Levyne-Offretite Intergrowths from Basalt near Beech Creek, Grant County, Oregon

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Abstract

Intergrowths of levyne and offretite occur in vesicles of the Picture Gorge Basalt near Beech Creek, Oregon. Levyne occurs as aggregates of thin, platy crystals, and the offretite occurs as white, silky, fibrous layers on the levyne. The offretite fibers grew normal to the (0001) of levyne, and, locally, replaced the levyne. Electron microprobe analyses of the zeolites yielded the formulas Ca$_{0.30}$Mg$_{0.6}$Na$_{0.5}$K$_{0.7}$Al$_{0.5}$Si$_{11.6}$O$_{37}$nH$_2$O for levyne and Ca$_{0.78}$Mg$_{0.17}$Na$_{0.3}$K$_{1.1}$Al$_{3.3}$Si$_{12.7}$O$_{37}$.nH$_2$O for offretite. Hexagonal cell parameters for the levyne are $a = 13.356(3)$ Å, $c = 22.88(1)$ Å, $V = 3.535(2)$ Å$^3$; and for the offretite, $a = 13.348(2)$ Å, $c = 7.59(2)$ Å, $V = 1.172(3)$ Å$^3$. Offretite had previously been recognized only from the type locality near Montbrison, France. Thus, the identification of offretite from the Beech Creek locality, as well as from other similar occurrences associated with levyne in basalts, indicates that it is not so rare as previously supposed.

Introduction

Offretite was first recognized by Gonnard (1890) as a new zeolite in amygdaloidal basalt at Mount Simionse near Montbrison, Loire, France. Except for a possible occurrence in basalt from Palau Island, Caroline Islands (Diirrfeld, 1911), no other occurrence of offretite has been reported. Erionite, a closely related (Bennett and Gard, 1962) but much more common zeolite, has been reported from amygdaloidal basalts and especially from diagenetically altered vitric tuffs (Sheppard and Gude, 1969).

Shimazu and Mizota (1972) described intergrowths of erionite and levyne in amygdaloidal basalts from Chojabaru, Iki Island, Japan, and from a locality in the United States designated as Beech Creek, Oregon. The identification of the erionite from Japan is supported by X-ray, optical, and chemical data; however, the identification of the Beech Creek material is doubtful and is supported only by a chemical analysis and incomplete X-ray data. Even the chemical analysis of the Beech Creek material given by Shimazu and Mizota (1972, p. 420) seems closer to that of offretite than to that of erionite. Furthermore, we have been studying the zeolites from the Beech Creek locality since 1971 and have identified intergrowths of levyne and offretite. This occurrence of offretite at Beech Creek is the only documented occurrence other than that near Montbrison, France.

Occurrence of Levyne and Offretite

Our specimens were collected from the Miocene Picture Gorge Basalt by A. L. McGuinness in 1964. The zeolite-bearing basalt flow crops out in a small quarry about 0.2 km east of Beech Creek in the NW¼ SW¼ sec. 18, T. 12 S., R. 31 E., Grant County, Oregon. A preliminary geologic map of the Long Creek quadrangle (Thayer and Brown, 1967) shows that the Picture Gorge Basalt dips gently northward at this locality. The basalt is dark gray and vesicular, and most vesicles are in the range of 5–20 mm. Thin sections show that the basalt has an intersertal texture and consists of calcic plagioclase laths, subophitic clinopyroxene, dark-brown glass, and minor olivine.

Levyne occurs in vesicles of the basalt as thin, platy, single crystals parallel to (0001) or more commonly as parallel aggregates of platy crystals that are mostly 1–7 mm in longest dimension. Individual crystals of levyne are 0.01–0.2 mm thick, but the aggregates of platy crystals are commonly 0.2–1.0 mm thick. The levyne forms a boxwork within
the vesicles (Fig. 1) and generally is separated from
the vesicle wall by a thin film of an unidentified
greenish-brown, 14 Å clay mineral.

