NIOBIAN PEROVSKITE FROM OKA, QUEBEC; A NEW CLASSIFICATION FOR MINERALS OF THE PEROVSKITE GROUP

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ABSTRACT

Niobian perovskite from the southwestern portion of the Oka complex has been found to contain from 14.5 to 44.9% Nb_2O_5. A chemical analysis of one perovskite sample gave the following results: CaO 25.95%; Na_2O 4.03%; rare earth oxides 2.03%; K_2O 0.03%; Nb_2O_5 43.90%; TiO_2 10.05%; Fe_2O_3 8.74%; MgO 2.20%; MnO 0.77%; SiO_2 0.45%; S 0.90%; and L.O.I. 0.65%. *X*-ray powder diffraction data indicate that this perovskite is orthorhombic with cell parameters $a = 5.448$, $b = 7.777$ and $c = 5.553$ Å, and space group *Pcmn*. The unit-cell size of the perovskite decreases with decreasing niobium content.

A classification scheme based on the valency of the *A* cation is proposed. According to this classification, minerals of the perovskite group are classified as lueshite, perovskite and loparite, respectively, depending on whether the *A* cation is monovalent (Na), divalent (Ca) or trivalent (Ce). The modifier *niobian* is used to designate varieties containing a substantial amount of niobium.

INTRODUCTION

Since shortly after the discovery of the niobium deposits at Oka, Quebec in 1953, one of the authors (E. H. Nickel) has been intermittently engaged in the investigation of certain mineralogical aspects of these deposits. During the course of a recent study of pyrochlore and perovskite from the property held by Columbium Mining Products Limited (Nickel, 1962), it was found that the perovskite varies widely in composition, and that some of it has an extraordinarily high niobium content. Consequently, a more detailed examination of the perovskite was made, leading to the results embodied in this paper.

The rather confusing use of varietal names in the literature and the lack of a suitable classification for minerals of the perovskite group soon became evident. A classification scheme for naturally-occurring perovskites was therefore developed.

The chemical analysis was made by one of the authors (R. C. McAdam). The other (E. H. Nickel) is responsible for the remainder of the investigation.

GENERAL GEOLOGY

The niobium deposits of the Oka district of Quebec lie within the Oka complex of carbonate and alkaline rocks. These rocks, which form an oval-shaped body about 4 miles in length and up to 1½ miles in width, are considered to be part of the Monteregian petrographical province of post-Middle Devonian age (Rowe, 1958). The niobium minerals, represented chiefly by pyrochlore, but also including niobian perovskite and niocalite, are disseminated irregularly throughout the body.

All of the niobian perovskite described in this paper was concentrated from samples taken from property held by Columbium Mining Products Limited in the southwestern part of the Oka complex. Sample A-1 was a mill sample taken from surface trenches; the other samples were diamond drill core assay rejects.

DESCRIPTION OF SAMPLES

The samples are all relatively fine-grained, and consist predominantly of white calcite with varying amounts of diopside, biotite and apatite. Accessory minerals include pyrochlore, niobian perovskite, magnetite, pyrrhotite, dolomite, nepheline and monticellite, as well as others occurring in extremely small quantities.

The niobian perovskite occurs primarily as small, black cubic crystals, generally less than 0.2 mm. to a side (Fig. 1). Most of the larger crystals are embayed by, and commonly contain inclusions of, other minerals,

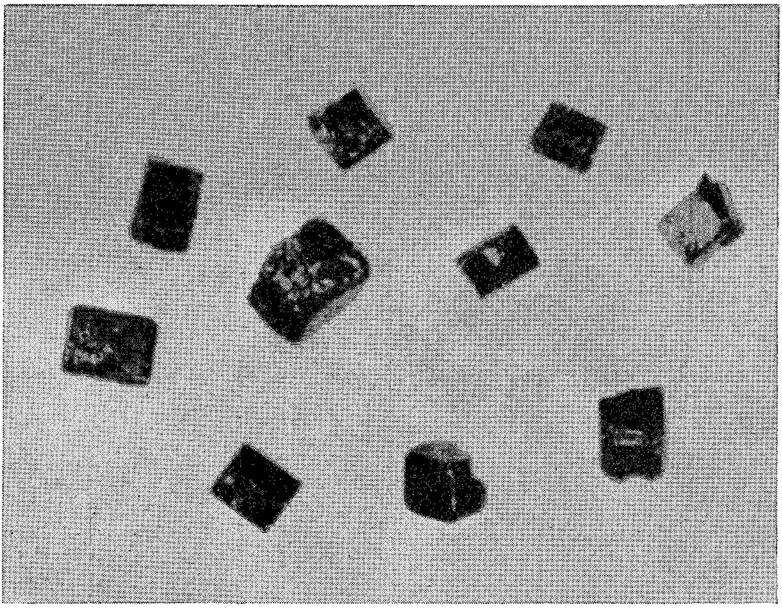

FIG. 1. Crystals of niobian perovskite. ×80.

