

## Phosphate minerals in pallasite meteorites

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**SUMMARY.** Phosphate minerals are widespread minor constituents of the pallasites. Both anhydrous primary and hydrous decomposition/alteration phosphates occur. The primary minerals, in decreasing order of abundance, are whitlockite, stanfieldite, and farringtonite, as well as a possibly new phosphate. The decomposition phosphates are compositionally heterogeneous and thus complex. Some may be new minerals. The phosphate minerals serve as the major repository for the alkali elements in pallasites, with individual crystals containing up to several percent of Na + K. Equilibrium established between coexisting phosphide and phosphate defines a relatively narrow range of  $f_{O_2}$  values.

PALLASITIC meteorites are essentially composed of Fe-Ni metal and olivine, with minor troilite; they have been considered remarkably simple mineralogically. Olivine is the only silicate that has been reported, although pyroxene has recently been observed as a minor phase (Buseck, 1977). DuFresne and Roy (1961) described farringtonite (essentially  $Mg_3(PO_4)_2$ ) from the Springwater pallasite and Fuchs (1969) reported stanfieldite ( $Ca_4(Mg,Fe)_5(PO_4)_6$ ) and whitlockite (ideally  $Ca_3(PO_4)_2$ ) from a few pallasites.

As part of a comprehensive study of the mineralogy and petrology of the pallasites, we have observed several phosphate minerals. They include the three phosphates mentioned above, as well as a few additional ones. Several of the latter, including ones containing small amounts of Ni or Cr, probably result from alteration of the primary pallasite minerals.

We have observed phosphates in 31 of 41 pallasites studied; it appears that they are essential, albeit minor, constituents of pallasitic meteorites. In addition to the phosphates, several other minor phases occur (Buseck, 1968, 1969).

The phosphate minerals are significant phases in pallasites for several reasons. Not only are they widespread, but they play an important role in that they serve as repositories for elements such as Na, K, U, and Th, which are not accommodated within the major minerals. Additionally, coexisting phosphates and phosphide can be used to define the fairly narrow range of  $f_{O_2}$  conditions under which the pallasites formed. The existence of a suite of anhydrous phosphates, rare in terrestrial mafic igneous rocks, is one of several features giving uniqueness to the pallasites.

### *Occurrence*

It is likely that phosphate minerals occur in all of the pallasites, for in many cases we have only been able to study single small (*c.* 1 cm<sup>2</sup>) polished sections from a given meteorite; such a small sample cannot be representative of these coarse-grained meteorites. Consequently we believe it probable that the pallasites that we were either unable to examine, or in which we observed no phosphates, actually do contain such phases.

Table I lists all the pallasites in which phosphates have been observed. Phosphates listed in the column labelled 'Identification uncertain' differ in composition from whitlockite, stanfieldite, and farringtonite. If analysed, their compositions can be determined by referral to Tables II to IV; others were observed by reflected light microscopy, but their compositions were not checked with the electron microprobe because of sampling problems (e.g., too large a specimen to fit into the instrument chamber). Wahl (1965) reported farringtonite in several pallasites,

TABLE I. *Survey of phosphate occurrences in pallasites*

Meteorite name	Whitlockite	Stanfieldite	Farringtonite	Identif. uncert.	Meteorite name	Whitlockite	Stanfieldite	Farringtonite	Identif. uncert.
Ahumada	X*	—	—	X*	Lipovsky	—	—	—	X
Albin	X*	X*	—	—	Marjalahti	X*	—	—	W
Antofagasta	X*	X*	—	—	Molong	—	—	—	X
Brahin	—	—	—	X*	Mt. Vernon	X* F	X* F	—	—
Brenham	X	X	—	—	Newport	—	F	—	X* W
Cold Bay	X	—	—	—	Ollague	X*	X*	—	—
Eagle Station	—	X*	—	—	Pavlodar	X	—	—	W
Esquel	—	—	—	X	Phillips Co.	—	—	F	X*
Finmarken	X	X	—	—	Rawlinna†	X*	X*	X*	—
Giroux	X	—	—	—	Salta	X	—	—	—
Glorieta Mtn.	—	—	—	X	Santa Rosalia	X* F	X* F	—	—
Huckitta	—	—	—	X W	Somervell Co.	X	—	—	—
Ilimaes	—	X	—	—	South Bend	X	—	—	—
Imilac	X*	X* F	—	—	Springwater	X*	X*	X* F	—
Itzawisis	X	—	—	—	Thiel Mtns.	—	X	—	—
Krasnojarsk	—	—	F	X					

X phosphate observed; X\* quantitative analysis performed; F, reported by Fuchs (1969), W, by Wahl (1965).

† See McCall (1968) for details of find.

but did not indicate the means used for identification. These meteorites are listed with a 'W' in Table I. Farringtonite was the only phosphate known from pallasites in 1965 and it is probable that he assumed any phosphate would be farringtonite. The phosphate occurrences listed by Fuchs (1969) are indicated with an 'F'. Fuchs mentioned several meteorites as containing only one phosphate. In these meteorites we have observed seven additional instances of phosphates that Fuchs did not find, reflecting the sporadic occurrence of these phases.

*Microscopy.* Many investigators have studied pallasites. Why have these widespread phases only been observed recently, and why have so many researchers overlooked them? The answer lies in the small size and remarkable resemblance that the phosphates have to the major non-opaque mineral, olivine. The similarity in reflectivity and colour is especially great in reflected light.

