MINERALOGICAL MAGAZINE, JUNE 1980, VOL. 43, PP. 789-95

Nomenclature of the phosphoferrite structure type: refinements of landesite and kryzhanovskite

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SYNOPSIS

THE ideal end-members reddingite, $Mn_3^{2+}(H_2O)_3(PO_4)_2$, phosphoferrite, $Fe_3^{2+}(H_2O)_3(PO_4)_2$, and kryzhanovskite, $Fe_3^{3+}(OH)_3(PO_4)_2$ form a complex triple series. Similarities in crystal axes and pronounced differences in site preferences have led to erroneous indexing of the powder data and subsequent errors in cell refinements. Writing the general formula $M(1)M(2)_2[(H_2O),(OH)]_3(PO_4)_2$, the following end-member names apply:

$M(1)$	$M(2)$	Name
Fe^{2+}	Fe^{2+}	phosphoferrite
Fe^{3+}	Fe^{2+}	unnamed
Fe^{3+}	Fe^{3+}	kryzhanovskite
Mn^{2+}	Mn^{2+}	reddingite
Fe^{2+}	Mn^{2+}	unnamed
Fe^{3+}	Mn^{2+}	landesite

Type landesite, $Ca_{0.4}Mg_{1.2}Mn_{7.2}^{2+}Mn_{0.5}^{3+}Fe_{2.7}^{3+}(OH)_{3.2}(H_2O)_{8.8}(PO_4)_{8.0}$, has $a = 9.458(3)$ Å, $b = 10.185(2)$ Å, $c = 8.543(2)$ Å, space group *Pbna*. R = 5.2% for 1821 independent reflexions (Mo-$K\alpha$ radiation). The distance averages are $M(1)$-O = 2.098 Å, $M(2)$-O = 2.205 Å, P-O = 1.539 Å. Cotype kryzhanovskite, $Ca_{0.5}Mg_{0.4}Mn_{3.8}^{2+}Fe_{7.3}^{3+}(OH)_{7.3}(H_4O)_{4.7}(PO_4)_{8.0}$, has $a = 9.450(2)$ Å, $b = 10.013(2)$, $c = 8.179(2)$. R = 7.2% for 1,703 independent reflexions (Mo-$K\alpha$ radiation). The distance averages are $M(1)$-O = 2.017 Å, $M(2)$-O = 2.115, P-O = 1.542.

Computed powder pattern intensities from the structure data admitted extensive revisions of earlier published Miller indices and revised powder data are presented.

[*Manuscript received 7 December 1979*]

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REDDINGITE, $Mn_3^{2+}(H_2O)_3(PO_4)_2$; phosphoferrite, $Fe_3^{2+}(H_2O)_3(PO_4)_2$; and kryzhanovskite, $Fe_3^{3+}(OH)_3(PO_4)_2$ are three end-members of an interesting solid-solution series involving two transition metals of the same formal charge (Mn^{2+},Fe^{2+}), and one transition metal of two different charges (Fe^{2+},Fe^{3+}), thus comprising a mixed-valence solid-solution series (Mn^{2+}, Fe^{2+}, Fe^{3+}). Detailed study on synthetic crystals of the two end-members phosphoferrite and kryzhanovskite established an isomorphism between the two and afforded comparison of bond distance and angle relationships between the $Fe^{2+}(H_2O)$ and $Fe^{3+}(OH)$ couples (Moore and Araki, 1976). An earlier study (Moore, 1971) on a natural kryzhanovskite crystal representing the series (Fe^{3+}, Mn^{2+}) suggested that the cations are extensively ordered over the two non-equivalent octahedral (M) sites in the structure type, with smaller cations preferring the M(1) site of equipoint rank number 4 on inversion centres and the larger cations distributed over the M(2) site of equipoint rank number 8 and with no symmetry. Thus, it appeared desirable to explore in detail and summarize the results for the compositions involving $Fe_3^{2+}(H_2O)_3(PO_4)_2$, $Fe_3^{3+}(OH)_3(PO_4)_2$, $Mn^{2+}Fe_2^{3+}(OH)_2(H_2O)(PO_4)_2$, and $Mn_2^{2+}Fe^{3+}(OH)(H_2O)_2(PO_4)_2$. Crystals of the first two yielded data of high quality, the X-ray structural results of which even established experimental location of hydrogen atoms (Moore and Araki, 1976). Type kryzhanovskite's composition is close to the third formula but, owing to inferior data and, worse still, a serious error in the entire study (Moore, 1971), a re-investigation seemed appropriate. The fourth composition is represented by the species landesite; we report here detailed investigations on both natural kryzhanovskite and landesite and incorporate, in the general discussion, the structural results available thus far on the entire series.

Cell parameters and powder data. Natural single crystals of kryzhanovskite (specimen from the type locality, see Moore, 1971) and landesite (Harvard University, 91214TYPE) were prepared for moving film methods and the best individuals selected for cell parameter refinement on a Picker FACS-1 automated four-circle diffractometer. Utilizing MoKα_1 radiation (λ = 0.70926 Å) with graphite monochromator, 24 high-angle reflections were submitted to least-squares refinement, the results of which appear in Table 1 along with the earlier published data on the synthetic end-members. The refined cell data are in poor agreement with the previously published results of Moore (1971), in particular kryzhanovskite's $\underline{c}$-axis which differs by 4.2%. The source of this error was eventually traced to the unfortunate juxtaposition of many non-equivalent powder lines and the subsequent difficulty in unambiguous assignment of Miller indices in the earlier study. Revisions of Miller indices for kryzhanovskite and landesite appear in Table 2 and were obtained from the refined single crystal data and the calculated powder patterns, the intensities of which were obtained from the atomic coordinate parameters, site distributions and isotropic thermal vibration parameters of this study. It is seen that agreement between observed and calculated data is now quite satisfactory, bearing in mind that a significant absorption effect occurs in the observed data, particularly for the kryzhanovskite. Of the 31 data earlier indexed for kryzhanovskite (Moore, 1971), 14 required new assignments; for landesite (Moore, 1964), of the 22 data, 6 required revisions. A further set of powder data has been published for synthetic phosphoferrite and kryzhanovskite (Moore, 1974). Calculation of the intensities from the structure parameters confirms the choice of indices reported therein.

