Grandreefite, pseudograndreefite, laurelite, and aravaipaite: Four new minerals from the Grand Reef mine, Graham County, Arizona

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ABSTRACT

Four new lead fluoride minerals are described from the Grand Reef mine, Laurel Canyon, Aravaipa mining district, Graham County, Arizona. They occur together in a vug surrounded by layers of quartz, fluorite, and galena. The new minerals are interpreted as resulting from the reaction of supergene solutions with galena and fluorite.

Grandreefite, Pb₂SO₄F₂, is orthorhombic, a = 4.439(4) Å, b = 13.575(13) Å, c = 4.333(4) Å, V = 261.1(4) Å³, space group F222, Z = 2. It occurs as colorless prismatic crystals striated parallel to [001], with a density of 7.0 (1) g/cm³ (meas.), 7.15 g/cm³ (calc.). Grandreefite is biaxial (+), very small 2V, with weak dispersion, r > v, α = 1.872(5), β = 1.873(5), γ = 1.897(5); orientation is X = c, Y = a, Z = b. The composition is PbO 82.9, SO₃ 13.8, F 7.1, sum 100.8 wt%. Grandreefite is isostructural with La₃SO₆, based on layers of the β-PbF₂ (fluorite) structure parallel to (010) with SO₄ groups between layers.

Pseudograndreefite, Pb₂SO₄F₂, is orthorhombic, a = 8.5182(5) Å, b = 19.5736(11) Å, c = 8.4926(5) Å, V = 1416.0(1) Å³, space group F222, Z = 4. It occurs as colorless square crystals tabular on {010}, with a density of 7.0 (1) g/cm³ (meas.), 7.08 g/cm³ (calc.). Pseudograndreefite is biaxial (+), 2V = 30(3)°, with strong dispersion, r > v, α = 1.864(5), β = 1.865(5), γ = 1.873(5); orientation is X = c, Y = a, Z = b. The composition is PbO 84.9, SO₄ 4.7, F 13.1, sum 102.7, less O = F 5.5, total 97.2 wt%. The structure of pseudograndreefite is very similar to that of grandreefite.

Laurelite, Pb(F,Cl,OH)₂, is hexagonal, a = 10.252(9) Å, c = 3.973(1) Å, V = 361.7(6) Å³, space group P6₃/m, Z = 6. It occurs as colorless needles with a density of 6.2(1) g/cm³ (meas.), 6.52 g/cm³ (calc.). Laurelite is uniaxial (+), with ω = 1.903(5), ε = 1.946(5). The composition is Pb 82.0, F 13.0, Cl 3.6, OH 0.9, total 99.5 wt%. The structure of laurelite is probably related to that of α-PbF₂.

Aravaipaite, Pb₃AlFe₆H₂O, is triclinic, with a = 5.842(2) Å, b = 25.20(5) Å, c = 5.652(2) Å, α = 93.84(4)°, β = 90.14(4)°, γ = 85.28(4)°, V = 827(2) Å³, space group P1 or P1̅, Z = 4. It occurs as colorless thin plates with perfect micaceous (010) cleavage and a density of 6.37 g/cm³ (calc.). Aravaipaite is biaxial (-), 2V = 70(3)°, with strong dispersion, r < v, α = 1.678(2), β = 1.690(2), γ = 1.694(2); Euler angles are φ = 67°, ψ = 60°, θ = 76°. The composition is Pb 73.8, Al 3.6, Fe 21.0, H₂O 3.0, total 101.4 wt%. The structure of aravaipaite may be related to that of β-PbF₂ with layers of the β-PbF₂ structure parallel to (010) and Al(F,H₂O) octahedra between layers.

INTRODUCTION

The Grand Reef mine is situated in Laurel Canyon, about 6 km northeast of Klondyke, in the Aravaipa mining district of Graham County, Arizona. The mine exploits a small epithermal lead-copper-silver deposit, which is hosted by a silicified breccia. The breccia is highly resistant, forming a precipitous cliff, locally known as the "reef," from which the name of the mine is derived. During the past 25 years, the mine has become well known among mineral collectors for a variety of rare minerals. The most notable of these is linarite, which has been found in well-formed crystals up to 5 cm in length. Jones (1980) provided an overview of the history, geology, and mineralogy of this deposit.

