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DIAGENESIS OF VOLCANOGENIC SEDIMENTS IN A TERTIARY SALINE LAKE; WAGON BED FORMATION, WYOMING

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ABSTRACT. Three diagenetic facies occur in the tuffaceous Eocene Wagon Bed Formation of Wyoming: (1) a fresh glass-smectite facies in fluvial and flood plain environments, (2) a clinoptilolite (+heulandite) facies in mixed fluvial, flood plain, and lacustrine environments, and (3) a K-feldspar–carbonate facies in lacustrine environments. The authigenic aluminosilicates formed after burial as a result of different pore fluid compositions inherited from these environments.

A local uplift restricted drainage in the basin and caused evaporative concentration of waters. The preponderance of shales and carbonates in the drainage area resulted in waters that when concentrated had saline but not alkaline compositions. Salinities were never sufficiently high to precipitate sodium or calcium sulphates.

From geochemical considerations we estimate that clinoptilolite-forming pore fluids have log Na+K/Ca+Mg mole ratios of about —0.3. When both K-feldspar and sepiolite coexist log K^+/H^+ activity ratios may have exceeded 3.0 and more likely 5.0.

Diagenetic reactions took place in moderately saline, but not highly alkaline pore fluids as evidenced by (1) the presence of calcium-rich zeolites, (2) high mobility of calcium ion during reaction of calcic zeolites to K-feldspar, (3) relatively low boron content of authigenic K-feldspar, and (4) absence of saline minerals indicative of alkaline waters.

INTRODUCTION

In recent years much has been written about authigenesis of volcanogenic sediments in saline, alkaline lakes; for example where lake waters are characterized by the condition $[\text{alkalinity}/2(Ca^{+2}+Mg^{+2})]>1$ (see summary in Surdam and Sheppard, 1978).[1] In contrast, little has been written about authigenic reactions in fresh, or saline lakes where $[\text{alkalinity}/2(Ca^{+2}+Mg^{+2})]<1$. In other words, lakes that upon evaporitic concentration would evolve to a saline but not alkaline lake, for example a $Na–SO_4–Cl$ lake such as the Great Salt Lake (see Hardie and Eugster, 1970). The occurrence of zeolites and authigenic K-feldspar in saline, alkaline environments has been emphasized in the literature, but there are numerous reports of these minerals in the absence of saline–alkaline indicators such as trona (see Hay, 1966). The diagenesis of volcanogenic sediments in the Wagon Bed Formation of Wyoming provides an outstanding case history of authigenic reactions and mineral formation in a fresh to saline lake deposit. Although saline, alkaline lakes provide an ideal habitat for authigenic silicates, it is now apparent that these same silicates form in a wide spectrum of lacustrine environments.

WAGON BED FORMATION: STRATIGRAPHY AND DEPOSITIONAL ENVIRONMENT

The Wagon Bed Formation (Van Houten, 1964) is a middle and upper Eocene succession of non-marine sedimentary rocks varying from about 40 to 210 m thick. The formation is exposed along the north-facing Beaver Rim escarpment on the southern edge of the Wind River Basin. Our study area extends eastward from Highway 287 to the Sweet-

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[1] In this context, alkalinity is defined (compare Stumm and Morgan, 1970, p. 130) as: alkalinity = $[HCO_3^-]_{total} + 2[CO_3^=]_{total} + [OH^-] - [H^+]$, where square brackets denote concentrations.

water-Natrona county line (fig. 1). Much of the following section draws on the excellent stratigraphic descriptions of Van Houten (1964) with supplementary data of our own.

The Wagon Bed Formation conformably overlies the Wind River Formation (lower Eocene) and is unconformably overlain by the White River Formation (Oligocene). Volcanic detritus of acid to intermediate composition is abundant in these formations and was derived from the Yellowstone-Absaroka volcanic field in northwest Wyoming (Van Houten, 1964).

Van Houten (1964) recognized five lithologic units in the Wagon Bed Formation *west* of the Conant Creek anticline, and these are summarized in table 1. East of the Conant Creek anticline, for about 27 km to the eastern limit of our study area, units 2 through 5 are not recog-

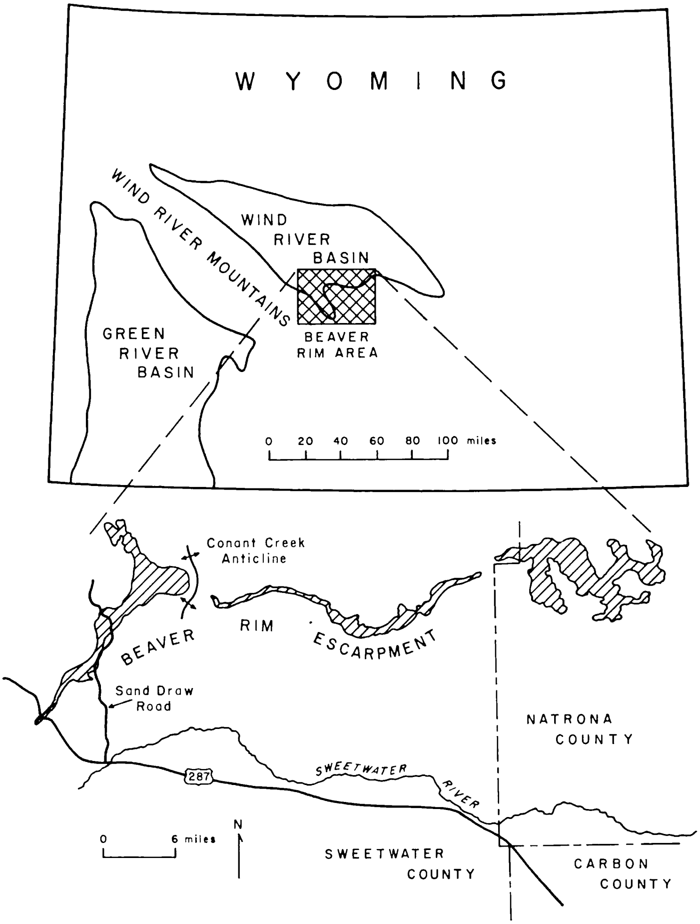


Fig. 1. Location map of Wagon Bed Formation along Beaver Rim escarpment, southern Wind River Basin, Wyoming.

