# 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 $Na_{2.3}K_{1.7}Ca_{0.5}Mg_{0.2}Al_{0.2}(Si_{30}Al_6)$ $O_{72} \cdot 24H_2O$ and $Na_{1.8}K_{1.4}Mg_{0.6}(Si_{31.6}Al_{4.4})$ $O_{72} \cdot 18H_2O$, 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, $(20\bar{1})$, not reported for heulandite. The optic orientation with OP parallel to (010) and $Z \wedge a = 30°$ to $45°$ is distinctly different from that of heulandite. Other properties are $2V_z = 32°-48°$ 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. Volitilization of the lighter elements was reduced to a minimum by using a 10 to 15 $\mu$m diameter spot size and by using low sample currents of 0.2–0.3 $\mu$A 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
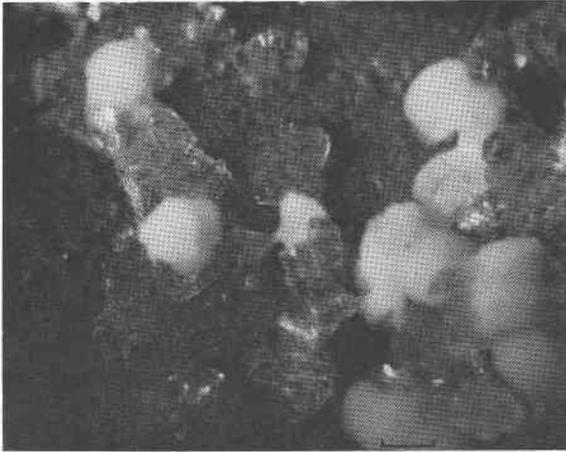


FIG. 1. A photomicrograph of ferrierite (white) and clinoptilolite from Agoura, California. Both minerals have grown on a chalcedony coating over montmorillonitic clay. Length of line is 1 mm.

oxide. The precision of this microprobe technique is generally less than $\pm 3$ 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 |
| $Al_2O_3$ | 11.66 | 11.89 | 11.74 | 8.51 | 9.39 | 10.71 |
| $Fe_2O_3$ | 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 |
| $Na_2O$ | 2.47 | 2.96 | 2.45 | 1.91 | 2.33 | 0.0 |
| $K_2O$ | 2.93 | 3.47 | 3.00 | 2.48 | 2.80 | 1.54 |
| $(H_2O)$[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 0's

| | | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| 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 |
| $H_2O$ molecules | | 24.0 | 23.2 | 23.9 | 18.2 | 18.2 | 18.7 |
| Σ charges of exchangable 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 electon 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 $H_2O$. Some of the $H_2O$ 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



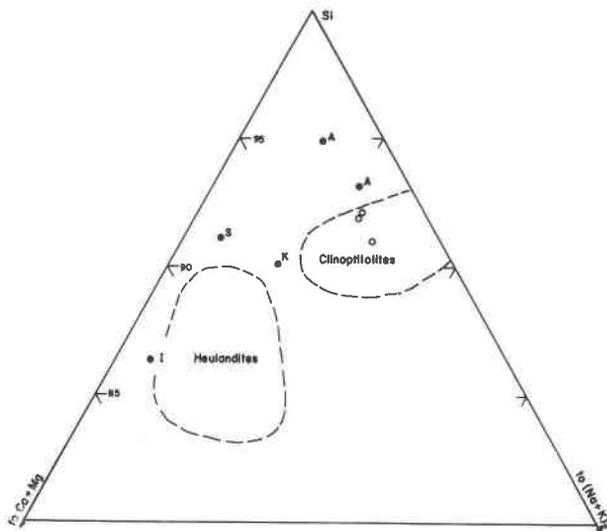FIG. 2. Ferrierite and clinoptilolite compositions plotted in the upper portion of the Si-$(Ca+Mg) - (Na+K)_2$ triangle. Agoura clinoptilolites are open circles. Ferrierites are solid circles: A, Agoura; K, Kamloops, British Columbia; S, Sonora Pass, California; and I, Italy. Heulandite and clinoptilolite 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 $Na/(Na+K)$ and $Ca/(Ca+Mg)$ ratios of these minerals. The two Agoura zeolites have nearly the same $Na/(Na+K)$ ratio, but differ widely in their $Ca/(Ca+Mg)$ 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 $Mg(H_2O)_6^{2+}$ 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
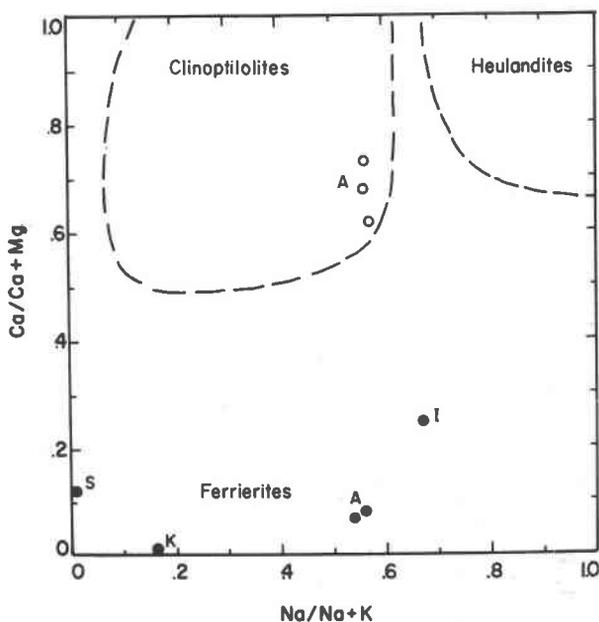


