

## Short Communication

## A High Pressure Phase of Magnesium Orthophosphate

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The crystal structure of  $\text{Mg}_3(\text{PO}_4)_2$  [space group  $P2_1/n$ ] was published in 1968 in this journal.<sup>1</sup> The cations are five- and six-coordinated, and the structure is far from densely packed with  $V=316.6 \text{ \AA}^3$  ( $Z=2$ ). This suggested the existence of a more closely packed modification, and in 1972 a denser phase was chemically prepared from  $\text{MgLiPO}_4$  and  $\text{MgSO}_4$  by Berthet *et al.*<sup>2</sup> This structure is isomorphous with *sarcopside*<sup>3</sup> and with nickel orthophosphate.<sup>4</sup> It was denoted " $\text{Mg}_3\Box(\text{PO}_4)_2$ " because of its structural relationship to *olivine*,  $(\text{Mg,Fe})_4(\text{SiO}_4)_2$ , but with ordered vacancies, " $\Box$ ", in the structure. The present study was undertaken to see if the sarcopside structure was formed when applying high pressures to  $\text{Mg}_3(\text{PO}_4)_2$ .

*Experimental.* The chemical preparations have already been described.<sup>5,6</sup> High pressure was then applied to  $\text{Mg}_3(\text{PO}_4)_2$  and  $(\text{Mg}_{0.8}\text{Fe}_{0.2})_3(\text{PO}_4)_2$  [ $30 \pm 1$  kbar (3 GPa),  $873 \pm 10$  K, 90 h] in a solid media press of the type described by Boyd and England.<sup>7</sup> X-Ray powder diffraction data were obtained with a Guinier-Hägg camera using  $\text{CuK}\alpha_1$  radiation and with KCl added as an internal standard. Mössbauer spectroscopy on  $(\text{Mg}_{0.8}\text{Fe}_{0.2})_3(\text{PO}_4)_2$  and its high pressure analogue were performed and analysed as described by Annersten *et al.*<sup>6</sup>

*Results and discussion.* The X-ray reflections could be indexed and the unit cell parameters refined based on the sarcopside structure, described in space group  $P2_1/a$  (*cf.* Table 1). For  $\text{Mg}_3(\text{PO}_4)_2$ -II the cell parameters are:  $a=10.25(2)$ ,  $b=4.72(1)$ ,  $c=5.92(1) \text{ \AA}$ ,  $\beta=90.9(1)^\circ$ ,  $V=287(1) \text{ \AA}^3$  ( $Z=2$ ), in good accordance with the data for " $\text{Mg}_3\Box(\text{PO}_4)_2$ ".<sup>2</sup> Data for  $(\text{Mg}_{0.8}\text{Fe}_{0.2})_3(\text{PO}_4)_2$ -II:  $a=10.26(1)$ ,  $b=$

Table 1. X-Ray powder data for the high pressure phases. Sarcopside structure ( $P2_1/a$ ). Relative intensities ( $I$ ): st=strong, m=medium, w=weak, vw=very weak.

$hkl$	$\text{Mg}_3(\text{PO}_4)_2$ -II		$(\text{Mg}_{0.8}\text{Fe}_{0.2})_3(\text{PO}_4)_2$ -II	
	$d/\text{Å}$	$I$	$d/\text{Å}$	$I$
0 0 1	5.911	vw	5.924	vw
1 1 0	4.304	w	4.309	w
2 0 1	3.849	m	3.849	m
0 1 1	3.700	vw	3.701	vw
1 1-1	3.473	w	3.474	vw
2 1 0				
1 1 1	3.455	w	—	—
2 1-1	3.014	st	3.020	st
0 0 2	2.966	m	2.960	m
3 1 0	2.769	vw	2.775	w
3 1-1	2.520	w	2.526	w
0 1 2				
3 1 1	2.497	vw	—	—
1 1-2	2.443	vw	2.448	vw
1 1 2	—	—	2.437	vw
2 1-2	—	—	2.268	vw
4 1 0	2.254	w	2.255	w
2 1 2	2.242	vw	2.245	vw
2 2-2	1.743	vw	1.751	vw
4 2 0	1.736	vw	1.742	vw
6 0 0	1.708	vw	—	—
2 1 3				

Table 2. Mössbauer parameters of  $^{57}\text{Fe}$  at room temperature. I= $(\text{Mg}_{0.8}\text{Fe}_{0.2})_3(\text{PO}_4)_2$ , and II=its high pressure analogue. CN=cation coordination number. Isomer shift (IS) relative to metallic iron.

