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# $^{57}$Fe MÖSSBAUER SPECTRA OF PEROVSKITE AND TITANITE

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## ABSTRACT

The $^{57}$Fe Mössbauer spectra of natural perovskite, and four natural and two synthetic samples of titanite containing small amounts of iron, have been recorded. In the natural samples, most of the iron is present as $Fe^{3+}$ in the octahedral Ti sites, but $Fe^{2+}$ in the Ti site is also present in some samples. In synthetic samples, $Fe^{3+}$ is present in approximately equal amounts in both the octahedral Ti and tetrahedral Si sites. An unusual degree of line-broadening is observed in the spectrum of natural titanite, and is probably due to structural defects from radiation damage and compositional or next-nearest-neighbor effects.

*Keywords:* titanite, perovskite, isomer shift, quadrupole splitting, octahedral site, tetrahedral site.

## SOMMAIRE

On présente le spectre Mössbauer du $^{57}$Fe d'une pérovskite naturelle et de six échantillons de titanite, quatre d'origine naturelle et deux préparés de mélanges contenant des petites quantités de fer. Dans les échantillons naturels, la plupart du fer se présente comme $Fe^{3+}$ dans les sites octaédriques du Ti; le $Fe^{2+}$ y est aussi dans certains cas. Dans les échantillons synthétiques, le $Fe^{3+}$ se trouve en parts approximativement égales dans les sites octaédrique du Ti et tétraédrique du Si. Un élargissement anomale des pics du spectre de la titanite naturelle serait dû à un endommagement structural par la radiation et à un effet de composition causé par l'influence des deuxièmes plus proches voisins.

(Traduit par la Rédaction)

*Mots-clés:* titanite, pérovskite, déplacement isomère, séparation quadrupole, site octaédrique, site tétraédrique.

## INTRODUCTION

Since the proposal was made to use perovskite $CaTiO_3$ (Ringwood *et al.* 1979) and titanite $CaTiSiO_5$ (Nesbitt *et al.* 1981, Hayward & Cecchetto 1982) as possible hosts for the immobilization of nuclear-fuel-reprocessing wastes, there has been a renewed interest in the crystal chemistry of these minerals. The space group of titanite is *P*2$_1$/*a*, and the unit cell is comprised of $TiO_6$ octahedra, $SiO_4$ tetrahedra and large irregular $CaO_7$ polyhedra (Speer & Gibbs 1976). Previous investigators (Černý & Povondra 1972, Staatz *et al.* 1977, Exley 1980) have reported a wide range of substitution for Ca and Ti, and little, if any, for Si. Recently, Hollabaugh & Rosenberg (1983) have documented the substitution of Ti for Si in Si-deficient synthetic titanite. The space group of perovskite is *Pm*3*m*, and the unit cell is comprised of a large $Ca^{2+}$ site surrounded by eight $TiO_6$ octahedra (Deer *et al.* 1966). Perovskite may also accept a wide range of substitution into its structure (Ringwood *et al.* 1979).

The technique of $^{57}$Fe Mössbauer spectroscopy has been used widely to determine the site preference and oxidation state of iron in minerals (Bancroft 1973, Hawthorne 1983). However, there have been no Mössbauer studies on natural samples of titanite or perovskite, perhaps partly because of their low iron content. As pointed out by Higgins & Ribbe (1976), such Mössbauer studies of titanite are required to confirm the oxidation state and assumed preference of iron for the Ti site. In this paper, we report the Mössbauer spectra of one natural perovskite, four samples of natural titanite and two of synthetic titanite.

## EXPERIMENTAL

The composition of the perovskite (Nesbitt *et al.* 1981) and of the natural samples of titanite is given in Tables 1 and 2. The Sebastapol and Gjerstad samples were kindly supplied by Dr. F.J. Wicks of the Royal Ontario Museum, and all of the samples were quantitatively analyzed using the electron microprobe and qualitatively analyzed using SIMS (Secondary Ion Mass Spectrometry).

