NEW DATA ON THE ANALCIME—WAIRAKITE SERIES

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ABSTRACT

DTA and TGA data and infrared absorption spectra are determined for analcime, wairakite, and a mineral having a composition intermediate between analcime and wairakite; the monoclinicity of the mineral with intermediate composition was also determined. Infrared absorption spectra of Si-O (1200–1000 cm⁻¹), and OH-O (around 3600 cm⁻¹) stretching bands for analcime and wairakite are quite distinct. Two OH-O distances for the analcime structure and four OH-O distances for the wairakite structure were established. An absorption due to OH bending deformations near 1630 cm⁻¹ was found similar for analcime and wairakite. Three absorption bands in the Si-O stretching region of 1200–1000 cm⁻¹ for analcime split into seven bands for wairakite, probably because of the lower symmetry of the wairakite structure. Chemical analyses, physical, optical, and X-ray diffraction data for two non-cubic analcime and the intermediate mineral of the analcime–wairakite series from Sugashima, Mie, Japan are given.

INTRODUCTION

Wairakite (CaAl₂Si₄O₁₂·2H₂O), the calcium analogue of analcime (Na₂Al₂Si₄O₁₂·2H₂O) was first described by Steiner (1955) using material found in drill cores at Wairakei geothermal area in New Zealand. X-ray diffraction data for wairakite were given by Coombs (1955). Since then, along with the studies of natural materials, synthetic wairakite has been studied by many investigators. Seki (1968) found differences between true monoclinic wairakite (fully–ordered wairakite) and synthesized tetragonal Ca–analcime (disordered wairakite). Seki (1968) further stated that almost all “wairakite” previously synthesized by many investigators was Ca–analcime. The stability field of true monoclinic wairakite was first determined by Liou (1970) over the temperature and pressure ranges of 200–500°C and 500–5000 bars Pfluid. The formation field of fully- and partly-ordered wairakite at temperatures and pressures much lower than those de-
determined by Liou, that is 200°-300°C and $P_{\text{vapor}}$ lower than 304 bars, was studied by Harada, Umeda, and Nagashima (1971). In his study on the low-grade metamorphic rocks of the Karmutsen Group, Buttle Lake Area, Vancouver Island, British Columbia, Surdam (1966) discovered some minerals intermediate between analcime and wairakite by electron microprobe; he established the existence of a continuous solid solution between analcime and wairakite. Harada and Sakurai (1967) also found a monoclinic mineral intermediate between analcime and wairakite (at Sugashima, Mie, southwest Japan, the lowest metamorphic grade of the Sambagawa metamorphic belt) containing 3.10 CaO and 11.87 percent Na$_2$O; they gave the results of wet chemical analysis, optical, and X-ray diffraction studies. Seki and Oki (1969) then discovered some minerals intermediate between analcime and wairakite in low-grade metamorphic rocks of the Tanzawa Mountains, central Japan; Seki (1971a, b) summarized the occurrence, chemical, and optical properties of the analcime-wairakite series.

This note presents new mineralogical data for the analcime-wairakite series including infrared absorption spectra, DTA-TGA curves, and new descriptions of an intermediate mineral of the series as well as of two non-cubic analcimes from Sugashima, Mie, Japan. The geology of this area was described by Saka (1970).

**AN INTERMEDIATE MINERAL OF THE ANALCIME-WAIRAKITE SERIES**

New information for two analcimes (Nos. 3 and 4) and an intermediate mineral of the analcime-wairakite series (No. 2) from Sugashima, Mie, Japan is given on Table 1. X-ray powder diffraction data for the intermediate species of the analcime-wairakite series (Nos. 1 and 2, Table 1) could be indexed assuming a monoclinic symmetry. This mineral exhibits the $hkl$ reflections of 200; 400, 004, and paired reflections of 332, 332; 422, 422; 434, 434; 521, 521. The separation of 400 and 004, characteristic of monoclinic wairakite, is not so distinct but is observed. The other reflections characteristic of minerals with monoclinic symmetry are clearly paired. The mineral is optically weakly anisotropic ($\gamma - \alpha = 0.002 \pm 0.001$) and two sets of twining lammellae, intersecting at almost right angles, are generally observed. Two other analcimes (Nos. 3 and 4, Table 1) exhibit very weak 200 reflection which is incompatible with the space group $O_h^{10} - Ia3d$, the space group of analcime, as discussed by Coombs (1955), although other peaks fit well to the space group $O_h^{10} - Ia3d$. The minerals also show the very weak birefringence ($\gamma - \alpha = 0.001 \pm 0.001$), but no twin lammellation was found. The analcimes should be lower in symmetry than normal cubic ($O_h^{10} - Ia3d$) analcime, but precise deter-
Table 1. Chemical Composition, Refractive Indices, and Unit Cell Data for Wairakite, Analcime, and Intermediate Minerals of the Analcime-Wairakite Series.

