Al-poor and Al-rich orthoamphiboles: a Mössbauer spectroscopy and TEM study

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Abstract

Mössbauer spectroscopy and electron microscopy were combined to study one Al-poor anthophyllite and one Al-rich gedrite. TEM show that Al-rich gedrite is not homogeneous and that the complexity of its Mössbauer spectrum is due to sub-microscopic intergrowth of chlorite and lizardite.

KEYWORDS: anthophyllite, gedrite, chamosite, lizardite, Mössbauer spectroscopy, TEM

Introduction

ANTHOPHYLLITE and gedrite have orthorhombic symmetry with *Pnma* space group. Both possess three regular octahedral sites *M*1, *M*2 and *M*3 with 1, 1 and *m* point symmetries, respectively. At the edge of this octahedral strip, there is the *M*4 site having point symmetry of 1. This site is coordinated to 8 anions in anthophyllite and to 6 anions in gedrite. In fact, the coordination number of *M*4 varies with its cation occupancy (see Hawthorne, 1981). For orthoamphiboles intermediate in Al content between anthophyllite and gedrite, i.e. for Al-rich anthophyllite, Seifert (1977) pointed out that the incorporation of Al into the *Pnma* amphibole structure decreases the distortion of the *M*4 polyhedron and increases the distortion of the *M*1, *M*2 and *M*3 polyhedra. This would result in separation of the absorption lines for *M*1, *M*2 and *M*3 in Al-rich anthophyllites, broadening the Mössbauer spectrum and even overlapping with the absorption line of *M*4. Seifert (1977) used this observation to conclude that reliable fitting of the Mössbauer spectrum of gedrite is not possible. Recently, however, Law (1989) fitted the spectra of gedrite and Al-rich gedrite using a model different than that adopted for anthophyllite. He found the two absorption lines of anthophyllite, A and C, corresponding to *M*1–*M*2–*M*3 and *M*4, respectively, insufficient to fit the spectra of gedrite and Al-rich gedrite. An additional absorption line, B, with isomer shift, IS, and quadrupole splitting, dq, intermediate between those of A and C, was consistently required to fit the Mössbauer spectra of gedrites and Al-rich gedrites. Furthermore, for Al-rich gedrites the intensities of A and C differ from those of anthophyllite. In sample 009 (Law, 1989), for example, the intensity ratio of the two absorption lines is reversed. Since anthophyllite and gedrite are structurally similar, Law attributed the complexity of the Mössbauer spectra of gedrite to the presence of Fe species in gedrite possessing different chemical environments.

Law (1989) does not rule out the presence of chain multiplicity defect and exsolution lamellae in some of the specimens, but he considers the orthoamphiboles as homogeneous phases for Mössbauer spectroscopy studies. However, a number of studies on both synthetic and natural amphiboles using high-resolution transmission electron microscopy, HRTEM, have demonstrated that the amphibole group of minerals are prone to different types of small-scale structural defects (Veblen, 1980; Maresch and Czank, 1983; Sharp and Buseck, 1988). These defects can not be detected by conventional techniques such as powder X-ray diffraction (XRD), optical microscopy and Mössbauer spectroscopy.

The aim of this paper is to present evidence to show that Al-rich orthoamphiboles may be unstable and that they may contain sub-microscopic intergrowths of other Al-rich phases. To this end we studied one Al-poor pink anthophyllite from Finnshyttebergsfältet in central Sweden and one Al-rich greyish black gedrite from Bergslagen in south-central Sweden using high-resolution transmission electron microscopy, HRTEM, Mössbauer spectroscopy and X-ray diffraction analysis, XRD. In addition a chamosite from Thüringen, German Democratic Republic, was studied using

Table 1. Mössbauer effect parameters of chain silicates and layer silicates where CS is the centroid shift relative to metalic iron (±0.01mm/s), dq is the quadrupole splitting (±0.01 mm/s), w is the full width at half maximum in mm/s and Ar is the relative area of the component doublets.