The synthetic samples were prepared by combining molar ratios of $TiO_2$, $SiO_2$ and $CaCO_3$ with a proportional decrease in the amount of $TiO_2$ to compensate for Fe substitution. Iron-metal powder was used, and two synthetic compositions were prepared, one containing 2 wt.% of iron, and one containing 0.8 wt.%, 95% enriched in $^{57}$Fe. HF was also added in an attempt to balance the charge difference between $Ti^{4+}$ and $Fe^{3+}$. $CO_2$ was released upon heating, and the oxides were then melted in a platinum crucible at 1400°C for three hours. The molten material was poured to form a glass slug, which was then crushed to a fine powder. The pow-

TABLE 1. COMPOSITION OF NATURAL SAMPLES*

| Specimen | Magnet Cove (perovskite) | Bear Lake (titanite) | Sebastapol (titanite) | Gjerstad (titanite) | Cardiff (titanite) |
|---|---|---|---|---|---|
| $SiO_2$ | 0.80 | 29.8 | 30.1 | 29.8 | 29.8 |
| CaO | 38.9 | 27.3 | 27.7 | 27.2 | 27.4 |
| $TiO_2$ | 42.3 | 35.5 | 33.7 | 32.0 | 28.2 |
| $Al_2O_3$ | 1.20 | 0.96 | 1.73 | 1.86 | 6.50 |
| FeO | 5.90 | 1.90 | 2.52 | 3.40 | 0.44 |
| $Na_2O$ | 0.12 | 0.29 | - | - | 0.06 |
| MgO | 0.02 | 0.19 | 0.25 | 0.08 | 0.14 |
| $K_2O$ | 0.04 | 0.01 | - | 0.01 | - |
| MnO | 0.16 | 0.06 | 0.17 | 0.23 | 0.15 |
| $Nb_2O_5$ | 5.90 | 0.26 | - | 0.18 | 0.52 |
| Total | 95.34** | 96.27† | 96.17† | 94.76† | 93.21† |

* in weight % oxides. ** Qualitative analysis by SIMS shows the presence of Y, Zr, La and Ce in significant amounts (≥ 0.1%).
† Qualitative analysis by SIMS shows the presence of Y, Zr, La, Ce, U, Th, Pb and F in significant amounts (≥ 0.1%).

TABLE 2. COMPOSITION OF NATURAL SAMPLES BY ATOMIC PROPORTION

| Specimen | Bear Lake (titanite) | Sebastapol (titanite) | Gjerstad (titanite) | Cardiff (titanite) | Magnet Cove (perovskite) |
|---|---|---|---|---|---|
| Ca | 1.01 | 1.03 | 0.949 | 0.965 | Ca 1.07 |
| Mn | 0.002 | 0.005 | 0.006 | 0.006 | Mn 0.004 |
| K | trace | - | trace | - | K 0.001 |
| Na | 0.019 | - | - | 0.021 | Na 0.006 |
| | 1.03 | 1.04 | 0.955 | 0.992 | 1.08 |
| Ti | 0.918 | 0.877 | 0.978 | 0.885 | Ti 0.818 |
| Al | 0.200 | 0.035 | 0.036 | 0.125 | Al 0.018 |
| Fe | 0.054 | 0.073 | 0.092 | 0.013 | Fe 0.127 |
| Mg | 0.010 | 0.013 | 0.004 | 0.037 | Mg 0.001 |
| Nb | 0.002 | - | - | 0.002 | Nb 0.034 |
| | 1.00 | 0.998 | 1.11 | 1.06 | Si 0.021 |
| | | | | | 1.02 |
| Si | 1.02 | 1.04 | 0.965 | 1.00 | |
| | 1.02 | 1.04 | 0.965 | 1.00 | |

