

# SHORT COMMUNICATIONS

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## An apatite high in lead from Wanlockhead, Strathclyde Region, Scotland

DURING curation of the recently acquired Sutcliffe-Greenbank collection of Leadhills–Wanlockhead minerals, three exquisite vanadinite specimens attracted attention due to an investing chalky-white mineral. Two of the specimens may possibly have passed through the hands of well known mineral collectors, viz. Alexander Rose (1781–1860) of Edinburgh, and Thomas Brown MD (1774–1853) from Waterhaughs and Lanfine, Ayrshire. The Rose specimen is roughly rectangular ( $9 \times 4 \times 1.5$ –2 cm) and approximately 70% of one surface is covered by the chalky-white mineral. A siliceous base, with ferruginous material and hydrocarbons, is coated by a 1 mm hematite layer on which a soft grey–brown layer has been deposited. Both the orangey–brown, globular vanadinite (<7 mm) and chalky-white mineral have developed upon the grey–brown layer. It is highly probable that vanadinite of this quality came from the High Pirn Mine at Wanlockhead.

Five samples of the chalky white mineral from different areas of the Rose sample yielded X-ray powder diffraction patterns of apatite, a close similarity with that of carbonate apatite being noted. Microchemical tests revealed the presence of  $\text{CO}_2$  and further investigation showed a high lead content. Apatite is an exceedingly rare mineral within the Leadhills–Wanlockhead orefield, the first recording being from Whyte's Cleuch, Wanlockhead (Temple, 1956), although no description was published.

### X-ray and chemical data

Indexed X-ray powder data for 33 lines are presented in Table 1 which indicate that the

mineral belongs to the apatite rather than the pyromorphite subgroup. Comparison with apatite data in the Powder Diffraction File reveals that apatites with a line at  $d$  3.04–3.08 Å are either carbonate, fluor or hydroxyapatites. Cell parameters refined from the powder data are  $a = 9.472$  Å,  $c = 6.904$  Å and cell volume  $536.42$  Å<sup>3</sup>.

Temple (1954) also described a white mineral, after galena, from Whyte's Cleuch, the X-ray pattern of which is almost identical to that of the plumboan apatite with which it is compared (Table 1). He called the white phase lead hydroxyapatite for the diffraction pattern matched very closely that of synthetic basic lead phosphate. It became apparent that X-ray data alone could not characterize the apatite. Only a single fluorite-bearing specimen has been reported (by Heddle, 1901) from the High Pirn Mine and this is not in the Heddle collection within the Royal Museum of Scotland. With closely associated vanadinite, and pyromorphite abundant at the locality, it was thought that the carbonate-bearing apatite probably contained a reasonably high chlorine content.

Results from a full chemical analysis by ICP/AES on a 15 mg sample, together with EPMA data, are detailed in Table 2. All electron microprobe analyses were undertaken on polished grains using a Camebax Cameca instrument utilizing galena, wollastonite, apatite and halite standards. Lead, calcium and phosphorus are the only major elements detected, whereas chlorine is present in moderate amounts. Water and carbon dioxide, both of which are tenaciously held by the apatite structure, were determined by CHN analysis. Fluorine was determined using an ion selective electrode on an active acid dissolution.

TABLE 1. X-ray powder diffraction data for plumboan apatite from Wanlockhead and Temple's (1954) lead hydroxyapatite.

d meas(A)	I est	hkl	d calc (A)	d meas (A)	I est
8.33	10	100	8.203		
5.28	5	101	5.282		
4.79	5	110	4.736		
4.03b	20	200	4.101	4.06	fs
3.457	30	002	3.452	3.56	vw
3.178	15	102	3.182	3.18	vw
3.076	15	210	3.100		
2.893	60	211	2.828	2.92	vs
2.800	100	112	2.789	2.82	vw
2.709	70	300	2.734		
2.631	10	202	2.641	2.68	vvw
2.526	5	301	2.542		
2.342	5	220	2.368	2.37	vw
2.252	20	221	2.239	2.20	w
2.139	5	302	2.143	2.13	w
2.067	5	113	2.069	2.02	w
1.998	5	203	2.007	2.01	vvw
1.939	20	222	1.953	1.96	vw
1.886	15	320	1.882	1.91	w
1.841	30	213	1.848	1.88	vw
1.801	15	410	1.790	1.82	vw
1.773	10	402	1.763	1.77	vvw
1.750	10	303	1.761	1.75	vvw
1.726	5	004	1.726	1.68	vvw
1.634	5	500	1.640	1.56	vw
1.529	5	403	1.531	1.51	vw
1.472	5	510	1.473	1.47	vvw
1.453	5	(304)	(1.459)		
		(324)	(1.457)		
1.424	5	(422)	(1.414)		
		(413)	(1.413)		
1.279	5				
1.258	5				
1.237	5				
1.217	5				