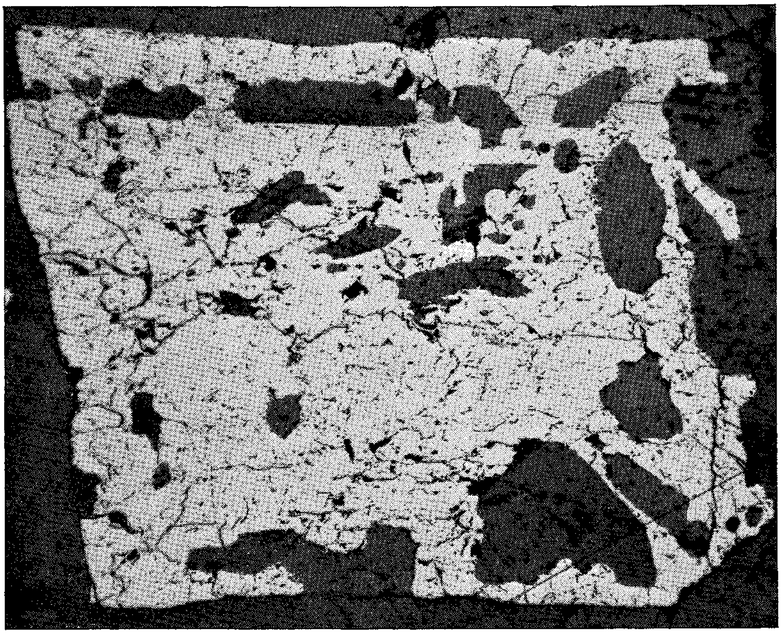

FIG. 2. Polished section of a large niobian perovskite crystal with calcite inclusions. ×65.

usually calcite (Fig. 2). A few crystals were found to be rimmed by extremely fine-grained pyrochlore, giving the impression that the niobian perovskite has been partially replaced by, or altered to, pyrochlore.

In transmitted light the niobian perovskite is dark greyish-brown and exhibits moderate anisotropism. Practically all of the crystals exhibit complex twinning.

The specific gravity of the analysed niobian perovskite, as determined by pycnometer, is 4.40. This is much higher than the theoretical specific gravity of pure $CaTiO_3$ (4.04), and can probably be attributed to its high niobium content.

PROCEDURE

Sample Preparation

Sufficient perovskite for a complete chemical analysis was obtained from only one sample, here referred to as A-1. A partial concentrate of the perovskite in this sample was produced by H. L. Noblitt, consulting metallurgist for Columbium Mining Products Limited, by means of flotation, tabling, and electrostatic separation. After further purification by heavy-liquid and magnetic separations, the sample was considered to be pure enough for chemical and *x*-ray diffraction analyses.

Small amounts of perovskite were also concentrated from a number of the diamond-drill core assay rejects by a combination of heavy-liquid, magnetic, and electrostatic separations. These concentrates, some of which had to be hand-picked during the final stages of concentration, were analysed for niobium.

X-ray Diffraction Methods

X-ray powder diffraction patterns of all the perovskite concentrates were made on 114.6 mm. Debye-Scherrer cameras using nickel-filtered copper radiation. The patterns were measured and shrinkage corrections made. The unit-cell dimensions were calculated from the (240, 321)–(123, 042) doublet in the neighbourhood of $2\theta = 58°$.

Single-crystal *x*-ray diffraction analysis was attempted by J. F. Rowland of the Mineral Sciences Division, but all the crystals selected up to the time of writing produced multiple diffraction patterns indicative of internal twinning. Investigation of the niobian perovskite by single-crystal methods is continuing, however, and it is expected that the results will be reported in another paper.

