

CLINOPTILOLITE AND FERRIERITE FROM
AGOURA, CALIFORNIA

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ABSTRACT

Coexisting clinoptilolite and ferrierite occur in cavities in an andesitic breccia near Agoura, Los Angeles County, California. The average cell contents of the clinoptilolite and ferrierite are $\text{Na}_{2.3}\text{K}_{1.7}\text{Ca}_{0.5}\text{Mg}_{0.2}\text{Al}_{0.2}(\text{Si}_{30}\text{Al}_6)\text{O}_{72}\cdot 24\text{H}_2\text{O}$ and $\text{Na}_{1.8}\text{K}_{1.4}\text{Mg}_{0.6}(\text{Si}_{31.6}\text{Al}_{4.4})\text{O}_{72}\cdot 18\text{H}_2\text{O}$, respectively. The clinoptilolite is similar in composition to reported analyses, whereas the ferrierite is far richer in Si and alkalis compared to published analyses.

The clinoptilolite crystals display a form, (20I), not reported for heulandite. The optic orientation with OP parallel to (010) and $Z \wedge a = 30^\circ$ to 45° is distinctly different from that of heulandite. Other properties are $2V_z = 32^\circ$ - 48° and $\beta = 1.479$. The small fibers (0.01 mm) of ferrierite prevent detailed optical study. Ferrierite cell dimensions and peak intensities may reflect compositional variation.

The earlier precipitation of calcite probably allowed these Si and alkali-rich zeolites to crystallize from water percolating through the breccia.

INTRODUCTION

The reported occurrences of clinoptilolite, the alkali and Si-rich zeolite with the heulandite structure, are restricted to altered rhyolite tuffs. It is commonly associated with opal, montmorillonite, calcite, and celadonite (Hay, 1966). In these tuffs the clinoptilolite is very fine-grained and identified only by X-ray diffraction methods. Ferrierite is a rare zeolite. Only two occurrences have been described in the literature (Graham, 1918, and Alietti, Passaglia, and Scaini, 1967), although others are known in California, Oregon, and British Columbia.¹ Ferrierite occurs in cavities in volcanic rocks and is associated with quartz (chalcedony) or calcite.

This paper describes a new occurrence of these two minerals, gives chemical data and physical properties, and offers an interpretation of their origin. A ferrierite from Sonora Pass, California, is also described.

OCCURRENCE AT AGOURA

Clinoptilolite and ferrierite occur in a breccia exposed in a quarry along Cornell Road, 6 miles southwest of Agoura in west Los Angeles County, California. The host rock is a brecciated porphyritic andesite, composed of microphenocrysts of plagioclase and hypersthene set in a glass-rich groundmass.

Cavities in the breccia are lined with a montmorillonitic clay covered by chalcedony. Some cavities have calcite also covered by chalcedony.

¹ A short manuscript prepared by the late R. M. Thompson describes a ferrierite from the north shore of Francois Lake, British Columbia. This ferrierite occurs as 1-2 mm radiating tuffs of minute needles on collinsite and carbonate fluorapatite.

The clinoptilolite occurs as clusters of platy crystals and is partially intergrown with tufts of very small (0.01 mm thick), soft, white ferrierite needles (Fig. 1).

CHEMICAL COMPOSITIONS

Analytical procedure. Polished grain mounts of each mineral were analyzed using an ARL electron microprobe analyzer. Volatilization of the lighter elements was reduced to a minimum by using a 10 to 15 μm diameter spot size and by using low sample currents of 0.2–0.3 μA at 15 kV. Silicate and oxide standards with reliable analyses were used. After correction for deadtime, background, and drift, the empirical correction factors of Bence and Albee (1968) were employed to convert corrected counts to weight percent