Phase	CN	IS mm/s	$\Delta E_Q$ mm/s	FWHM mm/s	Intensity %
I	5	1.12(1)	2.85(1)	0.29(1)	71.3
I	6	1.27(1)	1.50(1)	0.36(1)	28.7
II	6	1.19(1)	3.01(1)	0.26(1)	100.0

4.75(1),  $c=5.93(1) \text{ \AA}$ ,  $\beta=90.8(1)^\circ$ ,  $V=289(1) \text{ \AA}^3$ . As expected, the high pressure phases are much denser than the "ordinary" phases; the unit cell volume has decreased by 9.3 % for  $\text{Mg}_3(\text{PO}_4)_2$ -II and by 9.7 % for  $(\text{Mg}_{0.8}\text{Fe}_{0.2})_3(\text{PO}_4)_2$ -II.

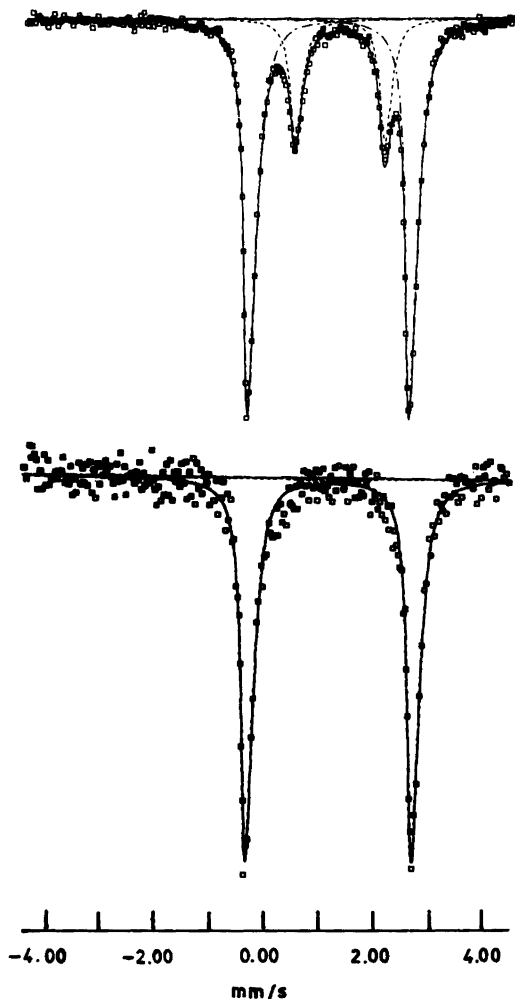


Fig. 1. Mössbauer spectrum of  $(\text{Mg}_{0.8}\text{Fe}_{0.2})_3(\text{PO}_4)_2$  at room temperature [inner doublet from five-coordinated  $\text{Fe}^{2+}$ ] and below for the respective high pressure phase.

The Mössbauer parameters (*cf.* Table 2) for  $(\text{Mg}_{0.8}\text{Fe}_{0.2})_3(\text{PO}_4)_2$ -II are indicative of only six-coordinated  $\text{Fe}^{2+}$  ions ( $\text{IS} = 1.19$  mm/s). Although there are two non-equivalent octahedral cation sites in the sarcopside structure, only one absorption doublet was observed (see Fig. 1). We have reason to believe, though, that both are populated by iron.<sup>6</sup> However, the slight difference in site symmetry may probably diminish the difference in quadrupole splitting so that only one doublet is observed. In fact, the same situation has also been observed for a structurally related  $(\text{Mg},\text{Fe})_4(\text{SiO}_4)_2$  olivine,<sup>8</sup>

where no cation ordering was found. The smaller isomer shift for  $(\text{Mg}_{0.8}\text{Fe}_{0.2})_3(\text{PO}_4)_2$ -II in comparison with the six-coordinated site in  $(\text{Mg}_{0.8}\text{Fe}_{0.2})_3(\text{PO}_4)_2$  suggests somewhat shorter metal–oxygen distances in the former compound.

As shown in the present paper and by Berthet *et al.*<sup>2</sup> the sarcopside structure is easily formed. Moreover, upon substitution of at least 30 % of the magnesium atoms in  $\text{Mg}_3(\text{PO}_4)_2$  by nickel, the same sarcopside type  $(\text{Mg}_{1-x}\text{Ni}_x)_3(\text{PO}_4)_2$  is formed. It was, however, not formed from magnesium orthophosphate kept at 3 kbar and 873 K for one week in a hydrothermal autoclave. Upon heating to about 1100 K at 1 bar,  $\text{Mg}_3(\text{PO}_4)_2$ -II rapidly transforms to “ordinary”  $\text{Mg}_3(\text{PO}_4)_2$ .

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