During the course of a detailed mineralogic and paragenetic study of the Grand Reef mine, Mr. William Besse (Besse, 1981) obtained an unusual specimen, which had...
been recovered in 1980 by Mr. Wayne Thompson under the auspices of Southwestern Mineral Associates. Mr. Besse brought the specimen to the attention of one of us (A.R.K.) with the observation that it might contain two minerals new to science. In the course of the present investigation, these two minerals, as well as two others on the same specimen, were determined to be new. The four new minerals are named grandreefite, pseudograndreefite, laurelite, and aravaipaite. Grandreefite is named for the Grand Reef mine. Pseudograndreefite is named for its close similarity to grandreefite in physical properties, composition, and structure. Laurelite is named for Laurel Canyon in which the Grand Reef mine is situated. Aravaipaite (à vâ' pâ it) is named for the Aravaipa mining district in which the mine is located.

The species and the names were approved by the Commission on New Minerals and Mineral Names, IMA, prior to publication. The type specimen containing all four species is deposited at the Natural History Museum of Los Angeles County (cat. no. 25414).

**Geologic and Mineralogic Setting**

The ore at the Grand Reef mine was emplaced in a heavily brecciated, nearly vertical fault zone. The breccia, consisting of rhyolite and schist fragments, has been silicified and contains specular hematite and fluorite as the principal gangue minerals. The most prevalent primary ore mineral is galena, with chalcopyrite, argentite, and pyrite being present in lesser amounts. Chalcocite, covellite, silver, and copper were products of supergene enrichment. In addition to the four new minerals described here, Besse (1981) listed 25 other minerals, most of which have resulted from oxidation.

In 1969 a bench was blasted near the top of the “reef” just south of a vertical stope known as the “glory hole.” The area of this bench has produced most of the mine’s well-crystallized oxidation minerals, predominantly sulfates. The type specimen of the four new minerals was found in this area.

The type specimen measures 10 × 7 × 4 cm, and the vug containing the new minerals is about 2 × 1.5 × 0.5 cm. A second specimen with a 5 × 2 × 1.5 cm vug was subsequently provided for examination by its current owner, Mr. Les Presmyk of Mesa, Arizona. The two specimens were discovered to be portions of the same vug. To date these are the only specimens known to contain any of these new minerals. Fragments of rock trimmed from the second specimen were also provided. A block of matrix measuring 27 × 25 × 15 cm was reconstructed from these fragments and the two vug sections.

The matrix is typical of the mineralization found in the bench area of the Grand Reef mine. Veins of galena follow irregular fractures in the breccia, and minor amounts of copper sulfides associated with the galena are altered principally to linarite and caledonite. The galena shows lesser alteration to anglesite. The vug containing the new minerals occupies the center of what was evidently once an interstice between breccia blocks. Although a portion of the rock surrounding the vug is missing, it is clear that the vug was completely surrounded by galena. An irregular and incomplete layer of fluorite is found inside the galena, followed by a complete layer of quartz surrounding the quartz-lined vug. Anglesite fills fractures in the quartz. A completely filled pocket surrounded by galena and containing only massive fluorite occurs a few centimeters away from the vug.

Isolated pockets in galena, sometimes containing vugs, are typical of the bench area of the Grand Reef mine, and the mineralization in these pockets is often quite distinct from that in the adjacent portions of the oxidation zone. Mr. Wayne Thompson (personal communication, 1988) has considered the vug containing the four new minerals to be an example of such an occurrence.

**Grandreefite (Pb₃SO₄F₂)**

**Appearance and physical properties**

The only crystal of grandreefite on the type specimen measures 1.5 × 3 × 4 mm parallel to the [100], [010], and [001] cell directions, respectively. The characterization of the mineral used fragments removed from this crystal, which is prismatic and striated parallel to [001]. The forms (120), (130), (293), (293), and (101) were observed and are depicted in Figure 1. Two bladelike crystals of grandreefite on the second specimen reach 7 mm in length.

Grandreefite is colorless and has a white streak. It is transparent with a subadamantine luster. No fluorescence in ultraviolet light was detected. The Mohs hardness is approximately 2½. The mineral is brittle with a conchoil fracture, and no cleavage was detected. The density, measured on a Berman balance using 3.43 mg of sample, is 7.0(1) g/cm³; the calculated density is 7.15 g/cm³.

**Optical properties**

The optical properties of grandreefite were determined by immersion using a Supper spindle stage. Over the course of a few minutes, the crystal surfaces became frosted because of reaction with the high-index immersion liquids. This required that observations be made rapidly and may have contributed to experimental error.
Grandreefite is optically biaxial (+). The indices of refraction measured in white light are \(\alpha = 1.872(5)\), \(\beta = 1.873(5)\), and \(\gamma = 1.897(5)\). The observed \(2V\) was very small; the calculated \(2V\) is 23°. Weak dispersion, \(r < v\), was observed. The optical orientation is \(X : c, Y : a, Z : b\). Coarse polysynthetic twinning was observed under crossed polarizers, but no twin law could be determined and no morphological or X-ray diffraction evidence for twinning was found.

