

Plumbogummite-group minerals from Mull and Morvern

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SUMMARY. Sandstones from Mull and Morvern, most of which are from the Greensand formation, have been shown by X-ray diffraction to contain minerals of the plumbogummite group in very small amounts in the $< 1.4 \mu\text{m}$ fraction. The minerals were concentrated by HF digestion of the clay minerals. X-ray spectrographic traces show concentrations of Sr, La, Ce, Yt, and Ba, and a semi-quantitative spectrochemical analysis also shows a concentration of Ca and Pb and the presence of numerous rare-earth elements. Individual minerals, which have a complex composition and can not be assigned to any one named species, are disseminated throughout the rocks as particles with an estimated size of between 0.1 and 0.25 μm .

MINERALS of the plumbogummite group are hydrated alumino-phosphates of Pb, Sr, Ca, Ba, and Ce and are isostructural with minerals of the alunite group of sulphates and the beudantite group of mixed sulphate-phosphates (Palache, Berman, and Frondel, 1951; Kato and Radoslovich, 1968). The formula is $X\text{Al}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ where X can be Pb (the mineral plumbogummite), Sr (goyazite), Ca (crandallite), Ba (gorceixite), or rare earths (florencite). The degree of inter-substitution of these cations is variable.

Plumbogummite-group minerals have been recorded from widely varying parageneses. The first reported occurrences were from 'favas', i.e. nodules found in diamantiferous sands (e.g. Hussak, 1906). Many occurrences are in sedimentary rocks (e.g. Milton *et al.*, 1958; Young, 1958) but others have been noted in igneous rocks, particularly carbonatites (Coetzee and Edwards, 1959; McKie, 1962), in ore veins (Tokody, Mándy, and Nemes-Varga, 1957), and in metamorphic rocks (Kempe, 1968). These minerals have also been found in soils by Norrish (1957) and others, and Norrish (1968) states that they must be regarded as one of the common forms of soil phosphate.

Nevertheless, these minerals are comparatively rare and the only recorded occurrences in Great Britain are of crandallite in a North Staffordshire tonstein (Wilson *et al.*, 1966), and of plumbogummite as an encrustation on vein quartz at Roughten Gill, Cumberland (Miers, 1896, 1900; Hartley, 1900; Förtsch, 1967), and associated with ore minerals in Cornwall (Kingsbury, 1952).

This paper reports the presence of rare earth members of the group in certain rocks from Morvern and the Isle of Mull, Argyll.

Geology and location of rocks studied. Twenty-seven rocks, mostly greensands, were investigated and plumbogummite-group minerals detected in eleven of these, of

which one originated from the Poll Luachrain area of Morvern, and the others from Gribun in western Mull and near Loch Don in south-eastern Mull. These eleven rocks are all fine-grained, glauconitic, calcareous sandstones, with the exception of one, which is a calcareous sandstone from the Great Estuarine Series.

Methods of investigation. Samples were crushed to $< 150 \mu\text{m}$ and the $< 1.4 \mu\text{m}$ e.s.d.[†] fraction separated by the standard sedimentation procedures of Mackenzie (1956) using a few drops of ammonia as a dispersant. To remove carbonates from calcareous samples a preliminary extraction was made with 25 % acetic acid (Gault and Weiler, 1955) and the residue washed with de-ionized water to remove acetates.

X-ray powder photographs of random and pressure-oriented aggregates of the clay fractions ($< 1.4 \mu\text{m}$) were obtained using 9-cm precision cameras with Fe-filtered Co-K α radiation from a Raymax diffraction unit.

The clay fractions were treated with HF in a manner similar to that of Norrish (1957). To prevent the formation of fluorite, however, apatite was removed by an overnight extraction with *N* formic acid. Washing with *N* NaOH, as recommended by Norrish, was omitted as artefacts sometimes formed. This method removed most clay minerals, except illite and muscovite, and so concentrated the plumbogummite-group minerals, where these were present. If Mg is present in the clay, HF treatment may produce $\text{NH}_4\text{MgAlF}_6$, which gives an X-ray diffraction pattern with *d*-spacings similar to plumbogummite-group minerals, but with quite different relative intensities. This compound can be removed with warm HCl.

Results

Mineralogy of fraction $< 1.4 \mu\text{m}$. The minerals most commonly present in the clay fractions were mica (usually glauconite or muscovite or both) and quartz, with chlorite and apatite in about half the samples, and kaolinite and a smectite in a few. Some of the Mull rocks also contained an uncharacterized 12 Å mixed-layer mineral.