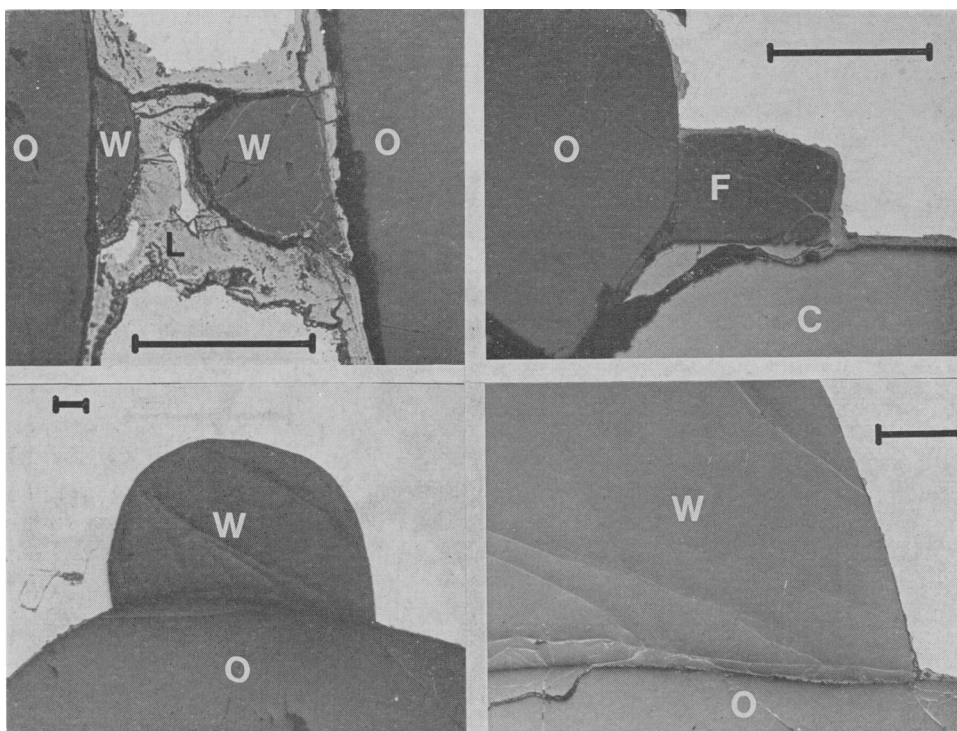
The phosphates may primarily be recognized on the basis of the relief developed at their contacts with olivine. However, a thin layer of embedding plastic looks very similar to phosphate, especially if the plastic overlies an olivine crystal. Optically, it is therefore difficult to confirm the presence of the phosphates. By using the electron microprobe it is, of course, possible to immediately check for the existence of these phases.

The most widespread phosphates in pallasites are whitlockite and stanfieldite. It is difficult to distinguish optically between them. Where they are adjacent, whitlockite appears very slightly harder, greyer, and less greenish than stanfieldite as seen in reflected light. Also, stanfieldite is commonly extensively fractured; in the Imilac pallasite these fractures stop at the margins of enclosed whitlockite.

*Interrelationships.* All the phosphates seem to have similar occurrences; they typically are at the peripheries of the olivine. Commonly they lie along the interstices between adjacent silicate crystals. These are also the places where troilite occurs, and in this instance the sulphide

generally separates the phosphates from the surrounding kamacite and taenite (fig. 1). It appears as if the phosphate solidified earlier than troilite, but later than olivine. The olivine crystal shapes thus predate the phosphates.

In the Albin pallasite, whitlockite and stanfieldite typically occur in direct contact with one another, with crisp, straight contacts showing no evidence of reaction. In all the observed



FIGS. 1 to 4: FIG. 1 (top left). Rounded grains, presumably former droplets, of whitlockite (W) attached to larger crystals of olivine (O). In this and subsequent figures, the white phase is kamacite or taenite; the material separating whitlockite from kamacite was troilite which has now been largely altered to 'limonite' (L). The black linear areas along the boundaries of these phases are cracks (formed by plucking during polishing or during weathering). The scale bar is 100  $\mu\text{m}$  long. *Somervell Co.* FIG. 2 (top right) Euhedral farringtonite (F) crystal at the junction between olivine (O) and chromite (C). The scale bar is 100  $\mu\text{m}$  long. *Rawlinna.* FIG. 3 (bottom left) Crystal of whitlockite (W) with a rounded outline (like a solidified droplet) resting on olivine (O). The scale bar is 100  $\mu\text{m}$  long. *Springwater.* FIG. 4 (bottom right). Detail of fig. 3. Note the smooth interface, and the rounded surfaces of both phases.

cases the whitlockite is situated between the stanfieldite and kamacite. In other meteorites both whitlockite and stanfieldite occur adjacent to kamacite (commonly there is a thin band of the ubiquitous 'limonite' terrestrial alteration product separating the metal from all the other phases).

An unusual occurrence for the phosphate is in the symplectic margins that surround some olivines in a few of the pallasites (Buseck, 1977). Whitlockite was observed in such regions in the Ahumada, Itzawisis, Marjalahti, South Bend, and Springwater pallasites. In these instances the phosphate coexists with troilite and chromite and occurs in grains only a few microns across. Generally the phosphates are in larger grains, ranging up to a few millimetres in diameter.

The only instances of phosphates that appear to be euhedral are the farringtonites in Rawlinna (fig. 2). Two such crystals are nearly rectangular in outline; both border on chromite and one occurs within 50  $\mu\text{m}$  of stanfieldite. The only farringtonite reported from a non-pallasite, the Barranca Blanca iron meteorite, also lies at the margin of chromite and kamacite (Bild, 1974).

Perhaps the most interesting textures are those suggesting that phosphate was liquid after the olivine had crystallized and thus represent a solidified residual melt. Such textures include: rounded phosphate grains suggestive of solidified droplets on the periphery of olivine crystals (figs. 3, 4); cusp-like regions of phosphate at the junctures of olivine crystals, with the portion facing the metal resembling a meniscus (fig. 5); and fillings of the narrow, parallel-walled veinlets or interstices that commonly separate adjacent olivine crystals (e.g., to the right of the 'S' in fig. 6). The phosphates are commonly 'plastered' onto the surfaces of large, smooth, rounded olivines. The olivine surfaces are typically unaffected by the partial coatings of phosphate, indicating a lack of reaction between the two phases. The olivines in some pallasites contain spherical inclusions that resemble former droplets. In Ilimaes some contain kamacite, troilite, and stanfieldite, with the phosphate on the same side of several inclusions. It appears as if the stanfieldite floated to the top of the droplets.