Offretite occurs as a silky white coating on the
levyne. Aggregates of the platy levyne, if broken
normal to the plates, also show layers of fibrous
offretite between the individual levyne plates. Under
a hand lens, these broken crystals show an alternation
of clear levyne and white offretite (Fig. 1). The
offretite has grown perpendicular to (0001) of
levyne (Fig. 2). Offretite layers are 2–80 μm thick
and consist of compact fibers that show pointed
terminations where they have grown on single
crystals of levyne (Fig. 3).

Some vesicles in the basalt are filled with colorless
chabazite. The chabazite generally fills the entire
vesicle and nowhere has been found associated with
the levyne-offretite intergrowths.

Fig. 1. Boxwork of levyne (pale gray) and offretite (white)
in a large vesicle in the Picture Gorge Basalt.

Fig. 2. Scanning electron micrograph showing fibrous
layers of offretite (O) that grew normal to a single crystal
of levyne (L).

**Chemical Composition of Levyne and Offretite**

Standard chemical analyses could not be per-
formed on the levyne or the offretite because of
the difficulty in obtaining sufficient quantities of pure
separates. Both zeolites were, however, amenable
to analysis by the electron microprobe. An ARL
model EMX-8M microprobe was used, and the elec-
tron beam was defocused to a diameter of 25 μm
to eliminate decomposition effects. Matrix correc-
tions of X-ray intensities were not made.

The electron microprobe analyses and unit cell
contents of the Beech Creek levyne and offretite
(U.S. National Museum No. R15766) are given
in Table 1. The mole ratio Al₂O₃: (Ca, Mg, Na₂,
K₂)O for zeolites should be unity, but this ratio is
1.16 and 1.15 for levyne and offretite, respectively.
Thus, both analyses show a slight excess of Al₂O₃
relative to the sum of the cation oxides. Divalent
cations are in excess of monovalent ones for both
zeolites, and the Si:Al ratio for levyne and offretite
is 1.69 and 1.99, respectively.
The reported compositions of erionites and offretites are represented in Figure 4. Erionites are more siliceous and alkali rich than offretites. Erionite generally has a Si:Al+:Fe3+ ratio greater than 3 and a Na+K:Na+K+Ca+Mg ratio greater than 0.5, whereas offretite has a Si:Al+:Fe3+ ratio less than 3 and a Na+K:Na+K+Ca+Mg ratio less than 0.5. Analysis 1 represents the offretite from the original locality near Montbrison, France. Analysis F is the Beech Creek offretite given in Table 1, and analysis C is a Beech Creek zeolite identified as erionite by Shimazu and Mizota (1972). Both analyses, F and C, clearly plot in the offretite field. Analysis D is an unidentified zeolite that was reported by Cross and Hillebrand (1885, p. 38) from the Table Mountain Shoshonite at Golden, Colorado. This zeolite is associated with levyne, and the brief published description and the analysis suggest that it is offretite.

Optical Properties and X-ray Powder Data

Levyne and offretite are uniaxial negative. Indices of refraction for the Beech Creek levyne are \( \mu = 1.498 \) and \( \epsilon = 1.494 \), and the indices for the offretite

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table
\end{align*}

**TABLE 1.** Electron Microprobe Analyses* and Unit Cell Contents of Levyne and Offretite from Beech Creek, Oregon

<table>
<thead>
<tr>
<th></th>
<th>Levyne</th>
<th>Offretite</th>
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<tbody>
<tr>
<td><strong>Electron microprobe analyses in weight percent</strong></td>
<td></td>
<td></td>
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<tr>
<td>SiO₂</td>
<td>48.8 (0.8)</td>
<td>53.5 (0.5)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>24.5 (1.6)</td>
<td>22.8 (0.6)</td>
</tr>
<tr>
<td>MgO</td>
<td>0.0</td>
<td>0.50 (0.01)</td>
</tr>
<tr>
<td>CaO</td>
<td>9.95 (0.40)</td>
<td>7.33 (0.36)</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.28 (0.15)</td>
<td>0.69 (0.50)</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.90 (0.43)</td>
<td>3.77 (0.10)</td>
</tr>
<tr>
<td><strong>Unit cell contents on the basis of O = 36</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>11.45</td>
<td>12.11</td>
</tr>
<tr>
<td>Al</td>
<td>6.78</td>
<td>6.08</td>
</tr>
<tr>
<td>Mg</td>
<td>0.00</td>
<td>0.17</td>
</tr>
<tr>
<td>Ca</td>
<td>2.50</td>
<td>1.79</td>
</tr>
<tr>
<td>Na</td>
<td>0.58</td>
<td>0.30</td>
</tr>
<tr>
<td>K</td>
<td>0.27</td>
<td>1.09</td>
</tr>
<tr>
<td>Si + Al</td>
<td>18.23</td>
<td>18.19</td>
</tr>
<tr>
<td>Si : Al</td>
<td>1.69</td>
<td>1.99</td>
</tr>
</tbody>
</table>

