THE PRESENT STATUS OF THE ANALCIME-POLLUCITE SERIES

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ABSTRACT

The compositions of natural pollucites known until recently cover the range Poll₆₉ - Poll₈₂. The finds of Cs-rich analcimes fill most of the gap Poll₆ - Poll₈. The largest of the three remaining gaps is that at the pollucite end, Poll₈₂ - Poll₁₀₀. The following nomenclature is proposed for the analcime-pollucite series: analcime for Poll₀ - Poll₆; cesian analcime for Poll₆ - Poll₅₅; sodian pollucite for Poll₅₅ - Poll₇₂, and pollucite for Poll₇₂ - Poll₁₀₀.

The stoichiometric relations in most analyzed analcime-pollucites are compatible with the requirements of Beger's (1969) structure model: Cs + H₂O = 1, Na < H₂O, Cs + Na < 1, Al < 1 and Si/Al > 2 (all per 6 oxygens of anhydrous subcell). Most of the H₂O contents are higher than predicted by Nel (1944; Na/H₂O = 1) but lower than expected by Neuvonen & Vesasalo (1960; H₂O = Na + 2× excess Si over 2). The tetrahedral composition Al₆₋₅Si₉₋₈₀ is rather constant in all members of the series, independent of the Na/CS/H₂O ratios. The average content of 0.90 univalent cations fits the tetrahedral content of Al₆₋₅.

The unit cell edge 13.64 - 13.71Å seems to be rather constant, but the intensities of x-ray powder diffraction reflections show considerable variations with the change in the Na + H₂O and Cs contents. All sodian pollucites are isotropic and produce cubic x-ray diffraction patterns, but the cesian analcimes show sectorial birefringence and splitting of those reflections that are doubled in monoclinic wairakite.

The relations between chemical composition and physical properties in the whole series follow the trends established earlier for sodian pollucites, but require a re-examination to provide more reliable determination curves.

INTRODUCTION

This study was prompted by the discovery of Cs-rich analcime in the Tanco pegmatite at Bernic Lake, southeastern Manitoba. Several samples were studied simultaneously by R. V. Gaines and J. Ito, and by the present author, and the results were summarized by the latter (Černý 1972). The compositions of these samples fall into the Na-rich half of the analcime-
pollucite series, and populate it almost continuously at least in terms of chemical completely (Fig. 1). The existence of such a series, position, has been assumed impossible structurally (Newnham 1967; Henderson & Taylor 1969; and other earlier authors), but is compatible with the structure proposed by Beger (1969).

This latter structure model, with cubic symmetry and space group Ia3d, has the analcime tetrahedral framework with cesium in the large voids around the 1,6b equipoint (at 1/6, 1/6, 1/6). The water molecules populate the same large voids that are not occupied by cesium. The sodium cations are located in equipoint 24c (at 1/4, 1/4, 0), between the water molecules. The water molecules and the sodium cations occupy the same positions as they do in analcime, but they occur only in randomly-distributed clusters whose outer members are restricted to water molecules.

This structure model is compatible with some peculiarities of pollucite stoichiometry, some of which have been recognized earlier: in contrast to the idealized formula (Cs,Na)AlSiO₄ * xH₂O, the actual compositions shows Cs + H₂O = 1, Na < H₂O, Cs + Na < 1, and Si/Al > 2.

The purpose of the present study was (1) to re-examine the population of the analcime-pollucite series in light of the recent find of cesian

