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Synthesis, Properties, and Structure of $K_2Ca(CO_3)_2$, Buetschliite

ADOLF PABST

Department of Geology and Geophysics, University of California, Berkeley, California 94720

Abstract

Synthesis of both the high- and low-temperature forms (fairchildite and buetschliite) by solid state reaction, one of five methods of synthesis used, suggests that the transition point is in the interval 505–585°C. Low-$K_2Ca(CO_3)_2$, buetschliite, crystallizes in the space group $R\bar{3}2/m$ (a 5.38, c 18.12 Å, $Z = 3$) with an eitelite-type structure.

Introduction

Buetschliite was recognized as a mineral and named by Milton and Axelrod (1947) who found it in wood-ash stones from half a dozen localities in the western United States. It has since been reported from several Canadian localities (Dawson and Sabina, 1958; Mandarino and Harris, 1965). Mrose, Rose, and Marinenko (1966) synthesized it and showed that it has the formula $K_2Ca(CO_3)_2$ and that it is a dimorph of fairchildite. They also reported it is rhombohedral and gave cell dimensions. The data in the Powder Diffraction File on card 21-980 are based on the spacings reported by Milton and Axelrod and indexed on the cell of Mrose *et al.*

Synthesis

The present study is based entirely on synthetic material, because natural material is difficult to procure, generally mixed with impurities, and/or partly decomposed. $K_2Ca(CO_3)_2$ grown from solutions as steeply rhombohedral crystals by Bütschli (1907, p. 294), his "Doppelsalz B," was presumably the equivalent of buetschliite. Niggli (1916, pp. 291–293) reported on the crystallization of $K_2Ca(CO_3)_2$ from the melt under a CO_2 pressure of one atmosphere. However, he did not recognize the dimorphism of $K_2Ca(CO_3)_2$ and supposed solid solution with $CaCO_3$ to be possible, a supposition not supported by later work. Eitel and Skaliks (1929) repeated the synthesis in a manner similar to that of Niggli. The density and refractive indices they reported show that the phase with which they were dealing is the equivalent of fairchildite.

The dimorphism of $K_2Ca(CO_3)_2$ was first recognized by Mrose *et al* (1966). They found a phase formed above 704°C to correspond to fairchildite and one below 704°C to correspond to buetschliite. Both phases were "synthesized from equimolar amounts of K_2CO_3 and $CaCO_3$ in closed but not sealed carbon crucibles." "Buetschliite also was formed at room temperature from a 40 percent solution of K_2CO_3 containing calcite." "Calcite" here refers to "powdered calcium carbonate—reagent grade" (Mrose, personal communication, March 20, 1973).

During this study buetschliite was synthesized:

(*A*) By slow but spontaneous transformation from fairchildite formed from fusion;

(*B*) By solid state reaction between finely ground and well-mixed K_2CO_3 and $CaCO_3$ in pellets heated for several days. Five runs were made: at 340 ± 10°C there was no reaction; at 420° and 505 ± 10° for 8 days and for 5½ days buetschliite was formed; but at 585 ± 10° for 4½ days only fairchildite was formed. This suggests that the transition point between the two forms may be substantially lower than one might conclude from the report of Mrose *et al* (1966).

(*C*) By the action of a saturated solution of $KHCO_3$ on Baker's (analyzed reagent) $CaCO_3$ at 66°C for 5 days. The $K_2Ca(CO_3)_2$ produced is microcrystalline.

(*D*) By action of a saturated solution of $K_2CO_3 \cdot 1\frac{1}{2}\ H_2O$ on Baker's (analyzed reagent) $CaCO_3$ for 138 hours at 55°C. This yielded many small single crystals of $K_2Ca(CO_3)_2$ adequate for X-ray diffraction in spite of invariably present inclusions of unreacted $CaCO_3$. (The difference in the action of $KHCO_3$ and $K_2CO_3 \cdot 1\frac{1}{2}\ H_2O$ saturated solutions is probably due to the fact that the former at 25°C has a concentration of about 27 percent K_2CO_3, the latter of about 53 percent K_2CO_3.)

(*E*) By action of a saturated solution of $K_2CO_3 \cdot 1\frac{1}{2}\ H_2O$ on small cleavage pieces of calcite, mostly 2 to 6 mm on edge, for 25 days at 60°C in a lightly stoppered Erlenmeyer flask. This yielded perfectly clear crystals suitable for goniometric study, some of which are shown in Figure 1. Repetition of the experiment using smaller calcite cleavage rhombs in the expectation that the greater calcite surface area would facilitate reaction did not yield a better crop of $K_2Ca(CO_3)_2$ crystals.