X-RAY DIFFRACTION ANALYSES

An *x*-ray diffractometer tracing of the analyzed niobian perovskite (A-1) is shown in Fig. 3. The measured powder diffraction data are given

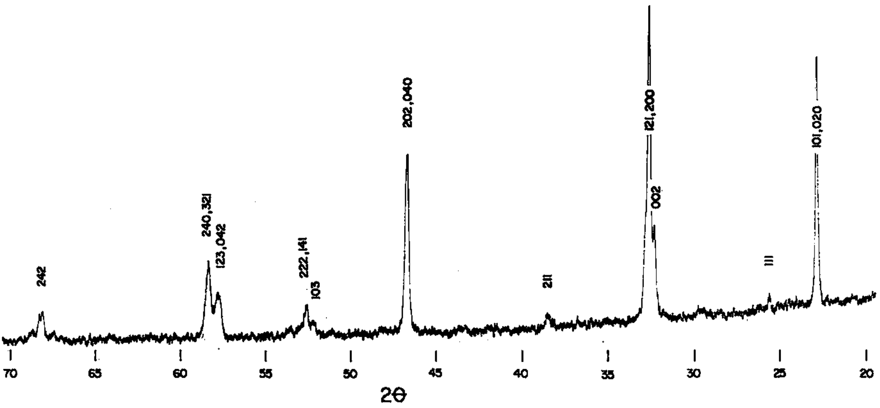

FIG. 3. *X*-ray diffractometer tracing of niobian perovskite A-1. Cu$K\alpha$ radiation; scanning rate $\frac{1}{4}$ degree per minute.

in Table 1. The numerical intensities given in Table 1 were measured from the peak heights on the diffractometer tracing, recalculated to a scale of 100. The intensities given as "w" (weak) appeared as weak lines on film, but were not resolved on the diffractometer tracing. The *d*-values were measured from the powder pattern films, and indexed with the *hkl* values for $CaTiO_3$ given by Coughanour *et al.* (1955). The few weak lines that cannot be indexed can be attributed to small amounts of impurities in the sample, chiefly pyrite and diopside.

TABLE 1. *X*-RAY POWDER DIFFRACTION DATA FOR NIOBIAN PEROVSKITE NO. A-1

I	$d_{\text{meas.}}$	*hkl*	$d_{\text{calc.}}$
79	3.887	101	3.888
		020	3.888
5	3.471	111	3.478
w	3.319	—	—
w	3.125	—	—
2	3.005	—	—
30	2.773	002	2.776
100	2.744	121	2.749
		200	2.723
w	2.608	012	2.615
w	2.421	201	2.445
4	2.339	211	2.333
w	2.281	022	2.260
w	2.207	220	2.231
w	2.152	131	2.157
w	2.079	122	2.087
		221	2.070
57	1.942	202	1.944
		040	1.944
w	1.915	—	—
w	1.888	212	1.886
w	1.835	—	—
4	1.750	103	1.753
9	1.737	222	1.739
		141	1.739
2	1.707	113	1.710
w	1.631	—	—
14	1.595	123	1.598
		042	1.593
25	1.579	240	1.582
		321	1.577
w	1.500	150	1.496
w	1.448	133	1.452
w	1.386	004	1.388
9	1.374	242	1.375
w	1.363	400	1.362
w	1.301	143	1.302
w	1.289	313	1.279
w	1.236	204	1.237
7	1.229	323	1.230
		161	1.230
w	1.193	—	—
w	1.179	431	1.178
w	1.128	044	1.130
w	1.116	440	1.115
w	1.087	170	1.089
		105	1.088
w	1.077	115	1.078
w	1.061	171	1.068
w	1.047	125	1.048
w	1.042	244	1.044
		163	1.042
w	1.036	361	1.036
w	1.033	521	1.031

There has been a diversity of opinion as to the best choice of unit cell for perovskite. The strongest lines can be indexed on a cubic cell with $a \sim 3.8$ Å. However, the anisotropism generally exhibited by perovskite indicates that the mineral is actually pseudocubic. Unit-cell symmetries suggested have been orthorhombic (Barth, 1925), monoclinic (Naray-Szabo, 1943) and tetragonal (Frank-Kamenetskii & Vesel'skii, 1961). However, an orthorhombic unit cell, with parameters $\sqrt{2}$, 2, and $\sqrt{2}$ of the simple cubic cell parameters and space group *Pcmn* is generally regarded as being the correct one (Megaw, 1954; Coughanour *et al.*, 1955; Kay & Bailey, 1957; Roth, 1957, etc.).

