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Paratooite-(La), a new lanthanum-dominant rare-earth copper carbonate from Paratoo, South Australia

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ABSTRACT

Paratooite-(La) is a new lanthanum-dominant rare-earth copper carbonate from the Paratoo copper mine, near Yunta, Olary district, South Australia. Paratooite-(La) occurs as sheaves and radiating sprays of blade-like to tabular pale blue crystals in thin fissures in a slaty country rock. Individual crystals are typically 50–200 μm in maximum dimension but <5 μm thick. Associated minerals include donnayite-(Y), kamphaugite-(Y), and bastnäsite-(La). Electron microprobe and CHN analyses gave: La_2O_3 26.47; Pr_2O_3 7.74; Nd_2O_3 8.15; Sm_2O_3 0.66; Gd_2O_3 0.85; Y_2O_3 0.72; CaO 7.57; SrO 3.15; Na_2O 3.3; CuO 5.77; F 0.24; CO_2 32.05; NO_2 1.12; −O=F −0.10; sum 100.03, yielding an empirical formula of $(La_{3.54}Ca_{2.94}Na_{2.32}Nd_{1.05}Pr_{1.03}Sr_{0.66}Y_{0.14}Gd_{0.10}Sm_{0.0.8})_{\Sigma 11.86}Cu_{1.58}(C_{15.84}N_{0.53})O_{47.76}F_{0.24}$. The simplified formula is $(REE,Ca,Na,Sr)_6Cu(CO_3)_8$ or possibly $REE_3(Ca,Sr)_2NaCu(CO_3)_8$. The mineral is pale turquoise-blue to pale blue in colour, transparent, with a pearly to vitreous lustre and a pale blue streak. No cleavage was observed but the morphology and TEM studies indicate a cleavage parallel to {100}. The Mohs hardness is estimated to be 4. The strongest lines in the X-ray powder pattern are [d_{obs} (I_{obs}) (*hkl*)]: 5.047 (53) (200); 4.786 (49) (021); 3.957 (43) (220); 3.468 (43) (012, 221); 2.927 (100) (202); 2.530 (52) (241); 2.344 (22) (420,103); 2.232 (20) (421). A synchrotron powder diffraction pattern was indexed on a primitive orthorhombic cell with a = 10.0862(5), b = 12.8088(6), c = 7.2360(4) Å, V = 934.8(1) Å^3 and Z = 2. The crystal structure of the new mineral could not be determined but powder diffraction data indicate the space group is probably *P*222, *Pmmm*, $P222_1$ or *Pmm*2. The measured density is 3.68(3) g/cm^3 and the calculated density is 3.78 g/cm^3. Paratooite-(La) is biaxial negative with α = 1.605(3), β = 1.696(3) and γ = 1.752(2); pleochroism is medium strong; X very pale bluish, Y and Z bluish (with greenish tint) with absorption $Z \approx Y >> X$. Paratooite-(La) is a supergene mineral which precipitated from mildly basic carbonated groundwaters. The mineral is named for the type locality.

Keywords: paratooite-(La), new mineral, rare-earth carbonates, Paratoo deposit, South Australia.

Introduction

The Paratoo Copper Mine is a small copper deposit located near the Paratoo Railway siding, some 30 km southwest of Yunta, on the western edge of the Olary Province of South Australia (32º41′S, 139º20′E). The deposit was worked intermittently between 1889 and the mid 1960s (Brown, 1908; Woodcock, 1966; Nixon, 1967). Further small-scale exploration work was also undertaken in the 1960s, but rare-earth mineralization at the site remained unrecognized until recently. Samples of a bright blue, spherulitic mineral collected and brought to our attention by Mr John Toma, an Adelaide mineral collector,

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proved to be a new yttrium rare-earth copper carbonate chloride hydrate, decrespignyite-(Y) (Wallwork *et al.*, 2002*a*). As part of the characterization of decrespignyite-(Y), additional material from the mine was collected by Maxine and Glynn Francis, of Whyalla, South Australia, on behalf of the South Australian Museum. Amongst the specimens they collected were some radiating sprays of a pale blue mineral which proved to be chemically and structurally distinct from decrespignyite-(Y), being a new lanthanum-dominant rare-earth copper carbonate. The characterization and description of this mineral, paratooite-(La) is the subject of this paper. The new mineral is named for the type locality, the Paratoo Copper Mine. The mineral and the name were approved by the Commission on New Minerals and Mineral Names (2005-020). The type material is held in the collection of the South Australian Museum, Adelaide (G29614).

