The Canadian Mineralogist
Vol. 33, pp. 67-75 (1995)

SPECTROSCOPIC DATA ON COEXISTING PREHNITE–PUMPELLYITE AND EPIDOTE–PUMPELLYITE

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ABSTRACT

X-ray absorption spectra in the Fe *K* near-edge region (XANES) and ^{57}Fe Mössbauer spectra were collected on two Fe-rich pumpellyite specimens from low-grade metamorphosed spilitic rocks from the Keweenaw Peninsula, northern Michigan, and on prehnite and epidote coexisting with pumpellyite. Spectroscopic data for prehnite, presented for the first time, are discussed in light of the pseudosymmetry of its structure. The data clearly show the prevailing role of Fe^{3+} in the crystal chemistry of the paragenetically associated Ca-silicates. This is in agreement with the overall oxidizing conditions typical of the low-grade metamorphic environment and the mineral assemblages characteristic of alteration zones in basaltic rocks as described by petrological analyses.

Keywords: pumpellyite, prehnite, epidote, crystal chemistry, XANES, Mössbauer spectroscopy, Keweenaw Peninsula, Michigan.

SOMMAIRE

Nous avons étudié les spectres d'absorption des rayons X dans la région près de la limite de l'énergie du rayonnement *K* du fer (XANES), ainsi que les spectres ^{57}Fe de Mössbauer de deux échantillons de pumpellyite riche en Fe, provenant de roches spilitiques de la péninsule de Keweenaw, dans la partie nord du Michigan, ainsi que ceux de la prehnite et de l'épidote coexistantes. Les données spectroscopiques sur la prehnite, présentées ici pour la première fois, sont évaluées à la lumière de la pseudosymétrie de sa structure. Les données démontrent clairement le rôle important du Fe^{3+} dans la chimie cristalline des silicates calciques de cette paragenèse. La présence du Fe^{3+} concorde avec le milieu oxydant des roches à faible degré de métamorphisme et les assemblages de minéraux typiques des zones d'altération des roches basaltiques, tels que décrits par analyses pétrologiques.

(Traduit par la Rédaction)

Mots-clés: pumpellyite, prehnite, épidote, chimie cristalline, XANES, spectroscopie de Mössbauer, spilite, péninsule de Keweenaw, Michigan.

INTRODUCTION

Twenty years ago, basic rules for a structural interpretation of the crystal chemistry of pumpellyite-group minerals were proposed (Passaglia & Gottardi 1973), essentially based on existing data for members of the series Al-bearing pumpellyite – Fe-bearing julgoldite series. Since then, several new end-members have been recognized: okhotskite (Mn end-member: Togari & Akasaka 1987), shuiskite (Cr end-member: Ivanov *et al.* 1981), V-bearing pumpellyite (Pan & Fleet 1992). Several studies also showed that there is an almost complete solid-solution between Fe-bearing pumpellyite and julgoldite (Kawachi 1975, Liou 1979, Schiffman & Liou 1983), and between Mn-bearing pumpellyite and okhotskite (Kato *et al.* 1981, Lucchetti 1983, Dasgupta *et al.* 1991).

The definition of an expanded compositional field for the mineral species isostructural with pumpellyite seems warranted. Furthermore, the structural basis for the allocation of a crystallographic site and an oxidation state to the octahedrally coordinated mixed-valence cations has been questioned on the basis of chemical and petrological studies (Cortesogno *et al.* 1984, Cho *et al.* 1986) and also on spectroscopic and structural evidence (Artioli *et al.* 1991, Artioli & Geiger 1994).

We here present data on Fe *K* near-edge X-ray absorption (XANES) and ^{57}Fe Mössbauer spectroscopy data for prehnite and epidote, respectively, associated with well-characterized specimens of Fe-rich pumpellyite. XANES spectra of the pumpellyite samples also are discussed. The data are compatible with an oxidizing environment of formation and indicate little or no crystallographic control on the oxidation state of Fe in the minerals and on the distribution of Fe among coexisting phases. The results are important in the thermodynamic modeling of low-grade metamorphic reactions involving pumpellyite-type minerals.

