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# STRONTIOWHITLOCKITE, $Sr_9Mg(PO_3OH)(PO_4)_6$, A NEW MINERAL SPECIES FROM THE KOVDOR DEPOSIT, KOLA PENINSULA, U.S.S.R.

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## ABSTRACT

Strontiowhitlockite, the Sr-dominant analog of whitlockite, occurs in the Kovdor deposit, Kola Peninsula, U.S.S.R., within cavities in a dolomite carbonatite vein that cross-cuts pyroxenite. Aggregates are pipe-like, with radial structure in cross-section, and are composed of rosettes of rounded crystals tabular on {001}, as much as 8 μm across. Associated minerals are dolomite, pyrite, collinsite and an unnamed Sr–Mg phospate. Strontiowhitlockite is dull white, transluscent, with a white streak. Cleavage is moderate on {001}. It is optically uniaxial (–), with ω 1.601(2), ε 1.598(2) for λ = 589 nm. By analogy with whitlockite, the mineral is hexagonal, *R*3*c*, with *a* 10.644(9), *c* 39.54(6) Å, *V* 3880 Å$^3$, *Z* = 6. The strongest five X-ray-powder diffraction lines [*d* in Å(I)(*hkl*)] are: 5.33(25)(110), 3.288(37)(0.0.12,214), 3.071(29)(030), 3.004(100)(0.2.10), 2.661(80)(220). Electron-microprobe analyses gave CaO 5.5, SrO 51.4, BaO 2.3, MgO 4.6, MnO 0.2, FeO 0.2, $P_2O_5$ 35.2, $H_2O$ 0.5 (by coulometry), total 99.9 wt.%. The ideal formula is $Sr_9Mg(PO_3OH)(PO_4)_6$. $D_m$ 3.64(2), $D_c$ 3.60 g/cm$^3$. The infrared-absorption spectrum includes the following bands: 1090, 1030, 955, 595, and 555 cm$^{-1}$.

*Keywords*: strontiowhitlockite, new mineral species, carbonatite, phosphate, whitlockite structure, Kovdor deposit, Kola Peninsula, U.S.S.R.

## SOMMAIRE

La strontiowhitlockite, analogue de la whitlockite avec le Sr comme cation dominant, a été découverte dans le gisement de Kovdor, situé dans la péninsule de Kola, U.R.S.S.; elle occupe des cavités d'un filon de carbonatite dolomitique qui recoupe une pyroxénite. Les agrégats de cristaux allongés montrent une texture transversale radiaire, et consistent de rosettes de cristaux arrondis aplatis sur {001}, et mesurant jusqu'à 8 μm en largeur. Lui sont associés dolomite, pyrite, collinsite et un phosphate de Sr–Mg sans nom. La strontiowhitlockite est blanc terne, translucide, avec une rayure blanche. Le clivage {001} est moyen. Elle est uniaxe négative, avec ω 1.601(2), ε 1.598(2) pour λ = 589 nm. Par analogie avec la whitlockite, c'est un minéral hexagonal, *R*3*c*, avec *a* 10.644(9), *c* 39.54(6) Å, *V* 3880 Å$^3$, *Z* = 6. Les cinq raies les plus intenses du cliché de diffraction [*d* en Å(I)(*hkl*)] sont 5.33(25)(110), 3.288(37)(0.0.12,214), 3.071(29)(030), 3.004(100)(0.2.10), et 2.661(80)(220). Les analyses à la microsonde électronique ont donné CaO 5.5, SrO 51.4, BaO 2.3, MgO 4.6, MnO 0.2, FeO 0.2, $P_2O_5$ 35.2, $H_2O$ 0.5 (par coulométrie), pour un total de 99.9% par poids. La formule idéale serait donc $Sr_9Mg(PO_3OH)(PO_4)_6$. Densité 3.64(2) mesurée, 3.60 calculée. Le spectre d'absorption infra-rouge montre des bandes à 1090, 1030, 955, 595 et 555 cm$^{-1}$.

(Traduit par la Rédaction)

*Mots-clés*: strontiowhitlockite, nouvelle espèce minérale, carbonatite, phosphate, structure de la whitlockite, gisement de Kovdor, péninsule de Kola, U.R.S.S.

