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ZEOLITES AND ZEOLITE ORE FROM UNION CARBIDE CORPORATION'S EZ NO. 225 PLACER MINING CLAIM, GRAHAM COUNTY, ARIZONA

by

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ZEOLITES AND ZEOLITE ORE FROM UNION CARBIDE CORPORATION'S EZ NO. 225 PLACER MINING CLAIM, GRAHAM COUNTY, ARIZONA

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INTRODUCTION

The placer mining claim EZ No. 225 of Union Carbide Corporation is located in sec. 13, T. 11 S., R. 28 E., G.&S.R. Meridian, Graham County, Arizona. The deposit on the above-mentioned claim was mined for its zeolite content. The remainder of this report consists of three parts: (1) General statement on zeolites, (2) Chabazite and erionite, and (3) Zeolite ore from Union Carbide Corporation's EZ No. 225 placer mining claim.

GENERAL STATEMENT ON ZEOLITES

Zeolites belong to a group of naturally occurring minerals known as framework silicates (Deer, Howie, and Zussman, 1963; Breck, 1973, p. 2; Breck and Smith, 1959, p. 85-87). The framework silicates include the feldspars and feldspathoids, as well as the zeolites. Specifically, zeolites are crystalline hydrated aluminosilicates of the alkali and alkaline earth elements. They have an infinitely extended framework structure that encloses interconnected cavities occupied by the relatively large cations and water molecules. The name to this remarkable group of minerals was given in 1756 by Baron Cronstedt, the Swedish mineralogist. The name is derived from the Greek <u>zein</u>, to boil, and <u>lithos</u>, stone, in allusion to the intumescence of most zeolites with a borax bead.

The cations, chiefly sodium, potassium, or calcium, and the water have considerable freedom of movement within the structure and give the zeolites their cation exchange and reversible dehydration properties. The porous framework of the zeolites enables them to act as molecular sieves for the separation of molecular mixtures according to the size and shape of the molecular compounds or for the selective adsorption of gases. These unique properties are utilized in diverse industrial and agricultural processes.

More than 30 distinct species of zeolites occur in nature. Numerous zeolites have also been synthesized, but many of these have no natural counterparts. Although the crystal habit is an adequate basis for the identification of some zeolites and optical properties for others, most zeolites can be positively identified only by X-ray methods. Routine X-ray diffractometer analysis of powdered samples is generally sufficient for positive identification. This method is particularly well-suited for the identification of zeolites in fine-grained sedimentary rocks where the individual minerals cannot be isolated.

Structure

The fundamental building block of the zeolites is a tetrahedron of four oxygens surrounding a relatively small silicon or aluminum atom. The framework structure of zeolites consists of SiO_4 and AlO_4 tetrahedra such that each oxygen is shared between two tetrahedra. Thus, the atomic ratio, O:(Al+Si), is equal to 2. Because aluminum has one less positive charge than silicon, the framework has a net negative charge and is neutralized by the exchangeable cations. Each sodium or potassium ion, with one positive charge, can neutralize one aluminum; but each calcium ion with two positive charges, can neutralize two aluminums. Feldspars and feldspathoids also have framework structures, but their structures are much more compact than those of the zeolites.

Chemical Composition

Most natural zeolites show considerable variations in chemical composition, including variations in the water content, the cation content, and the Si:Al ratio. The most common cations in natural zeolites are sodium, potassium, and calcium; however, barium, strontium, and magnesium are also found in some. Barium is the predominant cation in harmotome and edingtonite. Although potassium is present in many zeolites, it generally is not the predominant cation.

The actual number of sodium, potassium, and calcium atoms in the formula of a zeolite must be related to the Si:Al ratio by the charge relation, Na+K+2Ca=Al. Substitution of Al^{+3} for Si^{+4} in the framework of a zeolite requires the presence of a cation to maintain the charge balance. The maximum substitution of Al^{+3} for Si^{+4} results in a Si:Al ratio of 1. Thomsonite and gismondine are the only natural zeolites that have Si:Al ratios close to 1. A commercially important zeolite, type A, has been synthesized with a Si:Al ratio of 1. The minimum substitution of Al^{+3} for Si^{+4} is in mordenite and ferrierite which have a Si:Al ratio of about 5. Like the feldspars, zeolites show replacement of the type $CaAl \rightleftharpoons Na(K)Si$. Replacement of the type $Ca \rightleftharpoons 2Na(K)$ also occurs and does not involve the framework constituents. Replacement of the latter type can occur in zeolites at any time after their crystallization. The Si:Al ratio of a zeolite is probably determined at the time of crystallization, and is not subsequently modified because of the difficulty of moving Si and Al atoms in the framework.

Some workers have found a relationship between the water content of zeolites and the kind of exchangeable cation in the structure. In a general way - the water content of a zeolite increases with decreasing radius of the cation. The water content is also greater for a bivalent cation than for a univalent cation of the same radius.

Properties of Zeolites

Zeolites are colorless or white when pure, but many specimens are colored gray, pink, yellow, or green by minute inclusions of iron oxides, clay minerals, or other impurities. The specific gravity of zeolites is notably low as a consequence of their porous structures. Except for barium-rich zeolites, the specific gravity is 1.9 - 2.4; however, most zeolites are in the range of 2.0 - 2.3. Barium-rich zeolites such as harmotome and edingtonite have a specific gravity of 2.4 - 2.8. The hardness of zeolites is about 3.5 - 5.5.

Optical Properties

The indices of refraction of zeolites are relatively low for silicate minerals. Indices range from about 1.44 to 1.54, but most zeolites are in the range of 1.48 - 1.52. The indices of refraction are sensitive to changes in the water and cation contents as well as changes in the Si:Al ratio. Some zeolites, particularly the fibrous ones such as natrolite and mesolite, show first a decrease in indices on dehydration but then an increase in indices as dehydration proceeds. Substitution of alkalis for alkaline earths commonly cause a slight decrease in the indices. Indices of refraction decrease markedly with an increase in the Si:Al ratio. Such behavior has been well documented for analcime, chabazite, phillipsite, and thomsonite.