**Chemical data**

Grandreefite was analyzed with an electron microprobe utilizing synthetic PbO, celestite, and synthetic CaF\(_2\) as standards for Pb, S, and F, respectively. The analysis yielded PbO 82.9, SO\(_3\) 13.8, F 7.1, sum 103.8, less O = F 3.0, total 100.8 wt%. Single-crystal infrared spectroscopy indicated that no water was present in the mineral (<0.001 wt%). The empirical formula based upon O + F = 6 is Pb\(_{2.07}\)S\(_{0.86}\)O\(_{1.06}\)F\(_{2.90}\). The simplified formula, Pb\(_6\)SO\(_4\)F\(_5\), requires PbO 81.39, SO\(_3\) 14.60, F 6.93, sum 102.92, less O = F 2.92, total 100.00 wt%. Grandreefite decomposes in cold water.

**Crystallography**

Precession photographs showed grandreefite to be orthorhombic, with the space group \(I222\), \(I2_12_12_1\), \(Immm\), or \(I2mm\). The structure determination showed the space group to be \(I222\). The cell parameters were refined using four-circle diffractometer data, yielding \(a = 4.439(4)\), \(b = 13.575(13)\), and \(c = 4.333(4)\) Å. The cell volume is 261.1(4) Å\(^3\) and \(Z = 2\).

The X-ray powder-diffraction pattern was recorded using a Gandolfi camera of 114.6-mm diameter. CuK\(_\alpha\) radiation was employed, and the intensities were visually estimated. These data along with the calculated \(d\) values are given in Table 1.

**Comments on the structure**

Grandreefite is apparently isostructural with La\(_2\)O\(_2\)SO\(_4\) and may briefly be described as consisting of layers of the \(\beta\)-PbF\(_2\) (fluorite) structure parallel to (010), with SO\(_3\) groups between layers. The layer sequence corresponding to one unit cell is \([\text{SO}_3 - \text{Pb} - 2\text{F} - \text{Pb} - \text{SO}_3 - \text{Pb} - 2\text{F} - \text{Pb}]\). The La\(_2\)O\(_2\)SO\(_4\) structure was determined by Fahey (1976) using powder-diffraction data, but the positional parameters that he assigned to the sulfate oxygen site must be considered suspect because of the large temperature factor (15) for this atom. An attempt to solve the structure of grandreefite using single-crystal data failed to locate the oxygen site(s) and has resulted in an \(R\) value of 0.11. It is likely that absorption-correction problems are largely to blame, but it is possible that either rotational disorder or twinning has obscured the site. Efforts are still under way to completely solve the structure.

**Pseudograndreefite \((\text{Pb}_6\text{SO}_4\text{F}_{10})\)**

**Appearance and physical properties**

Pseudograndreefite occurs as square (pseudotetragonal) crystals tabular on (010). The tablets form a single sub-parallel aggregate on the type specimen measuring 4 \(\times\) 1 \(\times\) 4 mm parallel to the [001], [010], and [001] cell directions, respectively. The pseudograndreefite aggregate is in contact with the grandreefite crystal and appears to have partially overgrown the grandreefite. The forms (010), (100), (001), (210), and (012) were observed on pseudograndreefite crystals, as depicted in Figure 2. No twinning was detected.

The physical properties of pseudograndreefite are nearly identical to those of grandreefite. It is transparent and colorless with a subadamantine luster and a white streak. It exhibits no fluorescence in ultraviolet light and has a Mohs hardness of approximately 2½. It is brittle with a conchoidal fracture and no discernible cleavage. The density, measured on a Berman balance using 4.41 mg of sample, is 7.0(1) g/cm\(^3\); the calculated density is 7.08 g/cm\(^3\).
Optical properties

The optical properties of pseudograndreefite were determined by immersion using a Supper spindle stage. Pseudograndreefite exhibited the same surface deterioration in high-index immersion liquids noted for grandreefite.

