HINSDALITE PSEUDOMORPHOUS AFTER PYROMORPHITE, FROM DUNDAS, TASMANIA

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(With two text-figures)

ABSTRACT

Hinsdalite, $PbAl_3(PO_4)(SO_4)(OH)_6$ occurs as pseudomorphs after pyromorphite from the Dundas area. Determination of the mineral was made by the use of X-ray powder diffraction, spectroscopy, chemical spot testing and differential thermal analysis. Hinsdalite crystallizes in the rhombohedral system and the cell constants, $a_{rh} = 6.90$ and $\alpha = 61° 8'$ of the Dundas material agree closely with those of the type material from Colorado. The mineral can be synthesized in the laboratory either from a solution of its constituent ions or by alteration of pyromorphite. The unusual feature of the environment in which hinsdalite forms is the presence of large quantities of aluminium. In the Dundas case it is believed that weathering of eugeosynclinial sediments in the presence of soil waters of low pH and high humic acid content have made the aluminium available.

INTRODUCTION

Largely through the early efforts of Petterd (1910), the Dundas mineral field has earned mineralogical renown for its content of rare, oxidised zone minerals, amongst which the lead chromate, crocoite, is the best known. Investigation of several specimens of pyromorphite from the field has led to the recognition of yet another rare mineral, namely hinsdalite, $PbAl_3(PO_4)(SO_4)(OH)_6$. This mineral is one of a number of rare phosphate-sulphates collectively known as the Beudanite Group (Palache et al, 1951, p 1001).It was originally recognised by Larsen and Scaller (1911) in hydrothermal veins of the Golden Fleece Mine, Hinsdale County, Colorado.

OCCURRENCE

The Dundas hinsdalite occurs as sparse nests of pseudomorphs after the typical green pyromorphite of the Comet and other mines of the Zeehan-Dundas mineral province. Usually the pseudomorphs are solid although some occur merely as thin walled shells of hexagonal outline. Gibbsite is associated with the pyromorphite-hinsdalite assemblage. The occurrence appears to be only the second recorded for the mineral and the first in the oxidised zone, although other members of the Beudanite Group typically form in this environment.

CHEMICAL COMPOSITION

The small amounts of material available did not allow complete analysis to be made. Semi quantitative spectography established the presence of lead and aluminium as dominant metals with silver as a minor constituent. Chemical spot testing indicated the presence of phosphate and sulphate. Strontium, present in the type material, does not occur in that from Dundas.

MINERALOGICAL DATA

The fine grained nature of the pseudomorphs precluded accurate microscopic examination. The material was found to exhibit the anomalous biaxial segments characteristic of the minerals of the Beudantite Group (Figure 1). The mean refractive index was found to be 1.69.

Detailed study was undertaken by means of X-ray powder diffraction using a Philips Model 1050 X-ray Diffractometer. No data were on record for hinsdalite and the Australian Museum kindly donated type material to enable comparison to be made with the Dundas specimens. A check through the A.S.T.M. Card Index showed that there was a good match with the data of Card 2-0683, for plumbogummite, $PbAl_3(PO_4)_2(OH)_5.H_2O$. The diffraction data are given in Table 1. Selected spacings were determined more accurately by means of fixed-count techniques and cell data were computed from these results. The unit cell of hinsdalite is rhombohedral and contains one molecule. For the Colorado material $a_{rh} = 6.88$, $\alpha = 61° 8'$, the cell volume is 236A^3 and the calculated specific gravity 3.92. For the Dundas material $a_{rh} = 6.90$, $\alpha = 61° 8'$ the cell volume is 238A^3 and the calculated specific gravity 4.06. The differing values of specific gravity are due to the fact that the Cororado material contains strontium substituting for lead in a molecular proportion of about 1:5. The measured value of 3.65 for the mineral (Palache et al 1951, p 1004) is low and can probably be attributed to the presence of impurities in the sample used for the physical determination. Smith et al (1953) have noted a similar discrepancy in the case of hidalgoite, the arsenate analogue of hinsdalite.

The data of Table 1 show that determination of the minerals concerned on the basis of X-ray powder diffraction alone could be misleading.