## INTRODUCTION

Whitlockite was initially described by Frondel (1941) and was interpreted to be naturally occurring β-$Ca_3(PO_4)_2$ (Frondel 1943). Numerous investigations since then have been devoted to both β-$Ca_3(PO_4)_2$, its isostructural compounds, and whitlockite. Studies by Calvo & Gopal (1975), Schroeder *et al.* (1977) and Moore & Shen (1983) showed that whitlockite, ideally $Ca_9Mg(PO_3OH)(PO_4)_6$, differs from β-$Ca_3(PO_4)_2$. The mineral is related to a series of isotypic compounds with the general formula $A_9B(XO_3Y)(XO_3Y)_6(\square,OH,F)_3$, where cations of the *A* group are represented by $Ca^{2+}$, $REE^{3+}$, $Na^+$; the *B* group includes $Mg^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Al^{3+}$, *X* may be $P^{5+}$, $Si^{4+}$ or $Al^{3+}$, and *Y* represents $O^{2-}$, $OH^-$ or $F^-$. All of these isotypic compounds are synthetic. Cerite-(Ce), $Ce^{3+}{}_9Fe^{3+}(SiO_3OH)(SiO_4)_6(OH)_3$ (Moore & Shen 1983) is the only other mineral isostructural with whitlockite.

The new species, strontiowhitlockite, $Sr_9Mg(PO_3OH)(PO_4)_6$, is defined as the Sr-dominant (in the *A* group) analog of whitlockite. It was found in a specimen of dolomite carbonatite collected in the summer of 1985 from the Kovdor deposit, Kola Peninsula, U.S.S.R. Both the species and the name have been approved by the Commission on New Minerals and Mineral Names, I.M.A. The holotype specimen of strontiowhitlockite (1–2 mg of the mineral) is preserved in the Fersman Mineralogical Museum of the U.S.S.R. Academy of Sciences, Moscow (registration no. 558), and the grain mount used for microprobe analysis is on deposit in the Museum of Mines, Institute of Mines, Leningrad.

## OCCURRENCE

The Kovdor ultramafic alkaline complex, of Middle Paleozoic age (338–426 Ma), is located in the southwestern part of the Kola Peninsula, U.S.S.R. (67°35′N, 30°20′E), and is emplaced in Archean gneisses and granitic gneisses (1800–2000 Ma). The complex (40.5 km$^2$) is elliptical in shape and concentrically zoned (Kukharenko *et al.* 1965) from core to rim; dunites and "pyroxenized" and "phlogopitized" dunites in the core give way to jacupirangites and melteigites, melilite rocks, ijolites and other nepheline–pyroxene rocks, and an outside ring of fenites. The Kovdor magnetite–apatite–baddeleite deposit is located in the southwestern part of the complex; it is emplaced within contact of ijolites with fenites. In general, the igneous rocks exposed in the quarry (the Iron mine) are forsterite–magnetite (with apatite) ore-rocks and pyroxenites (jacupirangites). A variety of calcite–magnetite and dolomite–magnetite ores seem to be connected with a later, carbonatite stage of formation of the deposit. Accessory baddeleite is present in both forsterite–magnetite and carbonate-bearing ores.

Veins of carbonatite cross-cut rocks and ores, and are widespread throughout the deposit. The carbonatites can be divided into the following groups, based on mineralogical criteria (Krasnova & Kopylova 1988): calcite carbonatites with forsterite and phlogopite, calcite carbonatites with ferriphlogopite, dolomite carbonatites with zircon, and calcite–dolomite carbonatites with ilmenite. Dolomite carbonatites containing zircon are of pertinence here. There is hydrothermal phosphate mineralization after dolomite, including collinsite, bobierrite, vivianite (Kukharenko *et al.* 1965) and kovdorskite (Kapustin *et al.* 1981).

An interesting 60-m long vein of dolomite carbonatite that cross-cuts pyroxenites (jacupirangites) was exposed during mining operations in 1985 and includes numerous cm-size cavities involving phosphates, mainly carbonate fluorapatite as well as collinsite and bobierrite. Strontiowhitlockite (about 5–6 mg of the mineral) was found in a cavity 1 cm across in the central zone of the vein, in association with bud-like aggregates of strontian collinsite (6.3% SrO), octahedral crystals of pyrite and rhombohedra of dolomite. An unnamed Sr–Mg $CO_3$-bearing hydrous phosphate (hereafter referred to as Sr–Mg phosphate) is intimately intergrown with the strontiowhitlockite.

## PHYSICAL PROPERTIES

Strontiowhitlockite occurs as pipes and rose-like aggregates composed of rounded tabular crystals (Figs. 1, 2). Crystals as much as 5–8 μm across are flattened on {001}. Aggregates resembling pipes are the most interesting. At high magnification (Fig. 1b), the pipes, up to 2 mm long and 20 μm in diameter, show a radial structure, such that the [001] axis of each crystal is subparallel to the direction of pipe elongation. The inner channels of the pipes are occupied by "spindles" of the Sr–Mg phosphate, which exhibit a hexagonal cross-section.

