

## Composition of Pyromorphites from Broken Hill, New South Wales

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**ABSTRACT.** Twenty eight specimens of pyromorphite from the oxidised zone of the Broken Hill orebody, New South Wales have been analysed using EPMA methods. Material was selected to represent all of the varieties of pyromorphite which have been described by earlier workers as occurring in the deposit. Aside from minor  $\text{Ca}^{2+}$  substitution for  $\text{Pb}^{2+}$  and occasionally  $\text{VO}_4^{3-}$  for  $\text{PO}_4^{3-}$ , all specimens examined proved to be either pure end-member pyromorphite or arsenian pyromorphite with a maximum arsenate content corresponding to  $\text{pyr}_{2.1}\text{mim}_{0.9}$ . In one specimen phosphate-arsenate zoning is evident; minor vanadate is present in the more arsenian material. Calcium-lead zoning has been detected in a pale grey-coloured specimen. These zoning patterns indicate chemical variations in aqueous solution during crystal growth. The arsenate contents appear to be directly related to the original distribution of the primary arsenides and arsenic-bearing sulfosalts. The compositions have been related to those of the solutions from which they crystallised. Apatite is a major accessory in the primary ore and this would provide the requisite phosphate ions.

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The Broken Hill, New South Wales, Australia orebody is one of the largest and most productive base metal (Ag-Pb-Zn) deposits ever exploited. Leases were pegged on the outcrop in 1883 and mining has been continuous since that time. The centenary of ore production has recently been marked by a volume (Worner & Mitchell, 1982) which describes the geology and mining history, but which concentrates on mineralogical aspects of the orebodies.

The deposit is continuous over a strike length of about 7.3 km. Six separate lodes, which have been intensively folded and overturned, have been described (Plimer, 1982, 1984). Due to folding and erosion, the central portions of the lodes (confined essentially to the No.2 and No.3 lead lenses) were exposed, and in those bodies a well developed oxidised zone was formed. The surface expression originally consisted of a highly manganeseiferous gossan stretching for over 2.3 km along strike and varying from 6 to 23 m in width. Much of this material was removed during mining operations, particularly in the central leases where a large open cut was developed in part to relieve pressure on the underground workings. Little of the oxidised zone is intact (Plimer, 1982, 1984; Van Moort & Swensson, 1982) and underground access to remaining sections is virtually impossible. A recent report of complex suites of secondary minerals exposed during current mining operations has been provided by Birch & van der Heyden (1988). Nevertheless, much material is preserved in private and museum collections and is generally available for study.

One of the best contemporary descriptions of the oxidised zone ores is found in a report of Jaquet (1894), published prior to the commencement of open cut activities. The oxidised zone extended to between 60 and 120 m below the irregular surface outcrop, although oxidised ore did occur at greater depths in small channels and pipes. In the North Mine, leaching and oxidation is known to a depth of 300 m in the No.2 lead lens, and in the South Mine to 700 m. Little secondary enrichment at the base of the oxidised zone has occurred and in some cases lead carbonate (cerussite) ore was found in direct contact with the primary sulfides.

Pyromorphite specimens from all sections of the oxidised zone rank among the most spectacular ever discovered, and have been known since mining commenced; they vary widely in their colour and habit. Mimetite and vanadinite are also found in association with the pyromorphite and it has been assumed that compositional gradation is represented. Pyromorphite is known from all levels of the oxidised zone, but is most prominent from intermediate depths above a cerussite-rich zone (Plimer, 1982, 1984).

Early published analyses of Broken Hill pyromorphites and mimetites showed a range of compositions which reflect complete solid solution. More reliable and recent studies of a few specimens (Barclay & Jones, 1971; Birch & van der Heyden, 1988) confirm these early reports, but precise locality data for the specimens are lacking. Since it is generally appreciated that a more

thorough study would be desirable (Birch *et al.*, 1982), we have carried out the analytical work reported in this article. This study follows upon our recently published work concerning the nature of the pyromorphite-mimetite solid solution series (Inegbenebor *et al.*, 1989), which concentrated on solid state activity coefficients in the solid solution by way of distribution coefficient measurements. In essence, the series behaves ideally over the full range of stoichiometries, even though the two end-members are isostructural, but not strictly isomorphous (Baker, 1966; Keppler, 1969). We have attempted to relate the compositions of Broken Hill pyromorphites to their origin within the complex oxidised zone and to the compositions of the aqueous solutions from which they crystallised.