The 'decomposition phosphates', listed in the 'Identification uncertain' column of Table I, have a different occurrence from the anhydrous phosphates described above. In Albin the decomposition phosphate occurs along the contact between olivine and schreibersite, and extends into the fractures cutting schreibersite (fig. 7). The Brahin phosphates, although apparently anhydrous, have a similar occurrence. In Newport the decomposition phosphate is adjacent to weathered troilite and schreibersite, and invades fractures within the latter in a fashion suggesting it is a reaction product. The decomposition phosphates appear to have resulted largely from the terrestrial weathering of schreibersite, with occasional contributions from chromite.

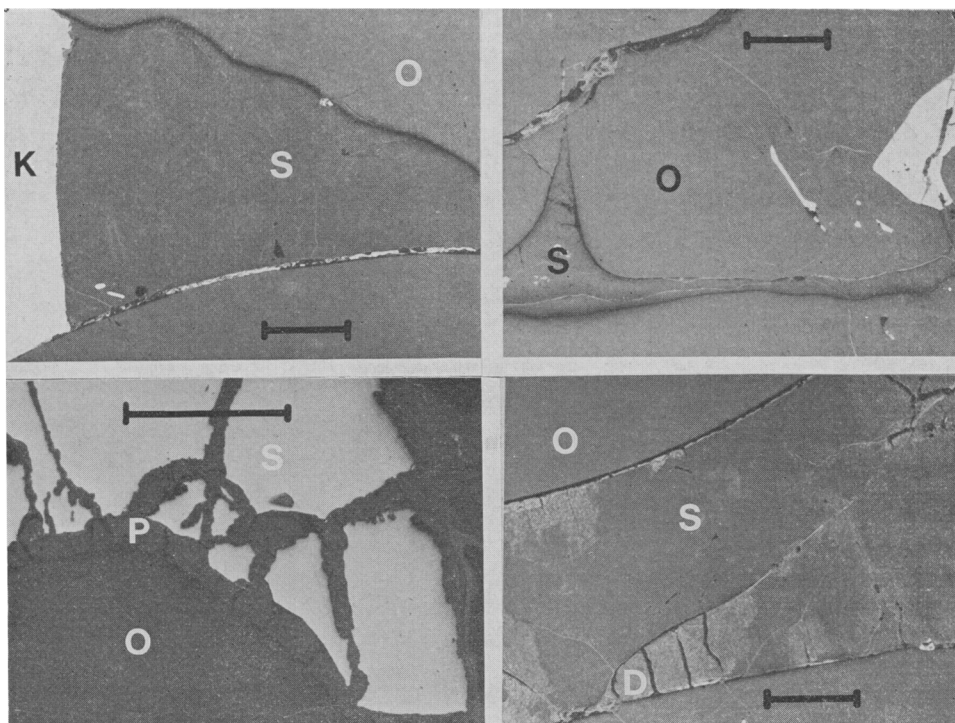
Except for the Brahin phosphates, the 'decomposition phosphates' listed in the previous paragraph contain Ni or Cr or both as well as apparently being hydrated. One of the decomposition phosphates (labelled 'Springwater (7)') differs in that neither Ni nor Cr could be detected. Also, rather than being near strongly weathered phosphides, 'Springwater (7)' occurs within a sizeable field of stanfieldite (fig. 8), which is essentially free of weathering products such as limonite. It looks as if 'Springwater (7)' formed by the decomposition of stanfieldite. As 'Springwater (7)' is more Fe-rich than stanfieldite, Fe must have been introduced, perhaps during terrestrial weathering.

The 'Springwater (7)' phosphate resembles stanfieldite fairly closely in reflected light. The decomposition phase appears to be slightly harder, although this is surprising if it is truly a hydrated reaction product. The 'Springwater (7)' phosphate has a gritty or grainy texture and it shows considerable compositional variation, depending on the degree of alteration of the host material. It is conceivably an intimate mixture of phases, thus accounting for its grainy appearance.

#### *Chemistry*

*Experimental.* All available phosphates were analysed for Ca, Mg, Fe, Mn, Na, K, P, and Si using the electron microprobe. Where appropriate, Ni and Cr were also measured. Apatite was used as a standard for Ca and P, garnet for Si, Fe, Mg, Mn, and obsidian for Na and K. Detection limits of the oxides (in wt. %) were 0.02 for Fe, Ca, Ni, Cr, Si; 0.03 for K; 0.05 for P, Mn, Mg; and 0.1 for Na. Standard corrections were applied. All samples were also monitored with an energy-dispersive analyser; elements other than those given above were not detected.

The results of 90 analyses of phosphates in 19 different meteorites are given in Tables II to IV. With the exception of phosphates that have formed as alteration or decomposition products, only analyses whose weight % totals to  $100 \pm 2$  are included. We believe that the apparent mass deficiencies of the alteration phosphates result from water of hydration, which, of course, is not detectable with the microprobe.



FIGS. 5 to 8: FIG. 5 (top left) Stanfieldite (S) in cusp-like region between two olivine (O) crystals. Note the smoothly rounded interface between the phosphate and kamacite (K), suggesting a solidified liquid. The scale bar is  $100 \mu\text{m}$  long. *Springwater*. FIG. 6 (top right). Typical occurrence of phosphate (stanfieldite—S) in interstices of adjacent olivine (O) crystals. The scale bar is  $100 \mu\text{m}$  long. *Santa Rosalia*. FIG. 7 (bottom left). Decomposition phosphate (P) in link-sausage-like shapes along the interface between olivine (O) and schreibersite (S). The scale bar is  $100 \mu\text{m}$  long. *Albin*. FIG. 8 (bottom right). Intimate intergrowth of stanfieldite (S) and decomposition phosphate (mottled, light grey regions—D). The small white grains are troilite and the large rounded crystals are olivine (O). The scale bar is  $100 \mu\text{m}$  long. *Springwater*.

It is possible that X-ray counts from olivine are included in some of the analyses. For the atomic proportions listed in Tables III and IV we assume that all of the Si derives from olivine. Using the relevant Fe and Mg values for olivine from Buseck and Goldstein (1969), appropriate amounts of these elements were subtracted to provide Si-free analyses. For the weight % values of 'olivine-corrected' analyses the residual summations were increased by normalization to their original measured values. The original measured  $\text{SiO}_2$  contents are indicated in Tables II and IV.