| Fe^{2+} (VI) | | | | | | | | | | | | Fe^{3+} (VI) | | | | Fe^{3+} (IV) | | | | |
| A | | | | B | | | | C | | | | | | | | | | | | |
CS	dq	w	A	CS	dq	w	Ar	CS	dq	w	Ar	CS	dq	w	Ar	CS	dq	w	Ar	Ref
1.15	2.81	0.26	0.08					1.12	1.79	0.26	0.92									1
1.14	2.68	0.26	0.19	1.10	2.38	0.30	0.51	1.09	1.85	0.34	0.23	0.34	0.60	0.38	0.04	0.18	0.30	0.34	0.04	2
1.15	2.74	0.25	0.14	1.16	2.39	0.35	0.41	1.13	1.93	0.37	0.33	0.26	0.35	0.72	0.12					3
1.12	2.70	-	0.44	1.10	2.45	-	0.27					0.39	0.67	-	0.23					4
1.13	2.68	0.40	0.29	1.13	2.28	0.40	0.36					0.42	0.65	0.60	0.25					5
1.15	2.79	0.40	0.45	1.16	2.21	0.32	0.33					0.37	0.65	0.82	0.22					6
1.14	2.66	0.28	0.85					1.22	1.83	0.26	0.15									7

Anthophyllite (1) and gedrite (2) from this study; gedrite (3) from Law (1989); chamosite (4,5) from Kodama et al. (1982) and Rozenson et al. (1979), respectively; lizardite (6) from Rozenson et al. (1979); chamosite(7) from this study. Note that dq of the second doublet of lizardite is lower than that of chamosite.

Table 2. Chemical analysis of anthophyllite and Al-rich gedrite. Note that the composition of the Al-rich gedrite in this study is similar to that of Law (1989).

K	Na	Ca	Co	Mg	Fe^{2+}	Fe^{3+}	Mn	Ti	Al$_{VI}$	Si	Al$_{IV}$	Ref
0.01	0.02	0.11	0.04	5.22	1.39	0.00	0.03	0.00	0.19	8.01	0.00	1
0.00	0.68	0.02	0.00	1.49	3.68	0.00	0.06	0.03	1.61	5.88	2.12	2
0.01	0.54	0.04	0.00	2.97	2.32	0.13	0.03	0.03	1.23	5.87	2.13	3

Anthophyllite and gedrite (1 and 2) this study; gedrite (3) Law (1989)

Mössbauer spectroscopy and XRD for comparison. The result of this study together with the Mössbauer parameters of lizardite and chamosite from the literature was used to explain the complexity of the Mössbauer spectrum of Al-rich orthoamphiboles.

Experimental

The homogeneity of the specimens was checked by X-ray powder diffraction analysis on a Philips automatic diffractometer using Cu-K radiation with silicon as internal standard.

The Mössbauer spectra of the specimens were all taken at room temperature using conventional techniques as described by Annersten *et al.* (1982). Electron microscopy was performed using a JEM 2000-EX operated at 200 kV with a point resolution of 2.7–3.0 Å. The apertures selected were 120μm for the condenser lens and 50μm for the objective lens, which corresponds to a minimum d_{hkl} spacing of 2.1 Å.

Results and discussion

HRTEM lattice images, selected area electron diffraction, SAED, and Mössbauer spectrum of the minerals studied are shown in Figs. 1 and 2. The Mössbauer parameters are listed in Table 1 and the chemical analyses in Table 2. For comparison the Mössbauer parameters of two chamosites (Kodama *et al.*, 1982; Rozenson *et al.*, 1979) and two lizardites (Rozenson *et al.*, 1979); and the chemical analysis of Al-rich gedrite (Law, 1989) are also included in the tables. Sample 016 (Law, 1989) was chosen because its chemistry is similar to the gedrite in this study.