### TABLE 1. UNIT CELL CONTENTS AND PHYSICAL PROPERTIES OF THE ANALCIME-POLLUCITE MINERALS

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Cation Sites</th>
<th>Water</th>
<th>Density (g/cm³)</th>
<th>2θ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analcime</td>
<td>CsNaAlSiO₄H₂O</td>
<td>CsNa</td>
<td>2</td>
<td>2.27</td>
<td>28.09</td>
</tr>
<tr>
<td>Pollucite</td>
<td>Cs₂Na₂Al₂Si₄O₁₀(PO₄)</td>
<td>CsNa</td>
<td>3</td>
<td>2.35</td>
<td>2.35</td>
</tr>
<tr>
<td>Polymorphite</td>
<td>CsNaAlSiO₄H₂O</td>
<td>CsNa</td>
<td>4</td>
<td>2.45</td>
<td>2.40</td>
</tr>
<tr>
<td>Analcite</td>
<td>CsNaAlSiO₄H₂O</td>
<td>CsNa</td>
<td>5</td>
<td>2.58</td>
<td>2.27</td>
</tr>
<tr>
<td>Pollucite</td>
<td>Cs₂Na₂Al₂Si₄O₁₀(PO₄)</td>
<td>CsNa</td>
<td>6</td>
<td>2.68</td>
<td>2.36</td>
</tr>
<tr>
<td>Polymorphite</td>
<td>CsNaAlSiO₄H₂O</td>
<td>CsNa</td>
<td>7</td>
<td>2.76</td>
<td>2.36</td>
</tr>
<tr>
<td>Analcite</td>
<td>CsNaAlSiO₄H₂O</td>
<td>CsNa</td>
<td>8</td>
<td>2.84</td>
<td>2.36</td>
</tr>
<tr>
<td>Pollucite</td>
<td>Cs₂Na₂Al₂Si₄O₁₀(PO₄)</td>
<td>CsNa</td>
<td>9</td>
<td>2.92</td>
<td>2.36</td>
</tr>
<tr>
<td>Polymorphite</td>
<td>CsNaAlSiO₄H₂O</td>
<td>CsNa</td>
<td>10</td>
<td>3.00</td>
<td>2.36</td>
</tr>
<tr>
<td>Analcite</td>
<td>CsNaAlSiO₄H₂O</td>
<td>CsNa</td>
<td>11</td>
<td>3.08</td>
<td>2.36</td>
</tr>
<tr>
<td>Pollucite</td>
<td>Cs₂Na₂Al₂Si₄O₁₀(PO₄)</td>
<td>CsNa</td>
<td>12</td>
<td>3.16</td>
<td>2.36</td>
</tr>
<tr>
<td>Polymorphite</td>
<td>CsNaAlSiO₄H₂O</td>
<td>CsNa</td>
<td>13</td>
<td>3.24</td>
<td>2.36</td>
</tr>
<tr>
<td>Analcite</td>
<td>CsNaAlSiO₄H₂O</td>
<td>CsNa</td>
<td>14</td>
<td>3.32</td>
<td>2.36</td>
</tr>
</tbody>
</table>

The table includes oxidation states of each element and the calculated density, calculated from the unit cell contents and physical properties of the analcime-pollucite minerals.
analcimes; (2) to check the crystallochemical requirements of Beger's structure on a broader scale; and (3) to re-examine the relations between chemical composition and physical properties in the series.

**Collection and Treatment of Data**

Chemical analyses, refractive indices, densities, and unit cell edges were collected from the literature, and x-ray powder diffraction data recorded for different members of the series. The chemical analyses were recalculated to atomic contents on the basis of 6 oxygens per anhydrous subcell; these are given along with physical properties in Table 1. For simplicity, the chemistry of individual specimens is characterized by their molecular percentage of the pollucite end member ("Poll") calculated as the atomic ratio \( \text{Cs} \times 100/(\text{Cs} + \text{Na} + \text{K} + \text{Rb} + \text{Ca} + \text{Mg}) \). The minor components K, Rb, Ca, and Mg are arbitrarily grouped with Na.

Rb and K could be grouped with Cs, because of the large size of Rb and the preferred occurrence of K in the 16b equipoint sites of anhydrous compounds. The pollucite percentage based on this grouping is shown in Table 1 as the "CRK" index, \( (\text{Cs} + \text{Rb} + \text{K}) \times 100/(\text{Cs} + \text{Na} + \text{K} + \text{Rb} + \text{Ca} + \text{Mg}) \). However, the Rb and K contents are very small in all samples and the crystallochemical role of K in pollucite is uncertain. Thus the simpler Poll index is used in this study; it can be seen in Table 1 that the differences between the Poll and CRK indices are small, except for samples 5, 13 and 15.

**Chemical Composition**

**Population of the analcime - pollucite series**

As shown in Figure 1, the classic pollucites cover the Pollas-Polle range, and a separate group of Na-richer minerals shows compositions between Pollas and Pollas. The few chemically analyzed cesian analcimes from Bernic Lake are scattered over the earlier gap Polla-Pollas. Judging from the refractive indices measured on 101 specimens, the cesian analcimes range continuously from about Polla to Pollas. Thus there seem to be just three relatively small gaps remaining at present: Polla - Pollas, Pollas - Pollas, and Pollas - Pollas. Only continued study of natural specimens will show if one or more of them are true. It is particularly interesting to note that, so far, no natural pollucite has been found with less than 18 mol. % analcime. The first gap, Polla - Pollas, seems to be populated by synthetic phases (Dr. T. Iiyama, personal comm. 1972).

