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Symmetry, twinning, and parallel growth of scolecite, mesolite, and natrolite

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ABSTRACT

Scolecite crystals consist of {110}, {010}, and {111} growth sectors with triclinic symmetry, although scolecite appears to be monoclinic by X-ray analysis. The crystals have twinning caused by an asymmetric arrangement of Ca and H_2O in the channel, and the (100) twin plane does not coincide with the sector boundary. The crystal has partly ordered (Al,Si) arrangements that are symmetrical with respect to the boundaries between the four {111} sectors; that is, the (Al,Si) arrangement allows sectoral (100) and (010) twins.

Natrolite crystals consist of {111} and {110} growth sectors, which correspond to smooth (111) and striated (110) faces. The optical extinctions are oblique to the **b** axis and parallel to the **c** axis, suggesting monoclinic symmetry, which can be attributed to (Al,Si) ordering. The {110} sectors show parallel intergrowths akin to twinning: one part is rotated 180° about the normal to (110) relative to the other. Sectors that grow in the opposite directions along the +**c** and −**c** axes show parallel intergrowths. Fine striations on the (110) face grow in the two directions corresponding to the +**c** and −**c** axes, producing the intergrowths. Mesolite crystals consist of only {111} sectoral twins, without {110} growth sectors, and are monoclinic.

INTRODUCTION

Scolecite, mesolite, and natrolite are acicular or fibrous common zeolites with chain structures. Although scolecite ($Ca_8Al_{16}Si_{24}O_{80}\cdot 24H_2O$) with growth sectors was thought to be triclinic in the 19th century (Des Cloizeaux, 1862; Luedecke, 1881), recent X-ray analyses have indicated monoclinic symmetry (Adiwidjaja, 1972; Fälth and Hansen, 1979; Smith et al., 1984).

Also, natrolite crystals ($Na_{16}Al_{16}Si_{24}O_{80}\cdot 16H_2O$) from various localities have been studied by many mineralogists since the 19th century. Some natrolite crystals, which are elongated along the **c** axis, show oblique optical extinction on (110),[1] suggesting monoclinic or triclinic symmetry (Brøgger, 1889). Hey (1932) summarized the many optical studies of natrolite and examined hundreds of crystals from most of the localities represented in the British Museum collection. From these data, he suggested that it could not be said that there was any satisfactory evidence for the existence of monoclinic natrolite with the symmetry axis *perpendicular* to the elongation. He did not mention monoclinic natrolite with the symmetry axis *parallel* to the elongation. Rinne (1890), however, described monoclinic natrolite whose optical extinction is inclined to the **b** axis in the (001) section. X-ray analyses suggest orthorhombic space group *Fdd*2.

Pabst (1971) summarized some papers on twinning in natrolite and described an intergrowth akin to twinning by X-ray analysis: the framework of one part is rotated about the normal to (110) 180° with respect to the other, that is, the **c** axes of the two lattices are parallel or nearly so whereas the **b** axis of one coincides with the **a** axis of the other and vice versa.

Mesolite ($Na_{16}Ca_{16}Al_{48}Si_{72}O_{240}\cdot 64H_2O$) appears monoclinic in optical studies, because the extinction is parallel to the elongation and is inclined to the **b** axis (Hey, 1933), whereas X-ray analysis suggests it to be orthorhombic (Adiwidjaja, 1972).

From optical studies of many minerals (e.g., Akizuki, 1981, 1984, 1986; Akizuki and Konno, 1985), Akizuki (1987) suggested a general mechanism for the formation of sectoral structures that involves atomic ordering produced on crystal surfaces during growth: charge balance is maintained along the two-dimensional structure exposed on the growth surface as well as within the crystal. If the tetrahedron forms after a large cation occupies the channel, the Al ion will preferentially occupy the tetrahedron, whereas if the tetrahedron forms prior to placement of the cation, a Si ion will occupy the tetrahedral site. If the growth face is inclined to the mirror or the glide plane, the two symmetry-related sites in a crystal will not be equivalent on the surface; thus ordering will occur, and the symmetry of the crystal will be reduced. The morphological mirror plane changes into a twin plane because of the symmetrically ordered arrangements. These

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[1] Throughout this paper, the Miller indices refer to monoclinic axes for scolecite and orthorhombic axes for natrolite and mesolite according to the recent X-ray studies, that is, the **c** axes are parallel to the elongations in the three crystals.