Since efforts to find an untwinned crystal suitable for single-crystal *x*-ray diffraction analysis were unsuccessful, no independent determination of the crystallographic symmetry could be made. However, the indexed powder pattern data are consistent with the orthorhombic space group *Pcmn.* The space group *Cmmm* proposed by Perrault (1960) does not appear to be acceptable, because several reflections forbidden by this space group are present in the powder pattern (in a personal communication dated February 13, 1963, Perrault stated that his space group determination had been made on a twinned crystal and that for this reason, he considered his results to be open to doubt). No evidence was found for a multiple unit cell, such as reported by Wood *et al.* (1962) for compounds in the $NaNbO_3$–$KNbO_3$ series.

The unit-cell parameters calculated from the powder pattern are $a = 5.448$, $b = 7.777$ and $c = 5.553$ Å. The *d*-values calculated from these cell parameters are in good agreement with the measured values.

CHEMICAL COMPOSITION

Chemical Analysis

The results of chemical and spectrographic analyses of the niobian perovskite A-1 are shown in Table 2.

TABLE 2. CHEMICAL AND SPECTROGRAPHIC ANALYSES OF NIOBIAN PEROVSKITE NO. A-1

Chemical analysis (1)		Semi-quantitative spectrographic analysis for trace constituents (2)	
CaO	25.95%	Ce	1.5%
Na_2O	4.03	La	0.3
Rare earth oxides	2.03	Zr	0.3
K_2O	0.03	Sr	0.2
Nb_2O_5	43.90	Y	0.1
TiO_2	10.05	Al	0.09
*Fe_2O_3	8.74	Ni	0.04
MgO	2.20	Gd	0.03
MnO	0.77	V	0.03
SiO_2	0.45	Dy	0.01
S	0.90	Yb	0.01
L.O.I. (less S)	0.65		
	99.70%		

*All the iron determined as Fe_2O_3.

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(2) ANALYST: Miss E. M. Kranck, Analytical Chemistry Subdivision.

The niobium content of this perovskite is unusually high. The titanium content is correspondingly low, as would be expected from a substitution of titanium by niobium. The iron content is also unusually high for perovskite. The Ta_2O_5 content was too low to be determined by wet chemical methods, but *x*-ray spectrographic analysis indicates that there is a minor amount present, estimated at between 0.1 and 0.5 per cent.

The chemical formula for the niobian perovskite, calculated from the analysis shown in Table 2, is: $(Ca_{0.75}Na_{0.21}R.E._{0.02})$-$(Nb_{0.54}Ti_{0.21}Fe_{0.16}Mg_{0.08}Mn_{0.02})O_{3.00}$ or, totalling the values within the brackets, $(Ca, etc.)_{0.98}(Nb, etc.)_{1.01}O_{3.00}$. In the calculations, the silica, sulphur and loss on ignition (L.O.I.) were excluded (as well as the corresponding amounts of CaO, MgO and Fe_2O_3), on the assumption that all the silica and sulphur are due to diopside and pyrite contamination.

The formula for the niobian perovskite, which can be generalized to $A_{0.98}B_{1.01}O_3$, is very close to that of perovskite, $CaTiO_3$, with the exception that most of the titanium has been replaced by niobium and iron, and that some of the calcium has been replaced by sodium.

The specific gravity calculated from the chemical analysis and the unit-cell parameters is 4.457. This agrees fairly well with the measured specific gravity of 4.40.

Variation in Niobium Content

Niobium analyses of the other perovskite samples show that there is a considerable variation in niobium content (Table 3). Variation in niobium content can be correlated, in a general way, with the unit-cell volume. This relationship is shown graphically in Fig. 4. Several points taken from the literature are also marked on the graph, namely, those established by Kay & Bailey (1957) for pure $CaTiO_3$, and by Perrault (1960) for two perovskites from the Oka district of Quebec (Perrault's *b*-parameters have been doubled to bring his unit cells into conformity with the unit cell used throughout this paper).

