Wagnerite with isokite from the Benson Mines, west-central Adirondack Highlands, New York

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Abstract

The rare fluophosphate minerals wagnerite, ideally Mg₂(PO₄)F, and isokite, ideally CaMg(PO₄)F, are intimately associated with magnetite-hematite deposits in sillimanite-, garnet-, and pyroxene-rich paragneisses and migmatites at the Benson Mines, near Star Lake in the west-central Adirondack Highlands of New York State. Coarsely crystalline wagnerite occurs in lenticular masses, typically 4 × 8 cm, delineated by sharply cross-cutting, sinuous, 2 cm-wide veins of fine-grained, fibrous to platy isokite and granular fluorapatite. These also penetrate transverse fractures across wagnerite lenses. Isokite formed from the introduction of Ca- and O-rich hydrothermal solutions into wagnerite. Both minerals are monoclinic: wagnerite crystallises in space group $P2_1/a$ with a = 11.945, b = 12.717, c =9.70 Å, $\beta = 108.18^\circ$, V = 1400.2 Å³, D(calc) = 3.291 g/cm³ for Z = 16; isokite crystallises in space group A2/a with a = 6.909, b = 8.746, c = 6.518 Å, $\beta = 112.20^\circ$, V = 364.7 Å³, D(calc) = 3.248 for Z =4. Optical properties for wagnerite are: $\alpha = 1.5845$, $\beta = 1.5875$, $\gamma = 1.6010$, $2V = 51^\circ$ (calc.) disp = r < v weak, absorption $\alpha < \beta > \gamma$ with $\alpha = col.$, $\beta =$ pale yel., $\gamma = v$. pale yel. For isokite only a mean index of refraction, n = 1.598, could be measured. Wet chemical analysis of wagnerite containing a calculated 11.4% of isokite as fine lamellae, gave the formula:

 $[Mg_{1.530}Fe_{0.199}^{2+}Ca_{0.111}Mn_{0.091}Fe_{0.034}^{3+}Al_{0.031}Na_{0.004}Ti_{0.001}]_{\Sigma 2.001}[P_{0.944}Al_{0.047}Si_{0.003}C_{0.006}]_{\Sigma 1.000}]_{\Sigma 2.001}[P_{0.944}Al_{0.047}Si_{0.003}C_{0.006}]_{\Sigma 2.001}[P_{0.944}Al_{0.047}Si_{0.003}C_{0.006}]_{\Sigma 2.001}[P_{0.944}Al_{0.047}Si_{0.003}C_{0.006}]_{\Sigma 2.000}]_{\Sigma 2.001}[P_{0.944}Al_{0.047}Si_{0.003}C_{0.006}]_{\Sigma 2.000}]_{\Sigma 2.001}[P_{0.944}Al_{0.047}Si_{0.047}Si_{0.047}C_{0.047}]_{\Sigma 2.001}[P_{0.944}Al_{0.047}Si_{0.047}C_{0.047}]_{\Sigma 2.001}[P_{0.944}Al_{0.047}Si_{0.047}C_{0.047}]_{\Sigma 2.001}[P_{0.944}Al_{0.047}Si_{0.047}C_{0.047}]_{\Sigma 2.001}[P_{0.944}Al_{0.047}Si_{0.047}C_{0.047}]_{\Sigma 2.001}[P_{0.944}Al_{0.047}Si_{0.047}C_{0.047}]_{\Sigma 2.001}[P_{0.944}Al_{0.047}Si_{0.047}C_{0.047}]_{\Sigma 2.001}[P_{0.944}Al_{0.047}Si_{0.047}C_{0.047}]_{\Sigma 2.001}[P_{0.944}Al_{0.047}Si_{0.047}C_{0.047}]_{\Sigma 2.001}[P_{0.947}C_{0.047}]_{\Sigma 2.001}[P_{0.947}C_{0.047}C_{0.047}]_{\Sigma 2.001}[P_{0.947}C_{0.047}C_{0.047}C_{0.047}]_{\Sigma 2.001}[P_{0.947}C_{0.047}$

 $[O_{3.965}(OH)_{0.035}]_{\Sigma 4.000}[F_{0.948}(OH)_{0.052}]_{\Sigma 1.000}.$

KEYWORDS: wagnerite, isokite, Benson mines, Adirondack Highlands, Grenville Province, New York.

