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## Distribution of Fe among octahedral sites and its effect on the crystal structure of pumpellyite

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**Abstract** Two pumpellyites with the general formula  $W_8X_4Y_8Z_{12}O_{56-n}(OH)_n$  were studied using  $^{57}\text{Fe}$  Mössbauer spectroscopic and X-ray Rietveld methods to investigate the relationship between the crystal chemical behavior of iron and structural change. The samples are ferrian pumpellyite-(Al) collected from Mitsu and Kouragahana, Shimane Peninsula, Japan. Rietveld refinements gave Fe(*X*):Fe(*Y*) ratios (%) of 41.5(4):58.5(4) for the Mitsu pumpellyite and 46(1):54(1) for the Kouragahana pumpellyite, where Fe(*X*) and Fe(*Y*) represent Fe content at the *X* and *Y* sites, respectively. The Mössbauer spectra consisted of two  $\text{Fe}^{2+}$  and two  $\text{Fe}^{3+}$  doublets for the Mitsu pumpellyite, and one  $\text{Fe}^{2+}$  and two  $\text{Fe}^{3+}$  doublets for the Kouragahana pumpellyite. In terms of the area ratios of the Mössbauer doublets and the Fe(*X*):Fe(*Y*) ratios determined by the Rietveld refinements,  $\text{Fe}^{2+}(\text{X}):\text{Fe}^{3+}(\text{X}):\text{Fe}^{3+}(\text{Y})$  ratios are determined to be 22:14:64 for the Mitsu pumpellyite and 27:8:65 for the Kouragahana pumpellyite. By applying the  $\text{Fe}^{2+}:\text{Fe}^{3+}$ -ratio determined by the Mössbauer analysis and the site occupancies of Fe at the *X* and *Y* sites given by the Rietveld method together with chemical analysis, the resulting formula of the Mitsu and Kouragahana pumpellyites are established as  $\text{Ca}_8(\text{Fe}_{0.88}^{2+}\text{Mg}_{0.68}\text{Fe}_{0.77}^{3+}\text{Al}_{1.66})_{\Sigma 3.99}(\text{Al}_{5.67}\text{Fe}_{2.34}^{3+})_{\Sigma 8.01}\text{Si}_{12}\text{O}_{42.41}(\text{OH})_{13.59}$  and  $\text{Ca}_8(\text{Mg}_{1.24}\text{Fe}_{0.65}^{2+}\text{Fe}_{0.46}^{3+}\text{Al}_{1.66})_{\Sigma 4.01}(\text{Al}_{6.71}\text{Fe}_{1.29}^{3+})_{\Sigma 8.00}\text{Si}_{12}\text{O}_{42.14}(\text{OH})_{13.86}$ , respectively. Mean *Y*–O distances and volumes of the  $\text{YO}_6$  octahedra increase with increasing mean ionic radii, i.e., the  $\text{Fe}^{3+} \rightarrow \text{Al}$  substitution at the *Y* site. However, change of the sizes of  $\text{XO}_6$  octahedra against the mean ionic radii at the *X* site is not distinct, and tends to depend on the volume change of the  $\text{YO}_6$  octahedra.

Thus, the geometrical change of the  $\text{YO}_6$  octahedra with  $\text{Fe}^{3+} \rightarrow \text{Al}$  substitution at the *Y* site is essential for the structural changes of pumpellyite. The expansion of the  $\text{YO}_6$  octahedra by the ionic substitution of  $\text{Fe}^{3+}$  for Al causes gradual change of the octahedra to more symmetrical and regular forms.

**Keywords** Pumpellyite · Iron · X-ray Rietveld analysis · Mössbauer spectroscopy

### Introduction

Pumpellyite is a rock-forming mineral occurring in low-grade metamorphic rocks and hydrothermally altered rocks. Pumpellyite group minerals have monoclinic  $A2/m$  symmetry, consist of isolated  $[\text{SiO}_4]$  tetrahedral and disilicate  $[\text{Si}_2\text{O}_6(\text{OH})]$  groups, and contain two symmetrically independent chains of octahedron, oriented parallel to the *b*-axis. The general formula of pumpellyite is represented as  $W_8X_4Y_8Z_{12}O_{56-n}(\text{OH})_n$  (Passaglia and Gottardi 1973). The seven-coordinated *W* site is primarily occupied by Ca, whereas the tetrahedral *Z* site is occupied by Si. Both the *X* and *Y* sites are octahedral, but the octahedra of the *X* site are larger than those of the *Y* site. The *X* site is occupied by both divalent and trivalent cations including  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Cr}^{3+}$ , whereas the *Y* site is occupied only by trivalent cations such as  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ . Pumpellyite group minerals are named after the most dominant *Y* site cation (Passaglia and Gottardi 1973); pumpellyite [with Al(*Y*)] (Palache and Vassar 1925), julgoldite [with  $\text{Fe}^{3+}(\text{Y})$ ] (Moore 1971), shuiskite [with  $\text{Cr}^{3+}(\text{Y})$ ] (Ivanov et al. 1981), and okhotskite [with  $\text{Mn}^{3+}(\text{Y})$ ] (Togari and Akasaka 1987). Recently, a  $\text{V}^{3+}$ -dominant member of pumpellyite group was approved as a new mineral (IMA No. 2005-018) by the Commission on New Minerals and Mineral Names.

Although iron cations in pumpellyite group minerals commonly exist both as  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , their oxidation state and distribution have not been determined in many

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cases due to the difficulty in the determination of Fe oxidation states and site occupancies by conventional chemical analysis. Artioli and Geiger (1994) studied Fe-rich pumpellyites from Keweenaw, Michigan (USA) and Bulla (Italy) using X-ray Rietveld and Mössbauer methods, and concluded that  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were distributed exclusively at the *X* and *Y* sites, respectively. In contrast, Akasaka et al. (1997) analyzed the Mössbauer spectra of Japanese Fe-rich pumpellyites from Tokoro (Hokkaido) and Mitsu (Shimane) and assigned  $\text{Fe}^{2+}$  to the *X* and *W* sites and  $\text{Fe}^{3+}$  to the *X* and *Y* sites, based on an assignment scheme differing from that of Artioli and Geiger (1994). Artioli et al. (2003) recently investigated julgoldite-( $\text{Fe}^{3+}$ ) from Bombay (India) using synchrotron X-ray Rietveld and  $^{57}\text{Fe}$  Mössbauer methods, and confirmed the distribution of  $\text{Fe}^{3+}$  at both the *X* and *Y* sites, which is consistent with the result by Akasaka et al. (1997). However, their  $\text{Fe}^{3+}$  Mössbauer doublets assignment model differs from those used by Artioli and Geiger (1994) and Akasaka et al. (1997). Moreover, their result raised a several problems for pumpellyite crystal chemistry. Firstly, 95% of the *X* site in the Bombay julgoldite was occupied by trivalent cations. This value deviates considerably from the common ratio (1:1) of divalent and trivalent cations at the *X* site. Secondly, preferential distributions of smaller  $\text{Al}^{3+}$  and larger  $\text{Fe}^{3+}$  in the larger *X* and smaller *Y* sites, respectively, contradict the general scheme of cation distribution in common pumpellyite group minerals formulated by Passaglia and Gottardi (1973).

We reinvestigated Fe-rich pumpellyites from Mitsu and Kouragahana, Shimane Peninsula, Japan to solve the problem of differing of  $^{57}\text{Fe}$  Mössbauer doublets assignment schemes outlined above, and to examine the crystal chemical behavior of Fe in pumpellyite group minerals. We determined the oxidation states and the site occupancies of Fe using  $^{57}\text{Fe}$  Mössbauer and X-ray Rietveld methods, respectively. This paper describes the crystal structures of the Mitsu and Kouragahana Fe-rich pumpellyites and our results for the assignment of  $^{57}\text{Fe}$  Mössbauer  $\text{Fe}^{3+}$  doublets at the *X* and *Y* sites. The relationship between Fe distributions at the *X* and *Y* sites and structural changes is also discussed. In this study, we classified the Mitsu and Kouragahana Fe-rich pumpellyites as pumpellyite-(Al). Hereafter, the pumpellyites from Mitsu and Kouragahana are described as 'MTS' and 'KGH', respectively.

## Experimental methods

### Sample preparation

The MTS and KGH were collected from hydrothermally altered gabbroic or dolerite sills, cropping out at Shimane Peninsula, Japan. Their occurrences of the Fe-rich pumpellyite and the associated minerals have been described by Kano et al. (1986) and Akasaka et al. (1997, 2003). In the pumpellyite-dominant parts of the samples,

needles of pumpellyite crystals form dark green to green cauliflower-like branches up to 0.5 mm in diameter. Crystal aggregates also occur. They are associated with prehnite, calcite, and augite. The pumpellyite aggregates were manually crushed down to grains 0.25–0.5 mm in diameter. Pumpellyite-dominant grains were then separated using a Franz Isodynamic separator. They were further purified by handpicking under a microscope, and treated with dilute HCl solution to remove calcite. The separated grains were crushed further to produce grains 100–150  $\mu\text{m}$  in diameter, and the above purification procedures repeated. Purity of the sample was then confirmed by X-ray powder diffraction analysis.

### Chemical analysis

Chemical compositions of the samples were determined using a JEOL JXA-8800M electron probe microanalyzer operated at an accelerating voltage of 15 kV, with beam current of  $2.00 \times 10^{-8}$  A and beam diameter of 1  $\mu\text{m}$ . The standards used were natural wollastonite for Si and Ca, synthetic  $\text{TiO}_2$  for Ti, synthetic spinel for Al and Mg, synthetic  $\text{Cr}_2\text{O}_3$  for Cr, synthetic  $\text{Ca}_3\text{V}_2\text{O}_8$  for V, synthetic hematite for Fe, synthetic MnO for Mn, synthetic NiO for Ni and natural anorthoclase for Na and K. Four natural minerals (clinopyroxene, kaersutite, pyrope, and uvarovite) with known compositions were also used as working standards to monitor the precision and accuracy of the analyses. The ZAF method was used for data correction for all elements.

