

AUTHIGENIC ZEOLITES AND K-FELDSPAR IN THE ESMERALDA FORMATION, NEVADA

RICHARD J. MOIOLA, *Mobil Research and Development
Corporation, Dallas, Texas 75221.*

ABSTRACT

Zeolites (analcime, clinoptilolite, and phillipsite) and K-feldspar of authigenic origin form a stratigraphically zoned succession in the 9065-foot sequence of the Esmeralda Formation (Miocene and Pliocene) in southern Big Smoky Valley, Esmeralda County, Nevada. Analcime and K-feldspar are confined to a 500-foot zone near the base of the sequence. Clinoptilolite, usually associated with opal, occurs within a 7700-foot zone above the analcime-K-feldspar bearing beds, and phillipsite is present in a thin zone at the top of the sequence. Clinoptilolite and phillipsite occur primarily as pseudomorphic replacements of vitric material, whereas analcime generally occurs as subhedral crystals that are thought to have formed directly from vitric material. K-feldspar is present predominantly as overgrowths on detrital grains of orthoclase and plagioclase.

The zeolites and K-feldspar formed after burial under the influence of groundwater solutions, and the different zones are thought to reflect primarily differences in the composition of the subsurface water in contact with the rocks at the time of alteration. The alkalinities and salinities necessary for the formation of the zeolites and K-feldspar are attributed to the solution and hydrolysis of vitric material in the altered rocks.

INTRODUCTION

Although zeolites are among the most common authigenic silicate minerals in sedimentary and pyroclastic rocks, their presence has only recently received appropriate attention. They occur in a wide variety of rock types, both marine and nonmarine, and are especially abundant in altered tuffs and tuffaceous sandstones of Cenozoic age (*cf.* Hay, 1966). Recent studies by Deffeyes (1959), Hay (1963, 1964), Hay and Moiola (1963), and Sheppard and Gude (1964, 1968), in particular, have demonstrated that zeolites, frequently associated with K-feldspar, are very common in the Tertiary and Quaternary continental strata of the western United States. They occur primarily as alteration products of volcanic glass and form readily during diagenesis by the reaction of the glass with interstitial water, which may have originated as either meteoric water (Hay, 1962) or connate water of a saline lake (Bradley, 1929; Hay, 1964).

Zeolites and K-feldspar of diagenetic origin are also commonly present in the Late Cenozoic strata of Esmeralda County, southwestern Nevada (Moiola, 1964a,b; Robinson, 1966). They are especially abundant in the Esmeralda Formation (Miocene and Pliocene) of southern Big Smoky Valley, north-central Esmeralda County, Nevada, where they form a zoned succession.

STRATIGRAPHY AND LITHOLOGY OF THE ESMERALDA FORMATION

The Esmeralda Formation of southwestern Nevada comprises a number of predominantly sedimentary continental sequences of Late Cenozoic age which were deposited in intermontane basins similar to those now present in the Basin and Range Province (Robinson, McKee, and Moiola, 1968). In southern Big Smoky Valley the formation consists of a thick sequence of sedimentary and pyroclastic rocks which crops out over an area of approximately 40 square miles. Neither the base nor the top of the Esmeralda Formation is exposed, but it is more than 9000 feet thick and can be divided into seven distinct units, A to G, of which the lower six are conformable (Figure 1).

Tuffaceous and volcanic sandstones and siltstones, tuffaceous shales and claystones, and volcanic-pebble and sedimentary-pebble conglomerates make up the bulk of the sedimentary strata in the sequence, and the associated pyroclastic rocks consist predominantly of rhyolitic vitric and lapilli tuffs. Thin beds of limestone occur at various intervals, and a 5- to 30-foot thick layer of olivine basalt is present in the upper part of unit G. Abrupt vertical and lateral facies changes are common throughout the sequence.

Units A and B consist predominantly of coarse-grained rocks that contain a very high percentage of Precambrian-Lower Paleozoic sedimentary rock fragments, some granitic detritus and little or no volcanic detritus. The rocks of unit C have a similar composition, but are much finer-grained. In contrast, the overlying units consist of fine- and coarse-grained rocks which contain varying amounts of Precambrian-Lower Paleozoic sedimentary rock fragments, little or no granitic detritus, and an abundance of volcanic rock fragments and pyroclastic material.

