FIRST OCCURRENCE OF BEUSITE IN AN IRON METEORITE: ITS COMPOSITION AND CRYSTAL STRUCTURE: Ian M. Steele, Joseph Pluth, Dept. of Geophysical Sciences, University of Chicago; Edward Olsen, Field Museum of Natural History, and Dept. of the Geophysical Sciences, University of Chicago; Andrew M. Davis, Enrico Fermi Institute, University of Chicago; all at Chicago, IL.

INTRODUCTION: The terrestrial beusite-graftonite series (1) occurs in pegmatites, always contains from 5 wt% to 14 wt% total of CaO+MgO, and represents the breakdown of a high temperature precursor. Graftonite, and its polymorph, sarcopside (2), occur also in meteorites (3) where they show only traces of CaO and MgO (Table 1 and Fig. 1). These meteoritic occurrences usually plot at or very near the iron end member of the binary $Fe_3(PO_4)_2$ — $Mn_3(PO_4)_2$. We report here the meteoritic occurrence of a Ca-free beusite with the empirical formula $Fe_{1.5}$ $Mn_{1.5}(PO_4)_2$. Its crystal structure is confirmed to be that of graftonite; a comparison with the the recently determined structure of Ca-rich beusite (4) shows that one of the three types of coordination polyhedra changes from 8 to 7 to 6 coordination depending on the Ca content illustrating the flexibility of the graftonite structure type.

OCCURRENCE: In meteorites the Fe-Mn-orthophosphates occur primarily, but not exclusively, in the group of iron meteorites classified as IIIAB (5). They are found as euhedral crystal inclusions within troilite nodules in turn enclosed by metal. They represent a small, late stage increase in oxygen partial pressure within the nodule volume which oxidizes some phosphorus alloyed in the Fe-Ni metal host (3). They appear to form as crystals within molten troilite nodules, in the approximately 500 C° interval between the solidification of the metal and the sulfide(6). The Mn-content is derived from the surrounding sulfide, due again to the local increase in the oxygen partial pressure, which is, in turn, due to the occlusion of trace amounts of oxygen from the surrounding metal mass.

This is the first known occurrence of beusite in a meteorite. It occurs as a euhedral crystal, 680 μm X 270 μm, separated by 18 μm from the nearest other phosphate crystal in the plane of the polished section. The other phosphates are mainly graftonite (Table 1), although two grains of an as yet uncharacterized alkali-bearing phosphate are also present. The meteorite is a IIIA iron, El Sampal, found in 1973 near Nueva Lubuka, Chubut Province, Argentina. The beusite composition (Table 1) lies exactly at the half-way point between the Fe and Mn end members. While this Mn-Fe equimolar composition is considered fortuitous, another phase, $Fe_2Mn(PO_4)_2$, has been found by us in the IIIB iron meteorite, Grant, and may represent an ordered compound (see later). The beusite in El Sampal contains excess ^{53}Cr ($\delta^{53}Cr$=31‰) from the decay of initial ^{53}Mn (7). Work is in progress for dating planetary core formation utilizing Mn-Cr isotope systematics (8).

CRYSTAL STRUCTURE: A small chip was excavated from the polished section and precession and automated diffractometer study gave space group and cell constants as: $P2_1/c$, a = 8.757(3), b = 11.381(4), c = 6.136(1)Å, β = 99.09(2). Using single crystal intensity data and starting positional parameters from graftonite (9), least squares anisotropic refinement resulted in a weighted R of 0.047. Final positional and isotropic parameters are given in Table 2. This confirms that low-Ca beusite from the El Sampal meteorite has the graftonite structure and this refinement allows a comparison among several refined graftonite structures to show the effect of substitution of a large cation in this structure.

The coordination of the 3 sites in the graftonite type structure has been noted to be variable and depend on how one defines coordination polyhedra. The M1 site has been described as 6, 7, or 8, M2 as 5, and M3 as 5 or 6 coordinated. The large ion, Ca, is ordered into the M1 site and the amount of Ca to a large measure determines the apparent coordination. For the high-Ca beusite (4), M1 is 8 coordinated while for the present refinement of low-Ca beusite, two M1-O distances (Figure 2) are great enough to allow 6-coordination. An intermediate Ca content in graftonite (9) shows M1 dimensions between these two extremes. For the structure of ferrous phosphate, another M1-O distance increases tending to make this site 5-coordinated as the radius of the cation becomes smaller. The observation of Fe_2Mn stoichiometry in graftonite in Grant (above and Table 1) suggests that the larger Mn cation may be ordered into M1 with the other two sites occupied by Fe. The ability of the graftonite structure to

accommodate a variety of cations without space group change is in part due to this coordination flexibility.