### X-ray powder diffraction data collection and Rietveld analysis

Samples were ground manually under alcohol in an agate mortar and pestle until the resultant particle size was less than 5  $\mu\text{m}$ . The powdered sample was then mounted on a glass sample holder with a  $20 \times 15 \times 0.5$  mm<sup>3</sup> cavity. Mounting for intensity profile collections was made by loading the powder from the front of the holder. Following the method of Raudsepp et al. (1990), a straightedge was used to level the sample surface to that of the holder. The surface was then finely serrated with a razor blade. This technique randomizes the orientation of any anisotropic crystals that are aligned during filling, while maintaining a generally flat surface. The quality of the mounted samples was assessed based on the X-ray rocking curves ( $\omega$ -scan) for the (115) pumpellyite. These were measured using a RIGAKU RINT automated X-ray powder diffractometer with a normal-focus Cu X-ray tube operated at 35 kV and 25 mA. The instrument was configured with a Bragg–Brentano goniometer equipped with incident- and diffracted-beam soller slits,  $0.05^\circ$  divergence slit, opening of anti-scatter and receiving slits, and a curved graphite diffracted-beam monochromator. Rocking curve profiles at  $30.680^\circ$   $2\theta$  were taken between  $10.340$

and  $20.340^\circ \theta$ , with a step interval of  $0.01^\circ$  and counting time of 5 s/step. The rocking curves obtained were smooth, indicating that the samples were fine-grained and uniform in size.

In collecting step-scan powder diffraction data for the Rietveld analysis, we employed the X-ray powder diffractometer described above equipped with incident- and diffracted-beam soller slits,  $1^\circ$  divergence and anti-scatter slits, and a 0.15 mm receiving slit. The normal-focus Cu X-ray tube was operated at 40 kV and 25 mA. The profiles were taken between  $5.00$  and  $150.00^\circ 2\theta$  with a step interval of  $0.02^\circ 2\theta$ . Counting times of MTS and KGH were 7 and 6 s/step, respectively.

The crystal structures of the pumpellyites were refined using the RIETAN-2000 program of Izumi and Ikeda (2000). Single crystal X-ray data for pumpellyite (Yoshiasa and Matsumoto 1985) was used as the initial parameters for the Rietveld refinement in this study. The cell parameters of the pumpellyites determined using a unit-cell parameter refinement program in the RIGAKU RINT system were used as initial values of the Rietveld analysis. The peaks were defined using the ‘‘Split Pearson VII function’’ of Toraya (1990) combined with profile relaxation. An asymmetric parameter is built into this profile function. Details of the profile functions are given by Izumi and Ikeda (2000). Nonlinear least-squares calculation using the Marquardt method was followed by the conjugate-direction method to check convergence at local minima (Izumi 1993). Preferred orientation was corrected using the March-Dollase function (Dollase 1986).

### $^{57}\text{Fe}$ Mössbauer spectroscopy

The  $^{57}\text{Fe}$  Mössbauer spectra of the pumpellyites were measured at room temperature, using 370 MBq  $^{57}\text{Co}$  in Pd as a source. The absorbers were about 300 mg of finely ground samples. The Mössbauer data were obtained using a constant acceleration spectrometer fitted with a 1,024 channel analyzer. The isomer shift was referred to a standard metallic iron foil, which was also used to calibrate Doppler velocity. The spectra were fitted to Lorentzians using the least squares method, with line width and intensities constrained to be equal at each site. The QBMOSS program of Akasaka and Shinno (1992) was used for computer analysis. The quality of the fit was judged using the  $\chi^2$  value and the standard deviations of the Mössbauer parameters.

## Results

### Chemical composition

Table 1 gives the average chemical compositions of MTS ( $n=17$ ) and KGH ( $n=34$ ), where  $n$  represents number of analytical data. Contents of  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_3$ ,

**Table 1** Average chemical compositions of the pumpellyite samples ( $n$  number of data)

Sample code	MTS		KGH	
	Mitsu, Shimane Peninsula		Kouragahana, Shimane Peninsula	
Locality				
	$n=17$		$n=34$	
	wt. %	s. d.	wt. %	s. d.
$\text{SiO}_2$	36.20	0.36	37.86	0.60
$\text{Al}_2\text{O}_3$	18.55	0.51	21.76	0.74
$\text{V}_2\text{O}_3$	ND		0.07	0.07
$\text{Fe}_2\text{O}_3^a$	15.99 <sup>b</sup>	0.64	9.93 <sup>c</sup>	0.93
MnO	0.17	0.07	0.06	0.03
MgO	1.36	0.19	2.56	0.40
CaO	22.46	0.31	22.91	0.47
$\text{Na}_2\text{O}$	0.10	0.04	ND	
	94.83		95.15	
$\Sigma$ cations = 32				
Si	12.00	0.07	12.18	0.12
Al	7.25	0.16	8.25	0.25
$\text{Fe}^{3+}$	3.99	0.16	2.40	0.24
$\text{V}^{3+}$			0.02	0.02
$\text{Mn}^{2+}$	0.05	0.01	0.02	0.01
Mg	0.67	0.10	1.23	0.11
Ca	7.98	0.07	7.90	0.11
Na	0.06	0.01		

<sup>a</sup>Total Fe as  $\text{Fe}_2\text{O}_3$

<sup>b</sup>The  $\text{Fe}^{2+}:\text{Fe}^{3+}$ -ratio given by Mössbauer method is 0.22:0.78:  $\text{Fe}^{2+}=0.88$ ,  $\text{Fe}^{3+}=3.11$  apfu;  $\text{FeO}=3.17$ ,  $\text{Fe}_2\text{O}_3=12.47$  wt. %

<sup>c</sup>The  $\text{Fe}^{2+}:\text{Fe}^{3+}$ -ratio given by Mössbauer method is 0.27:0.73:  $\text{Fe}^{2+}=0.65$ ,  $\text{Fe}^{3+}=1.75$  apfu;  $\text{FeO}=2.41$ ,  $\text{Fe}_2\text{O}_3=7.25$  wt. %

$\text{Cr}_2\text{O}_3$ , NiO, and  $\text{K}_2\text{O}$  in MTS and  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ , NiO,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  in KGH were less than the EPMA detection limits, and hence were neglected. Numbers of cations were calculated from the analytical data on the basis of 32 total cations. Although Fe is tabulated as total  $\text{Fe}_2\text{O}_3$  (15.99 wt.%) in MTS to display the standard deviation of Fe content ( $\pm 0.64$  wt.%), the  $\text{Fe}^{2+}:\text{Fe}^{3+}$ -ratio given by the Mössbauer analysis was 0.22:0.78, corresponding to  $\text{FeO}=3.17$  and  $\text{Fe}_2\text{O}_3=12.47$  wt.%. On the other hand, Fe content of KGH is  $10.21 \pm 0.93$   $\text{Fe}_2\text{O}_3$  wt.%, and the  $\text{Fe}^{2+}:\text{Fe}^{3+}$ -ratio was 0.27:0.73, corresponding to  $\text{FeO}=2.48$  and  $\text{Fe}_2\text{O}_3=7.45$  wt.%. Following Passaglia and Gottardi (1973), the formulae of MTS and KGH were calculated from the average compositions yielding:  $(\text{Ca}_{7.98}\text{Na}_{0.06})_{\Sigma 8.04}(\text{Fe}_{2.36}^{3+}\text{Fe}_{0.88}^{2+}\text{Mg}_{0.67}\text{Mn}_{0.05}^{2+})_{\Sigma 3.96}(\text{Al}_{7.25}\text{Fe}_{0.75}^{3+})_{\Sigma 8.00}\text{Si}_{12.00}\text{O}_{42.30}(\text{OH})_{13.70}$  and  $(\text{Ca}_{7.90}\text{Mn}_{0.02}^{2+}\text{Fe}_{0.08}^{2+})_{\Sigma 8.00}(\text{Fe}_{1.75}^{3+}\text{Fe}_{0.57}^{2+}\text{Mg}_{1.23}\text{Al}_{0.25}\text{V}_{0.02}^{3+})_{\Sigma 3.82}\text{Al}_{8.00}\text{Si}_{12.18}\text{O}_{42.38}(\text{OH})_{13.62}$ , respectively, where the OH contents were calculated based on the charge balance.

### Rietveld analysis

Details of data collection for the Rietveld analyses, the refined unit-cell parameters,  $R$ -factors, goodness-of-fit ( $S = R_{\text{wp}}/R_e$ ) and the Durbin–Watson  $d$  statistic are

**Table 2** Data collection and details of structure refinement

Sample code	MTS	KGH
Max. intensity (counts)	6,123	5,567
Space group	$A2/m$	
$a$ (Å)	8.8461(2)	8.8335(3)
$b$ (Å)	5.9657(2)	5.9381(3)
$c$ (Å)	19.2016(5)	19.1659(6)
$\beta$ (°)	97.462(2)	97.446(2)
$V$ (Å <sup>3</sup> )	1004.75(5)	996.85(6)
$Z$	4	4
$R_B$ (%)	3.55	1.92
$R_F$ (%)	1.24	0.82
$R_p$ (%)	6.07	5.78
$R_{wp}$ (%)	7.93	7.62
$R_e$ (%)	5.92	6.26
$S$	1.340	1.218
$D-W d$	1.174	1.394
Mass fraction		
Pumpellyite	1.000	0.760
Augite		0.125
Prehnite		0.112

Data collection: Step interval ( $^{\circ}2\theta$ ) 5–150°, step 0.02°

Details of structure refinement: Numbers within parentheses represent the standard deviations ( $1\sigma$ ) and refer to the last digit

$R_B$   $R$ -Bragg factor,  $R_F$   $R$ -structure factor,  $R_p$   $R$ -pattern,  $R_{wp}$   $R$ -weighted pattern,  $R_e$   $R$ -expected,  $S$  ( $= R_{wp}/R_e$ ) Goodness of fit (Young 1993),  $D-W d$  Durbin–Watson  $d$ -statistic (Hill and Flack 1987)