Camera diameter 114.6mm, CuK $\alpha$ , Ni filter. Above indexed on an hexagonal cell with  $a = 9.472 \text{ \AA}$  and  $c = 6.904 \text{ \AA}$ . b = broad.

Normalizing to 10 cations of calcium, analysis 8, Table 2, yields the following formula:  $(\text{Ca}_{8.78}, \text{Pb}_{1.22})_{10}[(\text{PO}_4)_{5.53}, (\text{CO}_3)_{0.44}]_{\Sigma 5.97}(\text{OH}_{1.70}, \text{F}_{0.73}, \text{Cl}_{0.13})_{2.56} \cdot 1.5\text{H}_2\text{O}$ . The Ca:Pb ratio is 7.25:1 with 12% of the Ca sites filled by Pb. Empirically the formula reflects the now well-established replacement of P by C in carbonate apatites, whereas F is five-and-a-half times greater than Cl. Cockbain (1968) reported that synthetic apatites produced at low temperatures can display non-stoichiometric features as do natural, low-temperature apatites, e.g. 'francolite'. For the latter, McConnell (1952) concluded that it can be hydrated, and putting 1.5 H<sub>2</sub>O into the plumboan apatite empirical formula produces a good charge balance.

Infrared, using a KBr pressed disc, reveals the presence of OH, H<sub>2</sub>O, CO<sub>3</sub> and PO<sub>4</sub> absorptions (Fig. 1 and Table 3). Thermogravimetric analysis in argon (Fig. 2) yielded results which are difficult to reconcile with CHN values, the salient features being a gradual loss to 635°C. Simpson (1964) reported a similar gradual loss up to 680°C for alkali carbonate apatites. The sharp event at 635°C may be a specific compound decomposing, whereas the final, large loss reflects Pb sublimation.

#### Discussion

Engel *et al.* (1975) showed that a complete solid solution series exists between Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>

TABLE 2. Analyses of plumboan apatite, from Wanlockhead.

	1	2	3	4	5	6	7	8
CaO	37.78	37.41	36.53	39.26	41.72	38.62	41.72	40.03
PbO	23.09	20.93	22.72	21.05	18.67	21.29	18.52	22.07
P <sub>2</sub> O <sub>5</sub>	30.78	30.18	29.91	30.67	32.41	30.79	32.12	31.91
SiO <sub>2</sub>	0.02	0.02	0.03	0.04	0.02	0.03	0.10	-
SO <sub>3</sub>	0.14	0.16	0.23	0.14	0.09	0.15	0.11	-
Cl	0.43	0.40	0.44	0.37	0.26	0.38	n.d.	0.39
F	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.10	1.14
	92.24	89.10	90.26	91.53	93.17	91.26	93.67	100.56
							99.41*	
							-O≡F,Cl	
							0.55	0.56
							98.86	100.00

n.d. = not determined.

\*Includes H<sub>2</sub>O<sup>-</sup> 0.72 and CO<sub>2</sub><sup>-</sup> 0.17, H<sub>2</sub>O<sup>+</sup> 3.32 and CO<sub>2</sub><sup>+</sup> 1.53 wt. %.

Analyses 1-5, five separate grains, single spot analysis per grain.

6, average of 1-5.

7, ICP/AES.

8, Analysis 6 excluding SiO<sub>2</sub> and SO<sub>3</sub> normalised to 100%, and includes 3.44% H<sub>2</sub>O<sup>+</sup> and 1.58% CO<sub>2</sub><sup>+</sup>.