Facies relationships, sedimentary structures, and fossils (freshwater molluscs, ostracods, fish) indicate that the Esmeralda Formation in southern Big Smoky Valley was deposited in an intermontane basin under alternating fluvial and lacustrine conditions. Molluscan assemblages collected at various intervals in the sequence and a potassium-argon date of 6.9 m.y. on biotite from a tuff in unit G indicate that the formation ranges from late Miocene (Barstovian and possibly Hemingfordian) to middle Pliocene (Hemphillian) in age (Robinson, McKee, and Moiola, 1968).

DISTRIBUTION OF AUTHIGENIC MINERALS

Authigenic K-feldspar and zeolites (analcime, clinoptilolite, and phillipsite) form three stratigraphic zones within the 9065-foot sequence of the Esmeralda Formation in southern Big Smoky Valley. Analcime and K-feldspar are confined to a 500-foot zone near the base of the exposed section. Clinoptilolite, usually associated with opal, occurs within a 7700-foot zone above the analcime-K-feldspar bearing beds, and phillipsite is present in a thin zone at the top of the sequence (Fig. 1).

The boundaries between the zones are distinct and do not transect bedding planes. The analcime-K-feldspar to clinoptilolite boundary is marked by a lithologic change from sandstones in unit B to shales and siltstones in unit C, and the boundary between the clinoptilolite and phillipsite zones is delineated by a slight angular unconformity between units F and G and a change from rhyolitic tuffs and tuffaceous sandstones to basaltic tuff-breccia. As a rule, individual altered beds within the various zones can seldom be traced over one-half mile laterally because of

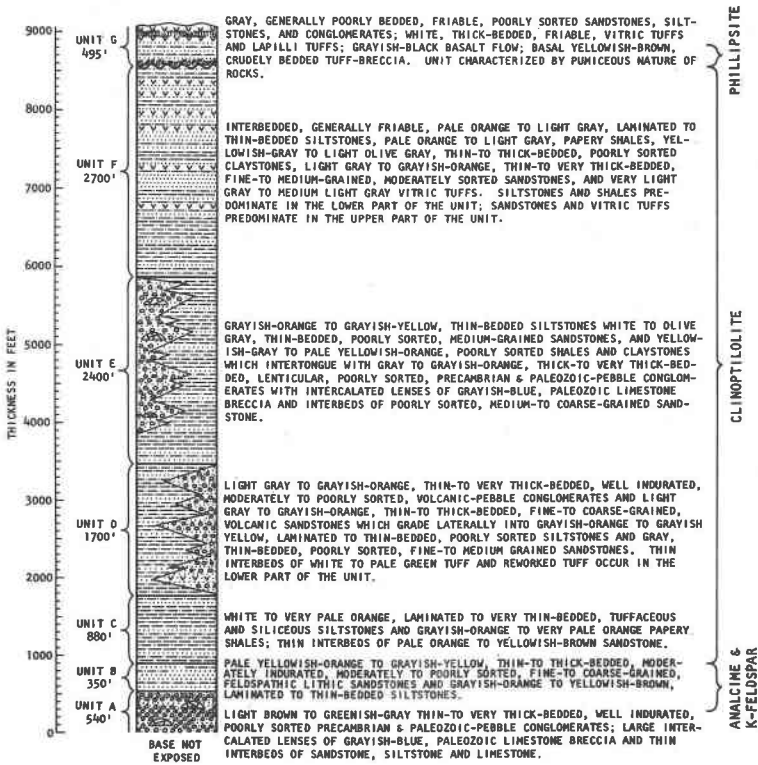


FIG. 1. Composite measured section of the Esmeralda Formation, southern Big Smoky Valley, Nevada showing distribution of zeolites and K-feldspar.

poor exposures and abrupt facies changes. An exception, however, is a distinct clinoptilolite-bearing 2-inch bed of fossiliferous tuffaceous sandstone near the top of unit C which can be followed for approximately 2 miles.

