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PETTERDITE, THE Cr-DOMINANT ANALOGUE OF DUNDASITE, A NEW MINERAL SPECIES FROM DUNDAS, TASMANIA, AUSTRALIA AND CALLENBERG, SAXONY, GERMANY

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Abstract

Petterdite is a newly discovered hydrated lead chromium hydroxyl carbonate, the Cr^{3+}-dominant analogue of dundasite, with a formula $PbCr_2(CO_3)_2(OH)_4 \bullet H_2O$. The type locality is the Red Lead mine, on the Zeehan–Dundas mining field in northwestern Tasmania, Australia. The mineral also occurs in small amounts at the Callenberg nickel deposit, Saxony, Germany. Petterdite forms thin crusts made up of tiny platy crystals up to about 15 μm across, associated with crocoite and anglesite at the type locality, and with crocoite, cerussite, bindheimite, pyromorphite, and relict galena at Callenberg. The petterdite crusts are pale greyish to pinkish violet and non-fluorescent; they have an earthy to pearly luster. The streak is pale violet, and the Mohs hardness is estimated to be about 2. Crystals are poorly developed, flattened on {010}, and slightly elongate along [001] or, less commonly, [100]. Most crystal terminations, in the direction of [001], have a frayed appearance. Cleavage is fair parallel to {100}, and possibly also parallel to {010}. Density could not be measured. Petterdite is biaxial negative, α 1.704(5), $\beta \approx 1.802$, and γ 1.842(5). The $2V_{calc.}$ is close to 62°, and the optical orientation is $X = a$, $Y = b$, $Z = c$, with pleochroism $X = Y$ colorless to pale greyish pink, Z greyish pink. Chemical analysis by a combination of electron microprobe and CHN gave (wt%) PbO 43.33, SrO 1.40, Cr_2O_3 22.64, Al_2O_3 3.65, Sb_2O_5 0.67, CO_2 18.3, H_2O (by difference) 10.01, total 100.00 wt%. The simplified formula is $PbCr^{3+}{}_2(CO_3)_2(OH)_4 \bullet H_2O$. Petterdite is orthorhombic, with unit-cell parameters a 9.079(3), b 16.321 (9), c 5.786(7) Å, V 857(1) $Å^3$. With Z = 4, the calculated density is 3.95 g/cm^3. The strongest six lines in the X-ray powder-diffraction pattern [d_{obs}(Å)(I_{obs})hkl] are: 7.937(100)(110), 4.686(50b)(021,111), 3.633(70)(131), 3.270(40)(221), 2.718(40)(022,060), 2.690(40)(241,301). The crystal structure has not been determined owing to the small size of the crystals. Petterdite is assumed to have space group *Pbnm* by analogy with dundasite. Both minerals have similar optical and physical properties. They are also isostructural with dresserite and strontiodresserite. Petterdite is a supergene mineral formed by the alteration of galena by solutions containing chromium and carbonate. The mineral is named after William Frederick Petterd (1849–1910) in recognition of his work on the mineralogy of Tasmania.

Keywords: petterdite, new mineral species, Red Lead mine, Tasmania, Australia, Callenberg Ni deposit, Germany, dundasite.

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Sommaire

Nous décrivons la petterdite, espèce minérale récemment découverte, un carbonate hydroxylé et hydraté de plomb et de chrome, l'analogue chromifère de la dundasite, ayant comme formule $PbCr_2(CO_3)_2(OH)_4 \cdot H_2O$. La localité type est la mine Red Lead, faisant partie du camp minier de Zeehan–Dundas dans le secteur nord-ouest de la Tasmanie, en Australie. On trouve aussi la petterdite en petites quantités au gisement nickelifère de Callenberg, en Saxe, Allemagne. Elle se présente en minces croûtes faites de petits cristaux en plaquettes jusqu'à environ 15 μm de taille, associée à crocoïte et anglésite à la localité type, et à crocoïte, cérussite, bindheimite, pyromorphite, et des reliques de galène à Callenberg. Les croûtes de petterdite sont gris pâle à violette rosâtre et non fluorescentes; l'éclat est terreux à nacré. La rayure est violette pâle, et la dureté est d'environ 2 (échelle de Mohs). Les cristaux sont pauvrement développés, applatis sur {010}, et légèrement allongés selon [001] ou, moins couramment, [100]. Dans la plupart des cas, les terminaisons des cristaux sont fibreuses dans la direction [001]. Un clivage médiocre est parallèle à {100}, et un autre peut-être à {010}. On n'a pu mesurer la densité. La petterdite est biaxe négative, α 1.704(5), β ≈ 1.802, et γ 1.842(5). L'angle $2V_{calc.}$ est proche de 62°, et l'orientation optique est $X = a$, $Y = b$, $Z = c$, avec schéma pléochroïque $X = Y$ incolore à rose pâle grisâtre, et Z rose grisâtre. Une analyse chimique réalisée par une combinaison de méthodes (microsonde électronique et technique CHN) a donné (en %, poids) PbO 43.33, SrO 1.40, Cr_2O_3 22.64, Al_2O_3 3.65, Sb_2O_5 0.67, CO_2 18.3, H_2O (par différence) 10.01, total 100.00%. La formule simplifiée serait $PbCr^{3+}{}_2(CO_3)_2(OH)_4 \cdot H_2O$. La petterdite est orthorhombique, avec les paramètres réticulaires a 9.079(3), b 16.321(9), c 5.786(7) Å, V 857(1) Å^3. Avec $Z = 4$, la densité calculée est égale à 3.95 g/cm^3. Les six raies les plus intenses du spectre de diffraction (méthode des poudres) [d_{obs}(Å)(I_{obs})hkl] sont: 7.937(100)(110), 4.686(50b)(021,111), 3.633(70)(131), 3.270(40)(221), 2.718(40)(022,060), et 2.690(40)(241,301). La structure cristalline n'a pas été déterminée à cause de la taille infime des cristaux. Nous préconisons que la petterdite répond au group spatial *Pbnm* par analogie avec la dundasite. Les deux minéraux se ressemblent dans leurs propriétés optiques et physiques. Ils auraient aussi la même structure que la dresserite et la strontiodresserite. La petterdite a une origine supergène, et s'est formée lors de l'altération de la galène par des solutions carbonatées contenant du chrome. Le nom du minéral honore William Frederick Petterd (1849–1910) pour son travail sur l'inventaire minéralogique de la Tasmanie.

