

## Geologic occurrence of zeolites and some associated minerals

R. L. Hay

Department of Geology, University of Illinois, 1301 West Green Street, Urbana, Illinois, U.S.A.

**Abstract** - The principal geologic settings of zeolites are (1) saline, alkaline lakes, (2) saline, alkaline soils, (3) deep-sea sediments, (4) low-temperature open hydrologic systems, (5) burial diagenesis, and (6) hydrothermal-geothermal systems. Volcanic ash layers alter rapidly to zeolites in saline, alkaline lakes, and relatively pure deposits can be formed. Silicic volcanic glass is altered slowly, and principally to smectite, in deposits of moderately saline, nonalkaline lakes, as demonstrated in sediments of Searles Lake, California. Vitric tuffs in saline, alkaline playa-lake complexes are characteristically zoned from an outer fresh-water zone with unaltered glass or glass altered to smectite, an inner saline zone with zeolites, and an innermost highly saline zone with analcime and/or alkali feldspar, most commonly K-feldspar. Large-scale zoning of saline, alkaline type is exhibited by the Upper Jurassic Morrison Formation in the San Juan Basin, New Mexico and Arizona.

Deep-sea sediments contain large volumes of clinoptilolite and phillipsite. The phillipsite predominates in Miocene and younger sediments and clinoptilolite in older sediments, possibly because clinoptilolite was favored in pre-Miocene sediments by more siliceous pore waters. Hydrolysis by ground water in open hydrologic systems can transform ash layers to bentonite or to zeolite-rich deposits. Temperature is the principal control on zeolite assemblages in burial-diagenetic and hydrothermal-geothermal systems. Igneous analcime has been documented in the Colima Volcanic Complex of Mexico.

### INTRODUCTION

Much work has been done on the geologic occurrence of zeolites over the past thirty years, and the distribution and origin of zeolites is generally well established [1-5]. Zeolites occur in many types of rocks but are most common in volcanoclastic sediments, and the largest and purest deposits are altered vitric tuffs. The principal geologic settings of zeolites are (1) saline, alkaline lakes, (2) saline, alkaline soils, (3) deep-sea sediments, (4) low-temperature open hydrologic systems, (5) burial diagenesis, and (6) geothermal-hydrothermal systems. Features common to all geologic settings are available SiO<sub>2</sub> and Al and a Ca + Na + K/H activity ratio higher than that in which a phyllosilicate would be formed. The species of zeolite formed depends principally on the nature of the Al-Si aluminosilicate source material (e.g. glass vs. crystalline materials), chemistry of the pore fluid, temperature, and time. Minerals commonly associated with zeolites are alkali feldspars, silica minerals, and phyllosilicates. Zeolites and associated minerals are commonly zoned, reflecting differences in water chemistry, temperature, or both.

### SALINE, ALKALINE LAKES

Zeolites are both common and widespread in deposits of saline, alkaline lakes in arid and semiarid regions [6]. Because of the high pH, silicic vitric tuffs alter rapidly and may form nearly pure deposits of zeolite, generally clinoptilolite, phillipsite, erionite, or chabazite. Vitric tuffs in playa-lake complexes are characteristically zoned: an outer fresh-water zone contains unaltered glass or glass altered to smectite; an inner saline zone contains glass altered to zeolites; and an innermost highly saline zone contains alkali feldspar, generally K-feldspar. An analcimic zone may lie intermediate between the zone with zeolites and that with alkali feldspar. Albite is locally common in Eocene and older deposits of saline, alkaline lakes, where it can replace analcime and other zeolites [2]. The apparent lack of albite in post-Eocene deposits is difficult to understand, as albite has formed at low temperatures in hypersaline marine sediments of late Miocene and early Pliocene age in the Mediterranean Sea [7].

Until recently, zoning had only been recognized in Cenozoic playa-lake complexes. Now, however, similar zoning has been demonstrated in the Upper Jurassic Morrison Formation of the San Juan Basin of New Mexico and Arizona [8]. Here the Brushy Basin Member of the Morrison Formation, 60-120 m thick, contains the southern part of a playa-lake complex at least 300 km in an east-west direction that is zoned from a broad smectite mudflat facies through a playa-margin zeolite facies with clinoptilolite into a central playa facies in