Cation Exchange

The ability of cations in zeolites to exchange with other cations in aqueous solutions was first reported by H. Eichhorn in 1858; and since then, a wide range of exchange behavior has been observed. The cation exchange properties depend on the size and charge of the cations and the structure of the zeolite. At relatively low concentrations and ordinary temperatures, the extent of cation exchange generally increases with increased charge and atomic number of the exchangeable cation. The extent of exchange is less predictable at high concentrations and high temperatures. The number of different cations which can undergo exchange increases as the zeolite structure becomes more open. For example, analcime shows extensive exchange with Na^+, K^+, NH_4^+, Tl^+, and Ag^+, limited exchange with Rb^+ and Li^+, but only slight or no exchange with Cs^+. Faujasite, one of the most open natural zeolites, shows extensive exchange with all the above cations as well as with bivalent cations and large organic cations. Many zeolites show only little or no structural modification of the framework during cation exchange. A drastic structural modification or even destruction of the structure accompanies the exchange of certain cations in some zeolites. The structure of synthetic type A zeolite is completely destroyed when exchanged with Ba^{+2}, Cu^{+2}, or Fe^{+3}. The thermal stability of some zeolites is improved by exchange with large cations such as Rb^+ and Cs^+. Chabazite, exchanged with these cations, remains stable above 1,000°C (Barrer and Langley, 1958).

Dehydration

The reversible dehydration property of zeolites was discovered by A. Damour in 1857. When most zeolites are heated, the water is given off continuously rather than in separate stages at certain temperatures. The dehydrated zeolite can then readsorb the original amount of water when exposed to water vapor. Recent investigations have shown that some zeolites such as phillipsite and gismodine lose and gain water in a stepwise manner (Hoss and Roy, 1960). These zeolites and others undergo drastic structural modifications during dehydration at temperatures below 200°C. Chabazite, on the other hand, dehydrates continuously and shows only a slight shrinkage of the cell parameters. Detailed structural studies of dehydrated Ca-chabazite (Smith, 1962) have revealed minor framework changes and major shifts of the calcium atoms. Apertures to cavities in the framework of chabazite also change in size and shape. Fully hydrated laumontite is rarely found in nature. On exposure to the atmosphere, laumontite readily loses about one eighth of its water and changes to a partially dehydrated form known as leonhardite which has distinctive optical properties.

Molecular Sieve Properties

When zeolites are dehydrated, the remaining crystalline solid is characterized by molecular-sized voids that have a large internal surface area. As early as 1909, F. Grandjean found that dehydrated zeolites could reversibly adsorb gaseous iodine, mercury, and ammonia as well as water. Weigel and Steinhoff in 1925 noted that dehydrated chabazite adsorbed methyl and ethyl alcohol but virtually excluded the relatively large molecules of acetone, ether, and benzene. The significance of this selective behavior was recognized by J. W. McBain, who proposed the term "molecular sieve" for the zeolites.

The molecular sieve properties of zeolites depend not so much on the size or volume of the voids in the framework but rather on the size of the apertures (windows) that connect the voids. The zeolites differ in the sizes of their apertures. For example, the aperture of analcime is 2.8 Å; whereas that of phillipsite is 4 Å and that of faujasite is 8 Å. The size of the apertures can be modified by controlling the temperature and the exchangeable cations. The framework of zeolites is not totally rigid, and the size of the apertures can be reduced by lowering the temperature. Cations are located in and near the apertures and therefore partially block them. Aperture size can be increased by reducing the number or size of the cations through cation exchange.

The charge on the cation influences the electrostatic fields within the zeolite and, therefore, affects the selective adsorption and catalytic properties.

Occurrence

Zeolites occur in rocks that are diverse in lithology and age, and they have formed in many different geological environments. The most common and, perhaps, best known occurrences are in the cavities and fractures of igneous rocks, particularly volcanic rocks. Most of the large, attractive zeolite specimens in museum collections have been obtained from igneous rocks. Zeolites are also found in metallic ore deposits and hot spring deposits such as those at Wairakei, New Zealand and Yellowstone National Park. In recent years zeolites have been recognized as important rock-forming constituents in low-grade metamorphic rocks and in a variety of sedimentary rocks (Hay, 1966). The zeolites in sedimentary rocks are very finely crystalline and do not appeal to mineral collectors; however, deposits of this type are voluminous and have economic potential for many industrial and agricultural processes.

Zeolites are among the most common secondary silicate minerals that occur in sedimentary rocks. Since the discovery in 1891 of phillipsite in deep-sea sediments, zeolites have been reported from many different sedimentary rocks and depositional environments. These zeolites are finely crystalline, commonly only 2 - 50 μm in size; and their recognition and identification was virtually impossible until the widespread use of X-ray techniques. Unlike the varied suite of zeolites in the cavities of basaltic rocks, the zeolites in sedimentary rocks are limited to nine species including analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. Analcime and clinoptilolite are by far the most common. Zeolites are particularly abundant in deposits of alkaline, saline lakes. These bedded deposits generally consist of two or more zeolites that are associated with clay minerals, silica minerals, or feldspar. Beds consisting almost entirely of one zeolite, however, have been found in the Cenozoic continental deposits in the desert areas of Western United States.

