

Phosphoran olivine from Pine Canyon, Piute Co., Utah

S. O. AGRELL^{1,3}, N. R. CHARNLEY² AND G. A. CHINNER¹

¹ Dept of Earth Sciences, Downing Street, Cambridge CB2 3EQ, UK

² Department of Earth Sciences, Oxford, OX1 3PR, UK

ABSTRACT

Olivines containing up to 6.1 wt.% P₂O₅ occur in association with apatite and an unnamed NaCaMg phosphate phase. Phosphoran olivine has been recorded only in pallasite meteorites and from one other terrestrial occurrence. The rarity of palpable phosphorus substitution for silicon may be related to the fact that in most terrestrial rocks, phosphorus is incorporated initially, and remains as, apatite; thus phosphorus excess in an undersilicated environment must be uncommon. However the highly capricious distribution of phosphorus in individual olivines from this and the meteoritic occurrences suggests disequilibrium, and questions whether phosphoran olivine is ever stable relative to combinations of P-free olivine and phosphate/phosphide minerals.

KEYWORDS: phosphorus, olivine, apatite, Pine Canyon, Utah.

Introduction

THE Pine Canyon breccia pipe, a syenitic intrusive into early Tertiary volcanic country rock in the Marysvale volcanic area of southern Utah, was discovered by S.O. Agrell in 1964 and mapped by him and P.D. Rowley in 1983 (Rowley *et al.*, 1994, pp. 19–20). The special interest in these rocks, of which a more comprehensive account is in preparation, lies in the nepheline-and spinel-rich 'skarn' assemblages which appear to represent hydrothermal fillings of cavities and veins in the brecciated country rock, pyrometamorphosed by subsequent igneous activity. The highly desilicated 'skarns' can be divided into two main groups: an aluminium-poor group characterised by olivine, and a corundum-rich group with a variety of rare-earth bearing minerals including hibonite, armalcolite and pseudo-brookite.

Two samples of float retrieved from the site by Agrell superficially resemble the olivine-rich group, but are unique in containing a phosphate

mineral similar in composition to the exotic magnesium phosphate farringtonite, in addition to olivines with a high content of phosphorus. The outcrop source of these rocks has not been found; their relation to the main skarn assemblages is thus unclear and they are being described separately in this paper.

The rocks are dense, black specimens which in thin section are seen to be made of over 70% of magnetite and green spinel in equal amounts. The spinels are magnesium rich, molecular percentages of end members varying within the ranges MgAl₂O₄, 75–80%; FeAl₂O₄, 8–12%; FeFe₂O₄, 8–15%.

Rock 102333 is of fairly regular grainsize with equidimensional oxides harbouring interstitial aggregates and rarer phosphate. 98794 is generally more fine grained, small magnetites studding a matrix of green spinel, with abundant olivine prisms. Irregular, colourless patches are predominantly of phosphates with occasional wedge-shaped, twinned olivines (Fig. 1) and, more rarely, magnetite-spinel grains much coarser than those of the matrix.

Phosphate minerals

These are not easily distinguished from low-birefringence olivine grains, or from each other,

³ Died January 29, 1996

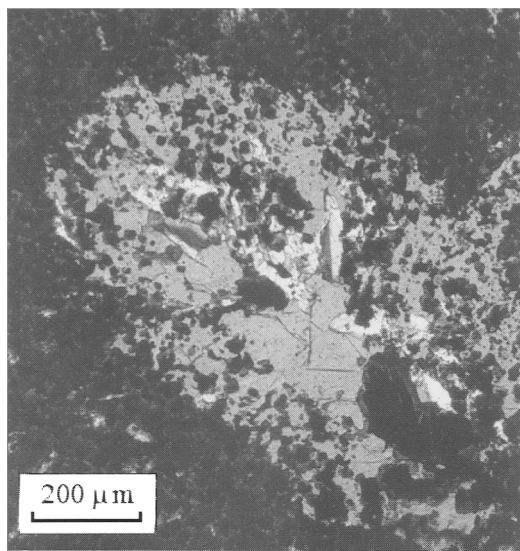


FIG. 1. Transmitted-light micrograph of 98794, with partly crossed polars. The dark matrix is of spinel and magnetite. Patches of phosphate contain inclusions of the matrix, and wedge-shaped, twinned crystals of olivine. Olivine and phosphate occur also as isolated crystals in the matrix.