The analcime-K-feldspar zone corresponds to the upper 150 feet of unit A and all of unit B. A total of 40 samples were analyzed by X-ray diffraction, 9 of which were also studied in thin section. K-feldspar was identified in 16 of the samples and analcime was identified in 29 samples. The two minerals were identified together in 12 samples. Analcime is found in sandstones and siltstones, but K-feldspar is only present in sandstones. They seldom form more than 2 percent of a sample.

Analcime and K-feldspar occur together, commonly in the same sample, in the upper part of the zone, but only K-feldspar is present in the lower part (*i.e.*, essentially the upper 150 feet of unit A). The analcime occurs as crystals which are thought to have formed either from vitric material or an alkali-rich zeolite precursor (*cf.* Hay, 1966). Absence

of analcime in the lower part of the zone is probably related to the absence of vitric material in the rocks of unit A. The K-feldspar is present primarily as overgrowths on detrital grains of feldspar.

The clinoptilolite zone corresponds to units C through F of the sequence. Clinoptilolite occurs in a wide variety of rock types (shales, siltstones, sandstones, conglomerates, limestones, tuffs) but is most abundant in tuffs and tuffaceous sandstones. Neither analcime nor K-feldspar is present in the clinoptilolite zone, but opal and "montmorillonite" (*i.e.*, any 14 Å clay mineral whose $d(001)$ spacing expands to 17–18 Å after solvation with glycol) are common.

Out of a total of 75 samples which were analyzed by X-ray diffraction, clinoptilolite was identified in 52, opal in 35, and "montmorillonite" in 30. Clinoptilolite is most abundant in the lower half of the zone. Opal is also more abundant in the lower half of the zone, but the abundance of "montmorillonite" increases upwards. Fresh glass is present in the uppermost part of the zone where several 1- to 8-foot beds of unaltered silver-gray vitric tuff occur, and relict glass appears in minor amounts in a few nonzeolitized samples in the middle of the zone.

The phillipsite zone corresponds to the lower part of unit G and is the poorest developed of the three zones. Phillipsite is present only in 3 beds of basaltic tuff-breccia and, with the exception of "montmorillonite", is the only authigenic silicate mineral in the zone. Unaltered vitric material occurs throughout the zone but is not present in the phillipsite-bearing beds.

DESCRIPTION OF AUTHIGENIC MINERALS

K-feldspar. Authigenic K-feldspar occurs predominantly as overgrowths on grains of orthoclase and on some grains of plagioclase (Fig. 2B,C). Rarely, it fills cracks in plagioclase crystals or partly replaces plagioclase. Very fine-grained, low birefringent aggregates of K-feldspar such as those described by Hay and Moiola (1963) from Searles Lake are not present in any samples. The K-feldspar is typically clear and colorless. Overgrowths show uniform extinction and are in optical continuity with the detrital feldspar.

The feldspar has a mean index of refraction of 1.518 and a $2V$ of approximately 40 degrees, suggesting that it is a relatively pure potash feldspar. X-ray diffraction patterns are those of a single-phase monoclinic potash feldspar (refer to Hay and Moiola, 1963, Figure 3, p. 324).

Analcime. Analcime generally occurs as colorless subhedral crystals 0.05 to 0.10 mm in diameter (Fig. 2A–C). Relatively perfect euhedral crystals up to 0.3 mm in diameter, however, are not uncommon (Fig.