X-ray diffraction lines (generally quite weak) at about 5.7 and 2.94 Å suggested plumbogummite-group minerals. After HF treatment, a set of diffraction lines at about 5.7, 3.49, 2.94, 2.71, 2.42, 2.17, 1.89, and 1.74 Å were present in addition to those of quartz and muscovite, confirming the presence of a mineral of this group. Occasionally the minerals were detected only after employing the HF concentration procedure, and in all instances this treatment was necessary for positive identification.

In attempting to identify the particular plumbogummite-group mineral present, chemical information was used to supplement the X-ray data, since the X-ray powder patterns of the various species are all very similar. It was not practical to perform a total chemical analysis from which the formula of the mineral could be calculated, because of the difficulty in obtaining a sufficient quantity of reasonably pure material.

In carrying out the standard spot test for phosphate (Feigl, 1953) on the clay fractions (after removal of apatite), the difficulty in bringing the plumbogummite-group minerals into solution was overcome by Na_2O_2 fusion (Young, 1958). The test proved

[†] e.s.d. = equivalent spherical diameter.

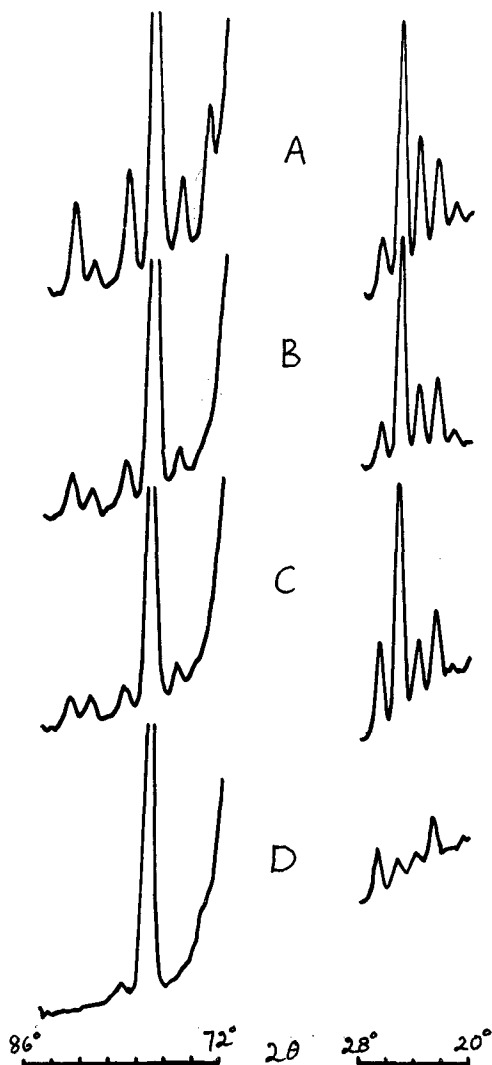


FIG. 1. X-ray spectrographic traces of untreated $< 1.4 \mu\text{m}$ fractions of four greensands. A, B (sample SP 17), and C contain a plumbogummite-group mineral, whereas D does not. The peaks, from left to right, are: in the 86 to $72^\circ 2\theta$ section, La- L_{α_1} , Sr- K_{α_3} , Ba- $L_{\beta_1} \pm$ Ce- L_{α_1} , Ti- K_{β} , La- L_{β_3} , and Ba- L_{β_2} ; and in the 28 to $20^\circ 2\theta$ section, Rb- K_{α} , Sr- K_{α} , Yt- $K_{\alpha} \pm$ Rb- K_{β} , Sr- $K_{\beta} \pm$ Zr- K_{α} , and Yt- K_{β} .

positive for all clay fractions whose diffraction patterns suggested the presence of plumbogummite-group minerals, and negative for the others.

Qualitative X-ray spectrographic traces (recorded on a Philips PW1540 spectrograph using Cr radiation and a LiF(200) analysing crystal) of untreated clay fractions show a greater concentration of Sr, La, Ce, Yt, and Ba in samples containing plumbogummite-group minerals (fig. 1). Scans over the Ca- K_{α} peak were also carried out but there was no definite trend of relative abundance of Ca in samples with or without plumbogummite-group minerals. This may be due to the variation in the amount of Ca present in the other minerals.

In order to obtain more detailed information about the nature of the plumbogummite-group minerals, one of the Mull samples (SP 17) from the Greensand formation at Gribun in which the mineral was detected in the untreated clay fraction, was selected for more intensive study. The results of a semiquantitative spectrochemical analysis (performed using the D.C. arc technique described by Mitchell, 1964) of the HF treated clay fraction of this rock (table I) show high concentrations of Ba, La, Pb, Sr, and Yt and the presence of numerous other rare earth elements and Ca, which is consistent with the presence of a plumbogummite-group mineral.