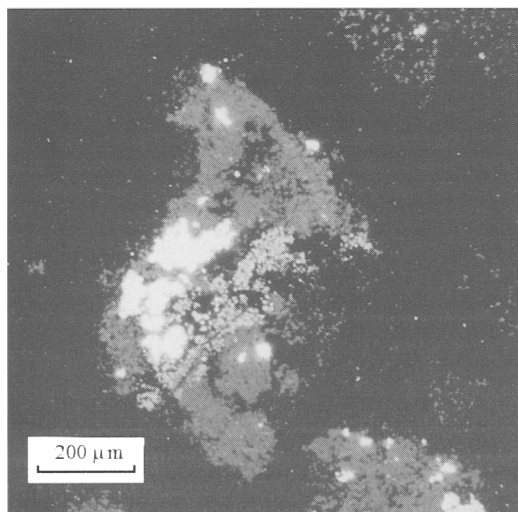


FIG. 2. Monochrome reproduction of transparency showing phosphate cathodoluminescence. The black background is of spinel, magnetite & olivine. White areas are blue- or white- luminescing apatite. Grey is the red-luminescing NaCaMg phosphate. A zone of green-fluorescing secondary Mg phosphate hydrates runs across the centre patch.

on transmitted light examination, but are readily differentiated by cathodoluminescence (Fig. 2). White - or blue - fluorescing apatite varies in composition from a halogen-free phase (presumably hydroxyapatite) to one containing 20 mol. percent of chlorapatite. A dull-red fluorescing phase is more abundant than apatite in some phosphate patches and also occurs spangling the matrix in tiny particles. Its composition as determined by electron micro-probe is given in Table 1; but for a palpable sodium content it could be regarded as a calcium magnesium phosphate intermediate between farringtonite $Mg_3(PO_4)_2$ and stanfieldite $Ca_4Mg_5(PO_4)_6$.

Buseck and Holdsworth (1977) noted a single grain of a closely comparable composition in the Springwater pallasite and more recently from the same meteorite Davis and Olsen (1991) have recorded "A $300 \times 600 \mu m$ rounded crystal of a new magnesium-calcium-sodium silicophosphate mineral attached to an olivine grain and in contact with troilite and schreibersite" which seems certain to be the same phase (Table 1). A sodium-bearing phosphate from a similar environment in the

TABLE 1. 'Unknown phosphates' from Pine Canyon, and Springwater pallasite (wt.%)

	Pine Canyon ¹	Springwater ²	Springwater ³
SiO ₂	0.21	2.79	2.33
P ₂ O ₅	50.36	47.1	48.92
Al ₂ O ₃	0.05	0.00	0.00
FeO	3.01	4.95	4.95
MnO	1.01	0.57	0.85
MgO	34.39	30.9	31.26
CaO	6.81	10.1	10.25
Na ₂ O	4.27	3.79	3.56
Total	100.11	100.2	102.15
Cations to 24(O)			
Si	0.02	0.39	0.32
P	5.91	5.61	5.71
Al	0.01	—	—
Fe	0.35	0.58	0.57
Mn	0.12	0.07	0.09
Mg	7.11	6.48	6.42
Ca	1.01	1.52	1.51
Na	1.15	1.03	0.95

1. Average of 20 analyses

2. Buseck and Holdsworth (1977)

3. Davis and Olsen (1991)

Total includes 0.01 K₂O, 0.01 Cr₂O₃

PHOSPHORAN OLIVINE

TABLE 2. Selected phosphoran olivines 102333 (wt.% oxides)

SiO ₂	40.03	38.68	38.24	37.04	34.91	35.52
P ₂ O ₅	0.31	1.70	2.29	3.96	4.29	6.15
MgO	48.50	49.42	49.21	47.69	47.01	47.58
MnO	0.44	0.42	0.45	0.61	0.50	0.52
FeO	9.80	9.08	8.86	11.01	10.55	10.79
Total	99.09	99.30	99.05	100.31	97.26	100.56
Cations to 4(O)						
Si	0.99	0.95	0.94	0.90	0.88	0.86
P	0.01	0.03	0.05	0.08	0.09	0.13
Mg	1.78	1.81	1.80	1.74	1.77	1.72
Mn	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.20	0.19	0.18	0.22	0.22	0.22
$\frac{Mg}{(Mg+Fe)}$ (%)	89.4	90.0	90.8	88.5	88.5	88.2

Zaisho pallasite (Buseck and Clark, 1984, p. 234) may also be related, but its composition seems sufficiently different for its identity with them to be suspect without X-ray information.