Occurrence

An outline of the general geology and mineralization style of the Paratoo deposit (32º41′S 139º20′E) is given by Nixon (1967). The Paratoo deposit is one of many small base-metal deposits located in the Adelaide Geosyncline, a rift basin containing a thick (up to 15 km) Neoproterozoic sedimentary sequence overlain by Lower Cambrian carbonates (Lambert *et al.*, 1987; Preiss, 1987). The Cambro-Ordovician Delamerian Orogeny marked the end of sedimentation. The Callanna Group (Willouran) contains the oldest sediments of the Adelaide Geosyncline. The Callanna Group consists of large amounts of mainly basaltic, sub-aqueous volcanic rocks overlain by thick evaporitic, halite-rich, mixed carbonate and clastic sequences. The evaporites now crop out as numerous diapirs that intrude the younger Neoproterozoic and Lower Cambrian sediments. Diapirism was probably initiated by sediment loading during the Neoproterozoic-Lower Cambrian and, along with the associated faults, reactivated during the Delamarian Orogeny (Dyson, 2001). The Burra Group (Torrensian) overlies the Callanna Group. The copper mineralization at Paratoo is hosted in the Auburn dolomite, a lenticular silty and carbonaceous dolomitic unit in the upper Burra group (Drexel *et al*., 1993). In the immediate vicinity of the deposit, there is a breccia with carbonate matrix and intrusive diorites. The breccia body has been interpreted as a diapir (e.g. Preiss, 1987; Nixon, 1967); however, the absence of clear fragments from the Callanna Group suggests an alternative origin as a breccia generated by the intrusion of the diorite, as first suggested by Holt (1970). Hence, our favoured model for the generation of the Paratoo copper deposit involves hydrothermal fluid circulation driven by the intrusion of the diorite. The primary mineralization consisted of chalcopyrite ± magnetite in thin (<10 cm) quartz veins, as well as impregnations of copper sulphides and native copper (Nixon, 1967; Holt, 1970). The deposit was subjected to deep weathering, and sulphides are rarely found in the surface workings; malachite and chrysocolla are the most common copper minerals. No primary Y- or *REE* mineral has been observed on any specimen from the mine workings and dumps, and the source of the *REE* and their mobility is not clear. Further work is in progress to decipher whether the *REE* were pre-enriched in the sediment, or were introduced with the hydrothermal fluid, or later during weathering. All other elements found in the secondary mineral assemblage are derived from the hydrothermal mineralization (mainly Cu), from the host rock (e.g. carbonate and probably the Sr found in paratooite-(La) and donnayite-(Y), or from the groundwater (e.g. Cl in decrespignyite-(Y)).

Paratooite-(La) occurs with a number of other rare-earth minerals including pale greyish globular kamphaugite-(Y), colourless to pale grey pseuohexagonal plates of donnayite-(Y) and pale greenish blue to pale blue globular bastnäsite-(La). All three species appear to have formed before paratooite-(La). Other minerals associated with paratooite-(La) include malachite, nontronite, and 'limonite' pseudomorphs after pyrite. Paratooite-(La) does not occur in direct association with decrespignyite-(Y). Other rare-earth minerals found at the deposit, but not in direct association with paratooite-(La), include pale white crusts and plate-shaped pseudomorphs of caysichite-(Y), pinkish-white acicular crystals of a Y-rich calcio-ancylite-(Nd) and thin seams of tengerite-(Y). More details of this interesting rare-earth mineral assemblage at the Paratoo Copper Mine will be published in the near future (Kolitsch *et al.*, 2006).