The points in Fig. 4 are scattered about a straight line drawn from the

TABLE 3. RELATIONSHIP BETWEEN UNIT-CELL PARAMETERS AND Nb_2O_5 CONTENT OF NIOBIAN PEROVSKITE

Sample No.	Nb_2O_5 Wt %	Unit-Cell Parameters (Å) *a*	*b*	*c*	Unit-Cell Volume (Å^3)
233	14.5	5.417	7.718	5.498	229.9
254	25.3	5.416	7.721	5.503	230.1
249	32.0	5.432	7.745	5.523	232.3
447	32.8	5.429	7.730	5.504	231.0
650	36.8	5.424	7.728	5.505	230.7
396	43.0	5.449	7.774	5.543	234.8
A-1	43.9	5.448	7.777	5.553	235.3
393	44.9	5.448	7.775	5.548	235.0

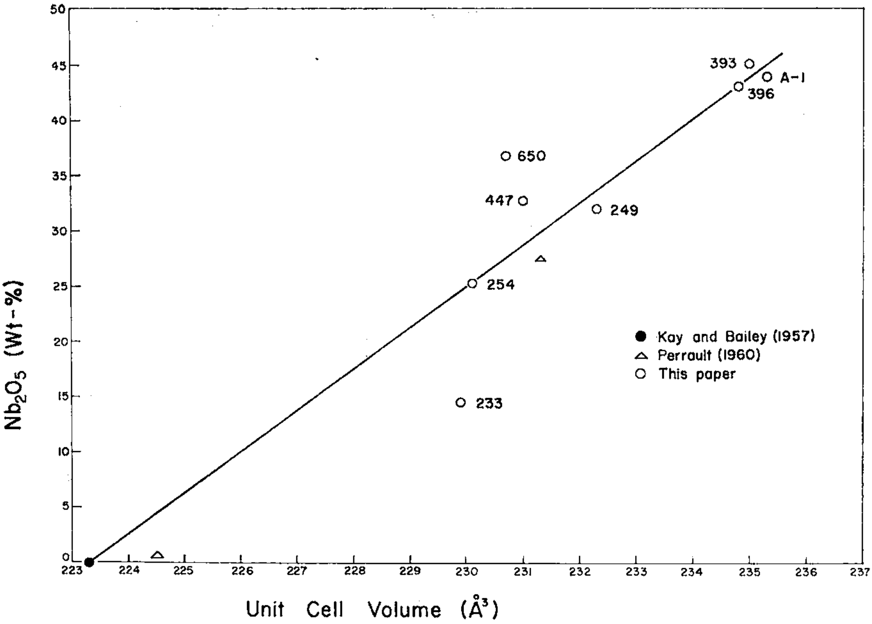

FIG. 4. Relationship between Nb_2O_5 content and unit-cell volume in niobian perovskite.

cell volume of $CaTiO_3$ to that of the perovskites with the highest niobium contents. Two of the points (233 and 650) are considerably displaced from the line. This is probably the result of compositional differences other than the simple replacement of titanium by niobium. Replacement of calcium by substantial amounts of rare earths, for example, could be expected to affect the size of the unit cell (Frank-Kamenetskii & Vesel'skii, 1961). There is a sufficient degree of correlation between niobium content and size of unit cell, however, to show fairly conclusively that substitution of titanium by niobium increases the parameters of the perovskite unit cell. A similar relationship has been noted by a number of authors, including Barth (1925), Murdoch (1951) and Ginzburg *et al.* (1958).

DISCUSSION

Perovskite-type compounds have received a considerable amount of attention in recent years, and many compounds with the perovskite or modified perovskite structure are known. A comprehensive review of this class of compounds has been given by Roth (1957).

The simplest perovskite structure is cubic, with one ABX_3 formula per unit cell, but only a very few binary oxides with this simple cell are known, perovskite itself being excluded. Many compounds are orthorhombic, with the unit cell proposed by Kay & Bailey (1957) and given here for the niobian perovskite. Some compounds give evidence of superstructures, resulting in unit cells that are multiples of this (Vousden, 1951; Wood *et al.* 1962; Galasso & Darby, 1962). Others have modified perovskite structures with tetragonal or rhombohedral symmetries (Roth, 1957).

Since the relationship between structural type and size of the constituent ions in perovskite was first noted by V. M. Goldschmidt (1926), a number of classifications have been proposed (Wood, 1951; Keith & Roy, 1954; Roth, 1957). These classifications are all based primarily on the size ratio of the A and B ions. The radii of the constituent ions of perovskite, niobian perovskite, and other naturally occurring perovskites, discussed in this paper, are such that they should all fall within the orthorhombic category. This has been shown to be the case for perovskite (Kay & Bailey, 1957, and others), $NaNbO_3$ (Vousden, 1951), and for niobian perovskite (this paper). Insufficient x-ray diffraction data have been published for other naturally occurring perovskites to draw any definite conclusions, but no convincing evidence to the contrary has been presented. Until such evidence is found, it must be assumed that naturally occurring perovskites belong to the orthorhombic group of perovskites.