Although the subtraction of the olivine 'molecule' from the analyses seems reasonable, it is not certain that all phosphates are free of minor Si. Some large phosphate grains produce minor Si counts. DuFresne and Roy (1961) noted the presence of Si in their spectrographic analyses of farringtonite. They speculated that it may be present in solid solution with P.

Olsen and Fredriksson (1966) detected no Si ( $< 500$  ppm) in another analysis of Springwater farringtonite; Fuchs *et al.* (1973) reported 0.09 and 0.07 wt. %  $\text{SiO}_2$  in Springwater and Krasnojarsk farringtonite. Further work will be required to resolve this potential problem of the extent of Si substituting for P.

TABLE II. *Electron microprobe analyses of phosphates from pallasitic meteorites*

Meteorite	No. of grains	FeO	CaO	MgO	MnO	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{P}_2\text{O}_5$	$\text{SiO}_2$	Sum	Source and No.
<i>Whitlockite</i>											
Ahumada (1)*	5	1.85	49.1	3.32	$< 0.05$	0.10	n.f.†	45.6	0.32	100.3	ASU(354.1.1b)
Ahumada (2)	1	1.69	48.2	3.91	n.f.	0.20	n.f.	46.0	0.21	100.2	ASU(354.1.1b)
Ahumada (3)	1	0.45	48.6	4.06	n.f.	0.30	n.f.	47.6	0.51	101.5	ASU(354.1.1b)
Albin (2)	2	0.92	49.2	3.90	0.07	0.85	0.05	45.9	0.15	101.0	USNM(934)
Albin (3)	5	0.26	48.7	3.67	0.14	0.94	0.06	46.8	0.10	100.7	ASU(314.3.1)
Antofagasta (2)	3	0.36	50.2	3.62	0.08	0.52	$\sim 0.03$	45.9	n.f.	100.7	ASU(656.1a)
Cold Bay (1)	1	2.11	45.4	6.43	$< 0.05$	1.08	$< 0.03$	43.5	1.94	100.5	USNM(633)
Imilac (2)	2	1.20	47.3	5.35	0.12	0.49	$< 0.03$	45.3	0.85	100.6	ASU(295a.1.A)
Marjalatti (1)	2	0.88	48.8	4.52	n.f.	n.f.	n.f.	45.2	n.f.	99.4	ASU(200a.2)
Marjalatti (2)	1	1.10	47.2	4.23	n.f.	n.f.	n.f.	47.3	n.f.	99.8	ASU(200a.1)
Mt. Vernon (3)	2	0.50	48.6	4.65	n.f.	0.26	n.f.	46.5	0.10	100.5	ASU(221a.1)
Mt. Vernon (4)	1	0.33	48.9	3.76	$< 0.05$	0.36	$\sim 0.03$	46.4	0.22	100.1	ASU(221a.2)
Ollague (2)	1	0.28	49.0	3.82	0.10	0.90	0.06	46.5	0.10	100.8	ASU(146a.1)
Rawlinna (8)	1	5.19	43.8	4.48	$< 0.05$	2.96	0.11	42.8	0.88	100.2	ASU(677.1)
Rawlinna (10)	1	3.13	44.2	5.18	0.10	2.80	0.11	44.7	1.29	101.5	ASU(677.1)
Santa Rosalia (3)	1	0.77	48.3	3.66	0.12	0.78	n.f.	46.7	n.f.	100.3	ASU(599.1.2)
Santa Rosalia (6)	2	0.47	48.7	3.65	n.f.	1.56	0.06	47.4	n.f.	101.8	ASU(599.1.1)
Somervell Co. (1)	2	0.50	48.7	3.76	n.f.	0.68	n.f.	46.8	0.08	100.5	USNM(1408)
Springwater (3)	1	1.49	44.5	4.50	$< 0.05$	3.16	$\sim 0.03$	46.0	0.80	100.5	ASU(135d.2.1)
Springwater (10)	1	1.59	46.1	3.75	$\sim 0.05$	3.10	0.09	47.1	0.09	101.9	ASU(135d.2.1)
Springwater (12)	1	1.87	47.0	3.36	$< 0.05$	2.64	0.09	44.3	0.09	99.3	ASU(135d.2.1)
<i>Starfieldite</i>											
Albin (4)	6	2.50	26.8	20.4	0.44	n.f.	n.f.	50.0	0.06	100.2	ASU(314.3.1)
Antofagasta (1)	3	2.61	27.6	21.2	0.47	n.f.	n.f.	48.9	0.08	100.9	ASU(656.1c)
Antofagasta (3)	1	2.49	27.3	21.1	0.44	n.f.	n.f.	49.0	n.f.	100.3	ASU(656.1a)
Eagle Station (2)	2	4.78	24.6	21.6	0.31	n.f.	n.f.	48.5	0.19	100.0	ASU(196a.1)
Eagle Station (1)	1	7.36	23.2	21.5	0.30	n.f.	n.f.	47.3	0.70	100.4	ASU(196b)
Imilac (1)	1	2.43	26.2	22.4	0.42	n.f.	$< 0.03$	49.8	0.59	101.9	ASU(295a.1.A)
Mt. Vernon (1)	2	2.42	26.8	21.7	0.33	n.f.	n.f.	49.4	n.f.	100.7	USNM
Mt. Vernon (2)	2	2.03	26.1	20.8	0.40	n.f.	n.f.	49.6	n.f.	98.9	ASU(221a.1)
Mt. Vernon (5)	1	2.04	26.9	21.2	0.30	n.f.	n.f.	49.0	0.16	99.6	ASU(221a.2)
Ollague (1)	2	2.60	26.4	21.5	0.41	n.f.	n.f.	48.6	n.f.	99.5	USNM(1612)
Rawlinna (9)	1	6.02	24.4	21.8	0.32	n.f.	n.f.	46.0	1.29	99.8	ASU(677.1)
Rawlinna (14)	1	6.89	24.6	20.5	0.25	$< 0.1$	$< 0.03$	46.7	0.11	99.0	ASU(677.1)
Santa Rosalia (1)	1	2.59	26.1	21.9	0.36	n.f.	n.f.	50.3	n.f.	101.3	ASU(599.1.3)
Santa Rosalia (2)	2	2.45	26.5	20.9	0.31	n.f.	n.f.	50.1	0.14	100.4	ASU(599.1.4)
Santa Rosalia (5)	1	2.58	25.8	21.0	0.35	n.f.	n.f.	49.6	n.f.	99.3	ASU(599.1.2)
Springwater (8)	1	3.68	25.9	20.8	0.66	$\sim 0.11$	n.f.	50.0	0.02	101.2	ASU(135d.2.1)
Springwater (9)	1	3.72	25.3	21.2	0.45	$\sim 0.10$	n.f.	50.5	0.02	101.3	ASU(135d.2.1)
Springwater (11)	1	3.76	25.4	21.2	0.58	$\sim 0.13$	n.f.	49.2	0.02	100.3	ASU(135d.2.1)
<i>Farringtonite</i>											
Rawlinna (12)	1	5.78	0.04	41.8	0.19	n.f.	n.f.	52.8	0.24	100.9	ASU(677.1)
Rawlinna (13)	1	5.67	0.07	40.5	0.14	n.f.	n.f.	52.2	0.05	98.6	ASU(677.1)
Springwater (1)	2	4.12	0.09	43.4	0.24	n.f.	n.f.	52.6	0.12	100.6	ASU(135a.1)
<i>Miscellaneous</i>											
Brahin (1)	1	49.6	n.f.	8.32	n.f.	n.f.	n.f.	36.5	3.73	98.2	ASU(744.1)
Brahin (2)	3	54.2	n.f.	4.23	0.06	n.f.	n.f.	40.2	0.31	99.9†	ASU(744.1)
Springwater (2)	2	4.95	10.1	30.9	0.57	3.79	n.f.	47.1	2.79	100.2	ASU(135d.7)