Strontiowhitlockite is white with a dull luster, translucent, and has a white streak. The hardness cannot be measured accurately owing to small

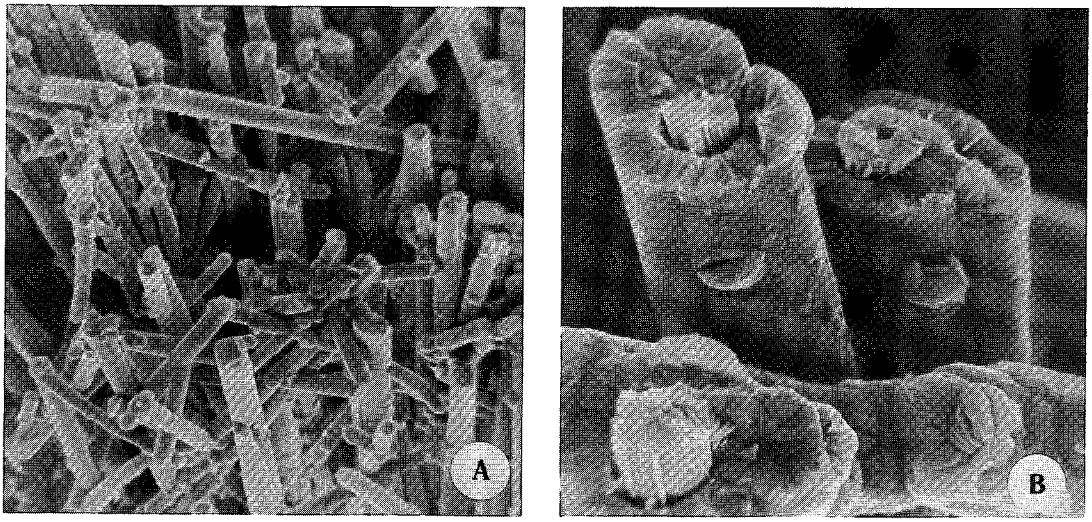

FIG. 1. Pipes composed of strontiowhitlockite with inner "spindles" composed of Sr–Mg phosphate. SEM image; width of field of view is 290 μm (A) and 40 μm (B).

crystal-size and composite nature. A moderate {001} cleavage (or parting) is present, and was observed by SEM. The measured density $D_m$ was determined by flotation of pipe fragments using a dilute Clerici - $H_2O$ solution, and found to be 3.64(2) g/cm$^3$; $D_c$ is 3.60 g/cm$^3$.

In immersion liquids, the mineral is colorless and nonpleochroic. The axial character cannot be observed directly because of small crystal-size, but pipes of the mineral show strong parallel extinction under crossed polarizers; the smaller index of refraction coincides with [001] of the crystals. If these data are taken into account along with the fact that the mineral is isostructural with whitlockite, strontiowhitlockite should be uniaxial (–), with a $\omega$ of 1.601(2) and a $\epsilon$ of 1.598(2) for $\lambda$ = 589 nm. Using the Gladstone–Dale constants (Mandarino 1979), the calculated index of compatibility is 0.012, indicating "superior" agreement of optical, physical and chemical data.

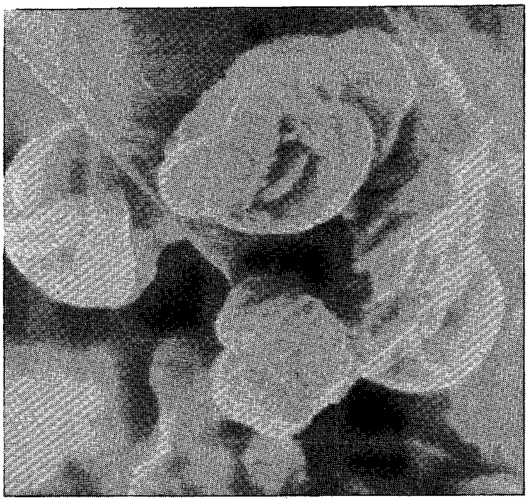

FIG. 2. Rose-like aggregates composed of strontiowhitlockite crystals. SEM image; width of field of view is 15 $\mu$m.

## CRYSTALLOGRAPHY

The strontiowhitlockite crystals are too small for single-crystal study, and only X-ray powder-diffraction techniques were used. Synthetic $\beta$-$(Sr_{2.57}Mg_{0.43})_{\Sigma 3.00}(PO_4)_2$ was prepared according to the method reported by Sarver *et al.* (1961) to compare its powder pattern with that of the mineral. Both patterns (Table 1) were obtained utilizing a DRON-2 diffractometer, 40 kV, 20 mA, 0.5°/s, with graphite-monochromatized Cu*K*$\alpha$ radiation. One extra reflection ($d$ = 2.930 Å, I = 25) attributable to Sr–Mg phosphate contamination was removed from the strontiowhitlockite pattern.

