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# An occurrence of lead oxycarbonate ($PbCO_3$.PbO) as a mine fire product at Broken Hill, New South Wales

THE progressive and controlled thermal decarbonatization of lead carbonate to lead oxide at elevated temperatures has been studied in considerable detail by a number of workers (see Grisale and White, 1964; Ware and Bayliss, 1962, and references therein). Thermal decomposition yields a number of lead oxycarbonates including $PbCO_3$.PbO as intermediate products. The conditions leading to the formation of the lead oxycarbonates are generally not found in nature, consequently these compounds are not known as minerals. In this note we report the identification of $PbCO_3$.PbO on specimens from the Kintore Opencut, Broken Hill, New South Wales. The Kintore Opencut is a large opencast mine development which straddles three of the original mining leases at Broken Hill, Blocks 9, 10 and 11. The opencut has been operated by Minerals, Mining and Metallurgy Ltd since 1984 to recover ore remnants and stope-fill left behind by the underground mining operations of the late 1800s and early 1900s. The complex secondary mineralogy exposed by this mining development has been reviewed by Birch and van der Heyden (1988).

FIG. 1. Lead oxycarbonate pseudomorphs after arrowhead twins of cerussite, up to 2 cm long. (Museum of Victoria Specimen M38235).

The lead oxycarbonate ($PbCO_3$.PbO) was found as part of old fill material, rather than *in situ*, at the north end of the opencut, on the 280 R.L. bench, about 60 m from the surface. It forms white, clay-like, slightly waxy pseudomorphs after reticulated and arrowhead cerussite twins up to 1 cm across (Fig. 1) and also occurs as irregular patches in the host rock matrix which is a granular quartz spessartine metamorphic rock known locally as "garnet sandstone". It is most likely that the lead oxycarbonate was formed by the roasting of cerussite during underground mine-fires on the Block 11 lease early in 1906 (van der Heyden, pers. comm., 1988). Minium has been reported as a post mine-fire product, also pseudomorphing cerussite (Skinner and McBriar, 1958; Birch *et al.*, 1983).

A powder X-ray diffraction pattern was obtained using a 100mm diameter Guinier-Hägg camera with Cu-*Kα* radiation, with Si as an internal standard. The reflections in the diffraction pattern were somewhat broad which is indicative of the very fine-grained nature of the material. The diffraction pattern was found to match those previously published for $PbCO_3$.PbO (Pannetier *et al.*, 1964; Grisale and White, 1964), but contained a number of additional reflections attributed to admixed cerussite and hydrocerussite. Since published powder X-ray diffraction patterns of $PbCO_3$.PbO are unindexed an attempt was made to find the unit cell for the Kintore material using the computer indexing program of Visser (1969). This was unsuccessful, but an orthorhombic unit cell was obtained using the powder pattern for the synthetic material of Pannetier *et al.* (1964). Using this cell it was then possible to index and refine the unit cell for the Kintore $PbCO_3$.PbO. The full indexed diffraction pattern for $PbCO_3$.PbO from the Kintore Opencut is presented in Table 1, the final cell parameters being $a = 9.323(9)$, $b = 8.996(9)$, $c = 5.143(6)$ Å. This unit cell is in accord with the optical measurements of Grisale and White (1964), which suggested orthorhombic symmetry. The $c$ parameter is similar to the *a* parameter of cerussite (5.14–5.15 Å), possibly indicating some common structural feature.

Table 1. Powder X-ray diffraction data for $PbCO_3.PbO$ from Kintore Opencut, Broken Hill, New South Wales.

| $I/I_o$ | $d._{obs}$ | $d._{cal}$ | hkl |
|---|---|---|---|
| 20 | 6.396 | 6.474 | 110 |
| 2 | 4.638 | 4.661 | 200 |
| 5 | 4.451 | 4.465 | 011 |
| 50 | 4.118 | 4.138 | 210 |
| 60 | 4.007 | 4.027 | 111 |
| 5 | 3.492 | 3.454 | 201 |
| 30 | 3.379 | 3.386 | 021 |
| 5 | 3.273 | 3.237 | 220 |
| 100 | 3.220 | 3.224 | 211 |
| 100 | 3.175 | 3.183 | 121 |
| 30 | 2.932 | 2.937 | 310 |
| 50 | 2.857 | 2.854 | 130 |
| 30 | 2.656 | 2.659 | 301 |
| 35 | 2.569 | 2.572 | 002 |
| 5 | 2.488 | 2.479 | 102, 131 |
| 20 | 2.329 | 2.331 | 400 |
| 25 | 2.290 | 2.289 | 321 |
| 25 | 2.255 | 2.252 | 202, 410 |
| 7 | 2.232 | 2.232 | 022 |
| 20 | 2.182 | 2.184 | 212, 140 |
| 10 | 2.158 | 2.158 | 330 |
| 20 | 2.063 | 2.066 | 411, 041 |
| 5 | 2.014 | 2.014 | 222, 141 |
| 15 | 1.935 | 1.935 | 312 |
| 15 | 1.911 | 1.911 | 132 |
| 5 | 1.885 | 1.885 | 241 |
| 5 | 1.819 | 1.822 | 340 |
| 10 | 1.736 | 1.732 | 431 |
| 15 | 1.720 | 1.721 | 511, 520 |
| 5 | 1.704 | 1.699 | 051 |
| 10 | 1.581 | 1.583 | 530 |

Cell parameters $a = 9.323(9)$ Å, $b = 8.996(9)$ Å, $c = 5.143(6)$ Å.