TABLE 1

Stratigraphy and depositional environments of the Wagon Bed Formation (modified after Van Houten, 1964)

Unit	Thick (meters)	Lithologies (listed in approximate order of abundance)	Sedimentary Structures	Mega Fossils	Depositional Environments
5	0-64	sandstone conglomerate siltstone claystone tuff	cross-bedding scour channels lag deposits	turtle bones	fluvial channel and flood plain
4	30-55	tuff claystone siltstone sandstone carbonate oil shale	thin bedding laminations flat-pebble conglomerate	Gar scales turtle bones nonmarine gastropods & pelecypods	lacustrine
3	30-60	tuff sandstone siltstone lignite	ripple cross-lamination cross-bedding channels	catfish bones	mixed fluvial and lacustrine
2	15-50	siltstone claystone conglomerate sandstone	channels lag deposits	petrified wood	flood plain and fluvial channel
1	3-6	claystone (kaolinitic, in part) sandstone	root casts burrows		paleosoil

nized. Unit 1 is similar in thickness and lithology to outcrops on the west side of the anticline. In the eastern area, the Wagon Bed Formation consists of a 75 to 85 m thick poorly-exposed sequence of sandstone, conglomerate lenses, poorly sorted mudstone, and vitric tuffs (Van Houten, 1964). Some of the tuffs are up to a meter thick and are probably equivalent to tuffs of unit 3 to the west of the anticline. The Wagon Bed Formation in these easterly outcrops represents mixed fluvial-flood plain deposits, similar to the deposits of unit 2. Notably, lacustrine-like sequences, such as those found in unit 4 and parts of unit 3, are absent east of the Conant Creek anticline.

The Conant Creek anticline was clearly a topographic high during deposition of the Wagon Bed, as evidenced by the wedging out of the formation onto Paleozoic carbonates at the anticline (Van Houten, 1964). Locally, the anticline supplied detritus to the Wagon Bed Formation west of the anticline as evidenced by the presence of coarse deposits of Paleozoic detritus in the formation (Van Houten, 1964, p. 36) and a general coarsening of sediments, particularly in units 2 and 4, in the vicinity of the anticline (Van Houten, 1964, pl. 4).

Regional drainage in the Wind River Basin was in a southeasterly direction during the middle and late Eocene (Love, 1970, p. 118-119), and thus the Conant Creek anticline and the Sweetwater uplift to the south created a significant hydrologic barrier along the southern edge of the Wind River Basin (see Van Houten, 1964, p. 54). The most compelling evidence for a hydrologic barrier is that lacustrine sediments are restricted to the west side of the anticline. In addition, the Wagon Bed is at maximum thickness about 10 km west of the anticline, indicating this area was a locus of deposition.

Directional transport indicators, although sparse in the Wagon Bed, are in general agreement with the above interpretation. Transport directions in units 2 and 3 are in part toward the axis of the anticline, suggesting that the Conant Creek anticline was not a significant topographic barrier during this time (fig. 2). In contrast, cross-bedding in units 4 and the lower 10 m of unit 5 are parallel to or away from the axis of the anticline, suggesting that the anticline was a topographic barrier during deposition of these units. Symmetrical ripple marks in units 3 and 4, presumably formed by wind generated oscillatory currents in shallow water, have crest-axes orientations varying from northeast-southwest to east-west and thus are compatible with northerly source for wind-blown ash from the Yellowstone-Absaroka volcanic field.

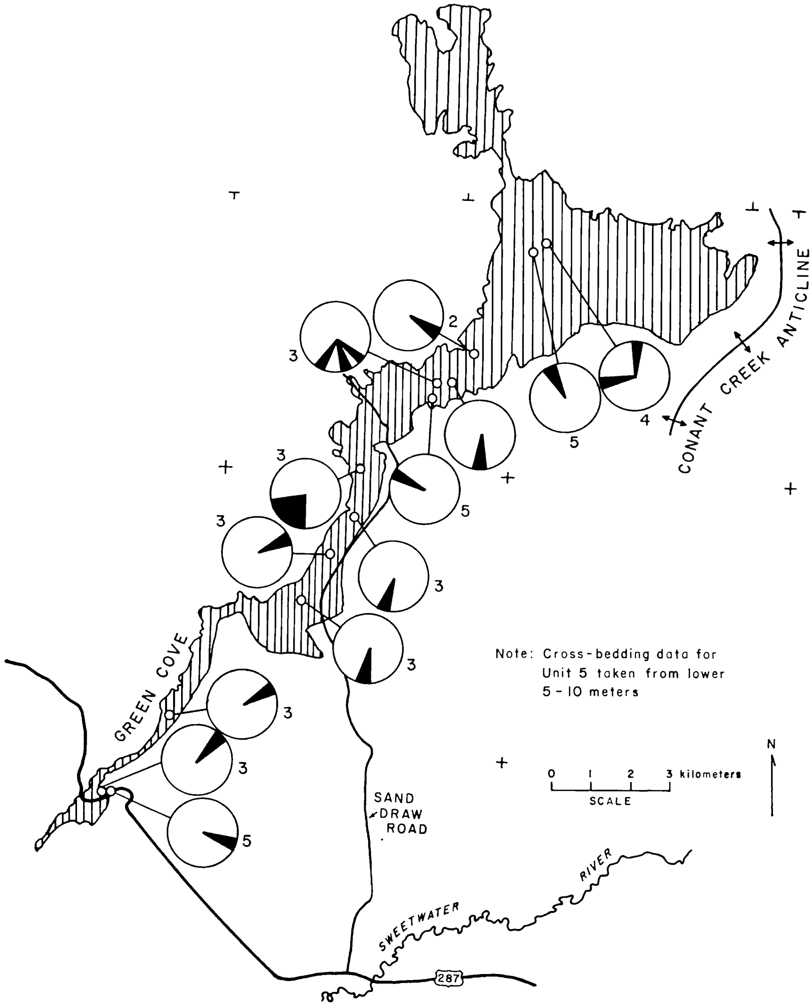
It is concluded that west of the Conant Creek anticline a lake or series of lakes began to form during deposition of unit 3, reached maximum development during deposition of unit 4, and finally disappeared during deposition of the upper part of unit 5. East of the anticline the area was generally well-drained and ponding did not occur.

AUTHIGENIC MINERALS

In the Wagon Bed, three diagenetic facies are recognized: (1) glass-smectite facies, (2) clinoptilolite (+heulandite) facies, and (3) K-feldspar–

carbonate facies. For reasons that will be discussed later, we believe that each of these facies and additional authigenic phases reflect important evolutionary stages in water chemistry during deposition of the Wagon Bed Formation. The distribution of volcanic glass and important authigenic minerals in the formation is summarized in figure 3. Details of the three diagenetic facies are discussed in the following section.

Glass-smectite diagenetic facies.—Diagnostic rocks of this facies consist of tuffaceous claystones with unaltered to partially dissolved glass shards. The shards have pale green clay rims and are set in a clayey,



Note: Cross-bedding data for Unit 5 taken from lower 5 - 10 meters

Fig. 2. Paleocurrent directions from cross laminated tuffs and sandstones in the Wagon Bed Formation. Numbers refer to Van Houten's (1964) stratigraphic units (see text). One to four measurements taken at each locality.