A variety of names based on compositional differences has been given to naturally occurring perovskites. A tabulation of these minerals, with their compositions expressed in numbers of atoms per ABO_3 formula, is presented in Table 4. In calculating the atomic proportions, SiO_2 and H_2O have been disregarded on the assumption that they are attributable to impurities, and all the rare earths have been calculated as cerium. The atomic proportions are all calculated on the basis of three oxygen atoms per formula.

Table 4 shows that there are wide compositional differences in naturally occurring perovskites. The A position in ABO_3 can apparently be occupied by calcium, sodium, or rare earth elements; the B position, chiefly by titanium or niobium. Other elements occur in smaller amounts. The departure from stoichiometry is also noteworthy. In practically all cases, the total A atoms are less than one and the total B atoms greater than one, which suggests that a certain proportion of the B atoms probably occupy A structural sites. Furthermore the number of A and B atoms taken together are generally less than two, the number required by the perovskite formula ABO_3. This indicates that not all the possible cation sites in the perovskite structure are necessarily filled.

This variation in composition and deviation from stoichiometry

TABLE 4. NOMENCLATURE AND COMPOSITION OF NATURALLY-OCCURRING PEROVSKITES

	Perovskite (Theoretical Composition)	Knopite (Holmquist, 1894)	Niobian Perovskite A-1 (This paper)	Dysanalyte (Knop, 1877)	Loparite (Kuznetsov, 1925)	Irinite (Borodin and Kazakova, 1957)	Niobolparite (Tikhonenkov and Kazakova, 1957)	Lueshite (Safiannikoff, 1959)	
Ca	1.00	0.68	0.75	0.52	0.15	0.06	0.04	0.02	
Na	—	0.01	0.21	0.17	0.46	0.35	0.58	0.64	
K	—	0.02	—	—	0.02	—	0.03	—	*A*
Ce*	—	0.05	0.02	0.05	0.35	0.25	0.27	—	
Th	—	—	—	—	—	0.08	0.01	—	
Ti	1.00	1.04	0.21	0.76	1.04	1.00	0.68	0.07	
Nb	—	—	0.54	0.26	—	0.08	0.34	0.98	
Fe	—	0.06	0.16	0.11	—	0.02	0.02	0.03	*B*
Mg	—	0.01	0.08	—	—	—	0.01	0.02	
Mn	—	0.01	0.02	0.01	—	—	—	—	
Zr	—	0.01	—	—	—	—	—	—	
O	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	
Total *A* Ions	1.00	0.76	0.98	0.74	0.98	0.74	0.92	0.66	
Total *B* Ions	1.00	1.13	1.01	1.14	1.04	1.10	1.05	1.10	

*All rare earths calculated as Ce.

presents difficulties in any strict scheme of classification. Until now new names have been given to compositional variants without compositional limits having been defined, and without the minerals having been placed within any systematic classification.

Ginzburg *et al.* (1958) have attempted to classify perovskite minerals on the basis of their niobium contents. They state that the varieties high in niobium are isometric with a substantial deficit in the *A* position, while the titanium varieties are pseudo-isometric and have a more nearly stoichiometric composition. However, no *x*-ray data are given to confirm the distinction between isometric and pseudo-isometric types, and furthermore, there are a number of inconsistencies in their grouping. Loparite is listed as being isometric, yet no niobium was reported in the original analysis of this mineral. Dysanalyte is given as pseudo-isometric, although it contains a substantial amount of niobium. Lueshite, which contains the highest niobium content of any perovskite-type mineral, is definitely orthorhombic (Safiannikoff, 1959), not isometric as required by the Ginzburg classification.

A more suitable classification is one based on the net valency of the cations in the *A* position. Since these cations are generally mono-, di-, or trivalent, compositions can be plotted on a ternary diagram. Figure 5 shows the perovskites of Table 4 plotted in this way. Cation deficiencies have had to be ignored, and the coordinates of the plotted points consequently represent percentages of the total cations in the *A* position, and not of the total number of possible sites.