## Experimental

Pyromorphite specimens in the collections of the Australian Museum, Sydney, were examined in hand specimen. From this collection, material which represented the various visually different varieties of the mineral were selected for analysis, particularly when accurate locality data were available. Curatorial information for each specimen analysed is given in Appendix II. In all, some 104 specimens were viewed; descriptive notes concerning these have been deposited with the Australian Museum and are available from the authors upon request. Twenty eight specimens were subsequently analysed. Material selected for analysis is readily identified with pyromorphite which has been described by other workers (Marsh, 1897; Smith, 1926; Birch *et al.*, 1982).

Small fragments (1-5 mm) of the pyromorphite samples selected for analysis were embedded in a drop of resin (Epotek 301) placed on a glass slide. A surface flat was ground and polished using 6, 3, 1 and 0.25 micron diamond paste, employing a Logitech LP3 machine with polishing attachments.

A Cambridge Instruments Microscan MK9 instrument (wavelength dispersive) was used for all analyses, employing a standard ZAF correction program. Operating conditions: accelerating voltage 20kV, beam current  $2.5 \times 10^{-8}$  A, Faraday cage detection, fully focussed beam. Primary standards used were apatite (Ca and P), galena (Pb), sylvine (K) and pure elemental (As and V). Aside from the latter two, these were correlated with a standard pyromorphite (British Museum (Natural History) specimen BM 1921, 470) whose composition had been confirmed by wet-chemical methods ( $P_2O_5$ , 15.84; Cl, 2.66; PbO, 82.07; sum, 100.57; less O = Cl, 0.59; total, 99.98%).

## Results and Discussion

A number of point counts were made on each

specimen analysed. The complete analytical data have been deposited with the Australian Museum, the British Museum (Natural History) and the National Museum of Wales, and are available upon request. Table 1 (see Appendix I) gives the average analyses for the samples together with the number of point count analyses used in each determination and the standard deviation for each chemical component. The limit of detection is at the 0.02% level, but lower *average* levels of some minor components have been calculated when some individual point counts were found to correspond to less than the detection limit. A comment is warranted concerning the accuracy of the data. We have included extra significant figures for the purposes of comparison, but have also included corresponding standard deviations so that the true accuracies of the analytical results can be readily assessed. This approach is of relevance with respect to some of the levels at which minor components are present in the samples.

Minor variations in Ca for Pb and As for P contents were found for all samples and this is reflected in the analytical results listed. Elemental mapping using back scattered radiation revealed no zoning in the specimens save for samples D27866 and D35040 as discussed in detail below. In the former specimen, an As-rich rim was detected and analyses for this rim and the As-depleted core of the sample are reported separately in Table 1 (see Appendix I). Ca-rich inclusions detected in D29326 are interpreted as small calcite grains.

A constant O = Cl factor (0.59) has been applied throughout. No other elements were detected. Chlorine analyses show that there is negligible substitution in the univalent anion site. Therefore a very simple method has been adopted in order to derive the stoichiometries of the samples. Analysed contents of CaO and PbO have been taken to represent an exact total of five divalent metallic cations in the lattice and ratios have been calculated accordingly. Similarly, the ratios of  $\text{PO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$  and  $\text{VO}_4^{3-}$  have been obtained by assuming that exactly three trivalent anions are present in the lattice. A list of derived stoichiometries for the samples is given in Table 2 (see Appendix I). Original specimens are retained in the collections of the Australian Museum, Sydney. Sample fragments used for analysis have been deposited in the collections of the National Museum of Wales, Cardiff (accession number NMW 88.6G).

The variety of colours and habits of pyromorphite reported from Broken Hill is remarkable. Nine varieties were listed by Smith (1926), and Marsh (1897) mentioned other variations in colour. Some correlations between the observations of both of these workers can be made; in other cases it is not certain if they referred to the same kind of material. However, reference to these and later reports, as mentioned below, permits the pyromorphite varieties for the most part to be characterised in terms of their spatial distribution in the oxidised zone. In this respect, the curatorial notes and labels present with the specimens (Appendix II) in the collections of the Australian Museum have been most illuminating, especially when viewed in the light of the large number

of pyromorphites from Broken Hill housed in that Institution.

