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Title page

Water incorporation in omphacite: concentrations and compositional relations in ultrahigh-pressure eclogites from Pohorje, Eastern Alps

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Abstract: Omphacite in ultra-high pressure (UHP) eclogites from the Pohorje Mountains in Slovenia, south-eastern Alps, has been investigated by electron microprobe (EMP), Infra-Red (IR) and Mössbauer spectroscopy to determine OH concentrations and related incorporation mechanisms. Results from polarized IR measurements reveal high contents of structurally-bound OH, varying from 530 to 870 ppm H₂O. Characterization of omphacite composition by EMP analysis and Mössbauer spectroscopy shows that all samples contain vacancies at the M2 position, which can be expressed as a Ca-Eskola component (Ca_{0.5}□_{0.5}AlSi₂O₆). The amount of the Ca-Eskola component displays a positive correlation with the OH concentration, which confirms results from previous studies. The occurrence of precipitated quartz rods in some samples indicates that primary omphacite contained a larger Ca-Eskola component. Extrapolation of the observed trend-line for the Ca-Eskola and OH contents point to an original OH concentration around 1500 ppm H₂O for these samples. The high water contents observed in omphacite are considered to be linked to the UHP origin of the eclogite rocks.

Key words: Omphacite; Ca-Eskola; eclogite; UHP; infrared spectroscopy; Mössbauer spectroscopy.

Introduction

The pyroxenes are one of the nominally anhydrous mineral groups that have been shown to generally contain low but significant contents of hydrogen, bound in their crystal structures as OH⁻ ions. The amounts of hydrogen incorporated in pyroxene are considered to be related to both intrinsic factors, such as sample composition and defect chemistry, as well as to external

ones such as T , P_{tot} and $P_{\text{H}_2\text{O}}$ conditions, thereby reflecting the equilibration environment. During recent years, hydrogen contents in pyroxenes have been extensively explored to gain information from a range of geological environments, including water storage mechanisms and circulation in Earth's mantle (*e.g.* Ingrin & Skogby, 2000; Bolfan-Casanova, 2005; Peslier, 2010) as well as magmatic water contents in volcanic systems (*e.g.* Wade *et al.*, 2008; O'Leary *et al.*, 2010; Weis *et al.*, 2015).

The modes of hydrogen accommodation in clinopyroxene are not yet fully understood. However, most incorporation models (*e.g.* Andrut *et al.*, 2007) have suggested that OH preferentially occurs on the underbonded O2 position, with charge compensation provided either by vacancies at the M2 position or charge-deficient substitutions such as Al replacing Si at the tetrahedral site. Among the pyroxenes, omphacite has been shown to frequently accommodate relatively high concentrations of OH (Skogby *et al.*, 1990, Smyth *et al.*, 1991; Katayama & Nakashima, 2003; Katayama *et al.*, 2006; Koch-Müller *et al.*, 2004; 2007; Konzett *et al.*, 2008a), approaching close to 1000 ppm H_2O . These high contents appear to be coupled to formation of structural vacancies via the so-called Ca-Eskola (CaEs) component, $\text{Ca}_{0.5}\square_{0.5}\text{AlSi}_2\text{O}_6$, which has been shown to be essential for OH incorporation in omphacite. Such a relation was first reported by Smyth *et al.* (1991) for a series of jadeite-rich omphacites from South-African kimberlites, where the amount of M2 vacancies was shown to be correlated with the absorbance of the OH-bands in FTIR spectra, and hence water concentration. This trend was further supported by Katayama & Nakashima (2003), who also found a positive correlation for OH absorbance and calculated CaEs components in a series of clinopyroxenes from deeply subducted crust occurrences in the Kokchetav UHP metamorphic terrane. In an experimental study of hydroxyl solubility in synthetic jadeite and Na-rich clinopyroxene, Bromiley & Keppler (2004) concluded that solid solutions of jadeite with diopside and in particular CaEs components lead to a drastic increase of water solubility, and

that these compositional effects were substantially larger than those imposed by pressure and temperature. Additional support for the importance of the CaEs component was provided by Koch-Müller *et al.* (2004) for a series of omphacites from Yakutian kimberlite pipes.

Even though the studies mentioned above have clearly demonstrated that the OH content in omphacite is frequently correlated with the CaEs component, a full characterization of the amount of CaEs has generally not been established. This has been caused by lack of Fe valence determination, which is needed to calculate an appropriate CaEs (and vacancy) component, and has lead to underestimation and often negative values of the CaEs component when all Fe has been assumed as Fe²⁺. In order to increase the understanding of OH incorporation in omphacite and the role of the CaEs component, we have here investigated a series of omphacites from UHP eclogites by FTIR spectroscopy and microprobe analysis, as well as Mössbauer spectroscopy to fully characterize the cation contents of the structural formulae.