It can be seen that the powder pattern of the mineral is close to that of $\beta$-$(Sr_{2.57}Mg_{0.43})_{\Sigma 3.00}(PO_4)_2$; strontiowhitlockite is related to this compound in the same manner as are whitlockite and synthetic $\beta$-$Ca_3(PO_4)_2$ (Gopal & Calvo 1972).

Strontiowhitlockite is hexagonal, space group *R*3*c* by analogy with whitlockite (Calvo & Gopal 1975). The powder pattern was indexed based on initial cell-parameters of cerite-(Ce) (Moore & Shen 1983); subsequent least-squares refinement (POLYCRYSTAL program, Institute of Catalysis, Siberia Branch of the U.S.S.R. Academy of Sciences) gave *a* 10.644(9), *c* 39.54(6) Å, *V* 3880(10) Å$^3$ and $Z$ = 6. Similar calculations for $\beta$-$(Sr_{2.57}Mg_{0.43})_{\Sigma 3.00}(PO_4)_2$ yielded *a* 10.606(2), *c* 39.37(1) Å, *V* 3835(2) Å$^3$ and $Z$ = 21. The relationship between this compound and strontiowhitlockite is discussed below.

## CHEMICAL COMPOSITION

An aggregate of the mineral was mounted and polished for electron-microprobe analysis. Quantitative analyses of both strontiowhitlockite and Sr–Mg phosphate were performed on a CAMECA MS–46 instrument with wavelength-dispersion spectrometers, using the following standards: lorenzenite (for Na), diopside (Ca), celestine (Sr), barite (Ba), pyrope (Mg), synthetic $MnCO_3$ (Mn), hematite (Fe) and fluorapatite (P). Instrumental conditions were: 20 kV accelerating voltage (25 kV for Sr), 20 nA beam current, 5 $\mu$m spot size. Each analysis is averaged using 10 spots, 10-s counting time per spot, with 10 s spent counting the background. No other elements with atomic number greater than 11 were detected, and no Li, Be and B were found by means of a laser microprobe (Carl Zeiss LMA–1 instrument). The analytical data were corrected by use of an "in house" program, and the results are shown in Table 2. As seen from the table, the chemical composition of both aggregate types of strontiowhitlockite is only slightly different owing to the substitution of Ca for Sr.

The determination of water in the mineral and the interpretation of the data were complicated by the heterogeneous nature of the strontiowhitlockite aggregates. Using SEM images, the phase composition of aggregates was estimated to be as follows: ~ 80 vol.% of pipe-like aggregates, ~ 10 vol.% of rosette-like ones and ~ 10 vol.% of Sr–Mg phosphate "spindles". Water (total $H_2O$) was determined by microcoulometric moisture analysis on 0.85 mg of heterogeneous aggregate. Two discrete events of water loss are observed. The first, between 70 and 120°C, centered at 100°C (~ 1.5 wt.%), seems to represent loss of molecular $H_2O$ contained in the Sr–Mg phosphate. The second weight-loss event, 0.5 ± 0.2 wt.%, occurs between 410 and 570°C, with a maximum rate of dehydration at 500°C; it is inter-

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR STRONTIOWHITLOCKITE AND $\beta$-$(Sr_{2.57}Mg_{0.43})_{\Sigma 3}(PO_4)_2$

