

SUMMARY AND CONCLUSIONS

The infrared absorption patterns covering the OH stretching frequencies of allophane, montmorillonite, illite and halloysite are presented.

The OH bond development in the allophane sample used is not sufficient to result in distinct bands of absorption.

As could be expected from the accepted structures of montmorillonite and illite, no evidence for unique OH bond directions was found. Indications are that a band of absorption at 3704 cm^{-1} may be useful in determining the octahedral filling of montmorillonite and illite.

For montmorillonite, two bands of absorption are creditable to adsorbed water. A broad band at 3440 cm^{-1} probably represents OH bonds within the water, whereas a relatively sharp band at 3635 cm^{-1} is considered indicative of OH bonding between the clay mineral surface and the water. These bands of absorption disappear at lower temperatures in the presence of sodium than in the presence of calcium, which agrees with previous findings.

Halloysite morphology did not lend itself to the sample study technique used. The resultant pattern has little interpretive usefulness.

As presented here, individual mineral absorption patterns appear unique; however, the applicability of this method for identification is doubtful.

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CHEMICAL COMPOSITION OF DIAGENETIC ZEOLITES FROM TUFFACEOUS ROCKS OF THE MOJAVE DESERT AND VICINITY, CALIFORNIA¹

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Zeolites are abundant rock-forming minerals in many tuffaceous rocks of Cenozoic age in the western United States. Some beds consist almost entirely of one or more zeolite (Deffeyes, 1959b; Regnier, 1960). In spite

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TABLE 1. X-RAY DIFFRACTION POWDER DATA FOR ZEOLITES
(DIFFRACTOMETER; COPPER RADIATION, NICKEL FILTER)

Clinoptilolite 1		Clinoptilolite 2		Erionite 3	
d(Å)	I	d(Å)	I	d(Å)	I
9.00	100	9.02	73	11.47	100
7.935	50	7.942	50	9.10	22
6.784	19	6.789	28	7.538	25
6.652	7			6.657	63
5.937	10			6.294	15
		5.890	16	5.731	14
5.243	13	5.243	19	5.350	16
5.126	30	5.129	35	4.559	19
		4.707	10	4.326	50
4.656	18	4.646	23	4.158	20
4.347	13	4.328	22	3.813	29
3.965	100	3.964	100	3.752	74
3.914	78	3.917	66	3.576	33
3.787	36	3.781	38	3.305	29
3.708	19	3.699	18	3.275	30
3.553	13	3.553	25	3.178	17
3.456	20	3.461	30	3.144	19
3.423	39	3.424	37	3.108	16
		3.121	23	2.923	14
3.078	26	3.070	18	2.860	40
3.042	12	3.054	14	2.843	63
2.978	58	2.975	48	2.815	52
		2.827	11	2.679	13
2.798	33	2.797	34	2.485	20
2.729	17	2.733	15	2.2048	9
2.715	15	2.725	15	2.1109	8
2.681	6			2.0822	5
2.454	18			2.0376	2
2.426	20			1.9827	4
2.169	10			1.9569	3
2.121	9			1.8846	9
2.089	6			1.8340	6
2.059	10			1.7723 α_1	12
2.015	14			1.7039	6
1.9955	8			1.6543 α_1	17
1.9581	15			1.5850 α_1	10
				1.5774	6
				1.5557	3
				1.4687	6
				1.4642	5
				1.2711 α_1	5

- Clinoptilolite; serial no. D100243. Gem Hill, SE $\frac{1}{4}$ sec. 26, T. 10 N., R. 13 W., Rosamond quad., Kern Co., Calif.
- Clinoptilolite; serial no. D100245. Last Chance Canyon, SE $\frac{1}{4}$ sec. 17, T. 29 S., R. 38 E., Saltdale quad., Kern Co., Calif.
- Erionite; serial no. D100244. Southern flank of Cady Mountains, SW $\frac{1}{4}$ sec. 6, T. 8 N., R. 5 E., Cady Mountains quad., San Bernardino Co., Calif.

of the abundance of such minerals, few analyses of these diagenetic zeolites have been published. Analyses of clinoptilolite are reported in Bramlette and Posnjak (1933, p. 170), Ames, Sand, and Goldich (1958, p. 31), Mason and Sand (1960, p. 346) and Hay (1963, p. 228). To the writers' knowledge, there are no previously published analyses of erionite from sedimentary environments. Publication of new chemical analyses of