Pseudograndreefite is optically biaxial (+). The indices of refraction measured in white light are $\alpha = 1.864(5)$, $\beta = 1.865(5)$, and $\gamma = 1.873(5)$. The observed $2V$ is $30^\circ$. Strong dispersion, $r > v$, was observed. The optical orientation is $X = c$, $Y = a$, $Z = b$. The lower indices of refraction, larger $2V$, and stronger dispersion are useful in distinguishing pseudograndreefite from grandreefite.

Chemical data

Pseudograndreefite was analyzed with an electron microprobe utilizing the same standards as for grandreefite. The analysis yielded PbO 84.7, SO3 4.9, F 12.4, sum 89.8 wt%. Single-crystal infrared spectroscopy indicated that no water was present (<0.01 wt%). The empirical formula based upon $O + F = 14$ is $Pb_{5.39}S_{2.27}O_{13}F_{1.09}$. The simplified formula, $Pb_7S_3O_{11}F_7$, requires PbO 87.57, SO3 5.24, F 12.42, sum 105.23, less O = F 5.23, total 100.00 wt%. Pseudograndreefite decomposes in cold water.

Crystallography

Precession photographs showed pseudograndreefite to be orthorhombic with the space group F222, Fmm2, or Fmmm. The structure determination showed the space group to be F222. The cell parameters were refined using four-circle diffractometer data yielding $a = 8.5182(5)$, $b = 19.5736(11)$, and $c = 8.4926(5)$ Å. The cell volume is 1416.0(1) Å³ and $Z = 4$.

The X-ray powder-diffraction pattern was recorded using a Gandolfi camera of 114.6-mm diameter and CuKα radiation. The intensities were visually estimated. These data and the calculated $d$ values are given in Table 2.

Comments on the structure

As for grandreefite, the pseudograndreefite structure has as yet resisted complete solution. All Pb and S atoms have been located, as have most F atoms; but the oxygen atoms in the presumed sulfate group and the "interlayer" F atoms have not been located. The resulting $R$ value is 0.11. The structure of pseudograndreefite is very similar to that of grandreefite and may briefly be described as consisting of layers of the $\beta$-PbF₂ (fluorite) structure parallel to (010) with SO₃ and F between layers. The layer sequence corresponding to one unit cell is [(2SO₃,4F)₄Pb₈-8F-4Pb₈-4Pb₂SO₄]₄Pb₈-8F-4Pb₈-4Pb₂SO₄]. Efforts are still under way to completely solve the structure.

Laurelite ($Pb(F,Cl,OH)_2$)

Appearance and physical properties

Laurelite occurs as needles up to 10 mm long and 0.05 mm in diameter, but most needles are much thinner and are typically grouped in parallel bundles. Laurelite needles in loose jackstraw-fashion fill the interior of the vug surrounding and atop the crystals of grandreefite and pseudograndreefite. Laurelite needles are also found included in plates of aravaipaite and, to a lesser extent, in crystals of pseudograndreefite.

The needles are prismatic parallel to [001] and have basal {011} terminations. Because of a combination of twinning, parallel growth, and narrowness, no distinct goniometer signals could be obtained from the prism faces. The crystals are twinned by rotation around [001].

Laurelite is colorless and has a white streak. It is transparent with a silky luster. No fluorescence in ultraviolet light was detected. The Mohs hardness is approximately 2. The tenacity can best be described as brittle, although the needles are slightly flexible. The fracture is conchoidal and an imperfect {011} cleavage was observed. A pyrometer was used for the density determination. The measurement on a 9-mg sample yielded 6.2(1) g/cm³. The calculated density is 6.52 g/cm³. The discrepancy may be attributable to the difficulty in handling the needles and to small sample size.

Optical properties

The optical properties of laurelite were determined by immersion. No crystals suitable for conoscopic observation were found, but the mineral is assumed to be uniaxial because of its hexagonal symmetry. The optic sign is positive, and the indices of refraction measured in white light are $\omega = 1.903(5)$ and $\epsilon = 1.946(5)$. Laurelite was stable in high-index immersion liquids during the course of optical study.
TABLE 3. X-ray powder-diffraction data for laurelite

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Note: 114.6-mm Gandolfi camera, CuKα radiation, visually estimated intensities, indexed with the aid of the precession-film data. *Reflections that were used in the least-squares refinement of the cell parameters.