FIG. 3. A Ca/(Ca+Mg) vs Na/(Na+K) plot of clinoptilolites and ferrierites. Symbols are the same in Fig. 2. Note that the Agoura clinoptilolites have the same Na/Na+K ratio as the ferrierites from the same locality.

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≃v.

$001 \wedge 101 = 66° 11'$

$001 \wedge 20\overline{1} = 47° 44'$
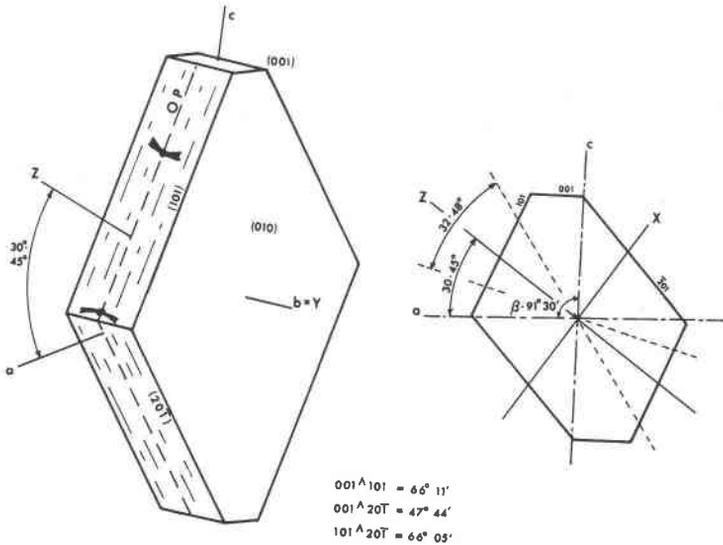
$101 \wedge 20\overline{1} = 66° 05'$

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 |
|---|---|---|---|
| $\alpha$ | 1.478 | — | 1.476 |
| $\beta$ | 1.479 | 1.478 | — |
| $\gamma$ | 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

| $hkl$ | $d_{(obs)}$ | $d_{(calc)}$ | $I/I_0$ | $hkl$ | $d_{(obs)}$ | $d_{(calc)}$ | $I/I_0$ |
|---|---|---|---|---|---|---|---|
| 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)
$a = 7.41 \ (\pm 0.01)$ Å
$b = 17.89 \ (\pm 0.04)$ Å
$c = 15.85 \ (\pm 0.03)$ Å
$\beta = 91° \ 29' \ (\pm 14')$
$V = 2100.3$ Å$^3$
$(\rho_{meas}) = 2.16 \ (\pm 0.02)$ 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 Na/Na+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

| | Agoura | | | Sonora | | | |
|---|---|---|---|---|---|---|---|
| hkl | $d_{(obs)}$ | $d_{(calc)}$ | $I/I_0$ | $d_{(obs)}$ | $d_{(calc)}$ | $I/I_0$ | $d^a$ |
| 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)

| | Agoura | Sonora Pass | Kamloops |
|---|---|---|---|
| $a$, Å | 19.015 ($\pm0.026$) | 19.177 ($\pm0.007$) | 19.156[b] |
| $b$, Å | 14.135 ($\pm0.007$) | 14.137 ($\pm0.005$) | 14.127 |
| $c$, Å | 7.486 ($\pm0.006$) | 7.490 ($\pm0.004$) | 7.489 |
| $V$, Å³ | 2011.9 | 2030.7 | |
| $\rho_{meas}$ g/cm³ | 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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