Detection of sulphate does not necessarily rule out the possibility of plumbogummite since the ion could be present by contamination. As plumbogummite contains water, differential thermal analysis coupled with X-ray procedures gives a more reliable result than chemical testing. Both hinsdalite and plumbogummite were synthesized from solutions of their constituent ions, and together with Colorado and Dundas hinsdalite, were subjected to differential thermal analysis. The results, shown in Figure 2, indicate that only the curve of plumbogummite contains a strong endothermic peak due to water loss.

MINERAL GENESIS

In the laboratory, formation of hinsdalite is effected by co-precipitation of lead sulphate and aluminium phosphate. With ageing at an elevated temperature this mixed precipitate gradually converts to hinsdalite as is shown by the equation below:—

$$PbSO_4 + 3AlPO_4 + 6H_2O \rightleftharpoons PbAl_3(PO_4)(SO_4)(OH)_6 + 2H_3PO_4$$

At Dundas, the formation of the mineral has been by means of alteration of pyromorphite. Comparison of the formulae of the two minerals shows that chemically only aluminium, sulphate and hydroxyl ions are needed to change pyromorphite into hinsdalite. Refluxing of finely ground pyromorphite with a solution of aluminium sulphate does in fact produce hinsdalite within 24 hours. Since the reaction in nature results in the formation of a pseudomorph it must take place at constant volume.

The volume of the pyromorphite unit cell is $630A^3$ and that of a hexagonal hinsdalite cell (triply primitive) is $708A^3$. The nearest approach to a volume constant reaction occurs when 9 molecules of pyromorphite are replaced by 24 molecules of hinsdalite (a cell ratio of 9:8). The resulting equation for the volume constant conversion is given below:—

$$\underset{\text{Pyromorphite}}{9Pb_5(PO_4)_3Cl} + 72Al_3^{+} + 24SO_4^{2-} + 144OH^{-}(+24Cl^{-})$$
$$\rightleftharpoons \underset{\text{Hinsdalite}}{24PbAl_3(PO_4)(SO_4)(OH)_6} + 21Pb^{2+} + 3PO_4^{3-} + 9Cl^{-}(+24Cl^{-})$$

The bracketed chloride ions in this equation serve no other purpose than the maintaining of electrical neutrality on both sides of the equation. The alteration has been subjected to physico-chemical studies (Baker, 1962) and these show that the proposed reaction results in an overall decrease in the free energy of the system. Such a reaction can thus take place spontaneously as required by the formation of hinsdalite in the oxidised zone of the Dundas mineral deposits.

The unusual condition which must be fulfilled for the formation of hinsdalite in either a hydrothermal or oxidised zone environment is that aluminium must be abundant. It is this condition which surely explains the rarity of the mineral. During differentiation of a magma the bulk of the aluminium is incorporated in the rock forming minerals. Unless the parent magma was unusually rich in aluminium, or that contamination in some way caused it to follow a peculiar differentiation path it is unlikely that this metal would appear as a constituent of the hydrothermal solution. In the weathering process aluminium has low mobility and tends to remain bound in the clay minerals.

The reason for the occurrence of aluminium in the Dundas environment and for its departure from the normal behaviour is not clear. Unfortunately little detail is known of the Dundas mineralization as the mines of the area ceased operations before systematic geological investigations were undertaken. The general environment is one of mineralization along contact zones between ultra-basic rocks and eugeosynclinal sediments and volcanics. The abundance of aluminium in the environment is clearly shown by the presence of a considerable quantity of gibbsite which is closely associated with the oxidised zone minerals of the area. Since aluminium is generally not incorporated in the mineral assemblages of ultra-basic rocks there remains only the Dundas sediments. Whilst no analyses of typical rocks are available the stratigraphic column consists, in considerable part, of greywackes, tuffs and shales all of which are likely to contain higher than average amounts of aluminium. The soil waters of parts of western Tasmania have pH values as low as 3.5 and they are relatively rich in humic acids. Such waters have a strongly corrosive action on the rocks with which they make contact, and weathering under these conditions could make large quantities of aluminium freely available.