Laurelite was analyzed with an electron microprobe utilizing synthetic PbF₂ for Pb and F and synthetic PbCl₂ for Cl. Water was determined on a Mitsubishi moisture titrator using a 3.35-mg sample. The water determination was nearly single, having diffuse streaked reflections about the c axis. The crystal most samples examined by the precession method yielded in parallel bundles and the pervasive twinning on <010>. No single crystals large enough for X-ray diffraction studies could be found. Because of the growth of needles in parallel bundles and the pervasive twinning on [001], most samples examined by the precession method yielded diffuse streaked reflections about the c axis. The crystal used in the cell determination was nearly single, having only one smaller twin crystal attached. Laurelite is hexagonal with possible space groups P6, P6, or P6/m. The cell parameters refined from the powder data are a = 10.252(9), c = 3.973(1) Å. The cell volume is 361.7(6) Å³ and Z = 6.

The X-ray powder-diffraction pattern was recorded using a Gandolfi camera of 114.6-mm diameter. CuKα radiation was employed and the intensities were visually estimated. These data, along with the calculated d values, are given in Table 3.

Comments on the structure
Laurelite has not yielded crystals adequate for structure determination. However, a structural relationship with α-PbF₂ (as well as the minerals cotunnite, laurionite, paraaraulionite, and fiedlerite) is indicated. The intense reflections 210, 140, and 420 on the h0k0 precession photograph of laurelite are consistent with an orthorhombic pseudocell having a = 6.73, b = 7.79, and c = 3.97 Å. This is analogous to the orthorhombic (pseudohexagonal) α-PbF₂ cell, which has a = 6.440, b = 7.651, and c = 3.899. The slightly larger dimensions of the laurelite pseudocell are consistent with the partial replacement of F by Cl. In the α-PbF₂ structure, Pb is 9-coordinated in tri-capped trigonal prisms. These prisms form face-sharing columns parallel to c, which are joined by sharing edges.

ARAVAIPAITE (Pb₄AlF₁₀·H₂O)

Appearance and physical properties
Aravaipaite occurs as thin plates, 0.001 to 0.1 mm thick, and up to 3 mm across. The plates are lamellar on [010], the only prominently developed face. The [041] face was also detected, but plate edges are usually rounded when not forming contacts with other crystals. A perfect micaceous [001] cleavage was observed, as were good [100], [001], and [101] cleavages. Figure 3 depicts a single-crystal bounded by the observed faces and cleavages. Polysynthetic twinning on [001] is always present.

Aravaipaite is colorless and has a white streak. It is transparent with a vitreous to pearly luster. No fluorescence in ultraviolet light was detected. The Mohs hardness is about 2. Thin plates are flexible, although not as much so as muscovite. The fracture is irregular.

The density could not be measured, as the mineral sinks in Clerici solution (ρ = 4.2 g/cm³), and the amount of material available is insufficient for density determination by other means. A cell content of four formula weights (Z = 4) was chosen because it provides a reasonable packing efficiency of 62%, compared with 54% for β-PbF₂ and 66% for the compound Pb₄AlF₁₀. This yields a calculated density of 6.37 g/cm³.

Optical properties
The optical properties of aravaipaite were determined by immersion using a Supper spindle stage. The polysynthetic twinning on [010] is obvious under crossed polarizers and considerably complicated the determination of optical properties. Utilizing the perfect [010] cleavage, a nearly single crystal with a very small attached twin was...
obtained for determination of optical properties. Aravaipaite was determined to be biaxial (−). The indices of refraction measured in white light are \(\alpha = 1.678(2),\ \beta = 1.690(2),\) and \(\gamma = 1.694(2).\) The observed 2\(V\) is 70(3)\(^\circ\); the calculated 2\(V\) is 66\(^\circ\). Strong dispersion, \(r < v,\) was observed. The optical orientation is specified by the Euler angles \(\phi = 67^\circ, \psi = 60^\circ, \theta = 76^\circ.\) Aravaipaite was stable in the immersion liquids during the period of optical study.

**Chemical data**

Aravaipaite was analyzed with an electron microprobe utilizing synthetic PbO, hornblende, and synthetic CaF\(_2\) for Pb, Al, and F respectively. The analysis yielded Pb 73.8, Al 3.6, F 21.0, total 98.4 wt%. The amount of aravaipaite available was insufficient for water determination by conventional methods, so recourse was made to single-crystal infrared spectroscopy that required only a single small plate of the mineral. The spectrum (Fig. 4) indicated about 3 wt% water. The uncertainty in this value is judged to be about 1 wt%, principally because of the uncertainty in the molar absorptivity. The intensity of the 1650 cm\(^{-1}\) band, corresponding to the H\(_2\)O bending mode, is 827(2) Å\(^2\) and \(Z = 4.\)

The X-ray powder-diffraction pattern was recorded using a Gandolfi camera of 114.6-mm diameter. CuKa radiation was employed and the intensities were visually estimated. These data along with the calculated \(d\) values are given in Table 4.