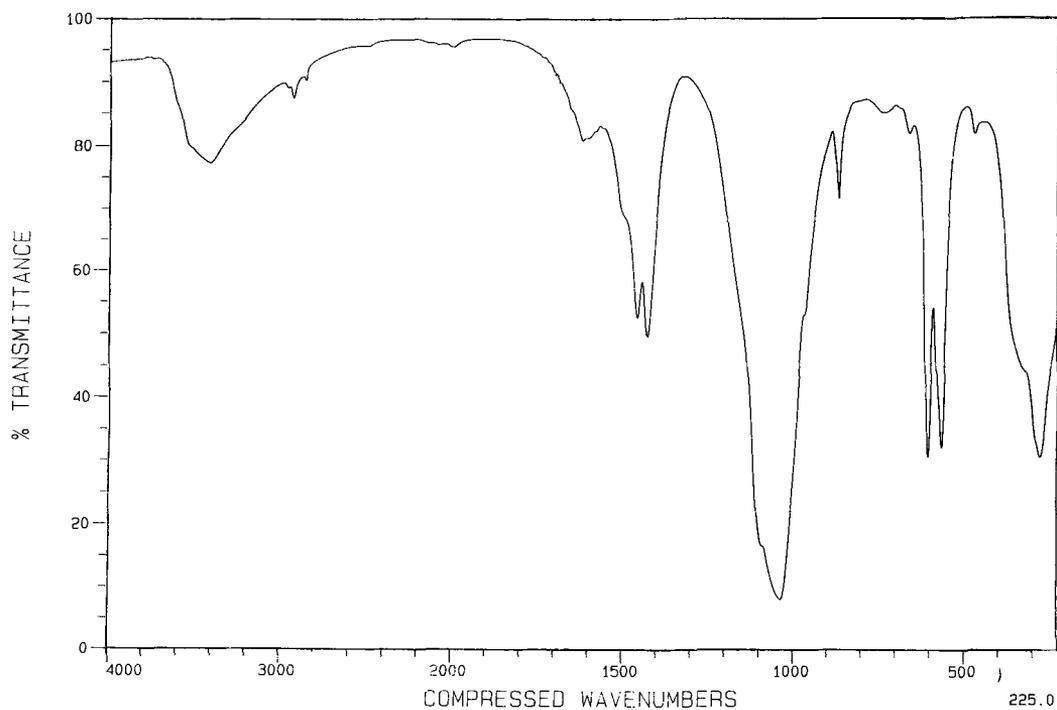


FIG. 1. Infrared spectrum of plumboan apatite.

TABLE 3. Infrared data for plumboan apatite from Wanlockhead.

	cm <sup>-1</sup>	%T	cm <sup>-1</sup>	%T
1	3412	78	6 865	73
2	1618	83	7 603	33
3	1454	55	8 564	34
4	1424	52	9 470	83
5	1033	9	10 274	34

and  $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ . Cell parameters, derived from synthesised compositions at 10 mol.% Pb increments, for the composition  $(\text{Ca}_9\text{Pb})_{\Sigma 10}(\text{PO}_4)_6(\text{OH})_2$  are  $a$  9.468 and  $c$  6.925 Å, cell volume 537.7 Å<sup>3</sup>, which are very close to those for the Wanlockhead material.

Analyses of apatites high in lead are difficult to locate within the literature. In their compilation of apatite analyses from numerous literature sources Smith and Leibovitz (1990) report a maximum

PbO content of 0.77%. The Wanlockhead apatite high in lead clearly demonstrates that a natural phase of composition  $(\text{Pb,Ca})_5(\text{PO}_4)_3(\text{OH})$  should exist which is the hydroxyl and phosphate analogue of hedyphane (Rouse *et al.*, 1984).