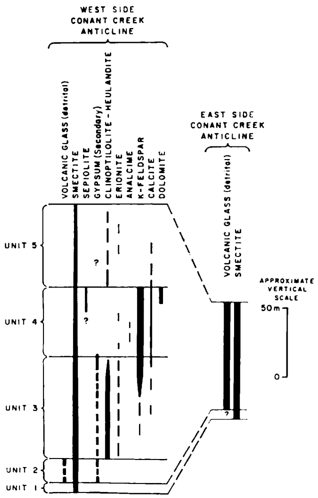


Fig. 3. Distribution of volcanic glass and important authigenic minerals in the Wagon Bed Formation. Dashed line implies mineral occurs sporadically within interval. Width of line is proportional to abundance in samples.

chiefly smectite-rich matrix. The clay matrix is presumably derived from alteration of very fine-grain ash. Crystals of zoned feldspars, chiefly plagioclase, quartz, biotite, and minor green-brown amphiboles are present in varying amounts. In some samples where the glass has been dissolved, silica was apparently precipitated as a cement of opal, chalcedony, and quartz in immediately overlying sandstone.

Clinoptilolite diagenetic facies.—Diagnostic rocks of this facies in unit 3 consist mainly of pure vitric tuffs and subordinate vitric-crystal tuffs and carbonaceous shales. In unit 5, diagnostic rocks range from tuffaceous sandstones to relatively pure vitric tuffs. Pyroclastic crystals consist mainly of brown biotite, subordinate plagioclase (oligoclase and andesine), and very minor amphibole. Volcanic glass in this facies has been replaced by very fine-grained clinoptilolite and/or heulandite. Minor clay is present in the matrix and as 5 to 10 μm rims about shard pseudomorphs. X-ray diffraction of the less than 2 μm size fraction separated from clinoptilolite and heulandite-rich tuffs indicate that the clay is dominantly a smectite, which expands to 17 Å upon glycolation. Some tuffs also contain a series of low intensity peaks from 24 to 17 Å after glycolation indicating the presence of interstratified clays, possibly illites, in these samples.

Heulandite,[2] the aluminous and usually calcium-rich end-member of the heulandite group, has not been reported from lacustrine environ-

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[2] We have distinguished heulandite from clinoptilolite by examining the intensity of the (020) lattice spacing on X-ray diffractograms before and after heating for 15 hrs at 450°C (see Boles, 1972). For the purpose of this paper, we classify a sample as clinoptilolite if greater than 50 percent of the original (020) peak intensity remains after heat treatment; as heulandite if the (020) peak is destroyed by the test; and as an intermediate composition phase if the (020) peak persists at less than 50 percent original intensity after the test. Samples of "intermediate" composition may also *represent* mixtures of heulandite and clinoptilolite.

TABLE 2
Anhydrous unit cell contents (72 oxygen) of zeolites from the Wagon Bed Formation. Compositions determined by electron microprobe.

	1	2	3	4	5	6	7	8
Si	29.12	29.20	29.40	27.83	27.54	28.07	28.26	28.62
Al	6.89	6.86	6.70	8.20	8.35	8.06	7.82	7.80
Ca	1.85	1.55	1.74	2.55	3.12	2.45	1.71	1.21
Mg	0.55	0.74	0.63	0.73	0.66	0.67	0.48	0.46
K	1.31	1.09	1.05	0.64	0.56	0.57	2.80	2.34
Na	0.76	0.96	0.56	0.86	0.67	0.76	0.31	0.43
Si/Al	4.23	4.26	4.39	3.39	3.30	3.49	3.61	3.67
Σ Na+K+ 2(Ca+Mg)	6.87	6.63	6.35	8.06	8.79	7.57	7.49	6.11
Sign of elongation mounted in Canada balsam or heated	slow to nearly isotropic			fast	fast	fast	slow	slow
birefringence	← ≤.005 →			← .010-.015 →				

Analyses 1, 2, 3: clinoptilolite, sample DE 151; analyses 4, 5, 6: heulandite, sample DE 185; analyses 7, 8: erionite, sample DE 151. Calculated on basis of 72 oxygen anhydrous unit cell.

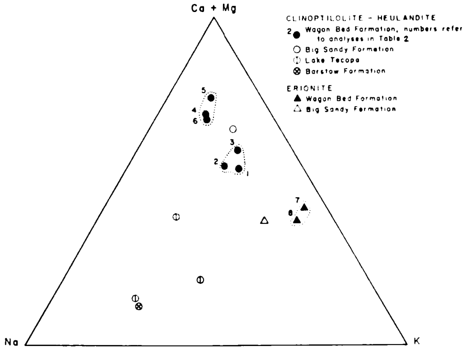

Fig. 4. Atomic proportions Ca + Mg, Na, and K in clinoptilolite, heulandite, and erionite from the Wagon Bed Formation (this paper). For comparison, zeolites from lacustrine rocks of Lake Tecopa, Big Sandy Formation, and Barstow Formation are shown (see Sheppard and Gude, 1968, 1969, 1973a).

ments to date, even though it is a common alteration product in marine sedimentary sequences (see Seki and others, 1969; Boles and Coombs, 1975). Heulandites and calcium-rich clinoptilolites are common in the Wagon Bed Formation.

Tests on 45 samples from the Wagon Bed Formation indicate that 36 percent are clinoptilolites, 42 percent are of intermediate composition, and 21 percent are heulandites. Table 2 gives spot EMA analyses of clinoptilolite and heulandite in two samples, confirming that the thermally stable samples are clinoptilolites and thermally unstable samples are heulandites (see classification scheme of Boles, 1972). The analyzed clinoptilolite has more divalent exchangeable cations, chiefly calcium, than monovalent cations (see fig. 4). Based on the thermal stability and chemical analyses described here, calcium is the dominant exchangeable cation in most samples of heulandite and clinoptilolite from the Wagon Bed Formation and the Si/Al ratio varies widely from sample to sample. In general heulandite and phases of intermediate composition appear to be more closely associated spatially with authigenic K-feldspar than is clinoptilolite.

Erionite is a relatively common minor constituent of the clinoptilolite diagenetic facies. At a few localities (for example, Van Houten, 1964, stratigraphic secs. 20 and 26), erionite is estimated to make up 30 to 50 percent of the total zeolite phase in altered tuffs. In hand specimens and thin section, erionite commonly occurs as needle-shaped crystals lining cavities and fractures in clinoptilolite-bearing tuff, suggesting it formed later than the bulk of the zeolites in the rock. In this tuff the erionite crystals have grown on clinoptilolite crystals (see table 2, analyses 1, 2, 3) and are therefore presumably later. The Wagon Bed erionites have lower Si/Al ratios and distinctly higher K/Ca+Mg ratios than coexisting clinoptilolite (see table 2 and fig. 4). A similar trend of potassium enrichment occurs between clinoptilolite and later-formed erionite in the Big Sandy Formation (see fig. 4).

K-feldspar–carbonate diagenetic facies.—The K-feldspar–carbonate diagenetic facies occurs throughout unit 4 and in the upper part of unit 3. Diagnostic rocks of this facies include altered vitric tuffs, tuffaceous sandstones, siltstones, claystones, carbonaceous shales, and bedded alkaline earth carbonates.

