Karenwebberite, Na(Fe^{2+},Mn^{2+})PO$_4$, a new member of the triphylite group from the Malpensata pegmatite, Lecco Province, Italy

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ABSTRACT

Karenwebberite, Na(Fe^{2+},Mn^{2+})PO$_4$, belongs to the triphylite group of minerals and corresponds to the Fe–equivalent of natrophilite or to the Na–equivalent of triphylite. It occurs in the Malpensata pegmatite dyke, Colico, Lecco Province, Italy. Karenwebberite is found as late–magmatic–stage exsolution lamellae up to 100 µm thick, hosted by graftonite and associated with Na–bearing ferrisicklerite and with an heterosite–like phase. Lamellae are pale green, with very pale grayish-green streak. The luster is greasy to vitreous, and lamellae are translucent (pale green) to opaque (dark green). Optically, the mineral is anisotropic, biaxial (+), $\alpha = 1.701(2)$, $\beta = 1.708(2)$, $\gamma = 1.717(2)$ (for $\lambda = 589$ nm), $2V_{\text{meas.}} = 87(4)°$, $2V_{\text{calc.}} = 41°$, $Z = b$. Pleochroism is moderate with X = dark grey, Y = brown, and Z = yellow. The mineral is brittle with a Mohs hardness of 4.5; in thin section it displays a perfect cleavage along {001} with an irregular fracture. Karenwebberite is non-fluorescent either under short–wave or long–wave ultraviolet light, and its calculated density is 3.65

g/cm^3. The mean chemical composition, determined by the electron–microprobe from 16 point analyses (wt. %), is: P_2O_5 41.12, $Fe_2O_3^*$ 7.00, FeO* 25.82, MgO 0.23, ZnO 0.11, MnO 9.31, CaO 0.10, Na_2O 14.66, total 98.41 (*: calculated values). The empirical formula, calculated on the basis of 1 P atom per formula unit from, is $(Na_{0.817}Ca_{0.003}\square_{0.180})_{\Sigma 1.000}(Fe^{2+}_{0.622}Mn^{2+}_{0.228}Fe^{3+}_{0.151}Mg_{0.010}Zn_{0.002})_{\Sigma 1.013}PO_4$. Karenwebberite is orthorhombic, space group P*bnm*, *a* =4.882(1), *b* = 10.387(2), *c* = 6.091(1) Å, V = 308.9(1) Å^3, and Z = 4. The mineral possesses the olivine structure, with the M1 octahedra occupied by Na, and the M2 octahedra occupied by Fe and Mn. The eight strongest lines in the X–ray powder pattern are [*d* in Å (intensities) (*hkl*)]: 5.16 (50) (020), 4.44 (90) (110), 3.93 (80) (021), 3.56 (90) (120), 3.04 (80) (002), 2.817 (100) (130), 2.559 (100) (131), and 1.657 (50) (061). The mineral is named in honour of Dr. Karen Louise Webber, Assistant Professor Research at the Mineralogy, Petrology and Pegmatology Research Group, Department of Earth and Environmental Sciences, University of New Orleans, Louisiana, U.S.A.

INTRODUCTION AND OCCURENCE

The triphylite mineral group is constituted by several Fe–Mn–bearing phosphates which are widespread in medium to highly evolved LCT granitic pegmatites, ranging from the beryl–columbite–phosphate subtype to the spodumene subtype, according to the classification of Černý and Ercit (2005). This group contains primary and weakly oxidized phosphates, as for example minerals of the triphylite–lithiophilite solid solution series [$Li(Fe^{2+},Mn)PO_4 - Li(Mn,Fe^{2+})PO_4$] and natrophilite [$Na(Mn,Fe^{2+})PO_4$], but the oxidation also frequently produces more oxidized phosphates as ferrisicklerite–sicklerite [$\square_{1-x}Li_x(Fe^{3+},Mn^{2+})PO_4 - \square_{1-x}Li_x(Mn^{2+},Fe^{3+})PO_4$] or heterosite–purpurite [$\square(Fe^{3+},Mn^{3+})PO_4 - \square(Mn^{3+},Fe^{3+})PO_4$].

Triphylite hosted by Triassic pegmatites embedded into the crystalline basement of the central Southern Alps had been recently described at Brissago (Switzerland) and Piona (Italy) (Vignola et al. 2008a, Vignola et al. 2010, Vignola et al. 2011a). In this paper, we report the description of a new Na–bearing mineral species belonging to the triphylite group, karenwebberite, $Na(Fe^{2+},Mn^{2+})PO_4$ (IMA 2011-015, Vignola et al. 2011b).

The mineral was found by one of the authors (P.V.) at the Malpensata granitic pegmatite, Colico commune, Lecco Province, north Italy. The Malpensata dyke, mined for ceramic feldspar and mica during 1943-1946, is located on the east side of the Piona peninsula, 1.2 km north of Olgiasca village and 200 m south of the Piona Abbey, at an elevation of 110 m above sea level (46°, 07’, 20’’ N; 9°, 10’, 33’’E). Malpensata dyke belongs to the Piona granitic pegmatite swarm, which is embedded into the high–grade metapelites (sillimanite–, biotite-bearing micaschists and gneisses) of the Dervio–Olgiasca Zone that constitutes the crystalline basement of the Central Southern Alps (Bertotti et al. 1999). The dyke consists of plagioclase (An_{08}) and quartz, with muscovite, schorl, and almandine-rich garnet as common accessories, and belongs to the beryl-columbite-phosphate sub-type of LCT granitic pegmatites referred to the classification of P. Černý (Černý and Ercit 2005, Vignola et al. 2010). Karenwebberite occurs as thin exsolution lamellae within graftonite nodules, which are enclosed in blocky plagioclase crystals located in the central portion (the most evolved one) of the dyke. These nodules were found in close association with cassiterite, Hf-rich zircon, tapiolite-(Fe), oxycalciomicrolite, ferrowyllieite and other evolved phosphates (Vignola et al. 2008b, Vignola et al. 2010).