TABLE 1. *Phosphoferrite series. Crystal cell data.*†

	1	2		3		4
	Phosphoferrite (synthetic)	Landesite (type)		Kryzhanovskite (cotype)		Kryzhanovskite (synthetic)
		a	b	a	b	
a(Å)	9.460(2)	9.458(3)	9.49(3)	9.450(2)	9.40(2)	9.518(4)
b(Å)	10.024(3)	10.185(2)	10.07(3)	10.013(2)	9.97(1)	9.749(4)
c(Å)	8.670(2)	8.543(2)	8.60(3)	8.179(2)	8.54(1)	8.031(3)
V(Å^3)	822.2	822.9	822.3	773.9	800.5	745.2
Axial ratios	0.9437:1:0.8649	0.9286:1:0.8388		0.9438:1:0.8168		0.9763:1:0.8238
n	1438	1821		1703	530	1316
R	0.024	0.052		0.072	0.086	0.036
R$_w$	0.046	0.041		0.045	---	0.055
M(1)–O(Å), obs.	2.160(2)	2.098(2)		2.017(3)	2.05(1)	2.014(3)
M(1)–O(Å), calc.	2.13	2.03		2.01		2.01
M(2)–O(Å), obs.	2.170(2)	2.205(3)		2.115(3)	2.16(1)	2.041(3)
M(2)–O(Å), calc.	2.13	2.18		2.11		2.01
P–O(Å), obs.	1.544(2)	1.539(2)		1.542(3)	1.53(1)	1.544(3)
specific gravity	--	3.026		3.31		--
density (g cm^{-3})	3.32	3.210	3.213	3.464	3.349	3.64

[1] Moore and Araki (1976). All calculated polyhedral M–O averages are based on $^{[6]}Fe^{2+}$–$^{[3]}O^{2-}$ and ionic radii from Shannon and Prewitt (1969). Errors in experimental bond distance averages are the mean of the individual distances.

[2a] This study. Calculated polyhedral M–O averages from the following site populations in the cell: M(1) = $1.2Mg^{2+} + 0.1Mn^{3+} + 2.7Fe^{3+}$, and M(2) = $0.4Ca^{2+} + 7.2Mn^{2+} + 0.4Mn^{3+}$.

[2b] Moore (1971). The specific gravity is from Berman and Gonyer (1930).

[3a] This study. Calculated polyhedral M–O averages from the following site populations in the cell: M(1) = $0.4Mg^{2+} + 3.6Fe^{3+}$, and M(2) = $0.5Ca^{2+} + 3.8Mn^{2+} + 3.7Fe^{3+}$.

[3b] Moore (1971).

[4] Moore and Araki (1976). The calculated polyhedral M–O averages are based on $^{[6]}Fe^{3+}$–$^{[3]}O^{2-}$

†For refinement, n = number of independent reflexions. The final cycle minimized $\Sigma_w||F_o|-|F_c||^2$ where w = $\sigma^{-2}(F)$.

