^{57}Fe Mössbauer spectroscopy of natural melilites

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ABSTRACT. — Natural melilites from volcanic rocks exhibit a Fe^{3+} doublet (IS = 0.31, QS = 1.12 mm/s at 298 K) and a Fe^{2+} doublet (IS = 0.97, QS = 1.10 mm/s at 298 K).

The systematic line broadening observed is related to next-nearest neighbours interactions. Fe^{3+} is preferentially ordered into the T(1) site.

Key words: natural melilites, Mössbauer spectroscopy, Alban Hills, Kaiserstuhl.

RIASSUNTO. — La spettroscopia Mössbauer consente di confermare la presenza di ferro ferroso e ferro ferrico nelle meliliti di rocce vulcaniche. Tali meliliti mostrano un doppietto Fe^{3+} (IS = 0.31, QS = 1.12 mm/s a 298 K) e un doppietto Fe^{2+} (IS = 0.97, QS = 1.10 mm/s a 298 K). A causa della complessa composizione chimica delle meliliti naturali le interazioni con gli immediati vicini determinano un significativo allargamento delle righe. Fe^{3+} occupa prevalentemente le posizioni T(1).

Parole chiave: meliliti naturali, spettroscopia Mössbauer, Colli Albani, Kaiserstuhl.

Introduction

Melilites, general formula $X_2ZT_2O_7$, with X mainly Ca and Na, Z = Mg, Fe^{2+}, Zn, Al, Fe^{3+}, and T = Si, Al, Fe^{3+}, are important rock-forming minerals in SiO_2-undersaturated volcanic rocks (e.g. Yoder 1973). In terms of crystal chemistry, an important feature is the incorporation of rather large and mostly divalent Z cations into a tetrahedral [T(1)] site. Mössbauer data on iron-bearing melilites have, so far, only been reported for synthetic specimens: Akasaga and Ohashi (1985) as well as Akasaga et al. (1986)

give hyperfine parameters for Fe^{3+}-bearing melilites, whereas Ito and Hafner (1974) report data on ferrous iron in $Ba_2FeSi_2O_7$ and $Sr_2FeSi_2O_7$ melilite end members. Because Seifert et al. (1987) observed incommensurate phases and a consequent splitting of ferrous Mössbauer doublets in synthetic åkermanite ($Ca_2MgSi_2O_7$) - Fe-åkermanite ($Ca_2FeSi_2O_7$) solid solutions, a Mössbauer study of natural melilites has been undertaken here.

Experimental techniques

Mössbauer spectra have been taken in the constant acceleration mode, a ^{57}Co in Rh source (held at room temperature, nominal activity 50 mCi), and a 1024 channel multichannel analyzer. Left-hand and right-hand spectra have been recorded separately in 512 channels each and fitted independently to sums of Lorentzian lines with a least-squares technique. Reported hyperfine parameters are the averages of the two sides. Metallic iron served as a velocity calibrant, and isomer shifts are reported relative to it. Absorbers were prepared from finely-ground powders (thicknesses 1 - 3 mg Fe/cm²) pressed between Al foil and kept at room temperature or 77 K, respectively.

Specimen description

Pure melilite separates were available from

the study of Federico and Gianfagna (1982) on melilites from ejecta and lavas from the Alban Hills, Italy. These authors also reported lattice constants and optical properties. From these samples, a highly oxidized specimen

TABLE 1

Structural formulae of the melilites studied, based on 14 cationic charges

	site	AR-52[a]	CC-B[a]	CB-G63[a]	Kaiserstuhl[b]
Si	T(2)	1.917	1.879	1.952	1.949
Al		0.083	0.121	0.048	0.051
Al	T(1)	0.268	0.353	0.283	0.361
Fe^{3+}		0.236[c]	0.072[c]	0.002[c]	0.030[d]
Fe^{2+}		0.004	0.095	0.159	0.163
Mn		0.004	0.012	none	0.009
Mg		0.416	0.432	0.532	0.416
Ca	X	1.705	1.737	1.774	1.663
Sr		0.014	0.022	0.021	n.d.
Na		0.278	0.235	0.203	0.338
K		0.013	0.020	0.021	0.006

[a] = taken from FEDERICO and GIANFAGNA (1982); [b] = sample from berghalite (nepheline-hauyne-melilitite) from Kaiserstuhl, FRG, supplied by J. KELLER, Freiburg. Analyst: D. ACKERMAND, Kiel; [c] = ferrous/ferric ratio from wet chemical analysis; [d] = ferrous/ferric ratio from Mössbauer spectroscopy; n.d. = not determined.

(AR-52) and two more or less reduced specimens (CC-B and CB-G 63) have been selected for the Mössbauer investigation. In addition, J. Keller (Freiburg, FRG) made available a sample from Kaiserstuhl (FRG).

Chemical analyses of the specimens used here are given in Table 1. For the Kaiserstuhl sample, no chemical determination of its ferric iron content was available. The purity of the hand-picked separates was always better than 99 per cent.