Table 2. Chemical Analysis of $PbCO_3.PbO$ from Kintore Opencut, Broken Hill, New South Wales.

| | 1 | 2 |
|---|---|---|
| PbO | 90.4<br>(89.7-91.1) | 91.03 |
| $SO_3$ | 0.1<br>(0.06-0.14) | --- |
| $CO_2$ | 9.7 | 8.97 |
| Total | 100.2 | 100.0 |

1. $PbCO_3.PbO$ from Kintore Open cut, Broken Hill, New South Wales. Pb and S determined by electron microprobe and $CO_2$ by TGA

2. $PbCO_3.PbO$

The chemical analysis of lead oxycarbonate from Kintore Opencut is presented in Table 2. Lead was determined using a JEOL electron microprobe at 15 kV with a nominal specimen current of 0.020 μA. The standards used were galena (Pb) and sphalerite (S). No other elements with an atomic number greater than eight were detected by wavelength spectroscopy. Carbon dioxide and water were determined by TGA with simultaneous mass spectrometry. The empirical formula calculated on the basis of 4 oxygens is $Pb_{1.91}C_{1.04}O_4$, in good agreement with the expected formula.

The thermal gravimetric analysis was performed under oxygen (flow rate of 40 ml/min) and with a heating rate of 10°C/min. A small amount of absorbed water and hydroxide (from the admixed hydrocerussite?) was evolved between 240/360°C, while $CO_2$ was given off in two steps with a small amount between 240 and 360°C and the main decarbonatization step occurring between 360 and 510°C. Above 510°C the sample was found to take up oxygen due to partial oxidation of the lead oxide, which then underwent reduction.

Lead oxycarbonate, $PbCO_3.PbO$, is a well known product of the thermal decomposition of cerussite. Grisale and White (1964) found that $PbCO_3.PbO$ forms from $PbCO_3$ via the intermediate phase $2PbCO_3.PbO$ in a $CO_2$ atmosphere. At 1 atmosphere of $CO_2$, $PbCO_3.PbO$ is stable between 283° (+/−15°) C and 373° (+/−15°) C; at the higher temperature $PbCO_3.2PbO$ is formed. Ware and Bayliss (1962) found that $PbCO_3$ decomposes to $PbCO_3.PbO$ at 340°C and $PbCO_3.PbO$ decomposes to $PbCO_3.2PbO$ at 390°C and this in turn goes to PbO at 440°C. However the temperatures of these reactions vary with the nature of the atmosphere under which the experiments were performed; for example in an oxygen-rich atmosphere these reactions occur at slightly higher temperatures.

There is no evidence from either the X-ray powder pattern (which shows traces of cerussite and hydrocerussite) or the TGA data for the Kintore lead oxycarbonate for the presence of either $2PbCO_3.PbO$ or $PbCO_3.2PbO$ in the samples. It is therefore possible that a considerable amount of air surrounded the cerussite when it underwent decarbonatization in the mine fire and that the temperature did not exceed 390°C. The small amount of hydrocerussite found with the lead oxycarbonate appears to be a post-fire product and may be the result of partial hydration of some of the $2PbCO_3.PbO$. It seems likely, since $PbCO_3.PbO$ and minium (Skinner and

McBriar, 1958) have been found as fire products at Broken Hill, that the lead oxycarbonates, $2PbCO_3.PbO$ and $PbCO_3.2PbO$, may also occur.

The status of the lead oxycarbonate from Broken Hill has been clarified by a vote of the IMA Commission for New Minerals and Mineral Names. It is not a mineral since it formed as the result of an artificial process (the mine fire).

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# Copper–aluminium analogues of hydrohonessite and honessite, and woodwardite relationships

AN old nickel mine at Craignure (NM 995011) about 12km southwest of Inveraray, Argyll and Bute District, Scotland, was worked before 1845 (Wilson, 1921). It lies on Forestry Commission ground, very close to one of the numerous, small tributaries of Abhainn Dubhan; and a forest road separates the mine adit to the north from small dumps just to the south. Primary ore collected from the dump close to the mine consists of rapidly oxidizing pyrrhotine and pentlandite, with chalcopyrite. Slightly downstream a small rock dump contains blue-green, copper–aluminium analogues of hydrohonessite and honessite which partially coat rocks at the surface of the dump. The general lithology of dump material is a chlorite schist with narrow quartz veins and calcite-rich bands. The hydrohonessite and honessite Cu–Al analogues form incoherent, multi-layer coatings, stringers, and pocket linings. On one specimen botanical debris is coated thus indicating a very recent origin.

Close on 40 X-ray powder photographs from tiny grains (unground) reveal coatings, in the main, to be mixtures of hydrohonessite and honessite/takovite-like phases. Reevesite is present also as fluffy, citron yellow coatings. The quality of X-ray powder photographs is rather poor (apart from reevesite) with broad reflections and high backgrounds. Nevertheless, when combined with infrared and chemical data it is possible