(Traduit par la Rédaction)

Mots-clés: petterdite, nouvelle espèce minérale, mine Red Lead, Tasmanie, Australie, gisement nickelifère de Callenberg, Allemagne, dundasite.

Introduction

The gossan mineralogy of the lead mines of the Zeehan–Dundas region (lat. 41°53'S, long. 145°25'E) in northwestern Tasmania, Australia, is so dominated by the lead chromate mineral crocoite that other species present have received little attention (Haupt 1988). An exception is dundasite, $PbAl_2(CO_3)_2(OH)_4 \cdot H_2O$, which was first described from these deposits by Petterd (1894). In the early 1980s, a small specimen of crocoite-bearing gossan containing an earthy, pale purplish mineral was collected at the Red Lead mine. Preliminary X-ray powder-diffraction studies at the Museum of Victoria showed that the purple mineral has a dundasite-like powder pattern, but no further follow-up studies were undertaken until 1998. Chemical analyses then revealed Cr dominant over Al, and after further detailed investigation, the mineral was confirmed as the Cr^{3+}-dominant analogue of dundasite, with an ideal formula $PbCr^{3+}{}_2(CO_3)_2(OH)_4 \cdot H_2O$. It is also isostructural with dresserite, $BaAl_2(CO_3)_2(OH)_4 \cdot H_2O$, and strontiodresserite, $SrAl_2(CO_3)_2(OH)_4 \cdot H_2O$. The mineral has been named petterdite after William Frederick Petterd (1849–1910), an amateur collector who published several significant catalogues on the mineralogy of Tasmania. The reinstated name supplants an obsolete use of petterdite (Twelvetrees 1902) for P-bearing mimetite (Anderson 1906, Ford & Kemp 1980). Both the mineral and mineral name, as well as supporting data, have been approved by the IMA Commission on New Minerals and Mineral Names. The type specimen of petterdite from Tasmania is lodged in the Museum Victoria collection (M38601). The mineral also occurs at Callenberg, Germany. Details of both these occurrences are provided in this paper. A specimen from Callenberg is deposited in the mineral collection of the Technische Universität, Bergakademie Freiberg, Germany.

In order to fully characterize petterdite, a combination of techniques was used, including electron-probe microanalysis, scanning and transmission electron microscopy, optical and infrared investigation and X-ray crystallography.

Occurrence, Physical and Optical Properties

The type specimen of petterdite, measuring 6 × 4 × 2.5 cm, consists of soft goethite enclosing corroded cavernous crocoite, which has replaced galena. Petterdite forms a thin (up to 0.5 mm), incomplete crust lining the cavity, in places extending to a delicate boxwork texture, suggesting it may have formed along original cleavage planes of galena. Small, transparent pale yellow crystals of anglesite occur in places on the petterdite. On other specimens from the Red Lead mine, petterdite occurs in two associations. In the most com-

mon, it is intimately intergrown with cerussite in fine-grained, pale lilac to grey botryoidal crusts up to about 2 mm thick. These aggregates have formed as coatings on galena (now totally leached) and are enclosed in limonite (which is probably pseudomorphic after siderite or ankerite). This association was locally common in the upper levels of the mine. The other association is similar to that shown by the type material and consists of thin bands or aggregates of petterdite intergrown with anglesite (commonly yellow) replacing galena (Fig. 1). The aggregates are a more intense lilac, reflecting the greater concentration of petterdite. Crocoite occurs in patches on and in this material but, significantly, rarely in direct association with petterdite. Pale pink Cr-bearing dundasite occurs in the same area, also in cavities in limonite, but does not seem to grade into petterdite. The Red Lead mine is the only confirmed locality for petterdite in the Dundas area, despite similar galena–crocoite–dundasite-bearing lodes occurring in several mines in the area.

Petterdite from the oxidation zone of a hydrothermal vein cutting serpentinite in the Callenberg Nord–1 open-cut, near Glauchau, Saxony, Germany, occurs with crocoite, cerussite, bindheimite, pyromorphite, and rare, relict galena. Callenberg is an occurrence of serpentinized ultramafic bodies mined for Ni (nickel hydrosilicates) (Rohde *et al.* 1978, Leonhardt & Leonhardt 1991).

Only scarce amounts of petterdite are known from either locality; about 50% of the petterdite on the type specimen has been consumed in the investigation.

Petterdite crusts are soft, earthy-looking and porous, and consist of thin, roughly rectangular, platy crystals up to 15 μm across at the Red Lead mine (Figs. 2, 3) and 5–10 μm across at Callenberg. The crystals, which are only loosely interlocked within the crusts, are poorly developed, flattened on {010} and slightly elongate along [001] or, less commonly, [100]. Most crystal terminations are corroded in the direction of [001], resulting in a frayed appearance. The color of petterdite ranges from pale greyish to pinkish violet, the streak is pale violet, the luster is earthy to pearly, and the crystals are translucent. No fluorescence under ultraviolet radiation was observed. The Mohs hardness could not be measured, but was assumed to be about 2, by analogy with dundasite. Cleavage is fair parallel to {100} and possibly also parallel to {010}. There is no evidence of twinning or parting, whereas fracture and tenacity could not be observed. Attempts to measure the density gave meaningless values, owing to the high porosity of the aggregates.