*The elements were analyzed at three different operating conditions, with spectral lines and analyzing crystals as follows: (1) FeKα -LiF, BaLα -LiF, and KAp -NaF at 15 kV and 30 nA; (2) CaKα -LiF, NaKα -LiF, and MgKα -KAP at 5 kV and 30 nA. Reference standards included albite, hornblende, three synthetic glasses, microcline, quartz, corundum, periclase, and anorthite.

**Standard deviations are given in parentheses. FeO is less than 0.1 weight percent, and BaO is less than 0.05 weight percent.**
are \( \omega = 1.495 \) and \( \epsilon = 1.491 \). All of the indices of refraction are \( \pm 0.001 \). Inasmuch as the Beech Creek offretite has grown normal to (0001) of the levyne, the \( c \) crystallographic axes of both zeolites are parallel. Offretite has negative elongation, a property that serves to distinguish it from erionite (Sheppard and Gude, 1969). In addition, the measured indices of refraction of the Beech Creek offretite are significantly higher than those of any reported erionite.

X-ray powder diffraction data for the Beech Creek levyne and offretite (Table 2) were obtained for pure separates hand picked from gently crushed levyne-offretite intergrowths. Because of the small quantities obtained by this method, the X-ray data were collected from collodion-membrane mounts of unoriented powder to which annealed fluorite had been added as an internal standard. Diagrammatic X-ray powder diffraction patterns for the Montbrison offretite, the Beech Creek offretite, and a typical erionite are shown in Figure 5. Although offretite and erionite have many lines in common, there are sufficient differences in the number and positions of the lines to distinguish the two zeolites. Figure 5 clearly shows that the Beech Creek zeolite studied here is offretite and not erionite.

Cell parameters for the Beech Creek levyne and offretite were obtained by a least-squares refinement of the X-ray powder diffractometer data utilizing the U.S. Geological Survey's FORTRAN IV computer program W9214. The resulting hexagonal cell parameters for levyne are \( a = 13.356(3) \) \( \AA \), \( c = 22.88(1) \) \( \AA \), and \( V = 3,535(2) \) \( \AA^3 \) and for offretite are

| Table 2. X-Ray Powder Diffraction Data* for Levyne and Offretite |
|----------------------|----------------------|
| **Levyne**           | **Offretite**        |
| \( h \) \( k \) \( l \) | \( d_{cal} \) (\( \AA \)) | \( d_{obs} \) (\( \AA \)) | \( h \) \( k \) \( l \) | \( d_{cal} \) (\( \AA \)) | \( d_{obs} \) (\( \AA \)) |
|----------------------|----------------------|
| 100                  | 11.57                | 11.58                | 100                  | 11.56                | 11.56                |
| 101                  | 10.32                | 10.36                | 101                  | 10.31                | 10.34                |
| 102                  | 8.14                 | 8.15                 | 102                  | 8.13                 | 8.14                 |
| 103                  | 6.68                 | 6.69                 | 103                  | 6.67                 | 6.68                 |
| 200                  | 11.41                | 11.41                | 200                  | 11.40                | 11.40                |
| 201                  | 10.51                | 10.52                | 201                  | 10.51                | 10.52                |
| 202                  | 9.50                 | 9.51                 | 202                  | 9.49                 | 9.50                 |
| 203                  | 8.69                 | 8.70                 | 203                  | 8.68                 | 8.69                 |
| 204                  | 7.79                 | 7.80                 | 204                  | 7.78                 | 7.79                 |

* Diffractometer, nickel-filtered CuK\( \alpha \) radiation, 1° divergence slit, 0.002-inch receiving slit, scanning speed of 1/2°/2 \( \theta \) per minute, fluorite internal standard. Calculated \( d \)'s less than 2.500 are reported only for observed reflections.