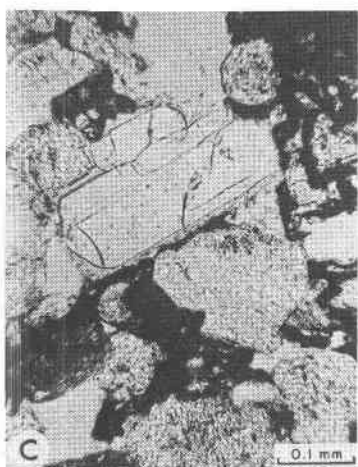
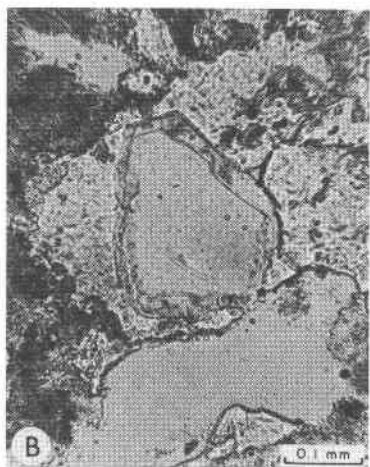
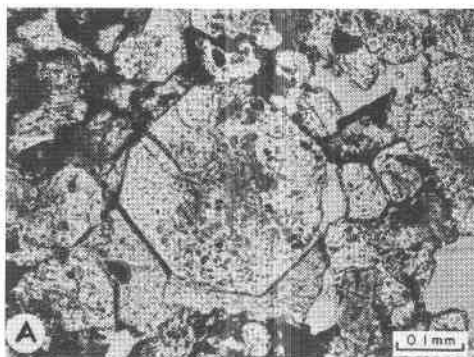


FIG. 2. Photomicrographs of sandstones from the analcime-K-feldspar zone. (A) Analcime crystals, (B) K-feldspar overgrowth on orthoclase grain, and analcime crystals, (C) K-feldspar overgrowths on plagioclase grains, and analcime crystals.

2A), and rather nondescript aggregates of small, roughly spherical crystals of analcime (less than 0.01 mm in diameter) occur in some samples. Nearly all of the crystals are completely isotropic, but most are crowded with minute dust-like inclusions. The analcime has an average refractive index of 1.486, which is intermediate between the indices of high-silica (1.484) and low-silica analcime (1.488) as reported by Iijima and Hay (1968, Table-1, p. 186). The analcime is thought to have formed directly from vitric material, although relict shards or other evidence of the former presence of vitric material in the analcime-bearing rocks are

lacking. The possibility that the analcime formed by the alteration of an alkali-rich zeolite precursor such as clinoptilolite (*cf.* Hay, 1966; Goodwin and Surdam, 1967; Sheppard and Gude, 1969) is less likely because of the absence of examples showing the replacement of any mineral by analcime.

Clinoptilolite. Clinoptilolite occurs chiefly as a pseudomorphic replacement of glass and as a cement in sandstones (Fig. 3A–C). It forms as much as 90 percent of some tuffs and occurs in trace amounts in a few limestones. On the average, however, most altered samples contain 5 to 10 percent clinoptilolite.

Clinoptilolite pseudomorphs of shards may be either hollow or solid. The larger pseudomorphs generally are the hollow ones. Hollow pseudomorphs characteristically consist of a very thin marginal film of “montmorillonite,” or occasionally a thin layer of opal, succeeded inwardly by a single layer of clinoptilolite crystals, 0.01 to 0.04 mm in length, oriented perpendicular to the shard wall (Fig. 2A). In most solid pseudomorphs, clinoptilolite crystals normal to the walls merge to form a solid mass. The clinoptilolite crystals in some pseudomorphs, however, are randomly oriented. These relationships demonstrate that the clinoptilolite replacements formed by crystallization in cavities from which the glass had already been dissolved. Clinoptilolite cement occurs in tuffaceous sandstones and conglomerates as lath-like masses of crystals, 0.01 to 0.03 mm in length, which are oriented approximately perpendicular to the edges of detrital grains of quartz, feldspar, and rock fragments (Fig. 3B,C).

The clinoptilolite has a beta index which ranges from 1.477 to $1.480 \pm .002$ and is stable at temperatures up to 700°C for at least 15 hours. These properties serve to distinguish it from heulandite which has a beta index of 1.488 or higher (Mason and Sand, 1960) and which undergoes a structural change to “heulandite-B” at about 230°C and is destroyed at 450°C (Mumpton, 1960). Neither heulandite nor any mineral with physical properties intermediate between heulandite and clinoptilolite (*cf.* Hay, 1963; Robinson, 1966) was identified in any of the samples that were analyzed.