TABLE 3. MÖSSBAUER PARAMETERS (mm $s^{-1}$)†

| Specimen | Oxidation State | Q.S. | I.S. | Γ |
|---|---|---|---|---|
| Magnet Cove perovskite | $Fe^{3+}$ * | 0.34 | 0.35 | 0.59 |
| Gjerstad titanite | $Fe^{3+}$ * | 0.92 | 0.39 | 0.94 |
| Sebastapol titanite | $Fe^{3+}$ *<br>$Fe^{2+}$ * | 0.94<br>1.72 | 0.39<br>1.18 | 0.84<br>0.95 |
| Cardiff titanite | $Fe^{3+}$ *<br>$Fe^{2+}$ * | 0.74<br>2.17 | 0.44<br>1.06 | 0.74<br>0.77 |
| Bear Lake titanite | $Fe^{3+}$ *<br>$Fe^{2+}$ * | 0.91<br>1.61 | 0.37<br>0.81 | 0.75<br>0.64 |
| Gjerstad (1100°C) titanite | $Fe^{3+}$ * | 1.13 | 0.41 | 0.81 |
| Bear Lake (ceramic) titanite | $Fe^{3+}$ * | 1.05 | 0.30 | 0.64 |
| 2% Fe Synthetic titanite | $Fe^{3+}$ *<br>$Fe^{3+}$ ** | 0.84<br>1.41 | 0.39<br>0.28 | 0.52<br>0.51 |
| $^{57}Fe$ Synthetic titanite | $Fe^{3+}$ *<br>$Fe^{3+}$ ** | 0.84<br>1.52 | 0.40<br>0.29 | 0.53<br>0.61 |

* Fe is in octahedral Ti site; ** Fe is in tetrahedral Si site.
† Errors are approximately 0.05 mm $s^{-1}$.

dered glass was then sintered in a furnace for three days at 1100°C to produce a polycrystalline ceramic. A similar process was also carried out to make a polycrystalline ceramic from a natural titanite. These samples were then characterized by X-ray powder diffraction and Mössbauer spectroscopy.

The Mössbauer samples were prepared by grinding the sample to a fine powder and transferring it to a plexiglass sample cell to obtain a maximum concentration of approximately 10 mg Fe/cm$^2$. Mössbauer spectra were obtained at 100 K and 295 K using the methods described in Bancroft (1973) and Bancroft & Brown (1975). A 25-mC $^{57}Co$ source annealed in palladium was used. Several million counts were accumulated for each spectrum. The spectra were fitted using a computer program adapted by L.P. Aldridge from that of A.J. Stone (in Bancroft *et al.* 1967), which complies with the criteria found in Bancroft (1973). The isomer shifts are quoted relative to Fe metal.

## Results and Discussion

The Mössbauer spectra are shown in Figures 1-9, and the Mössbauer parameters are summarized in Table 3. The Mössbauer spectrum of perovskite (Fig. 1) shows a simple doublet with an isomer shift characteristic of octahedral $Fe^{3+}$ (Bancroft 1973). The small quadrupole splitting indicates that the $Fe^{3+}$ is present in a site of close to cubic symmetry. The $Fe^{3+}$ can thus be assigned to the octahedral Ti site.

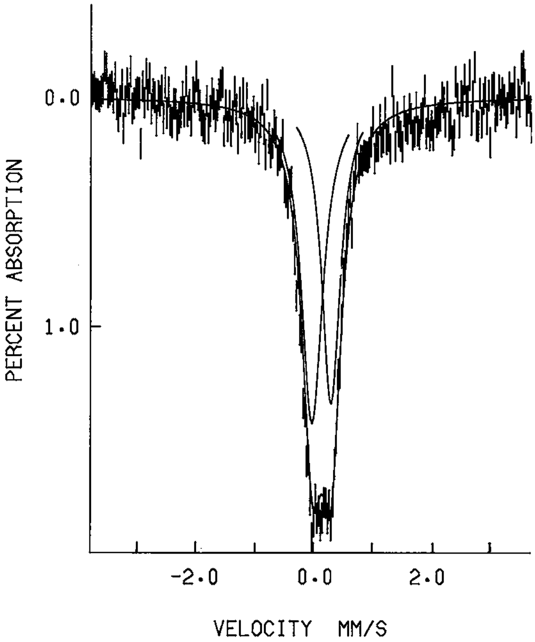

FIG. 1. Mössbauer spectrum of the natural perovskite from Magnet Cove.