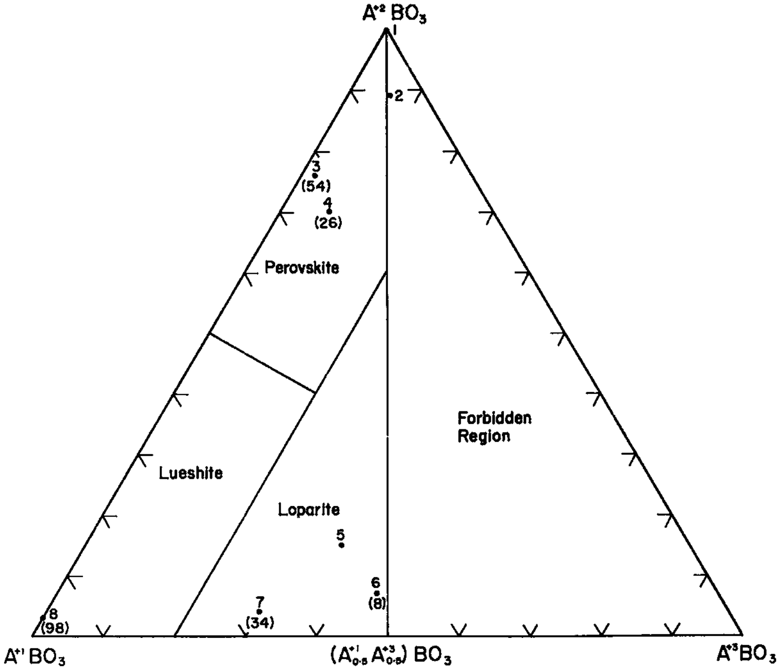

FIG. 5. Composition diagram (in atomic per cent) of perovskite minerals: 1—perovskite; 2—knopite; 3—niobian perovskite; 4—dysanalyte; 5—loparite; 6—irinite; 7—nioboloparite; 8—lueshite. Niobium contents (in atomic per cent) are indicate in brackets.

Variations in occupancy of the *B* position would have to be shown in the third dimension. Replacement of titanium by niobium could be shown on a tetrahedral figure or on a triangular prism, with niobium content perpendicular to the plane of the paper. Rather than cope with the difficulties of portraying such a figure in two dimensions, the niobium content (in atomic per cent) is indicated in brackets in Fig. 5. These values can be visualized as distances above the plane of the paper.

From Fig. 5 it is seen that the points tend to fall into three separate regions, one near the divalent corner (perovskite), one near the monovalent corner (lueshite) and one in the region $A_{0.5}^{+1}B_{0.5}^{+3}$ (loparite). This immediately suggests both a classification and a systematic nomenclature. The boundary between lueshite and perovskite has been drawn along the line $A^{+1}:A^{+2} = 1:1$. The boundary between loparite and the other two groups has been drawn rather arbitrarily at an A^{+3} content of 20 atomic per cent.

To reduce the proliferation of names given to perovskite variants, it is suggested that only these three names, with modifiers, if necessary, be used in reference to naturally occurring perovskites. If this suggestion is followed, the names knopite and irinite would be dropped, to be replaced by perovskite and loparite, respectively (Fleischer, 1955 has already stated that the name irinite is unnecessary). Dysanalyte would be "niobian perovskite." Other perovskite-type minerals described in the future could be fitted into this classification scheme, perhaps with modifications or extensions, as required.

The name lueshite presents a difficulty if the use of modifiers is strictly adhered to, since it is a sodium niobate by definition (Safiannikoff, 1959), and therefore the name "niobian lueshite" would be redundant. However, it is most unlikely that a sodium titanate with the perovskite structure will ever be found, since this would require an A cation deficiency of 50 per cent. Consequently, the name lueshite can safely be retained for sodium niobate, as originally proposed.

A portion of Fig. 5 is labelled "forbidden region" because of electrostatic requirements. In the perovskite formula ($Ca^{+2}Ti^{+4}O_3^{-2}$) there is a total positive charge of 6 to balance the negative oxygen charge of 6. When divalent calcium is replaced by monovalent sodium, the charge imbalance can be restored in several ways including replacement of the quadrivalent titanium by pentavalent niobium (as in lueshite), or by the replacement of some of the calcium by more highly-charged cations (as in loparite). These types of coupled replacement can be shown as follows:

$$Ca^{+2}Ti^{+4} \rightarrow Na^{+1}Nb^{+5}$$

or

$$Ca^{+2}Ti^{+4} \rightarrow (0.5\ Na^{+1}\ 0.5\ Ce^{+3})Ti^{+4}$$

Any compound in the "forbidden region" would have a net A valency greater than 2, which would require a B valency less than 4, making combinations with quadrivalent titanium or pentavalent niobium impossible, at least if all the sites are occupied. However, minerals could exist in the "forbidden region" if the net positive charge were reduced by cation vacancies or by a substitution of titanium by a less highly charged cation, such as iron or aluminum. Evidently the knopite, which occupies a position a short distance within the "forbidden region," does so because of a cation deficiency. Synthetic aluminates and ferrates of rare-earth elements are known (Roth, 1957), although no naturally-occurring varieties have yet been found.