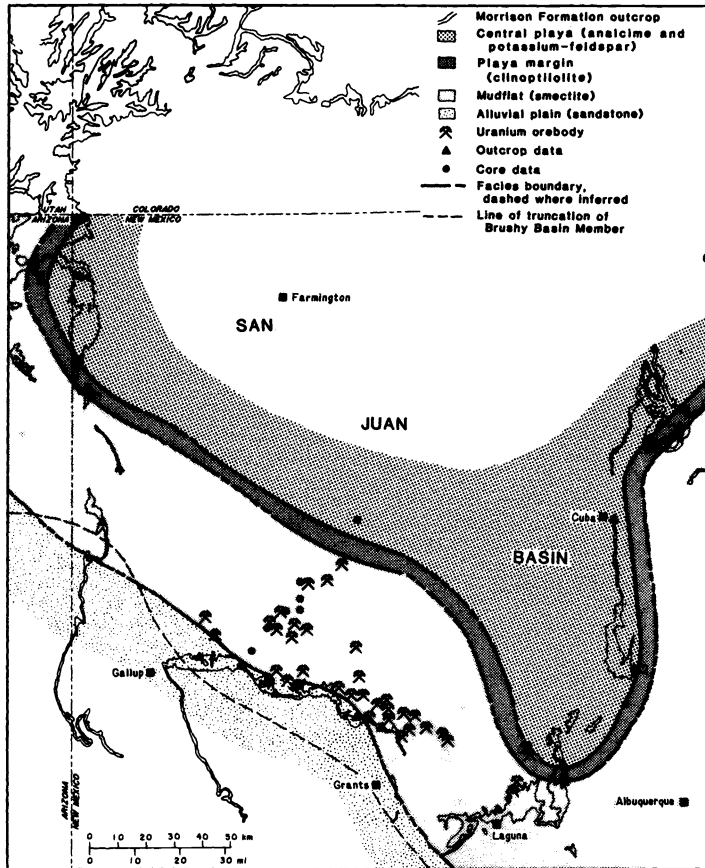


Fig. 1. Map showing the distribution of diagenetic facies in tuffaceous deposits of a playa-lake complex in the Brushy Basin Member of the Morrison Formation in the San Juan Basin of New Mexico and Arizona. The central playa facies contains albite in addition to K-feldspar and analcime. From [8], reproduced by permission of the American Association of Petroleum geologists.

which tuffs are altered to analcime, K-feldspar, and albite (Fig. 1). The clinoptilolite is pink to orange, probably because of pigmentation by hematite inclusions resulting from loss of iron in the tectosilicate framework over time. Large uranium ore deposits are found in the southern part of the complex, principally in sandstones of the mudflat facies. Primary ore deposits are attributed to fixation of uranium by humic acids from mudstones of the mudflat facies soon after Morrison deposition [8].

Mineralogic studies of core samples from Searles Lake, California have provided information about the time required for zeolite formed metastably to alter to K-feldspar in contact with highly alkaline brine and about the reaction of volcanic glass with saline nonalkaline pore fluid. Searles Lake is a saline, alkaline playa in the Mojave Desert of southeastern California that is noted for its wide variety and abundance of evaporites. Many drill cores have sampled the upper evaporite-rich section, and core KM-3 penetrated the entire thickness, 695 m, of lacustrine and playa sediments, which were deposited over the past 3.17 m.y. as shown by magnetic stratigraphy [9]. The lowermost stratigraphic unit (2.56-3.17 m.y.) was deposited in a deep-water lake, followed successively by units representing a playa (2.04-2.56 m.y.), a highly saline lake (1.28-2.04 m.y.), and a highly saline, alkaline playa-lake complex (0-1.28 m.y.). Silicic ash layers are altered to phillipsite and the closely related zeolite merlinoite in deposits about 10,000 to 100,000 years in age [10,11]. An ash layer about 140,000 years old is altered to a mixture of phillipsite and K-feldspar, and ash layers 0.50 to 1.83 m.y. in age are of K-feldspar. Assuming the vitric ash layers were altered to zeolites in 1,000 years or less, then phillipsite and merlinoite were partly altered to K-feldspar in 100,000 to 140,000 years and were wholly altered in less than 500,000 years.

The lowermost unit (Unit I) of core KM-3 shows the slow rate at which silicic vitric ash alters in contact with saline, non-alkaline pore fluid. Unit I is 142 m thick and consists largely of clays [9]. The pore water is moderately saline but not alkaline as judged from the fact that the only saline mineral is anhydrite, which occurs as disseminated crystals and nodules in the upper 115 m of the unit [11]. The temperature is 80°C at the base of Unit I [9]. Rhyolitic ash layers totalling 4-5 m are interbedded in the lower 50 m of Unit I, which has an age of about 2.96 to 3.17 m.y.. Most of the ash layers are of medium sand

size and consist of unaltered vitric shards with variable, generally small amounts of authigenic smectite. The finer grained ash layers are much more altered than the coarser layers. All but the lowermost of the finer grained layers are extensively altered to smectite and may contain coarse shards either etched or replaced by clinoptilolite. Clinoptilolite also lines cavities and is dispersed through the smectite. The lowermost ash layer consists of analcime pseudomorphs after coarse shards in a smectite matrix. The association of zeolites with smectite in the finer grained layers suggests that the chemical environment for zeolite crystallization was created by hydrolysis of the finer grained ash. Thus the alteration of glass is slow, comparable to that in deep-sea sediments, in contact with saline, nonalkaline pore fluid except where hydrolysis is enhanced by a fine grain size.