The mineral has been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association under number IMA 2011–015, and is named in honor of Dr Karen Louise Webber, who is Assistant Professor Research at the Mineralogy, Petrology and Pegmatology Research Group, Department of Earth and Environmental Sciences, University of New Orleans, Louisiana, U.S.A. Her research has focused on the cooling and crystallization dynamics of granitic pegmatites; in particular, she has demonstrated that crystal size is not a reliable indicator of crystallization time in pegmatites. For the analyses described in the following sections, two co-type specimens originating from the same hand sample were used. The two cotype specimens are kept in the mineralogical collection of the Museum of Natural History of Milano

(Italy), catalogue number M37902 and in the mineralogical collection of the Department of Geology of the University of Liège (Belgium), catalogue number 20385.

APPEARANCE AND PHYSICAL PROPERTIES

Karenwebberite forms pale to dark green (brownish if oxidized), transparent to translucent, exsolution lamellae up to 50–80 µm thick and 2–4 mm long, included in very pale–pink graftonite. In Figure 1 is shown the aspect of karenwebberite in thin section. Due to iron oxidation, this mineral progressively transforms into Na–bearing ferrisicklerite, $Na_{1-x}(Fe^{3+},Mn^{2+})PO_4$, which shows a dark brown color in thin section (Fig. 1). Lamellae of karenwebberite display a perfect cleavage along the {001} direction, as observed in thin section. The mineral is brittle and the Mohs hardness is 4.5(5), estimated by comparison with other minerals of the triphylite group. The lustre is greasy to vitreous and the streak is very pale grayish green. Karenwebberite is biaxial (+), α = 1.701(2), β = 1.708(2), γ = 1.717(2) (for λ = 589 nm), $2V_{\mathrm{meas.}} = 87(4)°$, $2V_{\mathrm{calc.}} = 41°$, with Z = *b*. Pleochroism is moderate with X = dark grey, Y = brown, and Z = yellow. Karenwebberite is non–fluorescent either under short–wave (254 nm) or long–wave (366 nm) ultraviolet light. Due to the small grain size, the density was not measured directly, but the density calculated from the empirical formula and single–crystal data is 3.65 g/cm^3. The compatibility index (Mandarino 1981), based upon the empirical formula, calculated density and average index of refraction, is 1 – (Kp/Kc) = 0.010, which corresponds to the superior category.

CHEMICAL COMPOSITION

Preliminary chemical investigations of karenwebberite were performed on a polished thin section using a Tescan Vega TS 5136 XM scanning electron microscope (SEM) equipped with an EDAX Genesis 4000 JXM energy dispersive spectrometer (EDS) at the “Centro interdipartimentale di microscopia elettronica” of the University of Milano-Bicocca.

Quantitative chemical analyses were performed on the same polished thin section using a JEOL JXA-8200 electron microprobe operating in wavelength–dispersive mode at the laboratory of the Department of Earth Sciences, University of Milano. The accelerating voltage was 15 kV, with a beam current of 15 nA, a spot size of 2 μm, and a counting time of 30 sec on the peaks and 10 sec on the background. Natural minerals were used as standards (graftonite KF16 for P, Fe, Mn and Ca; olivine USNM 2566 for Mg; rhodonite for Zn; and omphacite USNM 110607 for Na). The raw data were corrected for matrix effects using the ΦρZ method from the JEOL series of programs. The mean analytical results (average of 16 point analyses) are reported in Table 1. H_2O and CO_2 were not determined directly because of the small amount of material; anyway, these groups are absent from the mineral, as shown by the structural results (see below). The empirical formula, calculated on the basis of 1 P atom per formula unit with the Fe^{2+}:Fe^{3+} ratio constrained to maintain charge balance, is: $(Na_{0.817}Ca_{0.003}\square_{0.180})_{\Sigma 1.000}(Fe^{2+}_{0.622}Mn^{2+}_{0.228}Fe^{3+}_{0.151}Mg_{0.010}Zn_{0.002})_{\Sigma 1.013}PO_4$

The simplified formula is $Na(Fe^{2+},Mn^{2+})PO_4$, which requires Na_2O 17.86 wt%, FeO 27.74 wt%, MnO 13.49 wt%, P_2O_5 40.91 wt%, for a Fe:Mn ratio of 0.67:0.33 (based on refined site occupancies), reaching a total of 100.00 wt%.

X-RAY DIFFRACTION DATA AND CRYSTAL STRUCTURE DETERMINATION

Karenwebberite was first identified by powder X–ray diffraction using a Debye-Scherrer camera (diameter 114.6 mm, Fe*K*α radiation); the unit–cell parameters refined from the powder XRD pattern (Table 2) using the LCLSQ software (Burnham 1991) are: $a = 4.91(1)$, $b = 10.33(6)$, $c = 6.09(2)$ Å, and $V = 309(3)$ Å^3 ($Z = 4$, space group *Pbnm*).

The X–ray structural study of karenwebberite was carried out on an Oxford Diffraction Gemini PX Ultra 4-circle diffractometer equipped with a Ruby CCD–area detector (FUNDP, Namur, Belgium), on a crystal fragment measuring 0.04 × 0.09 × 0.13 mm. A total of 130 frames with a spatial resolution of 1° were collected by the φ/ω scan technique, with a counting time of 55 s per frame, in the range $7.84° < 2\theta < 58.16°$. A total of 861 reflections were extracted from these frames, corresponding to 397 unique reflections. The unit–cell parameters refined from these reflections, $a = 4.882(1)$, $b = 10.387(2)$, $c = 6.091(1)$ Å, and $V = 308.9(1)$ Å^3, are in good agreement with those refined from the X–ray powder diffraction data. Data were corrected for Lorenz, polarization and absorption effects, the latter with an empirical method using the SCALE3 ABSPACK scaling algorithm included in the CrysAlisRED package (Oxford Diffraction 2007).