Paratooite-(La) formed as a supergene mineral on narrow fissures of a fine-grained, inhomogeneous albitized dolomitic slatestone. The rare-earth carbonate assemblage contains caysichite-(Y) for which Hogarth *et al.* (1974) suggested transportation in mildly acidic carbonated groundwaters, with precipitation occurring when the pH was increased to a value approaching neutrality.

Both the association with malachite, donnayite-(Y) and chalcedony, and the presence of other minerals found at the mine site, such as chrysocolla, calcite, gypsum, celestite and baryte, suggest that mineral formation took place under conditions of intense weathering in an arid climate, probably at neutral or slightly basic pH and oxidizing conditions (Williams, 1990), with evaporation of saline groundwaters playing an important role. The pH probably did not exceed a value of 9.5 since this is the maximum value of groundwaters in the natural environment (Garrels and Christ, 1965). The presence of goethite pseudomorphs after pyrite also indicates that weathering processes have proceeded under arid conditions (Boyle, 1997). The absence of Ce in paratooite-(La) indicates that it was fractionated as Ce^{4+} elsewhere consistent with formation under oxidizing conditions.

Physical and optical properties

Paratooite-(La) forms sheaves and radiating sprays of blade-like to tabular pale blue crystals in thin fissures in the slaty country rock. Typically the mineral occurs on crusts of 'pseudohexagonal' donnayite-(Y) crystals (Fig. 1). Individual blade-like crystals are up to 200 μm long, 30 μm wide but <5 μm thick. The groups of free-grown crystals have a somewhat ragged appearance (Fig. 2). The colour of paratooite-(La) varies from a pale turquoise-blue (111 D of the Royal Horticultural Society colour (RHSC) chart to pale-blue (113 C) and the streak is pale-blue (112 D). The mineral is transparent with a vitreous to pearly lustre. In thin section paratooite-(La) is very pale blue. Optical properties were determined using Cargille immersion liquids in white light. Paratooite-(La) is biaxial negative with $\alpha = 1.605(3)$, $\beta = 1.696(3)$ and $\gamma = 1.752(2)$. Pleochroism is medium strong; X very pale bluish, Y and Z bluish (with greenish tint) with absorption $Z \approx Y >> X$. The 2V and the dispersion could not be measured but the calculated 2V is 72.6º. Neither short-wave (253 nm) nor long-wave ultraviolet light excitation (366 nm) resulted in notable discernible luminescence. The density was measured using the suspension method, with Clerici solution diluted with water, and found to be 3.68(3) g/cm^3. This value is somewhat lower than the calculated density of 3.78 g/cm^3 (calculation based on the empirical formula) and the difference is possibly due to small amounts of air being trapped in the radiating sprays of crystals. The Mohs hardness of aggregates of paratooite-(La) crystals is 2; that of the individual crystals could not be measured but is estimated to be 4, based on the hardness of other *REE* carbonates. No cleavage was observed but the morphology would suggest that cleavage would be on {100}. Transmission electron microscopy (TEM) studies also indicate a cleavage on {100}

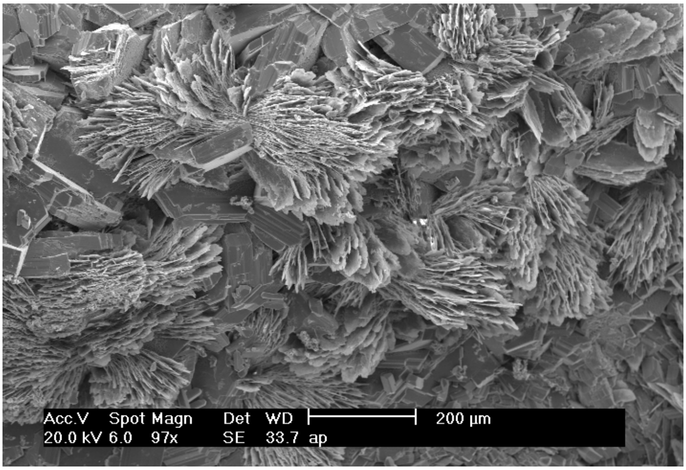

FIG. 1. SEM image of sheaf-like aggregates of paratooite-(La) crystals. The large thick plates intergrown with paratooite-(La) are donnayite-(Y) crystals.