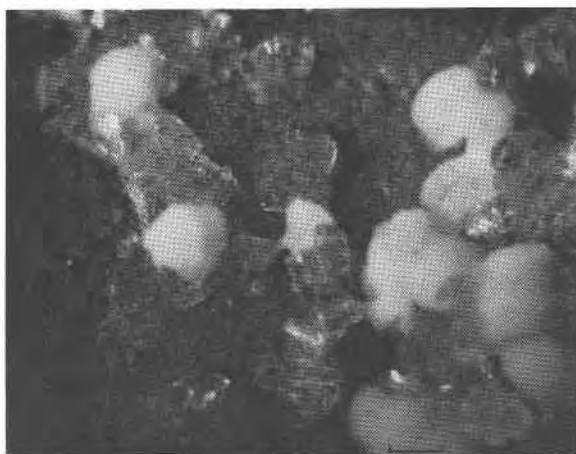


FIG. 1. A photomicrograph of ferrierite (white) and clinoptilolite from Agoura, California. Both minerals have grown on a chalcedony coating over montmorillonitic clay. Length of line is 1 mm.

oxide. The precision of this microprobe technique is generally less than ± 3 percent of the amount present, as estimated from alkali feldspars which were analyzed at the same time and for which reliable wet chemical analyses were available. The quality of the zeolite analyses can also be estimated from the charge balance between tetrahedral Al and Fe^{3+} and the exchangeable ions (Table 1).

Discussion of Results. Analyses and cell contents of separate crystals of clinoptilolite are given in Table 1, and these data are plotted on compositional diagrams of Figures 2 and 3. These analyses are similar in all respects to other published compositions.

The H_2O content listed in Table 1 is by difference. Therefore, the number of H_2O molecules in the unit cell was calculated from measured density, cell volume, and gram formula weight (from the analyses) (Wise, 1967). The variation in H_2O in the analyses is a result of the ease

TABLE 1. CHEMICAL ANALYSES^a AND CELL CONTENTS OF CLINOPTILOLITES AND FERRIERITES

	1	2	3	4	5	6	
SiO ₂	68.30	69.93	69.22	74.40	75.64	66.17	
Al ₂ O ₃	11.66	11.89	11.74	8.51	9.39	10.71	
Fe ₂ O ₃	0.02	0.02	0.04	0.04	0.01	0.99	
MgO	0.36	0.47	0.35	1.07	1.02	2.79	
CaO	1.03	1.07	1.16	0.13	0.14	0.55	
Na ₂ O	2.47	2.96	2.45	1.91	2.33	0.0	
K ₂ O	2.93	3.47	3.00	2.48	2.80	1.54	
(H ₂ O) ^b	13.23	10.19	12.04	11.46	8.67	17.25	
(total)	100	100	100	100	100	100	
Number of ions per unit cell with 72 O's							
Framework cations	{ Si	30.17	30.02	30.17	31.71	31.39	30.21
	{ Al	5.83	5.98	5.83	4.27	4.59	5.76
	{ Fe ³⁺	—	—	—	.01	—	—
Exchangeable cations	{ Al	.24	.03	.20	—	—	—
	{ Fe ³⁺	—	—	.01	—	—	.37 ^c
	{ Mg	.23	.30	.22	.68	.62	1.89
	{ Ca	.48	.49	.54	.05	.05	.26
	{ Na	2.10	2.45	2.07	1.56	1.87	—
{ K	1.64	1.88	1.65	1.33	1.47	.88	
H ₂ O molecules	24.0	23.2	23.9	18.2	18.2	18.7	
Σ charges of exchangeable ions	5.88	5.97	5.87	4.35	4.68	5.92	

1-3. Clinoptilolites from Agoura.

4, 5. Ferrierites from Agoura.

6. Ferrierite from Sonora Pass., California.

^a Data from electron microprobe analysis by W. J. Nokleberg.

^b Determined by difference.

^c This iron should be considered in the ferrous state, in order to achieve a balance of charge.

with which these zeolites give up H₂O. Some of the H₂O is lost in the vacuum of the electron microprobe analyzer.

Analyses and cell contents of two clusters of ferrierite crystals are given in Table 1. The data are also plotted in Figures 2 and 3. Another ferrierite from Sonora Pass was also analyzed, and the data are given in Table 1. It is obvious from Figure 2 that ferrierites have a wide range of compositions and that those from Agoura are the richest in Si and alkalis.