It is of interest to note that Petterd (op. cit. p. 139) has recorded the occurrence of plumbogummite at Zeehan. Some of this material was still available in the collection of The Tasmanian Museum and this institution kindly loaned it for examination. Under the binocular microscope the mineral is seen as an off-white resinous material developing at the expense of brown pyromorphite which coats partially decomposed galena. Thus in this case also the mineral occurs as an alteration product of pyromorphite. The results of mineral synthesis show that both hinsdalite and plumbogummite are produced quite readily. In the replacement of pyromorphite by either one, almost a quadrupling of the number of ions in a given volume is involved and as a result considerable ionic movement must take place. Whilst sulphides persist in the zone of oxidation there would be an abundance of sulphate in the environment and the formation of hinsdalite would be favoured. If the oxidation of the ore body was virtually complete to the existing water table and phosphate remained abundant then the formation of plumbogummite could take place.

The presence of silver in the Dundas hinsdalite is worthy of note. The Beudanite Group are chemical intermediates between the phosphates of the Plumbogummite Group on one side and the sulphates of the Alunite Group on the other. The theoretical 1:1 ratio of phosphate to sulphate is seldom achieved. If sulphate is in excess, the resulting decrease in the negative charge of the mineral is counteracted by replacement of part of the divalent metal ion (lead) by a mono-valent ion (silver). On the other hand if phosphate is in excess then the higher negative charge is counteracted by the substitution of neutral water for part of the hydroxyl content.

TABLE 1

X-Ray Powder Diffraction Data for Colorado and Dundas Hinsdalite and Plumbogummite

Hinsdalite Colorado		Hinsdalite Dundas		Plumbogummite ASTM Card 2-0683		Indices	
d(*obs.*)	I/I$_1$	d(*obs.*)	I/I$_1$	d(*obs.*)	I/I$_1$	hkl	d(*calc.*)
5.70	92	5.70	94	5.70	80	100	5.698
5.57	30	5.57	17	..	..	111	5.573
4.90	3	4.91	17	4.84	40	110	4.909
3.50	44	3.51	59	3.79	40	10$\bar{1}$	3.500
3.45	18	3.46	22	3.45	60	211	3.440
2.964	100	2.964	100	2.97	100	210	2.964
2.930	4	2.940	11	..	..	221	2.927
2.848	11	2.857	16	2.82	20	200	2.850
2.787	15	2.788	13	..	..	222	2.785
2.452	10	2.462	13	2.44	40	220	2.454
2.269	8	2.276	13	2.26	40	20$\bar{1}$	2.270
2.248	12	2.250	13	..	..	311	2.246
2.224	86	2.226	32	..	..	322	2.223
2.211	17	2.216	27	2.20	60	21$\bar{1}$	2.212
2.183	15	2.186	13	2.09	20	321	2.180
2.018	2	2.014	10	..	..	2$\bar{1}\bar{1}$ 11$\bar{2}$	2.120
2.010	10	..	..	2.01	40	310	2.009
1.978	9	1.981	5	..	..	332	1.975
1.900	36	1.901	22	1.89	50	300 22$\bar{1}$	1.900
1.857	1	1.861	4	..	..	333	1.857
1.750	16	1.753	15	1.75	50	20$\bar{2}$	1.750
1.722	8	1.724	4	1.70	20	422	1.720
1.668	4	1.672	3	1.66	40	31$\bar{1}$	1.670
1.655	11	1.657	5	..	..	421	1.653
1.642	29	1.643	6	1.63	40	432	1.640
1.614	8	1.616	4	..	..	433	1.611
1.502	4	1.504	4	1.50	40	410	1.503
1.491	4	1.493	2	..	..	22$\bar{2}$	1.492
1.480	22	1.481	4	1.48	50	420	1.482
1.465	24	1.467	8	1.45	50	442	1.464
1.426	4	..	..	1.42	40	400	1.425
1.392	3	..	..	..	..	444	1.389
1.373	4	..	..	1.37	40	31$\bar{2}$	1.372