Geological background and petrography

The investigated eclogites come from the Pohorje Mountains in Slovenia, at the south-eastern margin of the Alps (Fig. 1). The Pohorje Mountains is mainly formed by metamorphic rocks of continental basement type, predominantly micaschists, gneisses, marbles, and metaquartzites (Mioč & Žnidarčič, 1977; Kirst *et al.*, 2010), intruded by granodioritic to tonalitic plutons and pegmatites in the Miocene (Altherr *et al.*, 1995; Fodor *et al.*, 2008; Trajanova *et al.*, 2008; Uher *et al.*, 2014). Eclogites, partly amphibolitised, occur in the south-eastern part of Pohorje, together with meta-ultramafic rocks of the Slovenska Bistrica Ultramafic Complex (SBUC; Hinterlechner-Ravnik *et al.*, 1991; Janák *et al.*, 2006; De Hoog *et al.*, 2009), metasedimentary gneisses and marbles.

The first evidence for UHP conditions was documented in kyanite-bearing eclogites (Janák *et al.*, 2004). Subsequently, UHP conditions were determined for garnet peridotites from SBUC (Janák *et al.*, 2006) and finally, diamond was found in kyanite and garnet-bearing gneisses (Janák *et al.*, 2015a) hosting UHP eclogites and garnet peridotites. The UHP metamorphism in the Pohorje area resulted from subduction of the continental crust during the Late Cretaceous time (Janák *et al.* 2004), documented by geochronological data (c.100-90 Ma; Thöni, 2002; Miller *et al.*, 2005; Janák *et al.*, 2009).

The studied eclogites are medium to coarse-grained, with macroscopically visible reddish garnet, pale-green omphacite, bluish kyanite and pale zoisite, partly amphibolitised with dark-green amphibole. Microscopic observations show that primary minerals – garnet, omphacite, kyanite and phengite are variably replaced by retrograde ones forming symplectites, i.e. diopside + plagioclase after omphacite, plagioclase + biotite after phengite and sapphirine + corundum + spinel + anorthite after kyanite. Polycrystalline quartz inclusions in garnet, omphacite and kyanite surrounded by radial cracks indicate breakdown of former coesite. The most striking feature of omphacite is tiny needles and rods of quartz (Fig. 2). They display a parallel orientation with the c-axis, indicating exsolution from a pre-existing, more silicic clinopyroxene. Geothermobarometry on the peak metamorphic assemblage garnet + omphacite + kyanite + phengite + quartz/coesite records pressure and temperature conditions of up to 3.5-3.7 GPa and 800-850 °C (Vrabec *et al.*, 2012). More details on the kyanite eclogites from Pohorje can be found in Janák *et al.* (2004), Sassi *et al.* (2004) or Vrabec *et al.* (2012), including unusually Cr-rich minerals in these eclogites - kyanite, Mg-staurolite and corundum (Janák *et al.*, 2015b).

The investigated samples come from 6 localities in Pohorje (Fig. 1): Jurišna Vas (JV4, PO6), Novak (NO1), Tinjska Gora (PO4), Visole (VI04), Vranjekov Vrh (PO1) and Nova Gora (NG1), see Vrabec *et al.* (2012) for a more detailed map and sample location.

Experimental methods

Infrared spectroscopy

All the seven omphacite samples were measured by Fourier transform infrared (FTIR) absorption spectroscopy to characterize their OH vibrational bands. The spectrometer system consisted of a Bruker Equinox 55 spectrometer equipped with a halogen lamp source, a CaF₂ beam-splitter, a wire-grid polarizer (KRS-5) and an InSb detector. The crystals were oriented by morphology and optical microscopy and polished on two sides parallel to (100) and (010). To avoid cracks and turbid regions, the 100 to 200 μm thick crystals sections were mounted on circular 100-200 μm apertures under the microscope. Polarized absorption spectra were then acquired in the three principal optical directions (α , β , and γ) in the wavenumber range 2000-5000 cm^{-1} with a resolution of 4 cm^{-1} .