TABLE 2. CHEMICAL ANALYSES OF DIAGENETIC ZEOLITES

	1	2	3
SiO ₂	65.59	68.11	59.16
Al ₂ O ₃	13.07	12.41	13.44
Fe ₂ O ₃	1.12	.77	1.48
FeO	.16	.00	.05
MgO	.17	.19	.26
CaO	1.05	1.78	.21
Na ₂ O	2.26	2.39	6.03
K ₂ O	5.43	3.86	3.29
H ₂ O ⁺	5.65	5.01	8.01
H ₂ O ⁻	4.86	4.84	7.43
TiO ₂	.09	.03	.15
P ₂ O ₅	.03	.02	.03
MnO	.01	.01	.03
Cl	.02	—	—
F	.02	—	—
	—	—	—
Less O	99.53	99.42	99.57
	.01	—	—
	—	—	—
Total	99.52	99.42	99.57

1. Clinoptilolite; serial no. D100243; analyst: E. L. Munson; $\alpha = 1.477 \pm .001$, $\gamma = 1.481 \pm .001$. Gem Hill Formation of Miocene age. Mineralogy of original sample: clinoptilolite—75 per cent, crystal fragments (quartz, plagioclase, sanidine, biotite, and magnetite)—15 per cent, montmorillonite—10 per cent. Locality: Gem Hill, SE $\frac{1}{4}$ sec. 26, T. 10 N., R. 13 W., Rosamond quad., Kern Co., Calif.
2. Clinoptilolite; serial no. D100245; analyst: E. L. Munson; $\alpha = 1.478 \pm .001$, $\gamma = 1.482 \pm .001$. Member 2 of Dibblee (1952) of Ricardo Formation of Pliocene age. Mineralogy of original sample: clinoptilolite—80 per cent, crystal fragments (quartz, plagioclase, sanidine, biotite, magnetite, and zircon)—15 per cent, montmorillonite—5 per cent. Locality: Last Chance Canyon, SE $\frac{1}{4}$ sec. 17, T. 29 S., R. 38 E., Saltdale quad., Kern Co., Calif.
3. Erionite; serial no. D100244; analyst: E. L. Munson; $\omega = 1.469 \pm .001$, $\epsilon = 1.472 \pm .001$. Unnamed formation of Miocene(?) or Pliocene(?) age. Mineralogy of original sample: erionite—90 per cent, crystal fragments (plagioclase, quartz, sanidine, biotite, hornblende, magnetite, zircon, and apatite)—5 per cent, montmorillonite—5 per cent. Locality: southern flank of Cady Mountains, SW $\frac{1}{4}$ sec. 6, T. 8 N., R. 5 E., Cady Mountains quad., San Bernardino Co., Calif.

clinoptilolite and erionite from sedimentary rocks thus seems warranted because of the increased interest in the use of natural zeolites for industrial processes and as indicators of post-depositional sedimentary environments (Deffeyes, 1959a).

The zeolites occur as replacements of vitric material in vitric tuffs that contain varying percentages of angular crystal fragments (Table 2). The vitroclastic texture is plainly evident in thin section even though no original glass remains. Both vesicular and nonvesicular glass were present in the clinoptilolite-rich tuffs, but only fine particles of nonvesicular glass were present in the erionite-rich tuff.

The zeolites were separated from the other rock constituents by the following steps: First, the rock was crushed, ultrasonically disaggregated and dispersed and then wet sieved. Then the $-100+270$ mesh fraction was concentrated by repeated centrifuging in a heavy liquid mixture ($G \approx 2.2$) of bromoform and *n,n*-dimethylformamide. The final separations consisted of approximately 99 per cent zeolite and 1 per cent impurity, mainly montmorillonite and iron oxide. Identification of the zeolites was made from *x*-ray diffractometer patterns of powders (Table 1).

Chemical analyses of two clinoptilolites and one erionite appear in Table 2. None of the analyses are corrected for the minor amount of impurities.

