

Influence of metal cation order on magnetic order in manganogrunerite, $(\text{Fe,Mg,Mn})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$, a quasi-one-dimensional chain antiferromagnet

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ABSTRACT

The magnetic susceptibility of ordered and partially disordered manganogrunerites (composition $\text{Ca}_{0.1}\text{Mn}_{1.9}\text{Mg}_{1.25}\text{Fe}_{3.56}^{2+}\text{Fe}_{0.38}^{3+}\text{Si}_{7.81}\text{O}_{22}(\text{OH})_2$ and $\text{Ca}_{0.24}\text{Mn}_{1.57}\text{Mg}_{2.27}\text{Fe}_{2.76}^{2+}\text{Fe}_{0.32}^{3+}\text{Si}_{7.84}\text{O}_{22}(\text{OH})_2$) has been measured between room temperature and 5 K. The influence of disordering of metal cations over the $M(1,2,3)$ sites of the octahedral ribbon in these amphiboles is to dilute Fe^{2+} within the ribbon. We observe a reduction in both θ_p and T_N as a function of both increased $\text{Mg}/(\text{Mg}+\text{Fe})$ and metal cation disorder, linked to a reduction in the strength of magnetic coupling between and within the one-dimensional chains of the structure.

KEYWORDS: amphibole, order-disorder, antiferromagnet, dilution.

Introduction

CUMMINGTONITES $(\text{Fe}_x\text{Mg}_{1-x})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ represent a sub-group of the amphibole family. The cummingtonite series of amphiboles are monoclinic and in the system described by Leake *et al.* (1997) have compositions with $0.7 > \text{Mg}/(\text{Mg}+\text{Fe}) > 0.3$, with the general formula $(\text{Mg},\text{Fe}^{2+},\text{Mn})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$. The Fe-end-member, grunerite, has been described in terms of its magnetic characteristics as a quasi-one dimensional system, displaying ferromagnetic interactions between Fe^{2+} ions lying in the octahedral double chain that forms the backbone of the structure, with anti-ferromagnetic interactions between chains (Linares *et al.*, 1983, 1988). There have been few studies of the magnetic properties of amphiboles, but Eisenstein *et al.* (1975) were among the first to characterize these properties, focusing on the asbestos minerals amosite (actually a grunerite, under the nomenclature of Leake *et al.* (1997)) $(\text{Fe},\text{Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ and crocidolite $\text{Na}_2\text{Fe}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$. They saw two

different anti-ferromagnetic transitions at 7 K and 22 K, associated with easy axes parallel and perpendicular to oriented amphibole fibres. Indeed, it had been noted earlier that asbestos fibres could be aligned in a magnetic field (Timbrell, 1979; Cressey and Whittaker, 1984).

The amphibole structure can be thought of in terms of double chains of corner-sharing tetrahedra $(\text{Si}_4\text{O}_{11})_\infty$ parallel to the crystallographic z axis, with apices directed toward the octahedral double-chain ribbon. This double chain includes the three non-equivalent octahedral cation sites, $M(1)$, $M(2)$ and $M(3)$, with a fourth, larger, more distorted site at the periphery of the ribbon, termed $M(4)$ (Fig. 1). The multiplicity of the $M(1,2,4)$ sites is 2, with point symmetry 2. The $M(3)$ site has multiplicity of 1 and point symmetry $2/m$. A further cation position (the A site), occupied by large cations such as K^+ , Ca^{2+} and Na^+ , forms the large cavity between the basal planes of opposing chains of tetrahedra but is vacant in our samples.