To obtain absorption areas for the OH bands the measured spectra were fitted using the software Peakfit. A baseline subtraction was first applied before fitting with four Voigt-shaped bands that produced a good fit to the experimental spectra. Water concentrations were then calculated from the sum of the integrated absorption areas obtained in the α , β , and γ directions ($A_{\text{tot}}=A_{\alpha}+A_{\beta}+A_{\gamma}$) according to Beer's law using the calibrations of Koch-Müller *et al.* (2007), Libowitzky & Rossman (1997) and Bell *et al.* (1995).

Mössbauer spectroscopy

The samples were measured by Mössbauer spectroscopy in order to determine the oxidation state of iron, which is necessary for an accurate normalization of the structural formulae. Since the samples contained ubiquitous inclusions and turbid areas, the point-source technique (*e.g.* McCammon, 1994) was used. Small amounts (ca. 1-2 mg) of clear, inclusion-

free crystal fragments were selected under the microscope. The samples were finely ground, mixed with a thermoplastic resin and shaped to millimetre-sized cylindrical absorbers under mild heating. Mössbauer spectra were acquired using a conventional spectrometer system operated in constant-acceleration mode equipped with a ^{57}Co point source with a nominal activity of 10 mCi and an active area of 0.5 x 0.5 mm. The absorbers were mounted on strip tape and positioned close (< 1 mm) to the tip of the point source. Spectra were collected in 1024 channels over the velocity range -4.5 to 4.5 mms^{-1} , and were calibrated against an α -iron foil before folding and reduction to 256 channels. Spectral fitting was performed with the least-squares program MDA (Jernberg & Sundqvist, 1983), using a fitting model with two quadrupole doublets for Fe^{2+} and one doublet for Fe^{3+} .

Electron microprobe analysis

Electron microprobe analyses (EMPA) of the major elements (Al, Ti, Fe, Mg, Na, K, Si, Ca, Mn, Cr) were performed at the Department of Earth Sciences, Uppsala University using a FE-EPMA JXA-8530F JEOL superprobe. Between 10 to 30 spot analyses were performed on each sample using a beam current of 10 nA, an acceleration voltage of 15 kV and a beam diameter of $1\mu\text{m}$. A range of natural and synthetic compounds were used as standards: fayalite (Fe), periclase (Mg), pyrophanite (Mn, Ti) corundum (Al), wollastonite (Ca and Si), eskolaite (Cr), albite (Na) and orthoclase (K).

Results

The EMPA results show that the studied crystals are homogenous, whereas the compositions for the different samples show substantial variation (Table 1). The samples have rather typical omphacite compositions dominated by diopside (47-59 %) and jadeite (25-33 %) components,

with minor amounts also of hedenbergite (6-7 %), Ca-Tschermak (4-5 %), enstatite (3-4 %) and CaEs (3-5 %) components. In back-scatter electron images, some samples show the occurrence of micrometre-sized quartz-rods (Fig. 3), as previously described by Janák *et al.* (2004) and Vrabec *et al.* (2012) in other crystals partly from the same samples.

Polarized FTIR spectra of oriented omphacite crystals show intense absorption bands around 3470 and 3520 cm^{-1} , strongly polarized in the γ -direction (Fig. 4). Considerably weaker bands polarized in the α - and β -directions occur around 3620 cm^{-1} . For a few samples (*e.g.* NO1), additional weak but sharp bands occur around 3670 cm^{-1} , indicative of amphibole inclusions. These amphibole bands are stronger in spectra from regions close to cracks and grain boundaries, and in turbid regions. By masking off the IR-beam by small apertures (100-200 μm) such regions could be avoided. Using the molar absorptivity of 65 000 $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$ established for omphacite by Koch-Müller *et al.*, 2007, the recorded spectra correspond to water concentrations in the range 530 – 870 ppm H_2O (Table 1). Water concentrations calculated based on the wavenumber-dependent general calibration of Libowitzky & Rossman (1997) are in good agreement, with slightly higher values (up to 6 % higher). However, the calibration by Bell *et al.* (1995) results in concentrations which are approximately twice as high. Similar deviations were observed by Koch-Müller *et al.* (2004) for a series of omphacites from Yakutian kimberlite pipes. The Bell *et al.* (1995) calibration was based on an kimberlitic augite sample, which has considerably stronger bands at the higher wavenumbers (3620 cm^{-1}) than typical omphacite spectra, and the observed deviation is probably related to a wavenumber-dependence of the molar absorptivities. For the evaluation of the experimental data we have used the mineral-specific calibration of Koch-Müller *et al.*, 2007 which we consider to be that at present most accurate.

