Optical spectra of giant radiohaloes in Madagascan biotite

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Abstract

Studies were made of giant haloes in two biotite samples. Microphotometry at known wavelengths in the range 350–1100 nm gave comparative transmission data for material outside the haloes, in the bleached haloes, and within their inner edges. Mössbauer spectra were obtained for similar non-halo biotite samples. All results are consistent with the theory (Vance, 1978) that the bleached haloes formed through the reducing action on ferric iron of atomic hydrogen, produced by radiolysis.

Introduction

Bleached, giant pleochroic haloes have been reported in Madagascan biotite (Gentry, 1973, 1978). These haloes are centered on radioactive inclusions, as is the case for common pleochroic haloes, but because of the anomalous radii of the giant haloes, it was conjectured that the haloes derive from unknown nuclides which emit very energetic α-particles. Utilizing artificial α-radiation, X-ray diffraction, and radiography, together with visible and infrared spectroscopic measurements, Vance (1978) attempted to explain the giant haloes by “conventional” means. He ascribed the brown color of biotite to ligand-to-metal charge transfer of Fe<sup>3+</sup>, not Fe<sup>2+</sup> (Robbins and Strens, 1972), and argued that the bleaching derived from the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> at slightly elevated temperatures by atomic hydrogen produced by radiolysis (via α-particles emitted from the inclusion) of OH<sup>-</sup> ions in the biotite lattice. The rarity of the giant halo phenomenon was discussed in terms of an anomalously high diffusion rate of atomic hydrogen in Madagascan mica.

Experiments

In the present work, optical spectra of the halo regions were obtained to see if any further clues to the origin of the haloes would emerge. Two Madagascan biotites containing giant haloes (samples A and B—Vance, 1978) and two halo-free biotites from the same locality (samples C and D) were studied. Each sample was a cleavage fragment, about 40 μm thick. Viewed in transmission with white light, a halo consisted of a bleached, annular region surrounding an inclusion, the inner and outer edges of the annulus being about 25 μm and 60 μm respectively from the edge of the inclusion. Electron microprobe analysis of non-halo regions of sample A showed it to have a similar composition to those of samples C and D (Table 1), in agreement with expectations (Vance, 1978) based on the similarity of the optical spectra of samples C, D, and the non-halo regions of A and B. With other samples Gentry (1973, 1978) found no chemical difference between the halo region and the rest of the mica, but published no analytical figures. Samples A and B were too small to study by Mössbauer spectroscopy, but spectra were obtained at room temperature for C and D, using a constant-acceleration spectrometer. The spectra were similar and...

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Table 1. Microprobe analyses

<table>
<thead>
<tr>
<th></th>
<th>Sample A</th>
<th>Sample C</th>
<th>Sample D</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>37.4, 38.4</td>
<td>36.5-37.2</td>
<td>36.0-36.5</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.4, 3.5</td>
<td>4.2-4.3</td>
<td>5.3-5.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>11.9, 11.9</td>
<td>12.6-12.9</td>
<td>13.0-14.0</td>
</tr>
<tr>
<td>FeO</td>
<td>22.0, 22.3</td>
<td>21.2-21.8</td>
<td>19.4-19.8</td>
</tr>
<tr>
<td>MgO</td>
<td>10.6, 10.8</td>
<td>10.3-10.6</td>
<td>10.8-11.1</td>
</tr>
<tr>
<td>CaO</td>
<td>&lt;0.1</td>
<td>&lt;0.07-0.11</td>
<td>&lt;0.07</td>
</tr>
<tr>
<td>K₂O</td>
<td>9.5, 9.8</td>
<td>9.3-9.6</td>
<td>9.3-9.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>&lt;0.1</td>
<td>0.19-0.41</td>
<td>0.29-0.50</td>
</tr>
<tr>
<td>Total</td>
<td>94.8, 96.9</td>
<td>94.3-96.9</td>
<td>94.9-97.1</td>
</tr>
</tbody>
</table>

All results are in weight percent of oxide. Total iron is expressed as Fe₂O₃. Cr₂O₃ and MnO <0.08% for C and B, <0.1% for A. Sample D contained some H₂O, but the other samples contained little, if any, H₂O (Vance, 1978). Two separate determinations were made for sample A, each being an average for four separate points on the sample (beam size ~5 μm x 2 μm at sample). Values for C and D are each extremes for four separate determinations using a beam of 1.5 μm diameter at the sample.

Fig. 1. Room-temperature Mössbauer spectrum from sample C, a single-crystal flake. The source was ⁵⁷Co in Pd and the spectrometer was calibrated with a pure iron foil enriched to 90 percent in ⁵⁷Fe; this in turn was compared to a sodium nitroprusside absorber.