**Table 3** Site occupancies in  $W$ ,  $X$ , and  $Y$  sites

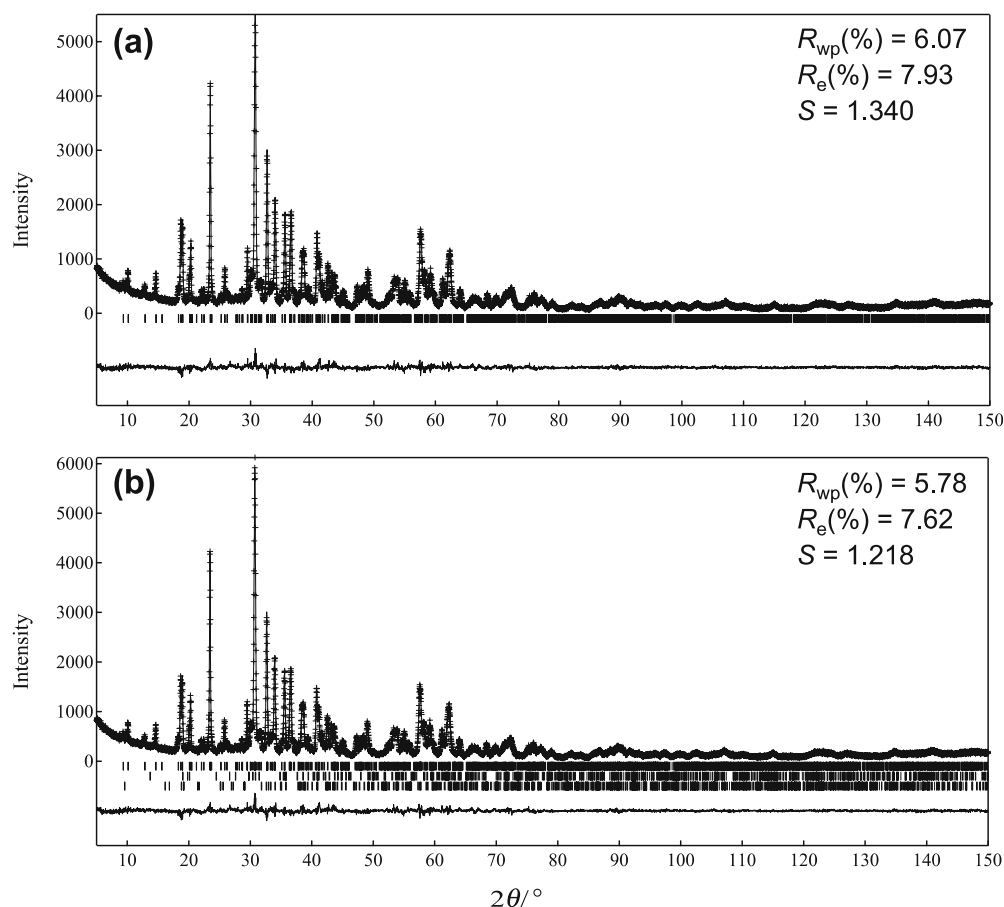
Site	MTS	KGH
$W1$	Ca 1.00	Ca 1.00
$W2$	Ca 1.00	Ca 1.00
$X$	Mg 0.17	Mg 0.31
	Fe 0.415(4)	Fe 0.278(6)
	Al 0.415(4)	Al 0.415(6)
$Y$	Fe 0.292(2)	Fe 0.161(3)
	Al 0.709(2)	Al 0.839(3)

The site occupancies of Ca and Mg were fixed by the chemical composition. Estimated standard deviations are in parentheses ( $1\sigma$ )

listed in Table 2. The refined powder patterns of MTS and KGH are given in Fig. 1a, b, respectively, indicating that the former is composed solely of pumpellyite and the latter is associated with small amounts of augite and prehnite. Thus, in the Rietveld refinement of KGH, augite and prehnite were added to improve  $R$ -factors, where structural parameters of augite after Peacor (1967) and prehnite after Akasaka et al. (2003) were used as the initial parameters. Errors are shown by estimated standard deviations of  $1\sigma$  (esd's).

In the structural refinements, Ca was fixed at the  $W$  site, Mg at the  $X$  site and Si at the  $Z$  site based on

**Fig. 1** Rietveld refinement plots for the Mitsu (a) and Kouragahana (b) pumpellyite-(Al). The Mitsu pumpellyite sample (MTS) was refined with single phase pumpellyite and the Kouragahana pumpellyite sample (KGH) with pumpellyite, augite, and prehnite. The crosses are the observed data, the solid line is the calculated pattern, and the vertical bars mark all possible Bragg reflections (Cu  $K\alpha_1$  and  $K\alpha_2$ ). In the plot of KGH (b), the vertical bars of the top, middle, and bottom correspond to the Bragg reflections of pumpellyite, augite, and prehnite, respectively. The difference between the observed and calculated patterns is shown at the bottom



**Table 4** Refined atomic positions

Atom	neq <sup>a</sup>	<i>W</i> <sup>b</sup>		MTS	KGH
O1	8	8 <i>j</i>	<i>x</i>	0.1213(6)	0.1424(8)
			<i>y</i>	0.236(1)	0.230(2)
			<i>z</i>	0.0737(3)	0.0730(4)
			<i>B</i>	0.4(2)	0.8(2)
O2	8	8 <i>j</i>	<i>x</i>	0.2578(8)	0.261(1)
			<i>y</i>	0.230(1)	0.234(1)
			<i>z</i>	0.2469(3)	0.2473(4)
			<i>B</i>	0.4	0.8
O3	8	8 <i>j</i>	<i>x</i>	0.3669(6)	0.3628(8)
			<i>y</i>	0.221(1)	0.231(2)
			<i>z</i>	0.4169(3)	0.4153(4)
			<i>B</i>	0.4	0.8
O4	4	4 <i>i</i>	<i>x</i>	0.1286(9)	0.126(1)
			<i>y</i>	1/2	1/2
			<i>z</i>	0.4425(5)	0.4436(6)
			<i>B</i>	0.4	0.8
O5	4	4 <i>i</i>	<i>x</i>	0.132(1)	0.137(1)
			<i>y</i>	0	0
			<i>z</i>	0.4592(5)	0.4584(6)
			<i>B</i>	0.4	0.8
O6	4	4 <i>i</i>	<i>x</i>	0.3664(9)	0.3650(9)
			<i>y</i>	1/2	1/2
			<i>z</i>	0.0463(5)	0.0459(5)
			<i>B</i>	0.4	0.8
O7	4	4 <i>i</i>	<i>x</i>	0.3730(9)	0.377(1)
			<i>y</i>	0	0
			<i>z</i>	0.0373(5)	0.0365(6)
			<i>B</i>	0.4	0.8
O8	4	4 <i>i</i>	<i>x</i>	0.0352(9)	0.039(1)
			<i>y</i>	0	0
			<i>z</i>	0.1786(5)	0.1799(3)
			<i>B</i>	0.4	0.8
O9	4	4 <i>i</i>	<i>x</i>	0.481(1)	0.485(1)
			<i>y</i>	1/2	1/2
			<i>z</i>	0.1743(5)	0.1750(6)
			<i>B</i>	0.4	0.8
O10	4	4 <i>i</i>	<i>x</i>	0.0712(9)	0.071(1)
			<i>y</i>	0	0
			<i>z</i>	0.3187(5)	0.3168(6)
			<i>B</i>	0.4	0.8
O11	4	4 <i>i</i>	<i>x</i>	0.5053(8)	0.512(1)
			<i>y</i>	1/2	1/2
			<i>z</i>	0.3155(5)	0.3144(6)
			<i>B</i>	0.4	0.8
<i>W</i> 1	4	4 <i>i</i>	<i>x</i>	0.2545(4)	0.2538(4)
			<i>y</i>	1/2	1/2
			<i>z</i>	0.3399(2)	0.3401(2)
			<i>B</i>	0.9(2)	0.5(2)
<i>W</i> 2	4	4 <i>i</i>	<i>x</i>	0.1881(3)	0.1870(4)
			<i>y</i>	1/2	1/2
			<i>z</i>	0.1544(2)	0.1557(2)
			<i>B</i>	1.0(2)	1.4(3)
<i>X</i>	4	4 <i>f</i>	<i>x</i>	1/2	1/2
			<i>y</i>	1/4	1/4
			<i>z</i>	1/4	1/4
			<i>B</i>	0.6(2)	1.4(3)
<i>Y</i>	8	8 <i>j</i>	<i>x</i>	0.2534(3)	0.2540(4)
			<i>y</i>	0.2510(8)	0.249(1)
			<i>z</i>	0.4946(1)	0.4956(2)
			<i>B</i>	0.6(2)	0.8(2)
Si1	4	4 <i>i</i>	<i>x</i>	0.0570(5)	0.0531(7)
			<i>y</i>	0	0
			<i>z</i>	0.0922(3)	0.0911(3)
			<i>B</i>	0.8(2)	0.9(3)
Si2	4	4 <i>i</i>	<i>x</i>	0.1638(5)	0.1644(5)
			<i>y</i>	0	0
			<i>z</i>	0.2496(2)	0.2495(3)

**Table 4** (Contd.)

Atom	neq <sup>a</sup>	<i>W</i> <sup>b</sup>		MTS	KGH
Si3	4	4 <i>i</i>	<i>B</i>	0.4(2)	0.5(2)
			<i>x</i>	0.4623(6)	0.4645(6)
			<i>y</i>	0	0
			<i>z</i>	0.4017(3)	0.4026(3)
			<i>B</i>	0.9(2)	0.3(2)

Estimated standard deviations are in parentheses ( $1\sigma$ )<sup>a</sup>Multiplicity<sup>b</sup>Wyckoff letter**Table 5** Selected interatomic distances (Å) and angles (°)

