American Mineralogist, Volume 67, pages 340–342, 1982

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

DON S. GOLDMAN
Owens-Corning Fiberglas
Technical Center
Granville, Ohio 43027

AND GEORGE R. ROSSMAN

Division of Geological and Planetary Sciences[1]
California Institute of Technology
Pasadena, California

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 α 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 β and 2400 nm α absorption bands both arise from Fe^{2+} in M4. The intensities of the 2400 nm α feature and the 1000 nm β 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, α and β 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 β band has the same origin as the 2300 nm α band, namely Fe^{2+} in the M4 site.

A further indication that the 1000 nm β 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 β 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

---

[1] Contribution No. 3661.

0003–004X/82/0304–0340$02.00

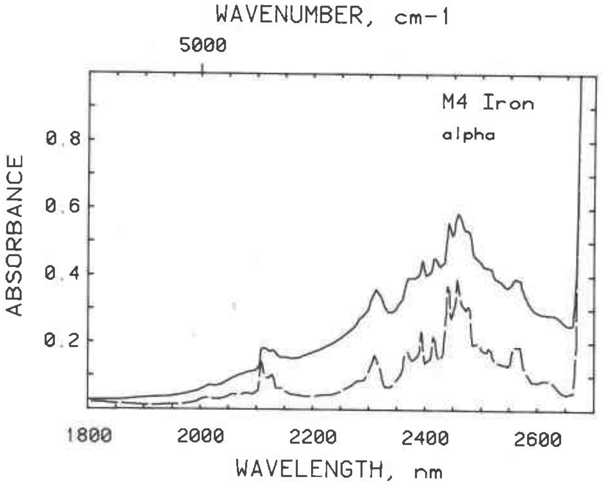

Fig. 1. Comparison of the optical absorption spectra of actinolite (UCB #14785) from near Berkeley, California, (solid line) and tremolite (CIT #459) from Caanan, Connecticut (dashed line). Both spectra are plotted for a sample 1.0 mm thick in α polarization. The increased absorption of the actinolite arises from Fe^{2+} in the M4 site.

site is nearly constant across the compositional range examined, and thus can be used analytically for M4 concentration determinations. The molar absorptivity values (ϵ) 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 ϵ values are: 2400 nm(α), ϵ = 17.9; 1000 nm (β), ϵ = 155. The ϵ 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 ϵ values determined this way are: 2400 nm(α), ϵ = 15.6; 1000 nm(β), ϵ = 135.

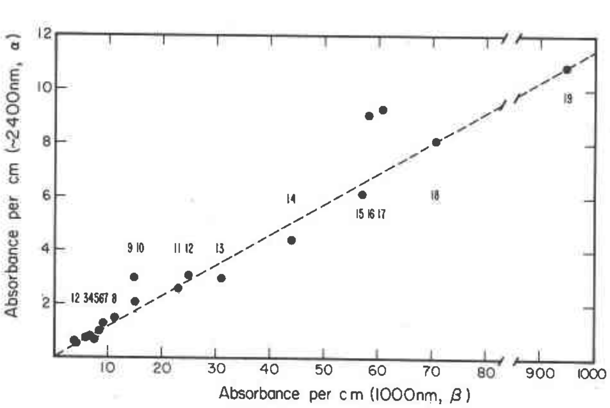

Fig. 2. Correlation of the intensities of absorption at ~2400 nm in α and ~1000 nm in β. Corrections for band overlap in the 1000 nm region were estimated visually. The dashed line, drawn between the origin and the grunerite point, is parallel to and just slightly below the least squares fit to the data. The absorbance of sample 19 in α is 109 per cm.