TABLE II. *Kryzhanovskite and landesite. Powder data.*†

KRYZHANOVSKITE										LANDESITE				
I(obs)	I(calc)	d(obs)	d(calc)	hkℓ	I(obs)	I(calc)	d(obs)	d(calc)	hkℓ	I(obs)	I(calc)	d(obs)	d(calc)	hkℓ
-	3	-----	6.184	101 -----	-	1	-----	1.810	143 -----	-	2	-----	6.340	101 -----
4	19	5.249	5.262	111 (111)	-	0	-----	1.799	251 -----	6	22	5.370	5.382	111 (111)
7	40	4.996	5.007	020 (020)	-	0	-----	1.767	342 -----	8	54	5.096	5.093	020 (020)
5	23	4.701	4.725	200 (200)	-	1	-----	1.767	152 -----	5	18	4.728	4.729	200 (200)
5	23	4.253	4.273	210 (210)	-	0	-----	1.758	413 -----	-	0	-----	4.374	021 -----
-	0	-----	4.270	021 -----	-	1	-----	1.757	224 -----	8	27	4.284	4.289	210 (210)
-	2	-----	4.090	002 -----	-	2	-----	1.754	333 -----	-	4	-----	4.272	002 -----
4	17	3.887	3.891	121 (121)	-	1	-----	1.744	432 -----	4	11	3.966	3.970	121 (121)
-	0	-----	3.787	211 -----	2	3	1.727	1.728	521 (314)*	-	1	-----	3.833	211 -----
-	0	-----	3.514	112 -----	-	0	-----	1.718	440 -----	0.5	0	3.631	3.636	112 (112)
2	8	3.433	3.436	220 (220)	-	0	-----	1.718	243 -----	4	16	3.464	3.465	220 (220)
10	100	3.156	3.168	221 (221)	-	0	-----	1.715	134 -----	-	3	-----	3.273	022 -----
-	3	-----	3.167	022 -----	3	4	1.691	1.691	512 (512)	10	100	3.207	3.211	221 (221)
2	32	3.071	3.092	202 (122)*	-	2	-----	1.690	314 -----	7	35	3.163	3.170	202 (202)
3	26	3.006	3.003	122 (212)*	-	2	-----	1.682	423 -----	5	23	3.090	3.093	122 (122)
2	3	2.940	2.955	212 (131)*	-	0	-----	1.681	441 -----	3	6	3.021	3.027	212 (212)
-	2	-----	2.939	301 -----	-	0	-----	1.681	252 -----	-	4	-----	2.993	131 -----
-	1	-----	2.937	131 -----	-	1	-----	1.669	060 -----	2	5	2.956	2.958	301 (131)*
-	1	-----	2.821	311 -----	-	1	-----	1.655	351 -----	3	1	2.836	2.840	311 (311)
5	16	2.723	2.726	230 (230)	-	2	-----	1.636	234 -----	4	29	2.758	2.758	230 (230)
-	6	-----	2.631	222 -----	-	1	-----	1.635	061 -----	3	15	2.721	2.727	103 (103)
4	11	2.623	2.620	103 (113)*	-	0	-----	1.623	522 -----	-	8	-----	2.691	222 -----
-	0	-----	2.586	231 -----	-	1	-----	1.623	324 -----	8	24	2.630	2.634	113 (231)*
-	2	-----	2.535	321 -----	3	3	1.613	1.612	531 (025)*	-	0	-----	2.624	231 -----
5	17	2.534	2.534	113 (132)*	-	2	-----	1.612	105 -----	2	4	2.557	2.559	132 (040)*
-	1	-----	2.503	040 -----	-	5	-----	1.611	161 -----	-	1	-----	2.558	321 -----
1	4	2.484	2.494	132 (023)*	-	1	-----	1.591	115 -----	-	1	-----	2.546	040 -----
4	8	2.400	2.421	312 (123)*	-	0	-----	1.591	343 -----	2	7	2.484	2.485	023 (023)
-	8	-----	2.394	023 -----	-	0	-----	1.591	153 -----	-	12	-----	2.461	312 -----
-	7	-----	2.394	041 -----	-	3	-----	1.584	442 -----	2	5	2.448	2.440	041 (312)*
-	3	-----	2.362	400 -----	-	5	-----	1.584	044 -----	4	17	2.400	2.404	123 (123)
4	10	2.323	2.321	123 (141)*	-	0	-----	1.575	600 -----	-	1	-----	2.372	213 -----
-	10	-----	2.320	141 -----	-	0	-----	1.574	433 -----	-	1	-----	2.365	400 -----
-	1	-----	2.299	410 -----	-	2	-----	1.574	260 -----	1	10	2.363	2.363	141 (213)*
-	1	-----	2.298	213 -----	2	6	1.560	1.562	352 (352)	-	0	-----	2.317	232 -----
-	1	-----	2.268	232 -----	-	0	-----	1.562	144 -----	-	1	-----	2.303	410 -----
-	1	-----	2.233	322 -----	-	2	-----	1.556	610 -----	-	0	-----	2.271	322 -----
-	12	-----	2.213	411 -----	2	4	1.552	1.555	025 (513)*	-	0	-----	2.242	240 -----
-	0	-----	2.212	240 -----	-	3	-----	1.553	503 -----	5	15	2.227	2.230	331 (240)*
5	10	2.207	2.206	331 (411)*	-	0	-----	1.546	404 -----	-	14	-----	2.224	411 -----
-	0	-----	2.137	420 -----	-	4	-----	1.545	261 -----	-	0	-----	2.200	223 -----
-	1	-----	2.136	223 -----	-	2	-----	1.545	062 -----	1	10	2.190	2.187	042 -----
-	2	-----	2.135	241 -----	-	4	-----	1.535	513 -----	1	4	2.165	2.169	241 -----
4	8	2.138	2.135	042 (042)	-	4	-----	1.534	125 -----	-	0	-----	2.145	420 -----
2	5	2.084	2.082	142 (142)	-	0	-----	1.528	611 -----	-	3	-----	2.136	004 -----
-	2	-----	2.067	421 -----	-	2	-----	1.528	414 -----	4	10	2.132	2.131	142 -----
2	3	2.058	2.061	303 (114)*	-	1	-----	1.528	215 -----	-	2	-----	2.126	133 -----
-	1	-----	2.061	133 -----	-	0	-----	1.528	450 -----	-	3	-----	2.113	303 -----
-	0	-----	2.046	402 -----	-	1	-----	1.527	253 -----	-	1	-----	2.080	421 -----
-	2	-----	2.045	004 -----	-	1	-----	1.526	532 -----	-	2	-----	2.069	313 -----
-	1	-----	2.019	313 -----	-	0	-----	1.525	334 -----	-	0	-----	2.069	402 -----
-	0	-----	2.004	412 -----	-	3	-----	1.525	162 -----	-	2	-----	2.041	114 -----
3	9	1.997	1.999	332 (332)	-	1	-----	1.502	620 -----	3	8	2.034	2.032	332 -----
-	2	-----	1.960	114 -----	5	7	1.503	1.502	451 (451)	-	0	-----	2.027	412 -----
-	3	-----	1.946	242 -----	-	12	-----	1.501	244 -----	-	3	-----	1.985	242 -----
-	2	-----	1.928	430 -----	-	1	-----	1.484	523 -----	-	2	-----	1.981	233 -----
-	3	-----	1.928	233 -----	-	1	-----	1.483	541 -----	-	0	-----	1.970	024 -----
-	11	-----	1.906	323 -----	-	0	-----	1.478	621 -----	3	13	1.952	1.952	323 -----
-	8	-----	1.906	341 -----	2	3	1.481	1.477	424 (315)*	-	1	-----	1.946	204 -----
-	0	-----	1.905	151 -----	-	2	-----	1.477	225 -----	-	4	-----	1.940	430 -----
-	4	-----	1.894	422 -----	-	0	-----	1.470	602 -----	-	0	-----	1.939	151 -----
-	1	-----	1.893	024 -----	-	0	-----	1.469	262 -----	-	7	-----	1.930	341 -----
-	2	-----	1.877	431 -----	-	1	-----	1.454	612 -----	-	1	-----	1.928	124 -----
-	1	-----	1.877	204 -----	-	0	-----	1.454	443 -----	-	6	-----	1.917	422 -----
-	0	-----	1.856	124 -----	-	2	-----	1.452	305 -----	-	4	-----	1.912	214 -----
-	2	-----	1.844	214 -----	-	1	-----	1.451	135 -----	-	0	-----	1.898	043 -----
-	0	-----	1.844	043 -----	3	3	1.453	1.451	361 (361)	-	2	-----	1.892	431 -----
-	0	-----	1.844	250 -----	-	2	-----	1.437	315 -----	-	0	-----	1.871	250 -----
2	2	1.842	1.841	501 (501)	-	0	-----	1.436	353 -----	-	0	-----	1.861	143 -----
2	3	1.807	1.811	511 (511)	-	0	-----	1.431	452 -----	-	5	-----	1.847	501 -----

†Fe/Mn radiation. 114.6 mm Gandolfi mount camera diameter. Film corrected for shrinkage but an absorption correction was not applied. Calculated intensities are from the single crystal refinements. Previously assigned Miller indices are in parentheses (see text), the erroneous assignments are starred.

It has been our experience that cell parameters obtained from single crystal high-angle diffractometric refinement using MoKα_1 radiation are quite satisfactory and along with calculated powder intensities directly from crystal structure parameters usually give much improved matches with earlier reported powder patterns. Many crystal structures, of which the phosphoferrite structure type is an extreme case, possess cell geometries and intensity distributions which render assignments of Miller indices to the powder patterns difficult at best and ambiguous at worst. Therefore, we recommend that powder patterns be routinely calculated as a part of any program in crystal structure analysis.

The difficulty of matching powder patterns for members of the phosphoferrite ternary series involving Mn^{2+}–Fe^{2+}–Fe^{3+} arises from the strong anisotropy and non-linearity of the three crystallographic axes with respect to the mean M–O distance averages. Although a linear relationship exists between the cell volumes and the cube of the mean M–O distance averages (Fig. 1a), the behaviour of each of the three crystallographic axes with respect to the mean M–O distance is very complicated (Fig. 1b). This doubtless arises from the highly ordered nature of the two non-equivalent sites with respect to three components with substantially different ionic radii, and that two of the components involve different formal charges. There is a pronounced tendency for the c̲-axis to substantially decrease with decreasing mean M–O distance and for the a̲-axis to remain relatively unaffected. Since natural members of the phosphoferrite structure type involve at least two other components as well (Ca^{2+} and Mg^{2+}), investigators on these compounds are advised to seek cell refinements via single crystal techniques rather than by indexed powder patterns.