Except for analcime, the zeolites are secondary or authigenic minerals. Analcime occurs as a primary mineral in certain alkalic igneous rocks, but it also is a secondary mineral in the cavities of basaltic rocks and in sedimentary deposits. Although zeolites in hot-spring deposits may have formed at temperatures as high as 250°C, most zeolites crystallized at temperatures considerably below 100°C. Conditions favorable for the formation of zeolites include alkaline water enriched in alkalis and a readily available source of silicon and aluminum. Zeolites form as a result of the reaction of interstitial fluid with glassy or aluminosilicate mineral constituents of the host rock. The interstitial fluid originated as either percolating meteoric water or connate water of a saline lake. Silicic volcanic glass in sedimentary deposits is particularly susceptible to alteration in the postdepositional environment. Rocks originally rich in shards of volcanic glass now commonly consist of zeolites that have preserved the original form of the glass particles. Those factors that determine which one of the many zeolites will crystallize in a rock are mostly unknown. However, the following factors are important: porosity, permeability, and composition of the host rock; depth of burial inasmuch as this affects the temperature and pressure; and chemisty of the interstitial fluid including the pH, salinity, and the proportion of cations.

CHABAZITE AND ERIONITE

Inasmuch as the ore from Union Carbide Corporation's EZ No. 225 placer claim (sec. 13, T. 11 S., R. 28 E., Graham County, Arizona) consists mainly of the zeolites chabazite and erionite, the chemistry, structure, physical properties, and occurrences of these zeolites are summarized on the following pages.

Chabazite

Chemistry

Chabazite has an ideal formula of $(Ca,Na_2)_6Al_{12}Si_{24}O_{72} \cdot 36H_2O$, but natural chabazites show considerable variation in the Si:Al ratio, the cation contents, and the H_2O content. Most chabazites have a Si:Al ratio of 1.9-2.5; however, a broader range of 1.4-4.1 has been reported. In general, the aluminous varieties occur in basaltic or alkalic mafic igneous rocks, whereas the siliceous varieties occur in silicic vitric tuffs of sedimentary deposits.

Passaglia (1970) recently studied the chemistry and physical properties of chabazites and concluded that most samples cluster near the calcium and sodium end-members, although there seems to be a complete range between the extremes. The sodic member has been called "herschelite," but its validity as a separate species is uncertain. Chabazites having potassium as the predominant cation are very rare, although some specimens contain as much as 5 weight percent K_2O. Those specimens that have the highest potassium contents also have high contents of strontium.

The water content for chabazite was shown by Passaglia (1970) to range from about 30 to 45 molecules per unit cell, based on a unit cell containing 72 oxygen atoms. The sodium-rich members have a lower water content than the calcium-rich members.

Structure

The structure of hydrated Ca-chabazite (space group: $R\bar{3}m$) as refined by Smith, Rinaldi, and Glasser (1963) is built of double 6-membered rings of tetrahedra that form hexagonal prisms. The centers of the prisms occupy the corners of the rhombohedral cell, and the prisms are linked to form one large cage per unit cell (Fig. 1). Each cage has six octagonal, two hexagonal, and twelve quadrilateral faces and is connected to six neighboring cages by apertures of 8-membered rings. The 8-membered rings are nearly circular and permit adsorption in all three directions but limit it by the minimum free diameter of about 3.9 Å. Dehydration of Ca-chabazite causes distortion of the 8-membered rings such that the free area is elliptical with dimensions of 4.4 Å by 3.1 Å. Water molecules cluster around the calcium atoms. During dehydration the calcium atoms move from the large cavities to the hexagonal prisms and cause some distortion of the framework. The structures of the Na-chabazite or chabazite with Si:Al ratios near 3 have not yet been determined.

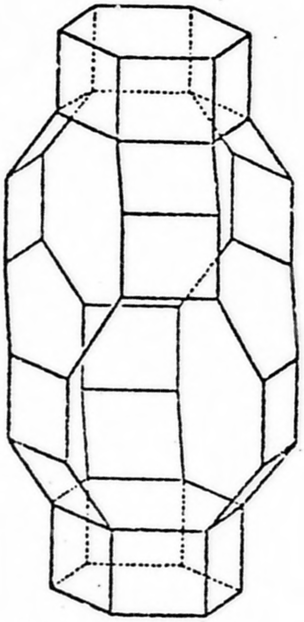

Figure 1.-Schematic representation of the chabazite cage. Aluminum and silicon atoms occupy each corner and are surrounded by oxygen atoms (from Barrer and Kerr, 1959, p. 1919).

Properties

As is true for most zeolites, the exchangeable cations, the Si:Al ratio, and the water content affect the physical properties of chabazite. According to Smith (1964, p. 3761), the properties depend markedly on the exchangeable cations. Twice as many univalent cations as bivalent cations are required to satisfy the electrical neutrality; and the number of aluminum atoms must equal the sum of the univalent cations plus twice the bivalent cations, if protons do not enter the structure.

Passaglia (1970) found that the indices of refraction decrease with an increase of the Si:Al ratio and an increase in the sodium content. Indices of refraction of aluminous varieties are in the range of 1.470-1.518; and the sodic members are at the lower part of the range and the calcic members are at the upper part of the range. Siliceous varieties have indices in the range of 1.460-1.474.

The hexagonal cell dimensions of the chabazite are affected by both the Si:Al ratios and the exchangeable cations. Passaglia (1970) found that the c dimension decreases with an increase in the Si:Al ratio and that a dimension increases with the number of exchangeable cations, especially when sodium is predominant. Most chabazites with Si:Al ratios less than 2.7 have c greater than 15.00 Å; whereas, most chabazites with Si:Al ratios greater than 2.7 have c less than 15.00 Å and as low as 14.80 Å. The a dimension shows a range of about 13.71-13.86 Å. Smith (1964) also showed that dehydration of chabazite causes a slight reduction in the cell size.

Dehydration and Thermal Stability

Barrer and Langley (1958), studying cation-exchanged chabazites, found that in many forms the basic structure of the zeolite remained unchanged during and for an interval after the loss of water. Bivalent cations show a greater retentivity for water than do univalent cations of comparable radius. Also, the larger the cation in the univalent series, the lower tends to be the temperature at which most of the water is lost. Thus, the lithium-, sodium-, potassium-, rubidium-, and cesium-forms lose water at respectively lower temperatures. The thermal stability of chabazite depends on the position of the cations in the dehydrated form because the water molecules are removed before the breakdown of the aluminosilicate framework. Barrer and Langley (1958) reported that the breakdown of the framework in univalent forms is postponed to increasingly higher temperatures as the size of the cation increases. In fact, the rubidium- and cesium-forms are stable under conditions of differential thermal analysis to at least 1,000°C. Ca-chabazite showed about the same thermal stability as the potassium-form.