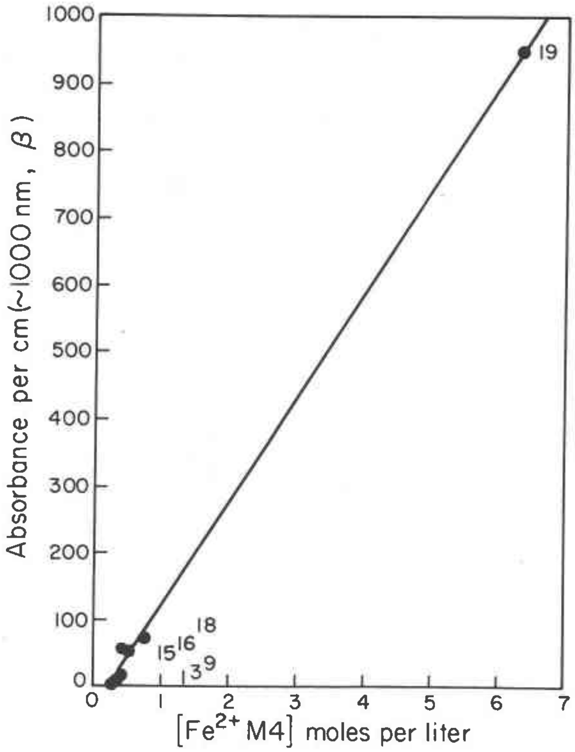

Fig. 3. Correlation of the content of Fe^{2+} in M4 obtained from Mössbauer spectra and the intensity of the 1000 nm β band of the optical spectrum. The solid line is a linear regression fit to the data (correlation coefficient = 0.999) which was used to compute the ϵ value.

The ϵ 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.

Table 1. Amphibole samples used in Figures 2 and 3

#	Name	Locality	Museum #
1	Richterite	Wilberforce, Ontario, Canada	8018
2	Tremolite	Macomb, New York	4924
3	Pargasite	Verona, Ontario, Canada	8037
4	Tremolite	St. Lawrence Co., New York	290
5	Pargasite	Oxbrow, New Jersey	MS 2858
6	Tremolite	Petaluma, California	109
7	Actinolite	Cloverdale, California	MS 2843
8	Tremolite	Haliburton, Ontario, Canada	MS 2824E
9	Tremolite	Mt. Bity, Madagascar	8038
10	Actinolite	Cloverdale, California	MS 2843
11	Actinolite	San Bernardino, California	309
12	Actinolite	Berkeley, California	299
13	Actinolite	Lone Pine Canyon, California	MS 2842
14	Pargasite	Chelan, Washington	1188
15	Actinolite	Chester, Vermont	6191
16	Actinolite	Zillerthal, Tyrol, Austria	4916
17	Actinolite	Washington	7222
18	Actinolitic-Hornblende	Kragero, Norway	7076
19	Grunerite	Heath Lake, Canada	7223

Museum numbers are Caltech reference collection numbers or, if proceeded by 'MS', UCLA reference collection numbers.

The data discussed above support our earlier assignment of both the 1000 nm band in β and the 2400 nm band in α 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 ≥ 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

Aldridge, L. P., Tse, J. S. and Bancroft, G. M. (1982) The identification of Fe^{2+} in the M(4) site of calcic amphiboles: discussion. American Mineralogist, 67, 000–000.

Burns, R. G. (1970) Mineralogical Applications of Crystal Field Theory. Cambridge University Press.

Burns, R. G. and Greaves, C. (1971) Correlations of infrared and Mössbauer site population measurements of actinolites. American Mineralogist, 56, 2010–2033.

Goldman, D. S. (1979) A reevaluation of the Mössbauer spectroscopy of calcic amphiboles. American Mineralogist, 64, 109–118.

Goldman, D. S. and Rossman, G. R. (1977) The identification of Fe^{2+} in the M(4) site of calcic amphiboles. American Mineralogist, 62, 205–216.

Goldman, D. S. and Rossman, G. R. (1979), Determination of quantitative cation distribution in orthopyroxenes from electronic absorption spectra. Physics and Chemistry of Minerals, 4, 43–59.

Manuscript received, July 30, 1981.
accepted for publication, October 28, 1981.