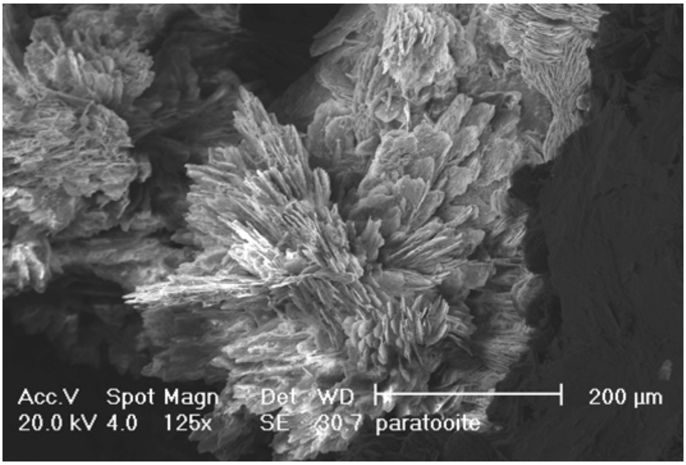

FIG. 2. SEM image of a single paratooite-(La) rosette, showing the indistinctly lath-like habit of the thin plates.

as crushed grain mounts fall in the [100] zone orientation.

Chemistry

Chemical analyses of paratooite-(La) were performed using a Cameca CAMEBAX SX51 electron microprobe operated at 15 kV and a specimen current of 20 nA. The spot size was set at 5 µm in order to reduce beam damage and volatilization. The standards used for wavelength-dispersive analysis were LaF_3, PrF_3, NdF_3, Y, Sm, Gd and Cu metals, wollastonite (Ca), celestite (Sr), albite (Na) and CaF_2 (F). Care was taken when selecting background positions to avoid overlaps with lines of *REE*. In addition to the elements reported above the following elements were sought but not found: Si, P, Al, Ce, Tb, Dy, Er, Lu, Ho and Cl. No other elements with $Z > 9$ were detected by a WDS scan. Carbonate, nitrate and water contents were determined by CHN analysis on a carefully hand-picked sample of ~20 µg from the type specimen. The CHN analysis showed 0.26% H which translates to 2.34% H_2O. However, the infrared (IR) and Raman spectra show no evidence of O-H stretching or H-O-H bending bands and the H_2O content maybe be due to absorbed water, or possibly due to a small amount of an impurity phase such as bastnäsite-(La). We have therefore chosen an anhydrous carbonate for the simplified formula. Analytical data are summarized in Table 1. Calculation of the empirical formula posed problems, as the mineral has no clear close relationship to any other mineral or synthetic compound. An inspection of the average volume occupied by anions (O,F,Cl) in various yttrium rare-earth carbonates gave a figure of ~19 Å^3 per anion. This indicated a formula based on 48 anions in the unit cell. The formula calculated on the basis of 48 anions give 1.58 Cu and 11.86 large cations. It is highly improbable that Cu and the *REE* would occupy the same crystallographic sites in the crystal structure, so we have adopted a composition

TABLE 1. Electron microprobe analysis of paratooite-(La).

Constituent	Wt. %	Range (48 anions)	Atoms
Y_2O_3	0.72	0.58–0.75	0.14
La_2O_3	26.47	25.4–27.3	3.54
Pr_2O_3	7.74	7.5–7.9	1.03
Nd_2O_3	8.15	7.5–8.4	1.05
Sm_2O_3	0.66	0.5–1.0	0.08
Gd_2O_3	0.85	0.7–1.0	0.10
CaO	7.57	6.9–8.1	2.94
SrO	3.15	2.6–3.7	0.66
CuO	5.77	5.6–6.2	1.58
Na_2O	3.30	3.2–3.6	2.32
F	0.24	0.0–0.5	0.24
CO_2*	32.05	32.05	15.84
NO_2*	1.12	1.12	0.53
$-H_2O$*	2.34	2.34	
O less for F	−0.10		
Total	100.03		