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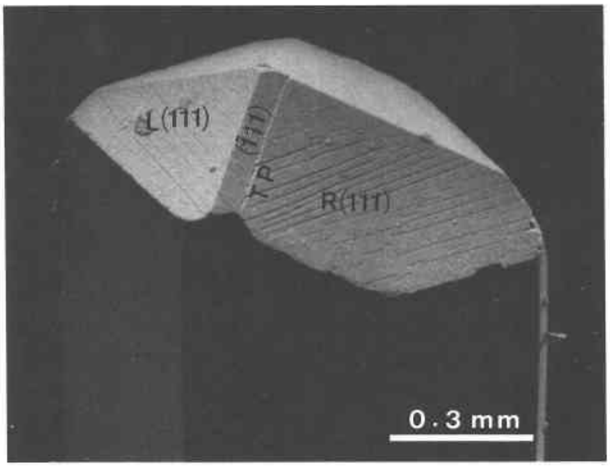

Fig. 1. Crystal form {111} and {110} of scolecite from Poona, India. The (100) twin plane is indicated by letters TP. *L*(111) and *R*(111) faces are related by the (100) twin (TP). The prism face is concave along the twin plane. SEM photomicrograph.

concepts are applied in this paper to scolecite, mesolite, and natrolite.

OPTICAL OBSERVATION

Scolecite

Scolecite crystals from three localities (Poona, India; Barufjard, Iceland; Teigarhorn, Iceland) were used for the study. Figure 1 shows a twinned crystal of scolecite as observed by SEM. Twins are commonly observed in scolecite, and the twin plane does not coincide with the intersection of the two (111) pyramidal faces with growth steps, though the twin was drawn by Dana (1892) as though it coincided with the sectoral boundary (SB-A in Fig. 2). Figure 2 shows the {111}, {010}, and {110} growth sectors in a thin section cut parallel to (001) in scolecite from Barufjard. Figure 3 shows a schematic sketch of the growth sectors and twins observed in the thin section cut parallel to (001). Since the vibration directions (*Y* and *Z*) are symmetrically inclined to the **b** axis through the crystal, triclinic symmetry is suggested for the crystal.

The {111} and $\{\bar{1}11\}$ sectors, which are correlated with the (111) and $(\bar{1}11)$ faces, respectively, are not related by twinning, because optical properties of the two are different. However, the *L*{111} and *R*{111} sectors, which correspond to the *L*(111) and *R*(111) faces shown in Figure 1, are related by the (100) twin (twin plane TP), not by the (100) sectoral boundary SB-A (Fig. 3). This twin (TP) is commonly observed in scolecite by optical and X-ray methods. The $\{\bar{1}11\}$ sector exists between the *R*{111} and *L*{111} sectors.

The optical orientations of the {111} and $\{1\bar{1}1\}$ sectors and the $\{\bar{1}11\}$ and $\{\bar{1}\bar{1}1\}$ sectors are symmetrically inclined with respect to the (010) sector plane (SB-B) (Fig. 3), that is, they are related to each other by (010) twinning. Also, the same relation exists for the {110} and $\{1\bar{1}0\}$ sectors, and for the $\{\bar{1}10\}$ and $\{\bar{1}\bar{1}0\}$ sectors. The {110} sectors consist of growth bands parallel to the surface, and the extinction angles vary within 3° from band to band in the (001) section.

The {010} sector consists of growth bands parallel to the (010) face, crossed by the (100) twinning. The extinction angles vary within 3° from band to band in the (001) section (Fig. 2). The large (010) faces are slightly concave in the scolecite from Poona, India. The {010} growth sectors are not observed in the crystal at all in spite of the predominant (010) face of the crystal. The (010) face is not produced by crystal growth on (010), but is the result of the growth of other faces. This crystal is triclinic as well. Scolecite from Teigarhorn, Iceland, shows texture similar to that of scolecite from Barufjard, though the texture in the {010} sector is simpler as shown schematically in Figure 3.