	MTS	KGH
<i>W</i> 1–O2 (×2)	2.409(6)	2.384(7)
<i>W</i> 1–O3 (×2)	2.360(6)	2.278(9)
<i>W</i> 1–O4	2.386(10)	2.41(1)
<i>W</i> 1–O8	2.541(8)	2.57(1)
<i>W</i> 1–O11	2.327(8)	2.40(1)
Mean	2.399(7)	2.386(9)
<i>W</i> 2–O1 (×2)	2.212(7)	2.25(1)
<i>W</i> 2–O2 (×2)	2.418(6)	2.387(8)
<i>W</i> 2–O6	2.766(9)	2.79(1)
<i>W</i> 2–O9	2.566(9)	2.61(1)
<i>W</i> 2–O10	2.416(8)	2.40(1)
Mean	2.430(7)	2.44(1)
<i>X</i> –O2 (×2)	2.139(7)	2.109(9)
<i>X</i> –O9 (×2)	2.074(7)	2.058(8)
<i>X</i> –O11 (×2)	1.947(6)	1.925(7)
Mean	2.053(7)	2.031(8)
<i>Y</i> –O1	1.920(6)	1.889(8)
<i>Y</i> –O3	1.913(6)	1.921(7)
<i>Y</i> –O4	2.034(7)	2.048(9)
<i>Y</i> –O5	1.914(6)	1.893(8)
<i>Y</i> –O6	1.992(7)	1.959(7)
<i>Y</i> –O7	1.942(6)	1.947(8)
Mean	1.953(6)	1.943(8)
Si1–O1 (×2)	1.652(7)	1.63(1)
Si1–O4	1.690(9)	1.64(1)
Si1–O8	1.694(9)	1.72(1)
Mean	1.672(8)	1.66(1)
Si2–O2 (×2)	1.607(6)	1.635(8)
Si2–O8	1.659(9)	1.618(9)
Si2–O10	1.648(9)	1.62(1)
Mean	1.630(8)	1.627(9)
Si3–O3 (×2)	1.611(7)	1.68(1)
Si3–O6	1.703(9)	1.69(1)
Si3–O9	1.606(9)	1.61(1)
Mean	1.633(9)	1.67(1)
O1–Si1–O1	116.7(6)	113.0(7)
O1–Si1–O4 (×2)	111.0(3)	112.4(4)
O1–Si1–O8 (×2)	108.8(3)	107.9(4)
O4–Si1–O8	99.1(5)	102.4(6)
O2–Si2–O2	117.0(6)	116.7(7)
O2–Si2–O8 (×2)	106.0(3)	106.3(4)
O2–Si2–O10 (×2)	109.6(4)	107.0(6)
O8–Si2–O10	107.6(4)	110.1(7)
O3–Si3–O3	109.7(6)	110.1(7)
O3–Si3–O6 (×2)	109.(3)	111.6(4)
O3–Si3–O9 (×2)	113.5(3)	110.7(4)
O6–Si3–O9	99.9(5)	101.9(6)

Note: Estimated standard deviations are in parentheses ( $1\sigma$ )



**Table 6** The refined and estimated bond lengths of the octahedral sites of samples MTS and KGH

Site	Cation <i>i</i>	<i>V<sub>i</sub></i>	<i>l<sub>0</sub></i> (Å)	<i>l<sub>ij</sub></i> (Å)	<i>g<sub>i</sub></i>	Estimated <i>X</i> -O and <i>Y</i> -O lengths (Å)	Observed mean bond lengths (Å)
MTS							
<i>Y</i>	Fe	+3	1.759	2.015	0.292	1.940	1.953(6)
	Al	+3	1.651	1.907	0.709		
Fe( <i>X</i> ) = 0.415Fe <sup>3+</sup>							
<i>X</i>	Mg	+2	1.693	2.099	0.17	1.984	2.053(7)
	Fe	+3	1.759	2.015	0.415		
	Al	+3	1.651	1.907	0.415		
Fe( <i>X</i> ) = 0.22Fe <sup>2+</sup> + 0.19Fe <sup>3+</sup>							
<i>X</i>	Mg	+2	1.693	2.099	0.17	2.002	2.053(7)
	Fe	+2	1.734	2.140	0.22		
	Fe	+3	1.759	2.015	0.19		
	Al	+3	1.651	1.907	0.415		
KGH							
<i>Y</i>	Fe	+3	1.759	2.015	0.161	1.924	1.943(8)
	Al	+3	1.651	1.907	0.839		
Fe( <i>X</i> ) = 0.278Fe <sup>3+</sup>							
<i>X</i>	Mg	+2	1.693	2.099	0.31	2.002	2.031(8)
	Fe	+3	1.759	2.015	0.278		
	Al	+3	1.651	1.907	0.415		
Fe( <i>X</i> ) = 0.16Fe <sup>2+</sup> + 0.12Fe <sup>3+</sup>							
<i>X</i>	Mg	+2	1.693	2.099	0.31	2.026	2.031(8)
	Fe	+2	1.734	2.140	0.16		
	Fe	+3	1.759	2.015	0.12		
	Al	+3	1.651	1.907	0.415		

Note: *V<sub>i</sub>*: Oxidation state of cation *i*. *l<sub>0</sub>*: bond valence parameter (Brown and Altermatt 1985; Brese and O'Keeffe 1991). *l<sub>ij</sub>*: expected bond length between cation *i* and anion *j* calculated using the equation  $V_i = \sum \exp[(l_0 - l_{ij})/0.37]$ . *g<sub>i</sub>*: refined site occupancy of cation *i*. Estimated *X*-O and *Y*-O lengths: calculated using the equation  $x = \sum (g_i \times l_{ij})$ . Estimated standard deviations are in parentheses (1σ)

published results for single crystal and Rietveld structural refinements of pumpellyite group minerals. Minor amounts of Mn and Na were ignored. Site occupancies of Al and Fe<sup>3+</sup> in the *X* and *Y* sites were refined using the following constraints: Al(*X*) = 1.0 - Mg(*X*) - Fe<sup>3+</sup>(*X*), Fe<sup>3+</sup>(*Y*) = [total Fe apfu - 4 × Fe<sup>3+</sup>(*X*)]/8 and Al(*Y*) = 1.0 - Fe<sup>3+</sup>(*Y*) where apfu means atoms per formula unit. The isotropic displacement parameters of oxygen were constrained to be equal. Refined site occupancies are shown in Table 3. The resulting atomic ratios in the *X* and *Y* sites of MTS are Mg0.17Fe0.415(4)Al0.415(4) and Fe0.292(4)Al0.709(4), respectively, and those of KGH are Mg0.31Fe0.278(6)Al0.415(6) and Fe0.161(6)Al0.839(6), respectively. The atomic positions are shown in Table 4, and selected interatomic distances and angles are given in Table 5.

The validity of the refined occupancies of Mg, Fe, and Al was examined in terms of the bond lengths estimated from the refined occupancies by using the bond valence sum rule (Brown and Shannon 1973):

$$V_i = \sum_j \exp\left(\frac{l_0 - l_{ij}}{0.37}\right),$$

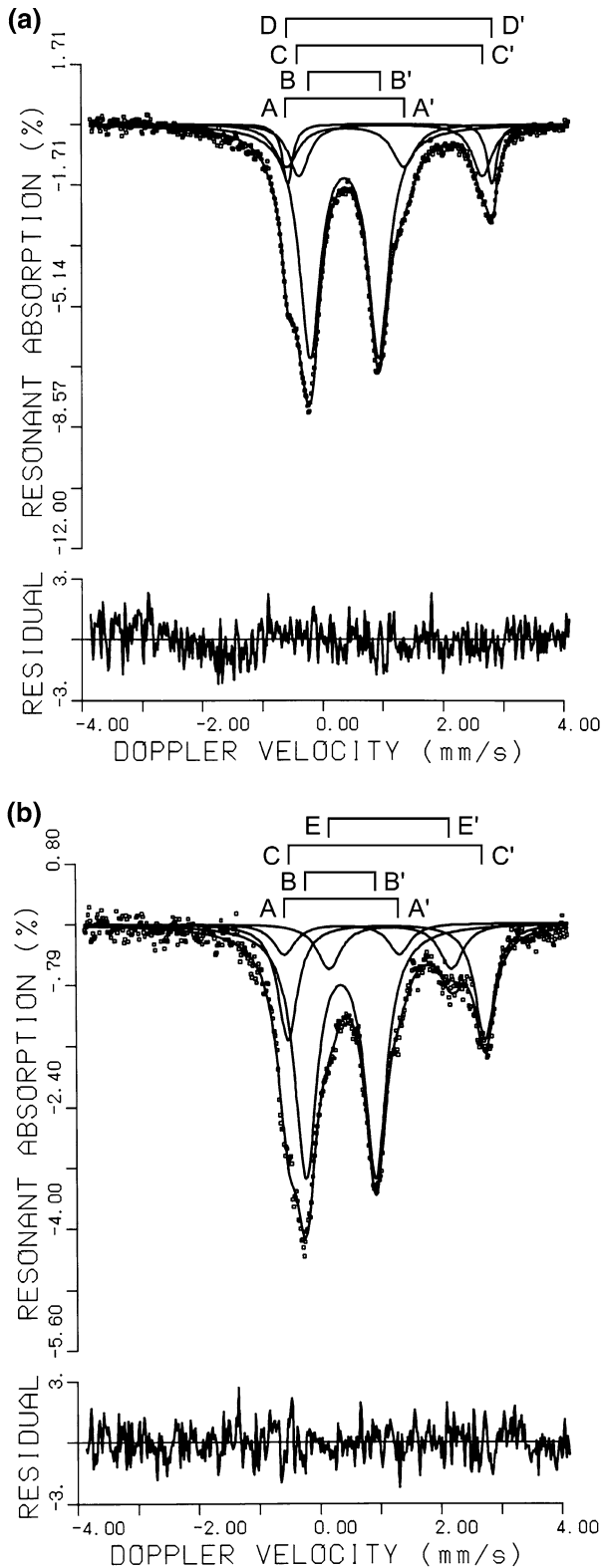
where *V<sub>i</sub>* is the valence or oxidation state of cation *i*, *l<sub>0</sub>* is the bond valence parameter (Brown and Altermatt 1985; Brese and O'Keeffe 1991) and *l<sub>ij</sub>* is the bond length between cation *i* and anion *j*. Based on this rule, Mg-O, Fe<sup>2+</sup>-O, Fe<sup>3+</sup>-O, and Al-O bond lengths at the octahedral sites were calculated to be 2.099, 2.140, 2.015, and

1.907 Å, respectively. Subsequently, *X*-O and *Y*-O bond lengths were derived using the equation  $x = \sum (g_i \times l_{ij})$ , where *g<sub>i</sub>* is the occupancy factor of cation *i*, and *l<sub>ij</sub>* is the bond length between cation *i* and anion *j*. On the assumption that all Fe is Fe<sup>3+</sup>, mean *X*-O and *Y*-O bond lengths of MTS were estimated 1.98 and 1.94 Å, respectively (Table 6). The expected mean *Y*-O distance is similar to the observed one ( $\langle Y-O \rangle = 1.95$  Å). However, the expected mean *X*-O bond length is considerably shorter than the observed value (2.05 Å). As shown in Table 6, the results for KGH are similar to those of MTS: the expected mean *Y*-O distance fits to the observed one, but the expected *X*-O is shorter than the observed value. These results indicate that the refined site occupancies and atomic positions at the *Y* site are consistent and that Fe is essentially ferric in the *Y* site, and suggest the presence of Fe<sup>2+</sup> at the *X* site.

