

Kanoite, donpeacorite and tirodite: Mn-Mg-silicates from a manganeseiferous quartzite in the United Arab Emirates

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Abstract: Kanoite, ideally $\text{MnMgSi}_2\text{O}_6$, donpeacorite $(\text{Mg},\text{Mn})\text{MgSi}_2\text{O}_6$, and tirodite $\text{Mn}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$, form augen-shaped grains or clusters in an oxidized quartzite (quartz + hematite + pyrophanite + ferrianbraunite), which is the granulite-facies equivalent of a chert-hosted sedimentary manganese deposit. Mn-bearing minerals were studied by electron microprobe analysis and single-crystal X-ray methods. Pyroxenes from these rocks vary in composition between $\text{Mn}_{0.89}\text{Mg}_{0.89}\text{Fe}^{3+}_{0.10}\text{Ca}_{0.07}\text{Na}_{0.05}\text{Si}_2\text{O}_6$ and $\text{Mn}_{0.60}\text{Mg}_{1.30}\text{Fe}^{3+}_{0.02}\text{Ca}_{0.05}\text{Na}_{0.01}\text{Si}_2\text{O}_6$, with the Mn-rich compositions comprising clinopyroxenes (kanoite) and the Mg-rich compositions comprising orthopyroxenes (donpeacorite). Clino- and orthopyroxenes were distinguished by X-ray single-crystal methods. Two kanoite single crystals were employed for X-ray crystal-structure refinement ($a = 9.725(2)$, $b = 8.876(2)$, $c = 5.263(1)$ Å, $\beta = 108.53(2)$, $Z = 4$, space group $P2_1/c$) leading to the crystal chemical formula $(\text{Mn}_{0.02}\text{Mg}_{0.98})(\text{Mn}_{0.78}\text{Mg}_{0.15}\text{Ca}_{0.07})\text{Si}_2\text{O}_6$ which confirms that the studied samples are highly Mn, Mg ordered clinopyroxenes. Tirodite, with the average composition $\text{Na}_{0.27}\text{Ca}_{0.15}\text{Mn}_{2.12}\text{Mg}_{4.37}\text{Fe}^{3+}_{0.19}\text{Al}_{0.10}\text{Si}_{8.07}\text{O}_{22}(\text{OH})_2$, is a retrogressive alteration product replacing kanoite and donpeacorite either along their rims or even completely in some cases.

Key-words: kanoite, donpeacorite, tirodite, crystal structure, crystal chemistry, granulite-facies metamorphism, United Arab Emirates.

Introduction

The aim of this study is mainly two-fold. Firstly, the assemblage kanoite-donpeacorite is petrographically described and petrologically discussed. Secondly, the new occurrence of well crystallized kanoite offers the possibility of a crystal chemical study leading to a discussion of the structural differences and correspondences of pyroxenes along the join MgSiO_3 - MnSiO_3 .

Stability relations of pyroxenes on the join MgSiO_3 - MnSiO_3 between 0.5 and 1.0 GPa and 700–110 °C have been studied by Iwabuchi & Hariya (1985). Above 700 °C, clinopyroxene forms a solid solution between 40 and 50 mol% MnSiO_3 . An orthopyroxene solid solution has been found

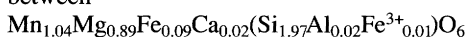
at 0.5 GPa between 0 and 25 mol% MnSiO_3 and at 1.0 GPa between 0 and 30 mol% MnSiO_3 . The narrow field between 25 (30) and 40 mol% MnSiO_3 is characterized by a two-pyroxene assemblage. Hydrothermal experiments at 0.1 and 0.2 GPa have also been performed by Huebner (1986) who confirmed the compositional range of orthopyroxene up to 30 mol% MnSiO_3 also at lower pressures. The natural analogue of clinopyroxene with the approximate composition $\text{MnMgSi}_2\text{O}_6$ is called kanoite and the Mn-rich orthopyroxene is called donpeacorite.

An experimental study on the stability of manganoan-cummingtonite (tirodite) at the composition $\text{Mn}_{2.35}\text{Mg}_{4.65}\text{Si}_8\text{O}_{22}(\text{OH})_2$ was undertaken by Dasgupta *et al.* (1985). Experiments under

Mn₃O₄-MnO buffer showed that, with increasing P,T conditions, the mineral transforms to Mn-clinopyroxene + quartz. At lower metamorphic grade, the mineral is replaced by tephroite and talc. Because the upper breakdown reaction showed a negative slope, the presence of the mineral would indicate temperatures below 650–700 °C and pressures below 0.5 GPa. However, as later studies by Maresch & Czank (1988) showed, the kinetics of reactions in this system pose a problem, and some of the unreversed runs of Dasgupta *et al.* (1985) may only be metastable products. In the detailed study by Maresch & Czank (1988), HRTEM techniques were used to show that amphiboles synthesized under similar conditions and with corresponding chemical composition exhibit heterogeneous stacking of tetrahedral chains, as well as chain arrangement faults and chain multiplicity faults. Even with long hydrothermal run durations, equilibrium was not reached. Thus, these synthetic amphiboles only poorly reflect the structural arrangement found in nature, but the T-X reaction loop depicted by Maresch & Czank (1988) may be a better estimate than earlier results.