Mössbauer spectra were obtained by the point-source method for all samples, and could be fitted satisfactorily by the three-doublet fitting model mentioned above.

Representative spectra are displayed in Fig. 5. The obtained hyperfine parameters are well in line with previous studies of omphacite (*e.g.* Li *et al.*, 2005), and are listed in Table 2, together with assignments and absorption ratios. The results show that the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio vary substantially, from 0.14 to 0.29 for the sample set. In line with Koch-Müller *et al.* (2007), the two fitted Fe^{2+} doublets can be considered to be caused by Fe^{2+} in the M1 site (outer doublet) and M2 site (inner doublet). However, the lack of resolution for these two doublets introduces a large degree of uncertainty in the obtained Fe^{2+} distribution. In spite of this, the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios are well constrained by the asymmetry of the two main high- and low-velocity components in the measured spectra, as the Fe^{3+} contribution occurs entirely within the low-velocity component and are hence not affected by uncertainties in the Fe^{2+} distribution over the M1 and M2 sites.

Structural formulae were calculated based on 12 positive charges taking all type of cations into account, including the $\text{Fe}^{2+}/\text{Fe}^{3+}$ distribution obtained from Mössbauer spectroscopy and the hydrogen content obtained from FTIR spectroscopy (Table 1). Without exception, this lead to cation sums less than 4 (excluding H^+), which demonstrate the occurrence of cation vacancies. CaEs ($\text{Ca}_{0.5}\square_{0.5}\text{AlSi}_2\text{O}_6$) components were then calculated as $\text{CaEs} = 2 \times \text{vacancies per formula unit}$, and varied from 2.5 to 4.6 % for the studied samples.

Discussion

In evaluating intrinsic pyroxene water contents based on the intensity of OH-bands in IR-spectra, it is important to identify absorption bands from possible contaminants. These may be caused by fluid or melt inclusions, as well as inclusions of hydrous minerals. Among hydrous mineral inclusions, amphiboles have been shown to occur relatively frequently in clinopyroxenes, particularly in samples from metamorphic rocks (*e.g.* Veblen & Buseck,

1981; Skogby *et al.*, 1990). Fortunately, amphibole OH-bands normally have a characteristic signature consisting of relatively sharp bands in the 3625-3725 cm^{-1} region (*e.g.* Skogby & Rossman, 1991; Della Ventura *et al.*, 2003), and can hence easily be distinguished from intrinsic clinopyroxene OH-bands that occur at lower wavenumbers. More problematic, however, is the possible occurrence of certain nanometer-sized sheet silicates. As demonstrated by Koch-Müller *et al.* (2004) using TEM and synchrotron-IR, absorption bands in the range 3600-3624 cm^{-1} of omphacite spectra can be caused by sub-micrometer inclusions of clinochlore and amesite. In particular, this seems to be the case when strong bands occur in this range (*e.g.* Katayama & Nakashima, 2003), and if not identified, may lead to significant overestimation of the omphacite water contents. Nevertheless, weak bands that normally occur in the 3620 cm^{-1} range of omphacite spectra (Skogby *et al.*, 1990; Smyth *et al.*, 1991, Konzett *et al.*, 2008a) may still be caused by intrinsic OH. This is not unexpected since absorption bands in this range, with the same pleochroism ($A_\alpha, A_\beta \gg A_\gamma$), are typical for diopside as well as augite (*e.g.* Skogby, 2006) which both occur as significant components in normal omphacite compositions. Furthermore, Bromiley & Keppler (2004) observed a major band at 3613 cm^{-1} in spectra of synthetic jadeite and Na-rich clinopyroxene which they interpreted to be caused by OH coupled to M2-site vacancies. In the present study, the relatively weak bands in the 3620 cm^{-1} range were therefore included in the calculation of omphacite water contents. The contribution from these bands was however minor, amounting to 20-30 ppm H_2O for the studied samples.

In general, the OH contents are expected to increase with the T , P_{tot} and $P_{\text{H}_2\text{O}}$ conditions, related to an increased amount of vacancies formed by stabilization of the CaEs component. An increase in OH contents with equilibration pressure was also found by Katayama & Nakashima (2003) for a series of clinopyroxenes from the Kokchetav UHP metamorphic terrane. Experimental studies (*e.g.* Gasparik, 1986; Konzett *et al.*, 2008b) have

shown that the CaEs component in omphacite in addition to bulk composition is also largely controlled by temperature and pressure conditions. However, it should be noted that the OH content of omphacite is not merely linked to equilibration pressure conditions. In their study of omphacites from Yakutian kimberlite pipes, Koch-Müller *et al.* (2004) noted that samples from the highest pressures environments (*i.e.* diamond-bearing eclogite xenoliths) showed the lowest OH contents, which they interpreted to be caused by either low water activities during crystallisation or, alternatively, to hydrogen loss during the uplift process.