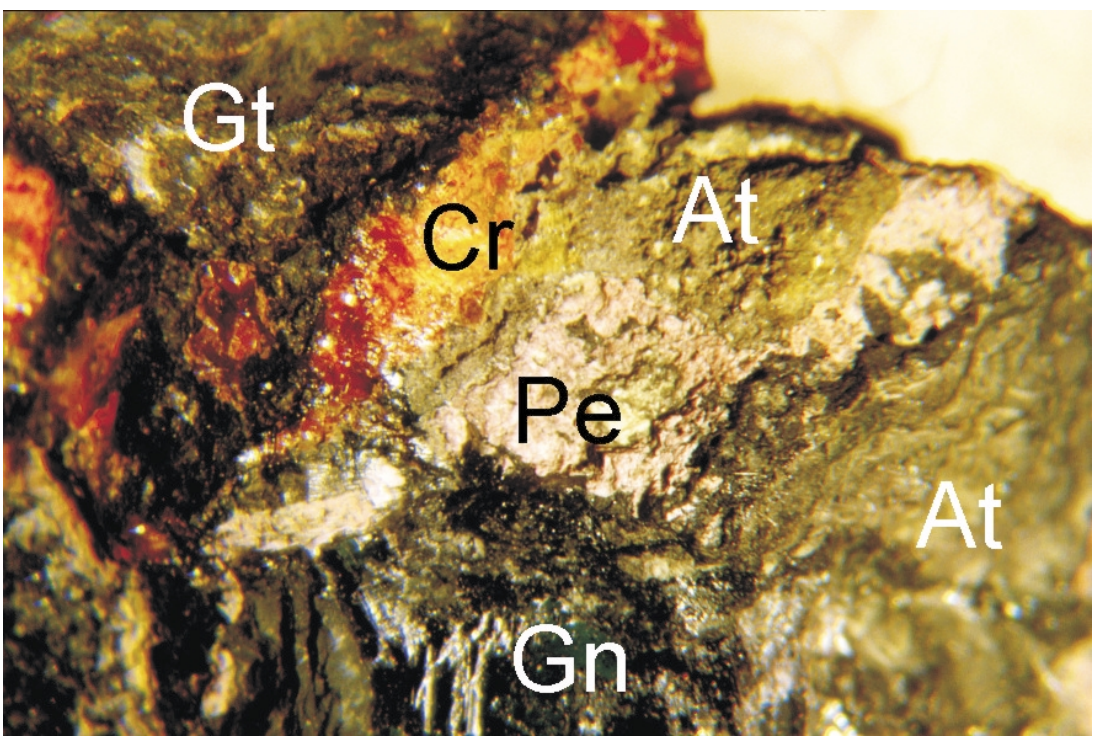

FIG. 1. Petterdite (Pe) forming a thin pink layer in grey-yellow anglesite (At) and cerussite, replacing galena (Gn), overgrown by red-yellow crocoite (Cr) and brown goethite (Gt). Field of view: 15 × 9 mm.

TABLE 1. COMPARISON OF DUNDASITE AND PETTERDITE

	dundasite [1]	dundasite [2]	petterdite [3]
Formula	$PbAl_2(CO_3)_2(OH)_4 \cdot H_2O$ or $\cdot 1.5H_2O$	$PbAl_2(CO_3)_2(OH)_4 \cdot H_2O$	$PbCr_2(CO_3)_2(OH)_4 \cdot H_2O$
a (Å)	9.05	9.08(1)	9.079(3)
b (Å)	16.35	16.37(2)	16.321(9)
c (Å)	5.61	5.62(1)	5.786(7)
V (Å^3)	830.1	835.4	857(1)
Space group	*Pbmm*	*Pbnm*	*Pbnm*
Strongest five lines in powder pattern [*d* (Å)(I)]	7.91 (100), 3.600 (80), 3.090 (60), 4.63 (50), 3.230 (50)	7.94 (100), 3.595 (41), 3.243 (23), 3.080 (18), 4.633 (18)	7.94 (100), 3.633 (70), 4.686 (50b), 3.270 (40), 2.718 (40)
D(meas.); (calc.)	3.10 – 3.55	not meas.; 3.716	(<3.9); 3.97 g cm^{-3}
Mohs hardness	2	not meas.	2 (est.)
α	1.602(2) – 1.603(3)	not meas.	1.704(5)
β	(–) – 1.716(3)	not meas.	~1.802
γ	1.750(2) – 1.742(3)	not meas.	1.842(5)
Birefringence	0.148 – 0.139	not meas.	0.138
Opt. character	neg.	not meas.	neg.
2*V* meas.; calc.	very large; ~50°	not meas.	not meas.; ~62°
Dispersion	none observed	not meas.	not observable
Orientation	*XYZ* = *abc*	*Z* = *c*	*XYZ* = *abc*
Elongation	positive	positive	positive (rarely negative)
X (color)	colorless	not meas.	colorless to pale greyish pink
Y (color)	colorless	not meas.	colorless to pale greyish pink
Z (color)	colorless	not meas.	greyish pink
Absorption	none observed	not meas.	*X* < *Z*
Habit	acicular along [001], slightly flattened	acicular along [001]	rectangular, platy {010}, slightly elongate along [001] or, less commonly, [100]
Twinning	none observed	none observed	none observed
Cleavage	{010} perfect	{010}	{100} fair; possibly also {010}

1) Beaumont & Guillemin (1960), Jambor *et al.* (1969) [PDF 21–936; space group *Pbmm*], Palache *et al.* (1951), Gaines *et al.* (1997). 2) Cocco *et al.* (1972) (structure solution) and PDF 33–731 (status: deleted). 3) This work.