Points close to the A^{+2}–$(A_{0.5}{}^{+1}A_{0.5}{}^{+3})$ join would not be expected to show substitution of titanium by niobium. On moving toward the A^{+1} corner, progressively greater substitution of titanium by niobium to balance the decreasing charge of the A ion would be expected. In a general way, this is the case, as shown by the niobium values in Fig. 5. A strictly systematic relationship does not exist because of partial substitution of other ions (notably iron), and by deviation from stoichiometry.

It is not yet clear whether there is a complete solid solution among the minerals shown in Fig. 5. Fig. 6 shows 39 perovskite analyses from the literature plotted on the composition diagram. Most of the points in the large cluster near the $A^{+2}BO_3$ corner are from analyses of Kola peninsula perovskites (Frank-Kamenetskii & Vesel'skii, 1961). Most of the other analyses were taken from Dana's System, ed. 7, and from

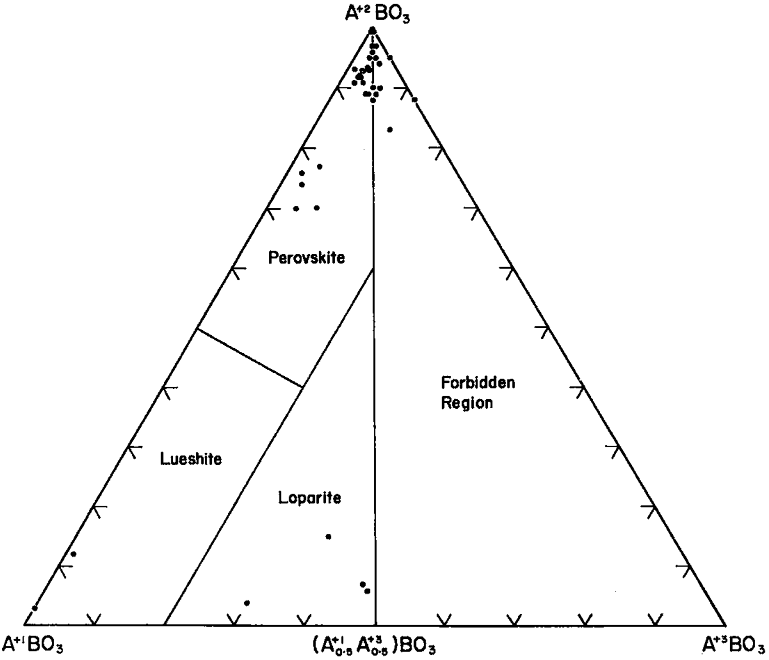

FIG. 6. Composition diagram (in atomic per cent) for 39 analysed perovskite minerals.

Murdoch (1951). The points in Fig. 6 fall into rather well-defined areas, with none in the central portion of the diagram. This suggests that there may be structural discontinuities separating the minerals in the different areas.

There are indications that some of the mineral variants are crystallographically distinct from $CaTiO_3$. Ginzburg *et al.* (1958) state that loparite and irinite are truly isometric, in contrast to perovskite, which is pseudo-isometric, although they provide no evidence to support this contention. Safiannikoff (1959) ascribes to lueshite, a unit cell twice the size of the perovskite cell (evidently following Vousden's usage), but his *x*-ray data can be interpreted equally well on the basis of the perovskite unit cell. Phase transitions have been found in synthetic perovskite-type compounds. Galasso & Darby (1962) found that cation ordering occurs in the *B* position when there is an appreciable difference in the ionic radii of the substituting ions. Wood *et al.* (1962) found three phases in the binary $NaNbO_3$–$KNbO_3$ system. Both types of phase transition result in orthorhombic unit cells that are multiples of the perovskite unit cell, and can be detected by the appearance of superstructure lines on *x*-ray diffraction photographs.

Further detailed work will be required to determine if and where phase transitions occur in naturally occurring minerals of the perovskite group. Although composition may be the determining factor, the effect of other variables, especially temperature of formation, cannot be ignored. It is hoped that the introduction of the tentative classification scheme presented here will stimulate a more intensive investigation of perovskite minerals.

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