| | STRONTIOWHITLOCKITE | | | $\beta$-$(Sr_{2.57}Mg_{0.43})_{\Sigma 3}(PO_4)_2$ | | |
|---|---|---|---|---|---|---|
| hkl | $d_{calc}$ | $d_{obs}$ | $I/I_{obs}$ | $d_{calc}$ | $d_{obs}$ | $I/I_{obs}$ |
| 104 | 6.742 | | | 6.715 | 6.74 | 10 |
| 110 | 5.322 | 5.33 | 25 | 5.303 | 5.32 | 65 |
| 202 | 4.489 | 4.50 | 5 | 4.473 | 4.48 | 10 |
| 018 | 4.356 | 4.34 | 4 | 4.338 | 4.35 | 11 |
| 1.0.10 | 3.634 | 3.633 | 17 | 3.619 | 3.620 | 75 |
| 122 | 3.431 | 3.437 | 10 | 3.419 | 3.420 | 60 |
| 208 | 3.371 | | | 3.358 | 3.361 | 30 |
| 0.0.12 | 3.295 | 3.288 | 37 | 3.281 | 3.286 | 40 |
| 214 | 3.286 | | | 3.274 | | |
| 300 | 3.073 | 3.071 | 29 | 3.062 | 3.062 | 50 |
| 0.2.10 | 3.001 | 3.004 | 100 | 2.989 | 2.988 | 100 |
| 128 | 2.848 | 2.841 | 17 | 2.837 | 2.836 | 32 |
| 306 | 2.785 | | | 2.775 | 2.774 | 35 |
| 220 | 2.661 | 2.661 | 80 | 2.652 | 2.651 | 90 |
| 2.1.10 | 2.614 | | | 2.604 | 2.602 | 50 |
| 226 | 2.468 | 2.461 | 5 | 2.458 | 2.462 | 6 |
| 2.0.14 | 2.408 | | | 2.398 | 2.395 | 7 |
| 1.0.16 | 2.387 | | | 2.377 | 2.375 | 7 |
| 3.0.12 | 2.247 | 2.246 | 26 | 2.238 | 2.238 | 50 |
| 404 | 2.244 | | | 2.236 | | |
| 2.1.14 | 2.194 | | | 2.185 | 2.186 | 30 |
| 0.2.16 | 2.178 | 2.171 | 8 | 2.169 | | |
| 048 | 2.089 | 2.084 | 23 | 2.081 | 2.080 | 40 |
| 3.1.11 | 2.083 | | | 2.075 | | |
| 2.2.12 | 2.070 | | | 2.062 | 2.062 | 37 |
| 324 | 2.068 | | | 2.061 | | |
| 1.1.18 | 2.031 | 2.034 | 8 | 2.022 | | |
| 4.0.10 | 1.991 | 1.991 | 26 | 1.984 | 1.984 | 55 |
| 143 | 1.989 | | | 1.981 | | |
| 238 | 1.944 | 1.940 | 29 | 1.937 | 1.937 | 50 |
| 1.2.17 | 1.936 | | | 1.927 | | |
| 416 | 1.924 | 1.922 | 17 | 1.917 | 1.918 | 45 |
| | | 1.865 | 12 | | 1.858 | 40 |
| | | 1.829 | 22 | | 1.830 | 25 |
| | | | | | 1.809 | 55 |
| | | 1.783 | 36 | | 1.779 | 35 |
| | | 1.728 | 9 | | 1.721 | 15 |
| | | | | | 1.710 | 18 |
| | | | | | 1.664 | 5 |
| | | 1.632 | 11 | | | |
| | | 1.608 | 10 | | 1.600 | 27 |
| | | 1.594 | 14 | | 1.589 | 35 |
| | | | | | 1.557 | 4 |
| | | 1.536 | 12 | | 1.532 | 5 |
| | | 1.503 | 8 | | | |
| | | 1.495 | 7 | | 1.494 | 9 |
| | | | | + 14 lines to $d$ = 1.176 | | |

TABLE 2. CHEMICAL COMPOSITION OF STRONTIOWHITLOCKITE AND THE Sr-Mg PHOSPHATE

| | | 1 | 2 | 3 |
|---|---|---|---|---|
| $Na_2O$ | wt.% | 0.0 | 0.2 | 0.0 |
| CaO | | 5.5 | 1.1 | 4.7 |
| SrO | | 51.4 | 58.0 | 47.5 |
| BaO | | 2.3 | 2.4 | 2.0 |
| MgO | | 4.6 | 4.4 | 3.0 |
| MnO | | 0.2 | 0.1 | 0.1 |
| FeO | | 0.2 | 0.2 | 0.3 |
| $P_2O_5$ | | 35.2 | 34.4 | 31.6 |
| $H_2O$ | | 0.5 | 0.6* | 10.8** |
| TOTAL | | 99.9 | 101.4 | 100.0 |

* Calculated assuming atomic ratio P:H = 7:1

** By difference, including $H_2O$ and $CO_2$ as well

1. Strontiowhitlockite, pipe aggregate
2. Strontiowhitlockite, rose-like
3. Sr-Mg phosphate, "spindles"

preted as resulting from decomposition of the $(PO_3OH)^{2-}$ group present in strontiowhitlockite. This temperature is lower than that for both natural and synthetic whitlockites, 700 and 1000°C, respectively (Gopal *et al.* 1974), but this may be due to the lower thermal stability of the strontiowhitlockite structure.

As noted above, pipe-like aggregates of strontiowhitlockite are predominant; consequently, all the high-temperature water, 0.5 wt.%, is added to the total of analysis 1.

## DISCUSSION OF THE FORMULA

Strontiowhitlockite is ascribed to whitlockite-like compounds mainly on the basis of X-ray powder data. In our usage, the term "whitlockite-like compounds" involves isostructures of both whitlockite (Calvo & Gopal 1975, Moore & Shen 1983) and $\beta$-$Ca_3(PO_4)_2$ (Sarver *et al.* 1961, Dickens *et al.* 1974, Schroeder *et al.* 1977); all are derived from the $\alpha$-$Ba_3(PO_4)_2$ structure type. The crystal structure of $\alpha$-$Ba_3(PO_4)_2$ was solved by Zachariasen (1948). It is composed solely of transitionally equivalent interconnected rods (chains) consisting of $PO_4$ tetrahedra and $BaO_x$ polyhedra. There are two distinct barium sites, Ba(I) and Ba(II). The Ba atom occupying the Ba(I) site coordinates to six nearby oxygen atoms [distorted $Ba(I)O_6$-octahedron] and six more distant oxygen atoms; therefore Ba(I) has in total a 12-fold coordination. The Ba atom occupying the Ba(II) site has 10-fold coordination. Every third Ba site in the structure is Ba(I), the remaining sites being Ba(II). The simplest repeat-unit along a chain is $PO_4$-Ba(II)-Ba(I)-Ba(II)-$PO_4$.