K-feldspar is most abundant in altered vitric tuffs in the upper part of unit 3 and in thin-bedded claystones of unit 4. Within unit 3, K-feldspar is commonly associated with the coarser-grained tuffs and tuffaceous sandstones. In contrast to the clinoptilolite facies, shard textures are poorly preserved or absent in K-feldspar bearing rocks. The K-feldspar forms an extremely fine-grained mosaic of crystals commonly less than 5 μm in diameter. Proportion and types of pyroclastic crystals are similar to those in tuffs of the other diagenetic facies suggesting that the original unaltered ash from all facies was similar.

Calcite[3] cement is commonly associated with K-feldspar in siltstones, mudstones, and sandstones of this facies but is comparatively rare in the clinoptilolite facies. In testing field samples with acid, we found that 60 percent of 55 K-feldspar bearing samples contain calcite, whereas only 6 percent of 116 clinoptilolite-bearing samples contain calcite. Calcite is very rare in K-feldspar bearing vitric tuffs in the upper part of unit 3.

Bedded dolomite and subordinate limestone occur in the upper part of unit 4, and at several localities these carbonates contain rip-up flat pebbles (up to several centimeters across) of clayey micrite and micrite. In thin section, much of the bedded fine-grained carbonate contains clasts of quartz, feldspars, and mica, organics, hematite, micrite, clay pellets, and sometimes oolites, and carbonate plates (shell fragments?). These detrital grains are set in an authigenic micrite matrix with patches of sparry carbonate in cavities. The rip-up clasts and the abundance of fine-grained detrital components in these carbonates suggest that during flooding the clasts were washed from a fringing mud flat into the adjacent lake, similar to the depositional environment ascribed to the Wilkins Peak Member of the Green River Formation by Eugster and Hardie (1975). Some of this detrital carbonate is probably also from reworked Paleozoic carbonates.

Preliminary studies of clay minerals in K-feldspar tuffs in the upper part of unit 3 indicate similar types of clays as found in the clinoptilolite facies, that is dominantly smectite, minor mixed-layer clays. A notable difference was found within the thin-bedded part of unit 4, where a light grayish-green waxy claystone contains coexisting K-feldspar and sepiolite. The sepiolite is a poorly crystalline variety, similar to that described by Caillere and Henin (1961). Similar appearing rocks occur elsewhere in the upper part of unit 4, and therefore sepiolite may be relatively common in this part of the section.

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[3] The $d_{(104)}$ spacing of the calcites indicates they have less than 3 mole percent magnesium (compare Goldsmith and Graf, 1958).

Analcime has only been found at Van Houten (1964) stratigraphic sections 22 and 23, where it occurs in two thin beds of tuffaceous siltstone. The analcime is disseminated in the matrix but also occurs as relatively coarse-grained crystals (up to 100 μm across) in cavities. The analcime coexists with K-feldspar and calcite. In contrast to the Wagon Bed Formation, analcime is a common phase in numerous saline–alkaline lacustrine environments (see Sheppard and Gude, 1968, 1969, 1973a; Surdam and Parker, 1972).

CHEMISTRY OF TUFFS

Table 3 gives partial bulk chemical analyses of vitric and altered vitric tuffs from the three diagenetic facies. The low subtotals in analyses 1 through 8 are largely explained by the abundance of water-rich authigenic phases in these samples. The relatively high potassium content of analysis 8 in table 3 is attributed, in part, to the abundance of pyroclastic biotite in this sample. Figure 5 shows that the tuffs are chemically similar to rhyolites or rhyodacites. Most samples are deficient in alkalies, particularly the clayey and zeolitic tuffs, compared with average rhyolites and dacites.

On an anhydrous basis, the average composition of tuffs from the three facies are similar, except for calcium, sodium, and potassium contents. High calcium reflects the presence of calcium-rich zeolites, whereas high potassium reflects the presence of authigenic K-feldspar. These differences in tuff chemistry must reflect interchange of elements between pore fluids and solid phases.

TIMING OF AUTHIGENIC SILICATE REACTIONS

The formation of K-feldspar or clinoptilolite has not been documented at the sediment-water interface of modern lakes. Hay (1966, p. 76) points out that youngest K-feldspar recognized is perhaps that found at Searles Lake with an estimated age of 60,000 to 100,000 yrs. The youngest reported occurrences of clinoptilolite are at Teels Marsh, Nev. in altered ashes less than about 10,000 yrs old (Hay, 1966) and at Lake Magadi, East Africa in beds 9100 yrs old (Surdam and Eugster, 1976).

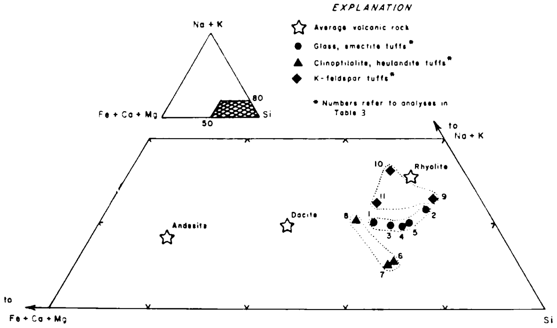

Fig. 5. Comparison between composition of tuffs from the Wagon Bed Formation and world averages of volcanic rocks (Nockolds, 1954).

At these localities only traces of clinoptilolite have been found. Erionite is commonly found as an abundant phase in the modern muds at Lake Magadi (Surdam and Eugster, 1976), but phillipsite is usually the most common zeolite found at the sediment-water interface in these types of environments (see Hay, 1966). From the above we conclude that clinoptilolite and K-feldspar did not form at the sediment-water interface in the Wagon Bed Formation.

RELATIONSHIP BETWEEN DIAGENETIC FACIES AND DEPOSITIONAL ENVIRONMENT

A number of workers have found relationships between authigenic mineral occurrences and depositional environment (for example, Hay, 1966; Sheppard and Gude, 1968, 1969, 1973a; Surdam and Parker, 1972). These studies also have emphasized the importance of fluid chemistry in controlling the alteration of glass to zeolites and zeolites to K-feldspar. In all these cases the most extreme alteration of glass (glass→zeolite→ K-feldspar) is associated with waters inferred to have the highest salinities and alkalinities, whereas unaltered glass is found only in the freshest waters. Perhaps one of the best documented sequences is at Pleistocene Lake Tecopa where fresh glass and clay are found at the margin of the lake associated with fresh-water diatoms and ostracods, and halite, trona, and molds of other salts are mainly associated with K-feldspar in the central part of the lake (Sheppard and Gude, 1968). In the Lake Tecopa deposits zeolites occupy an intermediate position between these two extremes.