#### Mössbauer analysis

The <sup>57</sup>Fe Mössbauer spectra of MTS and KGH are shown in Fig. 2 and the hyperfine parameters are listed in Table 7.

The spectrum of MTS consists of four doublets as reported by Akasaka et al. (1997). The doublets AA' [isomer shift (IS) = 0.38 and quadrupole splitting (QS) = 1.95 mm/s] and BB' (IS = 0.359 and QS = 1.140 mm/s) are attributed to Fe<sup>3+</sup>, and those of CC' (IS = 1.118 and QS = 3.387 mm/s) and DD'



**Fig. 2**  $^{57}\text{Fe}$  Mössbauer spectra of MTS (a) and KGH (b) at 298 K. The Mössbauer parameters refined are listed in Table 7

( $IS = 1.13$  and  $QS = 3.04$  mm/s) to  $\text{Fe}^{2+}$ . The doublet  $CC'$  is assigned to  $\text{Fe}^{2+}$  at the  $X$  site, because a doublet with  $IS = 1.09$ – $1.14$  mm/s and  $QS = 3.20$ – $3.35$  mm/s was

**Table 7**  $^{57}\text{Fe}$  Mössbauer hyperfine parameters

	MTS	KGH
Doublet	AA'	AA'
IS	0.38(1)	0.384(3)
QS	1.95(2)	1.896(5)
FWHH	0.48(3)	0.437(8)
Area ratio	14(1)	7(1)
Assignment	$\text{Fe}^{3+}(X)$	$\text{Fe}^{3+}(X)$
Doublet	BB'	BB'
IS	0.359(1)	0.353(8)
QS	1.140(3)	1.154(6)
FWHH	0.422(4)	0.437(8)
Area ratio	64(1)	58(1)
Assignment	$\text{Fe}^{3+}(Y)$	$\text{Fe}^{3+}(Y)$
Doublet	CC'	
IS	1.118(4)	
QS	3.387(8)	
FWHH	0.20(2)	
Area ratio	8(1)	
Assignment	$\text{Fe}^{2+}(X)$	
Doublet	DD'	CC'
IS	1.13(1)	1.115(8)
QS	3.04(3)	3.25(2)
FWHH	0.40(3)	0.386(2)
Area ratio	14(1)	24(1)
Assignment	$\text{Fe}^{2+}(X)$	$\text{Fe}^{2+}(X)$
Doublet		EE'
IS		1.18(1)
QS		2.02(3)
FWHH		0.468(4)
Area ratio		11(1)
Assignment		$\text{Fe}^{2+}(M)$ in Cpx
$\chi^2/\text{Freedom}$	1.27	1.21

Estimated standard deviations are in parentheses ( $1\sigma$ )

$IS$  isomer shift relative to metallic iron absorber (mm/s),  $QS$  quadrupole splitting (mm/s),  $FWHH$  full width at half height (mm/s),  $Area\ ratio$  %

assigned to  $\text{Fe}^{2+}$  at the  $X$  site by Artioli and Geiger (1994), Akasaka et al. (1997) and Artioli et al. (2003). The doublet  $DD'$  has  $QS$  (3.04 mm/s) different from those of  $\text{Fe}^{2+}$  in pumpellyites reported so far. However, it is rather close to that of  $\text{Fe}^{2+}$  at the  $X$  site, and the chemical composition of MTS shows no evidence for the significant substitution of  $\text{Fe}^{2+}$  for Ca in the  $W$  site. The  $DD'$  doublet should thus also be assigned to  $\text{Fe}^{2+}$  at the  $X$  site. Since  $QS$  of  $\text{Fe}^{2+}(X)$  of the doublet  $CC'$  is larger than that of the doublet  $DD'$ , the  $X$  site characterized by the doublet  $CC'$  is less distorted than that of the doublet  $DD'$ , although this slight difference in distortion of the  $X$  site cannot be detected by the X-ray structure refinement.

The  $\text{Fe}^{3+}$  doublets with Mössbauer parameters similar to those of the doublets  $AA'$  and  $BB'$  have been assigned to  $\text{Fe}^{3+}$  at the  $Y$  sites with different distortions by Artioli and Geiger (1994),  $\text{Fe}^{3+}$  at the  $X$  and  $Y$  sites, respectively, by Akasaka et al. (1997), and  $\text{Fe}^{3+}$  at the  $Y$  and  $X$  sites, respectively, by Artioli et al. (2003). Thus, it is difficult to assign the doublets  $AA'$  and  $BB'$  based on the published assignments. However, assignment of the doublets is possible when the distributions of Fe between the  $X$  and  $Y$  sites determined by the X-ray structural refinement are taken into consideration. The amounts

**Table 8** Estimated bond valence (v.u.) in samples MTS and KGH

Anion	Cation								Anion chemistry	
	W1	W2	X	Y	Si1	Si2	Si3	$\Sigma C^v$		
MTS										
O1		×2 0.46		0.53	×2 0.97				1.96	O <sup>2-</sup>
O2	×2 0.29	×2 0.28	×2 0.29				×2 1.09		1.95	O <sup>2-</sup>
O3	×2 0.32			0.54			×2 1.08		1.94	O <sup>2-</sup>
O4	0.30			×2 0.39	0.87				1.95	O <sup>2-</sup>
O5				×2 0.54					1.08	OH <sup>-</sup>
O6		0.12		×2 0.44			0.84		1.84	O <sup>2-</sup>
O7				×2 0.50					1.00	OH <sup>-</sup>
O8	0.21				0.86	0.95			2.02	O <sup>2-</sup>
O9		0.20	×2×2 0.35					1.10	2.00	O <sup>2-</sup>
O10		0.28					0.98		1.26	OH <sup>-</sup>
O11	0.35		×2×2 0.49						1.33	OH <sup>-</sup>
$\Sigma A^v$	2.08	2.08	2.26	2.94	3.67	4.11	4.10			
KGH										
O1		×2 0.42		0.55	×2 1.03				2.00	O <sup>2-</sup>
O2	×2 0.30	×2 0.30	×2 0.33				×2 1.01		1.94	O <sup>2-</sup>
O3	×2 0.39			0.51			×2 0.90		1.80	O <sup>2-</sup>
O4	0.29			×2 0.36	1.00				2.01	O <sup>2-</sup>
O5				×2 0.55					1.10	OH <sup>-</sup>
O6		0.11		×2 0.46			0.87		1.90	O <sup>2-</sup>
O7				×2 0.47					0.94	OH <sup>-</sup>
O8	0.19				0.81	1.06			2.06	O <sup>2-</sup>
O9		0.18	×2×2 0.38					1.08	2.02	O <sup>2-</sup>
O10		0.29					1.06		1.35	OH <sup>-</sup>
O11	0.29		×2×2 0.53						1.35	OH <sup>-</sup>
$\Sigma A^v$	2.15	2.02	2.48	2.90	3.87	4.14	3.75			

Note:  $\Sigma A^v$  is the valence of bonds emanating from cations summed over the bonded anions.  $\Sigma C^v$  is the valence of bonds reaching anions. The numbers in the left superscript give the number of identical bonds reaching the anion; the numbers in the right superscripts give the number of identical bonds emanating from cations. Estimated standard deviations are in parentheses ( $1\sigma$ )

of Fe in the X and Y sites of MTS determined by the Rietveld method are 1.66 and 2.34 apfu, respectively, giving Fe(X):Fe(Y)-ratio of 41.5:58.5 (%), where Fe(X) and Fe(Y) represent Fe content at the X and Y sites, respectively. Area ratios of the Mössbauer doublets AA', BB', CC', and DD' are 14:64:8:14 (%), which correspond to the amounts of Fe<sup>3+</sup>, Fe<sup>3+</sup>, Fe<sup>2+</sup>, and Fe<sup>2+</sup>, respectively, and the doublets CC' and DD' were attributed to Fe<sup>2+</sup> at the X site, as explained above. Thus, assignment of the doublets AA' and BB' to Fe<sup>3+</sup> at the X and Y sites (respectively) and the area ratios of the doublets lead to derivation of Fe<sup>2+</sup>(X):Fe<sup>3+</sup>(X):Fe<sup>3+</sup>(Y) ratios of 22:14:64 (%). These values are close to

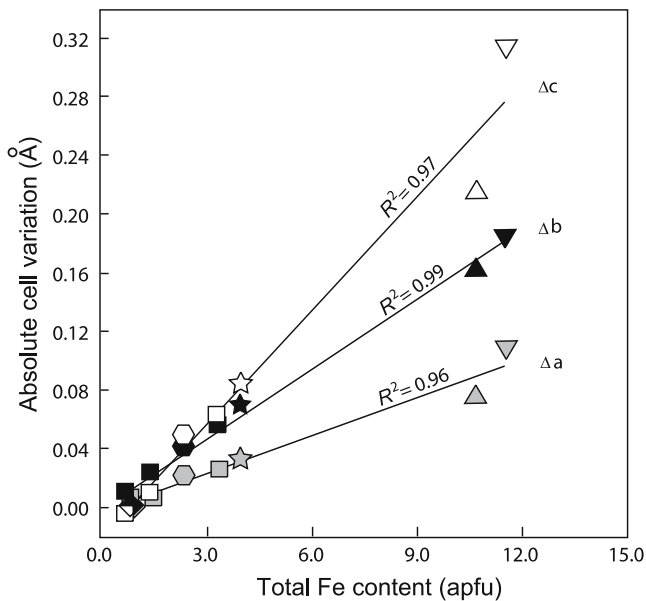
the Fe(X):Fe(Y)-ratio (=41.5:58.5) determined by the Rietveld method. Consequently, we assign the doublets AA' and BB' to Fe<sup>3+</sup> at the X and Y site, respectively (Table 7). By applying the Fe<sup>2+</sup>:Fe<sup>3+</sup>-ratio determined by the Mössbauer analysis and the site occupancies of Fe at the X and Y sites given by the Rietveld method, the formula of MTS is established as Ca<sub>8</sub>(Mg<sub>0.68</sub>Fe<sub>0.88</sub>Fe<sub>0.77</sub><sup>3+</sup>Al<sub>1.66</sub>)<sub>Σ3.99</sub>(Al<sub>5.67</sub>Fe<sub>2.34</sub><sup>3+</sup>)<sub>Σ8.01</sub>Si<sub>12</sub>O<sub>42.41</sub>(OH)<sub>13.59</sub>, where the OH content is calculated based on the charge balance.