**Si/Al ratio**

The slight deviation of the Si/Al ratio from the idealized value of 2 in several pollucites was recognized by Richmond & Gonyer (1938) and by Nel (1944). However, both authors did not...
realize how persistent this deviation was, and how constant its magnitude was, in all pollucites known to the dates of their respective studies.

Figure 2 shows the plot of the Si/Al ratios against the Poll contents. It is evident that the spread of the Si/Al values is well-centered around 2.33, i.e. Al_{0.90}Si_{1.10}, and two thirds of them lie between 2.22 (Al_{0.90}Si_{2.01}) and 2.44 (Al_{0.90}Si_{1.18}). This ratio appears to be independent of the Na and Cs contents. Thus the tetrahedral framework composition (Al_{0.90}Si_{1.10}O_4)^{0.90} can be considered typical for the whole series, undergoing only minor variations in individual members. As shown in the introduction, such a tetrahedral composition is required by the Beger structure model.

Presumably pure ferric analogues of pollucite were synthesized by Kopp et al. (1963), Kume & Koizumi (1965), and Kopp & Clark (1966), but natural pollucites are known to carry negligible Fe (sample 17 in Table 1).

Cationic content

As in the previously-known sodian pollucites, Na and Cs are also the most important cations in the cesian analcimes. K, Rb, Mg, and Ca are present only in very subordinate quantities (maximum atomic contents only 0.11, 0.05, 0.04, and 0.05, respectively, per 6 oxygens). Figure 3 shows the atomic contents of Cs plotted against those of Na plus minor cations; all the data closely follow the line connecting the 0.90 points, in accordance with the average anionic charge of -0.90. Deviations are caused by either slight variation in the Si/Al ratio, or by cationic deficiency which is rather common in zeolitic minerals (and may be apparent only because of lack of information about the possible H^+ and/or H_2O^+ contents). Formulas with high alkali excesses over Al (up to around 0.10) suggest faulty chemical analyses.

**H_2O**

The variations in the content of H_2O, not considered in detail by Richmond & Gonyer (1938), were related to the Na content by Nel (1944) in a simple way: the molecular content of H_2O equals the atomic content of Na (although his general formula does not reflect this relation properly): C_{Si,Na-Al-Si-O}(x+2y)H_2O. Neuvonen & Vesasalo (1960) have proposed a variation of the H_2O content in pollucite with the Si content, as found for analcime by Saha (1959): the molecular content of H_2O equals the atomic content of Na plus twice the excess of Si over 2: C_{Si,Na-Al-Si-O}(x+2y)H_2O.

The Na/H_2O ratios derived this way are, however, lower than those expected in the Na + H_2O clusters in Beger's structure. Figure 4 shows that most Na/H_2O ratios determined for...
natural analcime-pollucites plot between the lines based on Nel's and Neuvonen's & Vesasalo's proposals, and thus approach closely the range expected in Beger's structure. It must be kept in mind that the analytical error in determination of water in pollucite tends to lead to somewhat lower-than-actual contents of H$_2$O (Barrer & McCallum 1953), and particularly the H$_2$O contents of Cs-rich members of the series should be influenced by this error.

As shown in Figure 5, most of the Cs + H$_2$O contents per 6 oxygens of anhydrous subcell are close to 1. This fact, first pointed out by Nel (1944), is one of the characteristics following from the Beger structure model. In accordance with the lower-than-actual H$_2$O contents expected in most analyses, the distribution of Cs + H$_2$O totals shown in Figure 5 is not normal around 1.00, but frequencies are higher for slightly lower values.

General formula

The stoichiometric relations discussed above conform with the general formula proposed by Beger (1969), which reads (after reduction to the presently used subcell) Cs$_x$Na$_y$Al$_{2x+y}$Si$_{2x+9}$O$_{10}$•(1-x)H$_2$O.

Beger's limitation $2y \geq 1-x \geq y$ may be complemented by the empirical restriction of $x+y$ to $\sim 0.90$.

**Physical Properties**

**Refractive index and density**

Both these characteristics are known to increase with increasing Cs content. Their plots against mol. % Poll, shown in Figure 6, show a considerable scatter of data at the Cs-rich end of the series, which becomes, however, much less evident in a plot of $n$ versus density, shown in Figure 7. This suggests that in many studies either the material used for checking the physical properties was not representative of the bulk material used for chemical analysis, or the determination of alkalis was not accurate. Since no data are available for a synthetic pollucite with Al$_{0.05}$Si$_{1.16}$, and those known for other compositions deviate from expected values so much that they are evidently not reliable (Kume & Koizumi 1965; Kopp & Clark 1966; Kopp et al. 1963; Plyushev 1959), it is not possible to anchor the lines in Figures 6 and 7 at the Poll end of the scale in a similar way as at the Anal end (which was calculated from data by Saha 1959, 1961). The slope of these lines is only a visual estimate.