Of some interest is the fact that the variously coloured varieties of pyromorphite from Broken Hill have quite well defined levels of arsenate substitution associated with them. As might have been expected, this phenomenon may in turn be generally correlated with the availability of arsenic in the primary ores from which they were derived. These comprise the No.2 and No.3 lead lenses. Bulk analyses (Johnson & Klingner, 1975) show greater arsenic contents in the No.3 lead lens. This reflects the relative abundance of arsenopyrite and loellingite in these two lodes (Birch, 1982; Birch *et al.*, 1982). Loellingite shows variable degrees of replacement by arsenopyrite, but the two minerals have been noted to occur in massive patches over 30 cm across in the "garnet sandstone" of the North Mine. Arsenopyrite can be present at the 3 to 4% level in ore specimens from the No.3 lead lens (Plimer, 1984; Birch *et al.*, 1982). The "garnet sandstone" is a friable unit comprising small, somewhat round, pinkish spessartine crystals loosely cemented by blue quartz and biotite. It is particularly associated with the No.3 lead lens (O'Driscoll, 1953; Plimer, 1984) and constitutes a common gangue of that lode. These observations serve to illustrate the fact that arsenic is more abundant in the No.3 as compared to the No.2 lead lens. The particular observation to be made here is that higher arsenate levels are present in the pyromorphites from the former lode horizon.

Early specimens of pyromorphite from Broken Hill were from the upper levels of the Proprietary and Block 14 Mines and were canary yellow and greenish yellow in colour. Pale yellow-green to green pyromorphite was found rarely in the Junction Mine. Such material has been recently exposed in the Blackwood Opencut in Block 15 (Van Moort & Swennson, 1982), and is almost certainly derived from No.3 lead lens ore. Specimens D46990, D46595, D49648 and D43901 corresponding to this material have been analysed. The first two specimens have bright yellow to canary yellow pyromorphite crystals present, and the last two, squat yellow and yellow-green prisms of the mineral. Minor arsenate is seen to be substituted for phosphate, with somewhat more of the former in the yellow varieties. A similar pattern of substitution is found in other specimens (D41423, D29326, D41424 and D39778) which are almost certainly from the same environment but which have less precise locality information.

Two specimens from the Block 14 outcrop were analysed. Both consisted of yellowish-green arborescent aggregates of pyromorphite on a matrix of highly oxidised and weathered garnet sandstone. Both D38832 and D38842 are most probably derived from oxidised No.3 lead lens ore.

In all of these yellow or yellow-green pyromorphites from the northern end of the oxidised zone, and derived from the No.3 lead lens, the amount of arsenate substitution in the lattice is slight. Stoichiometries vary from  $\text{Pb}_{4.88}\text{Ca}_{0.12}(\text{P}_{2.99}\text{As}_{0.01})\text{O}_{12}\text{Cl}$

to  $\text{Pb}_{4.89}\text{Ca}_{0.11}(\text{P}_{2.90}\text{As}_{0.10})\text{O}_{12}\text{Cl}$ . Yellow material in general contains more arsenate than does the yellowish green variety.

Pyromorphite with several other habits and colours have been reported from the oxidised zone at the northern end of the outcrop. These include the celebrated smokey-grey, brownish grey and pinkish grey specimens from the Block 14 Mine consisting of aggregates of crystals up to 4cm in length (Marsh, 1897; Smith, 1926; Birch *et al.*, 1982). Several of these have been analysed (D37455, D32219, D33010 and D33011). Most of these specimens have grains of galena in the matrix; galena is sometimes the only other mineral observed in hand specimen. Similarities between the specimens and the excellent locality description (Appendix) for D37455 place these specimens as being derived from the No.2 lead lens (King & O'Driscoll, 1953). While the pyromorphite specimens in this category have flat terminations, other similarly coloured examples were recovered from the same general area and which have pointed terminations. These may form aggregates of branching acicular crystals which may merge to form botryoidal-like forms when the needle axis is particularly elongated.

Specimens D37454, D27870 and D30330 are typical of this latter group. All of the pyromorphites of these habits which have a grey colouration have, aside from minor substitution of Ca for Pb, stoichiometries close to the end-member composition. Lack of arsenate in the lattice can be correlated with their origin in oxidising ore from the No.2 lead lens. However, pale purple to ashen brown crystals from the British Mine (D19548 and D27869), also with negligible arsenate, have been analysed. The matrix for these specimens consists of decomposed gneiss and garnet sandstone although they may also derive from the No.2 lead lens (Henderson, 1953). Similar material from the South Mine can be placed with certainty. D30704 and D32084 both consist of pale-brown prisms of pyromorphite merging to nodular masses perched on secondary galena crystals to 2 cm. End-member pyromorphite composition is again evident, and reference to published mine plans and sections indicates that this material came from the No.2 lead lens between the No.1 and No.2 shafts in Block 8 (Kenny, 1923; Black, 1953; King & O'Driscoll, 1953).