The optical properties were determined using the type material. Petterdite is biaxial negative, with α = 1.704(5), β ≈1.802 and γ = 1.842(5). The optical angle could not be measured owing to the minute size of the crystals, but the calculated 2*V* is approximately 62°. No dispersion was observed, and the absorption is *X* < *Z*. The optical orientation is *X* = *a*, *Y* = *b*, *Z* = *c*, with pleochroism *X* = *Y* colorless to pale greyish pink, *Z* greyish pink.

TABLE 2. CHEMICAL COMPOSITION OF PETTERDITE

Constituent		Range	Ideal
PbO wt%	43.33	39.25 – 45.80	43.15
SrO	1.40	1.34 – 1.47	–
Cr_2O_3	22.64	22.46 – 22.82	29.38
Al_2O_3	3.65	2.84 – 4.83	–
Sb_2O_5	0.67	0.46 – 0.88	–
CO_2*	18.3		17.02
H_2O**	[10.01]		10.45
Total	[100.00]		100.00

* determined by CHN analyzer. ** calculated by difference.

These physical and optical properties for petterdite may be compared with those of dundasite, $PbAl_2(CO_3)_2(OH)_4 \cdot H_2O$ (Table 1) and of the closely related species dresserite, $BaAl_2(CO_3)_2(OH)_4 \cdot H_2O$, and strontiodresserite, $SrAl_2(CO_3)_2(OH)_4 \cdot H_2O$. The platy form of petterdite, because of the dominance of {010}, contrasts with the commonly acicular crystals of dundasite, flattened parallel to an unidentified form (presumably either {100} or {010}) (Beaumont & Guillemin 1960). Dresserite occurs as acicular crystals flattened parallel to {010}, according to single-crystal investigations by Jambor *et al.* (1969). The cleavage of petterdite, parallel to {100} and possibly {010}, contrasts with that of dundasite, given as parallel to {010} (Palache *et al.* 1951). No cleavage has been reported for dresserite or strontiodresserite.

The indices of refraction for petterdite are, as expected, much higher than those of dundasite, but the birefringence of both minerals is fairly similar (Table 1). Both petterdite and dundasite are biaxial negative, as are the isostructural species dresserite and strontiodresserite. The optical orientations of petterdite, dundasite and dresserite are identical, but differ from those reported for strontiodresserite.

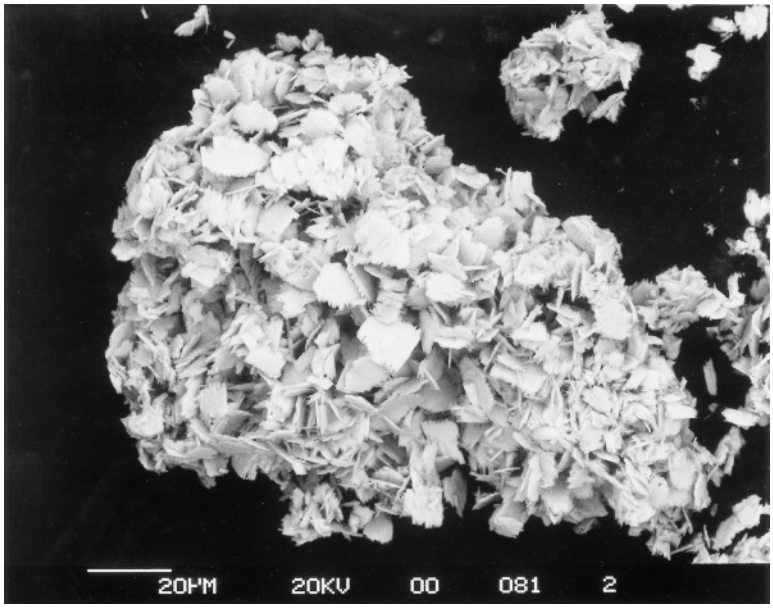

FIG. 2. SEM photomicrograph of petterdite crystals showing interlocking tabular crystals up to 10 μm in size. Scale bar: 20 μm.

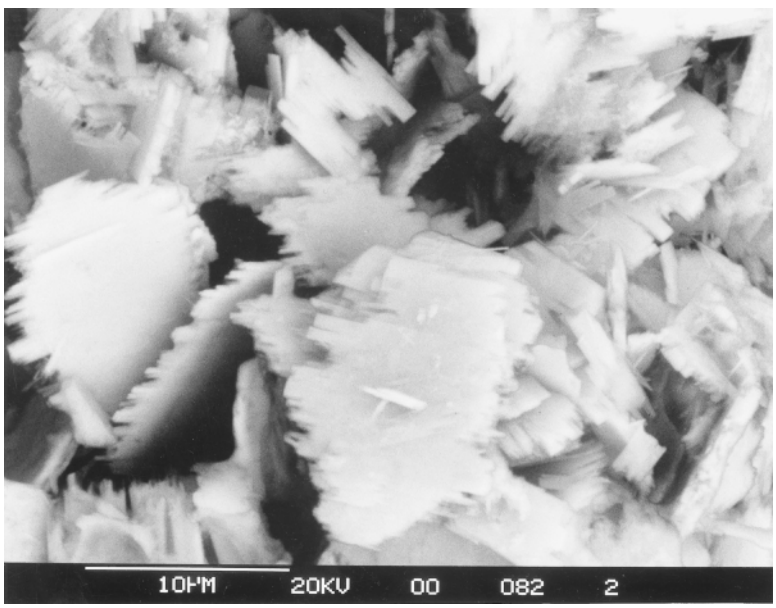

FIG. 3. SEM photomicrograph of single tabular crystals. Scale bar: 10 μm.