Fig. 5. Diagrammatic representation of X-ray powder diffractometer patterns for the Beech Creek offretite, the Montbrison offretite, and a typical erionite. Relative intensities are indicated by height of lines above baseline.
are $a = 13.348(2)$ Å, $c = 7.59(2)$ Å, and $V = 1,172(3)$ Å$^3$. These values are close to published cell parameters for the two zeolites. The $a$ dimension is nearly the same for both levyne and offretite, but the $c$ dimension for levyne is about three times that for offretite.

**Discussion**

The offretite from Beech Creek has clearly formed later than the levyne, and, at least locally, has replaced the levyne. Most clay minerals and zeolites in the vesicles of Cenozoic basalts formed after crystallization and cooling of the basalts (Nashar and Basden, 1965). The Beech Creek zeolites are probably no exception, and the constituents necessary for the zeolites were probably dissolved from the Picture Gorge Basalt by cool meteoric water. Compositional differences in the zeolites probably reflect the compositional differences in the solutions from which the zeolites crystallized. The relatively late offretite crystallized from a solution characterized by a higher potassium and Si:Al ratio but lower calcium and, especially, sodium contents than that from which the earlier levyne crystallized.

In addition to the levyne-offretite intergrowths from Beech Creek and possibly from Table Mountain, Golden, Colorado, other published descriptions of zeolites in basalts suggest that this association may be relatively common. Walker (1951, p. 776) described a satiny, fibrous mineral that formed from levyne in Tertiary basalts of County Antrim, Ireland. Although the alteration mineral was not identified, the reported habit and optical properties suggest to us that it is offretite. More recently, Chatterjee (1971) described and illustrated an unidentified fibrous mineral associated with levyne in the Deccan basalts near Bhopal, India. Neither optical nor chemical properties for the unidentified mineral were given by Chatterjee, but the mineral is probably offretite or perhaps erionite as suggested by Shimazu and Mizota (1972, p. 423).

A search of levyne in the collection of the Smithsonian Institution by one of us (J.S.W.) located two additional specimens that have a silky, white, associated mineral. X-ray powder diffractometer and optical studies indicate that both are offretite. These levyne-offretite specimens occur in basalt, probably the Picture Gorge Basalt, near Spray, Wheeler County, Oregon, and near Ritter, Grant County, Oregon. The Ritter material was described by Hewett, Shannon, and Gonyer (1928, p. 7), who tentatively identified the levyne but not the silky, white mineral.

R. W. Tschernich and W. S. Wise (written communication, 1973) have identified levyne-offretite intergrowths from many localities in the basaltic terranes of Oregon, Washington, and British Columbia. A description of the localities and the zeolite mineralogy is in preparation by these workers. Thus, offretite is not so rare as previously supposed. Many additional occurrences will undoubtedly be discovered by careful examination of levyne occurrences in basalt.

**Acknowledgments**

We thank A. L. McGuinness (San Mateo, California) for providing the Beech Creek specimens and a description of the locality. We also greatly appreciate the unpublished data provided by R. W. Tschernich (Snohomish, Washington) and W. S. Wise (University of California, Santa Barbara) on additional occurrences of levyne-offretite intergrowths. Louise Hedricks (U.S. Geological Survey) prepared the photomicrograph, and W. R. Brown (Smithsonian Institution) prepared the scanning electron micrographs.

**References**


Shimazu, Mitsuo, and Tadato Mizota (1972) Levyne and erionite from Chojobaru, Iki Island, Nagasaki Prefecture,


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