Stability

Crystals of $K_2Ca(CO_3)_2$, such as those shown in Figure 1, are instantly attacked when brought into contact with water. Exposed to moist air they are slowly attacked. However, Mrose reports that a crystal showed no change of structure after several years. The fact that buetschliite has been recognized as a mineral also shows that it may persist under natural conditions, perhaps because a very fine-grained coating of $CaCO_3$ formed by the initial action of water shields the interiors of buetschliite crystals from further action of moisture. Crystals of low-$K_2Ca(CO_3)_2$ may be preserved without change by immersion in toluene or some other organic liquid that prevents water from coming into contact with them. The high-temperature form, fairchildite, may be similarly protected from attack but in some cases changes spontaneously and slowly to the low-temperature form, some calcite forming incidentally. This process was followed by repeated X-ray examination of a crystal of the high-temperature form obtained from fusion. Nevertheless, even the high temperature form persists metastably as the mineral fairchildite.

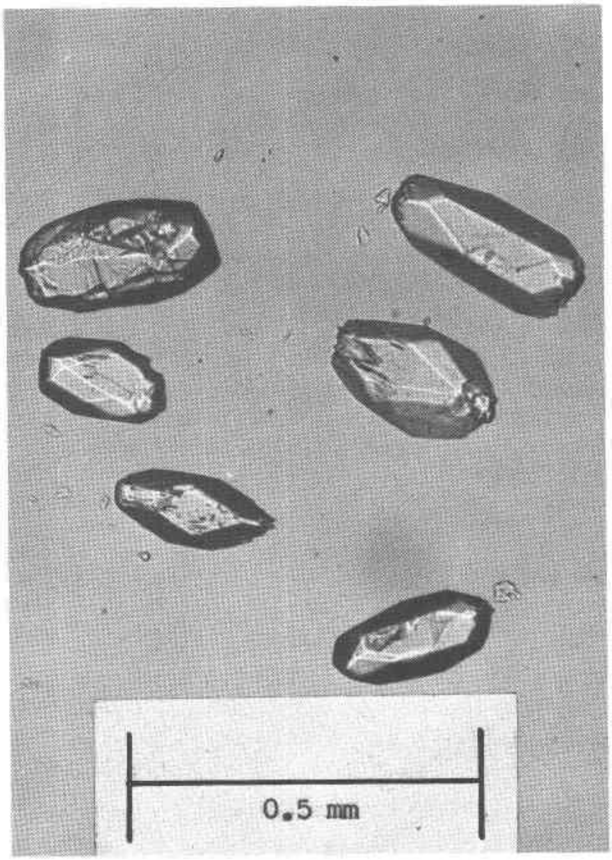

FIG. 1. Crystals of $K_2Ca(CO_3)_2$ formed by action of a saturated solution of $K_2CO_3 \cdot 1\frac{1}{2}\ H_2O$ on calcite cleavage chips. Crystals immersed in liquid with $n = 1.482$, polarized white light. Photograph by J. Hampel.

Morphology

Although synthesis by method D did yield some crystals on which a few faces could be identified in spite of the presence of coatings or inclusions, morphological observations were made mostly on crystals obtained by method E. Of ten crystals examined soon after mounting to avoid deterioration in moist air, only a few were found suitable for two-circle reflection goniometry. Accordingly such observations were supplemented by observations on crystals in immersion under the microscope, using a device similar to that described by Jones (1960) and a method of measurement adapted from that described by Gilbert and Turner (1949). The forms observed, in approximate order of importance, are: $\{10\bar{1}1\}$, $\{01\bar{1}2\}$, $\{0001\}$, $\{11\bar{2}0\}$, $\{11\bar{2}2\}$, (possibly other second order bipyramids), and $\{02\bar{2}1\}$. The pinacoid is also a cleavage form, and it is not always possible to distinguish growth forms from cleavage forms. The habit varies. Mostly it is determined by the dominance of the commonest rhombohedra, but a few crystals are more or less spindly, being bounded principally by faces of the second order prism with rhombohedral terminations.

The morphology is compatible with the symmetry $\bar{3}2/m$ and that of other rhombohedral classes. Etch figures on (0001) and $(000\bar{1})$ cleavage surfaces, such as were used to establish the centrosymmetry of eitelite (Pabst, 1973, Fig. 3), were not obtainable due to the rapid destruction of all crystal surfaces by moisture.