The CaEs component, and hence the amount of vacancies at the structural M2 site, display a positive correlation with the OH concentration in our samples (Fig. 6). This observation is in line with previous studies (Smyth *et al.*, 1991; Koch-Müller *et al.*, 2004; Katayama & Nikashima, 2003). Due to the determination of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios for the present study, the underestimation in calculation of the CaEs component, sometimes resulting in negative values, is here avoided. Although the regression line fitted to the experimental data points in Fig. 6 is associated with some uncertainty, the intercept with the y-axis (*i.e.* for CaEs = 0) indicates that an omphacite without the M2-vacancies may take up approximately 200 ppm H_2O , and that the water content thereafter will increase progressively with the amount of M2 vacancies. If the observed trend-line is extrapolated to the considerably higher CaEs components of up to 10 mol-% indicated by the composition of primary omphacite estimated from the modal content of the precipitated quartz rods mentioned above (Janák *et al.* 2004), an original water content of ca 1500 ppm H_2O is obtained. Due to the rather limited variation in OH contents and CaEs components for the studied samples, this extrapolation is associated with substantial uncertainty. However, the estimated content is in the similar range as that of ca 2000 ppm H_2O calculated by Smyth *et al.* (1991) for clinopyroxenes from South-African kimberlite samples, based on a vacancy-rich precursor composition reconstructed from exsolved garnet and kyanite.

In their study on hydroxyl contents in omphacite and omphacitic clinopyroxenes from the Siberian platform, Koch-Müller *et al.* (2004) observed a pronounced correlation between the absorbance of the OH-band at 3650-3540 cm⁻¹ and the amount of Al in the tetrahedral site. Such a correlation is not obvious for our sample series, however, the much more limited variation in Al contents for our sample set (Table 1) obscures a possible trend.

The OH concentrations here obtained, ranging from 530-870 ppm H₂O, are among the higher reported for omphacite, and somewhat higher than those reported by Konzett *et al.* (2008a) for three omphacite samples from Saualpe and Pohorje eclogites. Previous studies have indeed reported even higher concentrations, but some of these were based on calibrations that now have become obsolete (Skogby *et al.*, 1990; Smyth *et al.*, 1991) or on FTIR spectra with OH bands that appear to be associated with hydrous phases (Katayama & Nakashima, 2003). The high OH concentrations observed for the Pohorje omphacites are in line with equilibration under hydrous UHP conditions.

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437 **Title of tables**

438 Table 1. Chemical composition of omphacite based on microprobe and FTIR analyses.

439 Table 2. Mössbauer hyperfine parameters for omphacite.

440

441 Table 1. Chemical composition of omphacite based on microprobe and FTIR analyses.

	NO1	PO6	JV4	PO4	VI04	NG1	PO1
<i>Wt-% oxides</i>							
SiO ₂	55.19	55.36	54.87	55.52	55.27	55.42	55.35
Al ₂ O ₃	7.78	8.36	8.33	9.76	8.84	8.76	9.24
TiO ₂	0.13	0.13	0.12	0.13	0.12	0.13	0.12
Cr ₂ O ₃	0.28	0.05	0.11	0.02	0.18	0.13	0.15
MgO	12.39	11.75	11.63	10.56	11.19	11.47	10.98
FeO	1.69	2.00	1.93	2.01	1.86	2.04	1.86
Fe ₂ O ₃	0.47	0.60	0.65	0.79	0.83	0.38	0.69
MnO	0.02	0.03	0.02	0.07	0.03	0.02	0.02
CaO	18.91	18.28	18.08	16.53	17.50	18.01	17.45
Na ₂ O	3.59	3.99	3.87	4.77	4.36	4.04	4.41
H ₂ O	0.0535	0.0549	0.0636	0.0702	0.0769	0.0854	0.0866
Total	100.52	100.60	99.67	100.21	100.26	100.49	100.37
<i>Structural formulae normalised to 12 charges</i>							
Si	1.952	1.954	1.954	1.957	1.954	1.955	1.952
Al	0.324	0.348	0.349	0.406	0.368	0.364	0.384
Ti	0.004	0.004	0.004	0.004	0.004	0.004	0.004
Cr	0.008	0.001	0.003	0.001	0.005	0.004	0.004
Mg	0.654	0.618	0.617	0.555	0.589	0.603	0.578
Fe ²⁺	0.065	0.076	0.074	0.077	0.071	0.078	0.070
Fe ³⁺	0.016	0.020	0.022	0.027	0.028	0.013	0.024
Mn	0.001	0.001	0.001	0.003	0.001	0.001	0.001
Ca	0.717	0.691	0.690	0.624	0.663	0.681	0.659
Na	0.247	0.273	0.267	0.325	0.299	0.276	0.302
Total	3.986	3.987	3.981	3.977	3.982	3.978	3.978
H ₂ O (ppm)	535	549	636	702	769	854	866
<i>End-member components</i>							
Di	0.586	0.549	0.543	0.474	0.515	0.537	0.510
Jd	0.247	0.274	0.268	0.327	0.300	0.278	0.303
Hd	0.058	0.068	0.065	0.065	0.062	0.069	0.062
CaTs	0.048	0.046	0.046	0.043	0.046	0.045	0.048
En	0.034	0.033	0.039	0.045	0.034	0.038	0.034
Ca-Esk	0.027	0.025	0.038	0.046	0.036	0.043	0.043