Introduction and geologic setting

IN 1971 the senior author and the late Leo M. Hall collected several large rock specimens from the Benson Mines, near Star Lake, in the westcentral Adirondack Highlands, New York, where magnetite and hematite were mined from 1889 until the mid-1970s. Iron ores are associated with sillimanite-, garnet-, and pyroxene-rich paragneisses and migmatites, all of which are infolded in hornblende granitic and alaskitic orthogneisses that characterise this part of the Adirondack Highlands in the Grenville Province of Middle Proterozoic age. Associated with gneisses are fluorite-bearing granite pegmatite dikes and veins

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of diverse mineralogy that carry fluorite, calcite, quartz, malachite and other copper minerals. Buddington (1977), who favoured a hydrothermal origin for the ores, noted that the pegmatites are of two ages, older bodies that were regionally metamorphosed with the ore, and the gneisses and younger bodies that post-date the metamorphic rocks. Palmer (1970) considered that the ores were of sedimentary origin.

One large slab, roughly $15 \times 20 \times 30$ cm, collected at the surface of a pegmatite dike adjoining sillimanite-martite(hematite)-feldspar gneiss, contains the rare fluophosphate minerals wagnerite, Mg₂(PO₄)F (Coda *et al.*, 1967, Sheridan *et al.*, 1976) and isokite, CaMg(PO₄)F (Deans *et al.*, 1955, Fisher, 1957). Apparently monomineralic, vitreous, red-brown wagnerite occurs as typically 4×8 cm lenticular masses

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sharply cross-cut by 2 cm-wide veins of a finegrained, dark gray rock. A fracture lineation in the veins, parallel to their walls, transects prominent fractures developed across the short dimension of the wagnerite lenses (Fig. 1). Fibrous to short-prismatic plates and radial sprays of isokite are developed along vein contacts within fractured wagnerite. Fine-grained, granular fluorapatite is concentrated toward the vein interiors along with a small amount of hematite.

Chemical, optical and X-ray data

When optical, X-ray powder diffraction, and spectroscopic tests made in 1971 indicated that the lenticular masses were composed of the rare fluophosphate mineral wagnerite, a complete wet chemical analysis of the material was carried out in 1973 (Table 1). Allowing for minor substitutions, the atomic ratios show close correspondence with published data for wagnerite. Several extraneous reflections measured on the X-ray powder pattern, not accounted for by published data for wagnerite, were not identified and the

study was set aside. It was not resumed until after the retirement of the senior author in 1990, when a grain sample was sent to the U.S. Geological Survey for further X-ray study. There a Guinier-Hägg pattern was prepared, from which 69 reflections were measured. Of these, 53 indexed on the wagnerite lattice, 11 on the isokite cell, and 5 weak reflections remain unidentified. The patterns were made with Cr- $K\alpha_1$ radiation using Si powder (NIST SRM640a) as an internal standard. The wagnerite and isokite patterns were indexed with the aid of patterns calculated from the known crystal structures, as noted in Tables 2 and 3. The intensities were estimated from peak heights on densitometer traces made with a NONIUS Model II Microdensitometer. All these data are given in Table 3.