The Kaiserstuhl sample has also been investigated by electron diffraction by M. Czank (Kiel, FRG), to check for the presence of satellite peaks and an incommensurate phase (cf. Seifert et al. 1987), but none were found.

Results

Oxidized sample (AR-52)

The spectra consist of one very broad, nearly symmetrical doublet with little, if any, struc-

TABLE 2

Hyperfine parameters of natural melilites and of $Sr_2FeSi_2O_7$

I one ferric, one ferrous doublet

		AR52		CB-G63		CCB		Kaiserstuhl		$Sr_2FeSi_2O_7$
		298K	77K	298K	77K	298K	77K	298K	77K	298K
Fe^{3+}	T	0.041	0.034	0.006	0.004	0.005	0.005	0.003	0.004	-
	B	0.68	0.76	0.56	0.54	0.67	0.79	0.54	0.70	-
	IS	0.31	0.41	0.21	0.41*	0.42	0.52	0.26	0.30	-
	QS	1.12	1.12	0.33	0.42	0.75	0.87	0.48	0.55	-
Fe^{2+}	T	-	-	0.041	0.029	0.040	0.039	0.021	0.024	0.112
	B	-	-	0.42	0.66	0.40	0.58	0.37	0.48	0.31
	IS	-	-	0.97	1.12	0.96	1.09	0.97	1.09	0.97
	QS	-	-	2.33	2.75	2.35	2.80	2.39	2.84	2.60
M		0.43	0.16	0.28	0.54	0.33	0.51	0.36	0.49	0.01

II AR52, two ferric doublets

$Fe^{3+}(1)$		298K	77K	$Fe^{3+}(2)$		298K	77K
	T	0.026	0.016		T	0.023	0.024
	B	0.64	0.58		B	0.44	0.65
	IS	0.31	0.42		IS	0.29	0.41
	QS	1.37	1.46		QS	0.84	0.80
M		0.14	0.05				

III reduced melilites: one ferric, two ferrous doublets

		CB-G63		CCB		Kaiserstuhl
		298K	77K	298K	77K	298K
Fe^{3+}	T	0.003	0.002	0.005	0.005	0.003
	B	0.52	0.62	0.73	0.79	0.64
	IS	0.50	0.42*	0.31	0.32	0.26
	QS	0.45	1.13*	0.99	1.13*	0.49
Fe^{2+}	T	0.033	0.024	0.028	0.032	0.011
	B	0.34	0.52	0.32	0.43	0.24
	IS	0.99	1.13	0.98	1.10	0.97
	QS	2.45	2.92	2.46	2.90	2.52
Fe^{2+}	T	0.016	0.011	0.016	0.012	0.011
	B	0.41	0.78	0.43	0.63	0.37
	IS	0.99	1.17	0.94	1.09	0.95
	QS	2.04	2.19	2.13	2.26	2.24
M		0.02	0.22	0.13	0.10	0.09

* = constrained value; M = misfit in % (RUBY 1973); T = fractional dip; B = full width at half hight (in mm/s); IS = isomer shift (in mm/s, relative to metallic iron); QS = quadrupole splitting (in mm/s).

ture (Fig. 1). Fitting only one doublet, isomer shifts of 0.31 and 0.41 mm/s are obtained at 298 and 77 K, respectively, and a quadrupole splitting of 1.12 mm/s at both temperatures (Table 2). Because of the excessive line width in this fit, and because Fe^{3+} can, in principle, occupy both the T(1) and the T(2) positions (Akasaga and Ohashi 1985), two-doublet fits have been attempted as well (Fig. 1b and Table 2). However, the problem of line widths still persisted.