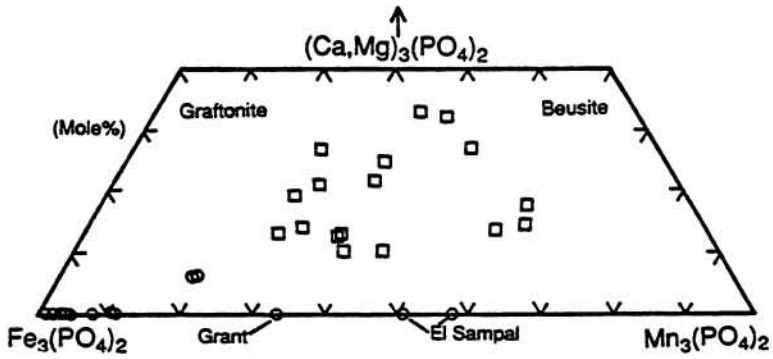

Fig. 1. Compositional range of terrestrial (squares) (1) and meteoritic (circles) beusites and graftonites. Data for El Sampal and Grant are noted. Meteoritic samples rarely have Ca and usually cluster near pure graftonite.

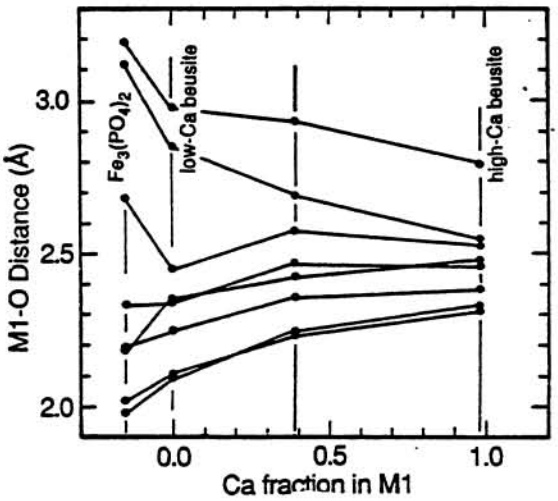

Fig. 2. Variation in bond lengths for 8 nearest oxygens in M1 coordination polyhedron versus the fraction of Ca in M1. As Ca decreases, the coordination changes from 8 in high-Ca beusite to 6 in the present sample as two oxygens move to distances greater than 2.8Å. For comparison, data are given for ferrous phosphate with Ca also 0.0 in M1 where the small Fe cation gives 5 short, one long, and two very long bond lengths. The intermediate Ca content is a structure of graftonite(9).

Table 1. Microprobe analyses of beusite and graftonites.

	Beusite	Graftonite	Graftonite
Oxide	El Sampal	El Sampal	Grant
P_2O_5	41.75(2.06)	40.13(2.02)	40.95(2.04)
CaO	0.07(.004)	0.03(.002)	0.06(.004)
MnO	29.31(1.44)	1.62(.082)	19.67(.980)
FeO	28.98(1.41)	57.59(2.86)	38.96(1.92)
Sum	100.11(4.92)	99.37(4.97)	99.64(4.95)

*Values in parentheses are atoms based on a total of 8 oxygens. Na_2O, MgO and SiO_2 less than 0.02 wt%.

Table 2. Positional and isotropic displacement parameters for beusite.

Atom	*x*	*y*	*z*	U_{eq}
P1	0.0911(2)	0.1372(1)	0.3932(2)	0.0109(4)
P2	0.6065(2)	0.0878(1)	0.8070(2)	0.0114(4)
M1	0.9457(1)	0.1165(1)	0.8441(2)	0.0194(3)
M2	0.7218(1)	0.0799(1)	0.3297(1)	0.0174(3)
M3	0.3639(1)	0.1918(1)	0.1260(1)	0.0140(2)
O1	0.0760(4)	0.0675(3)	0.1766(6)	0.015(1)
O2	0.4818(4)	0.1783(3)	0.8303(7)	0.016(1)
O3	0.9402(4)	0.2031(3)	0.4067(7)	0.016(1)
O4	0.7001(4)	0.1250(3)	0.6281(6)	0.015(1)
O5	0.2204(4)	0.2268(4)	0.3791(7)	0.019(1)
O6	0.7276(4)	0.0844(3)	0.0159(6)	0.014(1)
O7	0.1299(5)	0.0627(3)	0.6004(7)	0.017(1)
O8	0.5335(4)	-0.0343(3)	0.7588(7)	0.015(1)

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