It was noted that the X-ray sample, although a mixture, appeared microscopically quite homogeneous, as did the material in the original 1971– 73 examination; therefore, further microscopic work was carried out. Study of both thin sections and grain immersion mounts revealed that very thin plates, radial sprays, and anhedral grains of



FIG. 1. Fractured wagnerite lenses (clear areas–Wg), transected by fine-grained veins carrying isokite (barred–Is) and fluorapatite (dotted–Ap). Large wagnerite lens is 4×8 cm.

| Oxides | wt.% | Atoms per 5[O, (OH), F] | | | | |
|--------------------------------|--------|-------------------------|-------|--|--|--|
| P ₂ O ₅ | 38.58 | P | 0.944 | | | |
| As ₂ O ₅ | 0.01 | As | 0.000 | | | |
| SiO ₂ | 0.10 | Si | 0.003 | | | |
| CO ₂ | 0.15 | С | 0.006 | | | |
| Al_2O_3 | 2.30 | Al^{IV} | 0.047 | | | |
| | | Al ^{VI} | 0.031 | | | |
| TiO ₂ | 0.03 | Ti | 0.001 | | | |
| Fe ₂ O ₃ | 1.59 | Fe ³⁺ | 0.034 | | | |
| FeO | 8.23 | Fe ²⁺ | 0.199 | | | |
| MnO | 3.70 | Mn | 0.091 | | | |
| MgO | 35.52 | Mg | 1.530 | | | |
| CaO | 3.59 | Ca | 0.111 | | | |
| Na ₂ O | 0.08 | Na | 0.004 | | | |
| K ₂ Ō | 0.01 | Κ | 0.000 | | | |
| H_2O | 0.45 | Н | 0.087 | | | |
| F | 10.36 | F | 0.948 | | | |
| Sum | 104.70 | | | | | |
| O = 2F | -4.36 | | | | | |
| Total | 100.34 | | | | | |

Table 1. Chemical analysis of wagnerite, specimen no. 71-JSL-2, Benson Mines, New York

Analyst: Shiro Imai, Japan Analytical Co. Formula:

 $\begin{matrix} [Mg_{1.530}Fe_{0.199}^{2+}Ca_{0.111}Mn_{0.091}Fe_{0.034}^{3+}Al_{0.031}Na_{0.004} \\ Ti_{0.001}]_{\Sigma_{2.001}}[P_{0.944}Al_{0.047}Si_{0.003}C_{0.006}]_{\Sigma_{1.000}}[O_{3.965} \\ (OH)_{0.035}]_{\Sigma_{4.000}}[F_{0.948}(OH)_{0.052}]_{\Sigma_{1.000}} \\ Ratios \end{matrix}$

 $\begin{array}{l} Mg/(Mg + Fe^{2+} + Mn + Fe^{3+}) = 0.825 \\ Mg: Fe^{2+}: Mn: Fe^{3+} = 0.825: 0.107: 0.050: 0.018 \end{array}$

another mineral, isokite, were enclosed and sporadically distributed in host wagnerite.

Because isokite has indices of refraction that overlap those of wagnerite, it is difficult to resolve in fine grains and thin plates. Much of the wagnerite also contains a maximum of one per cent of thin (<0.05 μ m), discontinuous lamellae of an unidentified phase with higher index of refraction, and low to negligible birefringence; it may be associated with the unidentified reflections in the X-ray powder pattern. A rare grain of wagnerite contains very small (<0.5 μ m), equidimensional inclusions of fluorite, and occasionally magnetite. Optical data for wagnerite and isokite are given in Table 4.

Wagnerite from the Benson Mines would contain 11.4% isokite if the 3.59 wt.% of CaO of the chemical analysis (Table 1) is contained entirely in this phase. Because wagnerites from Bodenmais (Propach, 1976) and from Santa Fe Mountain (Sheridan et al., 1976) contain 4.1 and 1.36 wt.% CaO respectively, not all of the CaO in the Benson Mines sample need reside in isokite. Microscopic examination suggests that 11.4% isokite impurity may be high, although reasonable in regard to the X-ray patterns. X-ray and optical data in Tables 2 and 4 allow calculation of specific refractivities, K, for wagnerite and isokite from the Gladstone and Dale equation (Table 5). K may also be calculated directly from the chemical analysis (Table 1) by summing the specific refractivity constants (Jaffe, 1988) in proportion to the weight percentages of the analytical components (Table 5). Because the kconstant for CaO is greater than that for either MgO, FeO, or MnO (Table 5), replacement of

