RESOLUTION OF THE MÖSSBAUER SPECTRUM OF OXYKAERSUTITE

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INTRODUCTION

Mössbauer spectroscopy has been used extensively to characterize order-disorder relationships in silicates. A considerable amount of work has been done concerning dehydrogenation and oxidation in both natural (Hodgson et al. 1965; Addison & White 1968; Ernst & Wai 1970) and synthetic clino-amphiboles (Semet 1973). Although this technique gives accurate Fe³⁺/Fe²⁺ ratios, the Mössbauer parameters of Fe³⁺ in each of the three octahedral sites are similar enough to cause extreme overlap of the component doublets in the spectrum. Thus the resolution of the spectrum by least-squares techniques is rendered extremely difficult and the results are of unknown significance.

In an effort to provide Mössbauer parameters for Fe³⁺ in each of the octahedral sites in an oxy-amphibole, the Mössbauer spectrum of an oxykaersutite was resolved into three quadrupole-split doublets utilizing site-occupancy data derived from an X-ray crystal structure refinement (Hawthorne & Grundy 1973).

EXPERIMENTAL DETAILS

Mössbauer spectra were recorded at room temperature with an Austin Science Associates drive system used in conjunction with a Victoreen PIP400A multichannel analyser. The source used was ⁵⁷Co in a palladium matrix and the velocity scale was calibrated against the spectrum of iron foil. In order to reduce asymmetry effects in the spectrum due to sample orientation (Pollak et al. 1962), the sample was ground with sugar before mounting (Greaves et al. 1971). The velocity wave form was an asymmetric triangle and an absorber thickness of 5 mg/sq cm was chosen to avoid saturation effects (Burnham et al. 1971). Preliminary spectra run at 6 mm/sec confirmed the absence of Fe⁴⁺ as indicated by the chemical analysis (Hawthorne & Grundy 1973). Subsequent spectra were run at 2.5 mm/sec in an attempt to improve the resolution of the overlapping peaks. Spectra were also recorded at 77°K but were not used in this work as there was no significant improvement in resolution over the room-temperature spectra. The spectrum was fitted to component peaks of Lorentzian shape by least-squares refinement using a program written by Stone (1967); corrections were included in the least-squares procedure for base line sine component and drift.

LEAST-SQUARES REFINEMENT

The experimental spectrum shows one apparent quadrupole-split ferric doublet with only a slight asymmetry in the peak shapes. Least-squares refinement of a single doublet with the constraints of equal half-widths and equal areas converged to an \( \chi^2 \) value of 912. Subsequent refinement with the constraints removed converged to an \( \chi^2 \) value of 874; the fitted spectrum is shown in Figure 1 and the refined Mössbauer parameters are given in Table 1. Comparison of the \( \chi^2 \) value with the 1% and 99% points of the \( \chi^2 \) distribution (Table 1) shows that a single doublet fit to the spectrum is completely unsatisfactory.

It was clear from the results of the crystal structure refinement of the amphibole (Hawthorne & Grundy 1973) that ferric iron was present in all three octahedral sites, and consequently a three-doublet fit to the spectrum was attempted. In order to decrease the inter-parameter correlation in the least-squares procedures, judicious use of linear constraints was necessary. All the half-widths were constrained to be equal and the areas of doublet components were constrained to be the same. In addition, the area ratios were constrained to agree with the site population ratios derived from the crystal structure refinement on the assumption that the recoil free fraction of Fe⁴⁺ was the same for each site. Initial half-width and peak positions were chosen so that the Mössbauer parameters for the \( M(2) \) doublet were compatible with those in other resolved clino-amphiboles (unpublished data). Least-squares refinement resulted in convergence at a statistically acceptable \( \chi^2 \) value of 404; the fitted spectrum is shown in Figure 1 and the final Mössbauer parameters are given in Table 1. All attempts to remove any of the constraints resulted in extreme divergence, indicating an imminent singularity in the normal equations matrix.

DISCUSSION

The half-widths encountered in this refinement are considerably larger than those obtained...
from non-oxidized clino-amphiboles (unpublished data). This feature is also exhibited by the spectra of heat-treated amphiboles (Ernst & Wai 1970) and is probably the result of the wide range in next-nearest neighbour environments encountered in oxidized amphiboles.

The Mössbauer parameters derived above provide a basis for assessing the validity of peak assignments in oxy-amphibole spectra. In addition, they can also be used as initial parameters in the fitting of complex oxy-amphibole spectra and especially in those cases where there is a serious overlap of peaks.

![Mössbauer spectra recorded at room temperature for oxykaersutite. Fits shown for one and three doublets respectively.](image)

**TABLE 1. FINAL PARAMETERS‡ FOR THE TWO- AND SIX-PEAK FITS TO THE MÖSSBAUER SPECTRUM OF OXYKAERSUTITE***

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fe(^{3+})</th>
<th>Fe(^{3+})</th>
<th>Fe(^{3+})</th>
<th>(\chi^2)</th>
<th>%</th>
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<tr>
<td>Unconstrained two-peak fit</td>
<td>0.39</td>
<td>1.03</td>
<td></td>
<td>874 311</td>
<td>442</td>
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<tr>
<td>Isomer shift††</td>
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<td></td>
<td></td>
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<td>Quadrupole splitting</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Half-width</td>
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<td></td>
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<tr>
<td>Area ratio</td>
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<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fe(^{3+})</th>
<th>Fe(^{3+})</th>
<th>Fe(^{3+})</th>
<th>(\chi^2)</th>
<th>%</th>
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<tr>
<td>Isomer shift††</td>
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<td>0.39</td>
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<td>Quadrupole splitting</td>
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<td>0.51</td>
<td>0.51</td>
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<td>Area ratio*</td>
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<td>0.48</td>
<td>1.00</td>
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</table>

*All Mössbauer parameters are expressed in mm per sec and the assigned standard deviations are of the order 0.02 mm per sec.
††Isomer shifts are quoted relative to iron foil.
*Area ratios constrained to be equal to the site-population ratios (suitably modified to take account of differences in equipoint rank) derived from the x-ray results.

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**REFERENCES**


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