The Agoura ferrierites contain only 0.65 ions of Mg per unit cell. This is in distinct contrast to the other analyzed ferrierites, which have about 2.0 ions per cell and occupy specific sites in the channels (Vaughan, 1966). The Mg apparently is not an essential component of ferrierite.

The Sonora Pass ferrierite, similar to the Kamloops, British Columbia material, is zoned from colorless to red along the length of the needles. The red color of other zeolites, *e.g.* heulandite, appears to result from Fe^{3+} ions in tetrahedral sites. In order to balance charges and satisfy

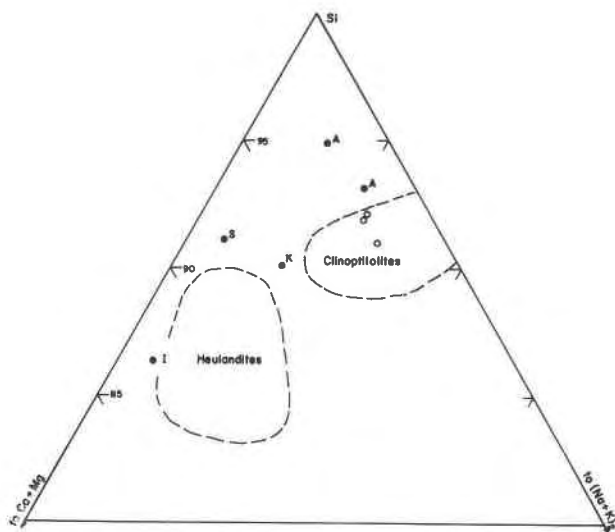


FIG. 2. Ferrierite and clinoptilolite compositions plotted in the upper portion of the $\text{Si}-(\text{Ca}+\text{Mg})-(\text{Na}+\text{K})_2$ triangle. Agoura clinoptilolites are open circles. Ferrierites are solid circles: A, Agoura; K, Kamloops, British Columbia; S, Sonora Pass, California; and I, Italy. Heulandite and clinoptilolite fields are from compilations given by Wise and Fisher (in preparation).

tetrahedral sites in the Sonora Pass sample, most of the Fe must be calculated as Fe^{2+} and considered as exchangeable ions. However, we are dubious of the validity of this calculation and hold the accuracy of the analysis in some doubt.

Because the two Agoura zeolites appear to have crystallized together, fractionation of exchangeable ions may have occurred. Figure 3 illustrates similarities and differences in the $\text{Na}/(\text{Na}+\text{K})$ and $\text{Ca}/(\text{Ca}+\text{Mg})$ ratios of these minerals. The two Agoura zeolites have nearly the same $\text{Na}/(\text{Na}+\text{K})$ ratio, but differ widely in their $\text{Ca}/(\text{Ca}+\text{Mg})$ ratios. The clinoptilolite has nearly all of the available Ca, whereas the ferrierite has

70 percent of the Mg. This fractionation may be a result of special sites for $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ ions in ferrierite (Vaughan, 1966); other cations cannot get into these sites.

CRYSTALLOGRAPHY AND OPTICAL PROPERTIES

The clinoptilolite crystals, which occur in clusters of platy crystals, exhibit (010), (001), (101) and $(20\bar{1})$ faces (Fig. 4). The $(20\bar{1})$ form has not been reported for heulandite (Goldschmidt, 1913–1923). The interfacial