Fig. 2. Diametral scan over halo region of sample A at 600 nm wavelength. Effective diameter of aperture = 3.5 μm. Regions H represent the bleached halo, I the inclusion. Length of traverse shown = 625 μm.

consisted almost entirely of two lines at 0.1 and 2.2 mm s⁻¹ (Fig. 1), in agreement with the Fe⁴⁺ lines found by Annersten (1974) and Bancroft and Brown (1975). The data were fitted reasonably well by a single Fe⁴⁺ doublet (a pair of Fe⁴⁺ doublets would have given a better fit), but the point of interest for the present purposes was that the Fe³⁺/Fe²⁺ ratio was very low, <2 percent.

Optical spectra of the halo regions in samples A and B were obtained with an apparatus described by Seal and Wasmund (1969). This is a monochromatic microscope photometer system which allows relative transmission measurements of areas of a thin sample defined by the demagnified transform of a diaphragm in the objective image plane. Most measurements were made with an effective limiting aperture of 14 or 28 μm diameter in the sample plane. Smaller effective apertures (down to 3.5 μm) were also tried but these gave increased noise from surface defects. The system includes quartz and glass prism monochromators and a motor-driven stage. Fixed wavelength diametral traverses were made across the halo regions and the wavelength resolution was ≤10 nm, depending on the source slit width and the wave-
Fig. 3. Absorption of sample A. Vertical lines give the absorption differences between the bleached halo and the nearby unbleached mica. Their absolute values depend critically on assumptions concerning the thickness of the mica in the halo region, but the form of the wavelength dependence does not. As error bars they show approximate limits of measurement error without regard to uncertainties in the thickness. The solid curve is the spectrum of the mica remote from the bleached halo. Similar results were obtained for sample B.

length-dependent system response. The scans were repeated at 20–50 nm wavelength intervals over the 350–1100 nm range. The main difficulties in producing quantitative absorption spectra were that small opaque inclusions were present and the thickness of the mica near the inclusion was not uniform, as evidenced in earlier X-radiographic measurements (Vance, 1978). The transmission data from one optical traverse are shown in Figure 2.

The main results to emerge from this work were (a) that there was no “extra” halo structure at wavelengths outside the visible region, (b) that there was little, if any, difference between the absorption spectrum of the mica outside the halo region and that between the inclusion edge and the inner edge of the bleached halo, and (c) that the difference in absorbance between mica outside the halo region and that in the bleached halo showed only a gentle variation with wavelength in the visible and near infrared (Fig. 3).

Specimen B was cleaved approximately in half to examine whether the increased optical transmission, especially in the ultraviolet, would provide more definitive information. This gave marked improvement in the quality of the data, but no substantive change in the results.

Discussion

The absorbance difference between the halo region and the rest of the mica was in approximate agreement with a result of Smith (1978) on the effect on the absorption spectrum of a biotite of reduction in molecular H₂ for 6 hr at 550°C, although this possibly showed that the absorbance difference continued to increase as the wavelength decreased below 500 nm. Thus the data were in accord with the mechanism of Vance (1978), i.e. ferric iron has been reduced to Fe²⁺. This should be true whether the optical absorption in the 17000–24000 cm⁻¹ range for biotite is largely due to ligand-to-metal charge transfer of Fe²⁺ (Vance, 1978) or to clusters of Fe³⁺ ions (Kliem and Lehmann, 1979); note that although our Mössbauer results on the Madagascan mica showed the Fe³⁺/Fe²⁺ ratio to be very low, there is no reason to suspect Fe³⁺ to be absent.

In general, the optical absorption spectrum of the Madagascan biotite was similar to those reported by others (Faye, 1968; Robbins and Strens, 1972; Smith, 1977, 1978; Kliem and Lehmann, 1979). However, unlike samples studied by most of these workers, virtually no discernible bands at 14000, 11000, and 9000 cm⁻¹ were present. These bands have been variously interpreted as arising from crystal-field transitions of Fe²⁺ ions (Kliem and Lehmann, 1979; Robbins and Strens, 1972), metal–metal charge transfer processes (Faye, 1968; Smith, 1977) involving both Fe²⁺ and Fe³⁺, or exchange-coupled Fe²⁺–Fe³⁺ pairs (Smith, 1978). The high Fe²⁺ (and low Fe³⁺) content of the Madagascan samples and the very small intensities of these bands would be consistent with Fe²⁺–Fe³⁺ charge transfer or exchange-coupled Fe²⁺–Fe³⁺ pairs, but not with Fe²⁺ crystal-field transitions being responsible for the bands.

No changes in the optical spectra of a piece of sample C and a non-halo piece of sample A were observed after they were heated in flowing H₂ for 4 hr at successive temperatures of 550, 650, and 700°C. This result is probably understandable in view of the low Fe³⁺/Fe²⁺ ratio found from the Mössbauer spectroscopy, but of itself it throws no light on whether atomic, as distinct from molecular, hydrogen causes the bleached, giant radiohaloes in Madagascan biotite. The insensitivity of the color of Madagascan biotite to radiation and heat-treatment has been discussed previously (Vance, 1978).

We conclude that our optical data are consistent with the mechanism of giant halo formation discussed by Vance (1978).
Acknowledgments

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References


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