* CO_2, NO_2 and H_2O were determined by CHN analysis. H_2O is probably due to adsorbed water or impurity (see text)

based on separate sites for the large cations and for Cu. The stoichiometry of the empirical formula, $(La_{3.54}Ca_{2.94}Na_{2.32}Nd_{1.05}Pr_{1.03}Sr_{0.66}Y_{0.14}Gd_{0.10}Sm_{0.08})_{\Sigma 11.86}Cu_{1.58}(C_{15.84}N_{0.53})O_{47.76}F_{0.24}$, looks odd due to a small excess of CO_2 and NO_2. We are uncertain as to whether the 0.34 wt.% N found in the CHN analysis is structurally bound or an impurity or artefact; if it is not included in the calculation of the formula then the stoichiometry is $(La_{3.62}Ca_{3.00}Na_{2.37}Nd_{1.08}Pr_{1.05}Sr_{0.68}Y_{0.14}Gd_{0.10}Sm_{0.08})_{\Sigma 12.12}Cu_{1.61}C_{16.20}O_{47.72}F_{0.28}$. The simplified formula is therefore $(REE,Ca,Na,Sr)_6Cu(CO_3)_8$, or possibly $REE_3(Ca,Sr)_2NaCu(CO_3)_8$, with $Z = 2$.

Paratooite-(La) quickly reacts with dilute HCl with effervescence. The mineral dissolves slowly in cold 10% HNO_3, but reacts rapidly, with effervescence and discolouration, when the solution is heated.

X-ray and electron diffraction studies

X-ray powder diffraction patterns of paratooite-(La) were obtained using a 100 mm diameter Guinier-Hägg camera with Cr-$K\alpha_1$ radiation (λ = 2.28970 Å) and Si as an internal standard. As part of an ongoing investigation into the determination of crystal structures of microcrystalline minerals by *ab inito* powder X-ray diffraction (XRD) methods, a powder diffraction pattern of paratooite-(La) was collected using synchrotron radiation (λ = 0.7012 Å) on a high-resolution powder diffractometer at the Photon Factory at Tsukuba, Japan (Wallwork *et al.*, 2002*b*, 2003). Attempts to solve the crystal structure from these data were not successful, but by fitting the diffraction pattern using the Le Bail profile fitting method with RIETICA (Le Bail *et al.*, 1988; Hunter, 1998) the following primitive orthorhombic unit cell was obtained: a = 10.0862(5), b = 12.8088(6), c = 7.2360(4) Å, V = 934.8(1) Å^3. The indexed powder diffraction data indicate no systematic absences except possibly $00l = 2n + 1$, which limits the space group to one of $P222$, $Pmmm$, $P222_1$ or $Pmm2$ (including $P2mm$ and $Pm2m$). The two different diffraction patterns are summarized in Table 2.

Electron diffraction patterns were obtained using a JEOL 200cx transmission electron microscope operating at an accelerating voltage of 200 kV. Diffraction patterns down the [100] axis were readily obtained and confirmed the b and c repeats but it was not possible to get electron diffraction patterns containing the a repeat due to the highly platy habit of the mineral. Diffraction patterns obtained are consistent with a primitive orthorhombic lattice.

Vibrational spectroscopy

Single-crystal laser-Raman spectra of paratooite-(La) were recorded in the range from 3800 to 100 cm^{-1} with a Renishaw Ramascope 1000 using a laser wavelength of 785 nm (red laser) and excitation through a Leica DMLM optical microscope (Si standard, spectral resolution ±4 cm^{-1}, minimum lateral resolution ~2 µm, unpolarized laser light, random sample orientation). A typical Raman absorption spectrum of