The spectrum of KGH is composed of three doublets of pumpellyite and one doublet of Ca-clinopyroxene. The doublets AA' (IS = 0.384 and QS = 1.896 mm/s) and



BB' (IS = 0.353 and QS = 1.154 mm/s) are attributed to  $\text{Fe}^{3+}$ , and those of CC' (IS = 1.115 and QS = 3.25 mm/s) to  $\text{Fe}^{2+}$  of pumpellyite. The doublet EE' with IS = 1.18 and QS = 2.02 mm/s is assigned to  $\text{Fe}^{2+}$  at *MI* site of Ca-clinopyroxene (Matsui et al. 1970; Bancroft et al. 1971; Akasaka 1990). Since the average chemical composition ( $n=5$ ) of augite as an impurity in the KGH sample is 50.54  $\text{SiO}_2$ , 0.38  $\text{TiO}_2$ , 3.49  $\text{Al}_2\text{O}_3$ , 0.10  $\text{V}_2\text{O}_3$ , 0.34 total MnO, 12.65 total FeO, 13.83 MgO, 19.10 CaO, 0.41  $\text{Na}_2\text{O}$ , 0.04  $\text{K}_2\text{O}$  and 100.84 wt.% total, all Fe is considered as ferrous iron. The amounts of Fe in the *X* and *Y* sites of KGH, determined by the Rietveld method, are 1.11 and 1.29 apfu, respectively, which is recalculated to Fe(*X*):Fe(*Y*)-ratio of 46.3:53.7 (%). Area ratios of the Mössbauer doublets AA', BB', and CC' are 8:65:27 (%), which correspond to the amounts of  $\text{Fe}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Fe}^{2+}$  in KGH, respectively. Thus, the  $\text{Fe}^{2+}$  (*X*): $\text{Fe}^{3+}$  (*X*): $\text{Fe}^{3+}$  (*Y*) ratio of 27:8:65 (%) derived from the assignments of the doublets AA', BB', and CC' to  $\text{Fe}^{3+}$  (*X*),  $\text{Fe}^{3+}$  (*Y*), and  $\text{Fe}^{2+}$  (*X*), respectively, is most close to the Fe distributions (Fe(*X*):Fe(*Y*) = 46.3:53.7%) determined by the Rietveld method. By using the same calculation scheme of the formula as MTS, the formula of KGH is established as  $\text{Ca}_8(\text{Mg}_{1.24}\text{Fe}_{0.65}\text{Fe}_{0.46}\text{Al}_{1.66})_{\Sigma 4.01}(\text{Al}_{6.71}\text{Fe}_{1.29})_{\Sigma 8.00}\text{Si}_{12}\text{O}_{42.14}(\text{OH})_{13.86}$ .

These results indicate that, in MTS and KGH,  $\text{Al}^{3+}$  cations are dominant both in the *Y* and *X* sites, and, thus, these pumpellyites are classified as 'pumpellyite-(Al)' in spite of the high  $\text{Fe}^{3+}$  contents.

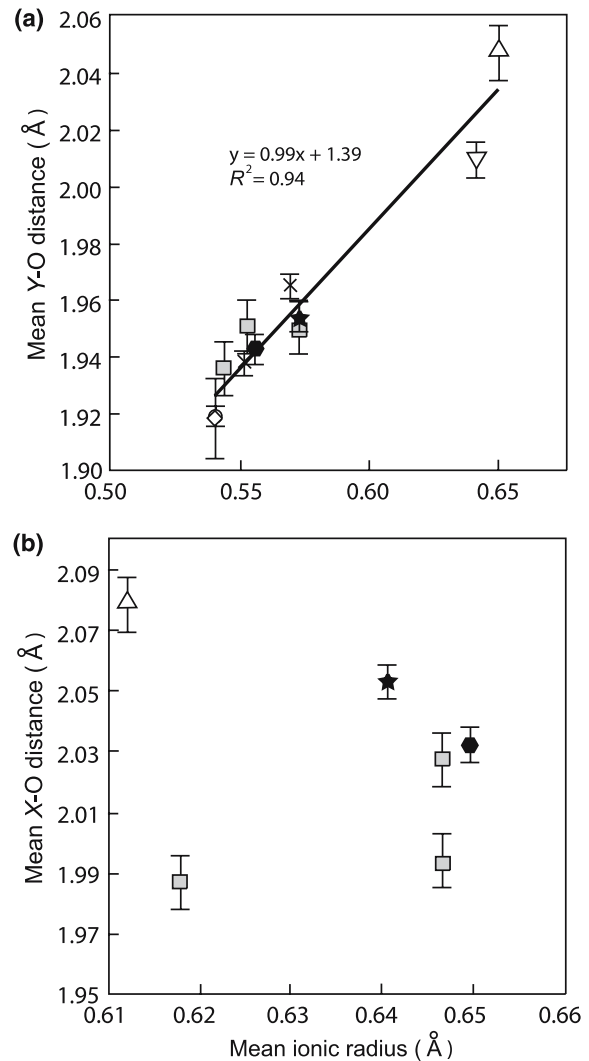


**Fig. 3** Variation of the unit-cell parameters as a function of the total Fe content (atoms per formula unit: apfu) in pumpellyites and juldolites. Gray symbols refer to the *a*-axis, closed symbols to the *b*-axis, and open symbols to the *c*-axis. Symbols and sources: inverted triangles (Allmann and Donnay 1973), diamonds (Yoshiasa and Matsumoto 1985), squares (Artioli and Geiger 1994), triangles (Artioli et al. 2003), stars (MTS of this study), and hexagon (KGH of this study)

## Discussion

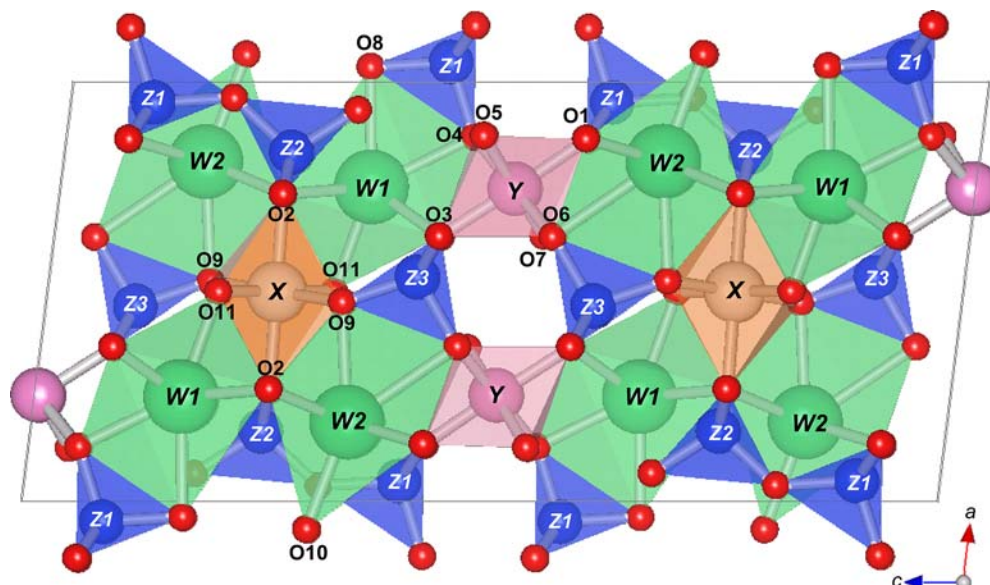
### Atomic configurations at the *X* and *Y* sites and local charge neutralization

As noted above, the expected *Y*-O bond distances of MTS and KGH derived from the refined occupancies of Fe and Al at the *Y* site using bond valence sum rule are consistent with the observed *Y*-O distances, indicating that the atomic configuration in the *Y* site is in harmony with the refined atomic positions and that Fe is essentially ferric in the *Y* site. However, in the case that all Fe



**Fig. 4** **a** The relationship between mean ionic radii at the *Y* site and mean *Y*-O distances. **b** The relationship between mean ionic radii at the *X* site and mean *X*-O distances. Mean ionic radii were calculated by using the ionic radii of Shannon (1976). Symbols and sources: open circle (Galli and Alberti 1969), open inverted triangle (Allmann and Donnay 1973), open diamond (Yoshiasa and Matsumoto 1985), gray squares (Artioli and Geiger 1994), crosses (Artioli et al. 1996), open triangle (Artioli et al. 2003), filled star (MTS of this study), and filled hexagon (KGH of this study)

**Fig. 5** Crystal structure of MTS on  $a$ - $c$  plane drawn with VICS developed by Dilanian and Izumi (Izumi 2005)



is assumed as  $\text{Fe}^{3+}$ , the expected  $X$ - $O$  distances were shorter than the observed values, suggesting the presence of  $\text{Fe}^{2+}$  in the  $X$  site. Thus,  $X$ - $O$  distances were re-estimated using the resulting atomic ratios of  $\text{Mg}:\text{Fe}^{2+}:\text{Fe}^{3+}:\text{Al}=0.17:0.22:0.19:0.415$  for MTS and  $0.31:0.16:0.12:0.415$  for KGH. As shown in Table 6, the  $X$ - $O$  distance of MTS is calculated to be 2.00 Å, close to the observed value of 2.05 Å, and that of KGH is calculated to be 2.03 Å, same as the observed value of 2.03 Å. Thus, the resulting  $\text{Fe}^{2+}:\text{Fe}^{3+}$ -ratio and the atomic configuration are consistent with the results of structural refinements.