An electron-optical study of the clay fraction of SP 17 revealed numerous very small grains (0.1 – $0.25 \mu\text{m}$), which were usually rounded but with no

definite shape although a few were roughly hexagonal. Diffraction from an area of a sample $< 0.25 \mu\text{m}$ (which was separated by centrifuging and subsequently HF treated) yielded the d -spacings listed in table II, column 1. These values are

very similar to those attributed to the plumbogummite-group mineral on the X-ray pattern.

The X-ray diffraction lines of the $< 0.6 \mu\text{m}$ fraction (table II, column 2), also separated by centrifuging, showed a greater concentration of the plumbogummite-group mineral than in the $< 1.4 \mu\text{m}$ fraction. The muscovite lines, which were still

TABLE I. *Semi-quantitative spectrochemical analysis of the $< 1.4 \mu\text{m}$ fraction of a Mull greensand (SP 17) after HF treatment. Results are expressed in ppm*

Ag	100	Co	3	La	$\gg 10\ 000$	Rb	200	Tl	20
Ba	10 000	Cr	300	Li	15	Sb	< 300	V	250
Be	< 3	Cu	60	Mn	200	Sc	6	Y	4000
Bi	< 30	Ga	15	Mo	2	Sn	10	Zn	< 1000
Ca*	c. 10 000	Ge	< 10	Ni	200	Sr	$\gg 10\ 000$	Zr	400
Cd	< 300	In	< 3	Pb	1500	Ti	12 000		

Other rare earth elements observed in the sample: Pr, Nd, Sm, Eu, Gd, and Yb.

* From an examination of the spectrograms (prepared for semi-quantitative analysis of trace elements) Ca appeared to be present in significant amount—probably about 1%.

TABLE II. *d-spacings of a plumbogummite-group mineral found in a Mull greensand*

1			2			1			2		
5.71 Å	5.68 Å	vs	2.45 Å	2.43 Å	m	1.77 Å	1.74 Å	m			
3.51	3.50	s	2.21	2.21	w	—	1.63	vw			
2.98	2.94	vvs	—	2.17	m	—	1.48	w			
—	2.83	vw	1.91	1.89	fs	—	1.46	w			
2.75	2.72	m									

1. *d*-spacings from electron diffraction pattern of $< 0.25 \mu\text{m}$ fraction of SP 17 after HF treatment.
2. *d*-spacings from X-ray diffraction pattern of $< 0.6 \mu\text{m}$ fraction of SP 17 after HF treatment.

present, are not recorded in the table. These *d*-spacings and relative intensities are similar to those on the A.S.T.M. cards for all the plumbogummite-group minerals, though not identical with any particular species.

Plumbogummite-group minerals could not be detected in the $> 1.4 \mu\text{m}$ fraction of any sample.

Discussion. As the semi-quantitative spectrochemical analysis of SP 17 shows that rare-earth elements, Sr, Ca, and Ba are all present in appreciable quantities, and, to a lesser extent, Pb, the plumbogummite-group mineral in this greensand can not be given a specific mineral name since X-ray spectrographic traces show that some or all of the elements Sr, La, Ce, Yt, and Ba have been concentrated in every instance. In addition, the composition varies from sample to sample as shown by variable X-ray spectrographic traces and X-ray diffraction patterns.

The particle size of the plumbogummite minerals detected in the rocks under investigation is $< 1.4 \mu\text{m}$, and for one sample (SP 17) is in the range $0.1\text{--}0.25 \mu\text{m}$. Optical examination of thin sections cut from these rocks failed to reveal anything that

could be identified as a plumbogummite-group mineral so the mineral must be disseminated throughout the rocks as very small particles. In some occurrences, however, plumbogummite minerals have been found concentrated in nodules, for example, gorceixite reported by Milton *et al.* (1958) in a glauconitic sand of Eocene age in Alabama occurred in irregular nodules up to several inches across.

In most occurrences, plumbogummite-group minerals seem to have formed under supergene conditions, although McKie (1962) suggests an alternative origin by crystallization during late-stage replacement processes for goyazite, florencite, and gorceixite in the African carbonatites he studied, and Kempe (1968) states that gorceixite in a Tanzanian schist is apparently of metamorphic origin. No textural evidence could be obtained to determine the origin of the plumbogummite-group minerals in the Mull and Morvern rocks. They may be detrital (they are extremely resistant chemically), or they may have formed during diagenesis or under supergene conditions at some later stage.

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