Chemical Composition

Chemical analysis for the major elements was undertaken on type material using a Cameca SX50 electron microprobe operating at 15 kV, with a specimen current of about 0.2 μA. The following standards were used: galena (Pb), strontianite (Sr), Cr metal (Cr), corundum (Al), hematite (Fe) and Sb metal (Sb). Analytical difficulties due to the small size of the crystals and the openness of the petterdite aggregates were partially overcome by defocusing the electron beam and moving it slowly over more dense portions of the aggregates during analysis. The four analytical datasets used to calculate the formula for petterdite (Table 2) were selected on the basis of highest analytical totals (lowest dehydration effects) and consistency of major-element contents. The empirical formula, calculated on the basis of 11 oxygen atoms, is $(Pb_{0.99}Sr_{0.07})_{\Sigma 1.06}(Cr^{3+}{}_{1.52}Al_{0.36}Sb_{0.02})_{\Sigma 1.90}(CO_3)_{2.12}(OH)_{3.62}\cdot 1.02H_2O$, giving a simplified formula of $PbCr^{3+}{}_2(CO_3)_2(OH)_4\cdot H_2O$.

The small amount of Sb determined in the analyses was assumed to be pentavalent because petterdite crystallized in an oxidizing environment and Sb^{3+} minerals are stable only up to moderately oxidizing conditions (Vink 1996). The substitution of Sb^{5+} for Cr^{3+} would also be likely on the basis of their similar ionic radii (radius of $^{[VI]}Sb^{5+}$ = 0.60 Å; radius of $^{[VI]}Cr^{3+}$ = 0.615 Å). Sb^{5+} also is known to substitute for Fe^{3+} and Mn^{3+}.

TABLE 3. COMPARISON OF ABSORPTION BANDS IN THE INFRARED POWDER SPECTRA OF PETTERDITE AND DUNDASITE

Petterdite	Dundasite [1]	Dundasite [2]
433 (m) cm^{-1}	440 (w), 455 (w) cm^{-1}	446 (s) cm^{-1}
504 (s)	485 (w)	479 (w)
541 (m)	542 (s)	542 (s)
592 (w)	576 (m)	576 (s)
626 (w)	615 (sh)	–
650 (sh)	667 (m), 675 (m)	671 (s)
744 (w)	753 (m)	727 (w), 750 (s)
812 (w)	–	–
830 (w)	826 (w)	825 (s)
852 (w)	843 (m)	844 (s)
881 (sh)	883 (m)	885 (s)
956 (w)	925 (sh), 965 (m)	925 (s), 967 (s)
1089 (w)	1083 (sh)	–
1122 (w)	1102 (m)	1100 (s)
1343 (vs), 1394 (sh)	1396 (vs)*	1400 (vs)
1493 (sh), 1516 (s)	1503 (m)*	1506 (w), 1523 (s)
1641 (w)	1643 (m)	1642 (s)
2072 (vw,b)	–	2115 (w), 2197 (w), 2277 (w)
2854 (w), 2924 (m), 2948 (w) **	3100 (m,b)	2858 (w), 2926 (w), 3076 (s)
3282 (w,b)	–	–
3470 (m)	3446 (s), 3510 (sh)	3450 (s)
3540 (m)	3600 (m)	3596 (s)

sh: shoulder, b: broad, w: weak, m: medium, s: strong, v: very.
Sources: [1] Farrell (1977); [2] Jones & Jackson (1993).
* These two strong peaks also show shoulders (*cf.* published spectrum) corresponding to those in petterdite.
** These spikes are probably due to a very minor contamination by hydrocarbon (*cf.* Figure 3; see also text for discussion).

A CHN analysis of several mg of hand-picked material yielded a satisfactory result for C but, for unexplained reasons, gave a H content of less than 0.1 wt%. There was insufficient material to repeat the analysis, so the H_2O content was calculated by difference. The electron-beam damage observed during electron microscopy confirms that water is lost easily from petterdite. This behavior appears to be common to related species; for example, the H_2O content of dundasite has been a matter of some debate. Most previous authors assumed the formula $PbAl_2(CO_3)_2(OH)_4\cdot 1.5H_2O$ (Beaumont & Guillemin 1960, Ford 1967), whereas the structure solution of Cocco *et al.* (1972) showed the formula to be $PbAl_2(CO_3)_2(OH)_4\cdot H_2O$. The H_2O content may, however, be slightly variable, as the H_2O molecules occupy channel sites along the *c* axis, where they are not coordinated by the cations (Cocco *et al.* 1972). The formula of dresserite is given as $BaAl_2(CO_3)_2(OH)_4\cdot 1.5H_2O$ (Jambor *et al.* 1969), and that of strontiodresserite, as $SrAl_2(CO_3)_2(OH)_4\cdot H_2O$ (Jambor *et al.* 1977). Mandarino (1999), however, gives formulae with one H_2O per formula unit. Jambor *et al.* (1977) suggested that all these minerals might absorb excess water, beyond the formula requirement of one H_2O.

Vibrational Spectroscopy

Infrared-absorption (IR) analysis of petterdite from the type locality was done by means of two Fourier-transform infrared (FTIR) spectra. Firstly, absorption spectra were acquired on a Perkin Elmer FTIR 1760X spectrometer equipped with KBr beam splitter and TGS detector. The conventional KBr pellet technique was employed for sample preparation. A CsI microfocus accessory was placed in the macro sample chamber for analysis. A total of 128 scans were done of the sample and the background in the range 400–4000 cm^{-1} at a resolution of 4 cm^{-1}. Secondly, absorption spectra were obtained using a Nicolet Continuum IR microscope equipped with a liquid-nitrogen-cooled MCT detector. The system was operated in the transmitted light mode, using 32× Reflachromat objectives (numerical aperture 0.65). Tiny single crystals of petterdite were placed on a ZnSe sample holder for analysis, and the sample-masking apertures were adjusted to an area of 10 × 20 μm. Background and sample were both measured for 300 s, in the range 750–4000 cm^{-1} at a resolution of 4 cm^{-1}; however, spectra can be interpreted only above 800 cm^{-1} because of the intense background at lower wavenumbers.