Kanoite, ideally MnMgSi₂O₆, was introduced as a new clinopyroxene ($a = 9.739$, $b = 8.939$, $c = 5.260$ Å, $\beta = 108.56^\circ$, $Z = 4$, space group $P2_1/c$) by Kobayashi (1977). The type locality is on the Oshima Peninsula in Hokkaido, Japan, where the mineral occurs in association with spessartine, manganoan cummingtonite ("tirodite"), pyroxmangite and quartz. At Balmat in New York state, U.S.A. (Brown *et al.*, 1980; Petersen *et al.*, 1984), kanoite occurs with magnesian rhodonite, braunite, hollandite, tirodite and donpeacorite (Petersen *et al.*, 1984). When Brown *et al.* (1980) compiled the Mn-Fe-Mg-Ca pyroxenes and pyroxenoids, they concluded from crystal-chemical considerations that some Mg-rich pyroxmangites described by Peters *et al.* (1977) from Buritirama in Pará (Brazil) are actually kanoites. In addition, Huebner (1986) assumed that in assemblage 5 of Klein (1966) – Mn-cummingtonites ("tirodite"), magnesioriebeckite, and Ca-poor rhodonite – the "extraordinarily magnesian rhodonite" might actually be kanoite, which was not known at that time.

All reported kanoites are from medium- to high-grade amphibolite-facies metamorphic belts. The reported chemistry is rather limited and varies between



(Kobayashi, 1977), $\text{Mn}_{1.02}\text{Mg}_{0.86}\text{Ca}_{0.12}\text{Si}_2\text{O}_6$ (Peters *et al.*, 1977), $\text{Mn}_{0.98}\text{Mg}_{0.86}\text{Fe}_{0.06}\text{Ca}_{0.06}\text{Si}_2\text{O}_6$ (Brown *et al.*, 1980), and $\text{Mn}_{0.87}\text{Mg}_{0.83}\text{Fe}_{0.15}\text{Ca}_{0.07}\text{Si}_{2.04}\text{O}_6$ (Klein, 1966). The crystal structure of kanoite was solved by Gordon *et al.* (1981) for a lamellar intergrowth of a $C2/c$ phase with the composition $\text{Mn}_{0.44}\text{Mg}_{0.88}\text{Ca}_{0.68}\text{Si}_2\text{O}_6$ and a $P2_1/c$ phase with the composition $\text{Mn}_{1.02}\text{Mg}_{0.86}\text{Ca}_{0.12}\text{Si}_2\text{O}_6$ (close to kanoite). This study showed that the Mn-rich M2 site in kanoite is seven-fold coordinated, whereas Mg concentrates on M1 with octahedral coordination.

Donpeacorite, (Mg,Mn)MgSi₂O₆, is an orthopyroxene ($a = 18.384(11)$, $b = 8.878(7)$, $c = 5.226(3)$ Å, $Z = 8$, space group $Pbca$) only described once from manganese-rich pods in marbles near Balmat, New York state (Petersen *et al.*, 1984). A crystal structure refinement (Petersen *et al.*, 1984) indicated that M1 is occupied only by Mg and M2 shows an Mg/Mn ratio of nearly 1:1.

Tiroadite, a manganese-bearing alkali amphibole of complex composition ($a \approx 9.70$, $b \approx 17.99$, $c \approx 5.30$ Å, $\beta \approx 103.5^\circ$, $Z = 2$, space group $C2/m$), is present at all localities where kanoite or donpeacorite has been described but it is called manganese-rich cummingtonite or magnesium-rich danemorite. Tiroadite was originally defined by Dunn & Roy (1938) from Tirodi, Maharashtra, India, where it occurs in assemblage with Mn-rich pyroxene (kanoite?), Mn-pyroxenoid and quartz (Dasgupta *et al.*, 1985). Significant Mn may be replaced by Ca and the mineral called tiroadite is commonly an intergrowth (exsolution) of different amphiboles (*e.g.* Ishida, 1985; Oberti & Ghose, 1993; Shau *et al.*, 1993). A crystal chemical study of a Mn-bearing alkali amphibole (tiroadite) from Tirodi, India, with no evidence of exsolutions or inclusions was presented by Oberti & Ghose (1993). This specimen indicates a composition half-way between (Ca-Na) and (Mn-Mg-Fe) amphiboles. Moessbauer data show all iron to be in the trivalent state.

Geological setting of the studied Mn-rich rocks

Manganese-bearing sediments and their metamorphic equivalents occur associated with the Semail Ophiolite in the Sultanate of Oman and the United Arab Emirates (Allemann & Peters, 1972; Glennie *et al.*, 1974; Ghent & Stout, 1981; Searle & Mal-

pas, 1980; Stössel & Ziegler, 1985; Bucher & Kurz, 1991; Kickmaier & Peters, 1991; Gnos, 1992).

Kickmaier & Peters (1991) have shown that pyrolusite and cryptomelane are the major phases of unmetamorphosed manganese-rich deposits in the Wahrah formation (Hawasina), indicating highly oxidizing conditions of formation. These manganese deposits occur in association with red cherts. Similar manganese deposits, transformed into metamorphic rocks during the upper Cretaceous obduction of the hot Semail ophiolite nappe (e.g. Boudier & Coleman, 1981; Searle & Malpas, 1980; Ghent & Stout, 1981), are found dispersed throughout the Oman Mountains. Two tectonic settings of metamorphic rocks can be distinguished comprising manganiferous quartzites.

A first group of occurrences is located beneath the ophiolite, characterized by a strong inverted thermal gradient of more than 1° per metre. A high-grade amphibolite-dominated zone (granulite- to amphibolite-facies) occurs adjacent to the basal thrust plane of the overlying peridotites, and grades into quartzite-dominated lithologies displaying amphibolite- to greenschist-facies metamorphism. The subophiolitic units are generally no more than a few hundred metres thick and manganiferous quartzites usually belong to the lower-grade metamorphic zone.