It has been suggested that non-convergent disorder of cations within the double chain of the amphibole structure at high temperatures could lead to their use as thermometric indicators, and to this end we have studied metal cation

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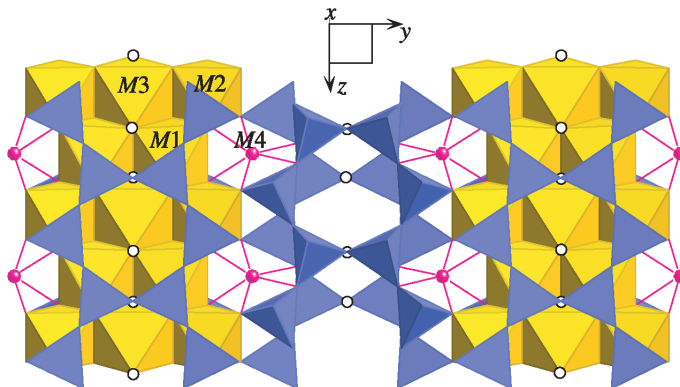


FIG. 1. Structure of grunerite. Fe^{2+} may enter the $M(1,2,3)$ sites of the octahedral ribbon as well as the $M4$ site to the side of the chain.

partitioning in Fe-bearing samples *in situ* at high-temperatures by powder neutron diffraction. We are focusing on metal-cation partitioning between the $M(4)$ site and the smaller octahedral sites $M(1)$, $M(2)$ and $M(3)$. Whittaker (1949) showed that, in crocidolite, Mg^{2+} occupies the $M(4)$ cation site in preference to Fe^{2+} . Ten years later using three-dimensional least-squares refinement of X-ray diffraction data from a grunerite, Ghose and Hellner (1959) reported almost complete occupation of the $M(4)$ site by Fe^{2+} and showed that surplus Fe^{2+} and Mg^{2+} were distributed randomly over the three remaining cation sites. Ghose (1961) later determined the crystal structure of a cummingtonite from Quebec with particular interest paid to cation distribution and disordering. Work on Fe-Mg ordering in a cummingtonite by Hirschmann *et al.* (1994) revealed a strong preference of Fe^{2+} for the $M(4)$ site relative to Mg. Here we explore the influence of high-temperature structural readjustments on the low-temperature magnetic behaviour of Fe-bearing amphiboles.

The magnetic behaviours of various Fe-bearing amphiboles have been investigated by a variety of techniques. Linares *et al.* (1983) used powder magnetic susceptibility measurements and Mössbauer spectroscopy to conclude that the magnetic structure of grunerite (the Fe end member) consists of ferromagnetic chains coupled by weaker antiferromagnetic interactions. Further compositions of amphibole along the $(\text{Fe}_x\text{Mg}_{1-x})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ binary were investigated using the same methods (Linares *et al.*, 1988) showing a composition-dependent change in T_N , the temperature at which the structure

orders anti-ferromagnetically. The heat capacity measurements through the low-temperature ordering transitions were interpreted in terms of a two-dimensional, randomly diluted Ising ferromagnet by Komada *et al.* (1995). The character of a lower-temperature transition at 4.5 K was investigated by Ghose *et al.* (1987), using neutron powder diffraction to observe the temperature-dependence of the intensity of the (010) magnetic peak. The transition was interpreted as being due to a spin canting at the $M(4)$ and $M(1)$ sites. Here, we explore the compositional dependence of T_N in Fe-bearing amphiboles further, and also investigate the influence of metal cation disorder and Fe-dilution on the magnetic behaviour.

Sample

We have studied two manganogrunerites (formerly termed dannemorites) from the collection of the Natural History Museum, London, which originate from near the village of Långban, an area of intensely mineralized Fe-Mn deposits in the Swedish Bergslagen Orefield. Their accession numbers are BM40798 and BM1980/280. The sample compositions are $\text{Ca}_{0.1}\text{Mn}_{1.9}\text{Mg}_{1.25}\text{Fe}_{3.56}^{2+}\text{Fe}_{0.38}^{3+}\text{Si}_{7.81}\text{O}_{22}(\text{OH})_2$ (BM40798) and $\text{Ca}_{0.24}\text{Mn}_{1.57}\text{Mg}_{2.27}\text{Fe}_{2.76}^{2+}\text{Fe}_{0.32}^{3+}\text{Si}_{7.84}\text{O}_{22}(\text{OH})_2$ (BM1980/280). Electron microprobe analyses were performed using a Cameca SX50 and sample compositions calculated by averaging 20 analyses of each specimen. Formula unit compositions were calculated on the basis of 23 oxygens. Both samples comprised prismatic crystals bound together in a massive bulk that