443 Fe valence ratios determined by Mössbauer spectroscopy.

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445

Table 2. Mössbauer hyperfine parameters for omphacite.

Sample	Assignment	cs	dq	fwhm	Int
NO1	Fe ²⁺ (1)	1.17	2.49	0.51	36.9
	Fe ²⁺ (2)	1.14	1.95	0.50	43.0
	Fe ³⁺	0.41	0.43	0.55	20.1
PO6	Fe ²⁺ (1)	1.16	2.56	0.50	30.6
	Fe ²⁺ (2)	1.13	2.01	0.51	48.2
	Fe ³⁺	0.41	0.40	0.52	21.2
JV4	Fe ²⁺ (1)	1.17	2.58	0.53	30.4
	Fe ²⁺ (2)	1.12	2.04	0.52	46.4
	Fe ³⁺	0.42	0.44	0.51	23.3
PO4	Fe ²⁺ (1)	1.14	2.59	0.52	36.3
	Fe ²⁺ (2)	1.17	1.94	0.51	37.6
	Fe ³⁺	0.41	0.46	0.52	26.1
VI04	Fe ²⁺ (1)	1.17	2.58	0.52	32.7
	Fe ²⁺ (2)	1.14	2.00	0.53	38.6
	Fe ³⁺	0.40	0.42	0.62	28.7
NG1	Fe ²⁺ (1)	1.16	2.61	0.50	31.4
	Fe ²⁺ (2)	1.15	1.97	0.51	54.2
	Fe ³⁺	0.42	0.41	0.53	14.5
PO1	Fe ²⁺ (1)	1.16	2.63	0.58	34.5
	Fe ²⁺ (2)	1.14	1.98	0.57	40.4
	Fe ³⁺	0.39	0.47	0.59	25.1

cs=centroid shift, dq=quadrupole splitting, fwhm=full width at half maximum, Int=percentage of total absorption area.

Figure captions

Fig. 1. Simplified geological map of Pohorje and adjacent areas (modified from Mioč & Žnidarčič 1997), showing location of investigated rocks (white stars) near Slovenska Bistrica.

Fig. 2. Microphotograph of omphacite (Omp) with quartz (Qz) rods and inclusion surrounded by radial cracks. Optical microscope, transmitted light, crossed polars. Sample PO6.

Fig. 3. Back-scatter electron image of omphacite (sample PO6) showing crystallographically oriented quartz-rods. Length of arrow 20 μm .

Fig. 4. Polarized FTIR spectra of omphacite normalized to 1 mm thickness. Spectra are vertically off-set for clarity. Sinusoidal shortwave variations are interference fringes. Note weak bands around 3670 cm^{-1} in the α and γ directions for sample NO1 caused by amphibole inclusions.

Fig. 5. Room-temperature Mössbauer spectra of omphacite with fitted sub-spectra. Blue and red sub-spectra are assigned to Fe^{2+} , green sub-spectra are assigned to Fe^{3+} .

Fig. 6. Plot of omphacite water content as a function of Ca-Eskola ($\text{Ca}_{0.5}\square_{0.5}\text{AlSi}_2\text{O}_6$) component.

Fig. 1

Fig. 2

Fig. 3.

Fig. 4.

514

515 Fig. 5.

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518 Fig. 6.

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