\* Number designates an analysed grain or set of grains.

† Includes 0.90% NiO.

‡ Not found.

The olivine-corrected empirical formulae based on 24 oxygens are given in Tables III and IV. Ni and Fe were assumed to be divalent and P pentavalent, except in the decomposition phosphates, where the Fe was assumed to be trivalent. The atomic proportions were recalculated to provide the compositional plot shown in fig. 9.

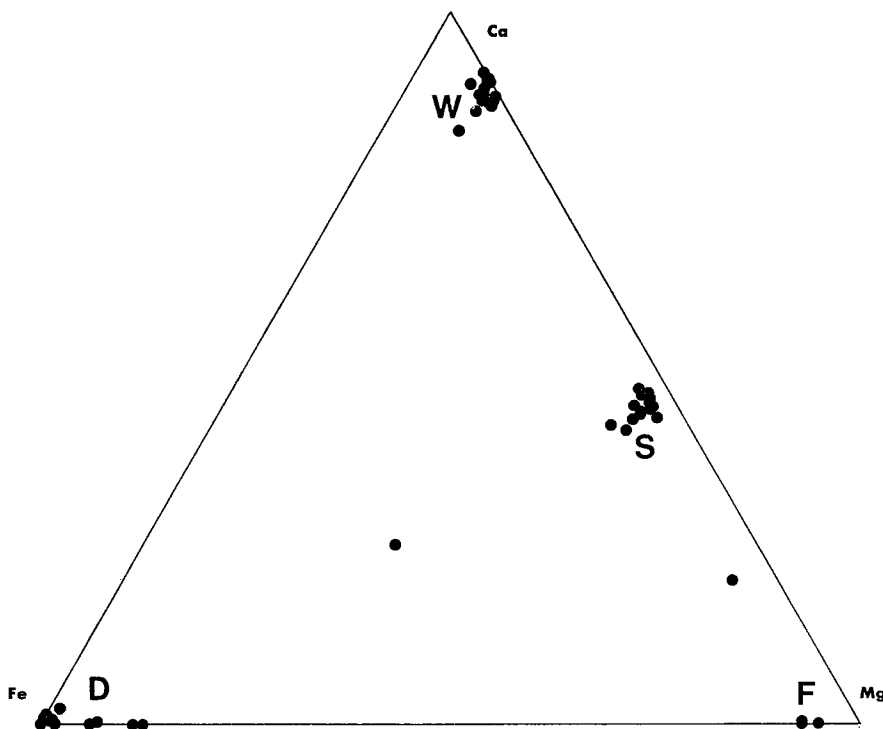


FIG. 9. Ternary composition diagram of the phosphate analyses shown in Tables III, IV. The analyses have been normalized to give  $\text{Ca} + \text{Mg} + \text{Fe} = 100$  (in atomic percents). Note the relatively well-defined fields of whitlockite (W), stanfieldite (S), farringtonite (F), and decomposition phosphates (D).

*Primary Phosphates.* 'Average compositions', based on the arithmetic means from Table III, are:

Whitlockite	Stanfieldite	Farringtonite
$\text{Fe}_{0.13}$	$\text{Fe}_{0.40}$	$\text{Fe}_{0.56}$
$\text{Ca}_{7.86}$	$\text{Ca}_{4.02}$	$\text{Ca}_{0.42}$
$\text{Mg}_{0.87}$	$\text{Mg}_{4.53}$	$\text{Mg}_{7.80}$
$\text{Mn}_{0.006}$	$\text{Mn}_{0.05}$	$\text{Mn}_{0.04}$
$\text{Na}_{0.31}$	$\text{Na}_{0.004}$	$\text{Na}_{0.28}$
$\text{K}_{0.007}$		
$\text{P}_{5.99}$	$\text{P}_{6.01}$	$\text{P}_{6.01}$
$\text{O}_{24}$	$\text{O}_{24}$	$\text{O}_{24}$

No single phase of these compositions was necessarily observed.

All whitlockite samples contain Mg and generally also the alkalis, Na and K. They contain little Fe and are essentially free of Mn. Components other than CaO, MgO,  $\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  account for a maximum of 1.8 wt. %. Calvo and Gopal (1975) suggest a formula for meteoritic samples of  $\text{Ca}_{18}(\text{Mg},\text{Fe})_2(\text{Na},\text{K})_2(\text{PO}_4)_{14}$ . Our 'average' whitlockite is similar, but slightly enriched in the divalent cations and depleted in the alkalis.