Optical properties

Both buetschliite and fairchildite are uniaxial negative. The anticipated refractive indices, assuming that CO_3 groups are all oriented normal to *c*, were calculated for both substances by the method devised in connection with the work on eitelite (Pabst, 1973, p. 213). For this it is necessary to calculate the effective refractive energies of the K_2CO_3 and $CaCO_3$ components for both ϵ and ω. For K_2CO_3 the indices reported by Milton and Axelrod (1947) and the density 2.428 were used, β and γ being averaged to yield an approximation to an ω value. For $CaCO_3$ the values for calcite were used. For fairchildite and buetschliite, the calculated densities given by Mrose *et al* (1966), 2.45 and 2.61 respectively, were used. The results of these calculations and the refractive indices of fairchildite and buetschliite as newly determined in Na light on crystals grown in connection with this work are shown in Table 1.

The good agreement of observed and calculated values for buetschliite indicates that the assumption that all CO_3 groups are oriented normal to *c* is correct for this substance. The lack of agreement in the case of fairchildite shows that such an assumption is not warranted in this case. Wickman (1949, p. 100) has shown that it is possible to take into account other orientations of CO_3 groups in the calculation of indices.

Space Group

The space group of buetschliite has been reported (Mrose *et al*, 1966) to be $R\bar{3}$. It has been shown by structure determination (Pabst, 1973) that eitelite, $Na_2Mg(CO_3)_2$, crystallizes in this space group. In view of the similarity of cell dimensions, cell content, and symmetry, it seemed probable that the structure of buetschliite is of the eitelite type. However, oscillation, Weissenberg, and precession patterns run on many synthetic buetschliite crystals indicated the Laue symmetry $\bar{3}2/m$. This was checked, for instance, by running pairs of zero-level precession patterns on the [$1\bar{2}0$] and [130] axes. These proved to be identical, whereas they should differ if the Laue symmetry were $\bar{3}$. It turns out that the space group of buetschliite was reported wrongly due to a misprint (Mrose, private communication, March 5, 1973).

Table 1. Calculated and Observed Refractive Indices of Fairchildite and Buetschliite

		Calculated	Observed	Differences
Fairchildite	ϵ	1.434	1.498	+0.064
	ω	1.563	1.533	-0.030
	$\omega - \epsilon$	0.129	0.035	0.094
Buetschliite	ϵ	1.462	1.453	-0.009
	ω	1.600	1.605	+0.005
	$\omega - \epsilon$	0.138	0.152	0.014

Structure Determination

In spite of the difference in space group, the structure of buetschliite may be of the eitelite type. In eitelite the oxygens of the CO_3 groups occupy general *x*, *y*, *z*, positions in $R\bar{3}$ (18*f*, hexagonal axes). The values of *x* and *y* were determined by considering the orientation of the CO_3 group over a range of ϕ values of only 30° (Pabst, 1973, p. 214, col. 2). If ϕ is at the limiting value of 30° (in the case of eitelite it is 18°), the 18*f* position of $R\bar{3}$ becomes the 18*h*, *x*, *x*, *z*, position of $R\bar{3}2/m$. This is the situation in buetschliite. The value of *x* is fixed by the C-O distance, assumed to be 1.283 as in dolomite (Steinfink and Sans, 1959). The origin being taken in Ca, the structure is fixed by the *z* parameters of K and CO_3. Preliminary values of these parameters were found, as in the case of eitelite, by one-dimensional F_o summations executed with Lipson and Beevers strips, using only the three highest F_o values for 000*l*—namely, $l = 6$, 9, and 15—and assigning each of the four possible independent combinations of signs. One of the resulting curves showed peaks interpretable in terms of an eitelite-type structure.

Satisfactory agreement of F_c and F_o was immediately obtained for the *hki*0 reflections with ϕ of CO_3 at 30° and after some adjustment of the preliminary *z* values for the 000*l* reflections. For both groups of reflections rather high temperature factors, more than double those for eitelite, were indicated, the thermal motion being much greater in the *c* direction than normal thereto. The intensities of other groups of reflections were estimated from zero-level precession patterns having *c** in common, as in the case of eitelite. The principal features of each pattern, *i.e.*, the strongest and weakest spots, could be predicted from the previously chosen parameters. For 36 observed reflections in the loci $10\bar{1}l$, $20\bar{2}l$, $30\bar{3}l$, $11\bar{2}l$, and $22\bar{4}l$, where *l* equals 15 to $\bar{15}$ and F_c is based on $B = 3$, *R* equals about 15 percent. However, test calculations on a limited group of reflections showed that it would