The crystal structure of karenwebberite was refined with SHELXTL (Sheldrick 2008) in space group *Pbnm*, starting from the atomic coordinates used by Losey et al. (2004) for triphylite. Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from the International Tables for X-ray Crystallography, Vol. C (Wilson 1992). For sake of simplicity, Mg, Zn, and Ca, which occur in low to trace amounts, were not taken into account in the crystal structure refinements. Finally, the relative occupancies of Na and vacancies on M1, as well as of Fe and Mn on M2, were refined. The refinements were completed using anisotropic displacement parameters for all atoms. The final refinement converged to $R_1 = 0.0785$ [$F_0 > 2\sigma(F_0)$] for 375 reflections and $R_1 = 0.0835$ for all 397 reflections. Further details on the intensity data collection and structure refinement are given in Table 3.

Karenwebberite possesses the olivine structure, and is isostructural with the pegmatite phosphates triphylite, lithiophilite, and natrophilite (Finger and Rapp 1969, Moore 1972, Losey et al. 2004, Fehr et al. 2007). The structure is characterized by octahedral chains parallel to the *c* axis (Fig. 2). The M1 octahedra are occupied by Na, while the M2 octahedra are occupied by Fe and Mn (Table 4). Bond distances and the most relevant bond angles are summarized in Table 5. It is noteworthy that this ordered distribution, with Na localized on the M1 site, is similar to the cationic distribution observed by Moore (1972) in natrophilite. The crystal–chemical formula of karenwebberite, calculated from the site occupancy factors (Table 4), is $Na_{0.68}(Fe^{2+}_{0.67}Mn_{0.33})PO_4$, and corresponds fairly well to the empirical formula calculated from the electron–microprobe analyses.

DISCUSSION

Karenwebberite is isostructural with olivine, and corresponds to the Fe–analogue of natrophilite, $NaMnPO_4$, or to the Na-equivalent of triphylite, $LiFePO_4$. The mineral is also a polymorph of marićite, $NaFePO_4$ (a = 6.861(1), b = 8.987(1), c = 5.045(1) Å, *Pmnb*), which shows a crystal structure distinct from that of olivine (Sturman et al. 1977; Le Page & Donnay 1977). A comparison of the physical properties of karenwebberite, with those of phosphates of the triphylite group, is shown in Table 6.

The polymorphic relationship between karenwebberite and marićite is also of particular interest, since this transformation is temperature–dependant, as shown experimentally by Corlett and Armbruster (1979). These authors confirmed that olivine–type $Na(Fe,Mn)PO_4$ phosphates are low-temperature polymorphs of marićite–type phosphates, and that the transition between the two polymorphs of $NaMnPO_4$ occurs around 325°C (P = 100 bars). Hydrothermal investigations performed on alluaudite–type phosphates at 1 kbar (Hatert et al. 2006 and 2011) also produced several marićite–type phosphates with various Fe/(Fe+Mn) ratios; their compositions are plotted in Figure 3. From this diagram, on which the transition temperature from natrophilite to its polymorph has been constrained according to the data of Corlett and Armbruster (1979), we can clearly observe a transition temperature of about 500–550°C between karenwebberite and marićite. Consequently, karenwebberite certainly crystallized below 550°C in the Malpensata dyke.

During the evolution of the oxidation condition in this pegmatite, karenwebberite progressively oxidized into a reddish–brown phosphate, as shown on the thin sections (Fig. 1). This phosphate shows a chemical composition significantly depleted in Na, compared to karenwebberite, and both phosphates are isostructural, as confirmed by single–crystal X–ray diffraction measurements. This secondary phosphate corresponds to a Na-bearing ferrisicklerite, according to its optical and structural properties, and its chemical composition evolves from $(Na_{0.69}\square_{0.31})(Fe^{2+}_{0.51}Fe^{3+}_{0.26}Mn^{2+}_{0.23}Mg_{0.01})PO_4$ to $(Na_{0.44}\square_{0.56})(Fe^{3+}_{0.49}Fe^{2+}_{0.30}Mn^{2+}_{0.23}Mg_{0.01})PO_4$ (Table 7). This oxidation mechanism, from karenwebberite to Na–bearing ferrisicklerite, is similar to that observed during the concomitant leaching of Li^+ and oxidation of Fe^{2+} in triphylite, leading to ferrisicklerite. It certainly took place during the late hydrothermal stages affecting the pegmatite, and corresponds to the substitution mechanism $Na^+ + Fe^{2+} \rightarrow \square + Fe^{3+}$, previously reported in alluaudite– and wyllieite–type phosphates by Quensel (1957), Fransolet et al. (1985, 2004), and Roda et al. (1996).

Figure 4 plots the chemical analyses of the oxidation products of karenwebberite, and shows a continuous depletion of Na from karenwebberite to Na–poor ferrisicklerite, with a constant Fe/(Fe+Mn) ratio. However, a lack of data is observed between ca. 0.44 and 0.14 Na atoms per formula unit, which can tentatively be related to the transformation of Na–poor ferrisicklerite to a heterosite–like phase. Indeed, as shown on Table 7, a progressive oxidation of Fe^{2+} to Fe^{3+} is observed for Na–bearing ferrisicklerite, whereas all iron and ca. 51 % of manganese are oxidized in the heterosite–like phase. This gap in data could have resulted from the sudden oxidation of manganese in these olivine–type phosphates.

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REFERENCES CITED

Anthony, J.W., Bideaux, R. A., Bladh, K. W. and Nichols, M. C. (1990) Handbook of Mineralogy. Mineral Data Publishing, Tucson Arizona, USA.

Bertotti G., Seward D., Wijbrans J., ter Voorde M. and Hurford A.J. (1999) Crustal thermal regime prior to, during, and after rifting: A geochronological and modeling study of the Mesozoic South Alpine rifted margin. Tectonics, 18/2, 185-200.

Burnham, C.W. (1991) LCLSQ version 8.4, least-squares refinement of crystallographic lattice parameters. Dept. of Earth & Planetary Sciences, Harvard University, 24 p.

Černý, P.and Ercit S. (2005) The classification of granitic pegmatites revisited. Canadian Mineralogist, 43, 2005-2026.

Corlett, M.I. and Armbruster, T. (1979) Structural relations between marićite and natrophilite in the system $NaFePO_4$-$NaMnPO_4$. GAC-MAC Join annual meeting, 4(44), 1979.