Regrettably none of these occurrences has yielded material adequate for more detailed examination and in the absence of structural data we can only speculate on the relation of the Pine Canyon/Springwater phosphate to its seeming relatives stanfieldite and farringtonite. The cation proportions of Table 1 could be approximated by the formula Na_{0.5}(NaCaMgFe)₉P₆O₂₄, with variable replacement of P by Si, the separation of the Na content in two halves implying its incorporation by the substitution □Ca → 2Na.

The hint of site preference suggested by the 4:5 ratio of Ca : Mg in stanfieldite is not repeated here, the Mg content being much closer to the 9 atoms per 24 oxygens of farringtonite; little however can be deduced from this, site occupancies in many phosphate groups being quite complex (e.g. for alluaudites; Moore and Ito, 1979).

Olivine

The prime novelty of the Pine Canyon specimens lies in the occurrence of olivine with a significant phosphorus content, a phenomenon known from four meteorite examples (Buseck and Clark, 1984, p. 230) and from one other terrestrial locality (Goodrich, 1984). The phosphorus values (Table 2) of up to 6.1 wt.% P₂O₅ (≡ 0.1 P atoms per 4 oxygens, see Table 2) are highly variable

sometimes even within a single grain (e.g. Fig. 3) and although higher values do tend to be in the vicinity of phosphate minerals, P-rich olivines may be juxtaposed against crystals essentially P-free (cf. Buseck and Clark, 1984, Fig. 2).

That phosphorus should replace silicon in tetrahedral coordination was an early prediction of crystal chemistry and has been established for

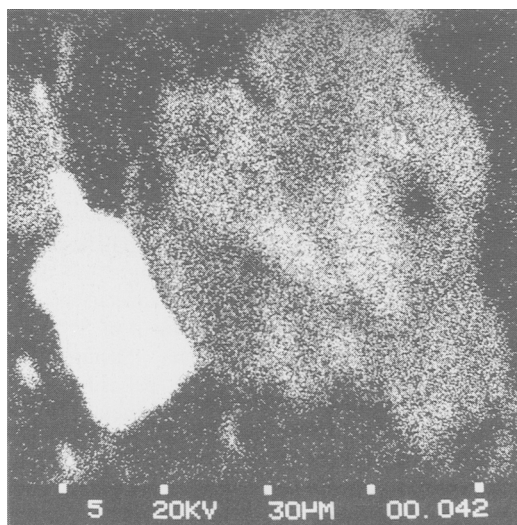


FIG. 3. X-ray picture of P_{Kα} radiation from olivines around a NaCa phosphate crystal. Phosphorus content of olivines variable (from 0 to ~3% P₂O₅); note that the highest values are not adjacent to the phosphate.

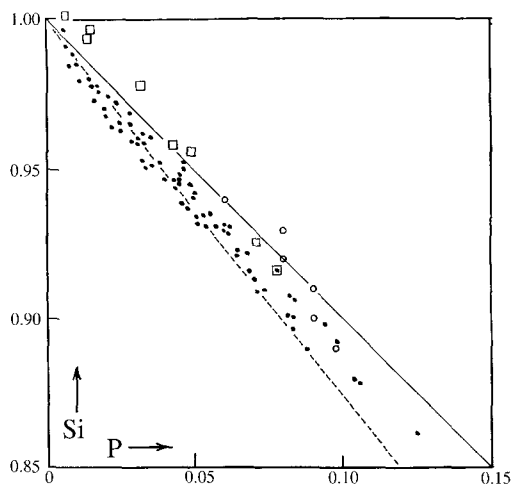


FIG. 4. Ionic P vs. Si of olivines on the basis of 4 oxygens. Solid dots, Pine Canyon; Open circles, pallasites; Open squares, Disko Island. The line marks full tetrahedral site occupancy $P + Si = 1$. Dotted line marks the vacancy substitution $5Si = 4P + \square$.