Raman spectra were obtained by means of a Renishaw RM 1000, a confocal, notch-filter-based Raman system equipped with a Leica DMLM series microscope, gratings with 1800 grooves per mm, and a Peltier-cooled charge-coupled device (CCD) detector. Spectra were excited with the 5145 Å line of an Ar^+ laser (0.3 mW measured after the objective). The Leica 100× objective (numerical aperture 0.95) was used.

Spectra were obtained in the "continuous extended scan" mode, in the range 100–4000 cm^{-1} (accumulation times about 30 minutes). The spectral resolution was better than 2.5 cm^{-1}.

Infrared-absorption and Raman spectra for petterdite are shown in Figure 4, and IR data are listed, together with data for dundasite, in Table 3. Both IR and Raman spectra are, with somewhat differing relative intensities, dominated by strong internal carbonate modes in the range below 1700 cm^{-1} and additional stray bands in the range 3400–3600 cm^{-1} that are assigned to O–H stretching vibrations. The group of three bands around 2900 cm^{-1} in the KBr IR spectrum is typical of C–H stretching vibrations. These bands are not observed in the single-crystal IR spectrum, nor is there any indication of C–H vibrations in the Raman spectrum. Therefore, these bands are interpreted as being due to contamination of the KBr pellet with minute amounts of hydrocarbons during preparation.

The IR spectrum is very similar to that of dundasite and also to spectra of dresserite and strontiodresserite (Farrell 1977, Jones & Jackson 1993). It also bears some similarities with that of the crystal-chemically related Ca–Al–carbonate alumohydrocalcite, $CaAl_2(CO_3)(OH)_4 \cdot 3H_2O$ (Jones & Jackson 1993). Observed bands (*cf.* Table 3) indicate the presence of CO_3 groups, OH and H_2O. Data are in good agreement with the features of the crystal structure of dundasite, which shows two different CO_3 environments, four distinct OH sites, metal–OH bonds and H_2O, with H bonds playing a

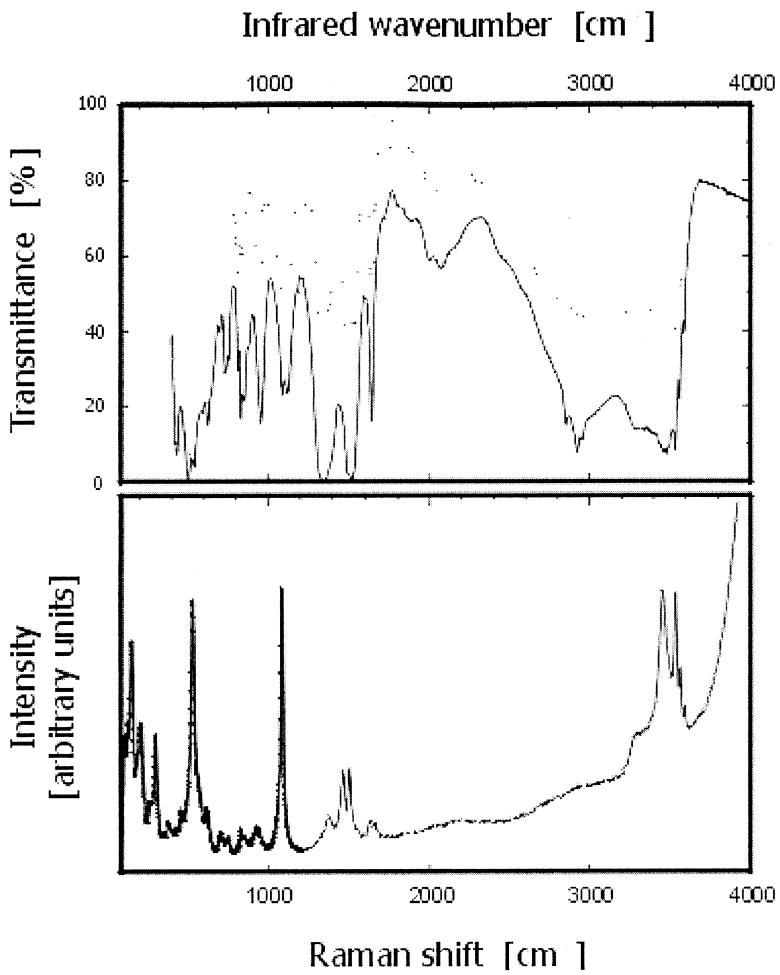

FIG. 4. Comparison of infrared-absorption (top) and Raman spectrum (bottom) for petterdite from the type locality. Infrared-absorption spectra were obtained from a single crystal (dotted line) and powder sample, which was prepared using the KBr pellet technique (solid line).