**Isotropic and anisotropic phases**

All sodian pollucites described in the literature and examined to date by the author are isotropic, but the newly-discovered cesian analcimes from Bernic Lake show sectorial birefringence (Černý 1972). Analcime, of course, is
known to be both isotropic and anisotropic (Coombs, 1955; Knowles et al. 1965; and others).

**Unit cell edge**

Saha (1959, 1961) found a rather broad variation of $a$ with changes in the Si/Al ratio in analcime. This suggests that in the natural Anal-Poll series with its restricted Si/Al range $a$ should be almost constant, provided the influence of the widely-changing Na/Cs ratio is negligible. The range of $a$ values quoted in literature is indeed only 3.64 - 3.71 Å. A more detailed discussion of these relations is not possible at present, as the available data come from different authors and were obtained by different (and frequently unspecified) methods. It would not be surprising if the actual range of $a$ was much smaller.

**X-ray powder diffraction data**

The relative intensities of x-ray powder diffraction reflections show considerable variations in the Anal-Poll series. Similar to the variations in alkali-rich beryls, recognized by Evans & Mrose (1966) and treated quantitatively by Bakakin et al. (1970), the substitution (and different allocation) of heavy Cs for Na influences profoundly the diffraction and absorption of x-rays in these minerals. Figure 8 shows x-ray powder diffraction patterns recorded under identical conditions for a series of samples with different Poll contents. Besides the increase in intensity of reflections 321, 440, 532, 631, and 721, and the decrease in that of 211, 220, 400, 222, 431, 521, 640 and 800 with increasing Poll content, the sodian pollucite patterns are generally weaker.

The x-ray powder diffraction patterns of optically isotropic sodian pollucites display cubic symmetry but those of the anisotropic cesian analcimes from Tanco show a broadening of the same reflections (422, 521, 640, and 800) that are doubled in the anisotropic, monoclinic wairakite CaAl$_2$Si$_4$O$_{10}$·2H$_2$O (Seki 1966, 1971; Seki & Oki 1969; Harada et al. 1972).

**SUMMARY AND CONCLUSIONS**

The preceding review establishes the natural analcime-pollucite group of minerals as an al-
most continuous isomorphous series. Only three small gaps seem to be present but these may disappear with continued research. The most prominent is that at the pollucite end of the series; the cesium-richest members in existence are sodian pollucites with more than 18 mol. % analcime.

The following nomenclature is proposed for the analcime-pollucite series: analcime for Poll<sub>p</sub>-Poll<sub>s</sub>, cesian analcime for Poll<sub>s</sub>-Poll<sub>ss</sub>, sodian pollucite for Poll<sub>ss</sub>-Poll<sub>ss</sub>, pollucite for Poll<sub>ss</sub>-Poll<sub>ss</sub>.

The stoichiometric relations derived from all published chemical analyses comply with the basic requirements of Beger's (1969) structure model: Cs + H<sub>2</sub>O = 1; Na + H<sub>2</sub>O, and thus Cs + Na < 1, which necessitates Al < 1 and Si/Al > 2. Most of the analyses show Al very close to 0.90 and Si/Al very close to 2.33.

The sodian pollucites are isotropic in accordance with the cubic space group Ia3d established by all structure refinements performed to date. However, the cesian analcimes are anisotropic, and their x-ray powder diffraction data are similar to those of monoclinic wairakite. A more detailed work on some of these Na > Cs phases may be useful to establish the possible structural causes of the anisotropism; these may be rather delicate and difficult to detect, as in the case of isotropic and birefringent analcimes (Knowles et al. 1965).

The relations between chemical composition and physical properties in the whole series follow the patterns established earlier for sodic pollucites. However, the presently available data show a rather wide scatter. A reexamination of refractive index, density, and a vs. chemical composition is being carried out at our Department.

To verify the continuity of the analcime-pollucite series, all new finds of different members of the series should be checked for their physical properties, and thoroughly examined if close to the gaps shown in Figure 1. This applies particularly to analcimes with possible low Cs contents from Li-rich pegmatites (Neuvonen & Vesasalo 1960; Rijks & v. d. Veen 1972), and to late hydrothermal "pollucites" from vugs (e.g. Richmond & Gonyer 1938; Miškovský 1955; Černý 1972).

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