SAMPLES

The two samples of pumpellyite were extracted from cavities and amygdales present in specimens of altered basalt collected near the type locality of pumpellyite, in the copper deposits of the Keweenaw Peninsula, Michigan (Palache & Vassar 1925). The rocks are typical spilitic basalts hydrothermally altered under conditions of low-grade metamorphism (Jolly & Smith 1969). The pumpellyite samples, labeled PmpK1 and PmpK3, are similar to those used in a preliminary spectroscopic study (Artioli *et al.* 1991) and were selected because the pumpellyite prisms are intimately associated with prehnite (cavity K1, Fig. 1), and with epidote (cavity K3, Fig. 2).

All minerals are readily recognizable under the optical microscope on account of their color and well-developed habit.

EXPERIMENTAL

After hand separation and grinding, the four mineral powders were checked for purity by X-ray powder diffraction. No extraneous phase was detected at the 1–2 wt% level in the prehnite of cavity K1 (labeled PrhK1) and the epidote of cavity K3 (labeled EpK3). A small amount of native copper is present in PmpK1, and the basal peaks of chlorite are barely visible above background in the powder pattern of PmpK3. The level of both impurity phases is such that they bear no detectable effects on the X-ray absorption experiments performed at the Fe *K* energies.

Chemical analyses were performed in the wavelength-dispersion mode on several crystals of epidote (EpK3) and prehnite (PrhK1) using an ARL–SEMQ

FIG. 1. SEM photograph of pumpellyite prisms on prehnite matrix in sample K1. Field of view: 0.28 mm × 0.36 mm.

FIG. 2. SEM photograph of well-developed prisms of pumpellyite which grew on large crystals of epidote in sample K3. Field of view: 1.11 mm × 1.43 mm.

TABLE 1. CHEMICAL COMPOSITION OF PREHNITE AND EPIDOTE COEXISTING WITH PUMPELLYITE*

	PrhK1	EpK3	PmpK1	PmpK3
SiO_2 wt.%	41.57	36.23	38.33	37.17
Al_2O_3	18.48	19.57	23.72	19.68
TiO_2	0.02	0.03	0.02	0.05
CaO	25.72	21.35	21.73	21.02
SrO	0.06	0.28	-	-
BaO	0.01	0.03	-	-
Na_2O	-	0.01	-	-
Fe_2O_3	8.51	18.41	4.22	8.96
FeO	-	-	1.62	3.45
MgO	-	-	3.16	2.40
Mn_2O_3	0.03	0.12	0.20	0.24
Cr_2O_3	0.02	-	-	0.02
NiO	0.01	0.04	-	-
Total	94.43	96.07	92.82	93.00
atomic proportions				
Si	5.81	2.86	12.18	12.11
Al	3.05	1.82	8.68	7.55
Ti	-	-	0.01	0.01
Ca	3.85	1.80	7.40	7.33
Sr	-	0.01	-	-
Ba	-	-	-	-
Na	-	-	-	0.01
Fe^{3+}	0.90	1.09	1.01	2.20
Fe^{2+}	-	-	0.43	0.94
Mg	-	-	1.49	1.17
Mn	-	-	0.05	0.06
Cr	-	-	-	0.01
Ni	-	-	-	-
OH	5.19	1.10	14.83	15.21
(O,OH) pfu	24.00	13.00	56.00	56.00

* The chemical composition of pumpellyite PmpK1 and PmpK3 is recalculated from Artioli et al. (1991). Symbols: Prh prehnite, Ep epidote, Pmp pumpellyite, pfu per formula unit.

electron microprobe. The experimental conditions were: 15 kV, beam current 20 nA and defocused beam (spot size ≈ 20 μm). The instrument was operated in the automatic mode, with on-line data reduction using the Ziebold & Ogilvie (1964) method, with the Albee & Ray (1970) correction factors. The compositional data are reported in Table 1.

X-ray absorption spectroscopy

The finely powdered samples were sedimented on a Millipore membrane as described in Quartieri *et al.* (1993a): the layer thickness was chosen so to obtain the best absorption contrast at the Fe *K* edge. Reagent-grade hematite (α-Fe_2O_3) (Willis & Rooksby 1952) was used as reference compound for octahedrally coordinated Fe^{3+}.