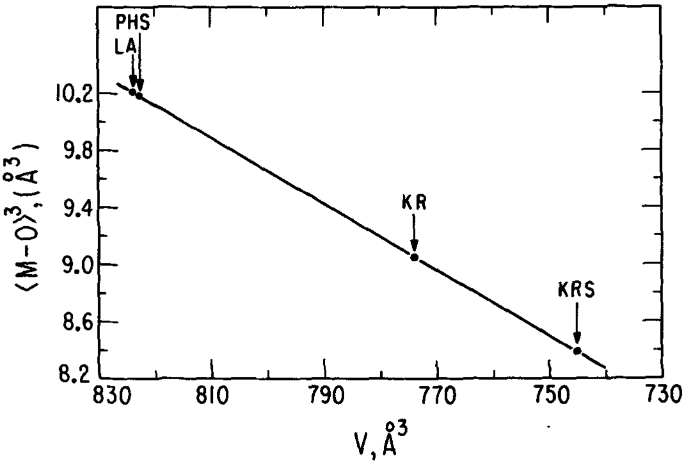

Fig. 1a. Plot of cell volume (V,Å) vs. cube of average M-O distance for landesite (LA), synthetic phosphoferrite (PHS), kryzhanovskite (KR) and synthetic kryzhanovskite. Note the linear relation throughout the series.

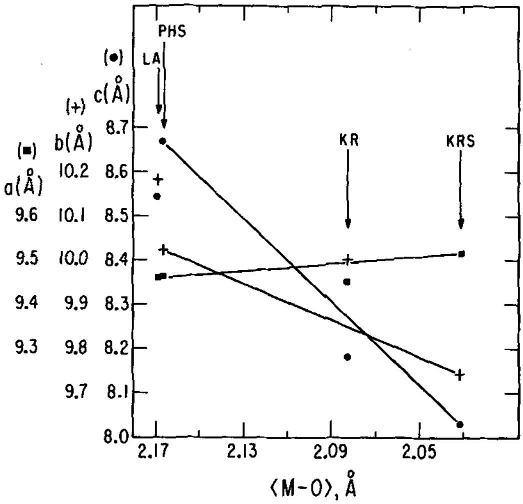

Fig. 1b. Plot of average M-O distance vs. cell edges *a*, *b* and *c* in Å. The PHS and KRS end-members have been connected with thin lines. Note the marked non-linearities, explaining in part the difficulty in indexing powder patterns.

Chemical composition. Very little type landesite and kryzhanovskite are available for complete wet chemical analysis. Therefore, we adopted for this study the analytical results of Berman and Gonyer (1930) and of Alekseev in Ginzburg (1950) for landesite and kryzhanovskite respectively. We adopted the cell contents on the basis of $\Sigma M = 12$ and $\Sigma P = 8$, resulting in the two compositions:

landesite $Ca_{0.4}Mg_{1.2}Mn^{2+}_{7.2}Mn^{3+}_{0.5}Fe^{3+}_{2.7}(OH)_{3.2}(H_2O)_{8.8}(PO_4)_{8.0}$

and

kryzhanovskite $Ca_{0.5}Mg_{0.4}Mn^{2+}_{3.8}Fe^{3+}_{7.3}(OH)_{7.3}(H_2O)_{4.7}(PO_4)_{8.0}$

The analytical results are summarized in Table 3.

TABLE III. *Chemical analyses for landesite and kryzhanovskite.*

	1 Landesite		2 Kryzhanovskite	
	a	b	a	b
CaO	1.41	1.39	1.74	1.50
MgO	3.04	3.07	1.00	1.30
MnO	32.09	33.65	16.69	16.39
Mn_2O_3	2.48	2.69	-	-
Fe_2O_3	13.54	13.91	36.10	34.62
P_2O_5	35.68	31.94	35.16	35.30
H_2O	11.76	13.60	9.31	9.70
Total	100.00	100.38	100.00	99.37

[1a] Calculated weight percentage for cell contents $Ca_{0.4}Mg_{1.2}Mn^{2+}_{7.2}Mn^{3+}_{0.5}Fe^{3+}_{2.7}(OH)_{3.2}(H_2O)_{8.8}(PO_4)_{8.0}$.

[1b] F. A. Gonyer analysis in Berman and Gonyer (1930). Total includes 0.13% insoluble.

[2a] Calculated weight percentage for cell contents $Ca_{0.5}Mg_{0.4}Mn^{2+}_{3.8}Fe^{3+}_{7.3}(OH)_{7.3}(H_2O)_{4.7}(PO_4)_{8.0}$.

[2b] Alekseev analysis in Ginzburg (1950). Total includes 0.56% insoluble.

In both instances, the calculated densities are substantially higher than the observed specific gravities (Table 1). Crystals of these species are invariably cracked and crenulated, and we advance the interpretation (vide infra) that the compositions represent oxidized phases, where oxidation postdated the original crystal growth of ferrous analogues.

Single crystal data. Three-dimensional single crystal data collection and refinement followed the same procedures as outlined in an earlier study (Moore and Araki, 1976). Data were collected to $\sin\theta/\lambda = 0.75$, scan speed 2.0° min^{-1}, background counting time 20 sec (stationary) on each side of the peak, base scan width 4.0°. The crystals, both approximately cubes in shape, were measured and corrected for absorption anisotropy by the Gaussian integral method (Burnham, 1966); Lorentz and polarization corrections were applied, the symmetry equivalent $|F_o|$ then averaged, yielding 1821 independent $|F_o|$ for landesite and 1703 independent $|F_o|$ for kryzhanovskite.

TABLE IVa. *Landesite (upper) and kryzhanovskite (lower). Atomic coordinate parameters.*

Atom	*x*	*y*	*z*
M(1)	0	0	0
	0	0	0
M(2)	0.06251(5)	0.10100(5)	0.63964(6)
	0.05105(7)	0.11205(7)	0.63602(8)
P	0.20733(7)	0.10506(7)	0.29235(9)
	0.20931(10)	0.10344(11)	0.28853(13)
O(1)	0.2155(2)	0.2526(2)	0.3294(3)
	0.2131(3)	0.2541(3)	0.3291(3)
O(2)	0.1051(2)	0.0378(2)	0.4074(3)
	0.1119(3)	0.0320(3)	0.4128(4)
O(3)	0.3566(2)	0.0444(2)	0.3087(3)
	0.3614(3)	0.0446(3)	0.3033(4)
O(4)	0.1585(3)	0.0878(3)	0.1227(3)
	0.1573(3)	0.0840(3)	0.1148(4)
OW(1)	-0.0945(4)	¼	½
	-0.0672(5)	¼	½
OW(2)	-0.0293(2)	0.3322(2)	0.1363(3)
	-0.0303(3)	0.3389(3)	0.1358(4)