The spectra of the natural samples of titanite (Figs. 2-5) are broad and less well defined. The Gjerstad spectrum (Fig. 2) is best fit to a broad doublet, but the fit is poor near the peak maxima, and there is obvious broadening in the peak shoulders. Once again, the isomer shift is characteristic of octahedral $Fe^{3+}$, and we can assign the $Fe^{3+}$ to the octahedral Ti site as previously postulated (Higgins & Ribbe 1976, Černý & Povondra 1972, Staatz *et al.* 1977). The larger quadrupole splitting (0.92 mm $s^{-1}$) is attributed to significant distortion of the $TiO_6$ polyhedron from octahedral symmetry, consistent with the $P2_1/a$ space group.

The Sebastapol, Cardiff and Bear Lake samples (Figs. 3-5) show some absorption at 2 mm $s^{-1}$, indicative of $Fe^{2+}$ in these samples. The fitting of two doublets to these spectra yields similar $Fe^{3+}$ isomer shifts and quadrupole splittings to those obtained for the Gjerstad spectrum. The isomer shift and quadrupole splitting of the $Fe^{2+}$ doublet indicate that $Fe^{2+}$ also is present in the Ti site.

In all four spectra, the linewidths are usually large (0.7-0.9 mm $s^{-1}$), and the fits to the $Fe^{3+}$ peaks especially are not satisfactory. The line shapes are clearly non-Lorentzian. There are three possible major causes of this broadening. Firstly, relaxation effects (either spin-spin or spin-lattice) are known to contribute to broad non-Lorentzian lines in $Fe^{3+}$ compounds (Wignall 1966, Bancroft & Sham 1976), but such line broadening is not known for $Fe^{3+}$ in minerals. We initially thought that the low concentration of $Fe^{3+}$ in these samples might be a contributing factor to the reduced spin-spin relaxation rate and the resulting broadening. However, we do not observe an increase in linewidth with decreasing Fe content (Tables 1, 3) for these titanite samples, as would be expected if spin-spin relaxation was important. For example, the Cardiff titanite, with by far the smallest Fe content, has the smallest $Fe^{3+}$ linewidth of the four natural samples. Spin-lattice relaxation would result in an increase in linewidth as the sample temperature decreases (Bancroft & Sham 1976). Mössbauer spectra at 100 K for the Bear Lake and $^{57}Fe$ synthetic samples gave the same linewidth as the 295 K spectra within the errors ($\pm 0.05$ mm $s^{-1}$). In addition, relaxation effects are not known to contribute to $Fe^{2+}$ broadening (Greenwood & Gibb 1971), and yet the $Fe^{2+}$ widths are just as broad as their $Fe^{3+}$ counterparts. All of the above evidence strongly suggests that relaxation is not an important contributor to our linewidths.

The second and third causes of line broadening are suggested by the large $Fe^{2+}$ linewidths. In minerals with more than one cation in a given site, large $Fe^{2+}$ line-broadening (and even separate peaks) arise from the varying electric-field gradients from so-called next-nearest-neighbor effects (Riedel

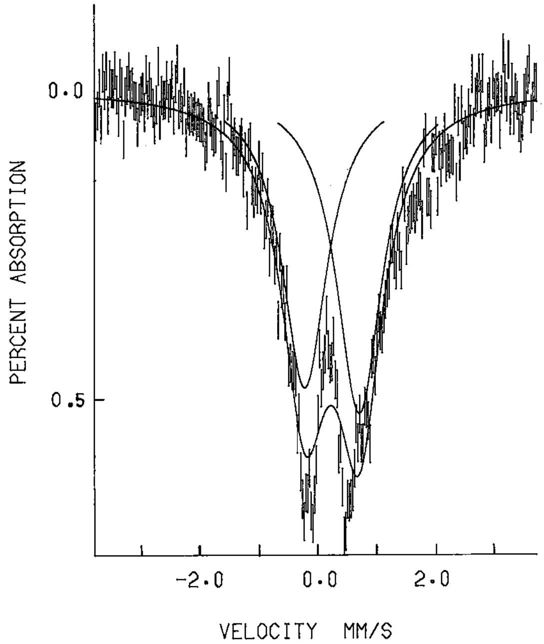

FIG. 2. Mössbauer spectrum of the natural titanite from Gjerstad, Norway.

