged from 1.95 to 2.58 and, as shown in Figure 5, a bimodal distribution of the Si/Al ratios was found.¹ It should be noted that the over-all range of Si/Al ratios determined in this study is smaller than that found by Iijima and Hay, and that 68 percent of the values found in this study are within the range of values found least often by Iijima and Hay (1968, p. 188).

Among 37 samples from the Wilkins Peak Member, sixteen contain analcime or analcime and quartz, fourteen contain analcime and albite, and seven contain analcime and K-feldspar. Of 30 samples from the Tipton Shale Member, 25 contain analcime or analcime and quartz, three contain analcime and K-feldspar, and two contain analcime and albite.

Figure 6A is a histogram of the distribution of Si/Al ratios of analcime in the Wilkins Peak Member. This histogram does not suggest the correspondence between feldspar content and Si/Al ratio in analcime noted by Iijima and Hay. Figure 6B shows a similar histogram for the distribution of Si/Al ratios in analcime from the Tipton Shale Mem-

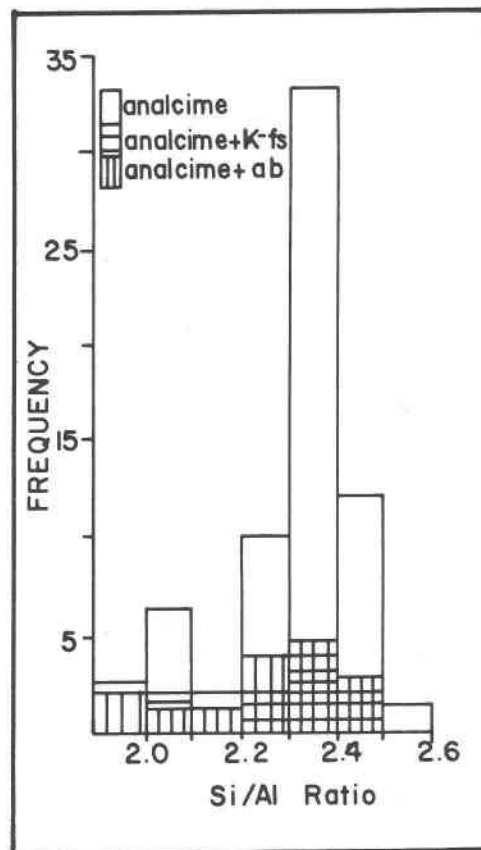


FIG. 5. Histogram of the distribution of Si/Al ratios of analcime in tuffs of the Green River Formation. Heights of columns equal total numbers of samples in each class. Number of samples containing only analcime equals total height of column minus the number of samples containing each feldspar.

ber. Again, there is no suggestion of the correspondence between mineral assemblage and Si/Al ratio noted by Iijima and Hay. Eighty percent of the samples containing analcime without authigenic feldspar have Si/Al ratios in excess of 2.30. But among samples containing analcime and albite, just as many have Si/Al ratios greater than 2.30 as have ratios lower than 2.30. Among samples containing analcime and K-feldspar, six have ratios greater than 2.30 and four have ratios lower than 2.30.

As a further test of the possible correspondence between mineral assemblages and Si/Al ratio, a modified "t" test was used to determine the statistical significance of the difference between the mean Si/Al ratios of samples containing only analcime versus samples containing analcime and each of the two feldspars. Table 2 shows the values for Si/Al ratios,

¹ A complete table of all $\Delta 2\theta$ values and Si/Al ratios may be ordered as NAPS Document Number 01980. The present address is Microfiche Publications, Division of Microfiche Systems Corporation, 305 East 46 Street, New York, N. Y. 10017. Please remit in advance \$1.50 for microfiche or \$5.00 for photocopies. Please check the most recent issue of this journal for the current address and prices.

Table 2.
Si/Al ratios and statistical values for calculation
of t tests for equality of means.