TABLE IVb. *Landesite (upper) and kryzhanovskite (lower): anisotropic thermal vibration parameters* ($\times 10^5$)†

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M(1)	261(5)	248(5)	491(7)	- 21(4)	- 44(6)	- 16(6)
	200(7)	349(8)	508(12)	- 39(7)	- 44(10)	- 48(9)
M(2)	328(4)	334(4)	474(6)	-173(4)	- 9(4)	41(4)
	419(7)	310(6)	543(9)	-161(6)	66(7)	- 47(8)
P	121(5)	183(5)	358(8)	- 21(5)	30(6)	- 8(6)
	109(8)	122(8)	370(14)	- 5(8)	11(9)	14(10)
O(1)	235(17)	175(14)	612(29)	26(16)	22(19)	4(19)
	250(26)	127(23)	588(45)	- 29(26)	- 20(29)	- 20(29)
O(2)	165(17)	291(17)	464(27)	- 69(15)	105(18)	36(19)
	146(26)	205(26)	585(45)	- 30(22)	88(29)	108(30)
O(3)	168(18)	286(18)	841(34)	61(16)	126(22)	12(22)
	115(27)	286(28)	641(47)	64(23)	49(31)	112(31)
O(4)	499(24)	788(29)	382(29)	-306(24)	38(23)	- 80(25)
	231(28)	357(31)	443(44)	- 77(24)	- 20(30)	-146(31)
OW(1)	555(35)	370(29)	700(48)	0	0	- 99(34)
	727(58)	196(40)	615(67)	0	0	13(47)
OW(2)	217(19)	349(19)	716(33)	- 57(15)	- 14(21)	-101(22)
	147(28)	243(26)	856(51)	- 53(22)	- 43(33)	149(34)

†Coefficients in the expression $\exp-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell]$. Estimated standard errors refer to the last digit except for those coefficients related by symmetry.

TABLE IVc. *Landesite and kryzhanovskite. Parameters for the ellipsoids of vibration.*[a]

		Landesite					Kryzhanovskite				
Atom	*i*	μ_i	θ_{ia}	θ_{ib}	θ_{ic}	B(Å^2)	μ_i	θ_{ia}	θ_{ib}	θ_{ic}	B(Å^2)
M(1)	1	0.104(1)	32(3)	62(4)	75(2)	1.13(1)	0.090(2)	19(2)	76(2)	77(2)	1.16(1)
	2	0.117(1)	118(4)	28(4)	93(3)		0.128(2)	71(2)	127(6)	137(6)	
	3	0.137(1)	104(2)	94(3)	15(2)		0.140(2)	88(3)	140(5)	50(5)	
M(2)	1	0.087(1)	139(1)	131(1)	85(1)	1.31(1)	0.097(2)	129(1)	141(1)	89(2)	1.40(1)
	2	0.131(1)	102(1)	84(1)	167(1)		0.131(1)	74(2)	104(2)	158(2)	
	3	0.158(1)	129(1)	41(1)	78(1)		0.163(1)	44(1)	126(1)	68(2)	
P	1	0.071(2)	15(2)	78(3)	98(2)	0.75(1)	0.070(3)	12(15)	79(16)	94(3)	0.62(1)
	2	0.099(1)	101(3)	15(3)	80(4)		0.079(3)	78(16)	168(14)	86(4)	
	3	0.116(1)	100(2)	82(4)	168(3)		0.112(2)	93(3)	95(4)	174(3)	
O(1)	1	0.092(5)	120(13)	30(13)	89(3)	1.11(3)	0.077(8)	75(12)	16(11)	86(5)	0.99(4)
	2	0.106(4)	31(13)	60(13)	94(4)		0.108(6)	164(11)	74(12)	94(8)	
	3	0.151(4)	86(4)	89(4)	5(3)		0.141(5)	95(8)	93(5)	5(6)	
O(2)	1	0.068(6)	152(3)	109(3)	70(3)	1.05(3)	0.067(9)	147(9)	117(9)	71(4)	0.97(5)
	2	0.129(4)	110(8)	20(8)	90(20)		0.101(7)	121(10)	34(9)	102(6)	
	3	0.137(4)	71(8)	83(20)	20(3)		0.149(5)	80(4)	71(5)	22(4)	
O(3)	1	0.075(5)	160(3)	73(4)	79(2)	1.41(4)	0.065(9)	164(6)	74(7)	88(5)	1.09(5)
	2	0.126(4)	74(4)	17(4)	97(3)		0.113(6)	77(7)	32(6)	119(6)	
	3	0.180(4)	78(2)	86(3)	13(2)		0.156(5)	81(4)	63(6)	29(6)	
O(4)	1	0.117(5)	73(45)	74(23)	23(51)	2.06(4)	0.086(8)	44(10)	59(5)	62(9)	1.15(5)
	2	0.120(4)	34(27)	66(16)	112(52)		0.114(6)	48(11)	108(8)	132(9)	
	3	0.224(4)	61(2)	151(2)	84(2)		0.153(6)	79(6)	143(5)	55(6)	
OW(1)	1	0.131(6)	90	153(7)	117(7)	1.85(5)	0.100(10)	90	3(10)	93(10)	1.68(8)
	2	0.159(5)	180	90	90		0.144(8)	90	87(10)	3(10)	
	3	0.168(6)	90	63(7)	153(7)		0.181(7)	0	90	90	
OW(2)	1	0.094(5)	160(5)	109(5)	96(3)	1.44(4)	0.075(8)	23(11)	68(10)	92(5)	1.26(5)
	2	0.132(4)	110(5)	32(5)	67(5)		0.105(7)	68(11)	150(9)	71(4)	
	3	0.169(4)	92(3)	66(5)	156(5)		0.177(5)	84(3)	109(4)	160(4)	

[a] *i* = *i*th principal axis, μ_i = rms amplitude, θ_{ia}, θ_{ib}, θ_{ic} = angles (deg.) between the *i*th principal axis and the cell axes *a*, *b* and *c*. The equivalent isotropic thermal parameter, B, is also listed. Estimated standard errors in parentheses refer to the last digit.

Structure determination and refinement. Inspection of the raw intensities led to extinction criteria consistent with the space group Pbna, which is uniquely determined. Weak extra reflexions (Moore, 1964) were sought but not found. Trial parameters were obtained from the earlier study (Moore and Araki, 1976) and the full-matrix least-squares refinement converged smoothly to the results in Table 1 for all observed non-equivalent reflexions, where

$$R = \frac{\Sigma||Fo|-|Fc||}{\Sigma|Fo|} \text{ and } R_w = \left[\frac{\Sigma_w(|Fo|-|Fc|)^2}{\Sigma wFo^2}\right]^{\frac{1}{2}}$$

Programs and procedures, including scattering curves used in the refinement were discussed earlier (Moore and Araki, 1976). Table 4a lists the atomic coordinates, 4b the anisotropic thermal vibration parameters, 4c the parameters for the ellipsoids of vibration, Table 5*the observed and calculated structure factors, and Table 6 the interatomic distances and angles for landesite, kryzhanovskite, and the previous reported synthetic end members.