TABLE 1—*continued*

Hinsdalite Colorado		Hinsdalite Dundas		Plumbogummite ASTM Card 2-0683		Indices	
d(*obs.*)	I/I$_1$	d(*obs.*)	I/I$_1$	d(*obs.*)	I/I$_1$	hkl	d(*calc.*)
1.366	8	..	..	..	..	522 441	1.367
1.351	6	..	..	..	..	532	1.350
1.321	3	..	..	1.32	20	31$\bar{2}$ 21$\bar{3}$	1.323
						41$\bar{1}$	1.320
1.295	7	..	..	..	..	54$\bar{3}$	1.291
1.286	9	..	..	1.28	40	40$\bar{1}$ 32$\bar{2}$	1.287
						42$\bar{1}$	1.284
1.258	8	..	..	1.26	20	544	1.254
1.200	9	..	..	1.20	40	520 4$\bar{1}\bar{1}$	1.202 1.200
1.185	8	..	..	1.19	20	553	1.181
1.173	3	..	..	1.17	20	554	1.173
1.147	1	..	..	..	..	533 552	1.144
1.141	2	..	..	1.14	20	31$\bar{3}$	1.143
						41$\bar{2}$	1.142
						500	1.140
1.121	6	..	..	1.12	40	622 643	1.123 1.119

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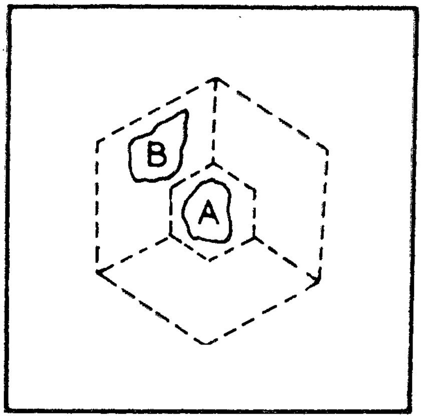

FIGURE 1 Optical anomalies in hinsdalite – core fragments "A" are uniaxial, peripheral fragments "B" are biaxial.

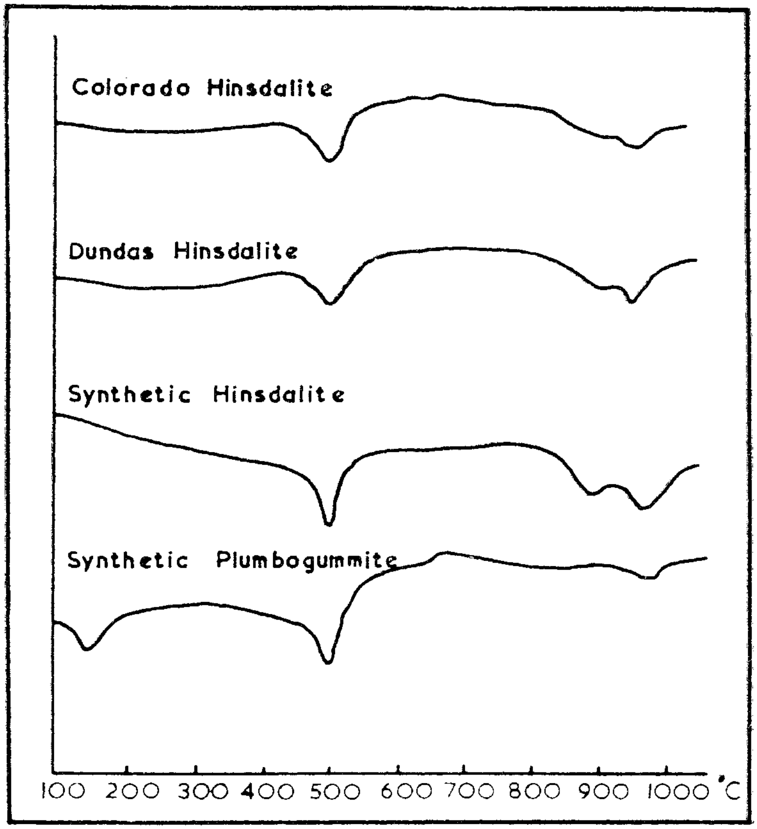

FIGURE 2 Differential thermal analysis curves for hinsdalite and plumbogummite.