Transmission electron microscopy study of the anthophyllite shows a very high degree of structural homogeneity with no chain multiplicity defect and no sub-microscopic exsolution or intergrowths of other phases (Fig. 1a). However, HRTEM and SAED of the Al-rich gedrite show both chlorite and lizardite coherently intergrown within its structure with a^* of gedrite parallel to c^* of chlorite and lizardite (Figs. 1b and c). Image
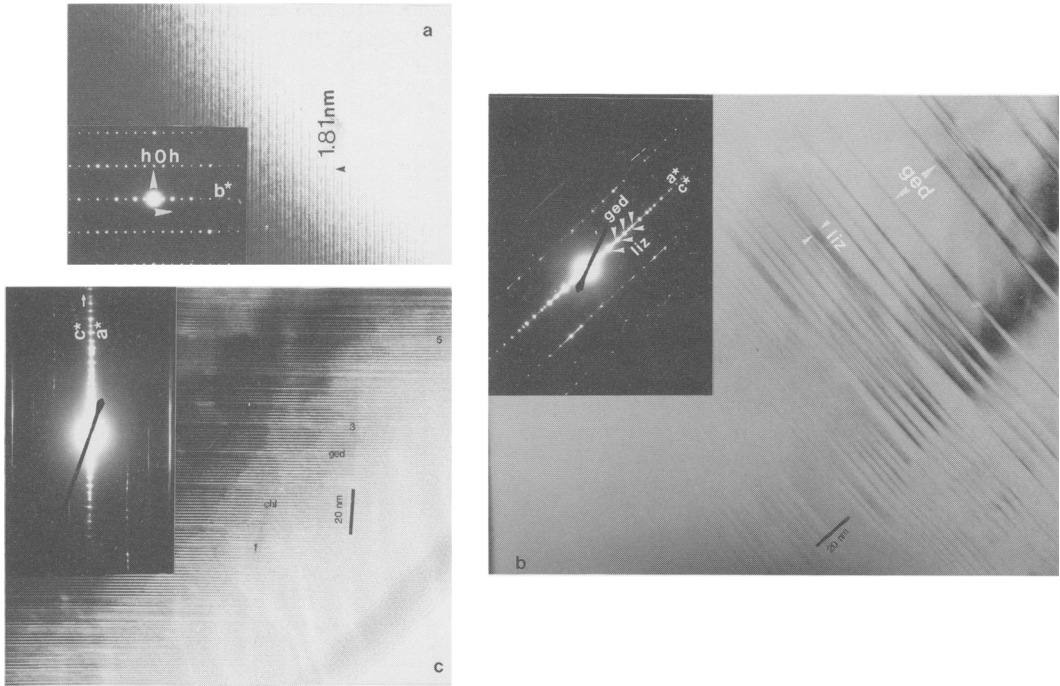
FIG. 1. HRTEM lattice fringes and SAED (insets) of anthophyllite and Al-rich gedrite. The diffraction spots correspond to the reciprocal of the inter-planar distances for the orientation given. Note that the anthophyllite show no structural defects (*a*), while the Al-rich gedrite contain coherent intergrowths of lizardite and chlorite with the a^* of gedrite parallel to c^* of lizardite and chlorite (*b* and *c*). The gedrite in (*c*) is heavily altered to chlorite with few (1, 3 and 5) gedrite units left while the alteration of gedrite to liardite is less severe (*b*).

interpretation of amphibole, chlorite and lizardite are similar to those presented by Veblen and Buseck (1981) and Cressey (1979).

The corresponding Mössbauer spectrum for anthophyllite shows a weak outer doublet, A, due to Fe^{2+} in the regular octahedral sites $M1$, $M2$, $M3$ and a strong inner doublet, C, due to Fe^{2+} in the more distorted $M4$ site (Fig. 2a); this result agrees with previous site assignment of anthophyllite (Seifert, 1977). The intensity ratio between the two lines agrees well with the Fe-site occupancy as determined by X-ray diffraction analysis (Seifert and Virgo, 1974). The Mössbauer spectrum of chamosite differs from that of anthophyllite (Fig. 2b). Here we have a strong outer doublet, A, and a weak inner doublet, C. The Mössbauer parameters of this particular example differ considerably from the Mössbauer parameters of chlorites found in the literature and the assignment of the lines and their crystallographic interpretation will be presented in a separate paper. The Mössbauer spectrum of the Al-rich gedrite appears to be a summation of the anthophyllite and chamosite spectra (Fig. 2c) Conse-

quently, three Fe^{2+} doublets would be required to fit the spectrum of the Al-rich gedrite. We fitted the spectrum of Al-rich gedrite using three Fe^{2+} and two low-intensity Fe^{3+} absorption lines and obtained Mössbauer parameters that are similar to those reported by Law (1989). We consider the Fe^{3+} lines to originate from the intergrowths and they will not be considered further in this study.