TABLE 2. Comparison of F_{obs} and F_{calc} Values for Two Groups of Reflections Used in Selection of Trial Parameters for Buetschliite

	F_{obs}	F_{calc}†		F_{obs}	F_{calc}††
00*6	35.5	-34.3	11*0	42.8	41.7
00*9	21.8	25.1	30*0	23.4	24.8
00*12	12.7	12.0	22*0	41.3	39.9
00*15	16.3	13.3	41*0	22.0	20.4
00*21	5.2	- 5.1	33*0	20.1	22.1
00*24	8.2	10.0	60*0	14.7	16.6
			52*0	12.1	10.9
	R = 10.1			R = 6.1	
	†B = 2.5			††B = 1.0	

be necessary to employ individual anisotropic temperature factors to obtain better agreement (see supplementary note at end). In view of (1) the uncertainty of visual intensity estimates, (2) the imperfection of the crystals connected with their limited stability, and (3) the common presence of inclusions or decomposition products, no attempt at such refinement was undertaken.

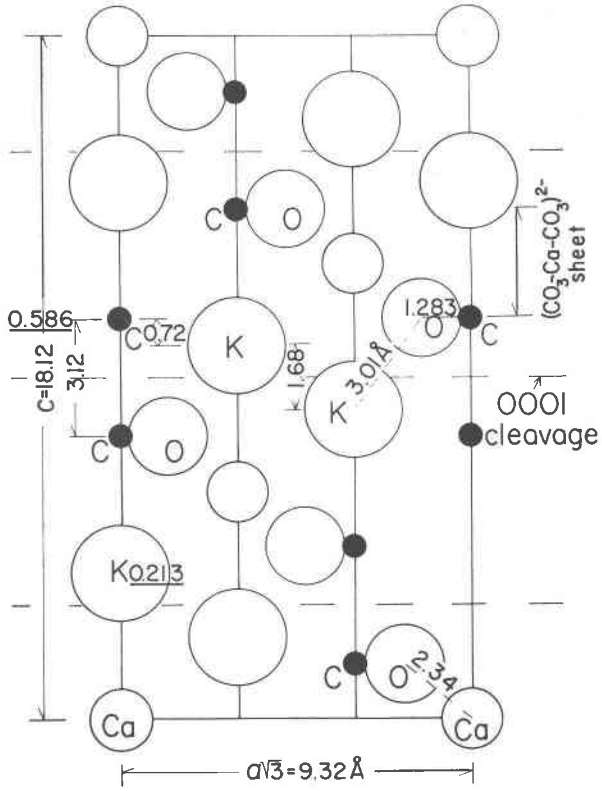

FIG. 2. Section through the structure of $K_2Ca(CO_3)_2$, buetschliite, along a mirror plane. The radii of the circles representing the various ions do not correspond to the radii of the ions on the scale of the drawing.

Table 2 shows the data on which the chosen parameters are based. The *R* values are slightly higher, and the *B* values much higher, than those given in the comparable table for eitelite (Pabst, 1973, Table 2). The structure parameters are:

Ca in 3*a* $\bar{3}m$ 0, 0, 0 (hexagonal reference system)
K in 6*c* 3*m* 0, 0, *z* $z = 0.213$
C in 6*c* 3*m* 0, 0, *z* $z = 0.586$
O in 18*h* *m* $x, \bar{x}, z$ $x = 0.138$, $z = 0.586$.

Volume Considerations

In connection with the study of eitelite, it was noted that its cell dimensions and cell content are comparable to those of dolomite (Pabst, 1973, Table 1[1]), the greater volume of the eitelite cell, 7.79 Å^3, being sufficient to accommodate one Na ion. One may also compare the cell volume and content of buetschliite to those of dolomite. In this case one would expect a much greater difference in volumes related to the substitution of 2K for Mg. All three structures may be compared as to their volume differences by the following relation:

$$\frac{V_{\text{buetschliite}} - V_{\text{dolomite}}}{V_{\text{eitelite}} - V_{\text{dolomite}}} = \frac{43.52}{7.79} = 5.587.$$

Calculating ionic volumes from their radii as given by Ahrens (1952), one gets a comparable relation:

$$\frac{V_{2K} - V_{Mg}}{V_{2Na} - V_{Ca}} = \frac{18.50}{3.58} = 5.17,$$

showing that the volume difference ratio of the structures is just about that required by the volume differences of the ions.