Samples Containing Only Analcime	Samples Containing Analcime and Albite	Samples containing K-feldspar	
2.38	2.47	2.43	
2.38	2.43	2.36	
2.48	2.32	2.06	
2.57	2.46	2.34	
2.47	2.13	2.25	
1.96	1.99	2.00	
2.32	2.35	2.30	
2.49	1.95		
2.19	2.04		
2.02	2.27		
2.06	2.30		
2.33	2.22		
2.28	2.23		
2.33	2.09		
2.31			
2.31			
sum =	36.88	31.25	15.74
\bar{X} =	2.31	2.23	2.52
s^2 =	0.0294	0.0297	0.1537

$$t = (\bar{X}_1 - \bar{X}_2) (s_1^2/N_1 + s_2^2/N_2)^{-1/2}$$

$$f = (s_1^2/N_1 + s_2^2/N_2)^2 \left((s_1^2/N_1)^2 (N_1 + 1)^{-1} + (s_2^2/N_2)^2 (N_2 + 1)^{-1} \right)^{-1}$$

N , \bar{X} and s^2 for each of the groups of samples used in the t test. For comparison of samples containing only analcime versus samples containing analcime and albite, $f = 29.4$, $t = 0.0048$, and the critical region is $t_{(0.975, 29)} = 2.045$, $t_{(0.025, 29)} = -2.045$. For comparison of samples containing only analcime versus samples containing analcime and K-feldspar: $f = 7.36$, $t = 2.52$, and this critical region is $t_{(0.975, 7)} = 2.365$, $t_{(0.025, 7)} = -2.365$. The test results indicated that the mean Si/Al ratio of samples containing analcime and albite is different from that of samples containing only analcime at all significance levels, whereas the mean for samples containing K-feldspar and analcime is not significantly different. However, a one-sided " t " test indicated that the mean Si/Al ratio of analcime associated with K-feldspar is greater than the mean for samples containing only analcime and that the difference for samples containing analcime and albite is insignificant. The ambiguity of these statistical tests suggests that the observed variations of Si/Al ratios in the samples are not related directly to the amount of feldspar in the samples.

Table 3 is a compilation of electron microprobe

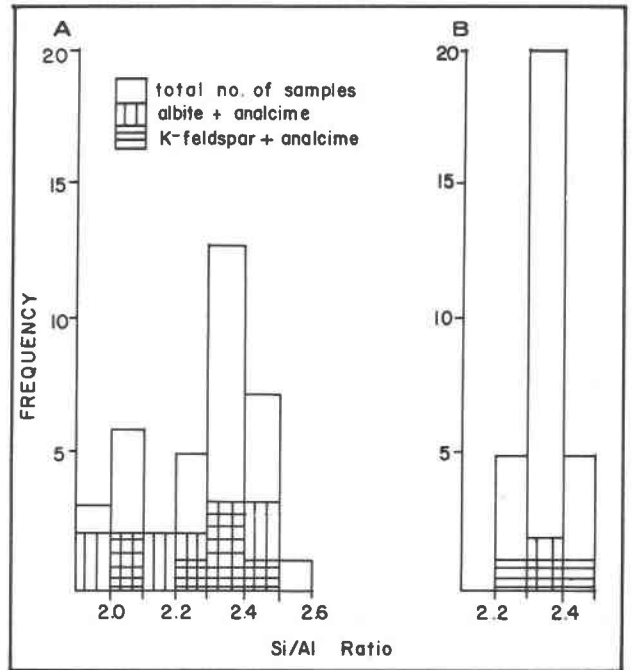


FIG. 6. Histograms of the distributions of Si/Al ratios, determined by X-ray, of analcime in tuffs of the Green River Formation. Total heights of columns equal total numbers of samples in each class. Number of samples containing only analcime equals total height of column minus the numbers of samples containing each feldspar.

A) Si/Al ratios of analcime from the Wilkins Peak Member, Green River Formation

B) Si/Al ratios of analcime from the Tipton Shale, Green River Formation

data for traverses of altered analcime grains. Traverses were made in 10 μm steps from the relatively fresh centers to the altered outer edges of the crystals. Only one of the traverses (Table 3, Number 3) indicates any tendency toward a loss of silica by the analcime as the K-feldspar is approached. The other three traverses show either little change or a slight increase of silica as the altering edge of the crystal is approached. Table 4 shows a comparison of electron microprobe and X-ray diffraction data. Si/Al ratios determined by the microprobe are generally higher than the ratios determined indirectly by X-ray diffraction. Indeed, many of the values determined with the microprobe are greater than the greatest values found by X-ray diffraction methods. Iijima and Hay (1968, p. 187) noted a similar discrepancy between the X-ray diffraction and electron microprobe determinations of Si/Al ratios. Saha's X-ray method for determining Si/Al ratios is probably more accurate than microprobe methods because it