One other grey pyromorphite, D35040, has been analysed. It matches perfectly the description of Marsh (1897) of "...clove brown to smoky grey..." hexagonal prisms from the North Broken Hill Mine, although no further details as to locality are available. The crystals are zoned about the c axis and in hand specimen this is seen as pronounced shading from lighter to darker grey bands of several generations. No arsenate was detected in this specimen, but elemental mapping by back scattered radiation techniques shows that the banding is due to variations of the degree of calcium substitution for lead. Barclay & Jones (1971) have remarked that only calcium appears to substitute for lead in Broken Hill pyromorphites and mimetites, and that this substitution is extremely limited. Of their seven analyses,

the greatest substitution observed corresponded to an empirical formula of  $[\text{Pb}_{0.93}\text{Ca}_{0.07}]$ . None of the pyromorphites analysed in the present study approaches this value and it is evident that the compositional variation which gives rise to the banding is subtle. It is not possible to put limits on the ratios of  $\text{Pb}^{2+}(\text{aq})$  to  $\text{Ca}^{2+}(\text{aq})$  which obtained (and varied) in solution during the crystallisation of the sample because the relevant solid state activity or distribution coefficients are not available. It is clear however that the composition of the solution did vary although negligible arsenate was present throughout the course of crystallisation (*vide infra*).

The more arsenian varieties of pyromorphite that we have analysed are from the Proprietary and Block 10 Mines. Some are coloured yellow, but others are orange-brown to deep brown, a hue which has not been commented upon by earlier workers. Recent material recovered from the Kintore open pit, which occupies sections of Blocks 9, 10 and 11, is white, and pale to dark brown and green (Birch & van der Heyden, 1988). The white material is arsenian (As, 3.15%) and calcian arsenian (As, 0.44%) pyromorphite. It is worth noting that orange mimetite is known to occur in the central blocks of the oxidised zone (Birch *et al.*, 1982). Exact locations for the specimens we have analysed are difficult to ascertain but the material is almost certainly derived from No.3 lead lens ore. Support for this is found in the fact that the only significant, if small, levels of vanadate in pyromorphite that have been encountered are associated with the most arsenian varieties. Vanadinite itself is known from Broken Hill and was recognised during early mining. Marsh (1897) reported that vanadinite was transitional to mimetite in the Proprietary Mine and that the two minerals were usually found in the same environment, lining vughs and fissures in garnet sandstone. Fawn coloured crystals are known from a section of ore which probably spanned Blocks 13 and 14 (Birch *et al.*, 1982) and these were associated with azurite, iodargyrite and bromian chlorargyrite. Reference to published sections in this vicinity (King & O'Driscoll, 1953) indicate that this material came from the No.3 lead lens. Further confirmation is provided by the report of Jaquet (1894). At about the time that orange to orange-brown mimetites and vanadinites were recovered from the Proprietary Mine only a little exploration work had been carried out on the "Eastern" lode (No.2 lead lens). The great majority of the ore raised from the Block 10 Mine was also derived from the No.3 lead lens as it passed into that lease from those held by the Proprietary Mine. Orange and pale brown phosphatian mimetites have been recently recovered from the Kintore open pit from the No.3 lead lens and a garnet sandstone immediately to the east, and remote from the No.2 lead lens. It was noted that "...mimetite is the most abundant arsenate at Kintore and is more common and widespread than pyromorphite..." (Birch & van der Heyden, 1988). On the basis of all these observations it seems reasonable to conclude that the pyromorphites we have analysed from the middle areas

of the oxidised zone come from No.3 lead lens ore and that their compositions reflect the relative abundance of arsenic in the primary ores from which they were derived.