proved to be phase pure after magnetic separation of crushed grains. Analyses of grains from different sections of the bulk sample showed no compositional variation within experimental error. As reported fully in Reece *et al.* (2002), both samples were investigated using *in situ* neutron powder diffraction at the ISIS spallation neutron source of Rutherford Appleton Laboratory, UK. Previous investigations of Fe-Mg amphiboles have shown that Fe²⁺ orders preferentially on to the large *M*(4) site. Investigations of samples that are richer in Mn, however, have shown that Mn has a higher preference for *M*(4) than either Fe or Mg (Reece *et al.*, 2000, 2002) but that Fe in such samples disorders from the smaller cation sites to the *M*(4) site at high temperatures. The high-temperature disordered cation distributions obtained on annealing samples to high temperature are retained during cooling. We have exploited this behaviour to obtain two samples of the same compositions as the unheated manganogrunerites, but with slightly different occupancies of Fe²⁺ in the octahedral double ribbon that is assumed to control the magnetic properties. The strongly opposing scattering lengths of Mn and Fe²⁺ of neutron radiation aid the accurate determination of individual average site occupancies. This enables us to link differences in magnetic behaviour to differences in site occupancies, furthering the understanding of the magnetic interactions within amphiboles, without the need to group Fe contained in the *M*(1,2,3) sites together.

Experimental methods

Magnetic susceptibility data were collected from powdered samples with a Quantum Design

SQUID magnetometer using a field of 0.1 T during both heating and cooling runs. The samples were cooled to the minimum temperature of 5 K, which was reached before the field was applied and heating commenced. Masses of 50.7 mg and 42.8 mg of untreated and disordered (heated during neutron diffraction experiments) sample BM1980,280 and 44.5 mg and 43.0 mg of the untreated and disordered BM40798 were used, respectively. An initial set of data was collected for each sample at 1.5 K intervals from 5 to 100 K at a heating rate of 2 K min⁻¹, then at every 4 K from 100 to 200 K at a rate of 3 K min⁻¹. A second data set was collected for the two BM40798 samples every ~0.5 K from 5 to 30 K at a rate of 0.5 K min⁻¹ and then every 4 K from 30 to 150 K at 5 K min⁻¹.

Results

The cell parameters and cation-site occupancies of the two samples at ambient temperature are given in Table 1. Also shown are the values of these parameters in the two samples obtained at high temperature, in the case of BM40798 (since no cooling data were collected) and at 300°C during cooling in the case of BM1980,280. Of the two samples, BM40798 is closer to the grunerite end-member and contains more Fe. The differences in magnetic properties of the two samples of differing composition, as well as their disordered counterparts, are expected to arise from differences in Fe distributions within the octahedral ribbon. In both BM40798 and BM1980,280, disordering is characterized by an increase in Fe at *M*(4) of some ~20–25%, due to exchange from *M*(1), *M*(2) and *M*(3) (Reece *et al.*, 2002). It is found that the details of the patterns of disordering on these latter three sites in the two

TABLE 1. Structural parameters (cell-edge lengths and Fe occupancy of the *M* sites in and beside the octahedral chain) of our two samples at room temperature and after heating to the highest temperatures of annealing.

	<i>A</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Volume (Å ³)	Fe <i>M</i> (4)	Fe <i>M</i> (3)	Fe <i>M</i> (2)	Fe <i>M</i> (1)
BM40798								
25°C	9.6273 (3)	18.3381 (6)	5.3424 (2)	921.97 (5)	0.342 (4)	0.580 (4)	0.490 (4)	0.753 (4)
600°C	9.6813 (3)	18.3823 (7)	5.3452 (2)	930.88 (6)	0.420 (5)	0.601 (5)	0.447 (5)	0.708 (5)
BM1980,280								
50°C	9.6068 (2)	18.2419 (5)	5.3326 (2)	913.11 (4)	0.307 (4)	0.507 (13)	0.419 (13)	0.480 (13)
300°C (cooling)	9.6255 (3)	18.2734 (5)	5.3347 (2)	917.25 (5)	0.381 (4)	0.418 (13)	0.416 (14)	0.453 (14)