Table 3.
Si/Al Ratios of Four Analcime Grains
Calculated from Electron Microprobe Analyses

Traverse Number	Distance in μm from Center of Crystal Toward Reacting Edge				
	0	10	20	30	40
1	2.38	2.50	2.36	2.77	2.87
2	3.03	2.97	2.55	2.84	
3	2.87	2.93	2.67	2.51	
4	2.61	2.64	2.70		

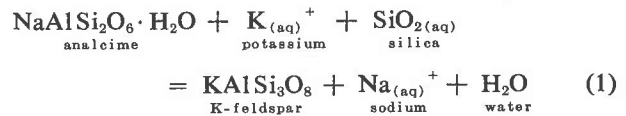
Analyses were made at 10 μm intervals from the relatively fresh centers of the grains to the highly altered outer edges. Analyses are of analcime grains which are altered to and surrounded by K-feldspar. Counting rates for potassium show no increase even within 10 μm of the altered edge of the analcime grain. Electron beam was 5 μm wide and operated at 15 kV, .003 μA sample current. Spots were counted for 10 seconds. Counting of Na or K showed no loss of volatiles during analysis with these techniques.

cannot be influenced by mineral impurities included in analcime grains. The discrepancy between X-ray diffraction and microprobe determinations can be explained by the presence in the analcime of inclusions of quartz or amorphous silica that are too small to detect with the microprobe.

Possible Causes of Variation of Si/Al Ratio. Sheppard and Gude (1969, p. 29) found that the Si/Al ratio of analcime in the Barstow Formation of California apparently depends on the Si/Al ratio of the precursor zeolite from which the analcime formed. Analcime associated with phillipsite has a lower Si/Al ratio than analcime associated with clinoptilolite. Figure 7 shows the number of Si atoms per unit cell of analcime from the Green River Formation, calculated from the data of this paper. The data of Sheppard and Gude (1969, p. 29) are shown for comparison, compositions of analcime from the Barstow Formation plot on the diagram in the range where Green River analcime compositions occur least frequently, and they have a narrow range of composition in contrast to analcime in the Green River Formation. It seems likely that brine composition determined the Si/Al ratios of Green River analcime because zeolites other than clinoptilolite, mordenite and analcime have not been found in the Green River Formation.

Experimental studies by Taylor (1930), Barrer (1950), Beattie (1954), and Saha (1959) suggest that the Si and water contents of analcime can be affected by the Si/Al ratio of the starting material from which the analcime formed, and by the Si/Al ratio, activity of water and potassium content of solutions in contact with the analcime during and after its formation.

The alteration of analcime to potassium feldspar in the Green River Formation is well documented. For the reaction:



the expression for the equilibrium constant is:

$$K = \frac{[\text{KAlSi}_3\text{O}_8][\text{Na}^+][\text{H}_2\text{O}]}{[\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}][\text{K}^+][\text{SiO}_2]} \quad (1a)$$

Taking the log of both sides of (1a) and adding $\log \text{H}^+/\text{H}^+$ to the right-hand side in order to conform to the parameters of Hess (1966, pp. 295, 299), (1a) becomes:

$$\log K = \log \frac{[\text{Na}^+]}{[\text{H}^+]} - \log \frac{[\text{K}^+]}{[\text{H}^+]} - \log [\text{SiO}_2] \quad (1b)$$

assuming that the activities of the solids and water are equal to 1, and molal concentrations of dissolved components are approximately equal to activities for dilute solutions. Clearly reaction (1) is strongly dependent upon the Na^+/K^+ concentration (activity) ratio and the concentration (activity) of SiO_2 in the solution. For concentrated brines, the activity of water would be less than 1 (Greenwood, 1961, p. 3939), and the expression for the equilibrium constant becomes:

$$\log K = \log \frac{[\text{Na}^+]}{[\text{H}^+]} \\ + \log [\text{H}_2\text{O}] - \log \frac{[\text{K}^+]}{[\text{H}^+]} - \log [\text{SiO}_2] \quad (1c)$$

Thus, higher concentrations of dissolved solids, by lowering the activity of water, favor the anhydrous feldspar phase of reaction (1).

Table 4.
Comparison of X-Ray Diffraction and Electron Microprobe
Analyses of Si/Al Ratios of Analcime Grains in Tuffs of the
Wilkins Peak Member, Green River Formation.