Powder X-ray diffraction analysis of the Al-rich sample used for Mössbauer spectroscopy shows a small 7 Å peak present. This is probably d_{002} of lizardite but it could as well be d_{002} of chamosite, since X-ray diffraction study of the chamosite showed d_{001} to be very weak. It means that the additional phase or phases in the Al-rich gedrite could be lizardite, chamosite or both. Nevertheless, both lizardite and chlorite have similar octahedral sites and related Mössbauer parameters. As Table 1 shows, the major difference in Mössbauer parameters between lizardite and chamosite is that the second Fe^{2+} site of lizardite shows slightly lower dq values.
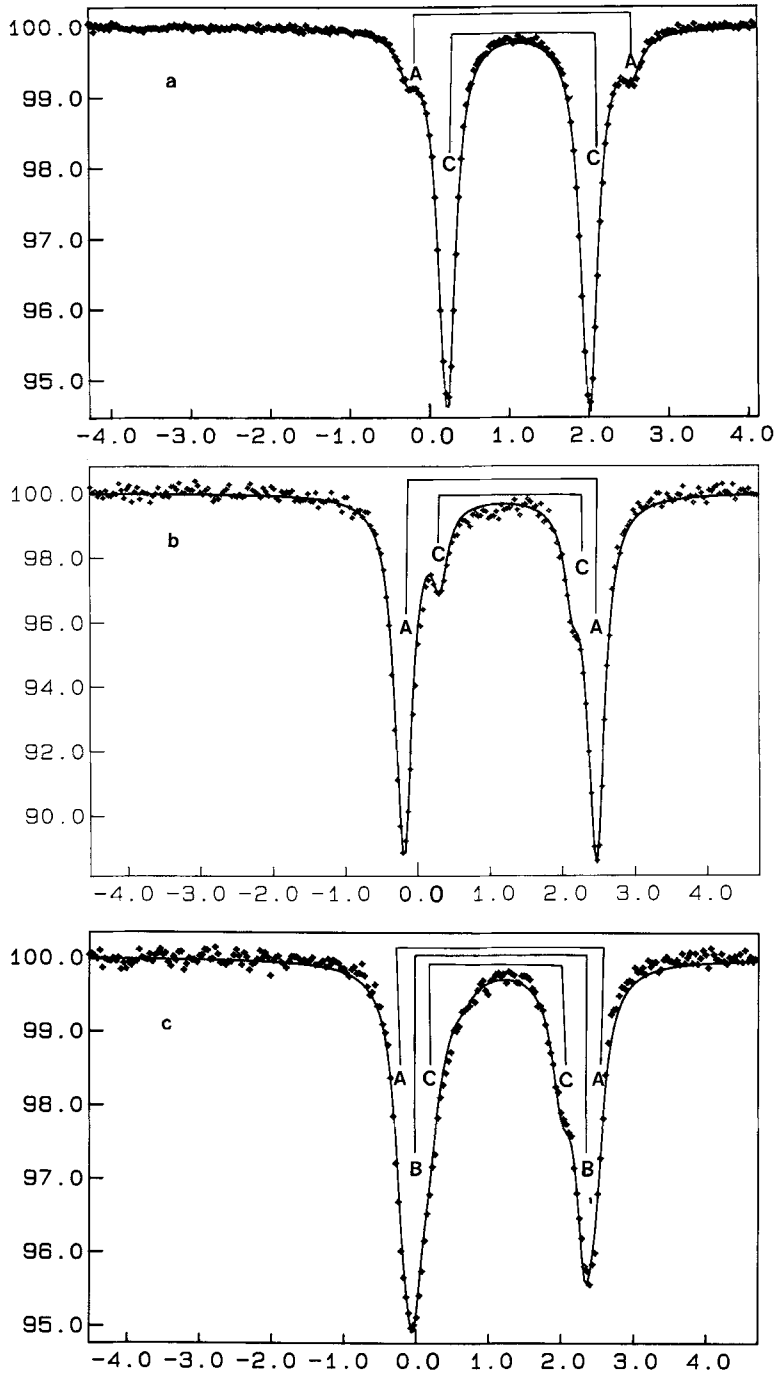
Using the information in Figs. 1 and 2, the

FIG. 2. Mössbauer spectra of (a) anthophyllite, (b) chamosite, and (c) Al-rich gedrite. The samples come from Finnshyttebergsfältet, Sweden; Thüringen, German Democratic Republic; and Bergslagen, Sweden, respectively. The Al-rich gedrite showed no additional phases under the petrographic microscope.