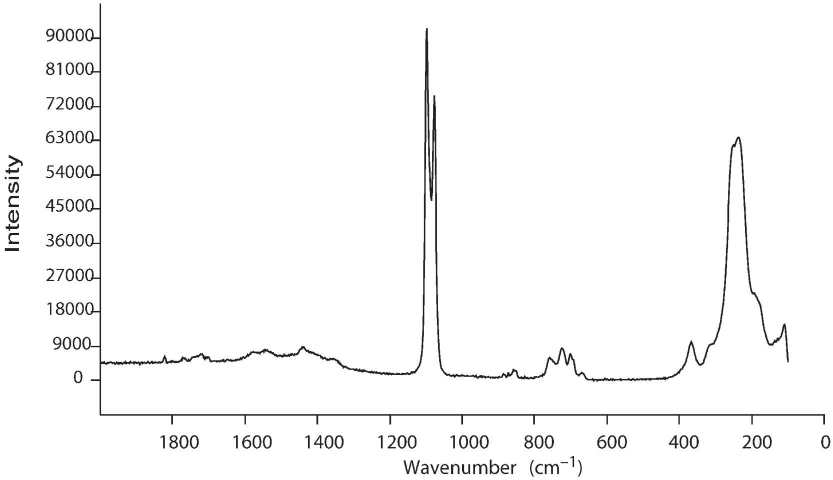

FIG. 3. Raman spectrum of paratooite-(La) showing two strong peaks at ~1100 cm^{-1} indicating at least two different CO_3 stretching bands.

TABLE 2. X-ray powder diffraction data for paratooite-(La).

	Synchrotron[1]		Guinier Hägg[2]			
I/I_o	d_{obs}	d_{cal}	d_{obs}	*h*	*k*	*l*
5	10.09	10.087		1	0	0
25	6.40	6.405	6.406	0	2	0
7	6.30	6.301	6.303	0	1	1
9	5.34	5.343	5.351	1	1	1
53	5.04	5.043	5.047	2	0	0
49	4.80	4.796	4.786	0	2	1
16	4.33	4.331	4.331	1	2	1
5	4.27	4.270	4.259	0	3	0
2	4.14	4.137		2	0	1
43	3.96	3.962	3.957	2	2	0
3	3.94	3.937		2	1	1
9	3.68	3.677	3.674	0	3	1
10	3.62	3.618		0	0	2
43	3.48	3.482	3.468	0	1	2
				2	2	1
3	3.45	3.455		1	3	1
6	3.36	3.362	3.372	3	0	0
13	3.20	3.202	3.190	0	4	0
5	3.15	3.150		0	2	2
16	2.97	2.971		2	3	1
				3	1	1
100	2.94	2.940	2.927	2	0	2
52	2.93	2.928		0	4	1
36	2.87	2.865		2	1	2
3	2.81	2.812		1	4	1
7	2.76	2.760	2.757	0	3	2
6	2.70	2.703	2.699	2	4	0
6	2.67	2.672		2	2	2
6	2.64	2.641	2.645	3	3	0
52	2.53	2.532	2.530	2	4	1
37	2.52	2.522		4	0	0
4	2.42	2.421		2	3	2
8	2.37	2.370		0	1	3
22	2.35	2.346	2.344	4	2	0
				1	0	3
14	2.34	2.341		4	1	1
8	2.26	2.257	2.254	0	2	3
20	2.23	2.232	2.232	4	2	1
14	2.17	2.166		2	4	2
3	2.15	2.145		2	1	3
32	2.13	2.135		0	6	0
				3	3	2
14	2.10	2.100		0	3	3
17	2.08	2.080		4	3	1
18	2.07	2.069		4	0	2
27	2.06	2.060		2	2	3
				1	3	3
28	2.05	2.048		0	6	1
				1	5	2
15	2.04	2.042		4	1	2
				3	5	0
16	2.02	2.017		5	0	0
25	2.01	2.007		1	6	1
4	1.99	1.993		5	1	0
56	1.97	1.969		4	2	2
4	1.95	1.952		3	4	2
5	1.94	1.939		2	3	3
				3	1	3
6	1.93	1.931		2	5	2
				0	4	3
42	1.91	1.911		4	4	1
22	1.90	1.897		2	6	1
10	1.89	1.892		1	4	3
3	1.87	1.874		3	2	3
5	1.86	1.862		4	3	2
23	1.81	1.809		1	6	2
				3	6	0
				1	7	0
				2	4	3
				4	5	0
28	1.79	1.791		0	1	4
				0	5	3
				4	4	2
				1	5	3
				2	6	2
				4	1	3
10	1.69	1.688		2	1	4
12	1.68	1.682		4	2	3
2	1.68	1.681		6	0	0
13	1.67	1.673		2	7	1
				3	4	3
				6	1	0
				0	3	4
8	1.66	1.661		5	4	1
				2	5	3
6	1.65	1.646		2	2	4
5	1.64	1.643		1	3	4
15	1.63	1.629		5	3	2
				6	2	0
4	1.62	1.624		6	1	1
8	1.61	1.614		4	3	3
				3	6	2
3	1.60	1.601		0	8	0
18	1.59	1.590		4	6	1
				6	2	1
5	1.58	1.575		0	4	4
5	1.57	1.569		3	7	1
19	1.53	1.531		4	4	3
				6	3	1
				2	8	0
19	1.52	1.525		6	0	2
				2	6	3
9	1.49	1.488		6	4	0
				4	6	2
10	1.48	1.483		6	2	2
				0	5	4
25	1.46	1.464		0	8	2
				1	5	4