A particular feature of this structure type is the instability produced because of a reduction of the cation radius (Gopal & Calvo 1973, Dickens *et al.* 1974), and because orthophosphates of divalent cations of radius smaller than that of $Sr^{2+}$ do not adopt the $\alpha$-$BaFe_3(PO_4)_2$ structure, but rather are derivative structures. In the case of $\beta$-$Ca_3(PO_4)_2$, there is the loss of one in every eight formula units per cell, in comparison with the "ideal" $\alpha$-$Ba_3(PO_4)_2$ type; the remaining seven units are distributed in a nonrandom way. The structure of $\beta$-$Ca_3(PO_4)_2$ thus contains a vacancy.

The crystal structure of whitlockite, $Ca_9Mg(PO_3OH)(PO_4)_6$ and cerite-(Ce), $REE_9Fe^{3+}(SiO_3OH)(SiO_4)_6(OH)_3$, are composed of rods (chains) of two distinct types (Calvo & Gopal 1975, Moore & Shen 1983). The repeat unit of rod II is quite identical in both structures and like that in $\alpha$-$Ba_3(PO_4)_2$; rod II is ordered and filled. However, the composition of rod I is different in whitlockite and cerite-(Ce). In the structure of whitlockite, rod I is composed of randomly distributed $MgCa_{1/2}(PO_4)_2$ and $MgH_2(PO_4)_2$ groups. As far as cerite-(Ce) is concerned, there are $Fe^{3+}(SiO_3OH)(OH)_3$ groups distributed along rod I in a nonrandom way. Empty sites exist along rod I in both whitlockite and cerite-(Ce) structures. The ratio of rod I to rod II is 1:3.

Crystallographic data for whitlockite and $\beta$-$Ca_3(PO_4)_2$ are quite similar: both compounds possess $R3c$ symmetry and have a hexagonal unit-cell containing 42 $PO_4$ groups, consisting of 6 formula units of whitlockite or 21 formula units of $Ca_3(PO_4)_2$; they are not distinguishable by an ordinary X-ray powder-diffraction study (Frondel 1943). As to our case, a structure solution for strontiowhitlockite is not possible because of the small grain-size, and consequently the question exists as to whether the formula for whitlockite or that of $Ca_3(PO_4)_2$ is correct. As reported by Gopal & Calvo (1972), careful powder diffractometry may be used to distinguish whitlockite from $\beta$-$Ca_3(PO_4)_2$, but it is inapplicable in our case, because a Sr-analog of $\beta$-$Ca_3(PO_4)_2$ is known (Sarver *et al.* 1961), but an Sr-analog of whitlockite is not. Thus, an X-ray powder-diffraction study does not solve the problem.

If the chemical composition is considered, the microcoulometry shows the presence of high-temperature water (interpreted as hydrophosphate) in strontiowhitlockite. Since the hydrogen is shown to be an essential constituent of the whitlockite structure but not of $\beta$-$Ca_3(PO_4)_2$ (Gopal & Calvo 1972), then the whitlockite-type formula is accepted for strontiowhitlockite, requiring seven P atoms (or a total of 28 oxygen atoms) per formula unit.