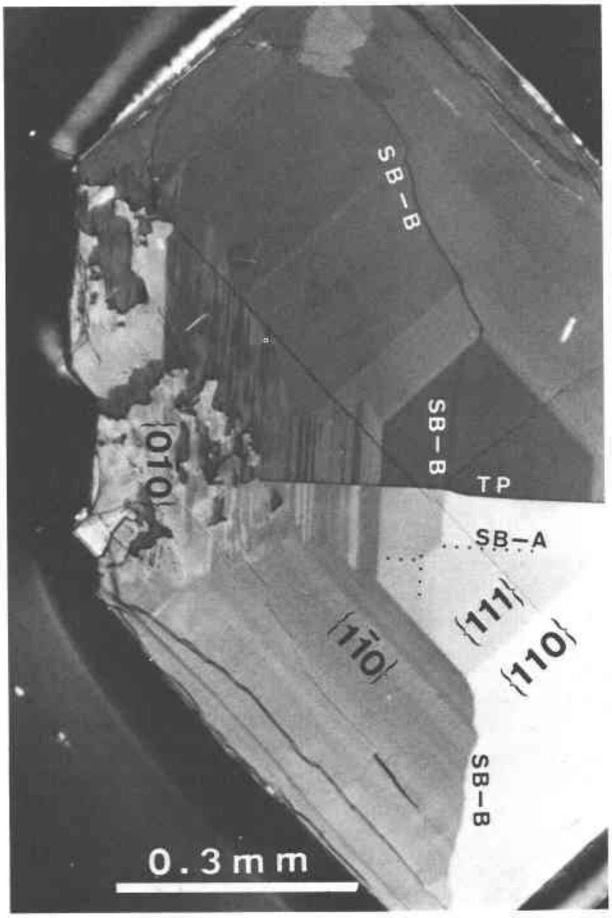

Fig. 2. Cross-polarized optical micrograph of the (001) section of scolecite from Barufjard, Iceland. The {111} sectors (core) and the {110} and {010} sectors (rim) are shown. The (100) twin plane is shown by the letters TP, and the sectoral twin boundaries are indicated by SB-A and SB-B. The {110} and {010} sectors consist of growth bands parallel to the faces. The growth bands in the {010} sector are crossed by the (100) twin. The optic axial angle ($2V_X$) is 38° throughout the crystal.

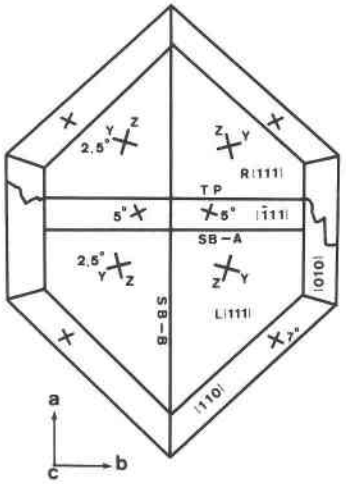

Fig. 3. Schematic sketch of growth sectors and twins in the (001) section of scolecite. The core corresponds to the {111} sectors and the rim to the {010} and {110} sectors. The symbols SB-A and SB-B show sectoral twin boundaries, and TP indicates the (100) twin plane. Optic vibration directions (*Y* and *Z*) and the inclinations of the *Y* direction to the **b** axis, which were measured in the (001) section, are shown in the sectors. The inclinations vary within ±1.5° in the {110} and {010} sectors, though the average values are shown.

Natrolite

Singly terminal prismatic natrolite crystals, having {111} and {110} forms, were studied in cross-polarized light. Natrolite crystals from Markovice, Czechoslovakia, and Kainagisa, Japan, show {111} and {110} sectors in a thin section cut parallel to (001). The optical vibration direction *Z* is parallel to the elongation of the crystal. In the {111} sector, the *X* directions are symmetrically inclined to the **b** axis as shown in Figures 4A and 4B, suggesting monoclinic symmetry. The difference between the two extinction angles is about 1° in the (001) section; that is, the *X* directions are inclined about 0.5° to the **b** axis. This suggests that the four {111} sectors are related by (100) and (010) twins.