Reduced samples (CB-G 63, CC-B, Kaiserstuhl)
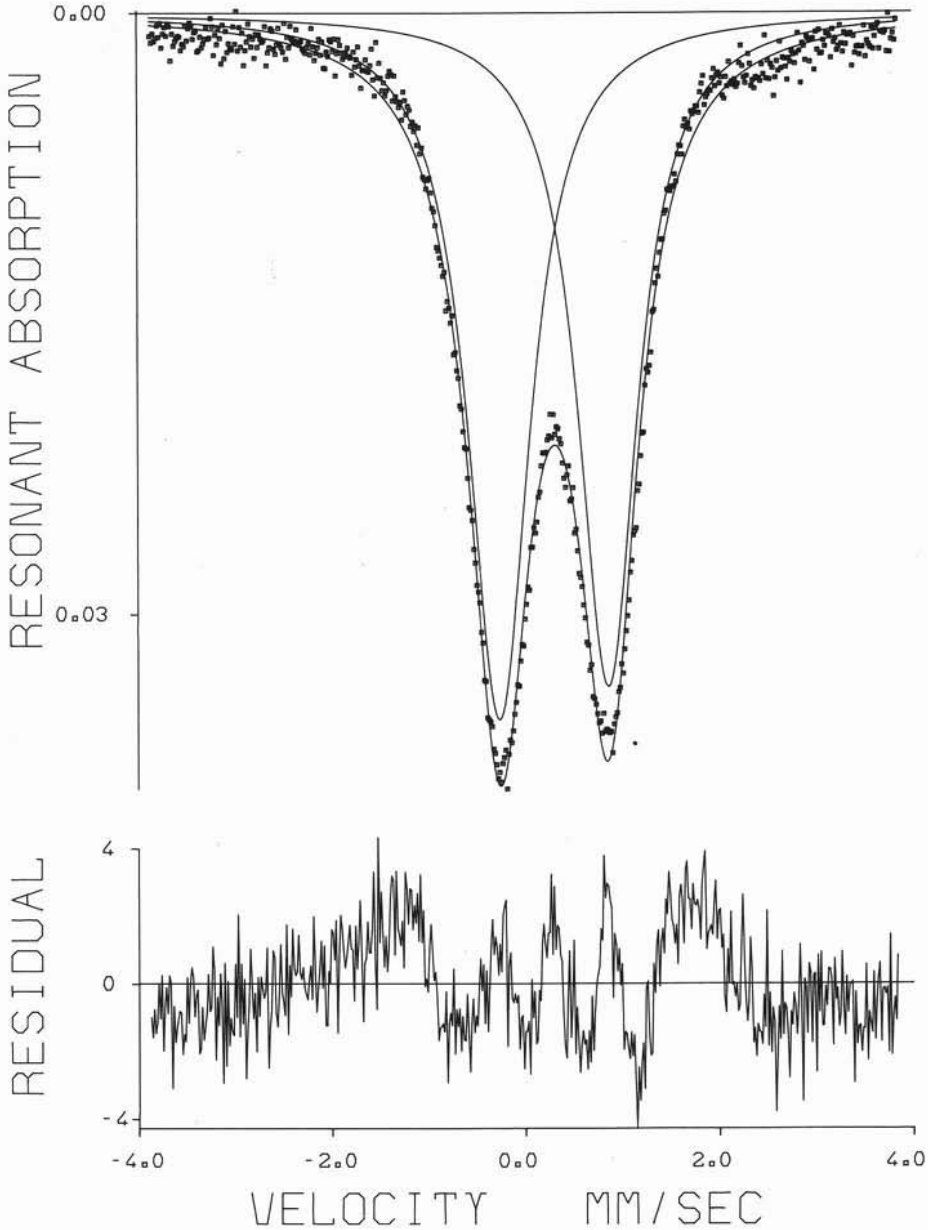
These three samples exhibit very similar

Fig. 1 a)

Fig. 1. — ⁵⁷Fe Mössbauer spectra of oxidized melilite AR-52, taken at 77K. a) fitted to one doublet; b) fitted to two doublets. The velocity scale is relative to Fe in Rh, for conversion relative to Fe metal add 0.11 mm/s. The residuals are the deviations of the calculated envelope from the experimental data, divided by the square root of the background. The unfitted small bump at a velocity close to 2.5 mm/s can be attributed to a trace of ferrous iron (cf. Fig. 2).