<table>
<thead>
<tr>
<th></th>
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<th>4</th>
<th>5</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>53.6</td>
<td>52.6</td>
<td>53.81</td>
<td>53.65</td>
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<td>55.9</td>
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<td>TiO₂</td>
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<tr>
<td>Al₂O₃</td>
<td>22.28</td>
<td>22.51</td>
<td>23.43</td>
<td>23.15</td>
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<td>23.0</td>
</tr>
<tr>
<td>FeO</td>
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<td>0.19</td>
<td>0.10</td>
<td>0.15</td>
<td>0.16</td>
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</tr>
<tr>
<td>MgO</td>
<td>none</td>
<td>0.47</td>
<td>0.07</td>
<td>0.08</td>
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<td>CaO</td>
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<td>none</td>
<td>1.77</td>
<td>0.40</td>
<td>0.80</td>
<td>0.47</td>
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<tr>
<td>Na₂O</td>
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<td>none</td>
<td>12.75</td>
<td>13.41</td>
<td>13.24</td>
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<tr>
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<td>0.07</td>
<td>0.16</td>
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<tr>
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<td>8.76</td>
<td>8.49</td>
<td>8.51</td>
<td>0.39</td>
<td>8.35</td>
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<td>Rem</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>TOTAL</td>
<td>99.34</td>
<td>99.50</td>
<td>99.71</td>
<td>100.28</td>
<td>99.66</td>
<td>100.39</td>
</tr>
</tbody>
</table>

1 Intermediate mineral of the analcime-wairakite series (analyzed by K. Nagashima and K. Nakao) from Sugashima (Harada and Sakurai, 1967).
2 Intermediate mineral of the analcime-wairakite series (analyzed by K. Nagashima) from Sugashima (this work); this corresponds to (Na₀.866Ca₀.142Mg₀.053)₁₀₂₄(Si₃.929Al₁.982Fe₂₀.035)₅.946₀.₀₂₃H₂O.
3 Non-cubic analcime (analyzed by K. Nagashima) from Sugashima (this work); this corresponds to (Na₁.918Ca₀.064Mg₀.008)₁₀₂₄(Si₃.969Al₁.972Fe₂₀.019)₀₂₃H₂O.
4 Non-cubic analcime (analyzed by K. Nagashima) from Sugashima (this work); this corresponds to (Na₁.869Ca₀.051Mg₀.009)₁₀₂₄(Si₃.969Al₁.972Fe₂₀.019)₀₂₃H₂O.
5 Cubic analcime (analyzed by K. Harada) from Mazé (Harada, Iwamoto, and Kihara, 1967).
6 Wairakite (analyzed by J. A. Richie) from Wairakei, N. Z. (Steiner, 1955)

Rem. is 0.05% SrO, 0.003% Rb₂O, and 0.017% CaO.

The determination of the crystal structure remains to be done. X-ray powder diffraction patterns of these analogs resemble analcime from Flinders described by Coombs (1955). The X-ray powder diffraction patterns for the intermediate mineral (No. 2, Table 1) containing 1.77 percent CaO and 0.47 percent MgO; analcime from Mazé, Niigata (Harada, Iwamoto, and Kihara, 1967; No. 5, Table 1) and wairakite from Waira-
kei, N. Z. (Steiner, 1955; Coombs, 1955; No. 6, Table 1) are shown in Figure 1. The chemical and physical data for the non-cubic analcimes, the intermediate minerals from Sugashima, cubic analcime from Mazé (Harada, Iwamoto, and Kihara, 1967), and wairakite from Wairakei (Steiner, 1955; Coombs, 1955) are compiled on Table 1.