The {110} sectors are divided into two parts with irregular boundaries. The *X* directions are symmetrically inclined about 1.5° to the **b** axis of the {111} sectors in the one part and to the **a** axis in the other part (Figs. 4A and 4B). The **b** axis of one part coincides approximately with the **a** axis of the other and vice versa. A relation between the two parts is explained in terms of parallel intergrowth, not by twinning along (110) (Pabst, 1971). Also, the {110} sectors are monoclinic. The $2V_Z$ value (57°) is consistent throughout the crystals.

The crystals from Puy-de-Dome, France, show only four {111} sectors in the (001) section, which are related by the (100) and (010) twinnings, though some crystals have very thin {110} sectors whose internal textures are not observable in detail between crossed polars. Since the difference in extinction angles between the sectors is about 2° in the (001) section, the optic axial planes are symmetrically inclined about 1° to the **b** axis through the crystal. The optical extinction is parallel to the elongation of the (110) section, suggesting monoclinic symmetry as well. The $2V_Z$ is 59°. Natrolite from Bound Brook, New Jersey, however, is homogeneous between crossed polars, suggesting orthorhombic symmetry.

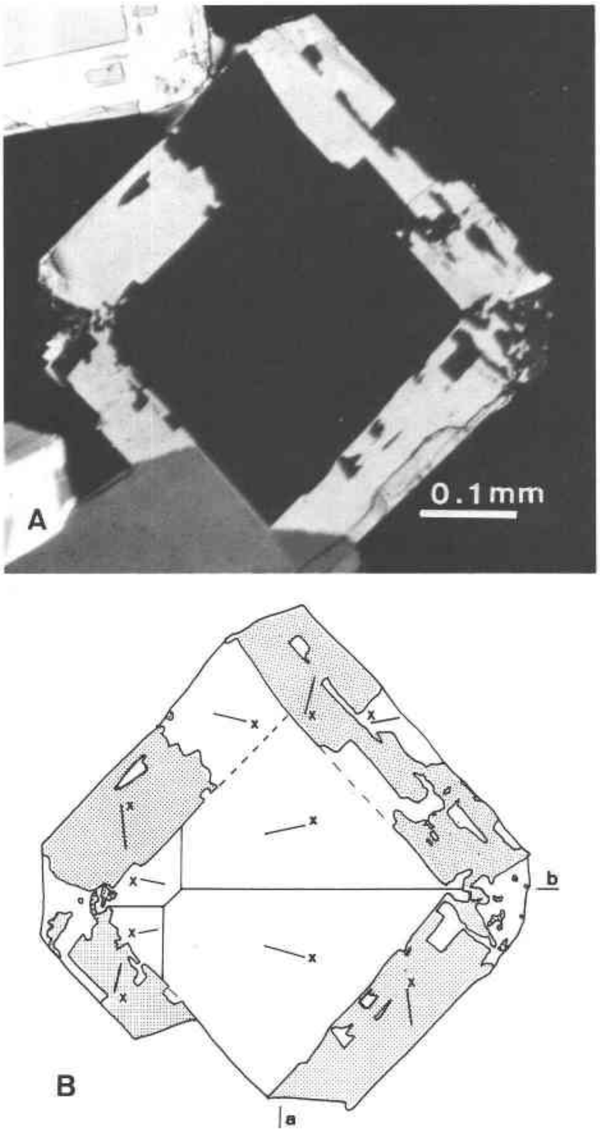

Fig. 4. Cross-polarized photomicrograph and sketch showing intergrowth in the {110} sectors (rim) and twin in the {111} sectors (core) in the (001) section of natrolite from Kainagisa, Kamogawa City, Japan. The crystal axes **a** and **b** are shown for the {111} sectors. The optic axial planes are shown by short lines. The optic vibration direction *Z* is normal to the plane of the paper, and the *X* direction is inclined about 1.5° to the **b** axis, though the angle as shown is exaggerated. The sectors showing light and dark contrasts in (**A**) and the sectors with and without shadow in (**B**) are related by the parallel intergrowth akin to (110) twinning, that is, the **a** axis of one part coincides approximately with the **b** axis of the other and vice versa.