The XANES experiments were performed at the PULS X-ray beamline of Frascati National Laboratories (Italy). The storage ring was operated at 1.5 GeV (yielding a critical energy of 1.5 keV); the typical beam-current was 40 mA. The incident X-ray beam was monochromatized by a channel-cut Si(111) crystal; no other optical elements are present on this beamline. Measurements were performed at the Fe *K* edge in the transmission mode, and the incident and the transmitted flux were measured using argon-filled ionization chambers. This experimental setting has been successfully used in detailed EXAFS analyses of mineral samples (Quartieri *et al.* 1993a), and the energy resolution at the Fe *K* edge is sufficient for the analysis of the near-edge features. In the present case, however, the relatively poor signal-to-noise ratio in the observed absorption spectra is essentially determined by the small quantity of sample available. The XANES region was scanned over the energy spectrum with a 0.40 eV step. The raw XANES spectra of the samples and reference compound were treated prior to examination by subtracting the pre-edge background with a linear function and normalizing to the absorption coefficient on the high-energy side of the curve. The normalization takes care of the effects resulting from the variable thickness of the samples.

Mössbauer spectroscopy

The same pulverized samples used for absorption spectroscopy were pressed into thin disks in a graphite press. ^{57}Fe Mössbauer spectra were measured at 298 K using a 20 mCi ^{57}Co source in a Rh matrix. The spectra were recorded over 1024 channels of a multichannel analyzer in the velocity range of ± 8 mm/s. They were fitted by a x^2 minimization procedure using a modified version of the MOSFUN program (Muller 1980); pseudo-Voigt profiles were approximated by the biquadratic function $1/[1 + \alpha x^2 + (1 - \alpha)\, x^4]$, $(0.5 < \alpha < 1$, where $\alpha = 1$ gives a Lorentzian profile and $\alpha = 0.5$ approximates a Gaussian function) (Muller 1980, and references therein). Doublets with equal areas for the high- and low-velocity peaks were used.

RESULTS

Fe K-edge absorption data

The XANES spectra collected for PmpK1 and PmpK3 (pumpellyite), PrhK1 (prehnite), and EpK3 (epidote) are reported in Figure 3. The data are compared with the absorption spectra of the Fe_2O_3 standard and the well-characterized pumpellyite from Hicks Ranch, California (labeled PmpHR: Galli & Alberti 1969, Artioli *et al.* 1991). The edge-feature energies reported in Table 2 correspond to the zeros of the first derivative of the spectra.

The near-edge X-ray absorption spectrum of Fe in several Fe-bearing minerals was extensively studied by Waychunas *et al.* (1983). It presents three or four well-defined features: a pre-edge peak, one or two broader maxima or shoulders, and a more or less structured edge-crest.

The pre-edge peak is assigned to the 1*s* Fe core state to 3*d* crystal-field molecular orbital transition; its energy is strongly influenced by the site geometry and

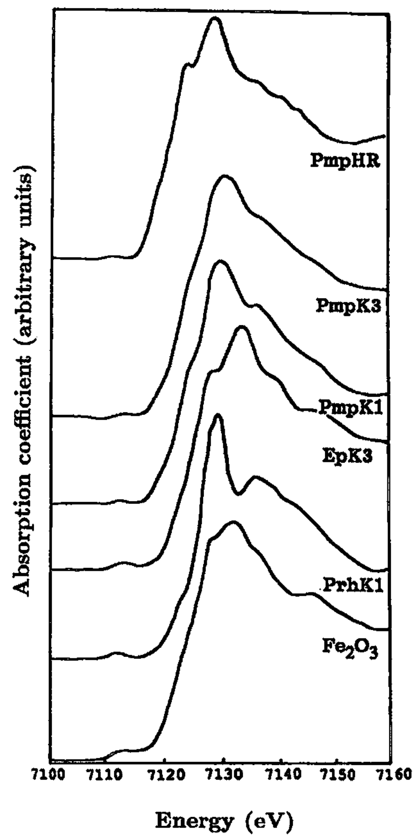

FIG. 3. XANES spectra on Fe *K*-edge. The photoelectron background-absorption profile has been removed, and all spectra have been normalized with respect to the high-energy side of the curve. Sample codes as in Table 2.