The analyses have been recalculated into atoms per unit cell, on the basis of 72 oxygen atoms, and are given in Table 3. Monovalent cations

TABLE 3. COMPOSITION OF UNIT CELL¹

Constituent	Atoms per unit cell		
	Clinoptilolite 1	Clinoptilolite 2	Erionite 3
Si	29.25	29.70	28.27
Al	6.87	6.38	7.57
Fe ⁺²	0.06	0.00	0.02
Mg	0.11	0.12	0.18
Ca	0.50	0.83	0.11
Na	1.96	2.02	5.59
K	3.09	2.15	2.00
H ₂ O ⁺	8.40	7.29	12.76
H ₂ O ⁻	7.23	7.04	11.84
O	72.00	72.00	72.00
Si+Al	36.12	36.08	35.84
Si/Al	4.26	4.65	3.73

¹ Fe³⁺, Ti, Mn, P, Cl and F were omitted in calculation of the unit cell.

TABLE 4. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES

	Clinoptilolite 1	Clinoptilolite 2	Erionite 3
B	<0.002	<0.002	0.002
Ba	.1	.1	.007
Be	.0001	.00015	.0003
Cr	0	0	.0001
Cu	.0007	.0015	.0005
Ga	.0015	.002	.003
La	0	0	.003
Pb	.001	.003	.0015
Sn ¹	.03	.01	.03
Sr	.03	.1	.003
V	.001	0	.003
Zr	0.005	0.003	0.007

Analyst: Joseph Haffty.

¹ Sn is assumed to be anomalously high because analyses of untreated tuff containing 75-90 per cent zeolite contains only 0.001 per cent Sn. The Sn apparently has been scavenged from the heavy liquid.

exceed divalent cations for both clinoptilolites and for the erionite. The potassium content of clinoptilolite is somewhat higher than that generally reported; however, Hay (1963) shows one clinoptilolite that contains as many as 2.53 potassium atoms per unit cell. The total water content for the analyzed zeolites is lower than the ideal value of 24 molecules per unit cell for clinoptilolite and 27 for erionite. Perhaps the low values are due to loss of weakly held water during storage in the low humidity of the Denver laboratory prior to analysis.

Semiquantitative spectrographic analyses of clinoptilolite and erionite appear in Table 4. Results are reported in per cent to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15 and 0.1, etc., which represents approximate midpoints of group data on a geometric scale. The assigned group for semiquantitative results will include the quantitative value about 30 per cent of the time. The symbol "<" with a number means less than the number shown—here usual detectabilities do not apply. Also looked for but not detected: Ag, As, Au, Bi, Cd, Ce, Co, Ge, Hf, Hg, In, Li, Mo, Nb, Ni, Pd, Pt, Re, Sb, Sc, Ta, Te, Th, Tl, U, W, Y, Yb and Zn.

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CRYSTALLOGRAPHIC DATA FOR THE IRON BORATE MINERAL, HULSITE¹

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The iron borate mineral, hulsite, from Brooks Mountain, Seward Peninsula, Alaska, was first described by Knopf and Schaller (1908). The chemical composition initially proposed for hulsite (Knopf and Schaller, 1908; Schaller, 1910) was later found to be incorrect (Schaller, written comm., 1955). The actual chemical composition is similar to that established for the ludwigite-vonsenite series of iron-magnesium-aluminum borates (Leonard and Vlisidis, 1960, 1961; Schaller and Vlisidis, 1961), *i.e.* $(\text{Fe}, \text{Mg})_2^{2+}(\text{Fe}, \text{Al})^{3+}\text{BO}_3\text{O}_2$. However, recent chemical studies by Schaller and Vlisidis (written comm., 1962) show that hulsite invariably contains tin (approximately 15 weight per cent SnO_2). Such sizeable amounts of tin have never been reported in analyses of members in the ludwigite-vonsenite series. Leonard, Hildebrand and Vlisidis (1962) state, "Tin is a minor constituent in quite a few members of the ludwigite-vonsenite series . . . and is a major constituent in the borate hulsite." Samples of hulsite from Brooks Mountain were kindly provided by W. T. Schaller for *x*-ray diffraction examinations, and the present note records the results.

The tiny hulsite cleavage fragments available (Schaller series no. H-5, least magnetic material, dimensions about $0.2 \times 0.2 \times 0.03$ mm) give excellent *x*-ray diffraction patterns. Single-crystal precession and Weissenberg techniques were used with Zr-filtered Mo radiation and Ni-filtered Cu radiation to obtain the diffraction data. Hulsite has monoclinic symmetry, and the diffraction data are compatible with space groups $P2$, Pm , and $P2/m$. Spatial considerations derived from accepted

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