The authigenic mineral distribution pattern in the Wagon Bed Formation can be related to the depositional environment of Wagon Bed sediments. In the fluvial and flood plain environments, where ground water presumably was relatively fresh, glass underwent only minor alteration to smectite during subsequent burial and diagenesis. In the lacustrine and in part fluvial-flood plain sediments volcanic glass was altered chiefly to clinoptilolite and heulandite. In the most obvious lacustrine sediments, glass was altered to K-feldspar through an intermediate zeolite. We will later suggest that this intermediate phase was clinoptilolite.

During the lake's history, waters were sufficiently concentrated to precipitate alkaline-earth carbonates both in the lake and on fringing mud flats. However, the salinity of the lake never evolved to the precipitation of saline (for example, calcium or sodium sulphate) or saline alkaline minerals (for example trona).

HYDROLOGY OF WAGON BED FORMATION

Importance of brines to diagenetic reactions.—The close relation between depositional environment and diagenetic facies suggests that fluid chemistry was a significant control on diagenetic reactions. Increasing temperature and pressure due to burial are relatively negligible controls on diagenetic reactions in the Wagon Bed Formation owing to the thinness of the stratigraphic section. Van Houten (1964) and J. D. Love (personal commun., 1968) concur that maximum burial depth is less than 600 m. Furthermore the least altered tuffs occur at the base of the Wagon Bed, opposite to what would be expected from burial metamorphic trends.

The importance of interstitial fluid chemistry is apparent from comparing bulk chemistries of altered vitric tuffs (table 3). Relative abundance of various pyroclastic crystal components suggests these tuffs were initially of similar bulk composition. Figure 6 illustrates the differences in proportions of sodium, potassium, and calcium in these altered tuffs from the three diagenetic facies. Obviously if the tuffs initially were of similar composition, they have undergone considerable interaction with interstitial fluids. If clinoptilolite tuffs represent an intermediate stage in the alteration of volcanic glass to K-feldspar, initial alteration of glass to clinoptilolite would tend to increase the Na/Ca ratio of the pore fluid relative to potassium, whereas alteration of clinoptilolite to K-feldspar would mainly increase the Ca/K ratio of the pore fluid, relative to sodium.

CONSTRAINTS ON LAKE WATER CHEMISTRY

Formation of clinoptilolite.—Theoretical considerations show that zeolites are favored over clays by relatively high alkali ion to hydrogen ion activity ratios and by relatively high silica activities (see Garrels and Christ, 1965). The general absence of authigenic carbonates in the clinoptilolite diagenetic facies suggests the pore fluids were undersaturated with respect to calcite and dolomite. In other words, the pH of the interstitial solutions, assuming equilibrium with atmospheric P_{CO_2} ($10^{-3.5}$ atm), was probably less than 8.5 (see Garrels and Christ, 1965).

Fluid compositions in which clinoptilolite has formed are reasonably well known in deep-sea sediments. Recent data show that deep-sea clinoptilolites strongly fractionate potassium relative to other exchangeable ions (Boles and Wise, 1978). Relative to potassium, sodium in the crystalline phase is lower by a factor of about 80, calcium by about 50, and magnesium by about 55 from the ionic proportions found in the interstitial fluids. We do not know how applicable these fractionation factors are to other environments, but we believe they may be a useful guide to fluid compositions in the absence of better data. Apply-

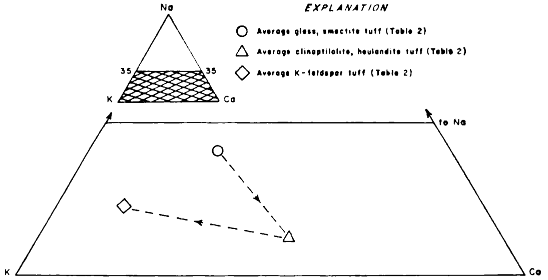

Fig. 6. Comparison of relative proportions of Ca, Na, and K in tuffs of the Wagon Bed Formation. Data from table 2. Arrows show direction of change in bulk composition with alteration of glass to zeolite to K-feldspar.

Table 3

Chemical analyses* of tuffaceous rocks from the Wagon Bed Formation

	Fresh glass-smectite tuffs					Average anhydrous vitric tuffs	Clinoptilolite tuffs			Average anhydrous clinoptilolite tuff	K-feldspar tuffs			Average anhydrous K-feldspar tuff
	1	2	3	4	5		6	7	8		9	10	11	
SiO_2	59.3	66.1	61.5	63.7	67.0	73.6	63.0	60.0	60.5	73.1	71.5	65.7	67.6	74.2
Al_2O_3	14.9	11.0	12.8	13.4	12.3	14.9	12.0	12.9	12.8	15.1	11.5	13.2	11.9	13.3
Fe_2O_3**	2.9	1.4	2.8	2.2	2.7	2.8	2.4	1.1	2.6	2.3	1.2	2.6	3.4	2.6
MgO	1.7	0.5	1.0	1.0	0.6	1.2	1.1	1.3	1.4	1.6	0.8	0.4	1.7	1.1
CaO	2.0	1.5	1.8	2.1	1.6	2.1	3.0	4.0	3.5	4.2	0.9	1.2	1.4	1.3
Na_2O	2.0	2.1	2.1	1.8	1.6	2.2	0.9	0.4	0.4	0.7	0.6	2.2	1.3	1.5
K_2O	2.6	3.3	2.3	2.6	3.1	3.2	1.6	1.8	4.3	3.1	5.5	6.0	4.9	6.0
Total	85.4	85.9	84.3	86.8	88.9	100.0	84.0	81.5	85.5	100.1	92.0	91.3	92.2	100.0

* Analyst: J. Murphy. Method: HF digestion and atomic absorption analysis.

** Total iron

ing the above factors to a Wagon Bed clinoptilolite (average of analyses 1 through 3, table 2), we calculate that the mole proportions of K/Na/Ca/Mg in the pore fluids may be about 1/53/75/31.

Jones (1965) has studied the evolution of closed basin waters at Deep Springs Lake, Calif., and found that the alkali/alkaline-earth ratio, pH, and total salinity increased with progressive evaporation from the mountains to the lake (fig. 7). Jones has shown that the decrease in alkaline earths with evaporation is due mainly to early precipitation of alkaline-earth carbonates. Hardie and Eugster (1970) showed by modeling evaporation of natural waters that early precipitation of alkaline earths will increase the alkali/alkaline earth ratio. The calculated alkali/alkaline earth ratio of pore fluids from which clinoptilolite crystallized in the Wagon Bed Formation (log Na+K/Ca+Mg = −0.3) suggests that pore fluids were relatively dilute and only slightly alkaline if the Deep Springs water can be used as an analogy (fig. 7).