spectra, with one asymmetrical doublet and a shoulder at a velocity close to 0.5 mm/s (Fig. 2). Consequently, these spectra have been fitted to one ferrous and one ferric doublet (Table 2). Again, half widths are much larger than the theoretical value, and the ferrous lines broaden with decreasing absorber temperature. Because of the complete overlap
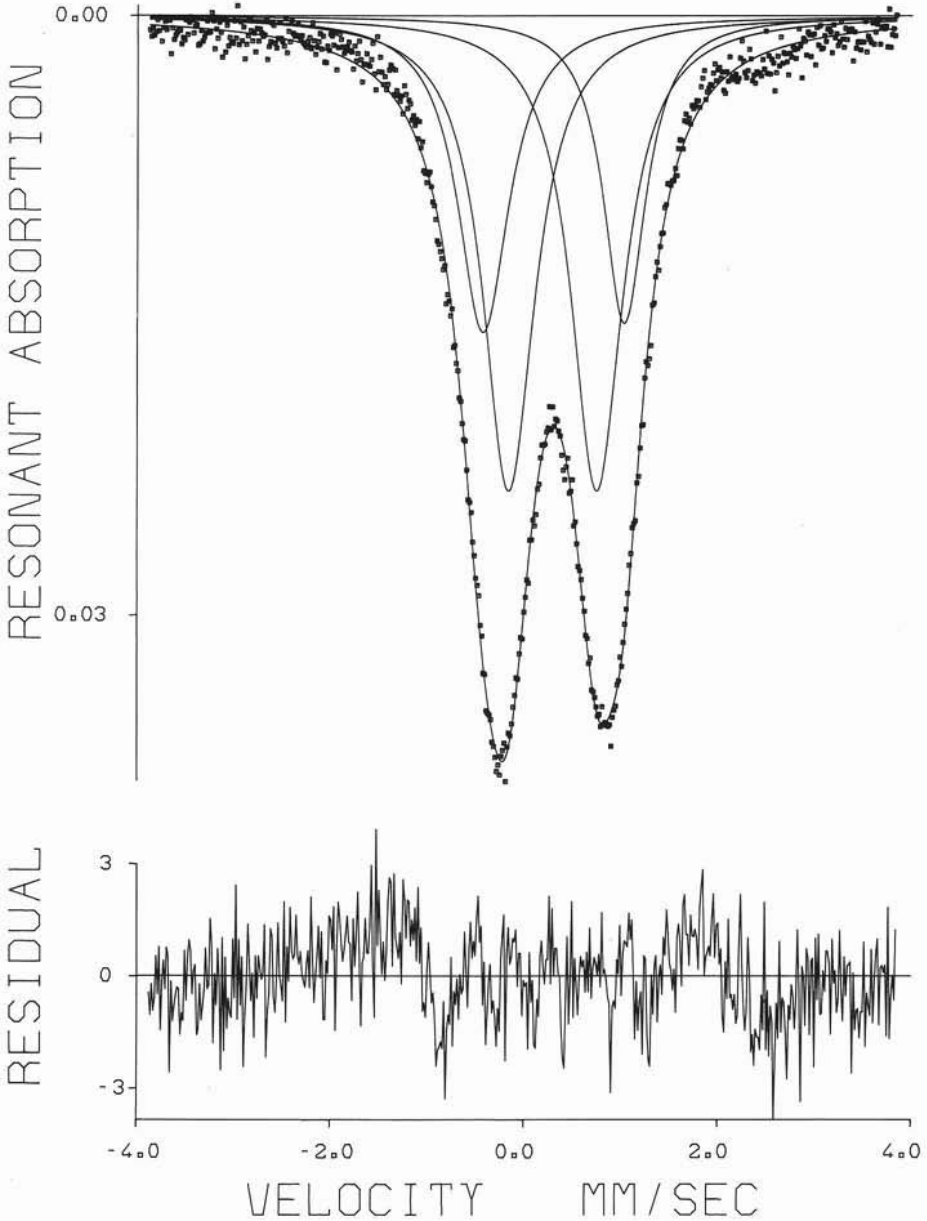
Fig. 1 b)

of the low-velocity ferric line with the ferrous line, hyperfine parameters of ferric iron in these samples are necessarily imprecise.

Although the standard melilite structure exhibits only one Fe^{2+}-bearing site [T(1)], two-doublet Fe^{2+}-fits have been attempted as well in view of the splitting of T(1) sites observed by Seifert et al. (1987) in the modulated melilite structure. As can be seen from Table 2 and Fig. 2, this lead to a general improvement of the fits, but still line widths are too high.
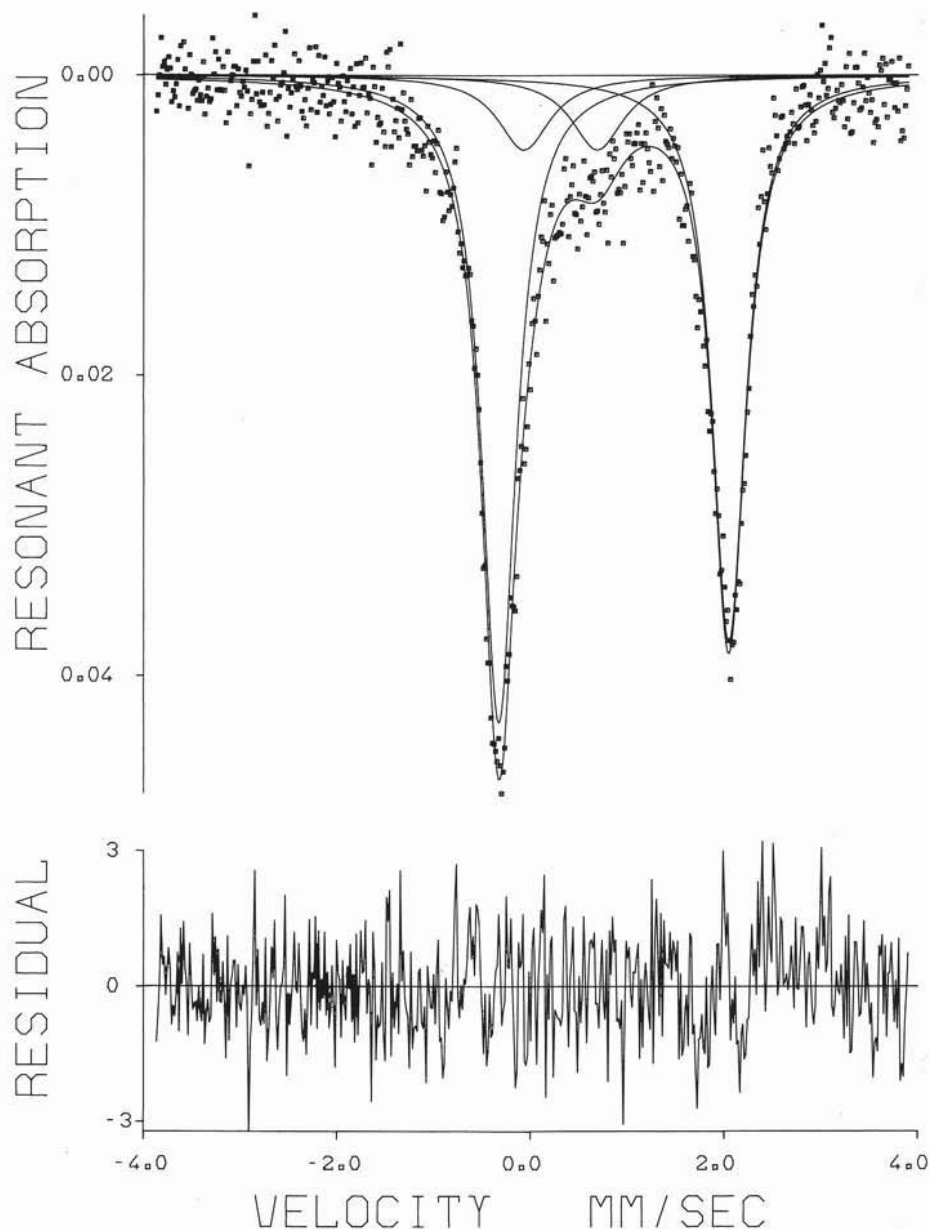
Fig. 2 a)