Fehr, K.T., Hochleitner, R., Schmidbauer, E. and Schneider, J. (2007) Mineralogy, Mössbauer spectra and electrical conductivity of triphylite, $Li(Fe^{2+},Mn^{2+})PO_4$. Physics and Chemistry of Minerals, 34, 485-494.

Finger, L.W. and Rapp, G.R. (1969) Refinement of the structure of triphylite. Carnegie Institution Year book, 68, 290-293.

Fransolet, A.-M., Abraham, K., and Speetjens, J.-M. (1985) Evolution génétique et signification des associations de phosphates de la pegmatite d'Angarf-Sud, plaine de Tazenakht, Anti-Atlas, Maroc. Bulletin de Minéralogie, 108, 551-574.

Fransolet, A.-M., Hatert, F., and Fontan, F. (2004) Petrographic evidence for primary hagendorfite in an unusual assemblage of phosphate minerals, Kibingo granitic pegmatite, Rwanda. Canadian Mineralogist, 42, 697-704.

Hatert, F., Fransolet, A.-M., and Maresch, W.V. (2006) The stability of primary alluaudites in granitic pegmatites: an experimental investigation of the $Na_2(Mn_{1-x}Fe^{2+}{}_x)_2Fe^{3+}(PO_4)_3$ solid solution. Contribution to Mineralogy and Petrology, 152, 399-419.

Hatert, F., Ottolini, L., and Schmid-Beurmann, P. (2011) Experimental investigation of the alluaudite + triphylite assemblage, and development of the Na-in-triphylite geothermometer: applications to natural pegmatite phosphates. Contributions to Mineralogy and Petrology, 161, 531-546.

Le Page, Y. and Donnay, G. (1977) The crystal structure of the new mineral marićite, $NaFePO_4$. Canadian Mineralogist, 15, 518-521.

Losey, A., Rakovan, J., Hughes, J.M., Francis, C.A. and Dyar, M.D. (2004) Structural variations in the lithiophilite-triphylite series and other olivine-group structures. Canadian Mineralogist, 42, 1105-1115.

Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. Canadian Mineralogist, 19, 441-450.

Moore, P.B. (1972) Natrophilite, $NaMnPO_4$, has ordered cations. American Mineralogist, 57, 1333-1344.

Oxford Diffraction (2007) CrysAlis CCD and CrysAlis RED, version 1.71. Oxford Diffraction, Oxford, England.

Palache, C., Berman, H. and Frondel, C. (1951) The system of Mineralogy, 7th edition, Vol. II. John Wiley and sons, New York.

Quensel, P. (1957) The paragenesis of the Varuträsk pegmatite, including a review of its mineral assemblage. Arkiv för Mineralogi och Geologi, 2(2), 9-125.

Roda, E., Fontan, F., Pesquera, A., and Velasco, F. (1996) The phosphate mineral association of the granitic pegmatites of the Fregeneda area (Salamanca, Spain). Mineralogical Magazine, 60, 767-778.

Sheldrick, G.M. (1990) SHELXTL, a crystallographic computing package, revision 4.1. Siemens Analytical X-Ray Instruments, Inc., Madison, Wisconsin.

Sheldrick, G.M. (2008) A short history of SHELX. Acta Crystallographica, A64, 112-122.

Sturman, B.D., Mandarino, J.A., and Corlett, M.I. (1977) Marićite, a sodium iron phosphate from the Big Fish River area, Yukon Territory, Canada. Canadian Mineralogist, 15, 396-398.

Vignola, P., Diella, V., Oppizzi, P., Tiepolo, M., and Weiss, S. (2008a) Phosphate assemblages from the Brissago granitic pegmatite, western Southern Alps, Switzerland. Canadian Mineralogist, 46, 635-650.

Vignola, P., Guastoni, A., and Diella, V. (2008b) Nb Ta Sn oxides association from the Malpensata granitic pegmatite, central Southern Alps (Lecco province, Italy): magmatic differentiation, crystallization mechanism and geochemical inference. Geophysical Research Abstracts, EGU2008-A-03866.

Vignola, P., Hatert, F., Fransolet, A.M., and Diella, V. (2010) The Na-rich phosphate minerals from Malpensata granitic pegmatite, Piona, Lecco province, Italy. Acta Mineralogica Petrographica, abstract series, 6, 609.

Vignola, P., Fransolet, A.M., Diella, V., and Ferrari, E.S. (2011a) Complex mechanisms of alteration in a graftonite + sarcopside + triphylite association from the Luna pegmatite, Piona, Lecco province, Italy. Canadian Mineralogist, 49, 765-776.

Vignola, P., Hatert, F., Fransolet, A.-M., Medenbach, O., Diella, V, and Ando', S. (2011b) Karenwebberite, IMA 2011-015. CNMNC Newsletter No. 10, October 2011, page 2551; Mineralogical Magazine, 75, 2549-2561.

Wilson, A.J.C. (1992) International Tables for X-ray Crystallography, Vol. C. Kluwer Academic Press, London, 883 p.

Figure captions

Figure 1. Exsolution lamellae of karenwebberite (light brown), oxidized into Na–bearing ferrisicklerite (dark brown) and included in graftonite. Malpensata pegmatite, Colico, Italy (plane polarized light microscopy; the length of the photograph is 1.5 mm).

Figure 2. The crystal structure of karenwebberite, projected along the *a* axis. The M1 octahedra are white, the M2 octahedra are light grey, and the PO_4 tetrahedra are dark gray.

Figure 3. Stability of natrophilite, karenwebberite and marićite in the Fe/(Fe+Mn) – T field. The points represent the chemical compositions of synthetic marićites reported by Hatert et al. (2006 and 2011), and the high–temperature stability limit of natrophilite has been constrained from the data published by Corlett and Armbruster (1979).

Figure 4. Ternary Na–$Fe_{tot.}$ –$Mn_{tot.}$ plot showing the electron–microprobe analyses of karenwebberite (black dots), Na-bearing ferrisicklerite (squares), and the heterosite–like phase (diamonds). The percentages correspond to atomic proportions.