Mössbauer parameters in Table 1 and the observation by Seifert (1977) on the effect of Al content on the dq of the two Fe^{2+} lines in anthophyllite, we can explain the complexity of the Mössbauer spectrum of Al-rich gedrite using a number of possible combinations. For example, line A of Al-rich gedrite = line A of chlorite + line A of orthoamphibole, line B of Al-rich gedrite = line B of chlorite, and line C of Al-rich gedrite = line C of orthoamphibole; or line A of Al-rich gedrite = line A of chlorite, line B of Al-rich gedrite = line A of orthoamphibole + line B of chlorite and line C of Al-rich gedrite = line C of orthoamphibole.

It is not easy to correlate the intensity distribution between the three Fe^{2+} doublets in Al-rich gedrite since a number of factors are involved. For example, variation in the Mössbauer parameters of orthoamphiboles with increasing amount of Al (Seifert, 1977), variation in the Mössbauer parameters of chlorite and the preference of Fe^{2+} between amphibole and chlorite and the ratio of the two phases in the sample are factors which cannot be estimated using either XRD or HRTEM. However, the results of electron microscopy indicate that Al-rich amphiboles usually contain other Al-rich phases as observed by Seifert (1977).

An additional factor, one that complements our finding that Al-rich amphibole may be unstable, comes from the experimental work on the stability of Al-rich tremolite in the tremolite–tschermakite join by Jenkins (1988). He was unable to synthesize pure tschermakite over the range of 6–15 kbar and 700–850°C. He demonstrated that there is a limit to the amount of the tschermakite component, $Al^{IV}_yAl^{VI}_ySi_{-y}Mg_{-y}$, that can be dissolved in tremolite and, that for exchange vectors where $y > 0.8$, other Al-rich phases such as anorthite, corrundum and chlorite stabilize together with tremolite. Similar behaviour is observed in layer silicates and was shown to be due to the structural mismatch between the tetrahedral and octahedral sheets (Ferrow, 1990). Amphiboles consist of I-beam-like structural units that are analogous to portions of the talc-like sheets in the layer silicates. It is possible that the same factors that control the solution of exchange component $Al^{IV}_yAl^{V}_ySi_{-y}Mg_{-y}$ in layer silicates control its solution in amphiboles. However, this is not the only exchange mechanism that incorporates Al^{IV} into the gedrite structure. It is also possible to incorporate more Al^{IV} in gedrite by solution of the edenite component, $Na^A_xAl^{IV}_xSi_{-x}$, where Na occupies the vacant A-site and where the excess charge is balanced by the replacement of Si by Al in the tetrahedral site. However, the magni-

tude of the second exchange vector is far less than that of the first one. For the gedrites (Table 2), for example, $x = 0.54$ and 0.68 while $y = 1.59$ and 1.44, respectively, which are greater than the maximum value of the exchange vector in tremolite.

Conclusion

The Al-rich gedrite from Bergslagen contain sub-microscopic intergrowths of other Al-rich phases such as chlorite and serpentine. The complexity of the Mössbauer spectrum of the Al-rich gedrites is partly due to the contamination of the sub-microscopic intergrowths. Thus the Mössbauer spectrum of gedrite can be fitted using the same model as the one adopted for anthophyllite provided the observations of Seifert (1977) are taken into account. However, even in this case we were not able to determine unequivocally which Fe^{2+} doublets belong to the host and the inclusions.

Furthermore, this study, together with the experimental result on the stability of Al-rich tremolite (Jenkins, 1988) suggest that Al-rich amphiboles may not be stable. If this is the case, our explanation could be extended to the Al-rich phases studied by Law (1989). However, only an experimental study on the stability of Al-rich orthoamphiboles combining XRD, Mössbauer spectroscopy and HRTEM could give a definite answer.

Finally, even if Mössbauer spectroscopy is an excellent experimental tool for studying mineralogical problems associated with Fe-bearing minerals, the technique requires reasonably homogeneous phases with few associated microdefects. Thus combining Mössbauer Spectroscopy with other techniques such as XRD and HRTEM is essential (Skogby and Ferrow, 1989).

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