Opal. Opal replaces glass in vitric tuffs and cements tuffaceous sandstones, siltstones, and conglomerates. It also completely replaces portions of a few 1- to 2-inch thick beds of tuffaceous siltstone, but such occurrences are extremely rare. Opal is common throughout the clinoptilolite zone but is most abundant in the lower part (units C and D); it rarely, however, forms more than 5 percent of any sample.

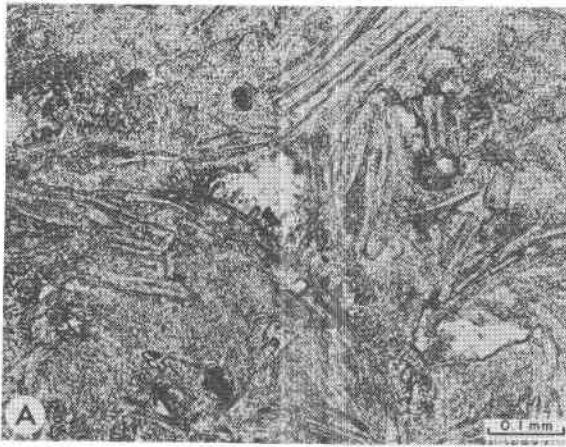


FIG. 3. Photomicrographs of tuff and tuffaceous sandstones from clinoptilolite zone. (A) clinoptilolite pseudomorph after glass shard, (B) clinoptilolite cement in tuffaceous sandstone, (C) close-up of clinoptilolite cement in tuffaceous sandstone.

Opal replaces the outer part of some glass shards, but shards that have been entirely replaced by opal are rare. The opal layer is generally succeeded inwardly by a layer of relatively coarse clinoptilolite crystals, but opal and clinoptilolite are intergrown in a few pseudomorphs. Opal cement typically forms colloform crusts on detrital grains, but occasionally it may also partly or completely replace detrital grains. Thin layers of "montmorillonite" may separate the opal from the detrital grains.

The opal is isotropic and has a refractive index that ranges between 1.420 and 1.440. X-ray diffraction patterns typically show a single strong peak at 4.09 Å which can be referred to the strongest reflection of cristobalite.

"*Montmorillonite*". The term "montmorillonite" is used for all 14 Å clay minerals in which the $d(001)$ spacing expands to 17–18 Å after solvation with glycol. "Montmorillonite" occurs throughout the clinoptilolite zone but it is most abundant in the upper part; it is also present in the overlying phillipsite zone. It is present in tuffs and tuffaceous sandstones, siltstones, and conglomerates in amounts ranging up to 10 percent and makes up as much as 99 percent of some claystones.

"Montmorillonite" partially replaces glass shards, coats detrital grains, and forms a fine-grained matrix in many tuffaceous rocks. It frequently occurs as a thin marginal replacement in shards pseudomorphed by clinoptilolite. Complete replacement of shards by "montmorillonite" is rare except in some claystones. Vitroclastic texture is preserved in some claystones, and it is assumed that the fine-grained "montmorillonite" matrix of most claystones is an alteration product of vitric dust and fine splinters of glass

Phillipsite. Phillipsite is a minor constituent in three beds of basaltic tuff-breccia in the lower part of unit G where it occurs primarily as a replacement of small pumice fragments. It has a mean index of refraction which ranges between 1.458 and 1.472 and occurs as aggregates of lath-shaped crystals 0.01 to 0.02 mm long. The crystals have parallel or nearly parallel extinction and are length slow. Fresh glass occurs throughout the phillipsite zone but is not present in the phillipsite-bearing beds.

PARAGENESIS OF AUTHIGENIC MINERALS

Age relationships can be reliably determined only for the authigenic minerals in tuffs of the clinoptilolite zone. A rather consistent order of formation of the diagenetic minerals can be established by studying the sequence of filling of cavities and shard molds, replacement relations, and the mutual intergrowth of minerals.

"Montmorillonite" was the earliest formed authigenic silicate mineral. It outlines shards replaced by clinoptilolite and opal, suggesting that it formed prior to dissolution of the glass. After the formation of "montmorillonite", the glass was dissolved and clinoptilolite and opal were subsequently precipitated in the open cavities. The occurrence of opal between "montmorillonite" and clinoptilolite in many pseudomorphs suggests that the bulk of the opal was precipitated before the clinoptilo-

lite. The intergrowth of opal and clinoptilolite in some shards suggests, however, that occasionally they were locally co-precipitated.