Crystal chemistry of the complex series. This study confirms the earlier conclusion (Moore, 1971) that cations of different radii are extensively ordered over the M(1) and M(2) sites in the phosphoferrite structure type and that the M(1) site accommodates the smallest cations. Paragenetic and physical evidence suggest that these compounds are oxidation products of pre-existing members of the reddingite-phosphoferrite series. Therefore, the principal divalent octahedral cations are arranged according to increasing ionic radius, $Mg^{2+} < Fe^{2+} < Mn^{2+} < Ca^{2+}$, assuming that all Fe^{3+} reflects the ordering scheme of Fe^{2+} prior to oxidation.

The peculiar distributions of the order of increasing individual polyhedral bond distances in Table 6 and the consequent non-linear relation-

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*On file with the Mineralogical Society

TABLE VI. *Polyhedral interatomic distances (Å) and angles (deg.) for the phosphoferrite series*[a]

	PHS		LA		KR			KRS	
M(1)									
2 M(1)-O(4)	2.012(2) Å	1	2.036(2)	1	1.949(3)	1	(1.96)	1.941(3)	1
-OW(2)$^{(4)}$	2.164(2)	2	2.086(2)	2	1.979(3)	2	(2.01)	1.957(3)	2
-O(3)$^{(1)}$	2.304(2)	3	2.171(2)	3	2.122(3)	3	(2.19)	2.144(3)	3
average	2.160 Å		2.098		2.017		(2.05)	2.014	
Δd_{M-O}	+0.000 Å		-0.062		-0.143			-0.146	
*2 OW(2)$^{(4)}$-O(3)$^{(2)}$	2.772(3)	76.6(1)*	2.749(3)	80.4(1)*	2.652(4)	80.5(1)	(2.66)	2.572(4)	77.5(1)
2 O(4)-O(3)	2.920(3)	84.9(1)	2.948(3)	88.9(1)	2.902(4)	90.8(1)	(2.96)	2.965(4)	92.9(1)
2 OW(2)$^{(4)}$-O(4)$^{(3)}$	2.945(3)	89.6(1)	2.878(3)	88.6(1)	2.737(4)	88.4(1)	(2.73)	2.688(4)	87.2(1)
2 O(4)-OW(2)$^{(4)}$	2.965(3)	90.4(1)	2.952(3)	91.5(1)	2.817(4)	91.6(1)	(2.88)	2.824(4)	92.8(1)
2 O(4)-O(3)$^{(2)}$	3.190(3)	95.1(1)	3.005(3)	91.1(1)	2.860(4)	89.2(1)	(2.93)	2.817(4)	87.1(1)
2 OW(2)$^{(4)}$-O(3)$^{(1)}$	3.507(3)	103.4(1)	3.253(4)	99.6(1)	3.132(4)	99.5(1)	(3.26)	3.199(4)	102.5(1)
average	3.050	90.0	2.964	90.0	2.850	90.0	(2.90)	2.844	90.0
$\Delta d_{O-O'}$	+0.000		-0.086		-0.200			-0.206	
P									
P-O(3)	1.539(2)	1	1.548(2)	4	1.558(3)	4	(1.52)	1.551(3)	3
-O(4)	1.543(2)	2	1.531(2)	1	1.516(3)	1	(1.59)	1.511(3)	1
-O(2)	1.544(2)	3	1.540(2)	3	1.547(3)	3	(1.54)	1.569(3)	4
-O(1)	1.660(2)	4	1.538(2)	2	1.546(3)	2	(1.47)	1.545(3)	2
average	1.544		1.539		1.542		(1.53)	1.544	
O(1)-O(4)	2.490(3)	107.2(1)	2.495(3)	108.8(1)	2.501(4)	109.5(2)	(2.50)	2.499(4)	109.7(1)
O(3)-O(4)	2.516(3)	109.5(1)	2.496(3)	108.3(1)	2.501(4)	108.9(2)	(2.51)	2.483(4)	108.4(1)
O(1)-O(3)	2.519(3)	109.3(1)	2.512(3)	109.0(1)	2.532(4)	109.3(2)	(2.44)	2.542(4)	110.3(1)
O(1)-O(2)	2.523(3)	109.3(1)	2.514(3)	109.6(1)	2.516(4)	108.9(2)	(2.44)	2.515(4)	107.8(1)
O(2)-O(3)	2.528(3)	110.2(1)	2.525(3)	109.8(1)	2.525(4)	108.8(2)	(2.49)	2.535(4)	108.6(1)
O(2)-O(4)	2.550(3)	111.4(1)	2.536(3)	111.3(1)	2.529(4)	111.3(1)	(2.60)	2.553(4)	112.0(1)
average	2.521	109.5	2.513	109.5	2.517	109.5	(2.50)	2.521	109.5