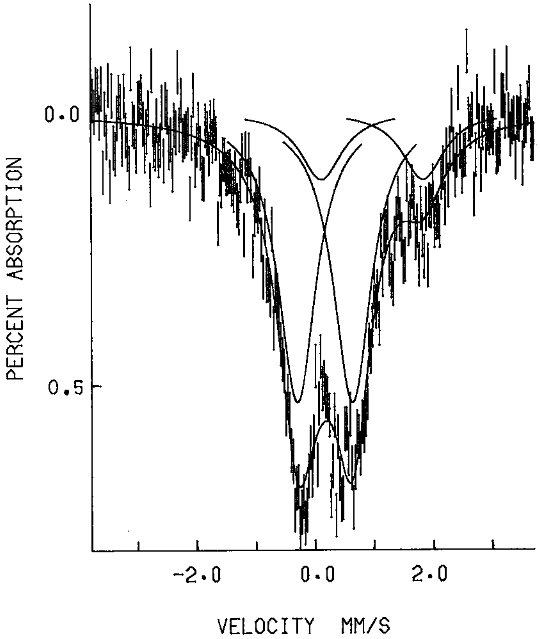

FIG. 3. Mössbauer spectrum of the natural titanite from Sebastapol Township, Ontario.

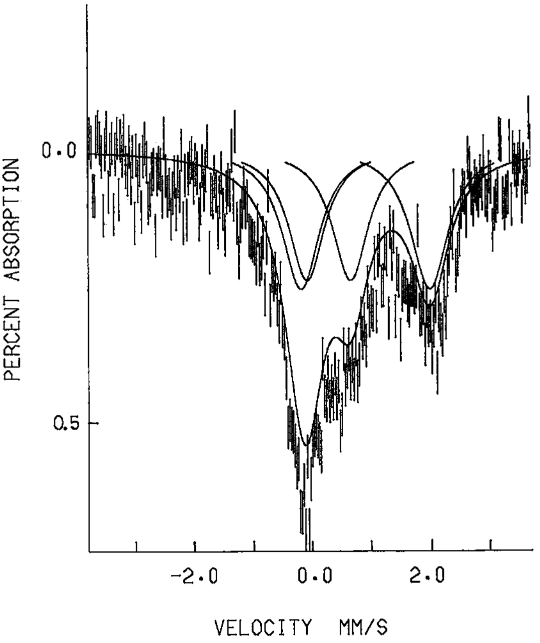

FIG. 4. Mössbauer spectrum of the natural titanite from Cardiff Township, Ontario.

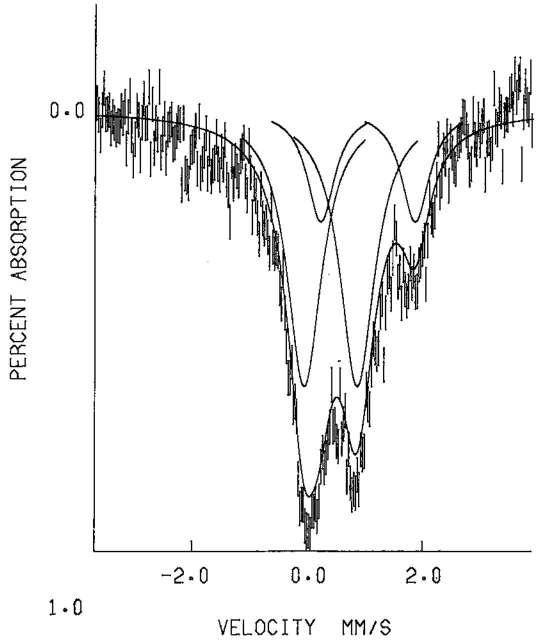

FIG. 5. Mössbauer spectrum of the natural titanite from Bear Lake, Ontario.

