The identification of Fe$^{2+}$ in the M4 site of calcic amphiboles: reply

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Experimental evidence indicates that absorption from Fe$^{2+}$ in the M4 site dominates the optical spectrum of most calcic amphiboles in the 1000 nm region in the spectrum. Contributions from Fe$^{2+}$ in M1, M2 and M3 occur in the 850–1150 nm region, but the intrinsic intensity of absorption by Fe$^{2+}$ in these sites is much less than that of Fe$^{2+}$ in M4.

The conclusions of Aldridge et al. (1982) rely in part upon site occupancy data for an actinolite from near Berkeley, California (Univ. Calif. Berkeley #14785). The chemical analysis of Burns and Greaves (1971) show that the sum of the formula proportions of Na + Ca + K + Mn equals 2.00, which was interpreted to indicate that Fe was excluded from the M4 site. Yet, the optical spectrum showed the intense 1000 nm band (Burns, 1970). Burns did not examine the Berkeley actinolite in the 2000 nm region where absorption from Fe$^{2+}$ only in the M4 site can occur.

We obtained a sample of the actinolite from the hand specimen used by Burns (1970) and Burns and Greaves (1971) and ran its optical spectrum in the 2000 nm region. Figure 1 compares the $\alpha$ spectra of the Berkeley actinolite and a tremolite which is free of Fe in the M4 site. The spectra demonstrate that the Berkeley actinolite has Fe$^{2+}$ in M4. An electron microprobe analysis of the sample we used indicated that the sum of Ca + Na was 2.03 and 0.03 K + Mn were also present, more than enough to fill the M4 site. We conclude that Fe$^{2+}$ can effectively compete for the M4 site. We also note that another sample which has a sum of Na + Ca greater than 2.00 (#3 of Goldman, 1979, possibly from the same locality as Berkeley #14785) shows absorption from Fe$^{2+}$ in the M4 site.

The results of detailed optical measurements of 19 calcic amphiboles which show absorption from M4 Fe$^{2+}$ in the 2400 nm region, including 13 actinolites and tremolites, establish that the 1000 nm $\beta$ and 2400 nm $\alpha$ absorption bands both arise from Fe$^{2+}$ in M4. The intensities of the 2400 nm $\alpha$ feature and the 1000 nm $\beta$ feature should be exactly correlated if both absorptions arise from just Fe$^{2+}$ in M4. This correlation is shown in Figure 2. For low-iron samples where vibrational overtones were a major component in the 2400 nm region, the tremolite data in Figure 1 were used as a baseline correction. For some of the samples (e.g., 7, 9, 16, and 17), multiple measurements made on different slabs or zones of the same crystal showed variation of a factor of 2 in the intensity of the M4 feature. Optical data of some samples were remeasured on slabs cut from portions of a single crystal as close together as possible. Because, in all cases, $\alpha$ and $\beta$ spectra were measured on separate slabs of the mineral, much of the deviation from the trend may be due to site-compositional inhomogeneity. The trend of Figure 2 is most directly interpreted to indicate that the majority of the intensity of the 1000 nm $\beta$ band has the same origin as the 2300 nm $\alpha$ band, namely Fe$^{2+}$ in the M4 site.

A further indication that the 1000 nm $\beta$ band is due to M4 Fe$^{2+}$ comes from the correlation between the intensity of the inner doublet of the Mossbauer spectrum attributed to Fe$^{2+}$ in M4 by Goldman (1979) and the intensity of the 1000 nm feature of the optical spectrum (Fig. 3). The correlation indicates that the 1000 nm $\beta$ band is caused primarily by Fe$^{2+}$ in the same site which causes the inner doublet. This site is M4.

The trend line in Figure 3 indicates that the intrinsic intensity of absorption of Fe$^{2+}$ in the M4
site is nearly constant across the compositional range examined, and thus can be used analytically for M4 concentration determinations. The molar absorptivity values ($\epsilon$) calculated from the slope of the trend line in Figure 3 can be used to determine the Fe$^{2+}$ content of the M(4) site. The $\epsilon$ values are: 2400 nm ($\alpha$), $\epsilon = 17.9$; 1000 nm ($\beta$), $\epsilon = 155$. The $\epsilon$ values can also be calculated independent of the Mössbauer data under the assumption that Fe$^{2+}$ fills the M4 site after Ca, Na, and K. From the grunerite point, the $\epsilon$ values determined this way are: 2400 nm ($\alpha$), $\epsilon = 15.6$; 1000 nm ($\beta$), $\epsilon = 135$.

The $\epsilon$ value for the 2400 nm band can be used to determine the amount of Fe$^{2+}$ in the M4 site of typical actinolites. For example, for the Berkeley sample (#3 of Goldman, 1979), the M4 Fe$^{2+}$ content is 0.4 wt.% FeO, or 7% of the total Fe, corresponding to 0.04 formula proportions of Fe$^{2+}$ in M4.

The additional area in the grunerite spectrum, which Aldridge et al. (1982) analyze, most likely results from quantitative error in the original intensity data (factor of 2 or 3). These quantitative errors, discussed by Goldman and Rossman (1979), result from the mixing of polarization directions inherent in a microscope spectrometer system with convergent light. They are most pronounced in the case of a sample which has strong absorption in one direction only (such as grunerite) and cause a loss of intensity which is disproportionally greater in the upper portion of an absorption band. The result is an apparent broadening of the band and a flattening of its top.
The data discussed above support our earlier assignment of both the 1000 nm band in $\beta$ and the 2400 nm band in $\alpha$ to Fe$^{2+}$ in M4. The correlation between the optical and Mössbauer data also strengthens the assignment of the inner Fe$^{2+}$ Mössbauer doublet to Fe$^{2+}$ in M4. The presence of M4 Fe$^{2+}$ in all the Fe-containing tremolites and actinolites we have studied, even those with $\geq 2.0$ Ca + Na, indicates that Fe$^{2+}$ has a much stronger preference for the M4 site than has been recognized in several earlier studies. This is analogous to the preference of Fe$^{2+}$ for the pyroxene M2 site which is structurally related to the amphibole M4 site.

References


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