Occurrence

Most of the natural chabazites studied and reported in the literature have been collected from metamorphic or igneous rocks, particularly of basaltic composition. These chabazites occur as megascopic crystals and are mainly calcic with Si:Al ratios of less than 2.7. Sodic chabazites (herschelite) with low Si:Al ratios generally occur in alkalic basaltic lavas. The chabazite that occurs in sedimentary deposits is generally siliceous and, on the basis of meager data, seems to range from sodic to calcic varieties. This chabazite is commonly finely crystalline ($< 10 \mu m$) and has formed from silicic vitric material during diagenesis of the sedimentary deposit.

Erionite

Chemistry

Erionite has an ideal formula of about $(Na_2,K_2,Ca)_{4.5}Al_9Si_{27}O_{72} \cdot 27H_2O$; but most natural erionites are more siliceous, and they show a considerable variation in cation content. Most erionites have a Si:Al ratio greater than 3, and most are alkalic. A compilation of eleven analyses of erionite by Sheppard and Gude (1969) showed that sodium was the predominant cation in more than half of the analyses and that calcium was predominant in only one analysis. The calcium-rich erionite was collected from a basalt in Japan; all of the other erionites were from tuffs in lacustrine deposits. Ferric iron seems to substitute for aluminum in erionites, as well as in other zeolites from sedimentary rocks. An analysis of erionite from a lacustrine tuff near Rome, Oregon, suggests that ferric iron can substitute for as much as 15 percent of the aluminum. The $Si:Al+Fe^{+3}$ ratio for the above-mentioned eleven erionite analyses showed a range of 2.9-3.7.

Structure

The structure of erionite (space group: $\underline{P6_3/mmc}$) as determined by Staples and Gard (1959) consists of a cage-like configuration of linked $(Si,Al)O_4$ tetrahedra that are bounded by 4-, 6-, and 8-membered rings (Fig. 2). Neighboring cavities are joined in the *c*-direction by a shared single hexagonal ring, instead of a double hexagonal ring as in chabazite. The cavities have a free length of about 15.1 Å and a free diameter of about 6.3 Å. Each cavity is connected with six others through elliptical windows with minor and major axes of about 3.5 Å and 4.7-5.2 Å, respectively, and with two others in the *c*-direction through windows with a free diameter of about 2.5 Å.

Properties

A decrease in the indices of refraction and cell dimensions of erionite can be correlated with an increase in the $Si:Al+Fe^{+3}$ ratio (Sheppard and Gude, 1969). The indices of refraction are in the range of 1.46-1.49, but most are less than 1.47. Cell dimensions for erionite are *a* = 13.21-13.26 Å, and *c* = 15.04-15.12 Å. Most erionites have *a* less than 13.23 Å and *c* less than 15.07 Å. Erionite shows about a one percent decrease in cell volume from the most aluminous analyzed specimen to the most siliceous specimen.

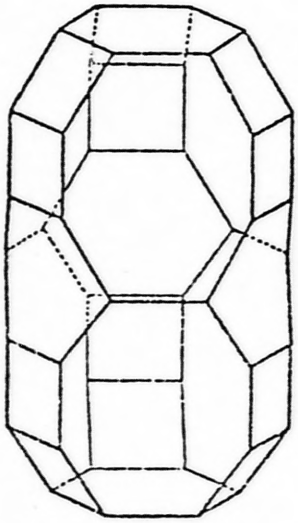

Figure 2.-- Schematic representation of the erionite cage. Aluminum and silicon atoms occupy each corner and are surrounded by oxygen atoms (from Barrer and Kerr, 1959, p. 1919).

Eberly (1964) found that cation exchange was only partially successful in erionite using lithium, sodium, magnesium, calcium, and strontium ions. The original potassium content, in particular, is difficult to reduce by cation exchange. The difficulty in reducing the original potassium content in erionite was confirmed by Peterson, Helfferich, and Blytas (1965) who found only slight potassium reduction during exposure to sodium and silver solutions. On the other hand, these investigators found that erionite underwent essentially complete exchange with potassium ions at room temperature. Apparently, a certain number of potassium ions occupy sites in the structure from which they cannot be removed without destroying the crystal structure. -

Natural erionite adsorbs nitrogen and straight-chain hydrocarbons but excludes the branched-chain isomers (Eberly, 1964). Regarding the adsorption of straight-chain hydrocarbons, Eberly found that natural erionite adsorbs considerably less n-heptane than either n-pentane or n-hexane. Apparently, this behavior is due to the relatively small volume and cylindrical shape of the adsorption cavities. Cation exchange was found to influence the adsorption capacity of erionite. Potassium-exchanged erionite had little or no adsorption capacity for n-pentane, n-hexane, and n-heptane and only slight capacity for nitrogen. The large potassium ions presumably block nearly all of the adsorption cavities. With calcium-exchanged erionite, however, more of the adsorption cavities are available to n-pentane and n-hexane and result in nearly doubling the adsorption capacity for n-pentane.

Occurrence

Erionite was considered an extremely rare zeolite prior to 1959 when it was found to be a common authigenic constituent in altered silicic tuffs of certain lacustrine deposits in Nevada. Erionite was originally described by Eakle (1898) from a silicic welded tuff near Durkee, Oregon. Since 1959, numerous occurrences of erionite have been discovered in upper Cenozoic lacustrine deposits in many of our western states. Several occurrences of erionite in basalt flows have been reported from Japan and Washington.