In a similar way, using the composition of a clinoptilolite from Lake Tecopa (Sheppard and Gude, 1968, p. 15) and the above fractionation factors, we calculate a log Na+K/Ca+Mg value of +0.9 for pore fluids from which clinoptilolite formed at Lake Tecopa. This suggests the Lake Tecopa clinoptilolite formed in more concentrated brines than clinoptilolite in the Wagon Bed Formation (see fig. 7). This conclusion is in

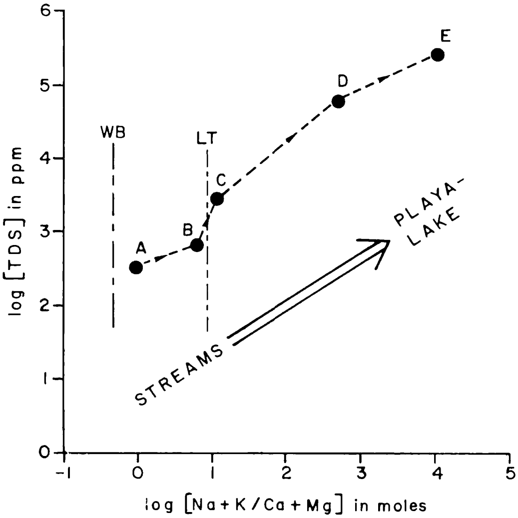

Fig. 7. Change in alkali/alkaline-earth ratio with total dissolved solids (TDS) of waters from Deep Springs Lake area (data from table 7 of Jones, 1965).

A = average of 53 waters with TDS <500 ppm, average pH = 7.7; B = average of 17 waters with TDS 500 to 1000 ppm, average pH = 7.9; C = average of 11 waters with TDS 1000 to 10,000 ppm, average pH = 8.3; D = average of 8 waters with TDS 10,000 to 100,000 ppm ppm, average pH = 9.1; E = average of 29 waters with TDS >100,000 ppm, average pH = 9.4; Vertical dashed lines are estimated compositions of waters from which clinoptilolite formed for the Wagon Bed Formation (WB) and Lake Tecopa (LT). See text for calculation procedure.

agreement with field observations as Lake Tecopa zeolites are associated with calcite and molds of gaylussite and/or pirssonite (hydrated $CaCO_3 \cdot Na_2CO_3$), whereas only sparse calcite is associated with Wagon Bed zeolites.

Heulandite is more commonly associated with sandy volcanoclastic units than clinoptilolite. Surdam and Stanley (1979) have shown that similar clastic wedges in the Green River Formation represent flooding periods. We believe these coarser facies in unit 3 of the Wagon Bed represent periods of influx of very fresh water into the lake. If so, alkali/alkaline earth ratios were probably lower in the lake waters during influx of the clastic sediments. Heulandites, owing to their relatively low Si/Al ratios, require lower alkali/alkaline earth ratios in the zeolite structure (see Boles, 1972). We speculate that heulandite formed, rather than clinoptilolites, in sediments affected by the fresher water influxes.

Reaction of clinoptilolite to K-feldspar.—A reaction that can be inferred in the upper part of unit 3 in altered tuffs is the conversion of calcium-rich clinoptilolite or heulandite to K-feldspar. Evidence supporting the zeolite→K-feldspar reaction in the tuffaceous rocks along the Beaver Rim is that in the rocks of unit 3 there is a reciprocal relation between clinoptilolite–heulandite and K-feldspar. Clinoptilolite or heulandite coexists with K-feldspar in a number of altered tuffs, suggesting that neither mineral is associated with specific glass compositions. K-feldspar tuffs represent a more advanced state of reconstitution than clinoptilolite tuffs as evidenced by the more complete destruction of relict shard texture and in some cases crystal components. Sheppard and Gude (1969, 1973a) have recognized K-feldspar replacement of clinoptilolite in thin sections of altered tuffs from other lacustrine environments.

The average clinoptilolite composition of table 2 is about $Na_{0.8}K_{1.2}Mg_{0.6}Ca_{1.7}Al_{6.6}Si_{29.4}O_{72} \cdot 24H_2O$ and for heulandite is about $Na_{0.8}K_{0.6}Mg_{0.7}Ca_{2.7}Al_{8.2}Si_{27.8}O_{72} \cdot 24H_2O$ (water content calculated from Boles, 1972, p. 1471). The reaction of clinoptilolite to K-feldspar (reaction 1) or heulandite to K-feldspar (reaction 2) is as follows:

$$5.4K^+ + \text{clinoptilolite} \rightarrow 6.6\ \text{K-feldspar} + 24\ H_2O + 0.8\ Na^+ + 0.6\ Mg^{++} + 1.7\ Ca^{++} + 9.6\ SiO_2 \qquad (1)$$

$$7.6K^+ + \text{heulandite} \rightarrow 8.2\ \text{K-feldspar} + 24\ H_2O + 0.8\ Na^+ + 0.7\ Mg^{++} + 2.7\ Ca^{++} + 3.2\ SiO_2 \qquad (2)$$

Both reactions are driven to the right by decreasing water activities, thus increasing salinity of pore fluids would facilitate K-feldspar crystallization. In addition, increasing the activity of K^+ would also favor the formation of K-feldspar.

Experimental studies have shown that zeolites are converted to K-feldspar or zeolites with low silica/alumina ratios when reacted with alkaline solutions (Sheppard and Gude, 1969; Mariner and Surdam, 1970; Boles, 1971). Studies of ancient lacustrine environments infer that pore fluids associated with K-feldspar tuffs were more alkaline than those associated with zeolitic tuffs (for example, Sheppard and Gude, 1968, 1969, 1973a; Surdam and Parker, 1972), and in cases where K-feldspar is associated with trona, it is believed that pH was 9 or greater.

The absence in the Wagon Bed of minerals indicative of saline–alkaline water, such as trona or gaylussite, suggests that this lake never became as concentrated or as alkaline as deposits such as the Green River Formtion or the Lake Tecopa rocks. Furthermore, K-feldspar tuffs in the upper part of unit 3 are depleted in calcium ion relative to clinoptilolite–heulandite tuffs (see fig. 6 and table 3), suggesting that calcium ion was mobile.

Calcite is relatively insoluble at high pH, for example at a pH of 9 or greater the calcium concentration of a fluid in equilibrium with calcite at 25°C, 1 atm total pressure, is less than 2 ppm (see Drever, 1972). Thus, the absence of calcite in K-feldspar tuffs in the upper part of unit 3 and the removal of calcium are inconsistent with highly alkaline conditions.

We have calculated the amount of calcium released from reactions (1) and (2) by assuming a tuff contains 60 percent clinoptilolite–heulandite by volume (density 2.2) and 30 percent pore fluid with no initial calcium in solution. If the zeolite is completely reacted to K-feldspar then the pore fluid would have a calcium concentration of 83,000 ppm [average value of reactions (1) and (2)], assuming all calcium is retained in the fluid. Such a pore fluid would be about two orders of magnitude oversaturated with calcite at a pH as low as 6.5 and P_{CO_2} as high as 10^{-1} (see Drever, 1972).