The stanfieldites are almost pure Ca-Mg phosphates having a Ca:Mg ratio ranging from 0.81 to 0.97 (atomic proportions). They all contain minor MnO (< 0.8 wt. %) and are

TABLE III. Atomic proportions of pallasitic phosphates shown in Table II, calculated to 24 oxygens; corrected for included olivine, based on the amount of SiO<sub>2</sub> in the analysis

Meteorite name	Fe	Ca	Mg	Mn	Na	K	P	O	Metal: phosphorus
<i>Whitlockite</i>									
Ahumada (1)	0.23	8.15	0.68	—	0.03	—	5.98	24	1.52
Ahumada (2)	0.21	7.94	0.84	—	0.06	—	6.00	24	1.51
Ahumada (3)	0.04	7.89	0.78	—	0.09	—	6.11	24	1.44
Albin (2)	0.11	8.06	0.85	0.01	0.25	0.01	5.95	24	1.56
Albin (3)	0.03	7.94	0.80	0.02	0.28	0.01	6.04	24	1.51
Antofagasta (2)	0.05	8.21	0.82	0.01	0.15	0.01	5.94	24	1.56
Cold Bay (1)	0.16	7.84	1.01	—	0.34	—	5.94	24	1.57
Imilac (2)	0.12	7.88	1.01	0.02	0.15	0.01	5.97	24	1.54
Marjalahti (1)	0.11	8.08	1.04	—	—	—	5.92	24	1.56
Marjalahti (2)	0.14	7.69	0.96	—	—	—	6.10	24	1.44
Mt. Vernon (3)	0.06	7.93	1.01	—	0.08	—	6.00	24	1.51
Mt. Vernon (4)	0.03	8.04	0.80	—	0.11	0.01	6.04	24	1.49
Ollague (2)	0.03	8.01	0.84	0.01	0.27	0.01	6.00	24	1.53
Rawlinna (8)	0.65	7.52	0.82	—	0.92	0.02	5.82	24	1.71
Rawlinna (10)	0.34	7.46	0.85	0.01	0.86	0.02	5.97	24	1.60
Santa Rosalia (3)	0.10	7.89	0.83	0.02	0.23	—	6.03	24	1.50
Santa Rosalia (6)	0.06	7.83	0.82	—	0.45	0.01	6.03	24	1.52
Somervell Co. (1)	0.06	7.94	0.83	—	0.20	—	6.04	24	1.50
Springwater (3)	0.15	7.40	0.83	—	0.95	0.01	6.06	24	1.54
Springwater (10)	0.20	7.46	0.82	—	0.91	0.02	6.03	24	1.56
Springwater (12)	0.004	8.03	0.71	0.01	0.88	0.01	5.93	24	1.64
<i>Stanfieldite</i>									
Albin (4)	0.30	4.12	4.34	0.05	—	—	6.08	24	1.45
Antofagasta (1)	0.31	4.23	4.54	0.06	—	—	5.95	24	1.54
Antofagasta (3)	0.30	4.20	4.53	0.05	—	—	5.98	24	1.52
Eagle Station (1)	0.57	3.84	4.64	0.04	—	—	5.97	24	1.52
Eagle Station (2)	0.86	3.69	4.57	0.04	—	—	5.95	24	1.54
Imilac (1)	0.27	4.01	4.62	0.05	—	—	6.03	24	1.49
Mt. Vernon (1)	0.29	4.10	4.62	0.04	—	—	5.99	24	1.51
Mt. Vernon (2)	0.25	4.05	4.49	0.05	—	—	6.08	24	1.45
Mt. Vernon (5)	0.24	4.18	4.54	0.04	—	—	6.02	24	1.50
Ollague (1)	0.32	4.10	4.64	0.05	—	—	5.97	24	1.53
Rawlinna (9)	0.70	3.96	4.56	0.04	—	—	5.91	24	1.57
Rawlinna (14)	0.85	3.92	4.51	0.03	—	—	5.88	24	1.59
Santa Rosalia (1)	0.31	3.96	4.62	0.04	—	—	6.04	24	1.48
Santa Rosalia (2)	0.29	4.07	4.43	0.04	—	—	6.08	24	1.45
Santa Rosalia (5)	0.31	3.99	4.52	0.04	—	—	6.07	24	1.46
Springwater (8)	0.44	3.96	4.42	0.08	0.03	—	6.05	24	1.48
Springwater (9)	0.44	3.85	4.48	0.05	0.03	—	6.08	24	1.46
Springwater (11)	0.45	3.92	4.55	0.07	0.04	—	6.01	24	1.50
<i>Farringtonite</i>									
Rawlinna (12)	0.64	0.01	8.32	0.02	—	—	6.01	24	1.50
Rawlinna (13)	0.65	0.01	8.24	0.02	—	—	6.04	24	1.48
Springwater (1)	0.46	0.01	8.63	0.03	—	—	5.96	24	1.53
<i>Miscellaneous</i>									
Brahin (1)	7.95	—	1.01	0.01	(Ni-0.13)	—	5.97	24	1.52
Brahin (2)	7.88	—	1.13	0.01	—	—	6.00	24	1.50
Springwater (2)	0.47	1.63	6.02	0.07	1.11	—	6.02	24	1.54



essentially free of the alkalis. Components other than CaO, MgO, P<sub>2</sub>O<sub>5</sub>, and MnO account for less than 0.2 wt. %. Guinier X-ray patterns of phosphate from Antofagasta and Imilac correspond to stanfieldite.

Farringtonite, although the first phosphate described from pallasites and probably the most abundant where it does occur, does not appear to be widespread. Only four of the analysed phosphate grains were farringtonite. Based on these limited data, the farringtonite is almost pure Mg phosphate (Table III). Fe is a minor constituent. Components other than MgO, FeO, and P<sub>2</sub>O<sub>5</sub> account for < 0.4 wt. %.