**Infrared Absorption Spectra**

Infrared absorption spectra were obtained using a Nippon Bunkō DS-401-G grating-type spectrophotometer with the KBr disk method for analcime from Mazé (No. 5, Table 1), an intermediate mineral of the analcime-wairakite series containing 3.10 percent CaO (No. 1,
Fig. 2. Infrared absorption spectra for (1) analcime from Mazé (No. 5, Table 1), (2) intermediate mineral of the analcime-wairakite series (No. 1, Table 1), and (3) wairakite from Wairakei, N. Z. (No. 6, Table 1). Numbers in parentheses represent corresponding OH-O distances.

Table 1) and wairakite from the type locality (No. 6, Table 1). Infrared absorption spectra for the three zeolites are quite distinct (Fig. 2). The data for analcime are in fair agreement with the data given by Oinuma and Hayashi (1967) as well as by Milkey (1960). Infrared absorption spectra for wairakite and an intermediate mineral of the analcime-wairakite series are given here. The OH-O distances calculated on the basis of the equations given by Lippincott and Schroeder (1955) as well as by Nakamoto et al. (1955) are also given. The absorption bands and OH-O distances for the zeolites are shown in Figure 1.

The first determination of the crystal structure of analcime was made by Taylor (1930). He showed that the H₂O molecules in analcime occupy 16-fold positions, surrounded by 12 O-ions at a OH-O distance of 3.5 Å. On the basis of his crystal structure analysis of pollucite, Naray–Szabó (1938) assumed that a part of the H₂O molecules in analcime should also occupy the 24-fold positions of octahedrally surrounded by 4 O-ions and 2 Na ions at the OH–O (or Na–O) distances of 2.3–2.4 Å instead of 16-fold positions advocated by Taylor (1930). Infrared absorption spectra for analcime represent the 3.06 Å and 2.97 Å OH–O distances. Both distances probably correspond to the
Fig. 3. TGA and DTA data for (1) analcime from Mazé (No. 5, Table 1), (2) intermediate mineral of the analcime-wairakite series (No. 2, Table 1), and (3) wairakite from Wairakei, N. Z. (No. 6, Table 1). Note: Weight loss of the TGA curves for the zeolites correspond well to the results of chemical analyses given in Table 1 (The weight of the starting materials—(1) 17.1 mg, (2) 16.8 mg, and (3) 16.9 mg, respectively).
16-fold positions in the analcime structure. 2.3–2.4 Å OH–O distances are not found in the infrared absorption spectra of analcime. The crystal structure of wairakite is not yet determined, but similarity of the crystal structure of wairakite with that of analcime is quite apparent. The OH–O distances of 3.15 Å, 2.97 Å, 2.86 Å, and 2.78 Å are found in the infrared absorption spectra of wairakite. These distances may result from occupancy of the 16-fold positions in sites of the wairakite structure.

Three absorption bands in the Si–O stretching region of 1200–1000 cm$^{-1}$ for analcime split into seven bands for wairakite probably because of the lower symmetry of wairakite.

**DTA AND TGA**

DTA and TGA curves were measured by an automatic thermal analyzer at a heating rate of 10°C/min. for analcime, wairakite, and the intermediate mineral of the analcime-wairakite series. The DTA and TGA data for analcime are in fair agreement with the data given by Otsuka et al. (1970) and by Koizumi (1953). DTA shows endothermic peaks at 280 and 340°C, and TGA shows that analcime loses its weight at temperatures from 200 to 370°C. The intermediate mineral of the analcime-wairakite series loses its weight at temperatures from 200 to 450°C, whereas wairakite loses it at temperatures from 300 to 700°C. The wairakite and the intermediate mineral lose their weight at a much higher temperature than analcime. The DTA for the intermediate mineral gives endothermic peaks at 310, 369, and 645°C, and the wairakite gives endothermic peaks at 470, 535, and 650°C which are at higher temperatures than that of analcime. The DTA and TGA data for analcime, the intermediate mineral, and wairakite clearly indicate that the increasing proportion of CaO in analcime plays a role in shifting the dehydration temperature of the series higher, as illustrated in Figure 3.

**Acknowledgments**

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**References**

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