phosphoran olivine by high-resolution structure determination (Self and Buseck, 1983); the negative correlation between P and Si in the phosphoran olivines shown in Fig. 4 gives striking confirmation. A concomitant charge-balancing change in octahedral site occupancy is not, however, so apparent, so in addition to the $M2Si \rightleftharpoons 2P$ substitution the tetrahedral vacancy scheme $5Si \rightleftharpoons 4P + \square$ may be involved.

The rarity of records of phosphoran olivine (despite the now almost universal application of the electron probe to routine petrography) does suggest that rather unusual circumstances are required to promote the replacement of Si by P. Previously recorded occurrences (Springwater, Rawlinna, Zaisho and Brachin pallasites, and immiscible silicate association with metallic iron; Goodrich (1984) accordingly argued low f_{O_2} as a factor in the formation of phosphoran olivine. The Pine Canyon occurrence, though reduced, is not unusually so: the oxygen fugacities were certainly nowhere near levels low enough to permit the appearance of native iron. Goodrich suggested in addition (1) high P_2O_5 contents (2) low silica activity. (2) seems certain to be necessary, but in the case of (1) it is probably not the magnitude of

P_2O_5 content which matters but its excess over the calcium available to form apatite or whitlockite. The phosphorus content of most terrestrial rocks is incorporated *ab initio* as apatite, so in them the excess is zero. Only in rare cases – the extra-terrestrial pallasites, in which phosphorus originates in phosphides, and Pine Canyon (P incorporated as hydrothermal Mg phosphate hydrates?) – is there phosphorus excess over Ca; this goes to form the rare phosphates, predominantly stanfieldite and farringtonite, and then into olivine.

The distribution of phosphorus in the olivine, however, does not show the regularity one might expect if it were determined by equilibrium distribution between silicate and phosphate phases. The highly variable and seemingly capricious contents illustrated by fig. 4 and by fig. 2 of Buseck and Clarke, 1984, indicate disequilibrium, presumably originally the product of some quirks of kinetics and preserved through the period of active diffusive exchange by the low silica activity of these highly undersaturated milieux. Thereby must arise a doubt, not to be resolved here, of whether phosphoran olivine really has a field of stability relative to that of P-free $(Mg,Fe)_2SiO_4$ in association with one or more phosphate/phosphide minerals.

References

- Buseck, P.R. and Clark, J. (1984) Zaisho — a pallasite containing pyroxene and phosphoran olivine. *Mineral. Mag.*, **48**, 229–35.
- Buseck, P.R. and Holdsworth, E. (1977) Phosphate minerals in pallasite meteorites. *Mineral. Mag.*, **41**, 91–102.
- Davis, A.M. and Olsen, E.J. (1991) Phosphates in pallasite meteorites as probes of mantle processes in small planetary bodies. *Nature*, **353**, 737–40.
- Goodrich, C.A. (1984) Phosphoran pyroxene and olivine in silicate inclusions in natural iron-carbon alloy, Disko Island, Greenland. *Geochim. Cosmochim. Acta*, **48**, 115–26.
- Moore, P.B. and Ito, J. (1979) Alluaudites, wyllicites, arrojadites: crystal chemistry and nomenclature. *Mineral. Mag.*, **43**, 227–35.
- Rowley, P.D., Mehnert, H.H., Naeser, C.W., Snee, L.W., Cunningham, C.G., Steven, T.A., Anderson, J.J., Sable, E.G. and Anderson, R.E. (1994) Isotope ages and stratigraphy of Cenozoic rocks of the Marysvale volcanic field and adjacent areas, West Central Utah. *U.S. Geological Survey Bull.* 2071.
- Self, P.G. and Buseck, P.R. (1983) High resolution

PHOSPHORAN OLIVINE

structure determination by ALCHEMI. *Proc. 41st
Ann. Meet. Electron Microscopy Soc. Amer.*, San Francisco Press. [Manuscript received 16 May 1997;
revised 7 July 1997]