Fig. 2. — [57]Fe Mössbauer spectra of reduced melilite CC-B. a) 298K spectrum fitted to one ferrous and one ferric doublet; b) 298K spectrum fitted to two ferrous, one ferric doublets; c) 77K spectrum fitted to two ferrous, one ferric doublets.

Discussion

Line broadening

A common feature in all the spectra taken is the remarkable line broadening of both the ferrous and ferric lines which does not exist in spectra of the synthetic melilites investigated so far. Chemical heterogeneity within a sample is only slight, as found by microprobe analysis. For instance, in sample
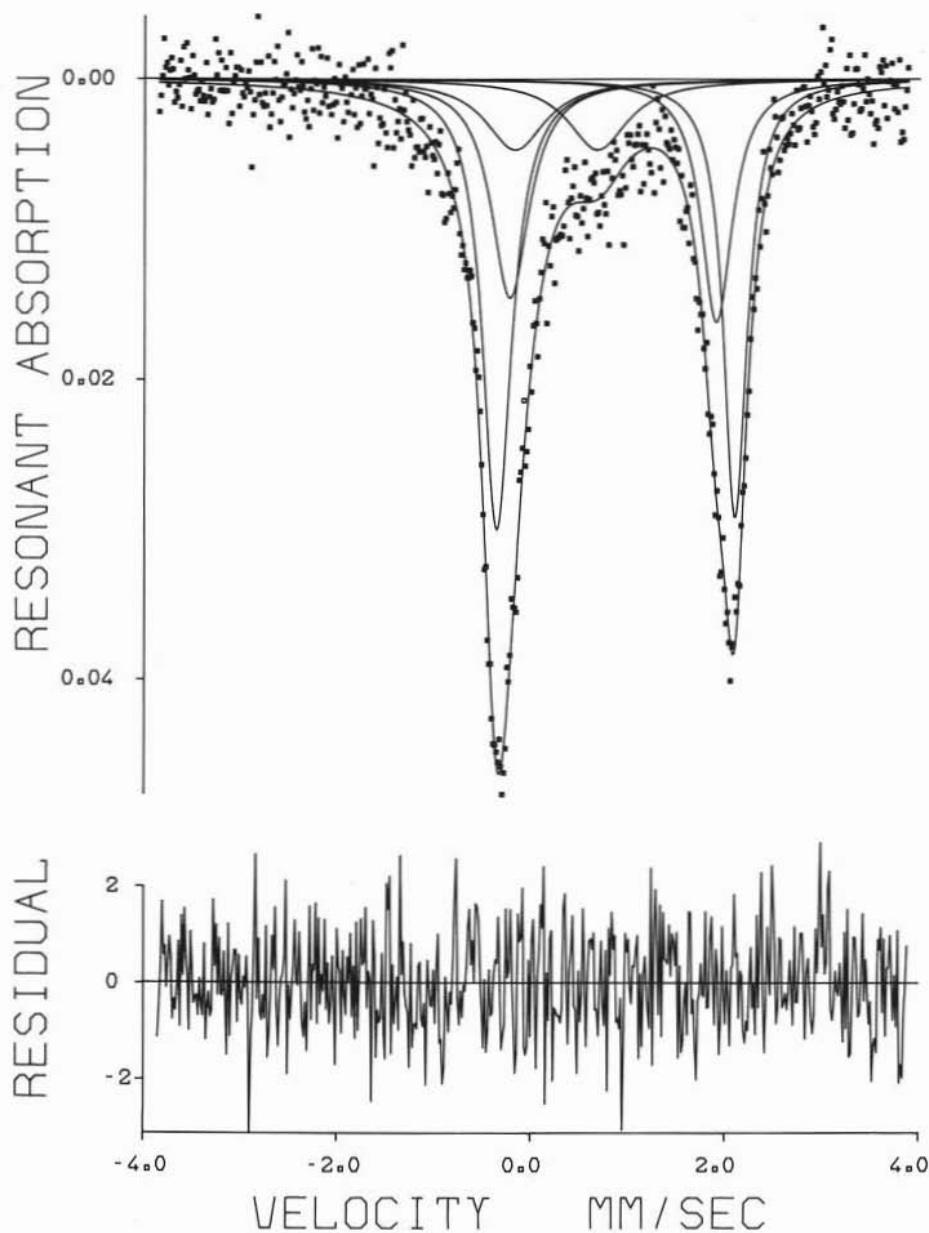
Fig. 2 b)