TABLE 4. X-RAY POWDER-DIFFRACTION DATA FOR PETTERDITE

Petterdite (This work)				Dundasite (Jambor *et al.* 1969)			Dundasite (PDF 33-731)		
I(rel)	d(meas)	d(calc)	hkl	I(rel)	d(meas)	hkl	I(rel)	d(meas)	hkl
-	-	-	-	5	8.85*	100*	-	-	-
100	7.937	7.934	110	100	7.91	110	100	7.94	110
30	6.091	6.069	120	30	6.07	120	11	6.08	120
50b**	4.686**	4.720	021	50	4.63	021	18	4.633	021
		4.675	111	20	4.57	111	16	4.587	111
20	4.533	4.540	200	20	4.52	200	11	4.54	200
30	4.373	4.373	210	20	4.36	210	6	4.375	210
10	4.099	4.080	040	5	4.11	121	4	4.092	040
20	3.964	3.967	220	20	3.96	220	4	3.97	220
5	3.736	3.722	140	<5	3.720	140	-	-	-
70	3.633	3.632	131	80	3.600	131	41	3.595	131
10b	3.495	3.489	211	5	3.490	230	-	-	-
		3.485	230						
20	3.336	3.334	041	20	3.300	041	8	3.308	041
40	3.270	3.272	221	50	3.230	221	23	3.243	221
<5b	3.175	3.130	141	-	-	-	-	-	-
30	3.084	3.072	150	60	3.090	141	18	3.08	150
20	3.038	3.036	240	30	3.030	240	10	3.04	240
30	2.975	2.976	310	40	2.968	310	13	2.976	310
10	2.887	2.893	002	20	2.800	002	8	2.810	002
40	2.718	2.727	022	20	2.729	060	4	2.728	060
		2.720	060						
		2.718	112						
		2.713	151						
-	-	-	-	5	2.697	151	5	2.701	151
40	2.690	2.687	241	50	2.666	241	14	2.674	241
		2.682	301	40	2.643	112	5	2.665	301
							4	2.658	022
							14	2.649	112
<5	2.641	2.646	311	-	-	-	4	2.630	311
		2.645	330						
-	-	-	-	<5	2.617	311	-	-	-
-	-	-	-	<5	2.524	321	-	-	-
20	2.440	2.440	202	<5	2.457	061	-	-	-
30	2.405	2.405	331	40	2.385	202	10	2.395	331
							10	2.389	202
-	-	-	-	<5	2.358	212	3	2.364	212
10b	2.340	2.337	222	10	2.337	260	3	2.339	260
		2.333	260						
-	-	-	-	-	-	-	2	2.317	042
-	-	-	-	<5	2.289	222	2	2.294	222
20	2.269	2.270	400	30	2.264	400	4	2.270	400
		2.258	170				3	2.265	170
10	2.223	2.226	232	20	2.218	350	5	2.222	350
10b	2.180	2.187	420	5	2.182	420	2	2.187	420
-	-	-	-	<5	2.158	261	-	-	-
30b	2.101	2.106	152	10	2.098	401	4	2.101	171
		2.104	171						
		2.094	242						
5	2.076	2.074	312	30	2.075	270	10	2.076	152
		2.074	270						
		2.072	351						
20	2.046	2.046	421	10	2.059	242	7	2.063	242
		2.040	080	20	2.035	421	2	2.046	080
				5	1.994	180	4	2.043	312
							6	2.038	421
10b	1.984	1.990	180	<5	1.978	440	3	1.9575	062
		1.984	440	10	1.956	062			
		1.982	062						
5b	1.933	1.936	162	<5	1.906	361	3	1.9228	081
		1.924	081						
20	1.874	1.877	023	10	1.867	441	3	1.8717	441
		1.876	441						
		1.874	113						
10	1.852	1.847	370	10	1.847	370	3	1.8505	370
10b	1.816	1.816	262	10	1.820	113	3	1.8261	023
							2	1.8233	113
30	1.781	1.786	402	10	1.796	262	5	1.7975	262
		1.782	133						
		1.780	172						
20	1.760	1.761	352	20	1.770	281	5	1.7705	281
		1.760	371	30	1.760	172	4	1.7658	402
							2	1.7577	371
5	1.746	1.744	043	40	1.741	460	3	1.745	460
		1.743	460						
10b	1.706	1.700	191	<5	1.716	530			
		1.697	432						
10b	1.648	1.651	531	+ 23 weak reflections					
10	1.588	1.587	550						
5	1.559	1.565	282						
		1.559	253						
		1.558	333						
5	1.530	1.531	512						
10	1.508	1.510	560						
		1.502	391						
5	1.489	1.493	462						
		1.484	2.10.1						
5b	1.467	1.468	481						
		1.467	173						
		1.464	1.11.0						
10b	1.440	1.446	004						
		1.446	423						
		1.441	621						
5	1.360	1.359	224						
		1.357	2.10.2						
10b	1.337	1.339	283						
		1.334	373						
20b	1.307	1.309	154						
		1.307	193						
		1.306	1.11.2						
		1.305	244						

* See text for discussion.

** This broad reflection is resolved into two reflections at d = 4.73 and 4.67 Å (I/I_{100} = 10 and 10, respectively) in the data measured with an automated X-ray powder diffractometer.

strong linkage role (Cocco *et al.* 1972). Some minor differences between the spectra of petterdite and dundasite are revealed upon closer inspection: obvious shifts of some peaks can be seen in the range 400–900 cm^{-1}, which represents a complex assemblage of peaks predominantly due to various lattice-vibration modes (*cf.* Farrell 1977). Some changes in the spectrum are also visible in the range 2800–3600 cm^{-1}, which reflects OH vibrations influenced by H bonding. As structural details for petterdite are not known, a more thorough discussion of the vibrational spectra is not possible.

The most intense Raman bands in the lattice region lie at 151, 207, 299, 532, and 1086 cm^{-1} (Fig. 4). (Note that the increasing background toward higher wavelengths in Figure 3 is due to luminescence phenomena.) These bands are interpreted as internal CO_3 modes, lattices modes, and combination modes involving the hydrous species. Apart from the 1085 cm^{-1} band, which is assigned to CO_3-stretching, a more detailed interpretation would be speculative owing to the dearth of structural information on petterdite. There are four narrow bands (strong modes at 3460 and 3535 cm^{-1}, and weak modes at 3565 and 3595 cm^{-1}) and a broad band at approximately 3300 cm^{-1} in the O–H stretching range. These bonds are assigned to OH groups located at four different sites (narrow bands) and to H_2O (broad band). The comparatively low frequencies suggest strong H bonding, in agreement with the IR data.