The second setting, occurring in a sheet of metamorphic rocks, up to 2 km thick, occupies an exceptional position enclosed in peridotites of the Bani Hamid area (Gnos & Kurz, 1994) near the northern end of the Semail Ophiolite (Fig. 1). This sequence is here referred to as the Bani Hamid metamorphic unit. In addition to amphibolites and quartzites the Bani Hamid unit contains meta-carbonates and calcsilicate rocks. The whole sequence underwent granulite-facies metamorphism. At peak metamorphic conditions, quartz-rich rocks were formed with two-pyroxene-magnetite-titanohematite, enstatite-($\pm$ sapphirine)-magnetite/spinel-titanohematite, or cordierite-($\pm$ sillimanite)-magnetite-titanohematite assemblages. These are associated with two-pyroxene amphibolites (granulites), diopside-amphibolites and wollastonite-grossularite-diopside ($\pm$ forsterite $\pm$ potassium feldspar $\pm$ spinel $\pm$ clinohumite) calcsilicate rocks and marbles (Allemann & Peters, 1972; Bucher & Kurz, 1991; Gnos & Kurz, 1994).

The absence of a thermal gradient across the metamorphic sequence points to an early em-

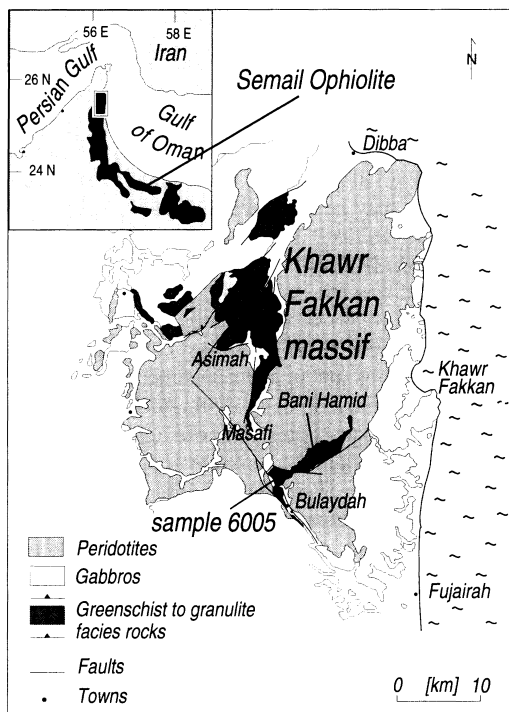


Fig. 1. Geological map of the northern end of the Semail Ophiolite showing granulite-facies metamorphic rocks (Bani Hamid unit) enclosed in peridotites of the Khawr Fakkan massif. The big black spot indicates the sample locality near the village of Bulaydah in the U.A.E.

placement in its present position and heating from the hot peridotite walls on both sides (Gnos & Nicolas, in press). Estimated peak metamorphic conditions for the Bani Hamid unit are $800\text{--}850^\circ\text{C}$ at $0.65\text{--}0.9\text{ GPa}$ (Gnos & Kurz, 1994). The metamorphic rocks of the Bani Hamid area underwent retrograde hydration during cooling, associated with decompression (Gnos & Kurz, 1994). Retrogressive alteration is clearly evident in the field by the widespread presence of muscovite in quartz-rich lithologies.

Manganese-rich samples (6005) were collected from metamorphic rocks in the Bani Hamid area, north of Bulaydah, in the United Arab Emirates. The samples are from a manganiferous horizon extending a few hundreds of metres and are located in diopside-bearing quartzites. The sample location is indicated by a black spot in Fig. 1.

Sample description

The investigated sample 6005 is a layered pyroxene-quartzite gneiss. Macroscopically buff-coloured, pyroxene or pyroxene-amphibole aggregates up to 5 mm in size and ore aggregates up to 15 mm occur dispersed in a compact quartz matrix. Albite may be present as isolated grains.

In thin section, augen-shaped grains or clusters of Mn-Mg-pyroxenes (5–25 vol%) occur randomly dispersed in association with ore aggregates (5–15 vol%) surrounded by quartz. All minerals of sample 6005 are plastically deformed. Where Mn-ores are minor constituents, the rocks cannot be macroscopically distinguished from enstatite-bearing quartzites. The ore aggregates consist of ferrian braunite, hematite and locally pyrophanite. Like the pyroxene grains, the ore forms boundin-shaped clusters within the quartz matrix. Traces of apatite are also observed. The pyroxenes commonly form poikiloblasts enclosing quartz and ore grains. Kanoite and donpeacorite appear extremely similar in petrographic thin sections and cannot be optically distinguished. Both are untwinned, colourless to light yellowish-brown in transmitted light. Pyrophanite is transparent and has a dark brown-reddish colour in thin section indicating traces of Fe^{3+} , since pure pyrophanite is green (Anne Feenstra, pers. comm.).

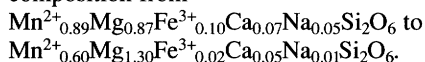
Retrogressive deformation associated with rehydration leads to a reduction in quartz grain size, smearing out of ore aggregates and the alteration or complete replacement of kanoite and donpeacorite by tirodite (Mn-Mg-amphibole). Tirodite is colourless transparent, optically similar to cumingtonite/tremolite, and forms bundles or clusters of fibrous crystals.

Whole-rock and mineral chemistry

Similar to the non-metamorphic manganese-bearing sediments described by Kickmaier & Peters (1991), sample 6005 is poor in Fe^{2+} and Ca (Table 1). Under prevailing oxidizing conditions iron is in the trivalent state and the minerals are essentially Mn-Mg- Fe^{3+} -silicates and -oxides. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ contents of the whole-rock sample were determined by wet chemical methods (di-pyridine method) (Bucher & Kurz, 1991) and the results are listed in Table 1.