Description of the Structure

Since all atoms are centered on mirror planes, the structure can be fully represented by a section through such a plane (Fig. 2). This figure is drawn to a scale based on the cell dimensions, a_h 5.38, c_h 18.12 Å, reported for buetschliite by Mrose *et al* (1966) and confirmed in this study. The principal features of the structure correspond to those of eitelite, and structure diagrams for the mineral (Pabst, 1973, Figs. 4 and 5) with a little modification would serve for buetschliite as well.

The calciums at one *z* level together with the CO_3

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[1] In this table the volume of the eitelite cell was mistyped as 116.67 Å^3 whereas it should be 115.67 Å^3.

groups immediately above and below make up a charged sheet $(CO_3—Ca—CO_3)^{2-}$ normal to *c* as indicated in Figure 2. Each Ca, at a site having symmetry $\bar{3}2/m$, is bonded to 6 CO_3 groups which are on the surrounding 3-fold axes, the Ca-O distance being 2.34 Å. O-O distances in the coordination group are: horizontally 3.16 Å with O-Ca-O 85° and diagonally 3.44 Å with O-Ca-O 95°.

The levels of CO_3 groups in neighboring $(CO_3–Ca–CO_3)^{2-}$ sheets are 3.12 Å apart in the *c* direction. The two K^+ ions per formula unit in this interval are at two different levels. The K^+ ions situated on the same 3-fold axis as the Ca^{2+} ions of a particular sheet are displaced towards the opposite sheet, being 0.72 Å from the CO_3 level of that sheet. Each K^+ ion thus has a markedly polar coordination. On the side closer to the CO_3 levels, it is bonded to three pairs of oxygens belonging to three different CO_3 groups, the K–O distances being 2.80 and the distances between oxygens in adjacent CO_3 groups being 3.16 Å. This situation is markedly different from that in eitelite in which there are only three oxygens at a minimum distance due to the lower symmetry and the different orientation of the CO_3 groups. Each K^+ ion is repelled by the Ca^{2+} ion that is located 3.86 Å from it on the same 3-fold axis. Consequently it is more distant from the $(CO_3–Ca–CO_3)^{2-}$ sheet that contains this Ca^{2+} and thus closer to the $(CO_3–Ca–CO_3)^{2-}$ sheet that does not. The K–O distance to the nearest oxygen is 3.01 Å for the more distant sheet and 2.80 Å for the nearer. The total coordination of K^+ may be stated to be 6 + 3 (see Fig. 3).

The Ca–O distance, 2.34 Å, is near the lower limit of such distances for Ca in 6-fold coordination (*Int. Tables for X-Ray Crystallography,* Vol. III, p. 260). The shorter K–O distance, 2.80 Å, is also close to the lower limit of such distances for K in 6-fold coordination, whereas the 3.01 distance is a bit above the upper limit. Presumably K should be considered to be bonded principally to the $(CO_3–Ca–CO_3)^{2-}$ sheet to which it is closer. The prominent cleavage parallel to (0001) passes between the K^+ ions at different levels in the space between successive sheets. The distance between the levels of the K^+ ions is 1.68 Å, very much greater than the corresponding distance between the levels of Na^+ ions, 0.96 Å, in eitelite, $Na_2Mg(CO_3)_2$. It seems probable that the lesser stability of buetschliite is related to this difference.

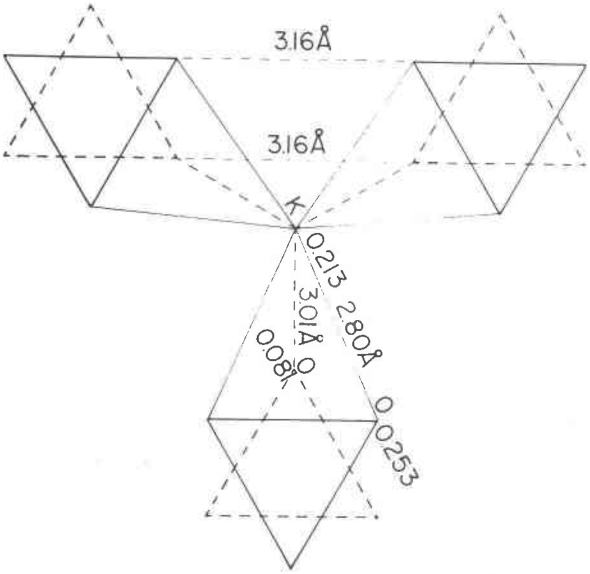

FIG. 3. Coordination of K^+ in buetschliite. The *z* levels of one potassium ion and of oxygens above and below it are indicated together with the K-O distances and the minimum O-O distances between oxygens of adjacent CO_3 groups at the same *z* level.