TABLE 2. ENERGY (eV) OF XANES FEATURES OF Fe IN PUMPELLYITE AND COEXISTING PREHNITE AND EPIDOTE*

Sample	1s → 3d (pre-edge)	2nd feature	3rd feature	edge crest
PmpK3	7112.5	7118.8	7123.3	7129.8
PmpK1	7112.9	7118.8	7123.8	7129.7
EpK3	7112.8	7122.4	7128.2	7132.8
PrhK1	7112.7	7122.7	7127.7	7130.0
PmpHR	7111.0	7118.0	7123.0	7128.4
Fe_2O_3	7113.1	7122.8	7127.8	7131.4

* Hematite was used as reference compound containing octahedrally coordinated Fe^{3+}. The XANES data are compared to those of the well-characterized pumpellyite from Hicks Ranch, California (Artioli et al. 1991).

the oxidation state of the Fe atom, and its intensity varies considerably with coordination state (Waychunas *et al.* 1983, Tossell *et al.* 1973, 1974).

Our XANES spectra reveal four main features: a pre-edge peak at 7111.0–7113.1 eV, a first shoulder in the energy range 7118.0–7122.8 eV, a second shoulder at 7123.0–7128.2 eV, and an edge crest at 7128.4–7132.8 eV. As can be seen from Table 2, the pre-edge peak has similar energy in all the samples, whereas in the PmpHR pumpellyite it is about 2 eV lower than the corresponding peak in hematite and in the other samples. A comparable shift in energy is shown by the edge crest. This evidence, as reported in other investigations on several Fe^{2+} and Fe^{3+} minerals (Calas *et al.* 1980, Calas & Petiau 1983, Brown *et al.* 1988, Waychunas *et al.* 1983, 1986), suggests that the prevalent state of oxidation of Fe in PmpHR is 2+, whereas in all the other samples it is 3+.

The quality of our XANES spectra is sufficient to reveal the prevalent state of oxidation of Fe in the samples examined. However, since the edge features of the two valence states of Fe largely overlap, we cannot rule out the presence of very small amounts of divalent iron in samples where trivalent iron is dominant. As discussed below, this possibility is certainly excluded for the EpK3 and PrhK1 samples by the Mössbauer data. The results obtained for the pumpellyite samples are in agreement with a previous interpretation of the X-ray absorption data for pumpellyite-group minerals (Artioli *et al.* 1991).

Mössbauer data

The room-temperature Mössbauer spectra of EpK3 and PrhK1 samples are reported in Figures 4a and 4b. Hyperfine parameters and statistical information on the fits for EpK3 and PrhK1 samples are reported in Table 3, whereas those regarding pumpellyite samples are reported in Table 2 in Artioli & Geiger (1994).

The Mössbauer spectra and the inferred distribution of Fe in the epidote-group minerals were extensively studied by Dollase (1973): in iron-rich epidote, piemontite and "oxyallanite", Fe^{3+} is found in two octahedrally coordinated sites, the major amount in *M*(3) and a minor amount in *M*(1); in a few cases, an additional minor Fe^{2+} peak was found. The valence state of the iron can be unambiguously determined by the isomer-shift values of these doublets.

The Mössbauer spectrum of epidote EpK3 (Fig. 4, Table 3) consists of two doublets whose isomer shift parameters reflect typical values for Fe^{3+} in octahedral coordination. No evidence of the presence of Fe^{2+} was found in our sample.