ZEOLITE ORE FROM UNION CARBIDE CORPORATION'S EZ No. 225 PLACER MINING CLAIM

Three representative samples of the zeolite ore were collected from Union Carbide Corporation's EZ No. 225 placer mining claim on June 14, 1972 in the presence of Pat Morgan and T. S. Ary (Union Carbide Corporation), H. F. Susie and R. A. McCally (U.S. Bureau of Land Management), and L. H. Godwin and R. S. Fulton (U.S. Geological Survey). These samples have been assigned the following field numbers: EZ-225-1, EZ-225-2, and EZ-225-3. Zeolite-bearing strata commonly overlie the ore bed, but these strata will not be discussed further in this report.

In the remainder of this report, data are presented on the chemistry and mineralogy of the bulk ore. The chemistry and some physical properties of chabazite and erionite, the chief minerals of the ore bed, are also presented and evaluated.

Chemistry of Bulk Samples of Ore

Each of the three bulk samples from the ore bed was analyzed, and the chemical analyses are given in table 1. The analyses do not show much variation, and they total reasonably close to 100 percent. The LOI (loss on ignition) is probably water inasmuch as ~~the~~ carbonate minerals were not detected in the bulk samples. The high content of water indicates that the ore consists of hydrous constituents, either gel-like materials or hydrous crystalline materials. Optical and X-ray studies showed that all of the samples consist mainly of hydrous crystalline materials (zeolites). For each sample, the sum of the alkali oxides nearly equals the sum of the alkaline-earth oxides. Both sums are about 4 weight percent.

Table 1.--Chemical analyses of ore from EZ No. 225 placer mining claim

[Weight percent]

	EZ-225-1	EZ-225-2	EZ-225-3
SiO_2	55.5	55.3	55.7
Al_2O_3	13.1	13.2	13.1
Fe_2O_3	3.43	3.40	3.32
MgO	1.00	0.98	0.96
CaO	3.02	3.25	3.23
Na_2O	3.00	2.85	3.07
K_2O	1.05	1.15	0.76
LOI	19.4	19.1	19.3
Total	99.50	99.23	99.44

SiO_2 determined gravimetrically by G. T. Burrow; Al_2O_3 determined colorimetrically by G. T. Burrow; total Fe as Fe_2O_3, MgO, and CaO determined by atomic absorption by Wayne Mountjoy; Na_2O and K_2O determined by IL flame photometer by Wayne Mountjoy; LOI determined at 900°C by G. D. Shipley.

Semiquantitative spectrographic analyses of the three bulk samples are given in table 2. Within the limits of error, these analyses confirm those given in table 1. In addition, these spectrographic analyses show contents of titanium, barium, manganese, and strontium that are sufficient to make up the difference between the totals shown in table 1 and 100 percent.

Mineralogy of the Ore

The mineralogy of the three samples of ore was determined from X-ray powder diffraction data, supplemented by examination of thin sections and scanning electron micrographs. The X-ray powder diffraction data permitted identification of the major mineral constituents and an estimate of the abundance of the constituents. Portions of the ore samples were first crushed to -100 mesh and then pelletized into a cellulose wafer. The wafer was then exposed to nickel-filtered copper radiation, and the data were recorded on a strip chart. Identification of the zeolite minerals was made by comparing the diffractometer records of pure zeolite minerals (standards) with the diffractometer records of the ore samples. The abundance of the zeolite minerals in each ore sample was based on the ratio of the peak heights of the zeolites in the ore to the peak heights of the zeolite standards.

The mineralogy of the three ore samples is given in table 3. The values reported are semiquantitative, and the actual values probably range from ±50 percent of those reported values less than 10 percent to ±10 percent of those reported values greater than 70 percent. Table 3 shows that the mineralogy of the three samples is similar and that the ore consists chiefly of zeolites. Zeolites make up about 95 percent of the ore, and chabazite is the predominant zeolite, followed by lesser amounts of erionite and clinoptilolite. Chabazite ranges from about 70 to 80 percent of the ore. No relict volcanic glass could be recognized in thin sections of the ore.

Table 2.--Semiquantitative spectrographic analyses of ore from EZ No. 225 placer mining claim

	EZ-225-1	EZ-225-2	EZ-225-3
	Weight percent		
Si	G	G	G
Al	10	10	10
Fe	2	2	2
Mg	.5	.7	.7
Ca	2	2	2
Na	2	2	3
K	1	1	1
Ti	.15	.15	.15
P	N	N	N
	Parts per million		
Ba	700	500	500
Be	2	2	1.5
Co	7	5	5
Cr	1	1	1.5
Cu	20	15	20
Ga	20	20	20
Mn	1,000	1,000	500
Ni	15	5	7
Pb	15	15	15
Sc	7	7	7
Sr	700	700	1,000
Y	N	N	10
Zr	200	200	200

Results are to be identified with geometric brackets whose boundaries are 1.2, 0.83, 0.56, 0.38, 0.26, 0.18, 0.12, etc., but are reported arbitrarily as mid-points of these brackets, 1.0, 0.7, 0.5, 0.3, 0.2, 0.15, 0.1, etc. The precision of a reported value is approximately plus or minus one bracket at 68 percent confidence/or two brackets at 95 percent confidence. G, greater than 10 percent; N, not detected. Analyst: Harriet G. Neiman

Table 3.--Mineralogic composition of bulk samples of ore

[Weight percent]

	EZ-225-1	EZ-225-2	EZ-225-3
Chabazite	75	70	80
Erionite	15	20	10
Clinoptilolite	5	5	5
"Others"	5	5	5

"Others" include plagioclase, clay minerals (including chlorite), clinopyroxene, magnetite, hematite, and amorphous iron oxides. Analyst: C. S. V. Barclay.