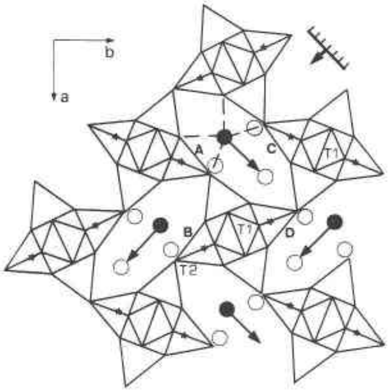

Fig. 5. Orthogonal projection on the (001) plane of scolecite with (Al,Si) ordering in which Al atoms are shown by stars. Solid and open circles represent Ca and H_2O, respectively. Dashed lines show chemical bonds between Ca and oxygen ions. Arrows show the Ca → $H_2O(3)$ vectors. Growth direction is indicated by the arrow at upper right. Modified from Alberti et al. (1982).

Mesolite

Singly terminated acicular mesolite crystals, which show {111} and {110} forms, were studied in cross-polarized light. Mesolite crystals from Atumi, Japan, consist of only {111} sectors in the (001) section, which are similar to the sectors observed in natrolite. The (110) face is not produced by crystal growth on (110), but is the result of growth of the (111) face. The optic vibration direction Y is parallel to the **c** axis, and the direction X is inclined about 10° to the **a** axis, suggesting monoclinic symmetry as shown by Hey (1933), though mesolite is orthorhombic according to X-ray analysis (Adiwidjaja, 1972).

DISCUSSION

Scolecite

Scolecite shows two kinds of twinning: one is (100) twinning caused by an asymmetric arrangement of Ca ions and H_2O molecules in the channel, and the other is sectoral twinning owing to a partly ordered (Al,Si) arrangement.

(100) twinning. Although the framework of scolecite has a glide plane parallel to (100), the distributions of water molecules and Ca ions are asymmetric with respect to that plane (Fig. 5), and therefore (100) twinning is allowed in scolecite. The topological framework around the channel of scolecite is equivalent in the four [110] directions (two directions through the center of each channel). Therefore, Ca and H_2O will occur at the same relative positions in the two-dimensional framework exposed on the four (110) faces of a crystal nucleus. If the Ca → $H_2O(3)$ vectors are oriented as shown in Figure 5 in the two-dimensional arrangement exposed on the (110) and $(1\bar{1}0)$ surfaces of the nucleus, the opposite vectors will be produced on the $(\bar{1}\bar{1}0)$ and $(\bar{1}10)$ surfaces, that is, they will be symmetrical with respect to (100). The three-dimensional structure develops on the twinned nucleus. Thus, the crystals always exhibit one twin plane (at TP) that does not coincide with the sector boundary (SB-A in Fig. 3). Since the origin of this twin is not due to the framework, the macroscopic crystal form is single, though the prism faces are re-entrant in some scolecite crystals.

Sectoral twinning. The sectoral twinnings of scolecite are explained by the following idea suggested by Akizuki (1987). The Ca ions are bonded directly to the oxygens of T_2 tetrahedra, but not to those of T_1 tetrahedra. Because of electrostatic charge balance and the Al-avoidance rule, the T_2 sites are alternately occupied with Al and Si ions, and the T_1 sites are occupied by only Si ions (Fig. 5). If the growth rate is very high, Al ions will metastably occupy some T_1 sites, and therefore the T_2 sites will have an abundance of Si, because of total charge balance. Thus, variously ordered structures can be metastably produced on the surface during growth. If the crystal grows in the direction indicated in Figure 5, the four tetrahedra (A, B, C, and D) will not be equivalent with respect to the Ca ions on the growth surface, resulting in a partly (Al,Si) ordered, triclinic structure, though the four sites are equivalent in the orthorhombic structure in which (Al,Si) arrangements are completely ordered (as shown in Fig. 5). The symmetry of the partly ordered structure is lower than that of the completely ordered structure.