The Mössbauer spectrum of prehnite (Fig. 4, Table 3) is even simpler: only one doublet is present, with a very small value of the quadrupole splitting parameter; the isomer shift unambiguously indicates that the oxidation state of Fe is 3+. The single doublet

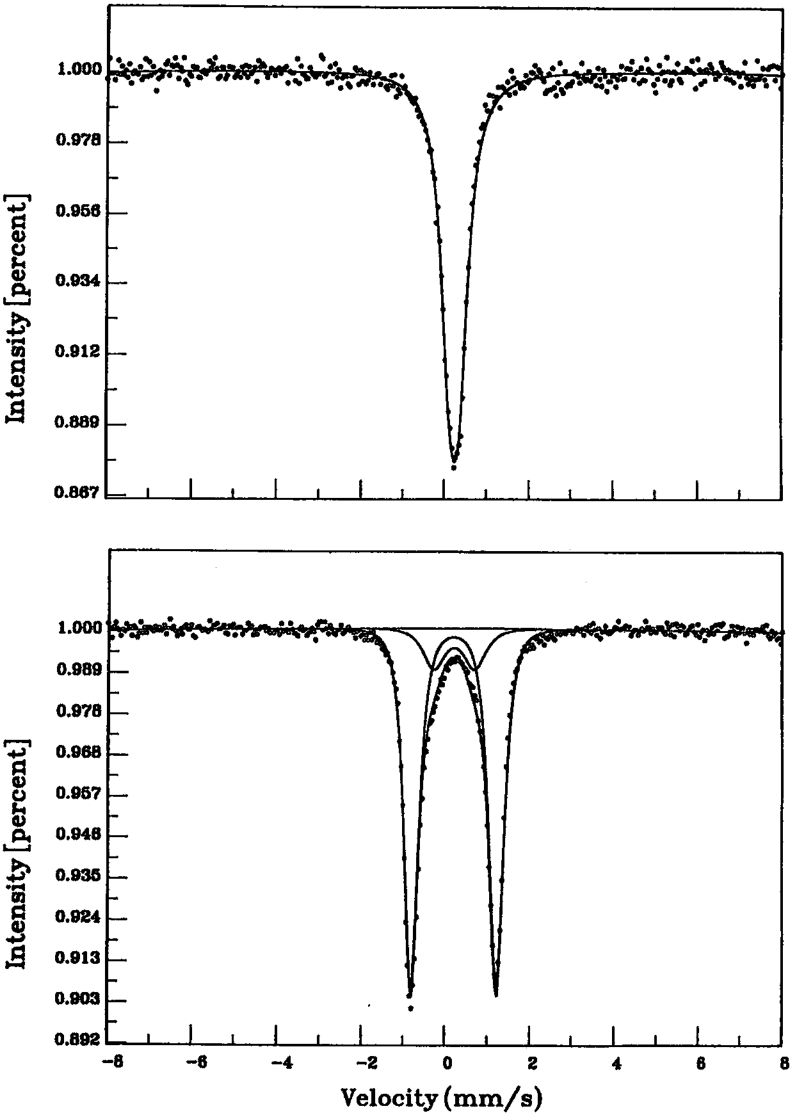

FIG. 4. ^{57}Fe Mössbauer spectra of prehnite PrhK1 (above) coexisting with pumpellyite PmpK1 and epidote EpK3 (below) coexisting with pumpellyite PmpK3.

indicates a unique crystallographic position for the iron cation, and the small quadrupole splitting suggests a highly symmetrical site-geometry. Prehnite has been described in at least three different space-groups: *Pncm* (Peng *et al.* 1959, Papike & Zoltai 1967), *P2cm* (Preisinger 1965, Balić Zunić *et al.* 1988), and *P2/n* (Baur *et al.* 1990). The ambiguity in the space group is determined by the Si,Al ordering scheme over the tetrahedrally coordinated sites; in all three models, the Al,Fe octahedral site is crystallographically unique. The octahedrally coordinated site indeed shows a more symmetrical environment in the centrosymmetric space-group *Pncm* (two independent cation–oxygen distances: Fe–OH = 1.91, Fe–O = 1.93 Å), than in the proposed noncentrosymmetric ones (*i.e.*, four different Fe–O distances in the space group *P2cm*, in the range 1.88–1.97 Å).