	Sample Number					
	CC68-16	TV68-3T	SC68-1	BF68-1	BF68-16	TV68-5
Average Microprobe Analysis	2.52	2.64	2.54	2.55	2.68	2.74
X-ray Analysis	2.22		2.06	1.99	2.25	
Number of Readings in Microprobe Average	18	12	64	9	10	13

Values listed for the electron microprobe are averages of all analyses for each sample, including the traverses of Table 3. All samples contain analcime, K-feldspar and quartz. Sample number CC68-16 includes traverse 1 of Table 3; sample number TV68-5 includes traverses 2, 3, and 4 of Table 3.

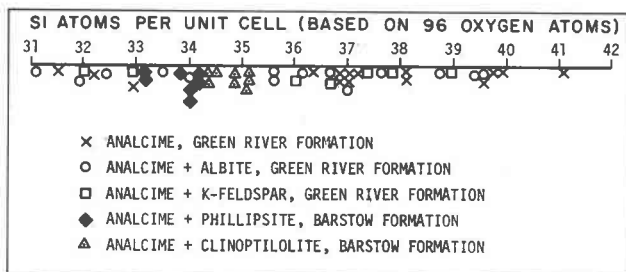


FIG. 7. Silicon contents of unit cells of analcime in the Green River Formation of Wyoming, and the Barstow Formation of California. Note the broad range of Si contents for the Green River analcime compared with those of the Barstow Formation. Design of figure is taken from Sheppard and Gude (1969, p. 29). All values calculated from X-ray diffraction determinations of Si/Al ratios.

Studies by Hess (1966, p. 303) and Garrels and Christ (1965, p. 369) suggest that under the conditions of (1b) above, the reaction of analcime to K-feldspar [reaction (1)] at 25°C. and 1 atm pressure should be at equilibrium near $\log [\text{Na}^+]/[\text{H}^+] = 9.5$, and $\log [\text{K}^+]/[\text{H}^+] = 7.5$ at $\log [\text{SiO}_2] = -4.0$ or $[\text{Na}^+]/[\text{K}^+] = 10^{2.0}$. The relationships of equation (1c) above and Hess's data indicate that under conditions of lower activity of SiO_2 , or higher $[\text{Na}^+]/[\text{H}^+]$ ratios, equilibrium between analcime and K-feldspar is reached at even lower values of $[\text{Na}^+]/[\text{K}^+]$. For example, using data from Hess (1966, p. 300, Fig. 1), the following relationships obtain for reaction (1):

$$\log \frac{[\text{Na}^+]}{[\text{H}^+]} = 11.0, \log \frac{[\text{K}^+]}{[\text{H}^+]} = 9.5, \text{ for}$$

$$\log [\text{SiO}_2] = -4.0. \text{ For } \log [\text{SiO}_2] = -5.0$$

$$\log \frac{[\text{K}^+]}{[\text{H}^+]} = 10.5, \text{ at } \log \frac{[\text{Na}^+]}{[\text{H}^+]} = 11.0.$$

Thus, at a pH of 9.5,

$$\frac{[\text{Na}^+]}{[\text{H}^+]} = \frac{[\text{Na}^+]}{[10^{-9.5}]} = 10^{11.0} \text{ and}$$

$$\frac{[\text{K}^+]}{[\text{H}^+]} = \frac{[\text{K}^+]}{[10^{-9.5}]} = 10^{9.5} \text{ at } \log (\text{SiO}_2) = -4.$$

$$\frac{[\text{K}^+]}{[\text{H}^+]} = \frac{[\text{K}^+]}{[10^{-9.5}]} = 10^{10.5} \text{ at } \log (\text{SiO}_2) = -5.$$

Therefore,

$$\frac{[\text{Na}^+]}{[\text{K}^+]} = \frac{10^{11.0}}{10^{9.5}} = 10^{1.5} = 32 \text{ at } \log (\text{SiO}_2) = -4$$

and

$$\frac{[\text{Na}^+]}{[\text{K}^+]} = \frac{10^{11.0}}{10^{10.5}} = 10^{0.5} = 3.2 \text{ at } \log (\text{SiO}_2) = -5.$$