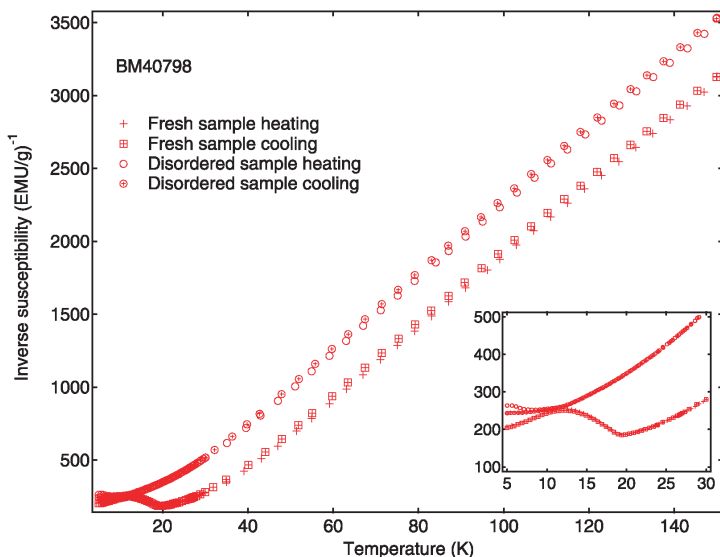


Fig. 2. Magnetic susceptibility of sample BM40798 in a 0.1 T applied magnetic field.

samples are different and that this is a result of the complex chemistry of the amphiboles and the strong partitioning behaviour of unequal amounts of Mn. For example, Fe shows little difference in site preference for $M(1)$, $M(2)$ and $M(3)$ in BM1980,280 while showing a strong preference for $M(1)$ in sample BM40798. Despite these differences, the occupancy of Fe on $M(1)$ has

decreased in both samples on disordering at high-temperature, albeit by a small amount.

Inverse magnetic susceptibility data for these four different samples are shown in Figs 2 and 3. The inverse susceptibility curve for sample BM40798 above 40 K shows typical Curie-Weiss behaviour for both the fresh and heat-treated samples with paramagnetic Curie tempera-

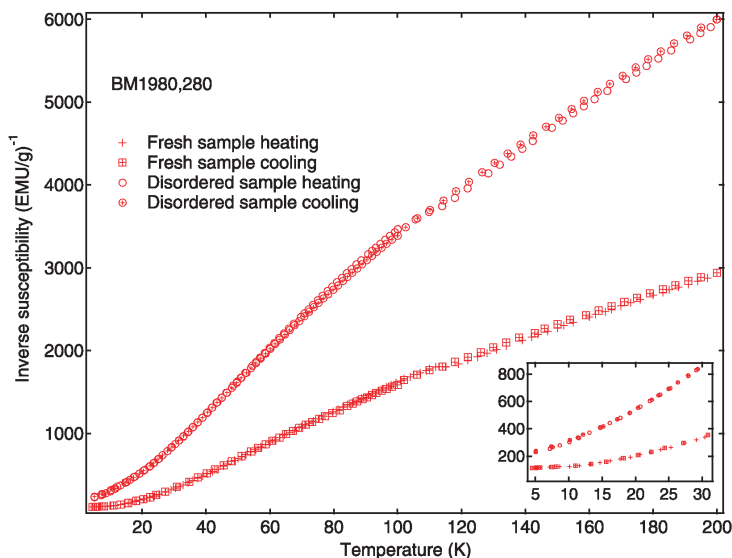


FIG. 3. Magnetic susceptibility of sample BM1980,280 in a 0.1 T applied magnetic field.

TABLE 2. Relationship between the Fe occupancy within the octahedral chain $[M(1,2,3)]$ and the observed T_N . Data for grunerite and cummingtonite are from Linares *et al.* (1983, 1988).