All minerals of sample 6005 were analysed using a wavelength-dispersive system on a CAM-ECAS-X 50 microprobe at the University of

Berne. Natural and synthetic minerals were used as standards. Working conditions for all elements were 15 kV, with a beam current of 20 μA . Fluorescence of the Mn-Mg-silicates was not observed under the microprobe beam. The mineral chemistry varies slightly within the sample, but none of the analysed mineral grains shows clear zoning. Representative mineral analyses for sample 6005 are reported in Table 1. Mg-Mn pyroxenes vary in composition from



Minor contents of Na and Fe^{3+} are attributed to an aegirine component and Ca indicates a minor diopside component. In order to distinguish kanoite and donpeacorite, analysed areas (electron microprobe analyses) of a polished petrographic thin section were cut out with a micromilling device (Medenbach, 1986) and subsequently studied with a single-crystal diffractometer. Pyroxene compositions are plotted in the MnSiO_3 - MgSiO_3 - FeSiO_3 - CaSiO_3 double-triangle in Fig. 2. The analysed pyroxenes with Mg/Mn higher than 1.9 are donpeacorites, while kanoites show variations from approximately 1 up to 1.23 if coexisting with donpeacorite. One intermediate analysis (Table 1, Dnp/Kan29) from the rim of a donpeacorite grain has an unclear status and could represent a kanoite-donpeacorite intergrowth.

Tiroadite occurs as an alteration product of kanoite and donpeacorite associated with fine-grained secondary ore minerals. Its average composition is $\text{Na}_{0.27}\text{Ca}_{0.15}\text{Mn}^{2+}_{2.12}\text{Mg}_{4.37}\text{Fe}^{3+}_{0.19}\text{Al}_{0.10}\text{Si}_{8.07}\text{O}_{22}(\text{OH})_2$ (Fig. 2). Ca, Na and Fe are very variable, which may indicate small impurities. The Mg/Mn ratios for tiroadites replacing donpeacorite are higher than those of kanoite. Pyrophanite and hematite have approximately endmember compositions. Pyrophanite contains traces of Fe^{3+} , hematite ($X_{\text{Hem}}0.94$ – 0.96) contains minor MnTiO_3 (pyrophanite) and probably also a minor Mn_2O_3 component. Ferrian braunite contains 18.9–21.1 wt.% Fe_2O_3 and traces of Ti and Al.

Single-crystal structure refinement

The kanoite crystals employed for structure refinement were selected from one of the rock chips used for electron-microprobe analyses. Both crystals were approximately $0.05 \times 0.12 \times 0.12$ mm in size. Data collection was performed on an ENRAF NONIUS CAD4 single-crystal X-ray diffractometer with graphite monochromated $\text{MoK}\alpha$

Table 1. Representative mineral and whole rock analyses of sample 6005.

wt.%	Dnp27	Dnp 28	Dnp/ Kan29	Kan1	Kan2	Kan3	Kan4	Kan9	Kan13	Tir10	Brn5*	Pm13	Hem8	wt.%	whole rock
SiO ₂	54.14	54.33	53.21	52.40	52.91	52.71	52.59	52.42	53.15	55.22	10.08	0.02	0.02	SiO ₂	82.92
TiO ₂	0.04	0.06	0.04	0.03	0.04	0.05	0.03	0.02	0.06	0.18	0.69	53.16	1.78	TiO ₂	0.38
Cr ₂ O ₃	0.04	0.05	0.01	0.00	0.02	0.00	0.01	0.03	0.00	0.05	0.03	0.04	0.03	Al ₂ O ₃	0.24
Al ₂ O ₃	0.80	0.82	0.62	0.29	0.30	0.32	0.42	0.38	0.42	1.48	0.23	0.00	0.00	Fe ₂ O ₃	4.94
Fe ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	20.52	0.00	97.35	FeO	0.02
FeO	0.55	0.62	0.25	1.60	1.19	0.93	1.19	0.65	0.55	0.85	0.00	46.18	0.00	MnO	9.74
MnO	20.35	19.55	23.76	27.81	27.80	27.56	27.00	26.22	25.67	16.21	63.17	0.05	2.80	MgO	2.11
MgO	22.81	23.98	20.76	15.22	15.59	15.94	15.97	17.79	17.86	21.40	0.31	0.00	0.00	CaO	0.27
NiO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	Na ₂ O	0.00
CaO	1.27	1.39	1.08	1.62	1.74	1.84	1.65	1.70	2.70	1.50	0.00	0.08	0.00	K ₂ O	0.00
Na ₂ O	0.09	0.10	0.06	0.43	0.30	0.28	0.32	0.25	0.28	0.93	0.00	0.00	0.00	P ₂ O ₅	0.07
K ₂ O	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	LOI	0.73
Total	100.09	100.91	99.80	99.40	99.89	99.63	99.18	99.46	100.69	97.85	95.06	99.53	101.98	Total	101.42
Si	1.993	1.979	1.994	2.027	2.030	2.025	2.026	2.004	2.004	7.828	1.004	0.000	0.000	(ppm)	
Ti	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.019	0.052	1.009	0.035	Nb	14
Cr	0.001	0.001	0.000	0.001	0.001	0.000	0.000	0.001	0.000	0.006	0.002	0.001	0.000	Zr	90
Al	0.035	0.035	0.027	0.013	0.014	0.014	0.019	0.017	0.019	0.247	0.027	0.000	0.000	Y	32
Fe ³⁺	0.017	0.019	0.008	0.052	0.038	0.030	0.038	0.021	0.017	0.101	1.538	0.000	1.903	Sr	16
Mn ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	4.381	0.000	0.027	U	27
Mn ²⁺	0.635	0.603	0.754	0.911	0.903	0.897	0.881	0.849	0.820	1.946	0.948	0.987	0.035	Rb	15
Mg	1.252	1.302	1.160	0.878	0.892	0.913	0.917	1.014	1.004	4.521	0.046	0.002	0.000	Th	34
Ni	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	Pb	0
Ca	0.050	0.054	0.043	0.067	0.072	0.076	0.068	0.070	0.109	0.228	0.000	0.000	0.000	Ga	8
Na	0.006	0.007	0.004	0.032	0.022	0.021	0.024	0.019	0.021	0.256	0.000	0.000	0.000	Zn	68
K	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.000	0.000	0.000	Cu	645
Mg/Mn ²⁺	1.972	2.159	1.538	0.964	0.988	1.018	1.041	1.194	1.224	2.323				Ni	71
														Co	53
														Cr	29
														V	9
														Ce	26
														Nd	9
														Ba	26
														La	45
														Sc	13