| Mineral Formula Space group | Waa (Mg, F P | gnerite e) ₂ [PO ₄]F 2 ₁ /a | Isokite CaMg[PO4]F A2/a | | |
|-----------------------------------|----------------------|---|-------------------------------|--------------------------|--|
| Unit cell | Refined ^a | Werfen ^b | Refined ^c | N. Rhodesia ^d | |
| a, Å | 11.945(1) | 11.957(8) | 6.909(1) | 6.91 | |
| b, Å | 12.717(1) | 12.679(8) | 8.746(2) | 8.75 | |
| c, Å | 9.702(1) | 9.644(7) | 6.518(2) | 6.52 | |
| β, deg. | 108.18(1) | 108.3(2) | 112.20(2) | 112.1 | |
| V, Å ³ | 1400.2(2) | 1388.1 | 364.7(1) | 365.25 | |
| D (X-ray) | 3.291 | 3.135 | 3.248 | 3.247 | |

Table 2. Unit cells of wagnerite and isokite

^a Least squares analysis of 47 wagnerite lines from specimen 71-JSL-2, Benson Mines, New York (Table 3), from composite pattern of mixed wagnerite and isokite.

^b Parameters of Coda et al. (1967), material from Werfen, Austria.

^c Least squares analysis of 13 isokite lines (Table 3) from composite pattern of New York material. $\sigma(2\theta) = 0.036$ deg.

^d Parameters of Deans and McConnell (1955) from Weissenberg patterns of amterial from Northern Rhodesia. Standard setting, transformed from their cell by (101/010/100). Similar unit cell dimensions for wagnerite were obtained by Propach (1976) on material from Bodenmais (Bavarian Forest), by Novák and Povondra (1984) from pyrope-rich rock from Skřinářov, central Czechoslovakia, and by Irouschek and Armbruster (1984) on material associated with sillimanite gneiss from Tessin, Switzerland.