These values indicate that at low silica concentrations the boundary for equilibrium between analcime and K-feldspar occurs at very low Na^+/K^+ ratios. However, holding all other parameters constant, a shift to higher silica concentrations favors the more siliceous K-feldspar phase (see Hess, 1966, p. 300). Either increased activity of silica or decreased Na^+/K^+ ratios in the brines could have caused analcime to react to K-feldspar. Mariner and Surdam (1970) showed that solutions of increasing alkalinity exposed to rhyolite glass have progressively lower Si/Al ratios, indicating that the solubility of alumina with increased pH increases more rapidly than the solubility of silica. Boles (1971) found in studies of the synthesis of analcime from clinoptilolite that although the Si/Al ratio of the analcime was directly related to that of the precursor clinoptilolite, the analcime product invariably had a lower Si/Al ratio. It seems likely that the Si/Al ratio of brines in contact with reacting zeolites and feldspars is more important in determining stability fields and reactions than total silica concentration. Increases in pH of the brines, by lowering the Si/Al ratio of the brine, should favor phases with lower Si/Al ratios. The Si/Al ratio of Green River analcime rarely rises to the Si/Al ratio of K-feldspar. Thus, brines of high pH should favor analcime over K-feldspar in spite of the increased concentration of total silica in high pH brines in contact with the reacting phases. It also seems likely that the Na^+/K^+ ratio of the brines is more important than the Si/Al ratio in determining the stability fields of analcime and K-feldspar in the Green River tuffs.

Variations in the Partial Pressure of CO_2

Trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) is present in the Green River Formation both as a primary, bedded evaporite mineral and in veins, rosettes and single crystals as an authigenic mineral.

Experimental studies reported by Bradley and Eugster (1969, pp. B38-B59) have shown that brines in the system $\text{Na}_2\text{CO}_3\text{-NaHCO}_3\text{-NaCl-H}_2\text{O}$ precipitate mostly trona and that halite saturation of such brines rarely occurs. In order to precipitate trona from such a solution, a bicarbonate quotient,

$$\frac{(\text{g HCO}_3^-)}{(\text{g HCO}_3^- + \text{g CO}_3^{--})}$$

of 0.15 must be maintained. This value is easily obtained by equilibrium of the brines with normal atmospheric concentrations of CO_2 . Interstitial brines trapped in sediments would be removed from equilibrium with the atmosphere, but addition to the brines of CO_2 from decaying organic matter could cause continued precipitation of trona without reaching the halite saturation level (Bradley and Eugster, 1969, p. B53).

Crystallization of trona and other authigenic sodium carbonate minerals used vast quantities of sodium. Fahey (1962, p. 22) estimates that $114 \times 10^9 \text{ kg}$ of shortite ($\text{Na}_2\text{CO}_3 \cdot 2\text{CaCO}_3$) are present in the rocks under every square mile of land surrounding the John Hay, Jr., well number 1 (Sec. 2, T. 18 N., R. 110 W.). This tonnage of shortite contains about $18 \times 10^9 \text{ kg}$ of sodium. None of the authigenic or primary carbonate minerals contain appreciable quantities of ions other than those necessary for stoichiometry. W. C. Culbertson (1970, personal communication) reported that analyses of bedded trona showed no more than 0.6 percent K_2O and that most analyses were in the range of 0.2 percent or

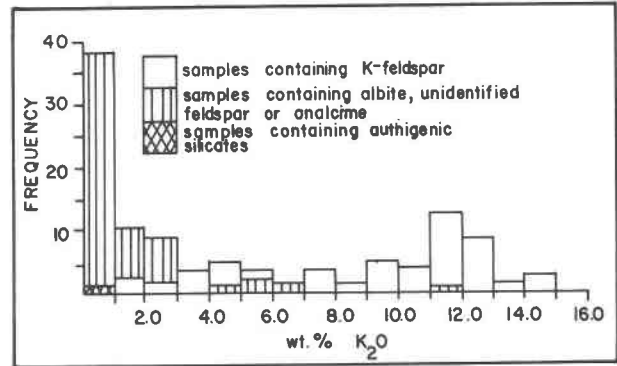


FIG. 9. Histogram of the distribution of potassium contents of tuffs in the Green River formation, Wyoming. Heights of columns equal total number of samples in each class. Note that only one sample that does not contain abundant K-feldspar has greater than 7 weight percent K_2O . Potassium contents determined by X-ray emission spectrographic analysis; J. Goodwin, analyst.

less of K_2O . Large amounts of potassium must have been present in the brines because many of the tuffs contain more than 7 percent K_2O . However, no potassium salts have been found in the Green River Formation (Milton and Eugster, 1959, p. 118–150; Fahey, 1962, p. 22–38). It seems probable, that crystallization of sodium carbonate minerals enriched the primary and occluded brines in potassium and caused a decrease in the Na^+/K^+ activity ratio of the brines.