In view of the greater uncertainty of the *z* parameters of buetschliite due to lack of refinement, the interionic and other distances given above are subject to much greater uncertainty than those reported for eitelite. However, even if the parameters should be in error by 0.005, a pessimistic estimate, interionic and related distances would still conform to the relations outlined. For instance, the distance between successive levels of K^+ ions might then be anywhere in the range 1.50–1.86 Å, still markedly different from the better established comparable distance, 0.96 Å, in eitelite.

Acknowledgments

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Supplementary Note

The structure determination is based on X-ray observations on crystals synthesized by method D. Better crystals, made by method E, were obtained in early April, 1973. Due to hindrances not connected with this study X-ray diffraction patterns from such superior crystals were not obtained until late July. Comparison of F_o's obtained from these patterns with those used earlier showed that errors in the F_o values used in the determination were no higher than was to be expected from the inherent uncertainty of visual estimates of intensities with the aid of photographic scales corresponding to known intensities. However, it may be that the indicated temperature factors include the effect of "frozen-in thermal movement" (Guinier, *X-ray Crystallographic Technology*, translated by T. L. Tippell, London, 1952, p. 245), in this case attributable to crystal imperfections that may be associated with the methods of synthesis.

References

Bütschli, O. (1907) Über die Einwirkung von konzentrierter Kalilauge und konzentrierter Lösung von kohlensaurem Kali auf kohlensauren Kalk, sowie zwei dabei entstehende Doppelsalze von kohlensaurem Kali und kohlensaurem Kalk. *Verhandlungen des Naturhistorisch-Medizinischen Vereins zu Heidelberg, N. F.* **8,** 277–330. [Erroneously cited by Niggli (1916, p. 292) as "Verh. naturw. Verein Heidelberg 2 8 (1907), 277." Year of publication erroneously given by Milton & Axelrod (1947) as 1905.]

Dawson, K. R., and Ann Sabina (1958) A Canadian occurrence of fairchildite and buetschliite. *Can. Mineral.* **6,** 290–291.

Dietrich, Richard V. (1971) An occurrence of buetschliite east of the Rocky Mountains. *Mineral. Rec.* **2,** 130–132. (reference added in proof).

Eitel, W., and W. Skaliks (1929) Über einige Doppelcarbonate der Alkalien und Erdalkalien. *Z. Anorg. Chem.* **183,** 263–286.

Gilbert, Charles M., and Francis J. Turner (1949) Use of the universal stage in sedimentary petrography. *Am. J. Sci.* **247,** 1–26.

Jones, F. T. (1960) Stage goniometer and cell for study of crystals by goniometry and X-ray diffraction without remounting. In, W. C. McCrone, Ed., *Proceedings Microscopy Symposium,* Chicago, p. 54.

Mandarino, J. A., and D. C. Harris (1965) New Canadian mineral occurrences: I. *Can. Mineral.* **8,** 377–381.

Milton, Charles, and Joseph Axelrod (1947) Fused wood-ash stones: Fairchildite (n.sp.) $K_2CO_3 \cdot CaCO_3$, buetschliite (n.sp.) $3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$ and calcite, $CaCO_3$, their essential constituents. *Am. Mineral.* **32,** 607–624.

Mrose, Mary, Harry J. Rose, Jr., and John W. Marinenko (1966) Synthesis and properties of fairchildite and buetschliite: Their relation to wood-ash stone formation. *Progr. Geol. Soc. Am. Meet., San Francisco,* p. 146.

Niggli, Paul (1916) Gleichgewichte zwischen TiO_2 und CO_2, sowie SiO_2 und CO_2 in Alkali, Kalk-Alkali und Alkali-Aluminatschmelzen. *Z. Anorg. Chem.* **98,** 241–326.

Pabst, Adolf (1973) The crystallography and structure of eitelite, $Na_2Mg(CO_3)_2$. *Am. Mineral.* **58,** 211–217.

Steinfink, H., and F. J. Sans (1959) Refinement of the structure of dolomite. *Am. Mineral.* **44,** 679–682.

Wickman, Frans E. (1949) The crystal structure of shortite, $Ca_2Na_2(CO_3)_3$. *Ark. Min. and Geol.* **1,** 95–101.

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