The local neutralization of charge in the structures of MTS and KGH was also examined in terms of the bond valence sum calculated after the method of Donnay and Allmann (1970) (Table 8). The bond valence sums of the  $W1$ ,  $W2$ ,  $Y$ , and  $Z$  sites of MTS and KGH are close to the expected values, and the sum of the  $X$  site is 2.26 and 2.48, respectively, indicating the presence of both divalent and trivalent cations in this site. The sums of  $O5$  and  $O7$  are sufficiently close to the expected value of 1 for an hydroxyl group, whereas those for  $O10$  and  $O11$  are 1.26 and 1.33 for MTS and 1.35 and 1.35 for KGH, respectively. These values are consistent with those for pumpellyite obtained by Yoshiasa and Matsumoto (1985). They suggested that the substitution  $\text{M}^{2+}(X) + \text{H}^+(\text{H}11) + \text{O}^{2-}(\text{O}11) \leftrightarrow \text{M}^{3+}(X) + \text{O}^{2-}(\text{O}11)$ , which reduces the number of hydrogen atoms, possibly occurs at the  $X$  site.

Relationship between unit cell parameters and mean bond lengths at the  $X$  and  $Y$  sites

Published studies of the pumpellyite–julgoldite series indicate that the unit-cell parameters  $a$ ,  $b$ ,  $c$ , and cell

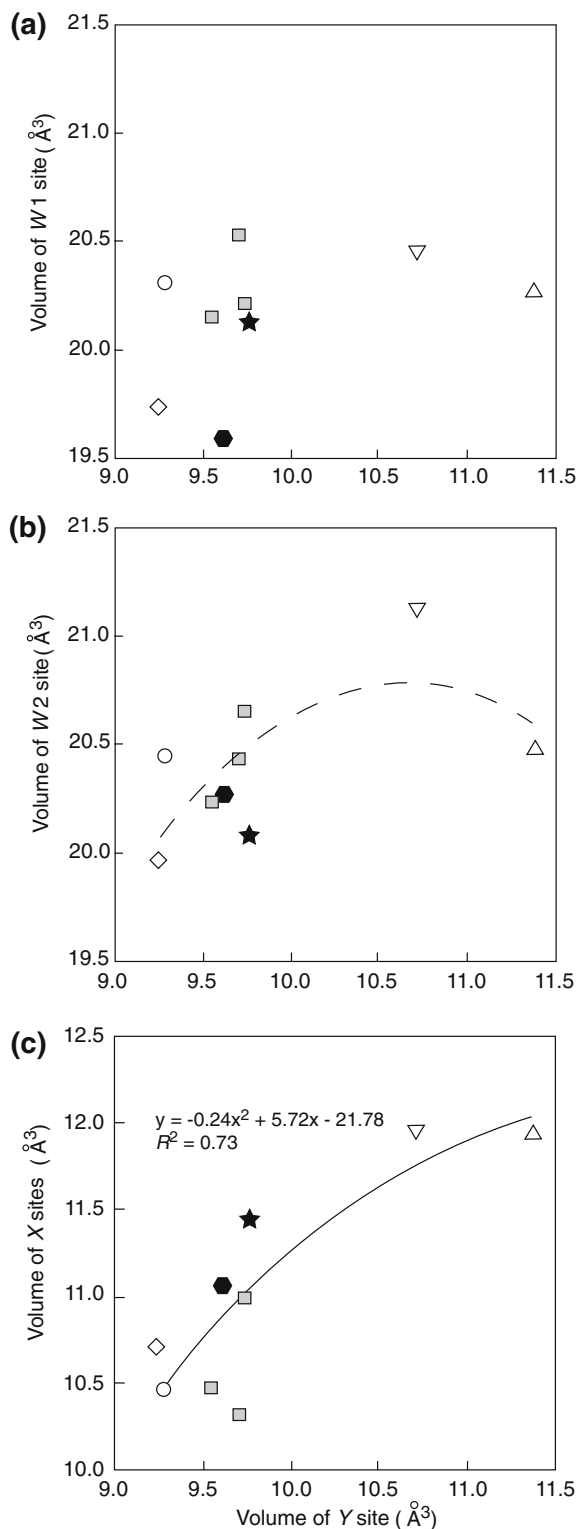
volume increase with increasing Fe content, and that  $\text{Al} \leftrightarrow \text{Fe}^{3+}$  substitution at the  $Y$  site has a significant effect on unit-cell parameters (Passaglia and Gottardi 1973; Artioli and Geiger 1994; Akasaka et al. 1997; Artioli et al. 2003). Cell parameters of MTS and KGH plot on the regression lines in the absolute cell variation—total Fe content diagram (Fig. 3), consistent with the positive relationships between cell parameters and total Fe contents.

The changes in bond lengths at the  $X$  and  $Y$  sites have not been clarified in terms of the ionic substitutions at these sites, however. The mean  $Y$ - $O$  distance correlate well with the mean ionic radius, calculated based on the ionic radii by Shannon (1976), as shown in Fig. 4a, which causes expansion of the  $Y$  site and increase of the unit-cell parameters. The edges of the  $\text{YO}_6$  octahedra may dominate the variation of each cell dimension as follows;  $\text{O}1$ – $\text{O}6$ ,  $\text{O}3$ – $\text{O}4$ ,  $\text{O}3$ – $\text{O}5$ ,  $\text{O}4$ – $\text{O}7$ , and  $\text{O}5$ – $\text{O}6$  edges for  $a$ -axis,  $\text{O}4$ – $\text{O}5$ ,  $\text{O}6$ – $\text{O}7$ ,  $\text{O}1$ – $\text{O}4$ ,  $\text{O}1$ – $\text{O}5$ ,  $\text{O}3$ – $\text{O}6$ , and  $\text{O}3$ – $\text{O}7$  edges for  $b$ -axis, and  $\text{O}1$ – $\text{O}5$ ,  $\text{O}3$ – $\text{O}7$ ,  $\text{O}1$ – $\text{O}4$ ,  $\text{O}3$ – $\text{O}6$ ,  $\text{O}5$ – $\text{O}6$  and  $\text{O}4$ – $\text{O}7$  edges for  $c$ -axis. Since the edges of  $\text{O}1$ – $\text{O}4$ ,  $\text{O}1$ – $\text{O}5$ ,  $\text{O}3$ – $\text{O}6$  and  $\text{O}3$ – $\text{O}7$  are not shared with other polyhedra (Fig. 5), they elongate more straightforward than the other shared edges with the  $\text{Fe}^{3+} \rightarrow \text{Al}$  substitution at the  $Y$  site, which easily causes the increase in the  $c$ -dimension than the  $a$ - and  $b$ -dimensions.

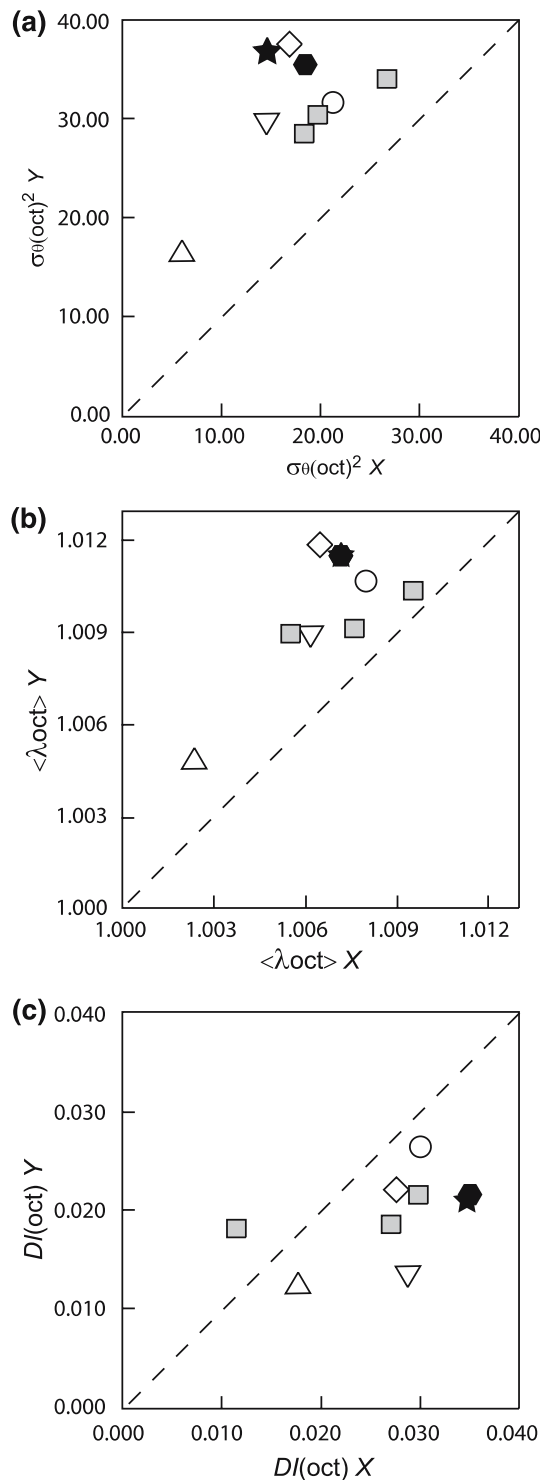
The relationship between the ionic substitutions and the structural changes at the  $X$  site is not simple, because both divalent and trivalent cations occur in this site and  $\text{M}^{2+}/\text{M}^{3+}$ -ratios differ from sample to sample. For example, mean ionic radii at the  $X$  site of MTS, KGH, and Bombay julgoldite-( $\text{Fe}^{3+}$ ) are calculated 0.641, 0.650, and 0.612 Å, respectively. However, in contrast to the expectation in terms of the mean ionic radii, mean  $X$ - $O$  distances of  $2.05 \pm 0.01$  Å (volume:  $11.5 \text{ \AA}^3$ ) for

MTS and  $2.031 \pm 0.008 \text{ \AA}$  (volume:  $11.1 \text{ \AA}^3$ ) for KGH are almost the same as the value of  $2.08 \pm 0.01 \text{ \AA}$  (volume:  $11.9 \text{ \AA}^3$ ) for Bombay juldite-(Fe<sup>3+</sup>), and, thus,