Sample	Fe/(Fe+M)	$X_{Fe^{2+}}$	$M(1,2,3)$	$X_{Fe^{2+}}$	$M(4)$	T_N (K)
Grunerite 9B	0.95		0.96		0.94	47.0±1
Cummingtonite DH7-490	0.49		0.35		0.88	6.5±1
Cummingtonite 118125	0.36		0.16		0.88	3.5±0.5
BM40798 fresh	0.54		0.61		0.34	19±1
BM40798 heat-treated	0.54		0.58		0.42	8±1
BM1980,280 fresh	0.42		0.46		0.31	/
BM1980,280 heat-treated	0.42		0.43		0.38	/

tures, θ_p , of 21 ± 1 and 10 ± 1 K, respectively, indicating predominantly ferromagnetic interactions, as expected. The inverse susceptibility follows a Curie-Weiss law with a Curie constant of $\sim 2.3 \text{ K emu}^{-1} (\text{g atom Fe})^{-1}$. The fresh (i.e. more cation-ordered) sample also shows a maximum in inverse susceptibility at 19 ± 1 K that, by analogy with the results of previous studies (Linares *et al.*, 1983, 1989; Ghose *et al.*, 1987), can be assumed to indicate the onset of antiferromagnetic ordering between the chains. The gradients of lines fitted to the paramagnetic regions of the fresh and the heat-treated BM40798 are the same and the difference in Curie temperature arises from the lateral shift to lower temperature of all inverse susceptibility data for the more disordered sample. Heating data collected from this disordered sample also suggest an anti-ferromagnetic transition at 8 ± 1 K, consistent with the ~ 11 K shift of the inverse susceptibility trend compared to that of the fresh sample. Cooling experiments for BM40798 do not show the lowest temperature transition, however.

Inverse susceptibility data for the ordered and disordered samples of BM1980,280 do not appear to follow the Curie-Weiss law so well, and show a change in the Curie constant within the paramagnetic region at ~ 100 K. It is worth noting, however, that the heating rate of the experiments was increased at this temperature, although if this has affected the recorded time-averaged susceptibility in this sample, it is strange that it has not also affected the more Fe-rich BM40798, from which data were collected in an identical manner. Furthermore, the Curie constant of the ordered sample differs from that of the disordered sample. Extrapolation of the high-temperature linear region for the ordered and disordered samples of

BM1980,280 do not give a positive Curie temperature, indicating an absence of ferromagnetic interactions.

None of the samples appear to experience the spin canting transition observed in pure grunerite, although the limit of the capability of the magnetic apparatus does not allow observation below 5 K. The values of T_N for the samples are given in Table 2 alongside values reported for other Fe-Mg-Mn group amphiboles by Linares *et al.* (1988). For the sake of comparison, the site occupancies of $M(1,2,3)$ are averaged for our samples. The values of T_N and composition are also shown in Fig. 4. The value of T_N of a sample with respect to composition is expected to lie on a curve connecting the data from Fig. 4. Clearly, the cation distribution in the amphibole structure plays an important role in determining T_N for a given composition. The degree of disorder in the system will depend upon composition, the temperature from which the host-rock has cooled and the speed at which it has cooled. With more

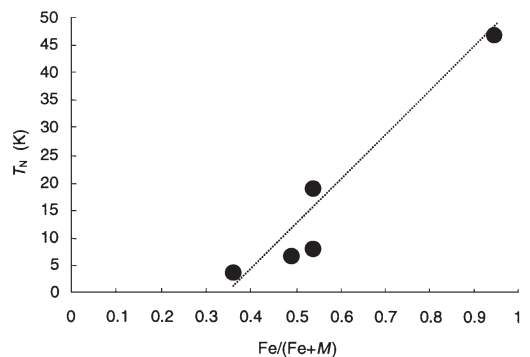


FIG. 4. The dependence of T_N upon the Fe content of various grunerites.

information regarding the 'blocking temperature', T_B , of cation disorder in amphiboles with respect to composition, these results indicate that it may prove possible to deduce the thermal history of the mineral from observations of T_N . In this sense, the anti-ferromagnetic behaviour of grunerite-like amphiboles provides an experimental method for the characterization of paragenesis of the host rock. Our results also demonstrate the influence of disordering within the chain, indicating that the anti-ferromagnetic interactions between chains become weaker with increased disorder of Fe. This demonstrates that it is unlikely that Fe-clustering occurs during the disordering process, and in this respect the behaviour of Fe in the double chain of the amphibole structure contrasts with recent observations of Fe-clustering in the sheet structure of micas.

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