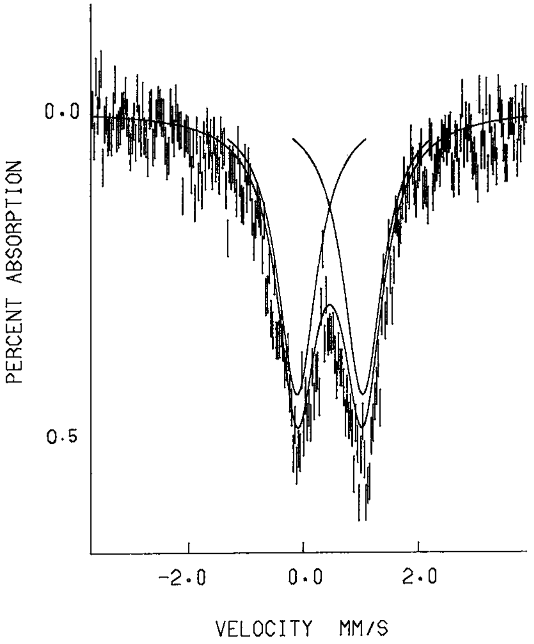

FIG. 6. Mössbauer spectrum of the natural titanite from Gjerstad, Norway, annealed at 1100°C for three hours.

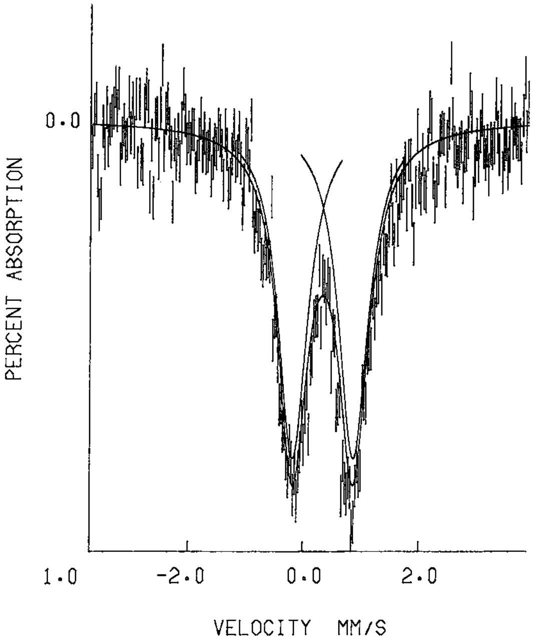

FIG. 7. Mössbauer spectrum of the natural titanite from Bear Lake, Ontario, melted at 1450°C and sintered at 1250°C to form a ceramic.

& Karl 1981, Aldridge *et al.* 1978). Varying electric-field gradients (and resulting line-broadening) would also arise from structural defects or metamictization in these radiation-damaged materials. The experiments described below demonstrate that these effects give significant line-broadening.

Figure 6 shows the effect of annealing the Gjerstad sample for 3 hours at 1100°C. Such annealing should help remove metamictization or structural defects. A significant decrease in linewidths (0.81 *versus* 0.94 mm $s^{-1}$) and better line-shapes result. In another experiment, to further remove any structural defects, the Bear Lake sample was melted to form a glass and then crushed to a fine powder and sintered at 1250°C for one week to produce an annealed polycrystalline ceramic titanite of natural composition. The spectrum (Fig. 7) shows a decrease in linewidth of about ~0.1 mm $s^{-1}$ from the untreated Bear Lake sample (Table 3). Metamictization and structural defects would thus appear to be significant contributing factors to the linewidths.

To examine the next-nearest-neighbor contribution to the linewidths, two synthetic samples of close to ideal $CaTiSiO_5$ in composition were prepared. The spectra (Figs. 8, 9) consist of two doublets with significantly different isomer shifts and quadrupole splittings; they have smaller linewidths than even the annealed natural samples. These smaller linewidths show that next-nearest-neighbor effects are indeed a significant cause of line broadening.

To obtain consistent $Fe^{3+}$ octahedral parameters for all titanite samples, the inner two and outer two peaks were matched. The isomer shift and quadrupole splitting for the inner doublet agree with the same parameters for $Fe^{3+}$ in the octahedral Ti site in natural samples (Table 3). The outer doublet gives a significantly lower isomer shift of 0.28 mm $s^{-1}$ and a larger quadrupole splitting of 1.41 mm $s^{-1}$. These parameters are just those expected for $Fe^{3+}$ in the Si site (Hafner & Huckenholz 1971, Bancroft 1973). Indeed, these spectra are very similar to that of ferridiopside (Hafner & Huckenholz 1971).