The empirical formula of strontiowhitlockite (anal. 1, Table 2) calculated on the basis of 28 atoms of oxygen, is: $(Sr_{6.96}Ca_{1.38}Ba_{0.21}Mg_{1.60}Mn^{2+}_{0.04}Fe^{2+}_{0.04})_{\Sigma 10.23}H_{0.78}P_{6.96}O_{28.00}$. The sum of (Mg,Mn,Fe) is 1.68, and this is substantially greater than 1.00 for ideal whitlockite. There is a similar situation for cerite-(Ce) from the rare-earth deposit at Mountain Pass, California (Glass *et al.* 1958), where calculation based on seven Si atoms yields 1.55 octahedral cations per formula. Moore & Shen (1983), who refined the structure of cerite-(Ce) from Mountain Pass, suggested that the discordance was a result of either the presence of impurities (the natural material was analyzed by the wet-chemical method) or additional structural sites occupied by octahedral cations (mainly $Fe^{3+}$). In the case of strontiowhitlockite, contamination by impurities is unlikely because the mineral was analyzed using an electron microprobe. However, the second possibility may apply to strontiowhitlockite. Additional octahedral cations may be introduced into vacant sites along rod I. Nevertheless, other suggestions could be proposed about the excess of octahedral cations. Of these, the first is the possible insertion of Mg into Sr sites, in fact, substitution of Mg for Sr. This is an unusual supposition because of an incompatibility in the crystal chemistry of $Sr^{2+}$ and $Mg^{2+}$. However, similar insertion of Mg into Ca sites is known and was studied by Schroeder *et al.* (1977), who refined the crystal structure of Mg-containing $\beta$-$Ca_3(PO_4)_2$. $\beta$-$(Sr,Mg)_3(PO_4)_2$ whitlockite-like compounds also are known (Sarver *et al.* 1961), but no structure determination was carried out. It is interesting that pure $Sr_3(PO_4)_2$ under normal conditions is an $\alpha$-polymorph, isostructural with $\alpha$-$Ba_3(PO_4)_2$ (Zachariasen 1948); $\beta$-$Sr_3(PO_4)_2$ is stable only above 1300°C (Sarver *et al.* 1961). In order for $\beta$-$Sr_3(PO_4)_2$ to stabilize under normal conditions, there must be substitution of cations of small ionic radius (*e.g.*, Mg) for Sr. This is an essential requirement for $Sr_3(PO_4)_2$ to exist in the whitlockite-like $\beta$-modification (Sarver *et al.* 1961).

Because strontiowhitlockite and cerite-(Ce) are isostructural with whitlockite and are close to the $\beta$-$Ca_3(PO_4)_2$ structure type, it could be expected that substitution Mg for Sr and of $Fe^{3+}$ for $Ce^{3+}$, respectively, may occur. However, one more explanation exists for excess Mg and Fe. The crystals may consist of domains of two different but related structure-types. Relevant to this proposal, an interesting observation was made by Sarver *et al.* (1961) on the $\beta$-$(Sr,Mg)_3(PO_4)_2$ compounds. The intensities of X-ray reflections on powder patterns decrease very markedly as Mg content is increased, and the compounds containing 20 to 30 mole % of $Mg_3(PO_4)_2$ have only diffuse powder-diffraction patterns. The authors suggested that this can be attributed to the difference between the X-ray scattering factors of $Mg^{2+}$ and $Sr^{2+}$. But this could also be attributed to a domain structure in the $\beta$-$(Sr,Mg)_3(PO_4)_2$ crystals.

As can be seen, it is not possible to give a simple explanation of excess octahedral cations in whitlockite-like compounds; future studies will reveal the correct explanation. For now, we have assumed the most likely pattern of substitution of Mg for Sr in strontiowhitlockite: $(Sr_{6.96}Ca_{1.38}Mg_{0.60}Ba_{0.21}Mn_{0.04}Fe_{0.04})_{\Sigma 9.23}Mg_{1.00}H_{0.78}P_{6.96}O_{28.00}$; the ideal formula of the mineral is thus $Sr_9Mg(PO_3OH)(PO_4)_6$.

## INFRARED-ABSORPTION SPECTROSCOPY

The infrared-absorption spectrum of strontiowhitlockite was obtained utilizing a UR–20 Carl Zeiss spectrophotometer. Spectra also were obtained on synthetic $\beta$-$(Sr_{2.57}Mg_{0.43})_{\Sigma 3.00}(PO_4)_2$ and natural whitlockite from the Tip Top pegmatite, Custer, South Dakota (Leningrad Mining Museum specimen number 1621/1). About 1 mg of each compound was ground and pressed into a KBr pellet, and the infrared-absorption spectrum was recorded over the region 400–3800 $cm^{-1}$ (Fig. 3).