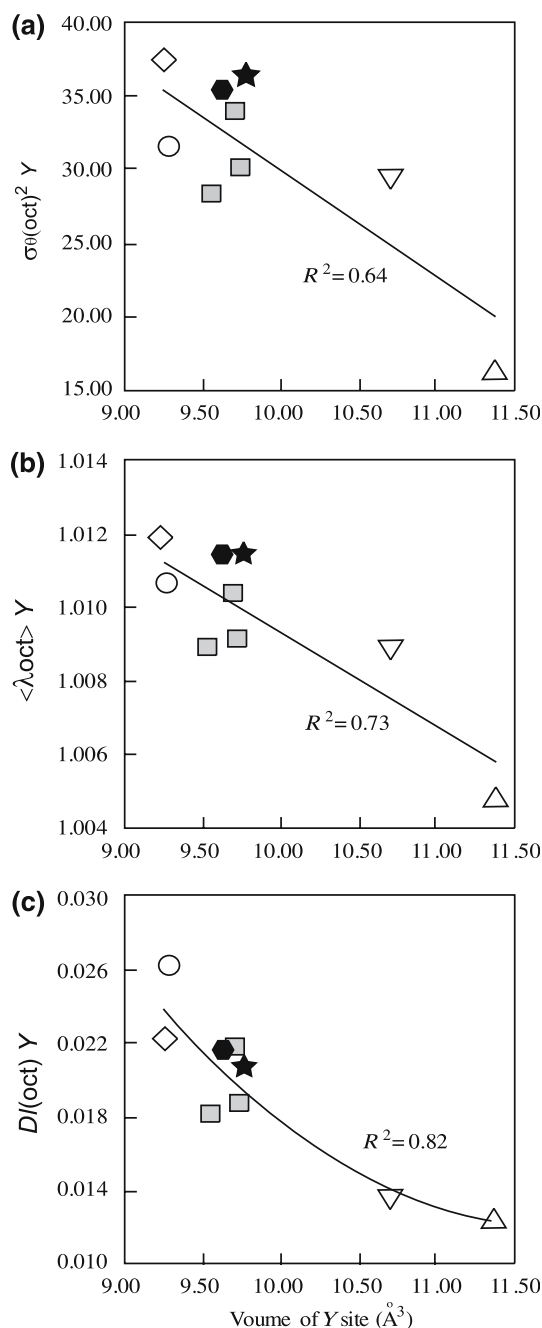
there is no correlation between the mean ionic radii and the mean  $X-O$  distances (Fig. 4b). The insignificance of ionic substitutions at the  $X$  site to the size of the  $XO_6$



**Fig. 6** Relationships of volumes of **a** the  $W1O_7$  polyhedra, **b** the  $W2O_7$  polyhedra, and **c** the  $XO_6$  octahedra versus that of the  $YO_6$  octahedra. Symbols and sources as in Fig. 4



**Fig. 7** Relationship of site distortions between the  $X$  and  $Y$  sites. **a**  $\sigma_{\theta(\text{oct})}^2 X - \sigma_{\theta(\text{oct})}^2 Y$ , **b**  $\langle \lambda_{\text{oct}} \rangle X - \langle \lambda_{\text{oct}} \rangle Y$ , and **c**  $DI(\text{oct}) X - DI(\text{oct}) Y$ . Definitions of the distortion parameters are shown in Table 9. Symbols and sources as in Fig. 4



**Fig. 8** Relationship between the volumes and distortions of the  $YO_6$  octahedra. **a**  $V_Y - \sigma_{\theta}(\text{oct})_Y^2$  (Robinson et al. 1971), **b**  $V_Y - \langle \lambda_{\text{oct}} \rangle_Y$  (Robinson et al. 1971), and **c**  $V_Y - \text{DI}(\text{oct})_Y$  (Baur 1974). Definitions of the distortion parameters are given in Table 9. Symbols and sources as in Fig. 4

octahedra may be interpreted in terms of the following facts: (1) the size of  $XO_6$  octahedra is essentially large; (2) all edges of octahedra of the  $X$  site are shared with the  $W1$  and  $W2$  polyhedra (Fig. 5), which prohibits changes of the size of the  $XO_6$  octahedra.

Due to the sharing of the O1–O6 edge between the  $Y$  and  $W2$  sites and of the O3–O5 edge between the  $Y$  and

$W1$  sites, the volumes of the  $W2O_7$  and  $W2O_7$  polyhedra increase with increasing the volume of the  $YO_6$  octahedra by the  $\text{Fe}^{3+} \rightarrow \text{Al}$  substitution at the  $Y$  site (Fig. 6a, b). The enlargements of  $W1O_7$  and  $W2O_7$  polyhedra elongate the edges shared with  $X$  site. Finally, the volume of the  $X$  site is influenced by that of the  $Y$  site (Fig. 6c).

#### Site distortion of the $X$ and $Y$ sites

In contrast to the previous Mössbauer studies of Fe-rich pumpellyite by Akasaka et al. (1997), the doublets AA' with  $\text{QS} = 1.896\text{--}1.95$  mm/s and BB' with  $\text{QS} = 1.14\text{--}1.154$  mm/s in our Mössbauer spectra are assigned to  $\text{Fe}^{3+}$  at the  $X$  and  $Y$  sites, respectively. This result supports the  $\text{Fe}^{3+}$  doublets assignments of Artioli et al. (2003) that the doublets with QS about 1.7 mm/s and about 1.1 mm/s to  $\text{Fe}^{3+}(X)$  and  $\text{Fe}^{3+}(Y)$ , respectively. However, these assignments seem to contradict the well known theoretical and empirical rule that the QS of  $\text{Fe}^{3+}$  at the distorted site is greater than that at the less distorted site (Bancroft et al. 1967). Using the polyhedral distortion indices of Robinson et al. (1971), Artioli and Geiger (1994) and Akasaka et al. (1997) indicated that site distortion of the  $Y$  site is greater than that of the  $X$  site. This requires larger QS for  $\text{Fe}^{3+}$  at the  $Y$  site than that at the  $X$  site. Thus, the distortions of the  $X$  and  $Y$  sites in pumpellyites were re-examined in terms of the bond length distortion parameters  $\langle \lambda_{\text{oct}} \rangle$  defined by Robinson et al. (1971), DI(oct) by Baur (1974), and the angular distortion parameter  $\sigma_{\theta}(\text{oct})^2$  by Robinson et al. (1971).

The angular distortion and bond length distortion parameters of MTS and KGH are listed in Table 9, along with those of pumpellyites and juldoldites from other localities. As pointed out by Artioli and Geiger (1994), the  $\sigma_{\theta}(\text{oct})_X^2 - \sigma_{\theta}(\text{oct})_Y^2$  and  $\langle \lambda_{\text{oct}} \rangle_X - \langle \lambda_{\text{oct}} \rangle_Y$  diagrams (Fig. 7a, b) reveal larger angular and bond length distortions of the  $Y$  site than those of the  $X$  site. However, in terms of the DI(oct) of Baur (1974), bond length distortions of the  $X$  site [excepting one sample from Artioli and Geiger (1994)] are larger than those at the  $Y$  site (Fig. 7c). In the case of their study of synthetic piemontite having three kinds of octahedral sites, Nagashima and Akasaka (2004) found that the DI(oct) parameter is more sensitive to bond length distortions than that of Robinson et al. (1974). The DI(oct) parameter may also be a more practical indicator of the bond length distortions of octahedra in pumpellyite.

All site distortion parameters, such as  $\sigma_{\theta}(\text{oct})^2$ ,  $\langle \lambda_{\text{oct}} \rangle$ , and DI(oct), for the  $Y$  site tend to decrease with increasing mean  $Y\text{--}O$  distance and volume of the  $Y$  site (Fig. 8). This observation confirms that expansion of the  $YO_6$  octahedra caused by ionic substitutions results in gradual change to highly symmetrical and regular form.

**Table 9** Angular and bond length distortions of the *X* and *Y* octahedral sites

Sample	<i>X</i> site			<i>Y</i> site			Reference
	$\sigma_{\theta}(\text{oct})^2$	$\langle \lambda_{\text{oct}} \rangle$	DI	$\sigma_{\theta}(\text{oct})^2$	$\langle \lambda_{\text{oct}} \rangle$	DI	
MTS	14.41	1.007	0.034	36.39	1.012	0.021	This study
KGH	18.41	1.008	0.035	35.25	1.011	0.022	This study
HR	21.08	1.008	0.030	31.63	1.011	0.026	Galli and Alberti (1969)
Julgoldite	14.55	1.006	0.029	29.59	1.009	0.014	Allmann and Donnay (1973)
Pumpellyite	16.83	1.007	0.028	37.46	1.012	0.022	Yoshiasa and Matsumoto (1985)
HR	18.20	1.006	0.011	28.39	1.009	0.018	Artioli and Geiger (1994)
K1	26.64	1.010	0.030	34.01	1.010	0.022	
BU	19.79	1.008	0.027	30.16	1.009	0.019	
Bombay julgoldite-(Fe <sup>3+</sup> )	5.98	1.002	0.018	16.30	1.005	0.012	Artioli et al. (2003)

Note: HR, K1, and BU are sample codes defined by Galli and Alberti (1969), and Artioli and Geiger (1994).  $\langle \lambda_{\text{oct}} \rangle = \sum_{i=1}^6 (l_i - l_0)^2 / 6$  ( $l_i$ : each bond length,  $l_0$ : center-to-vertex distance for an octahedron with  $O_h$  symmetry whose volume is equal to that of strained or distorted octahedron with bond lengths  $l_i$ ) (Robinson et al. 1971),  $\text{DI}(\text{oct}) = 1/6 \sum |R_i - R_{\text{av.}}| / R_{\text{av.}}$  ( $R_i$ : each bond length,  $R_{\text{av.}}$ : average distance for an octahedron) (Baur 1974), and  $\sigma_{\theta}(\text{oct})^2 = \sum_{i=1}^{12} (\theta_i - 90^\circ)^2 / 11$  ( $\theta_i$ : O–M–O angle) (Robinson et al. 1971)

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