The movement of pore fluids as indicated by the mobility of calcium and potassium ions prevented calcium concentrations from reaching the calculated values. The actual concentration for a given time interval would depend on the rate at which reaction (1) or (2) proceeds and the volume of fluid that moves through the rock during the interval. Figure 8 graphically depicts this relationship for the previous example and shows if 1 square meter of tuff completely reacted in 100 yrs, a flow rate of 10^5 cc/yr would have to be maintained in order to dilute the calcium concentrations to less than 1 ppm. The maximum reaction time, which is the age of the Wagon Bed Formation (about 45 m.y.), would require addition of at least 70 cc/yr of H_2O in order to maintain calcium at less than 1 ppm. Assuming 1000 ppm Ca as an upper limit, figure 8 shows that a probable minimum of 1 cc/yr of H_2O had to pass through the rock. The higher the $CO_3^=$ concentration in the pore fluid the greater the flow rate must be in order to maintain calcium concentrations below calcite saturation.

The vertical zonation of mineral facies in these rocks suggests that large scale vertical fluid movements have not occurred. Large scale horizontal fluid movement, however, cannot be ruled out. We believe the failure of calcite to crystallize upon the breakdown of a calcium zeolite to K-feldspar indicates conditions were not highly alkaline, and the reaction probably occurred at a pH less than 9. Some K-feldspar tuffs of unit 4 contain calcite suggesting conditions may have been more alkaline in those beds.

Composition of K-feldspar.—Authigenic K-feldspars from saline–alkaline environments have unusually high boron contents, with average values ranging from 950 to 3400 ppm (Sheppard and Gude, 1973b). The lowest average value is from the Pliocene Big Sandy Formation, where bedded saline deposits are absent, but crystal molds resembling gaylussite are present (Sheppard and Gude, 1973a). The high boron content of the feldspars is apparently inherited from the high boron content of concentrated pore fluids.

The maximum boron content in four K-feldspars from the Wagon Bed Formation has been calculated from the weight percent K_2O and B_2O_3 in the whole rock samples and by assuming all K_2O and B_2O_3 is in the K-feldspar. The maximum boron content in the samples is 190, 560, 790, and 890 ppm. These values are, in general, significantly less

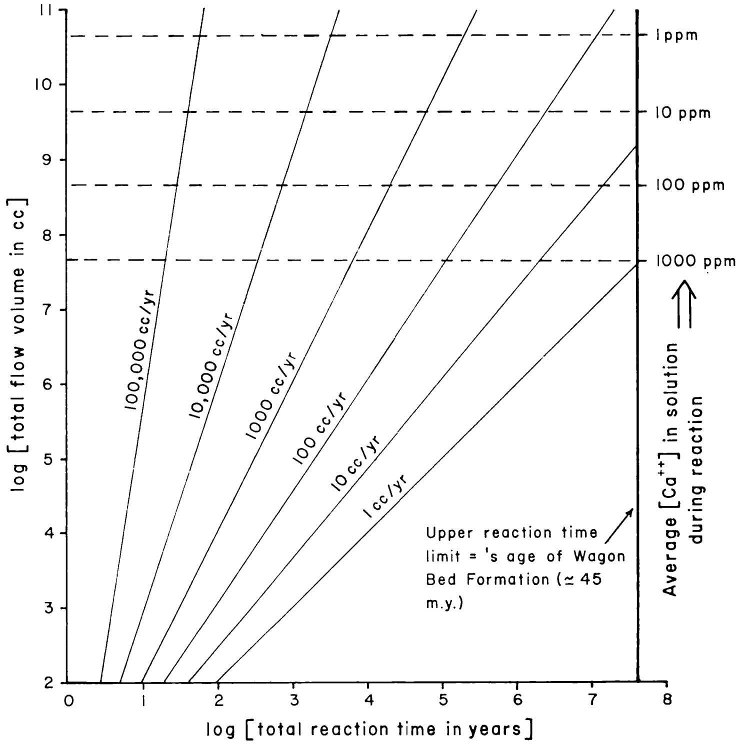

Fig. 8. Relationship between total flow volume, flow rate, total reaction time, and calcium concentration in solution for conversion of clinoptilolite–heulandite tuff to K-feldspar tuff. Calculations based on one square meter of tuff with 60 percent by volume clinoptilolite–heulandite and 30 percent by volume pore fluid. Initial pore fluid assumed to contain no calcium and pore volume remains constant. Zeolite converted to K-feldspar by reactions (1) and (2) in text.

than found by Sheppard and Gude (1973b) and suggest that K-feldspars in the Wagon Bed Formation did not form in strongly saline–alkaline solutions.

Smectite, sepiolite, and K-feldspar equilibria.—In the upper part of unit 4 there is an inferred reaction of smectite + silica to sepiolite + K-feldspar. There is no textural evidence for this reaction, aside from the fact that a bed of sepiolite + K-feldspar is in a sequence of beds containing smectite, quartz, and sometimes K-feldspar.

The composition of smectites in Beaver Rim sediments is not known. Assuming the composition of a smectite from altered rhyolitic and andesitic tuff described by Kerr and others (1950), and for simplicity assuming the smectite is potassium-rich and iron-free, we can place constraints on the pore fluid chemistry using the above reaction. The reaction is as follows:

$$\begin{aligned} K^+ + \text{potassium-rich smectite} + 1.25\ H_4SiO_4 \rightarrow H^+\ 2.5\ H_2O\ + \\ 1.5\ \text{K-feldspar} + 0.25\ \text{sepiolite} \end{aligned} \qquad (3)$$

where potassium-rich smectite has a composition of $K_{0.5}Al_{1.5}Mg_{0.5}Si_{4.0}O_{10}(OH)_2$ and sepiolite $Mg_2Si_3O_6(OH)_4$.

Standard free energies of formation for K^+, H_4SiO_4, H_2O, K-feldspar, and sepiolite are −67.7, −312.5, −56.69, −896.3, and −1020.5 kcal/mole (see Tardy and Garrels, 1974). Using the method of Tardy and Garrels (1974) for calculating free energies, a value of −1253.9 kcal/mole is calculated for potassium smectite.

The free energy change for reaction (3) in the standard state is +0.5 kcal/mole of reaction. It should be noted that the value of −1020.5 kcal/mole for sepiolite is based on a well-crystallized sepiolite. Free energy changes as much as 3.8 kcal/mole more positive have been calculated from solubility experiments on poorly crystalline sepiolite (Wollast, Mackenzie, and Bricker, 1968; Christ, Hostetler, and Siebert, 1973). The sepiolite in the Wagon Bed Formation is poorly crystalline and hence the standard free energy change for reaction (3) may be closer to +1.4 kcal.

The equilibrium constant for reaction (3), with the assumption that H_2O and solid phases have unit activities, is $K_{(3)} = a_{H^+}/a_{K^+}(a_{H_4SiO_4})^{1.25}$, which can be expressed as $\log a_{K^+}/a_{H^+} = -1.25 \log a_{H_4SiO_4} - \log K_{(3)}$. The value of $\log K_{(3)}$ ranges from about −1.0 for poorly-crystalline sepiolite to −0.37 for well crystallized sepiolite at 298°K (25°C) and 1 atm pressure according to the expression $\Delta G°_R = -1.364 \log K$.