Number of oxygen atoms or cations used for normalisation: Kanoite (6O), donpeacorite (6O), braunite (12O, 8cat), hematite (3O, 2cat), pyrophanite (3O, 2cat), tirodite (23O). The Fe²⁺/Fe³⁺ of the whole rock was determined by wet chemical methods. Analysis Dnp/Kan29 from the rim of a donpeacorite grain could represent a kanoite-donpeacorite intergrowth. * Microprobe analysis total is low because Mn is given as divalent oxide.

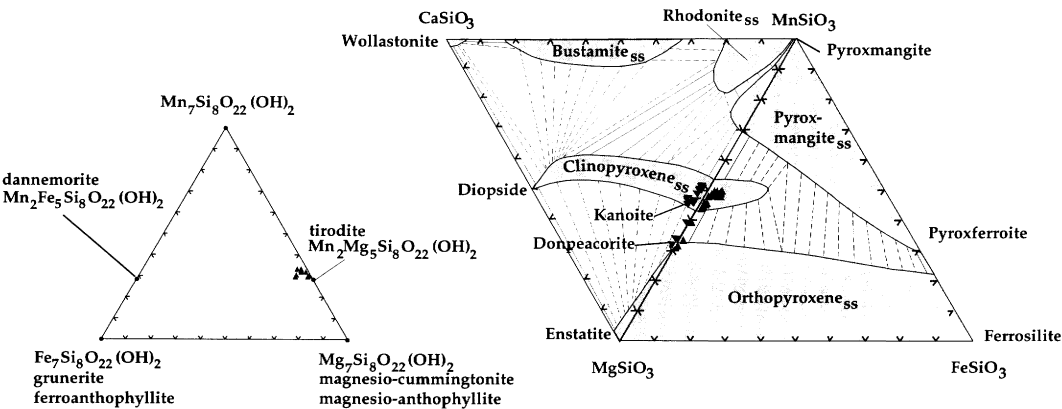


Fig. 2. Left: triangle for Mn-Fe-Mg amphiboles showing relations between tirodite, dannemorite and cummingtonite. Triangles indicate microprobe results from sample 6005. Right: pyroxene-pyroxenoid double-triangle for the system CaSiO₃-MgSiO₃-MnSiO₃-FeSiO₃ (Brown *et al.*, 1980; Petersen *et al.*, 1984) with minor corrections and showing the enlarged kanoite stability field. Black triangles indicate pyroxene analyses. The white areas are proposed miscibility gaps inferred from natural parageneses at 500–800 °C and 0.3–0.9 GPa (Brown *et al.*, 1980; Petersen *et al.*, 1984; this study). Solid lines indicate observed assemblages, dashed lines are inferred.

radiation. Because both crystals yielded nearly identical results, only data of one crystal are presented here. Cell dimension were determined from the angle settings of 25 reflections with $\Theta < 20^\circ$. The single-crystal X-ray reflections were extremely sharp, so a $1.0^\circ \Omega$ -scan was used for intensity collection. Diffraction data were collected up to $\Theta = 30^\circ$, yielding 1463 unique reflections of which 792 had $I > 2\sigma(I)$ used for structure refinement weighted $1/(\sigma^2(F) + 0.0001 F^2)$. Data reduction, including background and Lorentz-polarization correction, was carried out with the SDP program system (Enraf-Nonius, 1983). The structure was refined with the program SHELXTL (Siemens, 1990) using the start values from Gordon *et al.* (1981) and neutral atom scattering factors. Following the electron microprobe analyses described above, 0.07 Ca p.f.u. was assigned to the M2 position, and the Mg/Mn ratio was allowed to vary on M1 and M2. Because of the similarity of Mn, Fe and Mg, Al, Na scattering factors, the small Fe concentrations in kanoite are represented by Mn and the low Al, Na concentrations by Mg. All atoms were refined ($R = 2.48\%$, $R_w = 3.03\%$) with anisotropic displacement parameters. Atomic coordinates, populations and displacement parameters are given in Table 2, while selected interatomic distances are summarized in Table 3. The unconstrained structure refinement yields the composition M1: 0.976(5) Mg and 0.024(5) Mn, M2: 0.07 Ca, 0.775(6) Mn, and 0.155(6) Mg

Table 2. Atomic coordinates and isotropic displacement parameters, U_{eq} ($\text{\AA}^3$) for kanoite from the United Arab Emirates.