Scanning electron microscopy was useful in determining the texture of the ore and in determining the form and crystal size of the zeolites. Figure 3 shows the well-preserved vitroclastic texture of the ore. Although no glass remains, the shapes of shards and partial bubbles are plainly visible. A bed of volcanic ash was obviously the precursor for the zeolite ore. Figure 4 shows well-formed, relatively large clinoptilolite crystals and abundant irregular plates of minute chabazite crystals. Clinoptilolite crystals in this figure are 4-12μm long, and the plates of chabazite crystals are mostly 2-25μm long. Figure 5 shows well-formed clinoptilolite crystals, bundles of erionite rods, and abundant irregular plates of minute chabazite crystals. The bundles of erionite rods in this figure are about 10μm long. Figure 6 shows enlargements of the irregular plates of chabazite crystals. In this figure, individual crystals of chabazite can be recognized, and they are 0.5-0.8μm in size. The plates apparently are fragile aggregates of subhedral to euhedral chabazite crystals. Most of the chabazite in the ore bed is probably less than 1μm in longest dimension. Examination of thin sections and grain mounts of the ore samples showed that much of the clinoptilolite and erionite is larger than that shown in the scanning electron micrographs. Clinoptilolite is as large as 40μm, but most is 10-20μm long. The bundles of erionite rods are as long as 60μm, but most are 20-40μm long.

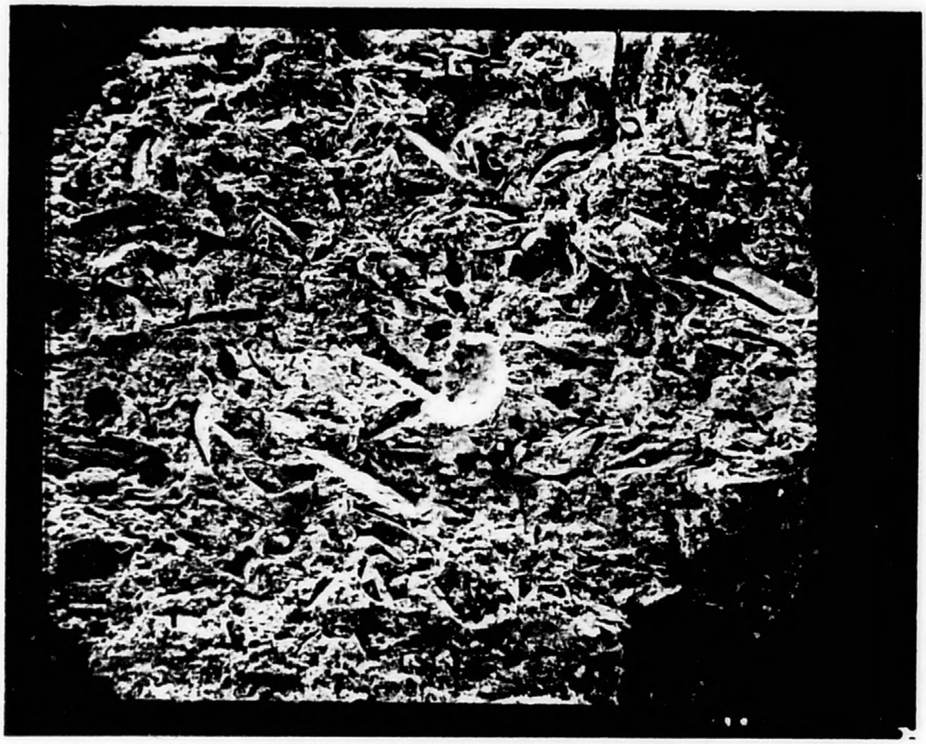

Figure 3.--Scanning electron micrograph of Sample No. EZ-225-2 showing vitroclastic texture. Magnification: X55. Micrograph by C. S. V. Barclay.

Figure 4.--Scanning electron micrograph of Sample No. EZ-225-2 showing relatively large clinoptilolite (Cl) crystals and irregular plates of minute chabazite (Ch) crystals. Magnification: X1,100. Micrograph by C. S. V. Barclay.

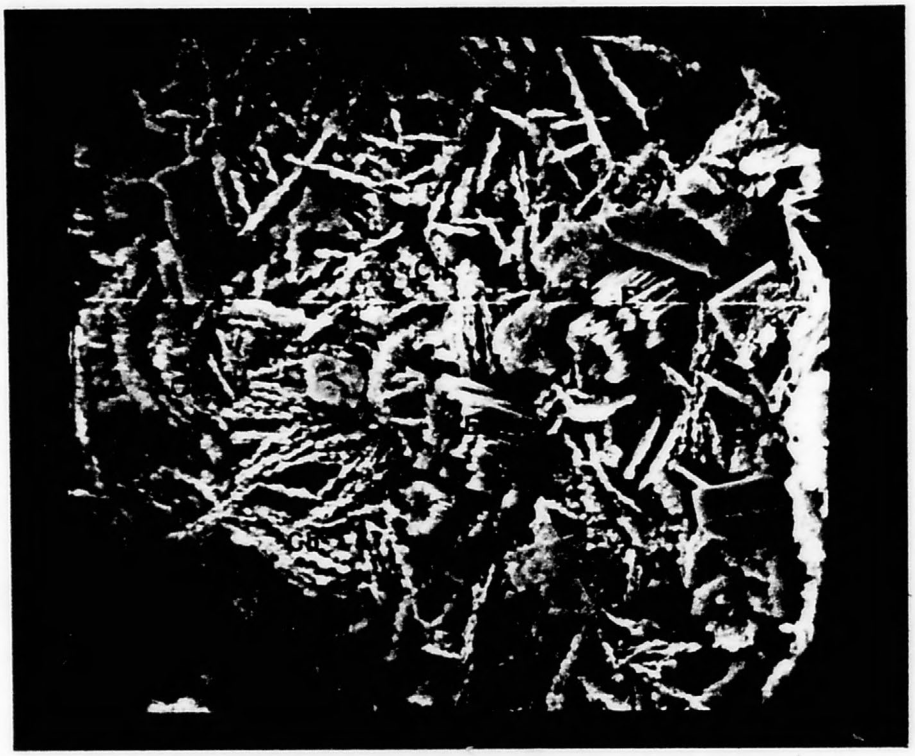

Figure 5.--Scanning electron micrograph of Sample No. EZ-225-2 showing relatively large clinoptilolite (Cl) crystals, bundles of erionite (E) rods, and irregular plates of minute chabazite (Ch) crystals. Magnification: X2,000. Micrograph by C. S. V. Barclay.