### SALINE, ALKALINE SOILS

Zeolites are formed at the land surface where the pH is 9.5 or higher as a result of the evaporative concentration of sodium carbonate in an arid or semiarid climate. Analcime has been documented as a reaction product of montmorillonite in modern saline, alkaline soils [12], and a wide variety of zeolites has formed at the land surface in sediments of Pleistocene and Holocene age in the vicinity of Olduvai Gorge, Tanzania. The climate at Olduvai Gorge is arid with seasonal rains, and soils are highly alkaline, at least during the drier part of the year. Analcime and less commonly phillipsite, chabazite, and natrolite have formed in non-tuffaceous claystones [13], and alkali-rich, low-silica tuffs have altered to phillipsite, chabazite, analcime, natrolite, dawsonite ( $\text{NaAl}(\text{OH})_2\text{CO}_3$ ), and illite [14].

### DEEP-SEA SEDIMENTS

Sea-floor sediments contain the largest volume of zeolites, and Kastner [15] has estimated that clinoptilolite averages 2 percent and phillipsite 1 1/2 percent of deep-sea sediments. Analcime is next in abundance. Phillipsite is generally associated with volcanic materials, principally basaltic; clinoptilolite occurs widely in both tuffaceous and non-tuffaceous sediments, particularly carbonates [15]. Phillipsite is found principally in Miocene and younger sediments at burial depths of less than 100 m but occurs in sediments as old as Cretaceous. Clinoptilolite is most common at depths of greater than 100 m and increases toward a maximum in upper Cretaceous sediments. Smectite is associated with phillipsite and clinoptilolite in altered vitroclastic sediments and may be the dominant alteration product. Analcime and K-feldspar increase with age and are most abundant in the oldest sediments sampled, of late Jurassic age [15]. Analcime and K-feldspar can be directly associated with glass, unlike nonmarine vitric tuffs, where they form from zeolite precursors. Glass is altered slowly in deep-sea sediments, and unaltered glass as old as Cretaceous has been found. The slow rate of alteration explains why K-feldspar can be precipitated directly in a solution from dissolving glass rather than from a metastable zeolite precursor which precipitates where glass dissolves more rapidly than feldspar can nucleate and crystallize. Reasons for the differing distribution of phillipsite and clinoptilolite are not yet established. The overall dominance of clinoptilolite in sediments older than Miocene has been attributed to reaction of phillipsite to clinoptilolite [16]. It may, however, reflect more siliceous pore water in pre-Miocene sediments. In support of this possibility, apparent peaks of siliceous sediments fall in the Eocene and Late Cretaceous [15].

### LOW-TEMPERATURE OPEN HYDROLOGIC SYSTEMS

Nonmarine tephra sequences commonly show a more or less vertical zonation of smectite and zeolites that reflects the chemical change in ground water moving through the system [17]. Solution and hydrolysis of vitric ash to smectite in the upper part of the system increases the pH,  $\text{a}_{\text{SiO}_2}$ , and Na + K/H activity ratio to the point where glass is altered to zeolites rather than smectite. In silicic tephra accumulations, zeolites (especially clinoptilolite) are generally found at a depth of greater than 200 to 500 m, whereas in alkali-rich, low-silica deposits zeolites may be formed at depths of a few meters or tens of meters. Open system-zeolites may be vertically zoned, with clinoptilolite, phillipsite, and chabazite in the upper zone and analcime in the lower zone. Although this paper is focussed on zeolites, it should be noted that many of not most montmorillonitic bentonites formed from silicic ash layers are a result of leaching in open systems. Where the pore fluid is static, as in deep-sea sediments, silicic glass is altered to a mixture of zeolite and smectite.

### BURIAL DIAGENESIS

In burial diagenesis, temperature is the dominant influence on zeolite zonation. Within silicic tuffs a common downward zonation is (1) fresh glass with smectite, (2) clinoptilolite and mordenite, (3) heulandite and analcime, and (4) albite and laumontite. Thickness of the zones varies according to the geothermal gradient, as shown by studies in the Green Tuff Region of Japan [18]. In areas of active diagenesis, temperatures of 30-50°C are found at the top of the clinoptilolite-mordenite zone, 84-91° at the top of the heulandite-analcime zone, and 120-124° at the top of the albite-laumontite zone [19].



Fig. 2. Photomicrograph of analcimic minette lava from Colima Volcanic Complex of Mexico [20]. Analcime forms colorless microphenocrysts about 80  $\mu\text{m}$  in diameter in a matrix of glass with crystals of clinopyroxene and opaque ores. Sample was provided by J. F. Luhr.