	LA		PHS		KR			KRS	
M(2)									
M(2)-O(1)$^{(4)}$	2.094(2)	1	2.066(2)	1	2.055(3)	1	(2.10)	1.989(3)	3
-O(2)	2.124(2)	2	2.121(2)	3	2.075(3)	2	(2.15)	2.059(3)	4
-O(2)$^{(3)}$	2.162(2)	3	2.108(2)	2	2.147(3)	5	(2.16)	2.114(3)	5
-O(3)$^{(2)}$	2.205(2)	4	2.132(2)	4	2.240(3)	6	(2.27)	2.204(3)	6
-OW(2)$^{(4)}$	2.209(3)	5	2.192(2)	5	2.077(3)	3	(2.14)	1.906(3)	1
-OW(1)	2.433(4)	6	2.399(3)	6	2.096(3)	4	(2.13)	1.973(3)	2
average	2.205		2.170		2.115		(2.16)	2.041	
Δd_{M-O}	+0.000		-0.035		-0.090			-0.164	
*O(2)-O(2)$^{(3)}$	2.654(4)	76.5(1)	2.641(3)	77.3(1)	2.630(5)	77.0(1)	(2.69)	2.610(4)	77.4(1)
*O(3)$^{(2)}$-OW(2)$^{(4)}$	2.749(3)	77.0(1)	2.772(3)	79.7(1)	2.652(4)	75.7(1)	(2.66)	2.572(4)	77.1(1)
O(1)$^{(4)}$-OW(2)$^{(4)}$	2.956(3)	86.7(1)	2.908(3)	86.1(1)	2.917(4)	98.8(1)	(2.96)	2.832(4)	93.3(1)
O(2)-OW(1)	2.976(3)	81.2(1)	2.909(4)	79.9(1)	2.853(4)	86.3(1)	(2.85)	2.748(4)	85.9(1)
O(2)$^{(3)}$-O(3)$^{(2)}$	2.989(3)	86.4(1)	2.968(3)	88.9(1)	2.957(4)	84.7(1)	(2.99)	2.956(4)	86.4(1)
O(2)$^{(3)}$-OW(1)	3.038(2)	82.5(1)	2.989(4)	82.8(1)	2.943(3)	87.8(1)	(2.96)	2.869(4)	89.1(1)
O(2)$^{(3)}$-OW(2)$^{(4)}$	3.204(3)	94.3(1)	3.149(3)	94.2(1)	3.076(4)	93.5(1)	(3.13)	2.892(4)	91.9(1)
O(1)$^{(4)}$-O(3)$^{(2)}$	3.269(3)	98.9(1)	3.145(3)	97.0(1)	3.182(5)	95.5(1)	(3.24)	3.050(4)	93.2(1)
O(1)$^{(4)}$-O(2)	3.271(3)	101.7(1)	3.236(3)	101.2(1)	3.155(4)	99.6(1)	(3.28)	3.039(4)	97.3(1)
O(1)$^{(4)}$-OW(1)	3.274(4)	92.3(1)	3.199(4)	91.2(1)	2.995(5)	92.4(1)	(3.04)	2.842(4)	91.7(1)
OW(1)-OW(2)$^{(4)}$	3.276(3)	89.6(1)	3.202(4)	88.3(1)	3.128(3)	97.1(1)	(3.24)	2.964(4)	99.6(1)
O(2)-O(3)$^{(2)}$	3.547(4)	110.0(1)	3.496(3)	110.6(1)	3.294(4)	99.5(1)	(3.46)	3.182(4)	96.5(1)
average	3.100	89.8	3.051	89.8	2.982	89.9	(3.04)	2.880	89.9
$\Delta d_{O-O'}$	+0.000		-0.049		-0.118			-0.220	

[a] Synthetic phosphoferrite and synthetic kryzhanovskite (KRS) from Moore and Araki (1976). Type landesite (LA) and cotype kryzhanovskite (KR) from this study. Octahedral shared edges are starred. Δd_{M-O} and $\Delta d_{O-O'}$ refer to the difference between the polyhedral average and the largest polyhedron in that category. Symmetrically related atoms are designated with superscripts and adopt the relations in Moore and Araki (1976). The order of increasing M-O and P-O distances are numbered 1, 2, 3, ···. Earlier data for KR (Moore, 1971) are listed in parentheses.

ships among the cell parameters with increasing oxidation in the series is entirely compatible with a bond length-bond strength model which adopts the empirical relationships of Baur (1970). It is convenient to represent the compositions ideally as follows: $M_3^{2+}(H_2O)_3(PO_4)_2$ (phosphoferrite, reddingite), $M_2^{2+}M^{3+}(OH)(H_2O)_2(PO_4)_2$ (landesite), $M^{2+}M_2^{3+}(OH)_2(H_2O)(PO_4)_2$ (type kryzhanovskite), $M_3^{3+}(OH)_3(PO_4)_2$ (kryzhanovskite end-member). We note that these "ideal" compositions reflect closely the analyses in Table 3 for landesite and kryzhanovskite types. We further note that the cell volumes decrease in the order PHS ≈ LA > KR > KRS*, that is in the order of the ideal compositions written above. Thus, in Table 6, the M–O and P–O distances were arranged in the same order. It is seen that non-linearities in cell parameters arise from permutations of the order of P–O and M(2)–O bonds (with respect to increasing distance) through the series. We note that there exist six possible "pure" combinations of coordinations of cations about the OW(1) and OW(2) anions: $M_2^{2+}H_2$ (Δp_O = +0.67), $M^{2+}M^{3+}H_2$ (Δp_O = +0.50), $M_2^{3+}H_2$ (Δp_O = +0.33), $M_2^{2+}H$ (Δp_O = -0.17), $M^{2+}M^{3+}H$ (Δp_O = -0.33), and $M_2^{3+}H$ (Δp_O = -0.50 e.s.u.). The combinations $M_2^{3+}H_2$ and $M_2^{2+}H$

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*It is convenient to use abbreviations: PHS = synthetic end-member phosphoferrite, LA = landesite, KR = kryzhanovskite (type), KRS = synthetic end-member kryzhanovskite.

cannot exist as the end-members, combination $M_2^{2+}H_2$ = PHS and combination $M_2^{3+}H$ = KRS. There are, in addition, the following combinations in solid solutions within non-equivalent sites: M(1), M(2) = M^{2+}, M^{3+}; OW = H_2O, OH^-. Thus, to sort out the possible combinations for intermediate members, we first note the distributions in M(1) and M(2), then ask which combinations of OW admit charge balance for the entire crystal.

In Table 1, the averaged M—O and P—O distances are compared with calculated distances from ionic radii tables (Shannon and Prewitt, 1969). The calculated values tend to be slightly smaller (0.01-0.03Å) for all entries except M(1)—O for LA where the value is smaller by 0.07Å. This doubtless arises from the fact that we based our ionic radii on $r_{[3]_O}$ = 1.36Å. Nevertheless, the M(2)—O = 2.205(obs) Å site in LA indicates complete population by the large cations at this site. The M(1)—O = 2.017(obs) Å in kryzhanovskite indicates complete occupancy by Fe^{3+}. Thus, we can write (as pure compositions) LA: M(1) = Fe^{3+}, M(2) = Mn^{2+}; and KR: M(1) = Fe^{3+}, M(2) = $Fe^{3+}_{0.5}Mn^{2+}_{0.5}$. These pure compositions were then used to assess the relationship in individual distance deviations from polyhedral average (Δd) with deviations from local electrostatic neutrality (Δp_O) in Table 7. Good agreement is achieved with the following combinations--LA: OW(1) = H_2O, OW(2) ≈ $H_{1.5}O$ and KR: OW(1) = OW(2) ≈ $H_{1.33}O$. Note that the order of Δp_O follows Δd in a consistent way, progressing along PHS—LA—KR—KRS.

We can trace the behaviour of the individual H atoms in more detail owing to the locations of these atoms in the earlier study (Moore and Araki, 1976) for the PHS and KRS. In that study, it was found that OW(2), which has two non-equivalent H atoms H(2a) and H(2b), loses H(2b); and that the H(1) pairs which are related by a 2-fold rotor, merge on the rotor for the pure KRS. Our present results are entirely consistent with the former study but add additional information: through progressive oxidation of M, H(2b) is progressively removed until it is about 1/3-occupied and then H(1) is progressively removed. Throughout, H(2a) remains intact.