In both synthetic samples, close to one half of the iron resides in the tetrahedral Si site. This was initially rather surprising, but cation substitution for Si in titanite has also been discussed by Hollabaugh & Rosenberg (1983). They noted that the substitution of Ti for Si is due to a Si deficiency in the synthetic samples. This substitution into the tetrahedral site may explain the larger-than-expected cell parameters of many specimens (to be published).

## CONCLUSIONS

From this work, it is evident that considerable care must be taken in controlling the stoichiometry of synthetic titanite. Along with the accepted substitution of $Fe^{3+}$ into the octahedral site, Mössbauer spec-

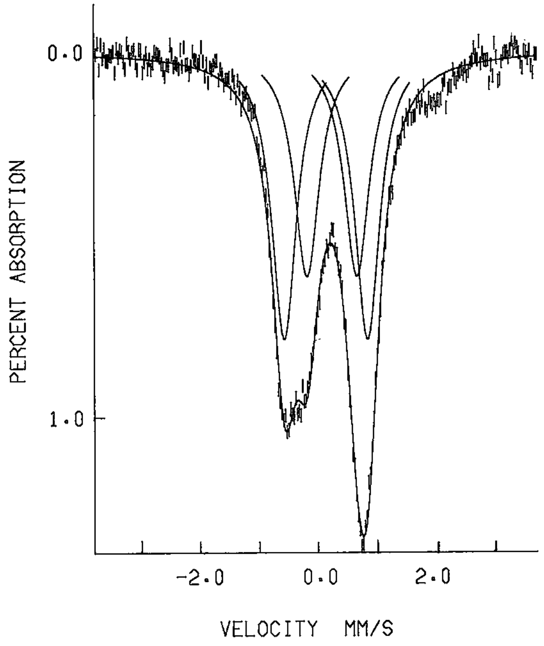

FIG. 8. Mössbauer spectrum of the synthetic titanite doped with 2 wt.% Fe.

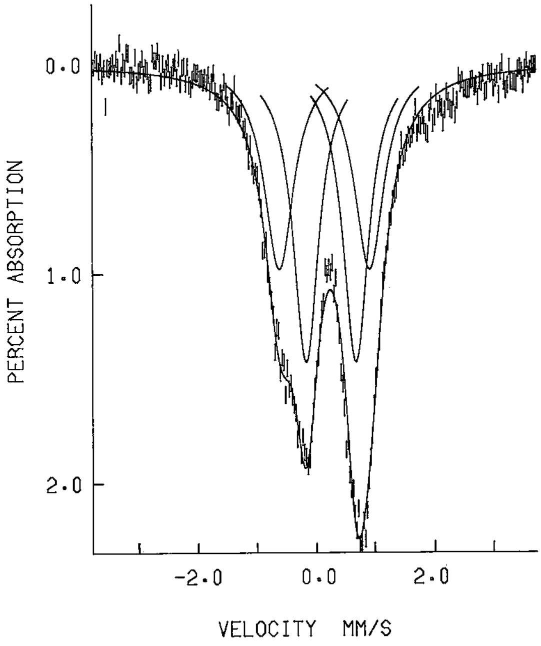

FIG. 9. Mössbauer spectrum of the synthetic titanite doped with 0.8 wt.% $^{57}Fe$.

troscopy has shown that $Fe^{3+}$ will also substitute into the tetrahedral sites in synthetic titanite. However, substitution into the tetrahedral sites was not seen in the natural samples examined, presumably because stoichiometric amounts of Si were available at the time of their formation. Substitution into the tetrahedral site may be the reason behind the enlarged cell-parameters that have been observed in many specimens.

Natural titanite also shows some substitution of divalent iron into the octahedral site, along with broadening of the linewidths. This broadening is due both to defects or metamictization from radiation damage and compositional next-nearest-neighbor effects.

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