Both yellow and brown-orange pyromorphites from the Proprietary Mine contain significant arsenate. Brown-orange, squat prisms (D35938) had the highest arsenate content analysed, together with minor vanadate. Three specimens of orange-brown pyromorphite prisms with a later yellow generation of the mineral were examined (D19544, D27866 and D29269). For D19544 and D29269, the orange and yellow phases were analysed, respectively. With D27866, both phases were analysed separately. At the interface, the crystals are seen clearly to be zoned as evidenced by back scattered electron image experiments. The yellow material is considerably more arsenian than is the orange-brown pyromorphite.

While mimetite is certainly found abundantly in some sections of the Broken Hill oxidised zone, we point out that not all of the orange material that might be judged to be that mineral is in fact mimetite; we have shown that orange to orange-brown examples of pyromorphite are also present. These two may be difficult to distinguish in hand specimen. Colour variation in mineral species may arise from a number of sources, and compositional variation is but one important contributor to the effect (Burns, 1970). In the case of pyromorphite-mimetite solid solutions, colours associated with arsenate substitution for phosphate *may* give rise to differing colours in a more-or-less regular fashion. In this connection it is worth recalling the results of Dunn (1982) concerning Bunker Hill, Idaho, USA pyromorphites (090-23-25 Shaft, 9 Level, Deadwood-Jersey Vein). Green, yellow-brown, orange and reddish orange varieties were analysed; these contained, respectively, 0.0, 0.0, 3.3 and 4.7-5.8%  $As_2O_5$ . These analytical data in conjunction with colour variations bear a resemblance to those obtained for the Broken Hill specimens, but further data are required in order to ascertain whether these patterns of colours reflect compositional trends.

While the complete pyromorphite-mimetite solid solution series is represented by specimens from the Broken Hill oxidised zone, all those analysed here are either pure end-member pyromorphite (ignoring minor calcium substitution) or arsenian pyromorphite. Indeed, most specimens which do contain arsenate are but feebly arsenian. The spread of stoichiometries does however correspond to a considerable range of arsenate to phosphate ratios in the aqueous solutions from which the solid phases crystallised. Distribution coefficients for the mimetite-pyromorphite solid solution series at 25°C have been reported (Inegbenebor *et al.*, 1989). The occurrence of carbonate minerals, especially cerussite, with pyromorphite at Broken Hill implies that the phosphate crystallised under neutral to slightly basic pH conditions where the conjugate anions  $HPO_4^{2-}$  and  $HAsO_4^{2-}$ (aq) predominate in solution. Application of the distribution coefficient results gives values for  $[HPO_4^{2-}]/[HAsO_4^{2-}]$  of from greater than about 900 for end-member

pyromorphite (corresponding to detection limits for As) to about 1.5 for the most arsenian specimen analysed (D35938). The availability of arsenate in solution will reflect the relative abundance of arsenides and other arsenic-containing sulfosalts in the primary ore as discussed above, and this in turn seems to correlate with the lens from which the specimens were derived. We do wish to point out however that solution chemistry may vary to a significant extent over quite small distances in the oxidised zone at Broken Hill.

Changes in arsenate *versus* phosphate compositions did occur with time during the crystallisation of at least some of the minerals examined. On the other hand, the end-member pyromorphites appear to have been formed from solutions of approximately constant composition, at least as far as arsenate and phosphate are concerned. This constant chemistry was maintained for a considerable time in some instances, in that buff coloured pyromorphites achieve considerable crystal size and no arsenate was detected anywhere in the largest crystals. These specimens have obviously, by virtue of their size, formed slowly. This is further borne out by the fact that calcium zoning has been observed in one of the specimens which displays rhythmic banding of calcium-rich and calcium-poor pyromorphite (although the absolute values of calcium contents are quite small, and the variation is not particularly pronounced). For such a compositional pattern to have developed, the pyromorphite crystals in this specimen would have to have been formed from solutions whose chemistry *did* vary subtly over some time, but which always contained much less arsenate than dissolved phosphate species.

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## APPENDIX I

Table 1. Analytical results for the Broken Hill pyromorphites.