TABLE 1. Averaged electron-microprobe analyses of karenwebberite

	Wt.% (average of 16 analyses)	Range	Stand. dev.	Empirical formula[§]	
P_2O_5	41.12	40.21 – 42.53	0.71	P (apfu)	1.000
Fe_2O_3[*]	7.00	-	-	Fe^{3+}	0.151
FeO[*]	25.82	24.89 – 27.10	0.67	Fe^{2+}	0.622
MgO	0.23	0.21 – 0.27	0.02	Mg	0.010
ZnO	0.11	0.04 - 0.19	0.04	Zn	0.002
MnO	9.31	8.92 – 9.54	0.21	Mn	0.228
CaO	0.10	0.05 - 0.20	0.04	Ca	0.003
Na_2O	14.66	13.95 – 16.12	0.63	Na	0.817
Total	98.35				

* FeO and Fe_2O_3 contents were calculated to maintain charge balance; [§] calculated on the basis of 1 P atom per formula unit (apfu).

TABLE 2. X-ray powder diffraction pattern of karenwebberite

$I_{obs.}$	$d_{obs.}$	$I_{calc.}$	$d_{calc.}$	*hkl*
50	**5.16**	**25**	**5.164**	**0 2 0**
90	**4.44**	**48**	**4.435**	**1 1 0**
80	**3.93**	**37**	**3.939**	**0 2 1**
20	3.79	8	3.823	1 0 1
90	**3.56**	**86**	**3.559**	**1 2 0**
80	**3.04**	**52**	**3.046**	**0 0 2**
100	**2.817**	**57**	**2.819**	**1 3 0**
100	**2.559**	**100**	**2.558**	**1 3 1**
30	2.386	25	2.389	2 1 0
40	2.302 {	15	2.314	1 2 2
		13	2.285	1 4 0
30	2.219	13	2.218	2 2 0
40	1.921	1	1.912	2 0 2
20	1.789	46	1.793	2 2 2
30	1.709	20	1.708	2 4 1
50	**1.657**	**25**	**1.656**	**0 6 1**
20	1.604 {	6	1.615	1 5 2
		15	1.596	0 4 3

Intensities were estimated visually. The eight strongest lines are in bold. Calculated intensities were calculated from the structural data with the SHELXTL-XPOW software (Sheldrick 1990).

TABLE 3. Experimental details for the single-crystal X-ray diffraction study of karenwebberite

Colour	Pale green
Dimensions of the crystal (mm)	*ca*. 0.04 × 0.09 × 0.13
a (Å)	4.882(1)
b (Å)	10.387(2)
c (Å)	6.091(1)
V (Å^3)	308.9(1)
Space group	*Pbnm*
Z	4
$2\theta_{min.}$, $2\theta_{max}$	7.84°, 58.16°
Range of indices	$-6 \leq h \leq 4$, $-9 \leq k \leq 13$, $-8 \leq l \leq 5$
Measured intensities	861
Unique reflections	397
Independent non-zero [$I > 2\sigma(I)$] reflections	375
μ (mm^{-1})	5.217
Refined parameters	43
R_1 ($F_o > 2\sigma(F_o)$)	0.0785
R_1 (all)	0.0835
wR_2 (all)	0.2055
S (goodness of fit)	1.269
Max Δ/σ in the last l.s. cycle	0.001
Max peak and hole in the final ΔF map (e/Å^3)	+1.12 and –2.20

TABLE 4. Final fractional coordinates and displacement parameters (Å^2) for karenwebberite

Site	*x*	*y*	*z*	$U_{eq.}$	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M1*	0	0	0	0.018(3)	0.008(4)	0.025(5)	0.021(5)	-0.003(4)	-0.007(3)	0.002(3)
M2**	0.9862(4)	0.2827(2)	¼	0.0103(7)	0.017(1)	0.010(1)	0.005(1)	0	0	-0.0008(7)
P	0.4334(8)	0.1034(4)	¼	0.0122(9)	0.017(2)	0.013(2)	0.007(2)	0	0	0.002(1)
O1	0.744(2)	0.111(1)	¼	0.019(2)	0.019(5)	0.024(6)	0.015(5)	0	0	0.006(5)
O2	0.166(3)	0.4648(9)	¼	0.020(2)	0.037(7)	0.010(5)	0.013(5)	0	0	-0.011(5)
O3	0.303(2)	0.1737(7)	0.052(1)	0.019(2)	0.026(4)	0.025(4)	0.005(3)	0.008(3)	0.000(3)	0.006(3)

Occupancy factors : * 0.68(3) Na; ** 0.67(8) Fe + 0.33(8) Mn.

TABLE 5. Selected bond distances (Å) and angles (°) for karenwebberite

M1-O1 x 2	2.284(8)
M1-O2 x 2	2.261(9)
M1-O3 x 2	2.354(8)
Mean	2.300
M2-O1	2.14(1)
M2-O2	2.09(1)
M2-O3 x 2	2.092(7)
M2-O3' x 2	2.266(8)
Mean	2.158
P-O1	1.52(1)
P-O2	1.52(1)
P-O3 x 2	1.550(7)
Mean	1.535
O1-P-O2	111.7(7)
O1-P-O3 x 2	112.6(4)
O2-P-O3 x 2	108.4(4)
O3-P-O3	102.6(6)
Mean	109.38

Table 6. Comparison of the physical properties for phosphates of the triphylite group