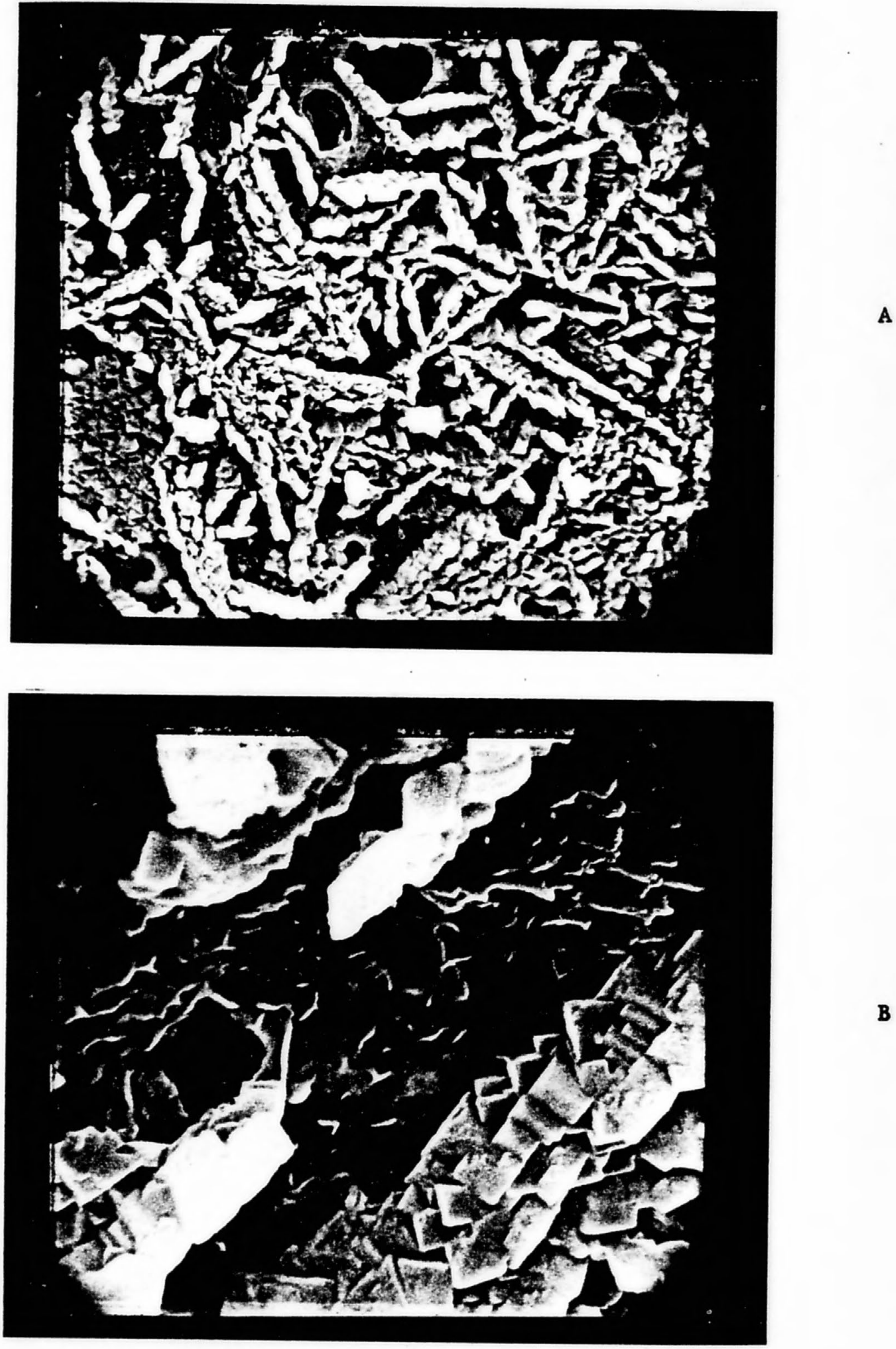

Figure 6.--Scanning electron micrographs of Sample No. EZ-225-1 showing irregular plates of minute chabazite crystals. A, magnification: X2,000; B, magnification: X10,000. Micrographs by C. S. V. Barclay.

Chemistry of Chabazite and Erionite

In order to obtain material for chemical analysis, an attempt was made to separate the chabazite and erionite from the bulk samples of the ore. About 100 grams of the bulk sample were ground to -200 mesh and then placed in a container of distilled water. Further disaggregation was accomplished by treatment for 15 minutes in an ultrasonic bath. Sand and Regis (1967) working with similar material, showed that chabazite concentrated in the very fine fractions and erionite concentrated in the coarse fractions. Therefore, the disaggragated ores were separated into various size fractions by sedimentation through a column of distilled water. By trial and error, combined with X-ray analysis of the size fractions, it was found that chabazite concentrated in the less than 1 μm-fraction and erionite concentrated in the 30 to 75 μm-fraction. Table 4 shows the mineralogy of these two size fractions for the three ore samples. The less than 1 μm-fraction for each sample consisted of nearly pure chabazite. The 30 to 75 μm-fraction consisted of 55-80 percent erionite. Chabazite was the chief impurity in the erionite-rich fraction, ranging from 10 to 35 percent.

The chabazite-rich and erionite-rich fractions from each of the three ore samples were chemically analyzed, and the results are given in table 5. The H_2O contents were not determined but were calculated by subtracting the sum of the analyzed constituents from 100. Therefore, the reported H_2O contents are probably higher than the actual H_2O contents of the zeolites.