Effect of Na^+/K^+ ratio

Electron microprobe studies of analcime from the Green River Formation indicate that there is no addition of potassium to the analcime within even 10 microns of the altered edge of the analcime crystal. Apparently, inversion of analcime to K-feldspar is not caused by a gradual exchange of potassium for sodium in the analcime structure. Instead, the reaction appears to be a rather sudden and complete reorganization occurring only under the proper conditions of Na^+/K^+ activity ratio, activity of water and Si/Al ratio.

Figure 8 shows diagrammatic plots of mineral content versus potassium content of tuffs from the Wilkins Peak Member collected in two different measured sections. These figures show that tuffs that contain K-feldspar have much higher potassium contents than tuffs that do not contain K-feldspar. Figure 9 is a histogram of the distribution of potassium contents in 108 samples of tuffs from the

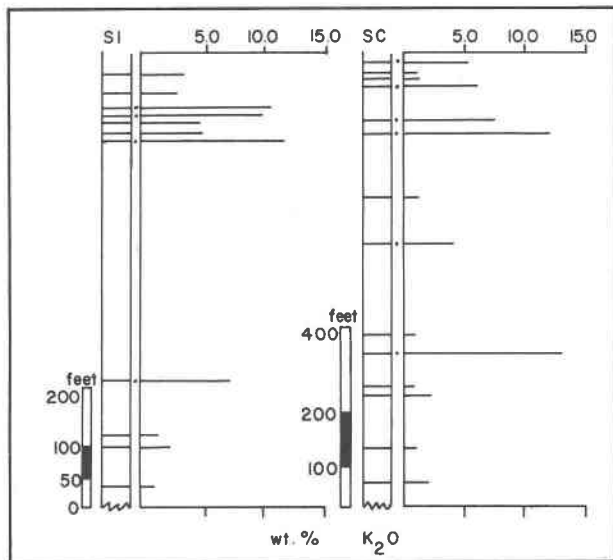


FIG. 8. Diagrammatic plots of stratigraphic locations, mineral contents and K_2O contents of tuffs from the Wilkins Peak Member, Green River Formation. Positions of lines in sections designate stratigraphic positions of tuffs below the top of the Wilkins Peak Member. Dots to the right of the tuffs indicate tuffs containing K-feldspar. Tuffs without dots contain only analcime. Tuffs containing K-feldspar always have higher wt percent K_2O than other tuffs. Tuffs chemically analyzed by X-ray emission spectrograph; J. Goodwin, analyst.

Table 5.
Average gain or loss of major cations in tuffs of the Green
River Formation, Wyoming

	1	2	3
Si	64.6	62.5	-2.1
Al	15.6	16.1	+0.5
K	3.2	12.8	+9.6
Na	5.2	2.8	-2.4
Mg	0.8	0.6	-0.2
Ca	2.5	2.6	+0.1
O	160.0	160.0	000.0

- 1) Numbers of cations per 160 oxygen atom unit cell in rhyolite from Aeolian Islands, Pietre Cotte, Monte della Fossa, Vulcano; rhyolite number 48 from Washington, 1917, p. 972; L. Ricciardi; analyst.
- 2) Average number of cations per 160 oxygen atom unit cell in 19 analyzed samples of altered tuff from the Green River Formation, Wyoming; J. Goodwin, analyst; Data from Goodwin (1971, table 6)¹.
- 3) Average numbers of cations per 160 oxygen atom unit cell gained or lost by Green River tuffs relative to analysis number 1. Analysis number 1 was chosen as a standard because of the close approach of its aluminum content to the average aluminum content of the Green River tuffs. Calculations of unit cells were made according to the methods of Barth (1952, p. 82-85).

Wilkins Peak and Tipton Shale Members. Of 56 tuffs containing analcime, albite, or other authigenic silicates without K-feldspar, 55 have potassium contents of less than 7 percent. The one sample of this group with a potassium content greater than 7 percent contains an indeterminate feldspar that was lumped with the analcime-albite group. Tuffs containing K-feldspar have a broad range of potassium contents, but 38 of these 52 samples have potassium contents greater than 7 percent. Thus, there is a rather clear division between samples containing K-feldspar and those containing other authigenic silicates.