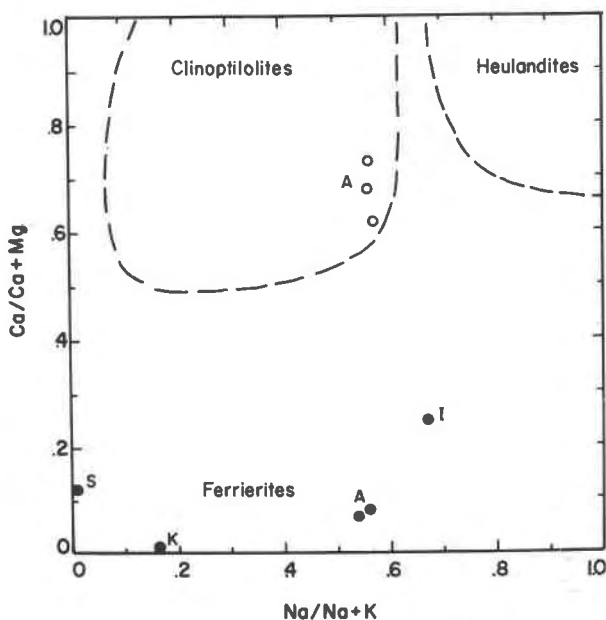


FIG. 3. A $\text{Ca}/(\text{Ca}+\text{Mg})$ vs $\text{Na}/(\text{Na}+\text{K})$ plot of clinoptilolites and ferrierites. Symbols are the same in Fig. 2. Note that the Agoura clinoptilolites have the same $\text{Na}/(\text{Na}+\text{K})$ ratio as the ferrierites from the same locality.

angles given in Figure 4 were calculated from unit-cell data, because the crystals are too small for accurate measurement.

The optical orientations and properties are distinctly different from those of heulandite (see Table 2 and Fig. 4). The optic plane is parallel to 010 (Y parallel to b). In heulandite the optic plane is normal to (010) with Z parallel to b . The positions of the Z and X directions in the clinoptilolite are somewhat variable in the 010 plane. Dispersion of the optic axes is strong with $r > v$ and appears to be axial dispersion. Heulandites, because of the different orientation, commonly display crossed dispersion with $r \approx v$.

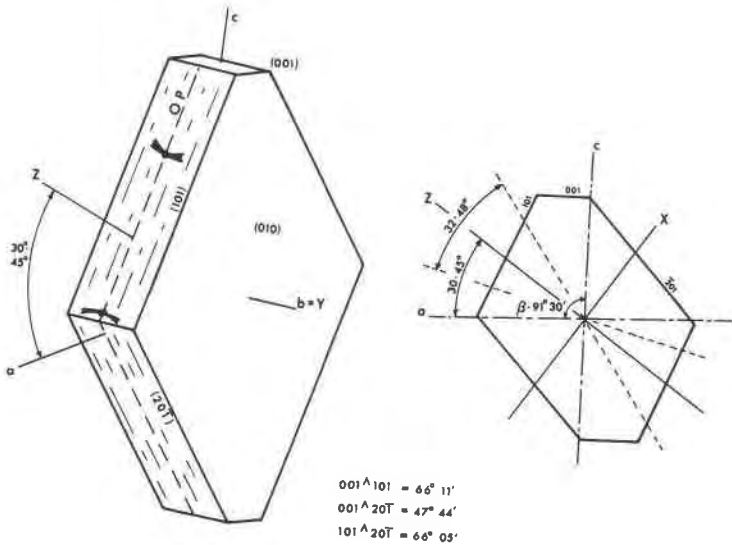


FIG. 4. Crystallographic and optical data for the Agoura clinoptilolite.

These properties are surprising, because heulandite and clinoptilolite have been considered isostructural (Hey and Bannister, 1934). At present there are insufficient data to say whether these differences in crystal form and optic orientation result from structural differences or merely the alkali- and silica-rich composition.

The ferrierite tufts are composed of such small needles that detailed study was not possible. The refractive indices are lower than other ferrierites, because of the high alkali content.