The resolution of the present Mössbauer data does not allow a completely unambiguous allocation of site-symmetry for the Fe cation. However, based on

TABLE 3. Fe MÖSSBAUER PARAMETERS AT 298 K FOR EPIDOTE EpK3 AND PREHNITE PrhK1 COEXISTING WITH PUMPELLYITE PmpK1 AND PmpK3, RESPECTIVELY

			$^{[VI]}Fe^{3+}$ in M3				$^{[VI]}Fe^{3+}$ in M1			
Sample	χ^2	α	A%	IS	QS	FWHM	A%	IS	QS	FWHM
EpK3	1.84	0.91	86.0	0.36	2.02	0.40	14.0	0.37	0.97	0.50
			$^{[VI]}Fe^{3+}$							
PrhK1	1.20	0.99	100	0.39	0.23	0.52				

Isomer shift relative to metallic iron (IS), quadrupole splitting (QS) and FWHM peak widths are in mm/s.

A%: relative absorption area in the site referred to the total resonant absorption area = 100.

α: parameter of the pseudo-Voigt profile (see text).

the fact that the lower site-symmetry is associated with a larger range in the associated bond-distances, the absence of the center of symmetry on the Fe site is assumed to be related to the increase of the observed Mössbauer peak-widths. The comparison of the Fe^{3+} Mössbauer line-width in prehnite PrhK1 (0.52 mm/s, Table 3) with those of the low-symmetry octahedrally coordinated environment of Fe^{3+} in epidote EpK3 (*M*1 site: 0.50 mm/s, Table 3) and in pumpellyite BU (*Y* site: 0.45–0.47 mm/s, Artioli & Geiger 1994) indicates, therefore, that a noncentrosymmetric geometry is likely to be more appropriate to describe the environment of iron in the Keweenawan prehnite.

The Mössbauer spectra of the pumpellyite samples are reported and discussed in detail in Artioli & Geiger (1994). The combined results of Mössbauer spectroscopy and full-profile Rietveld analyses of X-ray powder-diffraction spectra indicate that both Fe^{2+} and Fe^{3+} cations are present in the pumpellyite structure, and that they are essentially ordered on the *X* and *Y* octahedral sites, respectively. Specifically, the PmpK1 and PmpK3 pumpellyite samples contain divalent and trivalent iron in the approximate ratio 1:2.5.

The Mössbauer results are consistent with the information obtained from the XANES data, since both indicate the prevalence of Fe^{3+} in the samples studied. Moreover, the higher sensitivity of Mössbauer spectroscopy in detecting small amounts of divalent iron in the presence of predominantly trivalent iron cations (Quartieri *et al.* 1993b) allows us to exclude the presence of divalent iron in epidote EpK3 and in prehnite PrhK1 at the 1–2% level, and to determine the presence of a non-negligible amount of divalent iron in the structure of the coexisting pumpellyite.

DISCUSSION

The present spectroscopic data clearly show that iron in Fe-rich pumpellyite samples is mostly present in the trivalent state. Both X-ray absorption and Mössbauer data give good evidence that Fe^{3+} is prevalent in Fe-rich pumpellyite, be it associated with prehnite or epidote. The data also confirm that both prehnite and epidote coexisting with pumpellyite in low-grade metamorphic assemblages also contain a higher Fe^{3+}/Fe^{2+} ratio than pumpellyite (Schiffman & Liou 1983). As a matter of fact, the epidote and prehnite associated with pumpellyite are shown to be essentially pure ferric end-members. These findings indicate that the mineral assemblage formed under oxidizing conditions, which exerted a major control over the structural parameters of the secondary Ca-silicates.

Both pumpellyite and epidote have in principle very flexible structures, from the point of view of stoichiometry and charge-balance adjustements, by virtue of the presence of octahedral sites of different size and degree of distortion, and also in view of the possibility of OH groups substituting for oxygen atoms. In pumpellyite, in particular, the crystal structure can efficiently optimize the geometrical parameters and the distortion of the coordination polyhedra by simply adjusting the intracrystalline distribution of the octahedrally coordinated cations according to the oxidation conditions of the environment and the valence-dependent ionic radius. By correctly measuring the Fe^{2+}/Fe^{3+} ratio in pumpellyite-group minerals, it is then possible to estimate the $f(O_2)$ conditions of the environment during crystallization, and to clarify the correlation between the site distribution of the mixed-valence cations and the cell volume (Artioli & Geiger 1994). The correlation trend was previously misinterpreted because of the incorrect evaluation of the valence state of the cations in the literature (Passaglia & Gottardi 1973). Although Fe^{2+} has a larger ionic volume than Fe^{3+}, it is the more extensive substitution of Al by trivalent iron that controls the cell volume and distortion (Surdam 1969, Artioli & Geiger 1994). A misinterpretation of the structural formula of pumpellyite could lead to incorrect assumptions in the petrological analysis of assemblages of metamorphic minerals.