| | _ | W | i4 - a | | | | T1 | tob. | | | Obcomrad | |
|----------|---|----------------|---------|-----------|----------|--|----------|--------|----------------|---------------------|-----------------------|--------|
| h | ŀ | wagr | d(clc) | I(c c) | h | k | ISOK | d(c c) | <i>l</i> (clc) | d(obs) | Ubserveu ⁻ | 28 |
| <i>n</i> | ~ | l | | | <i>n</i> | ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~ | <i>i</i> | | | <i>u</i> (003) | 1(003) | |
| 0 | 2 | 1 | 5.234 | 12 | | | | | | 5.237 | 8 | 25.254 |
| -2 | 2 | 1 | 4.240 | 19 | | | | | | 4.236 | 11 | 31.356 |
| 0 | 3 | 1 | 3.851 | 7 | | | | | | 3.846 | 2 | 34.634 |
| 2 | 2 | 1 | 3.547 | 7 | | | | | | 3.547 | 11 | 37.658 |
| | | | | | | | | | | *3.527 ^d | 2 | 37.881 |
| 1 | 3 | 1 | 3.510 | 1 | | | | | | 3.509 | 5 | 38.075 |
| | | | | | 1 | 1 | 1 | 3.439 | 72 | 3.442 | 2 | 38.852 |
| 1 | 2 | 2 | 3.306 | 36 | | | | | | 3.307 | 53 | 40.509 |
| 3 | 2 | 0 | 3.251 | 16 | | | | | | 3.251 | 8 | 41.240 |
| | | | | | 2 | 0 | 0 | 3.198 | 29 | 3.199 | 10 | 41.937 |
| 0 | 4 | 0 | 3.180 | 1 | -2 | 2 | 2 | 3.176 | 5 | 3.178 | 15 | 42.234 |
| 2 | 0 | 2 | 3.131 | 57 | | | | | | 3.130 | 75 | 42.903 |
| -2 | 3 | 2 | 3.016 | 5 | 0 | 0 | 2 | 3.017 | 100 | 3.019 | 25 | 44.577 |
| 2 | 3 | 1 | 3.010 | 4 | - | - | _ | | | | | |
| -1 | 4 | 1 | 2.981 | 100 | | | | | | 2.982 | 100 | 45.148 |
| -4 | 0 | 2 | 2.844 | 71 | | | | | | 2.844 | 89 | 47.468 |
| 4 | 0 | 0 | 2.836 | 6 | | | | | | 2.839 | 2 | 47.503 |
| -2 | 2 | 3 | 2.818 | 11 | | | | | | 2.818 | 8 | 47.936 |
| | | | | | | | | | | *2.800 | 5 | 48.268 |
| | | | | | -2 | 0 | 2 | 2.781 | 31 | 2.781 | 5 | 48.616 |
| 2 | 4 | 0 | 2.774 | 7 | - | - | - | | | 2.775 | 11 | 46.736 |
| ō | 2 | 3 | 2.766 | 36 | | | | | | 2.766 | 28 | 48.896 |
| -4 | 2 | 1 | 2.703 | 16 | | | | | | 2,704 | 28 | 50.107 |
| - | _ | - | 20002 | | | | | | | *2.625 | 19 | 51,707 |
| 0 | 4 | 2 | 2 617 | 2 | | | | | | 2.615 | 4 | 51,919 |
| v | • | - | 2.017 | - | 2 | 2 | 0 | 2.582 | 44 | 2.582 | 11 | 52.650 |
| -2 | 4 | 2 | 2.555 | 3 | 2 | - | Ū | 2.002 | | 2.555 | 8 | 53.250 |
| -3 | 4 | 1 | 2 479 | 15 | | | | | | 2.480 | 14 | 54.992 |
| -2 | Ó | 4 | 2.414 | 7 | | | | | | 2.414 | 5 | 56.621 |
| ō | ě | 4 | 2.304 | 4 | | | | | | 2.305 | 5 | 59.575 |
| Ū | Ŷ | • | 2.501 | • | 1 | 3 | 1 | 2 2995 | 7 | 2 2995 | 11 | 59.718 |
| -1 | 2 | 4 | 2 2533 | 10 | • | 2 | | 2.2370 | | 2.2531 | 2 | 61.077 |
| -1 | 5 | 2 | 2 2502 | 2 | | | | | | 2.2512 | $\overline{2}$ | 61.134 |
| 2 | 4 | $\overline{2}$ | 2 2309 | 8 | | | | | | 2.2309 | 8 | 61.752 |
| ō | 5 | $\overline{2}$ | 2 2268 | š | | | | | | 2.2250 | 2 | 61.934 |
| · · | 2 | 2 | 2.2200 | Ũ | -2 | 3 | 1 | 2.2156 | 10 | 2.2158 | 11 | 62.222 |
| -5 | 2 | 2 | 2.2017 | 20 | - | U | - | | •• | 2.2014 | 14 | 62.671 |
| -3 | 2 | 4 | 2.1751 | 4 | | | | | | 2.1752 | 2 | 63.511 |
| č | - | • | 2.17.51 | • | | | | | | *2.1636 | $\overline{2}$ | 63.894 |
| -3 | 5 | 1 | 2.1401 | 1 | | | | | | 2.1369 | 2 | 64.791 |
| -4 | 4 | 2 | 2.1198 | 8 | | | | | | 2.1199 | 11 | 65.374 |
| 1 | 1 | 4 | 2.1029 | ĩ | | | | | | 2.1039 | 4 | 65,934 |
| 1 | 6 | Ó | 2.0835 | $\hat{4}$ | | | | | | / | | |
| 1 | 4 | 3 | 2.0828 | 10 | | | | | | 2.0827 | 17 | 66.694 |
| - | | - | | | 1 | 4 | 0 | 2.0691 | 16 | 2.0690 | 4 | 67.191 |
| 0 | 6 | 1 | 2.0646 | 10 | - | | • | | | 2.0658 | 17 | 67.311 |
| | - | | | | | | | | | *2.0391 | 5 | 68.311 |
| -2 | 6 | 1 | 1.9858 | 5 | | | | | | 1.9858 | 11 | 70.413 |
| -6 | 0 | 2 | 1.9802 | 5 | | | | | | 1.9801 | 5 | 70.647 |
| 2 | 0 | 4 | 1.9349 | 11 | | | | | | 1.9347 | 19 | 72.531 |
| -2 | 4 | 4 | 1.9224 | 4 | | | | | | 1.9217 | 11 | 73.133 |
| 2 | 6 | 1 | 1.8988 | 5 | | | | | | 1.8983 | 11 | 74.184 |
| 6 | 0 | 0 | 1.8914 | 7 | | | | | | 1.8917 | 11 | 74.504 |
| -6 | 2 | 1 | 1.8890 | 11 | | | | | | 1.8888 | 17 | 74.618 |
| 1 | 5 | 3 | 1.8693 | 1 | | | | | | 1.8795 | 2 | 75.475 |
| 0 | 4 | 4 | 1.8658 | 4 | | | | | | 1.8656 | 5 | 75.710 |
| -6 | 2 | 3 | 1.8172 | 3 | | | | | | 1.8171 | 5 | 78.104 |