TABLE 2 (*contd.*)

	Synchrotron[1]		Guinier Hägg[2]			
I/I_o	d_{obs}	d_{cal}	d_{obs}	*h*	*k*	*l*
				4	1	4
				6	4	1
				0	7	3
4	1.44	1.441		4	5	3
				6	3	2
2	1.43	1.433		4	2	4
4	1.38	1.383		1	9	1
				6	4	2
8	1.35	1.350		4	6	3
				6	2	3
2	1.32	1.325		5	5	3
3	1.31	1.313		1	9	2
8	1.30	1.299		6	6	1
5	1.29	1.293		7	4	1
8	1.28	1.281		2	9	2
27	1.27	1.267		6	4	3
				4	8	2
17	1.26	1.262		4	7	3
				0	10	1
				8	0	0
				0	5	5

[1] high-resolution powder diffractometer, synchrotron radiation (λ = 0.7012 Å), d_{obs} extracted by the Le Bail fit of diffraction pattern.

[2] 100 mm Guinier-Hägg camera, Cr-$K\alpha$ radiation (λ = 2.2909 Å); Si internal standard. Intensities determined from the Le Bail fit.

paratooite-(La) is shown in Fig. 3. It is dominated by two strong, narrow bands at 1095 and 1075 cm^{-1} that are assigned to stretching vibrations of CO_3 groups. The observation of two discrete bands instead of one, suggests that there may exist at least two different CO_3 sites with slightly differing symmetries in this carbonate structure. There were no Raman bands in the region between 3300 and 3500 cm^{-1}, consistent with an anhydrous composition (cf. Wallwork *et al.*, 2002*a*). Vibrational bands with frequencies <1000 cm^{-1} are very similar to those observed in decrespignyite-(Y) by Wallwork *et al.* (2002*a*) and are attributed to bending vibrations of the CO_3 groups, vibrations of the metal−oxygen polyhedra and lattice vibrations. The infrared spectrum was measured on a BioRad FTS40A infrared spectrometer on a powdered sample of paratooite-(La) between KBr discs. The spectrum shows a strong absorption band at 1490 cm^{-1} but no bands were observed in the 3300 to 3800 cm^{-1} region confirming the absence of H_2O or OH.

Relationship to other minerals

Paratooite-(La) is the second transition metal-bearing rare-earth carbonate mineral to be described, the other being decrespignyite-(Y), also from the Paratoo Copper Mine (Wallwork *et al.*, 2002*a*). To the best of our knowledge, there are no synthetic compounds of this type. Establishing possible structural relationships for paratooite-(La) is, therefore, somewhat difficult. A notable feature which emerges when paratooite-(La) is compared with other Y/*REE* minerals is that the refractive indices are similar to minerals of the bastnäsite-synchysite-parisite group. For example, the refractive indices for synchysite-(Nd) are 'Nx 1.61, Ny 1.66 and Nz 1.74' (Gaines *et al.*, 1997) while those of paratooite-(La) are α = 1.605(3), β = 1.696(3) and γ = 1.752(3). It is notable that in these highly birefringent carbonates, all carbonate groups are arranged either parallel to or perpendicular to the optic axis. The arrangement of carbonate groups in kamphaugite-(Y) is that of a corrugated sheet perpendicular to the optic axis and the birefringence accordingly is low. This suggests that, structurally, paratooite-(La) is probably more closely related to the bastnäsite-synchysite-parisite group than to kamphaugite-(Y) .