Table 4.--Mineralogic composition of less than 1µm- and 30 to 75µm - fractions of ore

[Weight percent]

Sample No.	EZ-225-1		EZ-225-2		EZ-225-3	
Size fraction	<1µm	40-70µm	<1µm	40-75µm	<1µm	30-75µm
Chabazite	>99	10-20	>99	20-30	>99	25-35
Erionite	---	70-80	---	65-75	---	55-65
Clinoptilolite	---	5	---	<5	---	5
"Others"	Tr	5	Tr	Tr	Tr	5

"Others" include plagioclase, clay minerals (including chlorite), clinopyroxene, magnetite, hematite, and amorphous iron oxides. Separations prepared by R. D. Hettinger; analyst: C. S. V. Barclay. Tr, Trace; ---, not detected.

Table 5.--Chemical analyses of chabazite-rich and erionite-rich fractions of ore

[Weight percent]

	Chabazite			Erionite		
	EZ-225-1	EZ-225-2	EZ-225-3	EZ-225-1	EZ-225-2	EZ-225-3
SiO_2	51.9	51.9	52.9	55.7	55.6	54.3
Al_2O_3	12.0	12.0	12.8	13.6	13.6	13.5
Fe_2O_3	5.74	5.30	4.56	2.38	2.59	2.66
MgO	1.18	1.17	1.09	0.85	0.86	0.89
CaO	3.24	3.46	3.38	3.02	3.29	3.20
Na_2O	3.63	3.68	3.46	3.09	2.91	3.04
K_2O	0.29	0.38	0.31	1.53	1.35	1.17
H_2O	22.02	22.11	21.50	19.83	19.80	21.24

SiO_2 and Al_2O_3 determined colorimetrically by G. T. Burrow; total Fe as Fe_2O_3, MgO, and CaO determined by atomic absorption by Wayne Mountjoy; Na_2O and K_2O determined by IL flame photometer by Wayne Mountjoy; H_2O calculated by difference.

The unit cell contents of the chabazite and erionite from the ore were calculated on the basis of 72 oxygen atoms and are given in table 6. Both zeolites in all three samples are alkalic. Sodium makes up about 54-56 percent of the cations in chabazite and about 46-49 percent of the cations in erionite. The sum of sodium and potassium in the chabazite and erionite is about 58-59 percent and about 60-64 percent, respectively. Inasmuch as sodium is the predominant cation in the chabazite and the erionite, both zeolites from this claim are considered sodium zeolites. The cation distribution in the three chabazite separates is about the same as that reported by Regis and Sand (1967) for an "intermediate sodium-calcium chabazite" from a lacustrine deposit in the San Simon basin, Arizona (the same deposit includes EZ No. 225 placer mining claim).

The molecular ratio Al_2O_3:(Ca,Mg,Na_2,K_2)O for zeolites should be unity; however, this ratio is 0.76-0.86 for the chabazite separates and 0.94-0.95 for the erionite separates shown in table 5. In other words, relative to the cation oxides, Al_2O_3 is deficient in all of the analyses, particularly the chabazite analyses. Inasmuch as ferric iron is known to substitute for aluminum in some natural zeolites, Fe_2O_3 was added to Al_2O_3. Most of the resulting ratios are greater than unity, but the ratios for the chabazites are greatly improved while the ratios for erionites show about the same departure from unityas that prior to the addition of Fe_2O_3. The molecular ratio Al_2O_3+Fe_2O_3:(Ca,Mg,Na_2,K_2)O is 0.98-1.05 for the chabazite separates and 1.05-1.06 for the erionite separates. Although some ferric iron may be in an impurity in the zeolite separates, all of it is treated as a zeolite framework constituent in table 6. Thus, the Si:Al+Fe^{+3} ratio is 2.81-2.86 for the chabazites and 3.03-3.13 for the erionites.

Table 6.--Composition of unit cell of chabazite and erionite from ore

[Atoms per unit cell calculated on the basis of 72 oxygen atoms]

	Chabazite			Erionite		
	EZ-225-1	EZ-225-2	EZ-225-3	EZ-225-1	EZ-225-2	EZ-225-3
Si	26.61	26.64	26.75	27.36	27.30	27.17
Al	7.25	7.26	7.63	7.87	7.87	7.96
Fe^{+3}	2.21	2.05	1.74	.88	.96	1.00
Mg	.90	.89	.82	.62	.63	.66
Ca	1.78	1.90	1.83	1.59	1.73	1.72
Na	3.61	3.66	3.39	2.94	2.77	2.95
K	.19	.25	.20	.96	.84	.74
H_2O	37.65	37.85	36.26	32.48	32.42	35.44
O	72.00	72.00	72.00	72.00	72.00	72.00
$Si+Al+Fe^{+3}$	36.07	35.95	36.12	36.11	36.13	36.13
$Si:Al+Fe^{+3}$	2.81	2.86	2.85	3.13	3.09	3.03

Other Properties of Chabazite and Erionite

Cell parameters for chabazite and erionite from Sample No. EZ-225-1 were determined by C. S. V. Barclay by a least-squares refinement of the X-ray powder diffraction data, utilizing the U.S. Geological Survey's FORTRAN IV computer program W9214. The resulting hexagonal cell parameters for chabazite are $a=13.728\pm0.003$ Å, $c=14.918\pm0.008$ Å, and $V=2{,}434.9\pm1.5$ Å^3. The hexagonal cell parameters for the erionite are $a=13.231\pm0.004$ Å, $c=15.020\pm0.007$ Å, and $V=2{,}277.1\pm1.7$ Å^3. These parameters seem consistent with the compositions of the zeolites.

Because of the small crystal size of the zeolites, particularly the chabazite, the indices of refractions could not be accurately determined. The mean index of refraction for erionite is 1.468-1.472. A mean index of refraction of less than 1.48 is all that could be determined for chabazite.

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