CC-B the maximum variability within the sample used is found with respect to Si ($\pm$ 0.026), Al ($\pm$ 0.065) and Mg ($\pm$ 0.036) where the figures give one estimated standard deviation of the concentration of the element per 7 oxygens, calculated from 11 point analyses of this sample. A later examination of a large fragment (measuring about $10 \times 6 \times 4$ cm) yielded larger variations (with FeO_{tot} ranging from 2.21 to 4.40 wt. % for sample CC-B, but this may be related to the big sample size. Despite of this we conclude that chemical heterogeneity of the sample on a macroscopic scale cannot be the cause of the anomalous
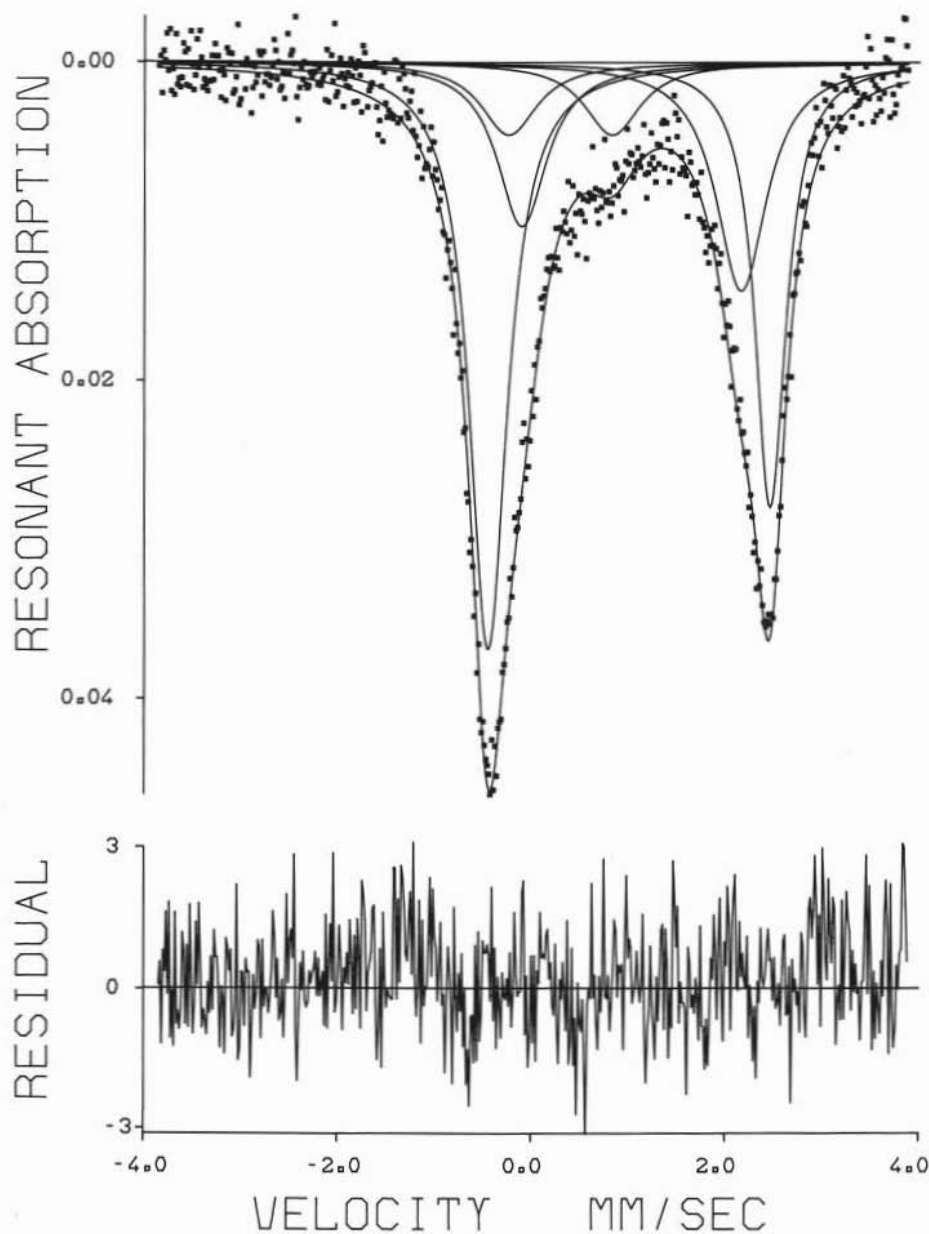
Fig. 2 c)