X-RAY DIFFRACTION DATA

Table 3 contains powder diffraction data for the clinoptilolite, as well as computed cell dimensions. These data are very similar to other

TABLE 2. OPTICAL PROPERTIES OF CLINOPTILOLITE AND FERRIERITE

	Clinoptilolite Agoura	Ferrierite Agoura	Ferrierite Sonora Pass
α	1.478	—	1.476
β	1.479	1.478	—
γ	1.481 (all $\pm .001$)	—	1.482
$2V_z$	32° to 48°		
Disp.	strong $r > v$		

TABLE 3. X-RAY POWDER DATA FOR THE AGOURA CLINOPTILOLITE

<i>hkl</i>	$d_{(obs)}$	$d_{(calc)}$	I/I_0	<i>hkl</i>	$d_{(obs)}$	$d_{(calc)}$	I/I_0
020	8.92 ^a	8.95	100	21 $\bar{1}$	3.55	3.554	6
002	7.97	7.92	3	051, 11 $\bar{4}$	3.48	3.46	3
10 $\bar{1}$	6.78	6.78	2	220	2.419 ^a	3.421	16
031	5.61	5.58	2	202	3.324	3.322	4
112	5.15	5.12	7	22 $\bar{2}$	3.168 ^a	3.169	14
130	4.65 ^a	4.645	14	222	3.119 ^a	3.114	15
10 $\bar{3}$	4.35	4.354	2	231	3.07	3.073	8
132	3.964 ^a	3.979	55	044	2.974	2.966	80
004	3.964 ^a	3.961	55	035	2.793 ^a	2.798	15
042	3.897 ^a	3.895	57	12 $\bar{5}$	2.793 ^a	2.794	15
14 $\bar{1}$	3.74	3.733	7	16 $\bar{1}$	2.728	2.730	33

^a Reflections used for cell dimension refinement.

Cell dimensions: (3 cycles least-squares refinement)

$a = 7.41 (\pm 0.01) \text{ \AA}$

$b = 17.89 (\pm 0.04) \text{ \AA}$

$c = 15.85 (\pm 0.03) \text{ \AA}$

$\beta = 91^\circ 29' (\pm 14')$

$V = 2100.3 \text{ \AA}^3$

$(\rho_{meas}) = 2.16 (\pm 0.02) \text{ gm/cm}^3$

clinoptilolites and heulandites; they do not reflect composition variations. Clinoptilolite, heated overnight at 400°C exhibits the lattice stability observed in other clinoptilolites by Mumpton (1960).

Table 4 presents powder diffraction data and computed cell dimensions for the Agoura, Sonora Pass, and Kamloops ferrierites. The low Mg and high alkali content of the Agoura ferrierite is noticeably reflected in a shorter a cell dimension and a change in certain peak intensities, especially (420), (330), (510), and (040). Steps were taken to minimize any preferred orientation in the powder mounts.

ORIGIN OF THE ZEOLITES

Ground water circulating through the tectonically shattered andesite probably dissolved some components from the glassy rock. Significant amounts of Si, Al, Mg, Ca, Na, and K could have been locally derived. A high activity of carbonate ions caused the early precipitation of calcite, thereby removing much of the Ca^{2+} ions and leaving the water alkali rich. The solutions, with which the zeolites were last in equilibrium, must have had an $\text{Na}/\text{Na}+\text{K}$ ratio similar to that observed in the zeolites. Neither zeolite possesses a structural mechanism for fractionating these two ions. However, Ca^{2+} and Mg^{2+} ions were fractionated, probably controlled by the Mg site in the ferrierite.