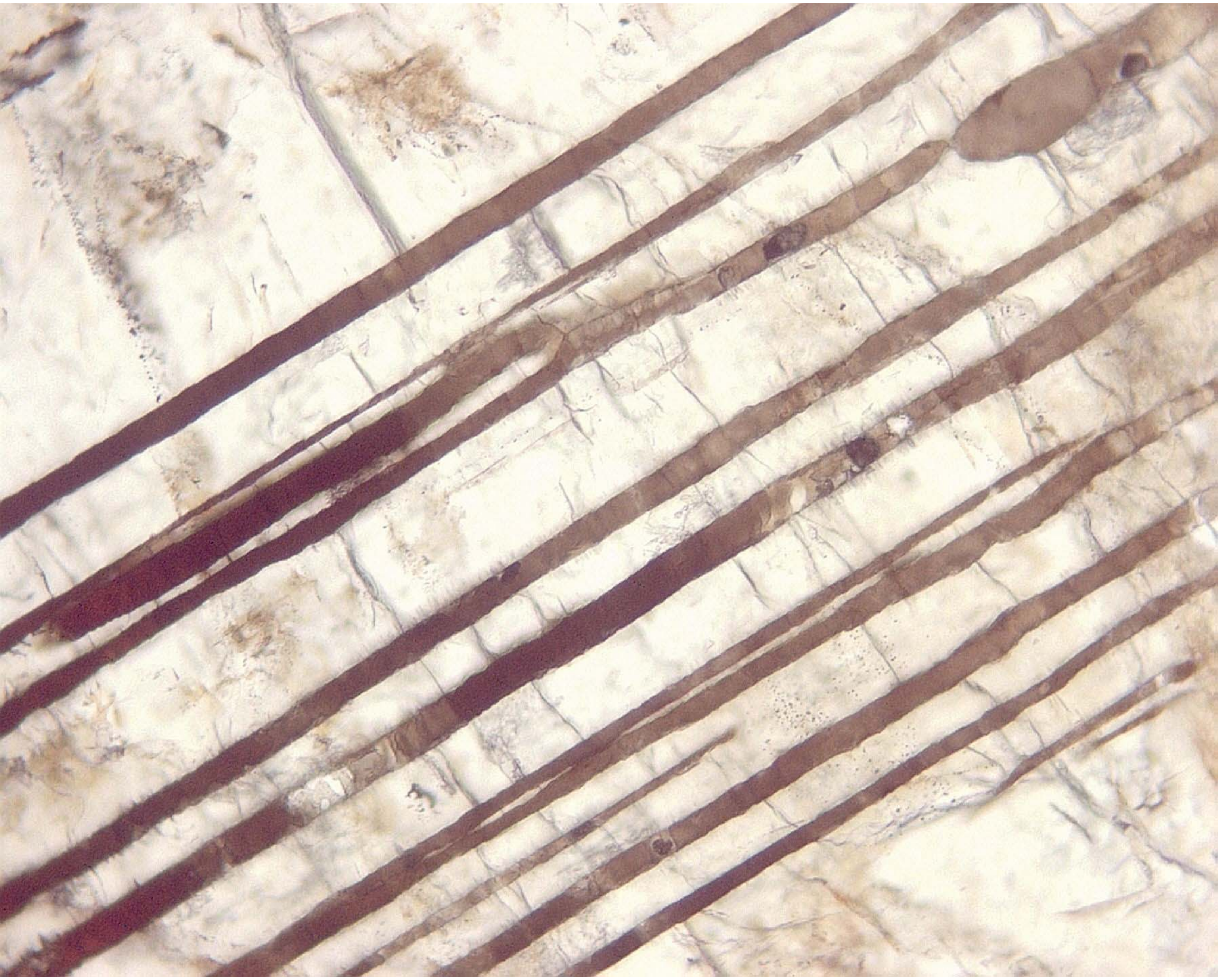
Mineral	Triphylite	Lithiophilite	Natrophilite	Karenwebberite
Reference	[1, 2]	[1, 2]	[3, 4]	This work
Ideal formula	$Li(Fe^{2+},Mn^{2+})PO_4$	$Li(Mn^{2+},Fe^{2+})PO_4$	$Na(Mn^{2+},Fe^{2+})PO_4$	$Na(Fe^{2+},Mn^{2+})PO_4$
Space group	*Pbnm*	*Pbnm*	*Pbnm*	*Pbnm*
a (Å)	4.6904(6)	4.7383(1)	4.987(2)	4.882(1)
b (Å)	10.2855(9)	10.429(1)	10.523(5)	10.387(2)
c (Å)	5.9871(4)	6.0923(4)	6.312(3)	6.091(1)
Z	4	4	4	4
Strong X-ray lines	5.175 (34)	5.236 (28)	5.24 (30)	5.16 (25)
	4.277 (76)	4.313 (56)	4.50 (60)	4.44 (48)
	-	-	4.05 (60)	-
	3.923 (26)	-	3.90 (30)	3.93 (37)
	-	-	3.66 (50)	3.79 (8)
	3.487 (70)	3.516 (71)	3.61 (10)	3.56 (86)
	3.008 (100)	3.051 (89)	3.15 (50)	3.04 (52)
	-		2.863 (80)	-
	2.781 (34)	-	-	2.817 (57)
	-	-	2.702 (20)	-
	-	-	2.604 (100)	-
	2.525 (81)	2.548 (100)	2.583 (100)	2.559 (100)
	-	2.492 (28)	2.487 (30)	-
Cleavage	{001} perfect, {010} imperfect	{001} perfect, {010} good	{001} good, {010} indistinct, {120} interrupted	{001} perfect
Density	3.54(4)	3.47(3)	3.41; 3.47 (calc.)	3.65 (calc.)
Optical sign	(+)	(+)	(+)	(+)
2V (°)	0-55	48-70	75(5)	87(4)
α	1.675-1.694	1.663-1.696	1.671(3)	1.701(2)
β	1.684-1.695	1.667-1.700	1.674(3)	1.708(2)
γ	1.685-1.700	1.674-1.702	1.684(3)	1.717(2)
Hardness	4-5	4-5	4.5-5	4.5(5)
Colour	Bluish grey to greenish grey	Yellowish brown, honey-yellow, grey	Deep wine-yellow	Pale green; brownish when oxidized