line widths.

On the other hand, we can expect line broadening from variations in chemistry on a microscopic, i.e. atomistic scale: Any T(1) tetrahedron is linked to three T(2) tetrahedra, and these may contain either Si or Al and possibly Fe^{3+}. Furthermore, the large posi-

tion X attached to a T(1) tetrahedron may be filled either by Ca or Na. Thus, a spectrum of electric field gradients will be possible, particularly because heterovalent substitutions are involved in the T(2) and X positions, and, consequently, a spectrum of hyperfine parameters can be expected for Fe in T(1) in-

stead of a sharp line. It should be noted in this context that the half widths of the Fe^{3+} in $T(1)$ are consistently higher than those of Fe^{3+} in $T(2)$ in the solid solutions studied by Akasaga and Ohashi (1985).

At least for the Kaiserstuhl sample it can be ruled out that the line broadening of the Fe^{2+} doublet at 298 K is due to incipient formation of a modulated structure, because this sample did not exhibit satellite reflections in the electron microscope. Furthermore, the 77 K Mössbauer spectra should exhibit two clearly resolved Fe^{2+} doublets (cf. Seifert et al. 1987) if the commensurate-incommensurate phase transition occurred in these samples around room temperature. We thus relate the line broadening of both the ferrous and ferric doublets at least mostly to next nearest neighbours interactions, although minor contributions of the effects of chemical heterogeneity on a macroscopic scale and in-cipient modulation of the structure at 77 K cannot be completely ruled out at present.

It is consistent with this concept of a spectrum of sites that fitting of more than one fer-ric and ferrous doublet yields better fits that are also statistically justified as judged from the decrease of the misfit parameter (Table 2). From the arguments given above it is not probable that these additional doublets describe specific sites, and in the following we will therefore rather use the one-doublet ferrous and one-doublet ferric fits describing the average positions.

Ferric iron

Fe^{3+} hyperfine parameters in melilites have been reported by Akasaga and Ohashi (1985) and Akasaga et al. (1986). In the first paper, they report, at 298 K, isomer shifts and quadrupole splittings of 0.095 to 0.15 mm/s and 1.086 to 1.256 mm/s, respectively, for Fe^{3+} in the $T(1)$ site and of 0.078 to 0.125 and 1.825 to 1.930, respectively, for Fe^{3+} in $T(2)$. In these ranges, the Sr-melilite sample has not been taken into account. According to these data, quadrupole splittings are more diagnostic for the assignment of Fe^{3+} to either $T(1)$ or $T(2)$, and the data for the AR-52 sample (Table 2) clearly suggest that the majority of Fe^{3+} in this sample resides in the

$T(1)$ position. Even the two-doublet ferric iron fit to this specimen does not support the concept of significant amounts of Fe^{3+} in $T(2)$. This conclusion contrasts to the slight preference of Fe^{3+} for $T(2)$ relative to Al observed by Akasaga and Ohashi (1985) in synthetic melilites.

The isomer shift of Fe^{3+} deserves a further comment: The value reported here (0.31 mm/s) fits well into the general relationship between average tetrahedral bond length and isomer shift (e.g. Steffen et al. 1984, their Fig. 3), with $T(1) - 0$ distances on the order of 1.926 Å ($Ca_2CoSi_2O_7$, Kimata 1983) to 1.762 Å ($CaNaAlSi_2O_7$, Louisnathan 1970), but disagrees with the values reported by Akasaka and Ohashi (1985) for both the $T(1)$ and $T(2)$ positions (cf. above). These authors explain the anomalously low value of the isomer shift of Fe^{3+} in $T(1)$ by π-bonding.

Their values could, however, be reproduced by us for a synthetic Ak50FAGe50 sample (i.e. $Ca_2Mg_{0.5}Fe^{3+}_{0.5}Al_{0.5}Si_{1.5}O_7$), so that the difference seems to be real.

Ferrous iron

In the one-doublet ferrous fits the quadrupole splitting and isomer shift is remarkably constant in the different natural samples (Table 2).