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References

Boyle, D.R. (1997) Iodargyrite as an indicator of arid climatic conditions and its association with gold-bearing glacial tills of the Chibougamau-Chapais area, Quebec. *The Canadian Mineralogist*, **35**, 23–34.

Brown, H.Y.L. (1908) *The Mines of South Australia*. Reprint of 4th edition, C. E. Bristow, Adelaide, Australia, 382 pp.

Drexel, J.F., Preiss, W.V. and Parker, A.J. (1993) The geology of South Australia. *Geological Survey of South Australia Bulletin*, **54**, 177–185.

Dyson, I.A. (2001) The diapir–base metal association in the northern Flinders Ranges. *MESA Journal*, **22**, 37–43.

Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B. and Rosenzweig, A. (1997) *Dana's New Mineralogy*, 8th edition, Wiley and Sons New York.

Garrels, R.M. and Christ, C.L. (1965) *Solutions, Minerals, and Equilibria*. Harper & Row, New York.

Hogarth, D.D., Chao, G.Y., Plant, A.G. and Steacy, H.R. (1974) Caysichite, a new silico-carbonate of yttrium and calcium. *The Canadian Mineralogist*, **12**, 293–98.

Holt, G.E. (1970) *Geology of the Paratoo diapir, S.A.* Unpublished Honours Thesis, Department of Economic Geology, The University of Adelaide, Adelaide, 28 pp.

Hunter, B.A. (1998) Rietica – A Visual Rietveld Program. *Commission on Powder Diffraction Newsletter*, **20**, 21.

Kolitsch, U., Pring, A., Brugger, J. and Elliott, P. (2006) Caysichite-(Y), donnayite-(Y), kamphaugite-(Y) and other rare-earth carbonates from the Paratoo copper mine, South Australia (in prep.).

Lambert, I.B., Knuston, J., Donnelly, T.H. and Etminan, H. (1987) Stuart Shelf–Adelaide Geosyncline copper province, South Australia. *Economic Geology*, **82**, 108–123.

Le Bail, A., Duroy, H. and Fourquet, J.L. (1988) Ab-initio structure determination of $LiSbWO_6$ by X-ray powder diffraction. *Materials Research Bulletin*, **23**, 447–452.

Nixon, L.G.B. (1967) Paratoo copper deposit. *Mining Review (Adelaide)*, Volume Date **1965**, No. **123**, 8–20.

Preiss, W.V. (1987) The Adelaide Geosyncline – late Proterozoic stratigraphy, sedimentation, palaeontology and tectonics. *Geological Survey of South Australia, Bulletin*, **53**.

Wallwork, K.S., Kolitsch, U., Pring, A. and Nasdala, L (2002*a*) Decrespignyite-(Y), a new copper yttrium rare-earth carbonate chloride hydrate from Paratoo, South Australia. *Mineralogical Magazine*, **66**, 165–172.

Wallwork, K.S., Pring, A., Taylor, M.R. and Hunter, B.A. (2002*b*) Structure solution of priceite, a basic hydrated calcium borate, by *ab initio* powder-diffraction methods. *The Canadian Mineralogist*, **40**, 1199–1206.

Wallwork, K.S., Pring, A., Taylor, M.R. and Hunter, B.A. (2003) Structure solution of the hydrated aluminum phosphate, kingite, by *ab initio* powder diffraction methods. *American Mineralogist*, **88**, 235–239.

Williams, P.A. (1990) *Oxide Zone Geochemistry*. Ellis Horwood, New York, 286 pp.

Woodcock, J.T. (1966) *Treatment of Oxidized Copper Ore from Paratoo, South Australia*. CSIRO Mineralogy Department, University of Melbourne, Ore Dressing Invest., Report No. **666**, 9 pp.

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