Atom	x/a	y/b	z/c	U_{eq}
M1	0.25052(9)	0.6543(1)	0.2339(2)	0.0047(4)
M2	0.25369(5)	0.02375(6)	0.23236(9)	0.0093(2)
SiA	0.04156(9)	0.34113(9)	0.2711(2)	0.0068(3)
SiB	0.54704(9)	0.83886(9)	0.2389(2)	0.0071(3)
O1A	0.8666(2)	0.33715(2)	0.1652(4)	0.0087(7)
O1B	0.3720(2)	0.8377(2)	0.1340(4)	0.0089(5)
O2A	0.1179(2)	0.5020(2)	0.3232(4)	0.0104(7)
O2B	0.6242(2)	0.9938(2)	0.3591(4)	0.0122(8)
O3A	0.1039(2)	0.2608(2)	0.5708(4)	0.0111(7)
O3B	0.6048(2)	0.7158(2)	0.4900(4)	0.0110(7)

M1: 0.976(5) Mg and 0.024(5) Mn
M2: 0.07 Ca, 0.775(6) Mn, and 0.155(6) Mg

which is in satisfactory agreement with the composition determined by electron microprobe analysis (Table 1, Kan 9).

Discussion

Mineral assemblage

The Mn-Mg-pyroxene-quartzite (sample 6005) is interpreted as a granulite-facies equivalent (800–850 °C; 0.65–0.9 GPa) of a chert-hosted sedimentary manganese deposit of the Neo-Tethys ocean.

Table 3. Selected interatomic distances (Å) and angles (°) of kanoite and related clinopyroxenes.

	kanoite (1)	kanoite (2)	Mn ₂ Si ₂ O ₆ (3)	Mg ₂ Si ₂ O ₆ (4)
M1 – O1A	2.048(2)	2.077(4)	2.133	2.030
O1A	2.144(2)	2.166(4)	2.255	2.142
O1B	2.171(2)	2.190(4)	2.274	2.179
O1B	2.048(2)	2.087(4)	2.157	2.066
O2A	2.024(2)	2.045(4)	2.114	2.044
O2B	2.033(3)	2.066(3)	2.131	2.078
ave	2.078	2.105	2.177	2.090
M2 – O1A	2.191(2)	2.197(3)	2.180	2.090
O1B	2.167(2)	2.177(4)	2.162	2.053
O2A	2.151(2)	2.161(4)	2.088	2.032
O2B	2.106(2)	2.122(4)	2.054	1.985
O3A	2.391(2)	2.421(3)	2.472	2.279
O3B	2.682(2)	2.715(3)	2.732	2.414
O3B	2.846(2)	2.865(3)		
ave	2.362	2.380	2.281	2.142
Si1A – O1A	1.614(2)	1.612(4)	1.614	1.610
O2A	1.593(2)	1.595(4)	1.602	1.589
O3A	1.644(2)	1.648(2)	1.648	1.646
O3A	1.660(2)	1.682(3)	1.660	1.665
ave	1.628	1.634	1.631	1.628
Si1B – O1B	1.614(2)	1.613(4)	1.616	1.615
O2B	1.598(2)	1.588(4)	1.598	1.586
O3B	1.653(3)	1.673(3)	1.665	1.676
O3B	1.669(2)	1.675(3)	1.670	1.676
ave	1.634	1.637	1.637	1.638
Si1A-O3A-Si1A	138.4(1)		139.4	133.3
Si1B-O3B-Si1B	134.9(2)		134.7	127.4

(1) this study, (2) Gordon *et al.*, 1981, (3) Tokonami *et al.*, 1979, (4) Ohashi & Finger, 1976.

The peak metamorphic assemblage kanoite ± donpeacorite + hematite + ferrian braunite ± pyrophanite indicates oxidizing conditions. The variations in the Mg/Mn ratio in different layers within the hand specimen are reflected by the presence of kanoite_{ss} or in layers with higher Mg/Mn ratio, by kanoite + donpeacorite. However, kanoite and donpeacorite could not be distinguished in thin section based on their optical properties. In poikiloblasts of random orientation, angles of ca. 88° between cleavage planes (110) and (110) in kanoite *versus* 51° and 129° between {110} cleavage planes in donpeacorite could not be determined. Kanoite (Kobayashi, 1977) is optically positive (2V_x = 130–135°) whereas donpeacorite (Petersen

et al., 1984) is optically negative (2V_x = 88°). However, donpeacorite forms a solid solution series with enstatite which is optically positive with 2V_x = 125°. Thus, the optic character is also not decisive for the distinction between Mn, Mg-pyroxenes.

The K_D [(Mg/Mn)^{Kan}/(Mg/Mn)^{Dnp}] of 0.64 measured here is slightly lower than a corresponding K_D of 0.73 determined by Iwabuchi & Hariya (1985) for hydrothermal run products at 700 °C and 1.0 GPa. The analysed pyroxene compositions are in agreement with the compositional ranges of the kanoite + donpeacorite and kanoite_{ss} stability fields of Iwabuchi & Hariya (1985). These experiments on the MgSiO₃-MnSiO₃-join show similar pyroxene compositions and association at 800 °C – 1.0 GPa.