Since the topological framework of scolecite is tetragonal, the (100) and the (010) mirror planes of the topological framework change into the (100) and (010) sectoral twin planes (SB-A and SB-B) in the triclinic topochemical framework with partly ordered (Al,Si) arrangement. The Ca and H_2O arrangements, however, are symmetrical with respect to the (100) twin plane (TP). These relations are shown by arrows below:

SB-A
←——— | ————→ Al,Si twinning
←———— | ——→ Ca,H_2O twinning
TP
L\{111\} | $\{\bar{1}11\}$ | R\{111\}

The L\{111\} and R\{111\} sectors are related by twinning, although the sectors are not in direct contact with each other. The {111} and $\{\bar{1}11\}$ sectors, however, are not related by twinning, and therefore their optical properties, such as extinction angle, are different (Fig. 3). The sector boundary (SB-B) corresponds to the composition plane of the sector twin with respect to only the (Al,Si) arrangement.

Natrolite

There are twice the number of Na ions in natrolite as Ca ions in scolecite, and they are related by a twofold screw axis in the center of the channel parallel to the elongation. Natrolite shows parallel intergrowths and sectoral twinning: the parallel intergrowths are attributed to an asymmetric arrangement of Na ions and H_2O molecules in the channel, and the sectoral twinning can be explained by a partly ordered (Al,Si) arrangement.

Parallel intergrowths. The intergrowths resembling twins are not observed in the {111} sectors of singly terminated prismatic natrolite, but do appear in the {110} sectors. Pabst (1971) observed by X-ray analysis that the best example of the intergrowth occurs in doubly terminated crystals, which show the same forms at both ends; that is, there is no morphological indication of the polarity of the **c** axis, though natrolite is piezoelectric (Ventriglia, 1953) and crystallizes in the space group *Fdd*2.

Crystal structures of zeolites are governed by kinetics on the crystal surfaces during growth, because the growth temperature is low. Since the topological structure ($I4_1/amd$) has a (001) glide plane, Na ions will be bonded at the equivalent positions in the two-dimensional frameworks exposed on both the (hkl) and $(hk\bar{l})$ faces during crystal growth. Since (Al,Si) ordering is affected by the Na ions on the surface during growth, not in the three-dimensional structure, the same (Al,Si) frameworks are produced on the (hkl) and $(hk\bar{l})$ faces of the doubly terminated crystal. The three-dimensional structure is metastably produced by a piling up of the two-dimensional frameworks and is maintained during growth because of the low temperature. Thus, the same form occurs at both the ends of the doubly terminated crystals.

Many nuclei with the natrolite structure are produced on the rough (110) surface and grow in opposite directions along the +**c** and −**c** axes, respectively, resulting in (110) faces with striations parallel to the **c** axis. Therefore, the {110} sectors show parallel intergrowths with complicated composition planes (Figs. 4A and 4B). The intergrowth of natrolite is similar in origin to the twinning of scolecite. However, the {110} sectors in scolecite show no intergrowths as observed in natrolite. This can be attributed to the large strain that would occur along the composition boundary of the intergrowth because scolecite is monoclinic.

Sectoral twinning. As discussed concerning scolecite, various (Al,Si) orderings are metastably produced on the surface of natrolite during low-temperature crystal growth. Since the (111) faces are symmetrically inclined to the topological mirror planes, the two symmetrically equivalent tetrahedra in the crystal will not be equivalent with respect to the Na ions on the (111) surface; thus, (Al,Si) ordering will metastably occur, and the symmetry of the crystal will be reduced to triclinic because of charge balance requirements along that surface. The topological mirror planes change into the sectoral twin planes. Although most of the natrolite crystals are monoclinic, some natrolites may be triclinic, because the optical extinction is oblique to the elongation in some of them (Brøgger, 1889). Natrolite from New Jersey, which is homogeneous between crossed polars, might have grown under conditions closer to equilibrium than natrolite with sectoral twins.