Specimen No.	n	PbO	CaO	Cl			
D19548	7	81.76(35)	0.32(13)	2.72(6)			
D27868	10	81.95(46)	0.27(21)	2.74(5)			
D27869	8	82.12(42)	0.21(7)	2.59(7)			
D27870	8	79.24(133)	1.65(62)	2.92(11)			
D30330	8	82.05(46)	0.28(12)	2.69(5)			
D30704	7	81.83(28)	0.21(16)	2.72(7)			
D32084	6	81.73(39)	0.26(7)	2.68(3)			
D32219	6	81.54(64)	0.67(43)	2.79(5)			
D33010	6	81.64(101)	0.79(51)	2.80(5)			
D33011	9	82.07(48)	0.46(17)	2.72(6)			
D35040	6	81.17(62)	0.76(25)	2.69(9)			
D37455	9	81.04(79)	0.63(52)	2.78(5)			
D37454	8	81.60(65)	0.31(29)	2.77(8)			
D38842	8	81.63(85)	0.49(23)	2.77(7)			
D41423	6	82.00(87)	0.33(46)	2.79(7)			
D38832	7	81.92(71)	0.48(30)	2.72(9)			
D43901	8	80.41(107)	0.82(39)	2.82(4)			
D41424	5	80.13(105)	0.63(38)	2.87(10)			
D39778	8	81.59(72)	0.18(27)	2.83(5)			
D35023	8	81.98(65)	0.30(20)	2.72(5)			
D49648	6	81.18(62)	0.41(21)	2.78(2)			
D29269	9	81.62(42)	0.24(21)	2.71(7)			
D29326	9	82.36(65)	0.31(31)	2.72(6)			
D46595	9	81.78(76)	0.15(10)	2.71(5)			
D46990	6	81.65(85)	0.45(26)	2.78(5)			
D19544	6	82.40(71)	0.10(9)	2.71(3)			
D27866 <sup>b</sup>	5	81.35(101)	0.14(12)	2.79(3)			
D27866 <sup>c</sup>	2	81.14(62)	0.02(3)	2.67(11)			
D35938	7	80.73(63)	0.03(5)	2.69(11)			
Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl		82.28		2.61			
		P <sub>2</sub> O <sub>5</sub>	As <sub>2</sub> O <sub>5</sub>	V <sub>2</sub> O <sub>5</sub>	sum <sup>d</sup>	O=Cl <sup>e</sup>	Total
D19548		15.77(49)	nd <sup>f</sup>	tr <sup>g</sup>	100.57	0.59	99.88
D27868		16.20(20)	nd	tr	101.16	0.59	100.57
D27869		16.03(14)	nd	0.01(2) <sup>h</sup>	100.96	0.59	100.37
D27870		16.65(63)	nd	tr	100.46	0.59	99.87
D30330		15.79(23)	nd	tr	100.81	0.59	100.22
D30704		15.13(96)	nd	nd	99.89	0.59	99.30
D32084		16.03(10)	nd	nd	100.70	0.59	100.11
D32219		16.52(31)	nd	0.01(1) <sup>h</sup>	101.53	0.59	100.94
D33010		16.46(42)	nd	tr	101.69	0.59	101.10
D33011		15.76(19)	nd	0.01(1) <sup>h</sup>	101.02	0.59	100.43
D35040		16.35(33)	nd	tr	100.97	0.59	100.38
D37455		16.12(49)	nd	tr	100.57	0.59	99.98
D37454		16.19(46)	0.03(8)	0.01(1) <sup>h</sup>	100.91	0.59	100.32
D38842		15.43(40)	0.01(1) <sup>h</sup>	tr	100.33	0.59	99.74
D41423		15.36(61)	0.12(10)	nd	100.60	0.59	100.01
D38832		15.07(69)	0.12(13)	nd	100.31	0.59	99.72
D43901		15.45(55)	0.20(34)	tr	99.70	0.59	99.11
D41424		15.70(47)	0.28(34)	tr	99.61	0.59	99.02
D39778		15.51(33)	0.35(40)	tr	100.46	0.59	99.87
D35023		14.98(35)	0.44(31)	nd	100.42	0.59	99.83
D49648		15.02(56)	0.46(37)	nd	99.85	0.59	99.26
D29269		14.69(65)	0.56(71)	0.02(2)	99.84	0.59	99.25
D29326		14.69(92)	0.61(35)	0.01(1) <sup>h</sup>	100.69	0.59	100.10
D46595		14.29(89)	0.78(44)	0.01(1) <sup>h</sup>	99.72	0.59	99.13
D46990		14.53(32)	0.80(39)	nd	100.21	0.59	99.62
D19544		13.65(84)	1.63(85)	0.03(4)	100.52	0.59	99.93

D27866 <sup>b</sup>	14.01(86)	1.53(74)	0.02(3)	99.76	0.59	99.17
D27866 <sup>c</sup>	11.37(32)	4.12(83)	nd	99.32	0.59	98.73
D35938	9.93(56)	6.70(62)	0.02(2)	100.12	0.59	99.53
Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	15.70			100.59	0.59	100.00

<sup>a</sup>In percent with standard deviations in parentheses; Australian Museum specimen numbers are given; n = number of point analyses.