 Table 3. Calculated X-ray powder data for wagnerite and isokite compared with observed data for specimen from Benson Mines, N.Y.

| | | Wagn | nerite ^a | | | | Isok | ite ^b | | | Observed | c |
|---------|---|------|---------------------|--------|----|---|------|------------------|--------|--------|----------|--------|
| h | k | 1 | d(clc) | I(clc) | h | k | l | d(clc) | I(clc) | d(obs) | I(obs) | 20 |
| 5 | 1 | 2 | 1.8047 | 2 | | | | | | 1.8050 | 2 | 78.732 |
| -5 | 4 | 3 | 1.7975 | 8 | | | | | | 1.7975 | 11 | 79.126 |
| -4 | 4 | 4 | 1.7788 | 4 | | | | | | 1.7783 | 8 | 80.149 |
| 0 | 2 | 5 | 1.7706 | 3 | | | | | | 1.7707 | 5 | 80.566 |
| -2 | 6 | 3 | 1.7574 | 3 | | | | | | | | |
| -4 | 2 | 5 | 1.7570 | 5 | | | | | | 1.7571 | 14 | 81.320 |
| 5 | 2 | 2 | 1.7526 | 2 | | | | | | 1.7524 | 5 | 81.584 |
| 0 | 6 | 3 | 1.7447 | 9 | | | | | | 1.7441 | 8 | 82.531 |
| 5 | 4 | 1 | 1.7287 | 7 | | | | | | | | |
| $^{-4}$ | 6 | 1 | 1.7284 | 11 | | | | | | 1.7281 | 25 | 82.983 |
| | | | | | 2 | 2 | 2 | 1.7197 | 22 | 1.7188 | 14 | 82.531 |
| | | | | | -2 | 4 | 2 | 1.7189 | 13 | | | |
| | | | | | -4 | 0 | 2 | 1.7043 | 16 | 1.7041 | 5 | 84.417 |
| 3 | 2 | 4 | 1.6795 | 16 | | | | | | 1.6790 | 22 | 85.977 |
| -5 | 5 | 3 | 1.548 | 1 | | | | | | 1.6552 | 8 | 87.525 |
| -3 | 7 | 1 | 1.6513 | 3 | | | | | | 1.6517 | 5 | 87.759 |
| 3 | 6 | 2 | 1.6322 | 2 | | | | | | 1.6325 | 2 | 89.062 |

Table 3-continued

^a Intensities calculated for wagnerite crystal structure of Coda *et al.* (1967), using refined unit cell of specimen no. 71-JSL-2 from Benson Mines, New York (footnote c).

