

*References*

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*Pyromorphite as a possible primary phase*

WITHIN the Newlands mining field, Cumberland, pyromorphite is particularly common in the outermost part of the lead-zinc zone, for example, in the Barrow vein system, and at Goldscope, Old Brandlehow, and Yewthwaite. This apparent connexion between the zoning of the primary and secondary mineralization, suggests that the pyromorphite may have been an original (primary) phase.

Removal of  $H_2S$  by precipitation of sulphides, by evaporation and by oxidation, will ultimately lead to the production of an ore fluid from which galena could not be precipitated, even with a high concentration of lead in solution. In these circumstances, minerals such as cerussite, anglesite, and pyromorphite could be precipitated as primary minerals. In the presence of soluble sulphide, these minerals would be converted to galena; they would not appear until the partial pressure of  $H_2S$  reached a very low value.

The ability of pyromorphite to form from aqueous chloride solutions was tested over the temperature range 20 to 480° C, at pressures up to 550 atm; details are given in table I.

TABLE I. Pyromorphite syntheses

Reactants	$P$ (atm)	$T$ (° C)	Time	Products
Cl,P ... ..	1	20	3 m	Pyr
Cl,P ... ..	1	100	3 d	Pyr
Cl,P,V ... ..	1	100	3 d	Pyr
Cl,V ... ..	1	100	3 d	Pyr
OH,P ... ..	1	100	3 d	Pyr
CO <sub>3</sub> ,P ... ..	1	100	3 d	Pyr
Cl,P ... ..	150	200	30 h	Pyr
Cl,P ... ..	180	340	13 h	Pyr
Cl,P ... ..	300	410	12 h	Pyr
Cl,P ... ..	550	480	12 h	Pyr unstable.

Cl— $PbCl_2$ ; OH— $Pb(OH)_2$ ; CO<sub>3</sub>—basic lead carbonate; Pyr = pyromorphite; V = ammonium metavanadate; P = ammonium dihydrogen phosphate; m = months; d = days; h = hours.

It was concluded that pyromorphite could form from such solutions up to about 450°C; consequently, there appears to be no reason why

pyromorphite should not form as a primary mineral, in the absence of sulphide ions.

Pyromorphite crystallizes from dry melts of lead chloride and lead phosphate, presumably at temperatures near the melting-point of lead chloride (501° C); the arsenic-rich variety has been made from solutions of lead arsenate and lead chloride (Palache, Berman, & Frondel, 1951).

Pronounced oxidation of the Skiddaw Slates has taken place near some of the low-temperature veins, with the production of haematite and pyrolusite. Under these conditions, hydrogen sulphide would oxidize to sulphate, leading to the precipitation of insoluble sulphates, such as baryte and anglesite, and the termination of the phase of sulphide deposition. Exhaustion of the sulphate radical could in turn cause the precipitation of the insoluble carbonates: cerussite, witherite, and calcite.

Oxidation at low temperatures, estimated at 50–140° C for these veins (Strens, 1962), would probably take place through redox reactions catalysed by manganese or iron. The most likely source of oxygen in these shallow veins would be percolating groundwater.

Whilst it is an undisputed fact that many occurrences of pyromorphite, cerussite, and anglesite are secondary, the possibility of primary origin must also be considered. Similar remarks apply to other secondary minerals, for example, malachite and azurite.

*Dept. of Geology,  
The University of California,  
Berkeley 4, California*

R. G. J. STRENS

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### *A natural occurrence of bayerite*

BAYERITE,  $\text{Al}(\text{OH})_3$ , is readily prepared by acidification of sodium aluminate solution with carbon dioxide or by ageing of aluminium gels, but no natural occurrence has as yet been reported.

Two samples containing bayerite were found in a sedimentary rock sequence of Cenomanian to Eocene age in Hartrurim, Israel<sup>1</sup> The presence of portlandite and ettringite in these rocks testifies to their

<sup>1</sup> Y. K. BENTOR, S. GROSS, and L. HELLER, *Amer. Min.*, 1963, vol. 48, p. 924.