<sup>b</sup>As-depleted core.

<sup>c</sup>As-rich rim.

<sup>d</sup>Ignoring standard deviations.

<sup>e</sup>See text.

<sup>f</sup>Not detected.

<sup>g</sup>Trace (average less than 0.02%).

<sup>h</sup>Some point analyses gave greater than 0.02% but others gave nd; average for all point analyses.

Table 2. Derived formulae for the Broken Hill pyromorphites.

Specimen No.	Calculated Formula
D19548	Pb <sub>4.891</sub> Ca <sub>0.109</sub> P <sub>3</sub> O <sub>12</sub> Cl
D27868	Pb <sub>4.950</sub> Ca <sub>0.050</sub> (P <sub>2.998</sub> V <sub>0.002</sub> )O <sub>12</sub> Cl
D27869	Pb <sub>4.938</sub> Ca <sub>0.062</sub> P <sub>3</sub> O <sub>12</sub> Cl
D27870	Pb <sub>4.617</sub> Ca <sub>0.383</sub> P <sub>3</sub> O <sub>12</sub> Cl
D30330	Pb <sub>4.820</sub> Ca <sub>0.180</sub> P <sub>3</sub> O <sub>12</sub> Cl
D30704	Pb <sub>4.815</sub> Ca <sub>0.185</sub> (P <sub>2.999</sub> V <sub>0.001</sub> )O <sub>12</sub> Cl
D32084	Pb <sub>4.842</sub> Ca <sub>0.158</sub> (P <sub>2.999</sub> V <sub>0.001</sub> )O <sub>12</sub> Cl
D32219	Pb <sub>4.949</sub> Ca <sub>0.051</sub> P <sub>3</sub> O <sub>12</sub> Cl
D33010	Pb <sub>4.935</sub> Ca <sub>0.065</sub> P <sub>3</sub> O <sub>12</sub> Cl
D33011	Pb <sub>4.923</sub> Ca <sub>0.077</sub> P <sub>3</sub> O <sub>12</sub> Cl
D35040	Pb <sub>4.933</sub> Ca <sub>0.067</sub> P <sub>3</sub> O <sub>12</sub> Cl
D37455	Pb <sub>4.850</sub> Ca <sub>0.150</sub> P <sub>3</sub> O <sub>12</sub> Cl
D37454	Pb <sub>4.931</sub> Ca <sub>0.069</sub> (P <sub>2.995</sub> As <sub>0.004</sub> V <sub>0.001</sub> )O <sub>12</sub> Cl
D38842	Pb <sub>4.883</sub> Ca <sub>0.117</sub> (P <sub>2.994</sub> As <sub>0.006</sub> )O <sub>12</sub> Cl
D41423	Pb <sub>4.920</sub> Ca <sub>0.080</sub> (P <sub>2.986</sub> As <sub>0.014</sub> )O <sub>12</sub> Cl
D38832	Pb <sub>4.886</sub> Ca <sub>0.114</sub> (P <sub>2.985</sub> As <sub>0.015</sub> )O <sub>12</sub> Cl
D43901	Pb <sub>4.805</sub> Ca <sub>0.195</sub> (P <sub>2.976</sub> As <sub>0.024</sub> )O <sub>12</sub> Cl
D41424	Pb <sub>4.848</sub> Ca <sub>0.152</sub> (P <sub>2.967</sub> As <sub>0.033</sub> )O <sub>12</sub> Cl
D39778	Pb <sub>4.956</sub> Ca <sub>0.044</sub> (P <sub>2.959</sub> As <sub>0.041</sub> )O <sub>12</sub> Cl
D35023	Pb <sub>4.928</sub> Ca <sub>0.072</sub> (P <sub>2.947</sub> As <sub>0.053</sub> )O <sub>12</sub> Cl
D49648	Pb <sub>4.901</sub> Ca <sub>0.099</sub> (P <sub>2.944</sub> As <sub>0.056</sub> )O <sub>12</sub> Cl
D29269	Pb <sub>4.942</sub> Ca <sub>0.058</sub> (P <sub>2.928</sub> As <sub>0.069</sub> V <sub>0.003</sub> )O <sub>12</sub> Cl
D29326	Pb <sub>4.929</sub> Ca <sub>0.071</sub> (P <sub>2.925</sub> As <sub>0.075</sub> )O <sub>12</sub> Cl
D46595	Pb <sub>4.964</sub> Ca <sub>0.036</sub> (P <sub>2.902</sub> As <sub>0.098</sub> )O <sub>12</sub> Cl
D46990	Pb <sub>4.893</sub> Ca <sub>0.107</sub> (P <sub>2.901</sub> As <sub>0.099</sub> )O <sub>12</sub> Cl
D19544	Pb <sub>4.976</sub> Ca <sub>0.024</sub> (P <sub>2.790</sub> As <sub>0.205</sub> V <sub>0.005</sub> )O <sub>12</sub> Cl
D27866 <sup>a</sup>	Pb <sub>4.966</sub> Ca <sub>0.034</sub> (P <sub>2.808</sub> As <sub>0.189</sub> V <sub>0.003</sub> )O <sub>12</sub> Cl
D27866 <sup>b</sup>	Pb <sub>4.995</sub> Ca <sub>0.005</sub> (P <sub>2.450</sub> As <sub>0.550</sub> )O <sub>12</sub> Cl
D35938	Pb <sub>4.988</sub> Ca <sub>0.012</sub> (P <sub>2.115</sub> As <sub>0.881</sub> V <sub>0.003</sub> )O <sub>12</sub> Cl