In the past, several petrological studies drew attention to the incongruency of a Fe^{2+}-rich pumpellyite (as interpreted from the assumed crystal-chemical rules) in assemblages of oxidized metamorphic minerals. The difficulties inherent to proper discrimination of the valence state of Fe (Zen 1974, Coombs *et al.* 1976, Nakajima *et al.* 1977, Artioli *et al.* 1991) obscured the effective crystal-chemical role of mixed-valence cations in the pumpellyite structure. Although it is known that most of the chemical variation of Fe-rich pumpellyite in low-grade metamorphism is due to a basic $Al \rightleftharpoons Fe^{3+}$ substitution (for example: Surdam 1969, Liou 1979, Evarts & Schiffman 1983, Cortesogno *et al.* 1984, Liou *et al.* 1985, Inoue & Utada 1991), the structural formula of pumpellyite commonly is interpreted on the basis of crystal-chemical rules (Passaglia & Gottardi 1973) derived according to the structural analysis of high-pressure Fe-poor pumpellyite coexisting with lawsonite from Hicks Ranch, California (Galli & Alberti 1969). This is one of the rare examples of pumpellyite in which the $Mg \rightleftharpoons Fe^{2+}$ structural substitution on the octahedrally coordinated *X* site is dominant. Furthermore, the partitioning of the two different oxidation states of iron over the crystallographically independent octahedral positions has not been recognized until recently (Artioli *et al.* 1991, Artioli & Geiger 1994). Preliminary data also show that the crystal-chemical role of Mn in the pumpellyite structure is very similar to that of Fe, as Mn^{3+} shows a clear preference for the *Y* octahedral site (Artioli *et al.* 1993).

It is common practice in the literature to allocate the total Fe or Mn content of pumpellyite, as resulting from electron microprobe or X-ray fluorescence analyses, to both the divalent and the trivalent states on the basis of charge balance alone. However, the varying degree of substitution of oxygen atoms by hydroxyl groups generally is unknown, and this may lead to serious errors in the estimate of the total anionic charge. It is virtually impossible to correctly allocate the valence state of the mixed-valence cations, especially Fe and Mn, in absence of an accurate measurement of the OH content by thermal or spectroscopic analyses, or without a direct measurement of the ratio of divalent to trivalent cations, as in the present study. The greater the proportion of mixed-valence cations in pumpellyite-type minerals, *i.e.*, in members of the pumpellyite–julgoldite and the pumpellyite–okhotskite series, commonly found in low-grade metamorphic assemblages, the larger is the error in the crystal-chemical interpretation of the chemical formula.

The issue also has some relevance in the definition of the thermodynamic properties of pumpellyite. It has been shown that petrogenetic grids for low-grade metabasites based on Fe-free pumpellyite result in an unrealistically small field of stability of prehnite + pumpellyite; more reliable results can be obtained by taking the Fe activity in pumpellyite into account (Frey *et al.* 1991). We trust that the data presented here and published recently clarify the crystal-chemical role of Fe in the pumpellyite structure and the genetically associated phases, and ultimately will lead to proper modeling of the reactions responsible for the formation of pumpellyite-group minerals.

ACKNOWLEDGEMENTS

The authors thank Italian MURST, INFM and CNR for financial support. We thank the staff of INFN–PULS (Frascati) for access to ADONE, and Dr. G. Antonioli for his help during the XANES data collection. Electron-microprobe analyses were kindly performed by Dr. G. Vezzalini at the Department of Earth Sciences of the University of Modena. Part of the computing time was made available by CICAIA, and SEM photographs were taken at CIGS of the University of Modena. Helpful suggestions and discussion were provided by the referees.

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Received November 25, 1993, revised manuscript accepted August 2, 1994.