Several phosphates do not fit the chemical constraints of the preceding minerals. 'Springwater (2)' is a phosphate that is intermediate in its Ca:Mg ratio (= 0.27) between stanfieldite and farringtonite (Table III). It contains significant Fe, Mn, and Na elements that appear to be incompatible in the other phosphates. Its metal to phosphorus ratio, 1.54, is only slightly greater than the theoretical value (1.50) for the preceding phosphates. It does not correspond to a known mineral.

The Brahin pallasite contains two grains that are almost pure Fe phosphate (Table III). They have minor MgO and NiO; total wt. % of the other elements is less than 0.1. The metal to phosphorus ratios are 1.50 and 1.52. The composition approximates Mn-free sarcopside, with one being slightly nickeloan. It is possible, although unlikely, that the Ni is actually in the adjacent schreibersite.

*Decomposition phosphates.* Five pallasites contain Fe-rich phosphates that appear to result from decomposition reactions—presumably caused by terrestrial weathering. Thirteen grains were analysed; the measured totals range from 75 to 87 wt. %. We believe that the mass deficiency is produced by water of hydration. This, plus the apparent variability in composition and the nature of their occurrence, is the basis for categorizing them as weathering products.

An interesting feature of the decomposition phosphates is that, with the exception of 'Springwater (7)', all contain Ni and four contain between 0.02 to 1.9 wt. % Cr. These four contain less Ni than the Cr-free phosphates. The latter have Ni contents ranging from 4.9 to 12.1 wt. %, i.e., the Ni is a significant component.

Based on their metal to phosphorus ratios, four of the decomposition phosphates {Albin (1), Phillips Co. (4), (5), (6)} could have similar stoichiometries to the other meteoritic phosphates, i.e.,  $M/P = 1.5 \pm 0.1$ . They most closely resemble the Brahin phases (Tables II, III), except that the latter are apparently anhydrous.

It is possible to speculate on the identities of some of the decomposition phosphates. However, because of the large number and complexity of known phosphates, it is difficult to be confident about these identifications. Structural work is clearly needed. Another complicating factor for identification is that some of the decomposition phosphates appear to be heterogeneous.

Areas in some specimens (e.g., Albin and Newport) resemble ludlamite,  $(\text{Fe, Mg, Mn})_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ;  $M/P = 1.5$  in composition, while others {(e.g. Phillips Co. (3))} resemble laubmannite  $(\text{Fe}_3^{\text{II}}\text{Fe}_6^{\text{III}}(\text{PO}_4)_4(\text{OH})_{12})$ ;  $M/P = 2.25$ . Caution must be expressed, however, in regard to assigning mineral names to materials as inhomogeneous as the decomposition products.

The following simple formula approximately describes those materials with  $M/P$  values near 1.5— $(\text{Fe, Ni, Ca, Mg})_x(\text{Na, K})_{6-2x}(\text{PO}_4)_2 \cdot Y\text{H}_2\text{O}$ , where  $x < 3$ . The values for  $Y$  were calculated assuming the deficiency in the summation is H<sub>2</sub>O and are listed in column 13 of Table IV.

'Springwater (7)' is distinct from the other decomposition phosphates in that it is free of Ni and Cr. In terms of its Ca/Mg ratio of 0.83 it most closely resembles stanfieldite. However, it contains appreciable FeO, has an anomalously high  $M/P$  ratio, and sums to only 85 wt. %. It thus appears to be yet another type of decomposition phosphate.

TABLE IV. *Electron microprobe analyses and atomic proportions of decomposition phosphates from pallasitic meteorites*

	Weight percent									
	1*	2	3	4	5	6	7	8	9	10
FeO	54.9	34.6	38.0	49.5	52.0	56.9	52.0	42.2	34.1	27.0
CaO	n.f.†	0.45	0.30	0.08	0.15	0.10	0.04	< 0.02	0.58	12.1
MgO	n.f.	n.f.	0.23	1.99	0.13	0.15	0.26	1.51	0.26	10.5
MnO	n.f.	< 0.05	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	0.31
Na <sub>2</sub> O	0.30	1.08	0.44	n.f.	n.f.	~ 0.10	~ 0.10	~ 0.10	~ 0.10	0.16
K <sub>2</sub> O	n.f.	2.11	1.06	n.f.	n.f.	0.10	0.10	0.10	0.10	~ 0.03
NiO	8.28	6.62	7.09	0.36	0.11	0.32	1.00	4.90	12.1	n.f.
Cr <sub>2</sub> O <sub>3</sub>	n.f.	n.f.	n.f.	1.25	1.92	0.56	~ 0.02	n.f.	n.f.	n.f.
P <sub>2</sub> O <sub>5</sub>	17.2	30.3	35.8	26.7	31.4	25.6	34.2	32.4	33.2	35.3
SiO <sub>2</sub>	0.45	0.20	0.77	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	0.06
Sum	81.1	75.4	83.7	79.9	85.7	83.8	87.7	81.2	80.4	85.5

Empirical formula subscripts—'olivine-free'												
	Metal:	Fe	Ca	Mg	Mn	Na	K	Ni	Cr	P	O	Mole fraction H <sub>2</sub> O‡
1	3.62	12.28	—	—	—	0.16	—	1.79	—	3.92	24	5.6
2	1.54	6.86	0.12	—	—	0.49	0.64	1.26	—	6.08	24	6.4
3	1.31	6.62	0.07	—	—	0.18	0.28	1.20	—	6.36	24	3.8
4	2.02	9.67	0.02	0.70	—	—	—	0.07	0.23	5.29	24	5.2
5	1.71	9.26	0.03	0.04	—	—	—	0.02	0.33	5.67	24	3.4
6	2.26	11.03	0.03	0.05	—	0.05	0.03	0.06	0.10	5.05	24	3.7
7	1.55	8.90	0.01	0.08	—	0.04	0.03	0.17	0.003	5.93	24	2.8
8	1.52	7.68	—	0.49	—	0.04	0.03	0.86	—	5.98	24	4.6
9	1.41	6.24	0.14	0.09	—	0.04	0.03	2.13	—	6.16	24	4.8
10	1.73	4.29	2.47	2.96	0.05	0.06	0.01	—	—	5.69	24	3.1

\* 1. Ahumada (4)—ASU (354.lb); 2. Albin (1)—USNM(939); 3. Newport (1)—ASU (89a.1); 4. to 9. Phillips Co. (1) to (6)—USNM (1695.11A); and 10. Springwater (7)—ASU (135d.2.1).