^b Intensities calculated for titanite crystal structure of Taylor and Brown (1976), and chemistry of isokite (CaMgPO₄F), in refined unit cell of New York material (footnote c).

^c Measured *d*-spacings (A) obtained from a Guinier-Hägg pattern, made with Cr- $K\alpha_1$ radiation ($\lambda = 2.2897$ Å) and Si internal standard, of specimen 71-JSL-2 from Benson Mines, New York. Peak intensities measured with a Nonius Model II Microdensitometer. Refined unit cells for wagnerite and isokite are given in Table 2.

^d Reflections marked by an asterisk are not indexed by either wagnerite or isokite.

| | | T. 114 | | | |
|-------|-----------------------|---------------------------|---------------------|-----------------|--|
| - | New York ^a | Sante Fe Mt. ^b | Werfen ^c | N. Rhodesia | |
| α | 1.5845 | 1.565–1.571 | 1.5678 | 1.590 | |
| β | 1.5875 | 1.567-1.572 | 1.5719 | 1.595 | |
| γ | 1.6010 | 1.578-1.585 | 1.5824 | 1.615 | |
| ŻVγ | 51° (calc) | 28–33° | 28°; 64° (calc) | 52°; 54° (calc) | |
| Disp. | r < v weak | r > v weak | r > v | r > v | |

Table 4. Optical properties of wagnerite and isokite

^a This report; pleoch.: α col., β pale golden yel., γ v. pale yel.; abs. $\alpha < \beta > \gamma$, $\beta = b$, OAP (010); clvg. (010) impf., (100) impf. For enclosed isokite plates, mean n = 1.598.

⁶ Sheridan *et al.* (1976).

^c Hegemann and Steinmetz (1927).

^d Deans and McConnell (1955); $\alpha \Lambda c = 32^{\circ}$.

wagnerite by isokite, as postulated here, should result in an increase in specific refractivity. Data of Table 5 verify that the specific refractivity calculated from the chemical analysis, 0.1803, is slightly larger than that for wagnerite, 0.1796, and much smaller than that for isokite, 0.1841. If the *k*-values for wagnerite and isokite are proportioned in the ratio 88.6:11.4, the resulting K =0.1801 is close to that calculated from the chemical analysis and tends to verify X-ray estimates of the isokite impurity.

Paragenesis

We suggest the paragenetic sequence to be: (1) growth of large wagnerite masses in pegmatite followed by (2) deformation of the pegmatite with infolded gneisses and magnetite deposits during regional metamorphism, with development of lenses or augen of wagnerite, and (3) fracturing of wagnerite with pervasive introduction of hydrothermal Ca- and O-rich solutions resulting in the partial conversion of wagnerite to isokite in

| | | Wagnerite | Isokite |
|---|-------------------------------|-----------|---------|
| n | (mean) ^a | 1.591 | 1.598 |
| D | (X-ray) ^b | 3.291 | 3.248 |
| Κ | (meas.) ^c | 0.1796 | 0.1841 |
| K | (chem. analysis) ^d | 0.18 | 03 |
| Κ | (88.6:11.4) ^e | 0.18 | 01 |

Table 5. Specific refractivity data for wagnerite, isokite, and their mixture

^a $(\alpha + \beta + \gamma)/3$, from Table 4.

^b From Table 2.

^c Specific refractivity, from law of Gladstone and Dale, K = (n - 1)/D.

^d Specific refractivity calculated from chemical analysis (Table 1), where $K = \Sigma kp$, k is the specific refractivity constant and p is weight per cent of each oxide constituent. Some relevant k-values are: for CaO, 0.226; for MgO, 0.200; for FeO, 0.185; for MnO, 0.190 (Jaffe, 1988).