Conclusions. The triple series reddingite-phosphoferrite-kryzhanovskite possesses the general formula $M(1)M(2)_2[H(1)_2O][H(2a)H(2b)O]_2[PO_4]_2$. The compounds are highly ordered with the smaller cations partitioned into the M(1) site. Progressive oxidation of the M cation leads to progressive removal of the H atoms in the order H(2b)—H(1), the H(2a) hydrogen remaining intact throughout oxidation. The ordered nature of the M cations and the preferential removal of the hydrogens lead to substantial non-linearities in the axial relations throughout the series and, subsequently, serious problems in correct indexing of the powder patterns in the absence of powder intensities calculated directly from the refined structures.

Nomenclature. The following nomenclature is advanced according to naming of end-members in the general formula $M(1)M(2)_2[(H_2O),(OH)]_3[PO_4]_2$:

	M(1)	M(2)	Name
1	Fe^{2+}	Fe^{2+}	phosphoferrite
2	Fe^{3+}	Fe^{2+}	unnamed
3	Fe^{3+}	Fe^{3+}	kryzhanovskite
4	Mn^{2+}	Mn^{2+}	reddingite
5	Fe^{2+}	Mn^{2+}	unnamed
6	Fe^{3+}	Mn^{2+}	landesite

There is no evidence that extensive Mn^{3+} exists in crystals of the phosphoferrite structure type. Note that type kryzhanovskite is at the dividing line between landesite and kryzhanovskite end-members and it is proposed that the name apply to all compositions where Fe^{3+} is the greatest fraction occupying both M(1) and M(2). Composition 2 may be unstable or, if it did occur, the conditions of its formation are predicted to be quite restricted. If M(1) and M(2) remain immobile components during the course of oxidation (cf. the triphylite-heterosite series, Eventoff et al., 1972; Alberti, 1976), then composition 5 quite likely exists in reddingites from Poland, Maine; and some reddingites from Branchville, Connecticut (see analyses 5 and 6 in Palache et al., 1951). But the matter of mobility of M(1) and M(2) cations has not been settled nor is the relationship between site occupancy and temperature known for the reddingite-phosphoferrite series. Owing to similarities in ionic radii and scattering power between Fe^{2+} and Mn^{2+}, it would appear that Mössbauer resonance spectroscopy would be the appropriate tool to investigate these intermediate compositions rather than X-ray diffraction.

TABLE VII. *The phosphoferrite series: electrostatic valence balance of cations about anions.*[a]

		Δp_O			
Anion	Coordinating cations	PHS	LA	KR	KRS
O(1)	H(2a)+P+M(2)	-0.25	-0.25	-0.17	-0.08
O(2)	P+2M(2)	-0.08	-0.08	+0.08	+0.25
O(3)	H(1) + P+M(1)+M(2)	+0.08	+0.25	+0.28	+0.33
O(4)	H(2b)+P+M(1)	-0.25	-0.17	-0.19	-0.25
OW(1)	2H(1)+2M(2)	+0.33	+0.33	-0.05	-0.17
OW(2)	H(2a)+H(2b)+M(1)+M(2)	+0.33	+0.22	+0.03	-0.17

	Δd_O					
	PHS			LA		
Anion	P	M(1)	M(2)	P	M(1)	M(2)
O(1)	+0.006	------	-0.104	-0.001	------	-0.111
O(2)	+0.000	------	-0.062,-0.049	+0.001	------	-0.081,-0.043
O(3)	-0.005	+0.144	-0.038	+0.009	+0.073	+0.000
O(4)	-0.001	-0.148	------	-0.008	-0.062	------
OW(1)	------	------	+0.229(×2)	------	------	+0.228(×2)
OW(2)	------	+0.004	+0.022	------	-0.012	+0.004

	KR			KRS		
Anion	P	M(1)	M(2)	P	M(1)	M(2)
O(1)	+0.004	------	-0.060	+0.001	------	-0.052
O(2)	+0.005	------	-0.040,+0.037	+0.025	------	+0.018,+0.073
O(3)	+0.016	+0.105	+0.125	+0.007	+0.100	+0.163
O(4)	-0.026	-0.068	------	-0.033	-0.073	------
OW(1)	------	------	-0.019(×2)	------	------	-0.068(×2)
OW(2)	------	-0.038	-0.038	------	-0.057	-0.135

[a] A bond length deviation refers to the polyhedral average subtracted from the individual bond distance. Refer to Moore and Araki (1976) for hydrogen nomenclature. The deviation of electrostatic bond strength sum from neutrality (p_O = 2.00 e.s.u.) assumed the following:

PHS: OW(1) = H_2O, OW(2) = $H(2a)_{1.0}H(2b)_{1.0}O$.
LA: OW(1) = H_2O, OW(2) = $H(2a)_{1.0}H(2b)_{0.5}O$.
KR: OW(1) = $H_{1.33}O$, OW(2) = $H(2a)_{1.0}H(2b)_{0.33}O$.
KRS: OW(1) = $H_{1.0}O$, OW(2) = $H(2a)_{1.0}H(2b)_{0.0}O$.

Acknowledgments. The kryzhanovskite data were from a fragment of the material provided by Professor A. S. Povarennykh and used in the earlier study (Moore, 1971). Professor Clifford Frondel kindly donated a fragment of the type landesite.

We appreciate support of this study by the National Science Foundation grant EAR-19483 (Geochemistry).

REFERENCES

Alberti (A.), 1976. *Acta Crystallogr.* B32, 2761-64.

Baur (W. H.), 1970. *Trans. Am. Crystallogr. Assoc.* 6, 129-55.

Berman (H.) and Gonyer (F.), 1930. *Am. Mineral.* 15, 375-87.

Burnham (C. W.), 1966. *Ibid*, 51, 159-67.

Eventoff (W.), Martin (R.), and Peacor (D. R.), 1972. *Ibid*, 57, 45-51.

Ginzburg (A. I), 1950. *Dokl. Akad. Nauk S.S.S.R.* 72, 763-66.

Moore (P. B.), 1964. *Am. Mineral.* 49, 1122-25.

__________, 1971. *Ibid*, 56, 1-7.

__________, 1974. *Nature Physical Sciences* 251, 305-6.

__________, Araki (T.), 1976. *Inorg. Chem.* 15, 316-21.

Palache (C.), Berman (H.), and Frondel (C.), 1951. *Dana's System of Mineralogy* 2, 727-31.

Shannon (R. D.) and Prewitt (C. T.), 1969. *Acta Crystallogr.* B25, 925-46.