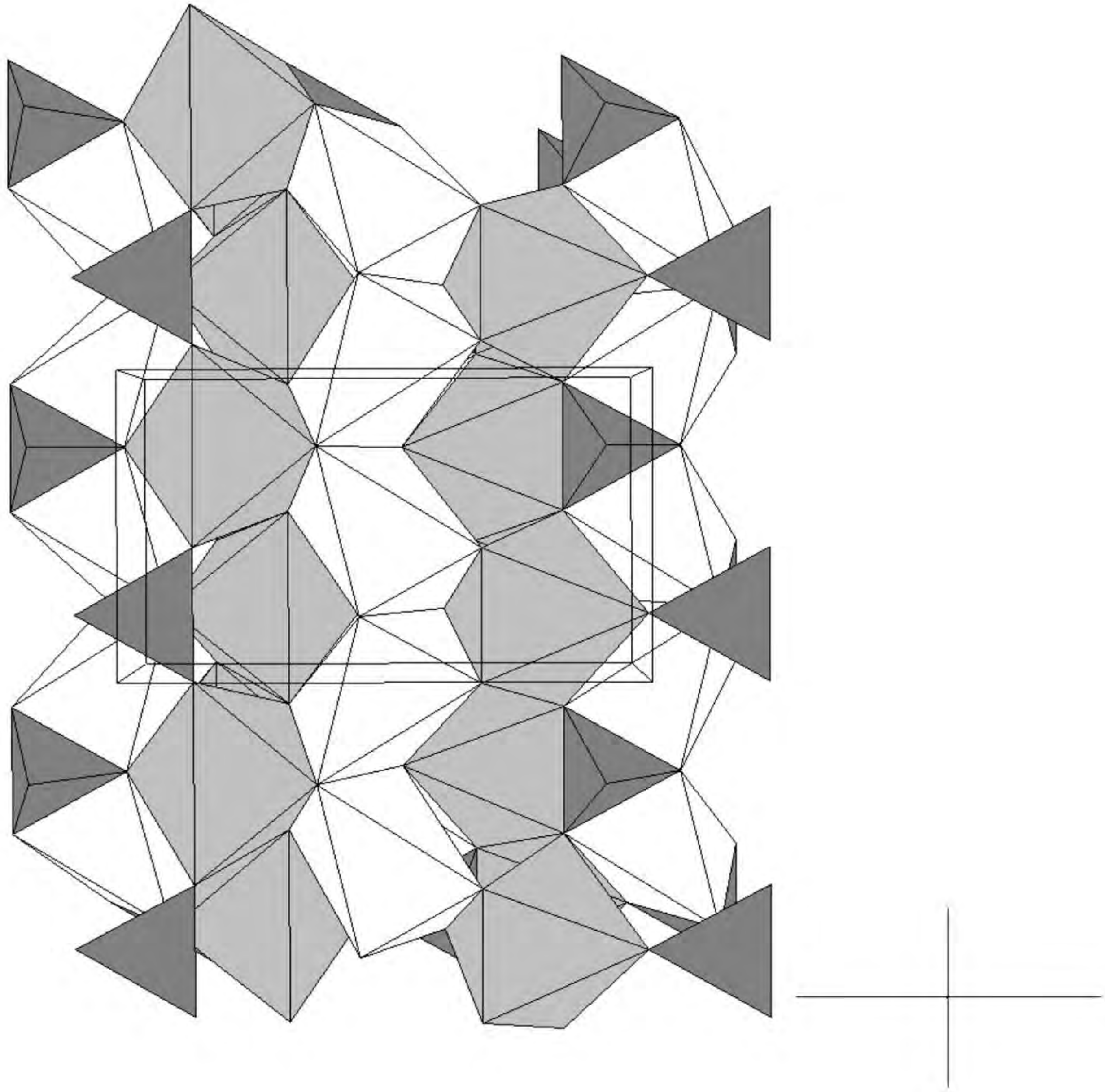
[1] Losey et al. (2004), [2] Anthony et al. (1990), [3] Moore (1972), [4] Palache et al. (1951).

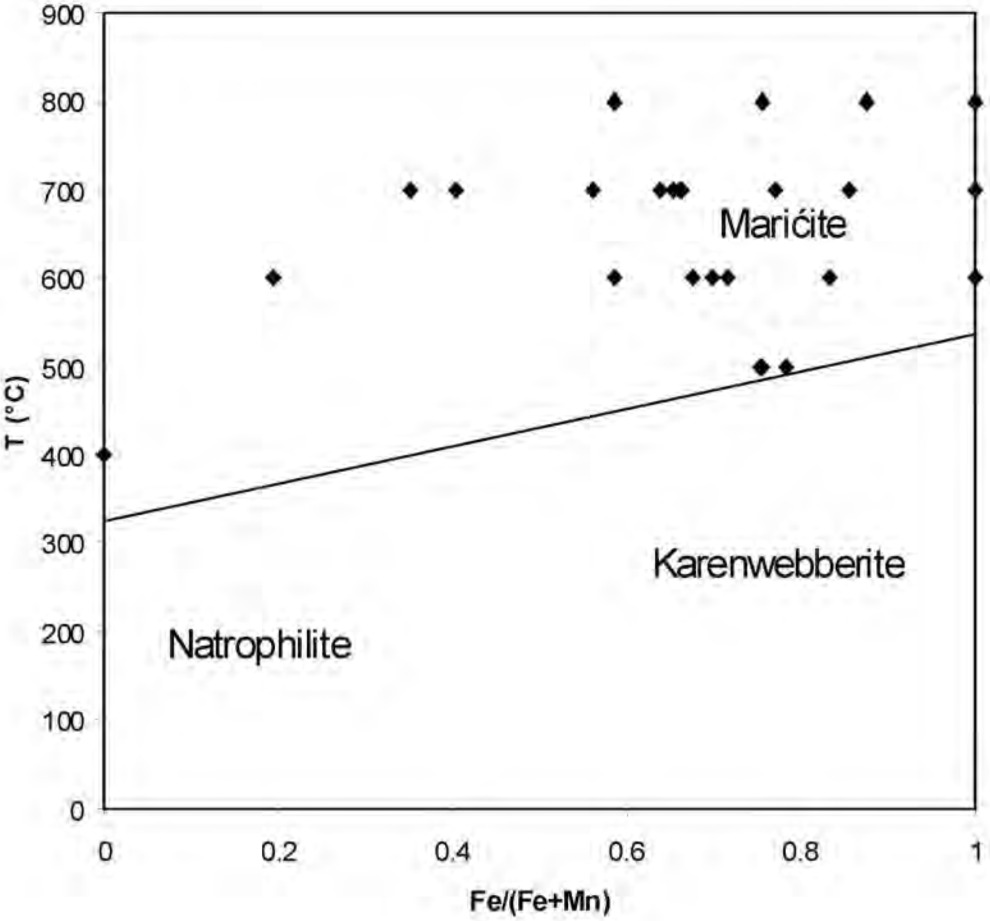
TABLE 7. Electron-microprobe analyses of Na-bearing ferrisicklerite and heterosite-like phase