Mesolite

Mesolite consists of an alternation of one natrolite plate with $Na_2(H_2O)_2$ and two scolecite plates with $Ca(H_2O)_3$. Although the vector Ca → $H_2O(3)$ in each channel is asymmetric with respect to the (100) plane, as shown in Figure 5, the vectors in the two scolecite plates are related by the (100) glide plane (Adiwidjaja, 1972), and therefore the morphological (100) twinning observed in scolecite is not produced in mesolite during growth. The {111} sectoral twinning can be explained by (Al,Si) ordering. If the {110} sectors are observed in mesolite specimens, parallel growth as found in natrolite may be observed in the crystal.

In natrolite, mesolite, and scolecite, the symmetry of the partly ordered structures is lower than that of completely ordered structures. Tetranatrolite, which was identified by X-ray (Krogh Andersen et al., 1969), may consist of partly (Al,Si) ordered structure, and its symmetry may not be tetragonal, but rather monoclinic or triclinic. Detailed optical study is required for tetranatrolite.

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REFERENCES CITED

Adiwidjaja, G. (1972) Strukturbeziehungen in der Natrolithgrouppe und das Entwässerungsverhalten des Skolezits. Dissertation, University of Hamburg.

Akizuki, M. (1981) Origin of optical variation in analcime. American Mineralogist, 66, 403–409.

——— (1984) Origin of optical variations in grossular-andradite garnets. American Mineralogist, 69, 328–338.

——— (1986) Al-Si ordering and twinning in edingtonite. American Mineralogist, 71, 1510–1514.

——— (1987) An explanation of optical variation in yugawaralite. Mineralogical Magazine, 51, 615–620.

Akizuki, M., and Konno, H. (1985) Order-disorder structure and the internal texture of stilbite. American Mineralogist, 70, 814–821.

Alberti, A., Pongiluppi, D., and Vezzalini, G. (1982) The crystal chemistry of natrolite, mesolite and scolecite. Neues Jahrbuch für Mineralogie Abhandlungen, 143, 231–248.

Brøgger, W.C. (1889) Die Mineralien der Syenitpegmatitgänge der Südnorwegischen Augit-und Nephelinsyenite, 65. Natrolith. Zeitschrift für Kristallographie und Mineralogie, 16, 598–640.

Dana, S.D. (1892) The system of mineralogy. Wiley, New York, 604 p.

Des Cloizeaux, A. (1862) Manuel de minéralogie. Dunod, Paris, 388 p.

Fälth, L., and Hansen, S. (1979) Structure of scolecite from Poona, India. Acta Crystallographica, 35, 1877–1880.

Hey, M.H. (1932) Studies on the zeolites. Part III. Natrolite and metanatrolite. Mineralogical Magazine, 23, 243–289.

——— (1933) A possible source of error in the determination of symmetry from optical extinction-angles. Mineralogical Magazine, 23, 367–370.

Krogh Andersen, E., Danø, M., and Petersen, O.V. (1969) A tetragonal natrolite. Meddelelser om Grønland, 181, 1–19.

Luedecke, O. (1881) Mesolith and skolezit. Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie, 2, 1–41.

Pabst, A. (1971) Natrolite from the Green River formation, Colorado, showing an intergrowth akin to twinning. American Mineralogist, 56, 560–569.

Rinne, F. (1890) Über die Umänderungen, welche die Zeolithe durch Erwärmen bei und nach dem Trübewerden erfahren. Sitzungsberichte der Koniglich Preussischen Akademie der Wissenschaften zu Berlin, 46, 1161–1207.

Smith, J.V., Pluth, J.J., Artioli, G., and Ross, F.K. (1984) Neutron and X-ray refinements of scolecite. In A. Bisio and D.H. Olson, Eds, Proceedings of 6th International Zeolite Conference, p. 842–850. Butterworths, Guildford.

Ventriglia, U. (1953) Simmetria della heulandite e piezoelecttricià di alcune zeoliti. Rendiconti della societa Italiana di Mineralogia e Petrologia, 9, 268–269.

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