† Not found.

‡ Determined by difference.

### Discussion

*Melt origin.* The textural evidence indicates that the phosphates were initially present as molten droplets, interstitial to the olivine crystal clusters or plastered onto the surfaces of olivines. The textures suggest that the phosphates have a fairly high surface tension and that they wetted the olivine, thereby explaining their adherence to the silicate. It also appears as if the phosphates have resided quiescently within the pallasites since this early stage of meteorite formation.

The occurrence of phosphate droplets on already crystallized olivines is reasonable if the phosphates melt congruently, as do farringtonite and whitlockite. Synthetic stanfieldite, however, melts incongruently (Ando, 1958) and is unstable above 1175 °C. There are two possible explanations: the pure Ca–Mg phase represented in the phase diagram of Ando may not be equivalent to natural stanfieldite, the minor elements present in the mineral permitting congruent melting; or the stanfieldite may have formed by solid state reactions from earlier 'droplets' of the Ca or Mg end members. The lack of compositional gradients suggests that the first is the more likely explanation.

*The question of equilibrium.* While there is abundant evidence of chemical disequilibrium in chondrites, the pallasites are remarkable for their apparent high degree of internal equilibrium

(Buseck and Goldstein, 1969). The situation becomes more complex, however, when the phosphates are considered. DuFresne and Roy (1961) indicated that farringtonite in the pallasites is evidence of gross disequilibrium, discussed in more detail in the following section. From the experimentally determined phase diagram for the system  $\text{Mg}_3(\text{PO}_4)_2\text{-Ca}_3(\text{PO}_4)_2$  it is clear that only two phases can coexist in equilibrium—whitlockite and stanfieldite, or farringtonite and stanfieldite (Ando, 1958).

Farringtonite was observed by us in two pallasites—Springwater and Rawlinna. Both meteorites also contain whitlockite and stanfieldite, clearly indicating a potential problem of equilibrium. The situation is yet more complex in Springwater as it contains a fourth and possibly a fifth anhydrous phosphate. Either the phase diagram of Ando is inappropriate or there are phases out of equilibrium with one another. Because of the other evidence of equilibrium, we believe that the presence of minor elements and the consequent compositional deviation from the binary system of Ando means that the experimental results from the system  $\text{Ca}_3(\text{PO}_4)_2\text{-Mg}_3(\text{PO}_4)_2$  are inapplicable.

*State of oxidation.* Schreibersite,  $(\text{Fe,Ni})_3\text{P}$ , is ubiquitous in the pallasites. Its coexistence with phosphates places restrictions on the  $f_{\text{O}_2}$  at which these minerals formed. The fact that many, if not all, of the pallasites contain both phosphide and  $\text{P}^{5+}$  compounds suggests that the pallasites formed under roughly uniform  $f_{\text{O}_2}$  conditions. The values are difficult to specify precisely because of thermodynamic uncertainties, especially for the more complex phosphates, which contain several minor elements. Olsen and Fredriksson (1966) calculated the position of the univariant curves governing the occurrence of  $\text{Fe}_3(\text{PO}_4)_2$  and farringtonite in iron and pallasitic meteorites. (Except for the tentative identification in the Brahin phosphate, sarcopsite has not been described from the pallasites, suggesting that the  $f_{\text{O}_2}$  was not sufficiently high to permit its formation.)

An interesting problem was posed by DuFresne and Roy (1961) in their initial report of farringtonite. They observed that the  $\text{P}^{5+}$  in farringtonite is rapidly reduced if the phosphate is melted in an Fe crucible. They concluded that the coexistence of farringtonite and metal in the pallasites means that these meteorites must have cooled extremely rapidly. This conclusion is at variance with both measured equilibrium element distributions and with observations regarding textures (Buseck and Goldstein, 1969; Buseck, 1977).

The calculations of Olsen and Fredriksson (1966) resolve this apparent dilemma; they show that there is a relatively narrow range of  $f_{\text{O}_2}\text{-}T$  conditions where farringtonite, schreibersite, and Fe can coexist stably (between curves 'M' and '4' in their fig. 3). This region severely limits the environment under which the pallasites formed. The relevant values were calculated from thermodynamic data provided by E. Olsen and are summarized in Table V (the lower limit values were extrapolated from 1100° to 1200 °K). The lower  $f_{\text{O}_2}$  limit is depressed as the olivine becomes more forsteritic, but the shift in  $f_{\text{O}_2}$  values is negligible over the compositional range of olivines in pallasites. For  $f_{\text{O}_2}$  values greater than the upper limit in Table V, magnetite or wüstite would occur rather than FeNi; with one possible exception, they have not been observed as primary phases in pallasites. For  $f_{\text{O}_2}$  values below those given for 'lower limit', farringtonite would no longer be stable, all the  $\text{P}^{5+}$  being reduced. Thus, farringtonite-bearing pallasites formed within the limits given in Table V. By analogy, it is likely that the other pallasites also formed within this or a comparable range of  $f_{\text{O}_2}$  limits.

### Conclusions

The phosphate minerals are minor in abundance but almost ubiquitous in occurrence in the pallasites. Several of the phosphates formed at an early stage of the development of the

TABLE V. *Limits of  $f_{O_2}$  at which farringtonite, schreibersite, and Fe can coexist*

T, °K	T, °C	Log $f_{O_2}$	
		Upper limit	Lower limit (Springwater)
1200	927	-16.3	-17.3
1000	727	-20.9	-22.5
800	527	-27.9	-30.4
600	327	-39.9	-43.6
400	127	-64.2	-69.9

pallasites, as indicated by textures representing a solidified residual melt. Assuming equilibrium between schreibersite and the phosphates, a relatively narrow range of  $f_{O_2}$  values for the pallasites is defined. The phosphates display a considerable range in composition and serve as a host for several minor elements that are absent in the other, compositionally simpler minerals of the pallasites. Conceivably phosphates also serve as a sink for the alkalis and other large ion lithophile elements in the Earth's lower mantle.

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