These temperature limits can vary considerably, and clinoptilolite can persist to much higher temperatures, and laumontite can form at temperatures as low as 50–60°C (J. R. Boles, 1985, personal communication). Ground-water movements can affect burial diagenesis through transport of constituents, as shown by chemical changes both within and across strata [18].

### HYDROTHERMAL-GEOTHERMAL

Zeolites can be formed at elevated temperatures, as high as 350°C, as a result of localized hydrothermal alteration. Present-day zeolitic hydrothermal alteration is known in many parts of the world, including Wairakei, New Zealand; Yellowstone Park, U.S.A.; and Iceland. Calcic zeolites such as mordenite, heulandite, laumontite, yugawaralite, and wairakite are characteristic of hydrothermal alteration. Because of the high temperatures, feldspathic rocks are common protoliths.

### IGNEOUS ANALCIME

Analcime has now been unequivocally documented as an igneous mineral [20]. It occurs as microphenocrysts in the unaltered glassy groundmass of very late Pleistocene or Holocene lava flows of minette composition in the Colima Volcanic Complex of Mexico (Fig. 2). Earlier reported occurrences of analcime phenocrysts in much older lavas are unreliable, as the analcime may be a low-temperature replacement of leucite. The  $\delta^{18}\text{O}$  value of the Mexican analcime phenocrysts is +8.8 o/oo [21], comparable to igneous feldspars. By contrast, analyzed analcime of low-temperature origin from saline, alkaline-lake deposits has  $\delta^{18}\text{O}$  values of +22.5 to +24.1 o/oo, in the range of low-temperature authigenic feldspars. Analcime "phenocrysts" in lavas of the Cretaceous Crowsnest Formation of Alberta, Canada, have  $\delta^{18}\text{O}$  values of +13.6 and +14.3 o/oo, which favor a metasomatic origin. These few isotopic measurements show that the oxygen-isotopic composition of zeolites has the potential for aiding genetic interpretations.

### REFERENCES

1. D.S. Coombs, A.J. Ellis, W.S. Fyfe, and A.M. Taylor, *Geochim. et Cosmochim. Acta*, **17**, 53 (1959).
2. R.L. Hay, *Geol. Soc. Amer. Spec. Pap.* 85 (1966).
3. R.L. Hay, in F.A. Mumpton, ed., "Natural Zeolites, Occurrence, Properties, Use", Pergamon Press, Oxford, 1978, p.135.
4. F.A. Mumpton, ed., *Min. Soc. Amer. Short Course Notes*, **4**, (1977).
5. A. Iijima and M. Utada, *Japan J. Geol. Geogr.*, **42**, 61 (1972).
6. R.C. Surdam, *Min. Soc. Amer. Short Course Notes*, **4**, 65 (1977).
7. M. Kastner in W.B.F. Ryan and others, *Initial Reports of the Deep Sea Drilling Project*, **13**, U.S. Govt. Printing Office, Washington, D.C., 721 (1972).
8. C.E. Turner-Peterson, *Amer. Assoc. Petrol. Geol. Bull.*, **69**, 1999 (1985).
9. G.E. Smith, V.J. Barczak, G.F. Moulton, and J.C. Liddicoat, *U.S. Geol. Surv. Prof. Pap.* 1256 (1983).
10. R.L. Hay and R.J. Moiola, *Sedimentology*, **2**, 312 (1963).
11. S.G. Goldman, unpub. M.S. thesis, Univ. California, Berkeley (1984).
12. N.A. Baldar and L.D. Whittig, *Proc. Soil Sci. Amer.*, **32**, 235 (1968).
13. R.L. Hay, *Proceed. 5th Intl. Conf. on Zeol.*, L.V. Rees, ed., 155 (1980).
14. R.L. Hay, *Min. Soc. Amer. Spec. Pap.*, **3**, 237 (1970).
15. M. Kastner, in Emiliani, C., ed., "The Oceanic Lithosphere", Wiley, N.Y., 1981, p.915.
16. J.R. Boles and W.S. Wise, in F.A. Mumpton, ed., "Natural Zeolites, Occurrence, Properties, Use", Pergamon Press, Oxford, 1978, p.235.
17. R.L. Hay and R.A. Sheppard, *Min. Soc. Amer. Short Course Notes*, **4**, 93 (1977).
18. M. Utada, *Sci. Pap. College Education, Univ. Tokyo*, **21**, 189–221 (1971).
19. A. Iijima and M. Utada, *Advances in Chemistry Series 101, Molecular Sieve Zeolites - 1*: *Amer. Chem. Soc.*, 342 (1971).
20. J.F. Luhr and I.S.E. Carmichael, *Contr. Min. Pet.*, **76**, 127 (1981).
21. H.R. Karlsson, *Geol. Soc. Amer. Abst. with Program*, **17**, 622 (1985).