X-Ray Crystallography

X-ray powder-diffraction data for type petterdite (Table 4) were recorded using a Gandolfi camera 114.6 mm in diameter with Co$K\alpha$ radiation (λ = 1.79021 Å). The data were indexed and refined on the basis of an orthorhombic unit-cell with *a* 9.079(3), *b* 16.321(9), *c* 5.786(7) Å, *V* 857(1) $Å^3$ and assuming space group *Pbnm* (see below). The indexing is based on a theoretical powder pattern, calculated with the program Lazy Pulverix and using the structural positional parameters of dundasite (Cocco *et al.* 1972) and the above unit-cell parameters. The axial ratios for this unit cell are *a*:*b*:*c* 0.5563:1:0.3545. Another sample, measured with a 100-mm Guinier–Hägg camera and Cr$K\alpha$ radiation (Si internal standard), gave similar unit-cell parameters: *a* 9.050(7), *b* 16.325(20), *c* 5.795(2) Å, *V* 856(2) $Å^3$. X-ray data were also obtained for material from Callenberg using an automated powder diffractometer (Cu$K\alpha$ radiation, secondary monochromator, silicon sample holder); these gave a unit cell with parameters *a* 9.065(7), *b* 16.374(7), *c* 5.765(4) Å, *V* 855.8(8) $Å^3$, similar to those obtained for the type material. The diffractometer trace showed strong preferred orientation and unambiguously indicated that the platy face of the crystals is {010}. Because of this preferred orientation, a weak 020 reflection was also recorded at about 8.2 Å (this reflection is not present on either the Gandolfi or Guinier–Hägg film). No 100 reflection was recorded in

any of the three datasets, in agreement with the proposed space-group (*Pbnm*). With $Z = 4$, the calculated density for type petterdite is 3.947 g/cm^3 (for the empirical formula and the unit-cell volume derived from the Gandolfi film data).

A comparison of the indexed X-ray powder data for petterdite and dundasite (Table 4) clearly shows the close structural relationship between the two species. The unit-cell parameters *a* and *b* are similar for both minerals, whereas *c* is much larger for petterdite. In the dundasite structure, chains of edge-sharing $(Al,Cr)O_6$ octahedra run parallel to the *c* axis (Cocco *et al*. 1972). As the radius of six-coordinate Cr^{3+}, 0.615 Å (Shannon 1976), is larger than that of Al^{3+}, 0.535 Å, the chains of octahedra are obviously longer, therefore the *c* axis is longer and, consequently, the unit-cell volume is larger.

The choice of space group *Pbnm* for petterdite is based on that established for dundasite (Cocco *et al*. 1972). Although on PDF card 21–936 (citing Jambor *et al*. 1969), the space group of dundasite is given as *Pbmm*, this space group is not explicitly stated by Jambor *et al*. (1969). The only reflection in their powder pattern that would exclude space group *Pbnm* is a very faint reflection at $d = 8.85$ Å (I = 5), indexed as 100. It seems probable that this reflection is due to some impurity or measurement error, since the difference between this and the calculated value, $d = 9.05$ Å, is rather large, whereas an adjacent reflection at $d = 7.91$ Å (I = 100) agrees well with the calculated value (7.92 Å).

The space group of the closely related mineral dresserite, $BaAl_2(CO_3)_2(OH)_4{\bullet}H_2O$, is given by Jambor *et al*. (1969) as *Pbmm*, *Pb*2$_1$*m*, or *Pbm*2, based on evaluation of "poor quality" Weissenberg and precession photographs. Equally poor single-crystal photographs of dundasite "adequately indicate that it has the same space group as dresserite" (Jambor *et al*. 1969). PDF card 20–617 (citing Jambor *et al*.) gives the space group of dresserite as *Pbmm*. Jambor *et al*. (1977), in a re-examination of dresserite, noted that on precession films, weak *h*0*l* diffraction spots with $h \neq 2n$ are present; they concluded that dresserite has space group *Pbmm*. However, the structure of dresserite has not been successfully determined, and its powder data would also conform to space group *Pbnm*. The space group of the (possibly isostructural) mineral strontiodresserite, $SrAl_2(CO_3)_2(OH)_4{\bullet}H_2O$, could not be determined by Jambor *et al*. (1977); Roberts (1978), who investigated crystals free of any satellite reflections by the precession method, found systematic extinction conditions consistent with the space group *Pbnm* or *Pbn*2$_1$ for strontiodresserite.

A TEM study of type petterdite was conducted with a Philips CM200 electron microscope at 160 and 200 kV, but failed to shed additional light on the space-group problem, as the crystals quickly dehydrate under the beam and become amorphous after 2–10 seconds. Nonetheless, the briefly observable diffraction patterns are in accord with orthorhombic symmetry and a primitive lattice.

Origin

At both known localities, petterdite is a supergene mineral found in voids previously occupied by galena or in small crevices a few mm away. These features indicate that petterdite is a product of complex redox reactions associated with alteration of galena by Cr-bearing meteoric solutions. As the source of the Cr was crocoite containing Cr^{6+}, these solutions were probably nearly neutral to slightly reducing in order to provide Cr^{3+} for petterdite. A possible reaction is $3CrO_4^{2-} + 3PbS + 2CO_2 + H_2O + 3O_2 + 4H^+ \rightarrow PbCr^{3+}{}_2(CO_3)_2(OH)_4{\bullet}H_2O + 2Pb^{2+} + 3SO_4^{2-}$. The excess lead released into solution would precipitate as either cerussite or anglesite, depending on the solution's composition. During early oxidation of galena, sulfate would be high in solution and anglesite would dominate; with extended oxidation, the removal of all sulfate in solution would make cerussite the more stable phase (after removal of galena).

Conclusions

Petterdite is the Cr-dominant analogue of dundasite and is also isostructural with dresserite and strontiodresserite. The color and crystal habit of petterdite distinguish it from dundasite, although the powder patterns of both minerals are relatively similar. A complete solid-solution may exist between the two minerals.

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