<sup>a</sup>As-depleted core.

<sup>b</sup>As-rich rim.

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## APPENDIX II

## Locality Information for the Specimens Analysed

These data, used in conjunction with other mineralogical information to locate origins of the pyromorphite specimens analysed, are taken from the records of the Australian Museum. The curatorial notes are included here because of their importance in placing the specimens in terms of lead lenses Nos 1 and 2. The specimen numbers are the same as in the body of the text: BH = Broken Hill, NSW = New South Wales.

- D46990: Pyromorphite, Blackwoods open cut, BH, NSW
- D46595: Pyromorphite, yellow on matrix, Blackwoods open cut, BH, NSW
- D49648: Pyromorphite, Blackwoods open cut, MIM leases, BH, NSW
- D43901: Pyromorphite on large crystal of cerussite, Blackwoods open cut, South Mine, BH, NSW
- D41423: Pyromorphite, North Mine lease, BH, NSW
- D29326: Pyromorphite (yellow) on ironstone gossan, Block 14 Mine, BH, NSW
- D41424: Pyromorphite, yellowish green, North Mine leases, BH, NSW
- D39778: Pyromorphite, small crystals on manganese oxides, BH, NSW
- D38832: Pyromorphite, yellow crystals on matrix, East side of outcrop, Block 14, BH, NSW
- D38842: As for D38832
- D37455: Pyromorphite, light yellow ashen brown crystals, almost transparent, show perfect basal termination, West Lode, 400 foot level, Block 14 Mine, BH, NSW
- D32219: Pyromorphite, BH, NSW
- D33010: As for D32219
- D33211: Pyromorphite, Proprietary Mine, Block 14 Mine, NSW
- D37454: Pyromorphite, crystallised ashen coloured, crystals show pointed terminations, mammillated structure, 200 foot level, Block 14 Mine, BH, NSW
- D27870: Pyromorphite, North Mine, BH, NSW
- D30330: Pyromorphite with galena, BH, NSW
- D19548: Pyromorphite, British outcrop, BH, NSW
- D27869: Pyromorphite, British Mine, BH, NSW
- D27868: As for D27869
- D30704: Pyromorphite on secondary galena, South Mine, BH, NSW  
Pyromorphite in secondary galena, unknown small yellow crystals, Section 5Cc, 525 foot level, South Mine, BH, NSW
- D32084: Pyromorphite, 525 foot level, South Mine, BH, NSW
- D35040: Pyromorphite, BH, NSW
- D35023: Pyromorphite, brownish yellow, BH, NSW
- D35938: Pyromorphite, crystalline on manganic ironstone, variety campylite, BH, NSW
- D19544: Pyromorphite with mimetite, Proprietary Mine, BH, NSW
- D27866: Pyromorphite on ironstone, Proprietary Mine, BH, NSW
- D29269: Pyromorphite, Proprietary Mine, BH, NSW