TABLE 4. X-RAY POWDER DATA FOR THE AGOURA AND SONORA PASS FERRIERITES

<i>Agoura</i>				<i>Sonora</i>			d^a
<i>hkl</i>	$d_{(obs)}$	$d_{(calc)}$	I/I_0	$d_{(obs)}$	$d_{(calc)}$	I/I_0	
110	11.33	11.34	3	—	11.38	—	11.33
200	9.47	9.51	50	9.56	9.59	80	9.61
020	7.07	7.07	38	7.06	7.07	12	7.00
011	6.59	6.61	3	6.61	6.61	8	6.61
310	5.75	5.78	15	5.83	5.82	21	5.84
220	5.64	5.67	14	5.71	5.69	8	—
121	—	—	—	—	4.97	—	4.96
400	4.75	4.75	2	—	4.79	—	4.80
130	4.56	4.57	1	—	4.58	—	4.58
031	3.977	3.987	35	3.99	3.99	29	3.99
420	3.943 ^c	3.944	35	3.971 ^c	3.968	60	—
411	—	—	—	—	—	—	3.88
330	3.778 ^c	3.781	65	3.794 ^c	3.793	55	3.79
510	3.661	3.672	12	3.700 ^c	3.702	37	3.69
040	3.537 ^c	3.534	100	3.533 ^c	3.534	100	3.54
202	3.480 ^c	3.483	18	3.489 ^c	3.489	50	3.47
501	—	—	—	—	—	—	3.42
240	3.313 ^c	3.312	35	3.317 ^c	3.316	13	3.31
600	—	—	—	—	—	—	3.20
312	3.140 ^c	3.142	12	3.151	3.150	9	3.15
521	—	—	—	3.073 ^c	3.074	13	3.07
431	3.048	3.055	12	—	—	—	—
530	—	—	—	2.976 ^c	2.975	22	2.97
402	2.945 ^c	2.941	11	—	—	—	—
051	2.644 ^c	2.645	7	—	—	—	2.64
350	2.582 ^c	2.582	10	—	—	—	2.58

Cell dimensions: (3 cycles least-squares refinement)

	<i>Agoura</i>	<i>Sonora Pass</i>	<i>Kamloops</i>
a , Å	19.015 (± 0.026)	19.177 (± 0.007)	19.156 ^b
b , Å	14.135 (± 0.007)	14.137 (± 0.005)	14.127
c , Å	7.486 (± 0.006)	7.490 (± 0.004)	7.489
V , Å ³	2011.9	2030.7	—
ρ_{meas} g/cm ³	2.14	2.13	2.136

^a From Staples (1955).^b From Vaughan (1966).^c Reflections used in cell dimension refinement.

With quartz present at the time of zeolite crystallization, the solution must have been saturated with respect to Si. It is not clear why two Si-rich zeolites should have crystallized instead of just one, as in other occurrences of each of these minerals. The variations in exchangeable ions reported for both heulandite-clinoptilolites and ferrierites, argues these ions have little control on the building of a Si-O framework. Perhaps the relative activities of Si and Al are of primary importance in controlling the formation of a particular type of zeolite structure.

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REFERENCES

- ALIETTI, A., E. PASSAGLIA, AND G. SCAINI (1967) A new occurrence of ferrierite. *Amer. Mineral.*, **52**, 1562-1563.
- BENCE, A. E., AND A. L. ALBEE (1968) Empirical correction factors for the electron microanalysis of silicates and oxides. *J. Geol.*, **76**, 382-403.
- GOLDSCHMIDT, V. (1913-1923). *Atlas der Krystallformen*, vol. 4. Heidelberg,
- GRAHAM, R. P. D. (1918) On ferrierite, a new zeolite mineral, from British Columbia; with notes on some other Canadian minerals. *Proc. Trans. Roy. Soc. Can., 3rd Ses., Sect. IV*, 185-190.
- HAY, R. L. (1966) Zeolites and zeolitic reactions in sedimentary rocks. *Geol. Soc. Amer. Spec. Pap.* **85**.
- HEY, M. H., AND F. A. BANNISTER (1934) Studies on the zeolites. Part VIII "Clinoptilolite," a silica-rich variety of heulandite. *Mineral Mag.*, **23**, 556-557.
- MUMPTON, F. A. (1960) Clinoptilolite redefined: *Amer. Mineral.*, **45**, 351-369.
- STAPLES, L. W. (1955) X-ray investigation of ferrierite, a zeolite. *Amer. Mineral.*, **40**, 1095-1099.
- VAUGHAN, P. A. (1966) The crystal structure of the zeolite ferrierite. *Acta Crystallogr.*, **21**, 983-990.
- WISE, W. S. (1967) A heulandite with excess water. *Mineral Mag.*, **36**, 64-69.
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