The values also closely agree with those reported for the «normal» $T(1)$ site in the modulated $Ca_2MgSi_2O_7$ - $Ca_2FeSi_2O_7$ melilites (Seifert et al. 1987). On the other hand, in $Sr_2FeSi_2O_7$ and $Ba_2FeSi_2O_7$ (Table 2, and Ito and Hafner 1974) quadrupole splittings differ strongly, pointing to a strong influence of the size of the X cation on the geometry of the Z site. Even in the two-doublet fits of the natural melilites the isomer shift ranges (at 298 K) from only 0.94 to 0.99 mm/s. These values are consistent with an exclusively tetrahedral coordination of Fe^{2+} (cf. Bancroft 1973).

Ferric/ferrous ratios

At low temperatures, the area ratio of the Fe^{3+} doublet relative to the total area under the envelope is closely proportional to the molar ratio of ferric to total iron, whereas at

higher temperatures relations may be complicated through different recoil-free fractions of the Fe species. Thus area ratios calculated from the 77 K spectra can be compared to the wet chemical Fe analyses available for the AR-52, CC-B and CB-G 63 samples (Table 3).

TABLE 3

Wet chemical molar Fe^{3+}/total Fe ratios and area fractions of Mössbauer Fe^{3+} doublets

sample	chemical analysis	Mössbauer data, 77 K 4-lines fits	6-lines fits
AR-52	0.99	1.00	-
CC-B	0.43	0.15	0.14
CB-G63	0.01	0.11	0.02
Kaiserstuhl	n.d.	0.18	n.d.

n.d. = not determined.

In agreement with the wet chemical analyses, no significant amounts of ferrous iron can be observed in the AR-52 sample (cf. lack of absorption at about 2.0 mm/s in the Mössbauer spectrum of Fig. 1). In the more reduced samples, the Fe^{3+} concentrations will be overestimated in four-line fits because the asymmetry of the Fe^{2+} peak will enhance the apparant Fe^{3+} lines. Considering the potential sources of error in the wet chemical and Mössbauer techniques, and the small absolute concentrations of Fe^{3+}, the agreement can still be considered satisfactory for the reduced CB-G 63 sample. On the other hand, a clear discrepancy exists for CC-B where the Mössbauer data suggest much lower ferric contents than the chemical analysis. The latter determination has been repeated on 100 mg sample, and the earlier results have virtually been confirmed.

Attempts failed to calculate the ferric/ferrous ratio from the microprobe analyses by the additional constraint Σ cations = 5, probably because of the low total amounts of Fe. We cannot, at present, explain this discrepancy.

Conclusions

The presence of both ferrous and ferric iron in many volcanic melilites has been confirmed from the Mössbauer data. Ferric iron predominantly and ferrous iron exclusively enter the T(1) site. In the complex chemistries of natural melilites next-nearest neighbors interactions lead to a significant increase in line widths. The anomalously low isomer shifts of tetrahedral ferric iron observed in synthetic melilites are lacking in the natural specimens.

REFERENCES

AKASAKA M., OHASHI H. (1985) - *⁵⁷Fe Mössbauer study of synthetic Fe^{3+}-melilites.* Phys. Chem. Minerals *12*, 13-18.

AKASAKA M., OHASHI H., SHINNO I. (1986) - *The distribution of Fe^{3+} and Ga^{3+} between two tetrahedral sites in melilites, Ca_2 $(Mg,Fe^{3+},Ga,Si)_3O_7$.* Phys. Chem. Minerals *13*, 152-155.

BANCROFT G.M. (1973) - *Mössbauer spectroscopy. An Introduction for Inorganic Chemists and Geochemists.* McGraw Hill, London.

FEDERICO M., GIANFAGNA A. (1982) - *The melilites of the ejecta and lavas from the Alban Hills (Rome, Italy).* Rend. Soc. Ital. Min. Petrol. *38*, 1387-1400.

ITO H., HAFNER S.S. (1974) - *Synthesis and study of gadolinites.* Am. Mineral. *59*, 700-708.

KIMATA M. (1983) - *The crystal structure and stability of Co-åkermanite, $Ca_2CoSi_2O_7$, compared with the mineralogical behaviour of Mg cation.* N. Jb. Miner. Abh. *146*, 221-241.

LOUISNATHAN S.J. (1970) - *The crystal structure of synthetic soda melilite, $CaNaAlSi_2O_7$.* Zeitschr. Krist. *131*, 314-321.

RUBY S.L. (1973) - *Why misfit when you already have x^2?* Mössbauer Effect Methodology 8, 263-276.

SEIFERT F., CZANK M., SIMONS B., SCHMAHL W. (1987) - *A commensurate-incommensurate phase transition in iron-bearing melilites.* Phys. Chem. Minerals *14*, 26-35.

STEFFEN G., SEIFERT F., AMTHAUER G. (1984) - *Ferric iron in sapphirine: a Mössbauer spectroscopic study.* Am. Mineral. *69*, 339-348.

YODER H.S. JR. (1973) - *Melilite stability and paragenesis.* Fortschr. Miner. *50*, 140-173.