Figure 9 shows the equilibrium relationships between the phases as a function of $\log a_{K^+}/a_{H^+}$ and $\log a_{H_4SiO_4}$. Also plotted are some average water compositions from the Deep Springs playa area assuming concentrations are equal to activities (Jones, 1965). Progressive concentration of waters would stabilize K-feldspar and sepiolite relative to potassium smectite. Most natural waters are saturated with respect to quartz (approx 10 ppm SiO_2), and the presence of detrital and authigenic quartz in the Wagon Bed Formation suggests a minimum $\log H_4SiO_4$ value of about

—3.8. Some of the most extreme dissolved silica concentrations are in saline–alkaline lakes where values as high as 1000 ppm SiO_2 (that is for total silica as H_4SiO_4, log $H_4SiO_4 = -1.77$) or greater have been reported (Jones, Rettig, and Eugster, 1967). We consider this value to be an upper limit of dissolved silica in the Wagon Bed Formation. Silica values were probably less than this judging from the fact that sodium carbonate salts are precipitating in lakes where extreme dissolved silica concentrations are found.

From the above analysis, and the upper line in figure 9, we conclude that pore fluids present during formation of K-feldspar and sepiolite locally exceeded log $[K^+]/[H^+]$ values of about 3.2 but more likely exceeded about 5. The calculations show that at pH values ranging from 7 to 9, potassium activities could have been relatively low (10^{-4} to 10^{-2}) to stabilize K-feldspar–sepiolite assemblages with respect to potassium smectite. The absence of sepiolite at many localities in the upper part of unit 4 may be due to the presence of dolomite, a possible magnesium sink.

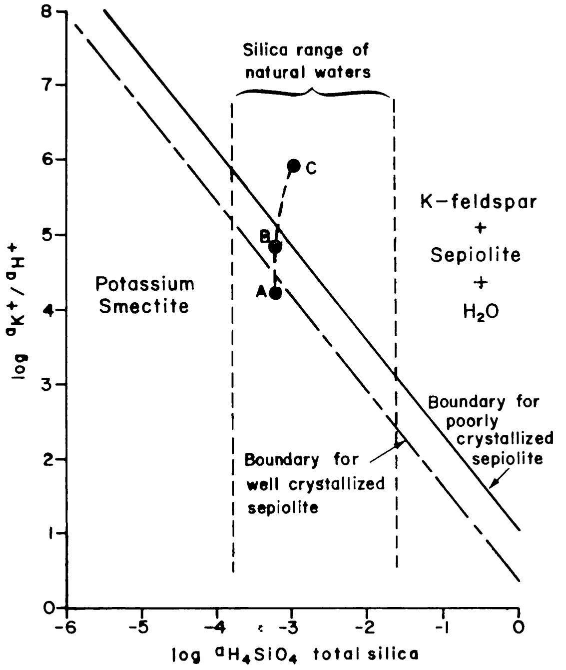

Fig. 9. Potassium smectite and K-feldspar + sepiolite equilibria as a function of log a_{K^+}/a_{H^+} and log $a_{H_4SiO_4}$ (total silica) at 1 atm total pressure, 25°C. Solids and H_2O assumed to have unit activities. See text for calculations. Points A, B, and C are average water compositions from Deep Springs Lake area, arrows in direction of increasing salinity (see fig. 7).

EVOLUTION OF HYDROCHEMISTRY

In a number of Tertiary lakes, for example Eocene Lake Gosiute (Green River Formation) and Pleistocene Lake Tecopa, K-feldspar altered tuffs are associated with sodium carbonate saline minerals and hence are inferred to have been characterized by highly alkaline conditions. Modern examples of such lakes commonly show pH above 9 and sometimes exceeding 10 (Jones, Rettig, and Eugster, 1967). In this regard, the Wagon Bed lake was apparently less alkaline than these lakes owing to differences in chemistry of influx waters. The formation of the Wagon Bed lake and its inferred restricted outflow was largely due to the Conant Creek anticline which blocked easterly drainage. Weathering and erosion of Mesozoic and Paleozoic sediments progressively exposed by uplift of the anticline may have largely controlled the chemistry of influx waters.

The Wagon Bed onlaps Madison limestone outcrops (Mississippian) at the Conant Creek anticline (see Van Houten, 1964). The sequence once overlying the Madison consists of about 240 m of Paleozoic sediments, approximately half of which are limestone and dolomite (Keefer and Van Lieu, 1966). The overlying Mesozoic section is 2700 m thick, and the upper 2100 m is largely Cretaceous shales (Van Houten, 1964). This post-Mississippian section was removed mainly during Wagon Bed deposition. Although the Paleozoic-Mesozoic section exposed on the anticline represented only a local source of sediments to the Wagon Bed Formation west of the anticline, its control on groundwater chemistry may have been important owing to its proximity to the lake. Thus it is suggested that the chemistry of influx waters during unit 2 and unit 3 deposition was influenced by shaley source rocks and during deposition of unit 4 was influenced by carbonate-rich source rocks. The presence of *secondary* gypsum veins in units 2 and 3 and authigenic carbonates in unit 4 is compatible with this conclusion.

Hardie and Eugster (1970) have calculated that evaporative concentration of waters associated with shales and limestones ultimately will result in sodium chloride or possibly sodium sulphate brines. Such brines would not be strongly alkaline, as is the case for sodium carbonate brines. Thus the absence of trona or other saline minerals in the Wagon Bed Formation is due not only to the absence of intensive evaporation but may also be due to inappropriate initial water chemistry. By the same reasoning, the rarity of analcime in the Wagon Bed Formation may be due to relatively low sodium activities. Because bedded saline minerals other than calcite (and dolomite) are absent from Wagon Bed deposits, we conclude that evaporative concentration of this lake never proceeded beyond a juvenile stage. In this regard the Wagon Bed lake waters may have had compositions similar to the relatively dilute water found on the outer playa fringe of Deep Springs lake where calcite and dolomite have crystallized (see Jones, 1965).

SUMMARY

It is concluded that waters in Wagon Bed sediments were not highly alkaline (pH probably less than 9). Evidence supporting this conclusion is: (1) relatively high calcium activities as indicated by the presence of calcium-rich zeolites; (2) high mobility of calcium ion as indicated by the loss of calcium from tuffs in which calcium–zeolites reacted to form K-feldspar; and (3) absence of saline minerals indicative of alkaline waters (for example trona or other sodium carbonate phases). The relative low boron content of authigenic K-feldspar from the Wagon Bed Formation also suggests the feldspar did not form in strongly saline–alkaline waters. Although the lack of thermodynamic data on zeolite stability prevents us from making a more quantitative analysis of the Wagon Bed fluid chemistry, from the above considerations it is clear that authigenic minerals in the Wagon Bed Formation represent an example of diagenesis in a relatively dilute to saline lake.

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