Table 5 shows the average gain or loss of major cations in 18 analyzed samples of altered tuff from the Green River Formation, relative to a rhyolite. All of the analyzed tuffs contain at least some K-feldspar and the table clearly shows that large amounts of potassium must have been added to the tuffs in order to form K-feldspar. The most likely

source for the additional potassium is the brines in contact with the tuffs at the time of alteration.

Conclusions

Saline minerals are generally absent in exposures of the Green River Formation near the eastern boundary of the study area, but become progressively more common toward the west (see Culbertson, 1966, p. B162). Thus, the brines must have had increasingly higher concentrations of dissolved saline minerals toward the west. This increased concentration of dissolved solids would have lowered the activity of water progressively toward the west, thus favoring the formation of less hydrous, less siliceous analcime toward the west (Saha, 1959, p. 310). Mariner and Surdam (1970, p. 979) have shown that for alkaline solutions in contact with volcanic glass or zeolites the Si/Al ratio of the solution decreases with increasing pH. Thus, if the pH of the brines in Lake Gosiute increased toward the west, analcime with lower Si/Al ratios would have been favored.

The reaction mechanism for the formation of K-feldspar from analcime did not cause a desilication of the analcime. The east-west trend in Si/Al ratios of analcime and its correspondence with increased authigenic feldspar content in the rocks observed by Iijima and Hay (1968, pp. 184-190) appears to be coincidental. Analcime with low Si/Al ratios formed toward the west because increased concentrations of dissolved solids, and perhaps increased p_{CO_2} , caused an increase in the pH of the brines and therefore a decrease in the Si/Al ratio of the brines in contact with the tuffs at the time the analcime formed. These conditions also favored the precipitation of sodium carbonate minerals which caused a decrease in the Na^+/K^+ activity ratio in the brines. Ultimately, K-feldspar formed from analcime where the Na^+/K^+ activity ratio fell to low enough values. These conditions occurred most commonly within or near the primary saline mineral facies toward the western end of Iijima and Hay's section and, coincidentally, where analcime with low Si/Al ratios had formed earlier.

Acknowledgments

Research was conducted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in geology at the University of Wyoming, and supported by grants from the Penrose Bequest of the Geological Society of America and a grant to Professors Ronald B. Parker and Ronald C. Surdam from the American Chemical Society-Petroleum Research Fund (ACS-PRF No. 3809-A2). Mr.

¹A complete table of all chemical analyses, mineral assemblages, and calculated Barth unit cell contents may be ordered as NAPS Document 01980. The present address is Microfiche Publications, Division of Microfiche Systems Corporation, 305 East 46th Street, New York, N. Y. 10017. Please remit in advance \$1.50 for microfiche or \$5.00 for photocopies. Please check the most recent issue of this journal for the current address and price.

William Culbertson of the United States Geological Survey assisted in sampling the cores at the Survey office in Denver and provided valuable information on the stratigraphy of the Green River Formation. Arthur J. Gude, 3rd, and Richard A. Sheppard of the United States Geological Survey in Denver, and Richard L. Hay of the University of California discussed several aspects of the research. Gerald U. Dineen, J. Ward Smith and the staff at the United States Bureau of Mines, Laramie Petroleum Research Center, donated time and equipment which made the project possible. Professors Surdam, Parker, Blackstone, McGrew and Howatson provided valuable technical assistance as members of my research advisory committee. M. Dane Picard critically reviewed early drafts of the manuscript. The conclusions are the author's own.