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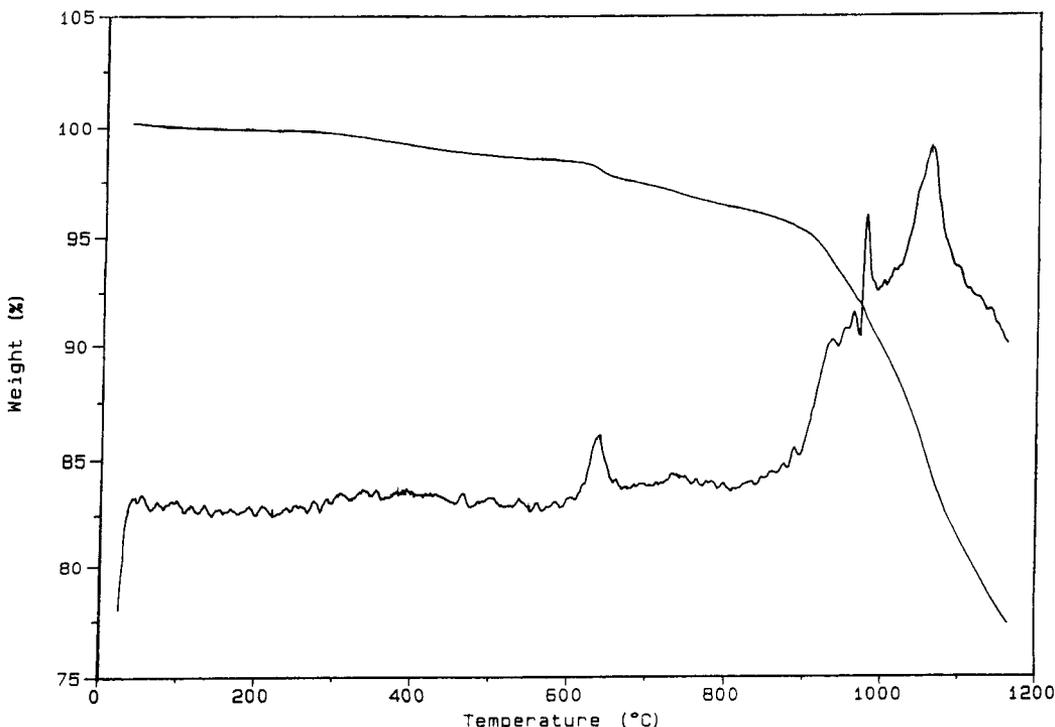


FIG. 2. Thermogravimetric curve of plumboan apatite, heating rate 10°C/min. in argon.

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## The compositional range of magmatic Mn-garnets in the Galway Granite, Connemara, Ireland

An alkali-feldspar leucogranite, called the Murvey Granite, is exposed in the central and marginal zones of the early Devonian, I-type (Caledonian) Galway Granite in the west of Ireland (Fig. 1). Previous studies have shown that some aplites within the leucogranite contain garnets and that a garnet-bearing variety of the Murvey Granite (Garnetiferous Murvey Granite) is also locally developed at the edge of the batholith (Wright, 1964; Thornton, 1964; Leake, 1967; Coats and Wilson, 1971; Lawrence, 1975; Leake, 1974). Wright (1964) stated that there can be little doubt that these manganiferous garnets constitute a primary phase and are not the result of contamination. Leake (1967) presented the results of microprobe studies of the garnets hosted by the Garnetiferous Murvey Granite and the aplites, exposed at the western end of the batholith, and highlighted the presence of compositional zoning

with Mn and Ca-rich centres and Fe and Mg-rich margins — see Fig. 2. Leake (1967) also reported that the garnets obviously crystallized from the granite magma and concluded that the zoning was clearly not related to metamorphic conditions, but was instead governed by the Rayleigh fractionation principle.

Our communication presents new compositional data from microprobe studies of garnets hosted by a pegmatite and an aplite exposed in a working quarry located in the centre of the non-garnetiferous Costelloe Murvey Granite (Fig. 1). The horizontal pegmatite is composed of alkali feldspar, quartz and biotite, and is up to 25 cm thick. Cherry red garnet euhedra between 2 and 5 mm in diameter are sporadically developed in the pegmatite and locally occur in clusters of up to ten crystals. The geochemistry of this pegmatite has been published by Whitworth and Feely (1989).