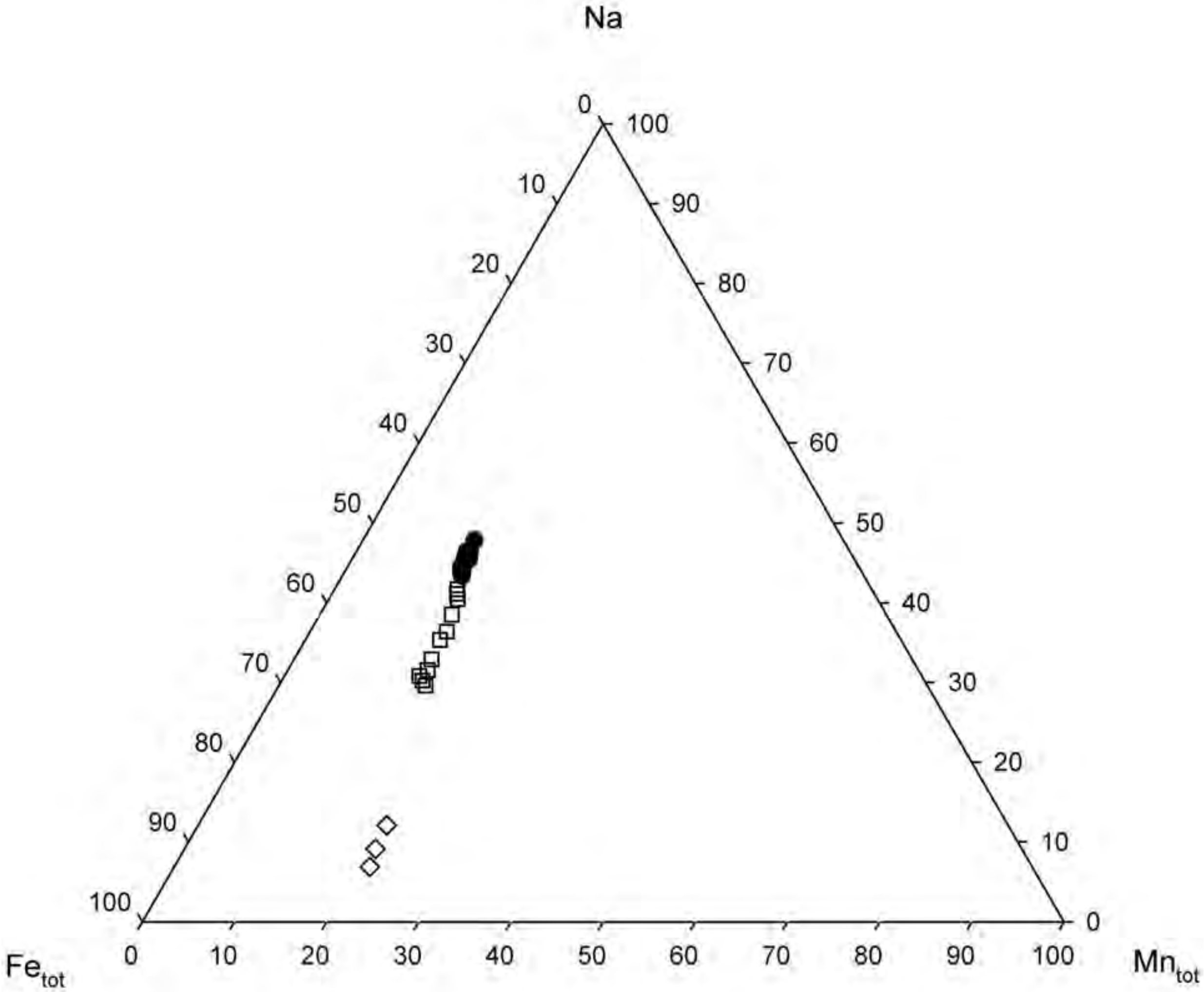
	a (2)	b (6)	c (2)	d (3)
P_2O_5	42.96	43.72	44.11	46.58
$Fe_2O_3^*$	12.71	21.14	24.44	40.06
$Mn_2O_3^*$	-	-	-	6.06
FeO^*	22.16	15.46	13.43	-
MgO	0.25	0.27	0.26	0.27
ZnO	0.10	0.17	0.10	0.13
MnO^*	10.07	9.88	10.03	5.18
CaO	0.09	0.09	0.10	0.08
Na_2O	13.00	10.03	8.39	2.10
Total	101.34	100.76	100.86	100.46
Cation number on the basis of 1 P atom per formula unit				
P	1.000	1.000	1.000	1.000
Fe^{3+}	0.263	0.430	0.492	0.764
Mn^{3+}	-	-	-	0.117
Fe^{2+}	0.510	0.349	0.301	-
Mg	0.010	0.011	0.010	0.010
Zn	0.002	0.003	0.002	0.002
Mn^{2+}	0.234	0.226	0.227	0.111
Ca	0.003	0.003	0.003	0.002
Na	0.694	0.526	0.436	0.103
ΣM2	1.019	1.019	1.032	1.004
ΣM1	0.697	0.529	0.439	0.105

Analyses in weight percents; the number of point analyses is indicated in parentheses. * FeO, Fe_2O_3, MnO, and Mn_2O_3 contents were calculated to maintain charge balance. a: Na-rich ferrisicklerite; b: Intermediate ferrisicklerite; c: Na-poor ferrisicklerite; d: Heterosite-like phase.






900
800
700
600
500
400
300
200
100
0
T (°C)
0
0.2
0.4
0.6
0.8
1
Fe/(Fe+Mn)
Marićite
Karenwebberite
Natrophilite


Na
Fe$_{tot}$
Mn$_{tot}$
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
60
70
80
90
100
100
90
80
70
60
50
40
30
20
10
0