ORIGIN OF AUTHIGENIC MINERALS

Experimental work by Hemley (1959, 1962) and studies of Quaternary saline lakes by Hay and Moiola (1963, 1964) and Moiola and Hay (1964) have shown that the formation of authigenic K-feldspar and zeolites rather than clay minerals is stimulated by relatively high alkali-ion to hydrogen-ion activity ratios and by relatively high silica activities. Hay (1963, 1964) also has demonstrated that these conditions can most likely be attained in the depositional environment of a saline, alkaline lake or in the post-depositional environment as a result of solution and hydrolysis of rhyolitic vitric material by subsurface water. In addition, these conditions can also prevail in certain hydrothermal solutions, and the possibility of a hydrothermal origin for zeolite-K-feldspar assemblages should be considered.

Several criteria suggest that hydrothermal solutions were not responsible for the formation of the zeolites and K-feldspar in the Esmeralda Formation in southern Big Smoky Valley. The widespread distribution of altered rocks, absence of typical hydrothermal minerals such as alunite and kaolinite, and the fact that authigenic minerals are not localized within or along fractures but generally follow bedding planes all argue against a hydrothermal origin. The idea of an origin in a saline, alkaline lake environment can also be discarded. Many of the altered beds appear to have been deposited under fluvial conditions. In addition, the complete absence of saline minerals and the common presence of freshwater molluscs and fish remains in the sequence suggest that when lacustrine conditions prevailed, the lake water was neither alkaline nor highly saline. The above data suggest, therefore, that the authigenic minerals in the Esmeralda Formation formed after burial under the influence of groundwater solutions.

Alteration of the Esmeralda Formation could have taken place at depths as great as 8500 feet if it is assumed that the lowest occurring authigenic minerals were buried under the entire overlying section. Maximum temperature at this depth would be 100°C, assuming an average gradient of 1°C per 100 feet and an average surface temperature of 15°C. Hydrostatic pressure corresponding to a depth of 8500 feet would be approximately 250 atmospheres, assuming that the water table lay within 100 feet of the surface and that no impermeable layers barred the free flow of water. Presumably, however, most alteration took place at considerably lower temperatures and pressures.

The different authigenic mineral zones are thought to primarily reflect

differences in the composition of subsurface water in contact with the rocks at the time of alteration. Clinoptilolite probably required a relatively high Si to Al activity ratio and a relatively high Na+K to H ratio. Precipitation of opal in conjunction with clinoptilolite indicates the existence of solutions supersaturated with respect to quartz, tridymite, and cristobalite. Phillipsite probably required lower activity ratios of Si to Al and Na+K to Ca than clinoptilolite.

The early formation of "montmorillonite" was probably favored by a relatively low Na+K to H activity ratio (Hemley, 1962). This activity ratio was probably at its lowest level at the time of deposition of the sediments. Formation of "montmorillonite" by an initial marginal hydrolysis of glass would cause an increase in the pH and the concentration of alkali ions (Hay, 1963). This would raise the Na+K to H activity ratio of the pore water and provide a more suitable environment for the formation of zeolites. If these assumptions are correct, then the Na+K to H ratio of the groundwater solutions probably increased as alteration proceeded. In addition, the Na+K to H activity ratio probably also increased with depth resulting in the formation of analcime and K-feldspar. Fluctuations in the Na to K ratio probably controlled the formation of analcime and/or K-feldspar.

The high alkalinities and salinities necessary for the formation of the zeolites and K-feldspar are thus attributed to the solution and hydrolysis of vitric material in the altered rocks by groundwater solutions (*cf.* Hay, 1963). This interpretation is supported by petrographic evidence of dissolution of the glass prior to the formation of the zeolites. The subsurface water responsible for the diagenesis in the Esmeralda Formation is therefore thought to have originated as meteoric water which subsequently acquired the composition necessary for the formation of zeolites and K-feldspar by leaching vitric material as it passed downward and through the strata of the Esmeralda Formation.

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