^e Weighted K-values for 88.6% wagnerite, 11.4% isokite.

fracture zones. Thus, ferroan wagnerite plus hydrothermal solutions might yield isokite plus hematite according to the scheme:

$$\begin{array}{l} (Mg_{1-x}Fe_x)_2(PO_4)F + [CaO + O] \\ & \text{wagnerite} \\ & \rightarrow CaMg(PO_4)F + Fe_2O_3 \\ & \text{isokite} \\ \end{array}$$

Wagnerite, $Mg_2[PO_4]F$, magniotriplite, (Mg,Fe,Mn)₂[PO₄][F,OH], triplite, $Mn_2[PO_4]F$, and triploidite, $Mn_2[PO_4](OH)$ are structurally related fluophosphate minerals commonly occurring in pegmatite and in hydrothermal vein deposits. Coda *et al.* (1967) found that wagnerite from Werfen, Austria, crystallised in space group $P2_1/a$ with Z = 16 and a *b* axis of 12.679 Å (Tables 2 and 3). Tadini (1981), in a single-crystal study of magniotriplite from Albères in the Pyrénées, found that it crystallises in space group A2/a with Z = 8 and a *b*-axis dimension of 6.432 Å, one-half that of wagnerite. Tadini (1981) concluded that these minerals are related by an order-disorder relationship, whereby F atoms are ordered in the wagnerite structure, and disordered in the A2/astructure of magniotriplite. On this basis they assigned the manganese fluophosphate minerals triploidite to $P2_1/a$, and triplite to A2/a.

As might be expected, the (Fe + Mn)-rich members have higher mean indices of refraction (n), density (D), molecular refractivity (R), larger molar volume (V_m) , and b-axis dimensions than the Mg-rich members (Table 6).

In conclusion, it may also be noted that isokite (CaMg[PO₄]F), titanite (CaTi[SiO₄][F,O,OH] above 220 °C, durangite (NaAl[AsO₄]F), tilasite (CaMg[AsO₄]F), and malayaite (CaSn(SiO₄)O) are isostructural minerals that crystallise in space group A2/a or C2/c (Table 2, this report; Deans *et al.*, 1955; Speer and Gibbs, 1976; Taylor and Brown, 1976; Takenouchi, 1971).

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Table 6. Systematic increase in unit cell dimensions, molar volume, density, mean index of refraction (n), and molecular refractivity (R) with decrease in Mg/(Mg + Fe + Mn) ratios in wagnerite and triplite

| | Mg/(Mg + Fe + Mn) | b, Å | $V_{\rm m},{\rm cm}^3$ | $D, g/cm^3$ | n (mean) ^a | R, cm^3 |
|----------------------------------|-------------------|---------------------|------------------------|-------------------|-----------------------|--------------------|
| Wagnerite, P2 ₁ /a, Z | 2 = 16 | | | | | |
| Werfen | 0.98 | 12.679 | 52.25 | 3.14 | 1.574 | 29.99 |
| Sante Fe Mt. | 0.97 | 12.671 | 52.07 | 3.16 | 1.576 | 29.99 |
| Benson Mines | 0.825 | 12.717 | 52.71 | 3.29 | 1.591 | 31.14 |
| Magniotriplite, 12/a | Z = 8 | | | | | |
| Hållsjöberget ^d | 0.66 | 12.762 ^b | 53.06 | 3.43 | 1.618 | 32.73 |
| Turkestan ^e | 0.44 | 12.830 ^b | 53,96 | 3.66 | 1.650 | 35.18 |
| Albères ^f | 0.44 | 12.864 ^b | 54.01 | 3.68 | 1.655 | 35.37 |
| Triplite | | | | | | |
| Mica Lode ^g | 0.35 | 12.908 ^b | 55.98 | 3.62 ^c | 1.653 ^c | 36.34 |

^a Mean index of refraction $(\alpha + \beta + \gamma)/3$.

^b Value cited is 2b. Triplite minerals (12/a) have b unit cell dimension 1/2 that of wagnerite ($P2_1/a$).

^c Values reduced where Mn > (Fe + Mg).

^d Henriques (1957).

^e Ginzburg et al. (1951).

^f Fontan (1981).

^g Waldrop (1967).

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