References

- BARRER, R. M. (1950) Ion-exchange and ion-sieve processes in crystalline zeolites. *J. Chem. Soc. (London)*, 2342.
- BARTH, T. F. W. (1952) *Theoretical Petrology*. John Wiley and Sons, New York. 1st ed.
- BEATTIE, I. R. (1954) Structure of analcite and ion-exchanged forms of analcite. *Acta Crystallog.* **7**, 357-359.
- BOLES, R. (1971) Synthesis of analcime from natural clinoptilolite and heulandite. *Amer. Mineral.* **56**, 1724-1734.
- BRADLEY, W. H. (1929) The occurrence and origin of analcite and meerschaum beds in the Green River Formation of Utah, Colorado, and Wyoming. *U. S. Geol. Surv. Prof. Pap.* **158-A**.
- (1964) Geology of the Green River Formation and associated Eocene rocks in southwestern Wyoming and adjacent parts of Colorado and Utah. *U. S. Geol. Surv. Prof. Pap.* **496-A**.
- , AND H. P. EUGSTER (1969) Geochemistry and paleolimnology of the trona deposits and associated authigenic minerals of the Green River Formation of Wyoming. *U. S. Geol. Surv. Prof. Pap.* **496-B**.
- CULBERTSON, W. C. (1966) Trona in the Wilkins Peak Member of the Green River Formation, southwestern Wyoming, pp. B159-B164. In United States Geological Survey, 1966, Geological Survey Research, 1966. *U. S. Geol. Surv. Prof. Pap.* **550-B**.
- FAHEY, J. J. (1962) Saline minerals of the Green River Formation, with a section on X-ray powder data for saline minerals of the Green River Formation by Mary E. Mrose. *U. S. Geol. Surv. Prof. Pap.* **405**.
- GARRELS, R. M., AND C. L. CHRIST (1965) *Solutions, Minerals, and Equilibria*. Harper and Row, New York. 450 pp.
- GODDARD, E. N., *et al.* (1948) *Rock Color Chart*. National Research Council, Washington, D. C. 6 pp.
- GOODWIN, J. H. (1971) *Authigenesis of silicate minerals in tuffs of the Green River Formation, Wyoming*. Unpublished doctoral dissertation, University of Wyoming.
- GREENWOOD, H. J. (1961) The system $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O-Argon}$: Total pressure and water pressure in metamorphism. *J. Geophys. Res.* **66**, 3923-3946.
- HAY, R. L. (1963) Stratigraphy and zeolitic diagenesis of the John Day Formation of Oregon. *Univ. Cal. Publ. Geol. Sci.* **42**, 199-262.
- (1966) Zeolites and zeolitic reactions in sedimentary rocks. *Geol. Soc. of Am. Spec. Pap.* **85**.
- HESS, P. C. (1966) Phase equilibria of some minerals in the $\text{K}_2\text{O-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system at 25°C. and 1 atmosphere pressure. *Amer. J. Sci.* **264**, 280-309.
- IJIMA, A., AND R. L. HAY (1968) Analcime composition in tuffs of the Green River Formation. *Amer. Mineral.* **53**, 184-200.
- KERR, P. F. (1959) *Optical Mineralogy, 3rd ed.* McGraw-Hill, New York. 442 pp.
- MARINER, R. H., AND R. C. SURDAM (1970) Alkalinity and formation of zeolites in saline alkaline lakes. *Science*, **170**, 977-980.
- MILTON, C., E. C. T. CHAO, J. J. FAHEY, AND M. E. MROSE (1960) Silicate mineralogy of the Green River Formation, Wyoming, Colorado, and Utah. *Rep. of the 21st Session, Int. Geol. Congr., Norden, Part XXI*, 171 ff.
- MILTON, C., AND H. P. EUGSTER (1959) Mineral assemblages of the Green River Formation, pp. 118-150. In P. H. Abelson, Ed., *Researches in Geochemistry, Vol. 1*. John Wiley and Sons, New York.
- SAHA, P. (1959) Geochemical and X-ray investigation of natural and synthetic analcites. *Amer. Mineral.* **44**, 300-313.
- SHEPPARD, R. A., AND A. J. GUDE, 3RD (1969) Diagenesis of tuffs in the Barstow Formation, Mud Hills, San Bernardino County, California. *U. S. Geol. Surv. Prof. Pap.* **635**.
- TANK, R. (1969) Clay mineral composition of the Tipton Shale Member of the Green River Formation (Eocene) of Wyoming. *J. Sediment. Petrology*, **39**, 1593-1596.
- TAYLOR, W. H. (1930) Structure of analcite ($\text{NaAlSi}_3\text{O}_8 \cdot \text{H}_2\text{O}$). *Z. Kristallogr.* **74**, 1-19.
- WASHINGTON, H. S. (1917) Chemical analyses of igneous rocks. *U. S. Geol. Surv. Prof. Pap.* **99**.

Manuscript received May 24, 1972; accepted for publication, August 15, 1972.