Most surprising in this context are the experimental results of Dasgupta *et al.* (1985). In hydrothermal runs of bulk composition Mn_{2.35}Mg_{4.65}Si₈O₂₂(OH)₂ these authors found a clinopyroxene phase Mn_{0.808}Mg_{1.135} in equilibrium with Mn-cummingtonite and a clinopyroxene phase Mn_{0.659}Mn_{1.358} in equilibrium with quartz. From our analyses combined with X-ray single-crystal identification and the experimental data of Iwabuchi & Hariya (1985) and Huebner (1986), it can be assumed that the phase with 0.808 Mn p.f.u. observed by Dasgupta *et al.* (1985) is kanoite, whereas the pyroxene with 0.659 Mn p.f.u. is donpeacorite. However, Dasgupta *et al.* (1985) measured unusual clinopyroxene cell dimensions by X-ray powder and single-crystal methods (Table 4; 9) that are neither in agreement with kanoite nor with donpeacorite. Nevertheless, the cell volume agrees fairly well with their Mn_{0.659}Mg_{1.358} composition and the authors specifically state that these dimensions are considerably different from kanoite. However, if we transform the clinopyroxene cell of Dasgupta *et al.* (1985) to an orthopyroxene cell with *a* = 18.308, *b* = 8.825, *c* = 5.234 Å, we obtain a β angle of 89.48° (Table 4; 9a). Thus it is very likely that the pyroxene in equilibrium with quartz observed by Dasgupta *et al.* (1985) is actually an orthopyroxene corresponding to donpeacorite, which would be in agreement with the experimental data of Iwabuchi & Hariya (1985), Huebner (1986), as well as observations on natural assemblages.

In sample 6005, tirodite (also identified by cell dimensions obtained from X-ray single-crystal data: *a* = 9.52(1), *b* = 18.01(1), *c* = 5.291(5) Å, β = 102.2(2)°) is replacing both Mn-pyroxenes.

Table 4. Cell dimensions of pyroxenes along the join $\text{MgSiO}_3\text{--MnSiO}_3$.

	M1, M2	a(Å)	b(Å)	c(Å)	$\beta(^{\circ})$	V(Å ³)
(1)	Mn ₂	9.864(2)	9.179(2)	5.298(1)	108.22	455.6
(2)	Mg _{1.04} Mg _{0.84} Fe _{0.10} Ca _{0.03}	9.739	8.939	5.260	108.56	434.1
(3)	Mn _{1.02} Mg _{0.86} Ca _{0.12}	9.76(2)	8.93(9)	5.27(2)	108.60(7)	435.3
(4)	Mn _{1.00} Mg _{1.00}	9.732(2)	8.934(1)	5.245(2)	108.52(2)	432.4
(5)	Mn _{0.90} Mg _{1.10}	9.719(2)	8.917(2)	5.248(1)	108.51(2)	431.3
(6)	Mn _{0.86} Mg _{1.14}	9.724(3)	8.911(2)	5.247(2)	108.60(3)	430.9
(7)	Mn _{0.80} Mg _{1.13} Ca _{0.07}	9.725(2)	8.876(2)	5.263(1)	108.53(1)	430.7
(8)	Mg ₂	9.605(1)	8.813(1)	5.166(1)	108.46(1)	414.8
(9)	Mn _{0.66} Mg _{1.36}	9.499(2)	8.825(15)	5.234(3)	105.5	422.8
(9a)	Mn _{0.66} Mg _{1.36} , transformed	18.308	8.825	5.234	89.48	845.6
(10)	Mn _{0.62} Mg _{1.27} Fe _{0.01} Ca _{0.05} Na _{0.01}	18.361(5)	8.861(2)	5.229(1)	90	850.7
(11)	Mn _{0.57} Mg _{1.43}	18.352	8.877	5.224	90	851.0
(12)	Mn _{0.56} Mg _{1.41} Ca _{0.03}	18.384(11)	8.879(7)	5.226(3)	90	853.1
(13)	Mn _{0.29} Mg _{1.71}	18.291	8.848(1)	5.203(1)	90	842.0
(14)	Mg ₂	18.214(4)	8.818(2)	5.177(4)	90	831.5
(15)	Mg ₂	18.225(2)	8.818(1)	5.179(1)	90	832.3

(1) synthetic pyroxene (Tokonami *et al.*, 1979), (2) kanoite (Kobayashi, 1977), (3) kanoite exsolutions, cell dimensions in original paper are erroneous (Gordon *et al.*, 1981), (4) synthetic kanoite (Huebner, 1986), (5) synthetic kanoite (Ghose *et al.*, 1975), (6) synthetic kanoite (Huebner, 1986), (7) kanoite (this study), (8) synthetic clinoenstatite (Ohashi & Finger, 1976), (9; 9a) synthetic clinopyroxene (Dasgupta *et al.*, 1985), (10) donpeacorite (this study), (11) synthetic Mg-Mn-orthopyroxene, average of four analyses (Huebner, 1986), (12) donpeacorite, *Pbca* orthopyroxene, chemistry varies between $\text{Mn}_{0.56}\text{Mg}_{1.41}\text{Ca}_{0.03}\text{Al}_{0.01}\text{Si}_2\text{O}_6$ and $\text{Mn}_{0.63}\text{Mg}_{1.32}\text{Ca}_{0.03}\text{Al}_{0.01}\text{Si}_2\text{O}_6$ (Petersen *et al.*, 1984), (13) synthetic Mn-Mg orthopyroxene, average of four analyses (Huebner, 1986), (14) orthoenstatite (Hawthorne & Ito, 1977), (15) orthoenstatite, average of two analyses (Huebner, 1986).

Tiroidite replacing Mg-rich pyroxene has commonly higher Mg/Mn values. The $K_D[(\text{Mg}/\text{Mn})^{\text{Kan}}/(\text{Mg}/\text{Mn})^{\text{Tr}}]$ varies from 0.46 to 0.64 which can only partly be explained by the compositional variation of kanoite. The corresponding K_D values from analyses of natural assemblages published by Klein (1966), Kobayashi (1977) and Peters *et al.* (1977) vary between 0.39 and 0.48. The two available donpeacorite-tiroidite pairs in sample 6005 show a $K_D[(\text{Mg}/\text{Mn})^{\text{Dnp}}/(\text{Mg}/\text{Mn})^{\text{Tr}}]$ of 0.65, slightly different to the value of 0.59 obtained by Petersen *et al.* (1984). The variation probably reflects changes in P,T and fluid composition during tiroidite formation. The retrogressive growth of tiroidite over a wide P,T range is underlined by the formation of hydrous minerals in all other quartz-rich lithologies of the area. Anthophyllite and talc replacing enstatite as well as the formation of andalusite indicate cooling during decompression of the Bani Hamid unit (Gnos & Kurz, 1994). The retrograde minerals occur in shear zones, while the formation of white micas indicates migrating potassium- and sodium-bearing fluids which were probably derived from the underlying subducting plate.