The strong absorption bands within the region

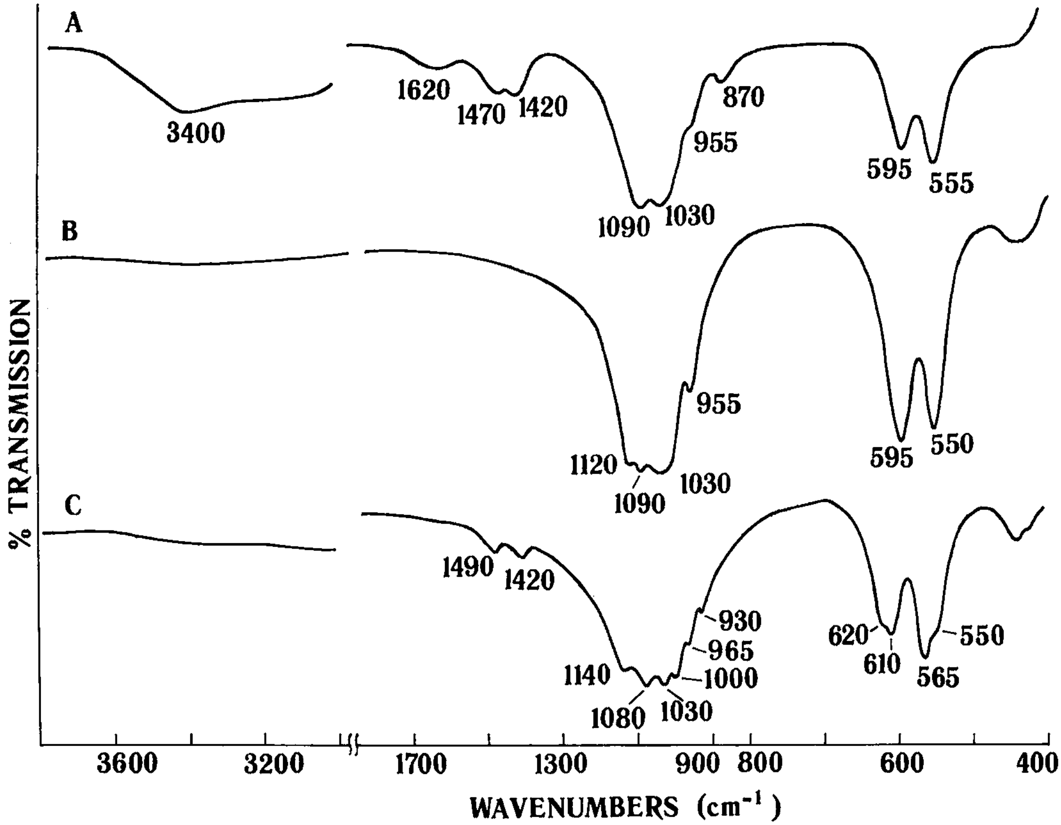

FIG. 3. Infrared-absorption spectra of strontiowhitlockite with 10% Sr-Mg phosphate impurity (A), synthetic β-$(Sr_{2.57}Mg_{0.43})_{\Sigma 3.00}(PO_4)_2$ (B) and whitlockite (C).

1140–930 cm$^{-1}$ are attributed to stretching modes of $PO_4^{3-}$ tetrahedra, and the absorption bands ranging from 620 to 550 cm$^{-1}$ are attributed to bending modes of $PO_4^{3-}$. It is to be noted that the strontiowhitlockite aggregate contains about 10 vol.% of Sr–Mg phosphate impurity. This would probably not affect the position and configuration of the absorption bands in the strontiowhitlockite spectrum. In general, the spectra of the mineral and β-$(Sr_{2.57}Mg_{0.43})_{\Sigma 3.00}(PO_4)_2$ are very similar, indicating the structural similarity of these compounds. However, the spectrum of strontiowhitlockite includes a weak additional band attributed to $CO_3^{2-}$ anions (1470, 1420 and 870 cm$^{-1}$) and bonded water (3400 and 1620 cm$^{-1}$). These constituents cannot be essential in the mineral because the analytical total is about 100 wt.% (anal. 1, Table 2). Thus, we believe that $CO_2$ and $H_2O$ can be attributed to the Sr–Mg phosphate.

The spectrum of whitlockite also is similar to the spectra of Sr-dominant compounds, but there is a more obvious multiple splitting of the bands. This could mean either the perfection of whitlockite crystals, compared with strontiowhitlockite and β-$(Sr_{2.57}Mg_{0.43})_{\Sigma 3.00}(PO_4)_2$ , or a difference in crystal symmetry among Sr- and Ca-dominant members; X-ray single crystals are required to answer this question. Some $CO_2$ contained in whitlockite is revealed by the 1490 and 1420 cm$^{-1}$ bands.

In conclusion, it will be noted that the absorption bands are affected by Ca-for-Sr substitution. It can be seen clearly with bending modes (620–550 cm$^{-1}$) that this compositional shift is about 10–15 cm$^{-1}$ among Sr and Ca end-members.

## SR–MG PHOSPHATE

The spindles of Sr–Mg phosphate are too thin (about 10 μm in diameter) and their quantity is too sparse for a proper study to be carried out. As far as the chemical composition is concerned (anal. 3, Table 2), the ratio of the cations may be represented as: $(Sr_{7.21}Ca_{1.32}Ba_{0.21})_{\Sigma 8.74}(Mg_{1.17}Fe_{0.07}Mn_{0.02})_{\Sigma 1.26}P_{7.00}$. This formula is much like that of the whitlockite structure-type. However, the low analytical total compared to that of strontiowhitlockite shows that these are distinct compounds. The sharp phase-boundary between the minerals (Fig. 1b) also provides evidence of this. It is possible that strontiowhitlockite and the Sr–Mg phosphate are closely related structurally.

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