**Comments on the structure**

Aravaipaite crystals adequate for structure determination were not found. However, a structural relationship with \(\beta\)-PbF\(_2\) is indicated. The formula, cell dimensions, and perfect cleavage suggest that the structure may be based upon layers of the \(\beta\)-PbF\(_2\) (fluorite) structure parallel to (010) with Al(F,H\(_2\)O) octahedra between layers. Note that the \(a\) and \(c\) cell dimensions are 5.842 and 5.652 Å, respectively, and \(\beta\) is very close to 90\(^\circ\). (The \(\alpha\)\(\beta\) precession photograph is pseudotetragonal.) The unit cell of \(\beta\)-PbF\(_2\) is cubic with \(a = 5.940\) Å.

**Gladstone-Dale compatibility**

The Gladstone-Dale compatibility indices, \(1 - (K_p/K_o)\), for grandreefite, pseudograndreefite, laurelite, and aravaipaite are \(-0.061, -0.017, -0.136,\) and 0.100, respectively (Mandarino, 1981). These suggest that the compatibility among the density, average index of refraction, and composition is adequate only for pseudograndreefite.
The Gladstone-Dale relationship should probably not be considered a valid measure of compatibility for these minerals because current knowledge concerning the interaction of Pb with halogen elements is incomplete.

**Paragenesis**

The new minerals are interpreted as resulting from the reaction of supergene solutions with galena and fluorite. This is suggested by their compositions, by their spatial proximity to galena and fluorite, and by the presence of anglesite fracture-filling in the quartz surrounding the vug. The presence of Pb²⁺ in solution is clearly critical to the formation of the new minerals. Because of the strong tendency of this ion to combine with sulfate or carbonate, its mobility in systems dominated by these anions is very limited. Close proximity of galena to a source of fluoride ion is seemingly necessary for the formation of the new minerals.

Of apparent importance as well is the isolation of the vug from acidic sulfate-rich solutions, which permeated most of the adjacent oxidation zone. Otherwise either anglesite would have formed in preference to the lead fluorides or earlier-formed lead fluorides would have been destroyed by the later solutions. In this regard, it is presumed that the quartz, fluorite, and galena layers on the specimen formed a continuous envelope around the vug. This view is supported by observations on other isolated vugs in the bench area (Wayne Thompson, personal communication, 1988).

The secondary calcium fluoride minerals gearksutite and creedite were reported from the mine by both Jones (1980) and Besse (1981). Besse reported gearksutite to be moderately common in the bench area as a very late stage, chalky cavity filling. Besse (personal communication, 1988) also reported the occurrence of prosopite in an isolated vug in the bench area. None of these minerals is found in association with the new lead fluoride minerals described here, although small amounts of gearksutite are present in the matrix surrounding the vug. The conditions present in this isolated vug must have favored the formation of secondary lead fluorides rather than calcium fluorides, since Ca would have been available from the alteration of the fluorite.

The new minerals probably crystallized from the same supergene solution as it evolved under approximately closed system conditions within the vug. Although the crystallization ranges undoubtedly overlapped considerably, growth interrelationships suggest the following crystallization order: grandreefite → pseudograndreefite → laurelite → aravaipaite. The trend among these minerals is toward decreasing amounts of F and water. The increase in water content follows the normal tendency toward increasing water li-

ation with decreasing temperature. The decrease in sulfate and increase in F suggest that the sulfate was selectively incorporated into the earlier phases. The selective incorporation of Cl in laurelite is probably attributable to the preference of Cl for the α-PbF₂ (PbCl₂) structural arrangement. The Al in aravaipaite was probably present in the invading supergene solution and was progressively concentrated as the earlier lead fluoride minerals crystallized.

The combination of conditions that resulted in the formation of these four new minerals thus far appears to have been unique, since only one vug containing these minerals has been recognized during nearly a century of mine operation and a quarter century of intense interest in this mine on the part of mineral collectors. The common association of galena and fluorite in this and countless other deposits throughout the world further testifies to the unusual set of conditions that must have existed for these four minerals to form. It should be noted, however, that the new minerals are inconspicuous in comparison to the brightly colored secondary copper minerals, which are of particular interest to collectors at the Grand Reef mine. Specimens with colorless needlelike crystals consistent in appearance with laurelite have been reported by at least two other persons who have collected minerals at the Grand Reef mine, but they discarded the specimens thinking them insignificant.

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