Crystal chemistry of kanoite

Two structure refinements on kanoite are available from the literature (Ghose *et al.*, 1975; Gordon *et al.*, 1981). Unfortunately, the results of Ghose *et al.* (1975) on a synthetic kanoite with the composition $\text{Mn}_{0.9}\text{Mg}_{1.1}\text{Si}_2\text{O}_6$ are only presented in the form of an abstract. In this sample, M1 has 0.118(3) Mn and 0.882 Mg; M2 has 0.782 Mn and 0.228 Mg. These populations are very similar to those for natural kanoite studied here. The natural kanoite of Gordon *et al.* (1981) has the composition $\text{Mn}_{1.02}\text{Mg}_{0.86}\text{Ca}_{0.12}\text{Si}_2\text{O}_6$, with Mg strongly enriched on M1. Average M1-O and M2-O distances of the Balmat kanoite (Table 3, column 2) are ca. 0.02 Å longer than the corresponding distances of kanoite from the United Arab Emirates. This can be explained by the higher Ca content of the Balmat sample which can be placed on M2, leading to a higher Mn concentration on M1 and thus increasing M1-O as well. The characteristics of the kanoite structure are very similar to related *P2₁/c* structures. The atomic displacement parameters for M2 are significantly higher than those for M1. Bond valence calculations (Table 5) using the pa-

Table 5. Bond valences and valence sums for cations and anions in kanoite.

	O1A	O1B	O2A	O2B	O3A	O3B	Σ
M1	0.386 0.298	0.277 0.386	0.412	0.402			2.160
M2	0.340	0.364	0.380	0.429	0.198	0.091 0.058	1.860
Si1A	1.033		1.082		0.937 0.907		3.959
Si1B		1.027		1.073		0.925 0.885	3.910
Σ	2.057	2.053	1.874	1.904	2.042	1.959	

rameters of Brown & Altermatt (1985) indicate underbonding for M2 but overbonding for M1. O2A and O2B – which are three-fold coordinated by M1, M2, and Si –, are underbonded and form the shortest M1-O, M2-O and Si-O distances in the structure. The longest Si-O distances are observed for O3A and O3B, bridging Si1A and Si1B. These long Si-O3 distances become possible because O3 bonds to additional M sites, thus increasing the valence sums.

Mg₂Si₂O₆ (clinoenstatite), MgMnSi₂O₆ (kanoite), and Mn₂Si₂O₆ (clinopyroxene synthesized at 10 GPa, 1200 °C by Tokonami *et al.* (1979)) all crystallize in space group *P*2₁/*c*. Kanoite from the United Arab Emirates has the same mean M1-O distance (Table 3) as clinoenstatite (Ohashi & Finger, 1976). If the six shortest M2-O distances are considered, kanoite has the same mean M2-O distance as synthetic Mn₂Si₂O₆ (Tokonami *et al.*, 1979). Because Mg-O distances are the shortest and Mn-O distances are the longest M1-O and M2-O distances found in the *P*2₁/*c* pyroxenes it is worth testing some general relationships described in the literature.

Cameron & Papike (1980) assumed from an analogy with *Pbca* orthopyroxenes that *P*2₁/*c* pyroxenes have a negative correlation between the Si-O (bridging) bond length and the mean M1, M2 octahedral radius. Based on the series of Mg, Mn *P*2₁/*c* clinopyroxenes, however, this cannot be confirmed. Si1A-O (bridging) is 1.654 Å for Mn₂Si₂O₆ and 1.655 Å for Mg₂Si₂O₆, with 1.652 for MgMnSi₂O₆ (kanoite). Thus, there is no correlation between Si1A-O (bridging) and M-O. Although Si1B-O (bridging) is 1.667 Å for

Mn₂Si₂O₆ and 1.676 Å for Mg₂Si₂O₆, it is 1.661 Å for kanoite, indicating that this correlation is not simply linear. Nyfeler *et al.* (1995), comparing pyroxene-related structures with Mn on M1, concluded that there is no simple correlation between the size of the M2 site and the length of the tetrahedral chain (or the Si-O-Si angle). A striking variation can be seen in Si-O-Si angles in the Mg, Mn *P*2₁/*c* series. Both kanoite and synthetic Mn₂Si₂O₆ have M2 occupied by Mn, whereas kanoite has Mg on M1. Both structures have very similar Si-O-Si angles (Table 3). The corresponding angles for clinoenstatite (Mg on M1 and M2) are about 6° shorter. Cameron & Papike (1980) further suggested that there is a slight negative correlation between mean ionic radius (M1, M2) and mean Si-O distance. However, mean Si1A-O = 1.631 Å for Mn₂Si₂O₆, and mean Si1A-O = 1.628 Å for both Mg₂Si₂O₆ and MgMnSi₂O₆ (Table 3). Mean Si1B-O = 1.637 Å for Mn₂Si₂O₆, 1.638 Å for Mg₂Si₂O₆ and 1.634 Å for kanoite. These data indicate that correlations in *P*2₁/*c* pyroxenes are much more complex than hitherto considered.

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