

## Mössbauer spectroscopy and molecular orbital calculations on iron bearing omphacite.

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Omphacite is an important mineral in petrology due to its occurrence in rocks metamorphosed under high pressure conditions. It has a wide thermobaric range of stability and is commonly used as thermobarometer in HP and UHP rocks. The accurate estimation of iron content in omphacite is very important to both geothermobarometry and the calculation of redox conditions in the mantle (Poyer et al. 2004). Microprobe analysis can give a good estimation of the total iron content, however, it can not provide a reliable distinction between Fe<sup>2+</sup> and Fe<sup>3+</sup>. Mathematical corrections of the Fe<sup>2+</sup>/Fe<sup>3+</sup>-ratio based on formula stoichiometry have been shown to be inaccurate (Poyer et al. 2004).

The ordering of Fe<sup>2+</sup>/Fe<sup>3+</sup> in the crystal structure is important, as it influences the physical properties of the mineral. Omphacite is a solid solution of jadeite, NaAlSi<sub>2</sub>O<sub>6</sub>, and diopside, CaMgSi<sub>2</sub>O<sub>6</sub>. Fe<sup>2+</sup> is incorporated in the structure as hedenbergite, CaFe<sup>2+</sup>Si<sub>2</sub>O<sub>6</sub>, and Fe<sup>3+</sup> in the form of acmite, NaFe<sup>3+</sup>Si<sub>2</sub>O<sub>6</sub>. At high temperature omphacite has the same space group as the end members of the solid solution, namely C2/c. This structure requires cation disorder within the M1, as well as within the M2 sites. The M1 site is a relatively undistorted octahedron whereas the M2 site is an irregular polyhedron of 8-fold coordination. At lower temperatures there is a tendency for the cations to order within the M1 and M2 sites. At sufficiently low temperatures, omphacite at intermediate compositions (Na0.5Ca0.5)(Al0.5Mg0.5)Si<sub>2</sub>O<sub>6</sub> is a cation-ordered pyroxene with two distinct M1 and two distinct M2 sites, labeled M1, M11 and M2, M21 (Matsumoto et al., 1975). This reduces the symmetry to P2/n due to the difference in size of the two main M1 cations occupants, Al and Mg, and their presence in approximately equal numbers. The degree of Mg, Al ordering on M1 sites is coupled with Ca, Na ordering on M2 sites. In this paper the role of Fe-substitution in the interpretation of the Mössbauer spectra is investigated, based on theoretical calculations of hyperfine parameters and compared to measured spectra of a known composition.

A natural iron bearing omphacite with composition Ca0.49 Na0.525 Mg0.424 Al0.43 Fe<sup>2+</sup>0.076 Fe<sup>3+</sup>0.056 Ti0.0024 Mn0.005 Si1.989 O<sub>6</sub> from Syros, Greece, has been investigated by Mössbauer spectroscopy at different temperatures. The interpretation of the spectra is based on electronic structure calculations in the local spin density approximation. The calculations emphasize that large clusters, extending beyond the second coordination sphere of iron, are necessary for a reliable description. As suggested by the model calculations, different environments around the Fe<sup>2+</sup> octahedra give rise to slightly different hyperfine parameters, especially affecting the quadrupole splitting. Hence, the measured spectrum has been evaluated based on quadrupole splitting distribution. The calculated values, as well as the temperature dependence are in quantitative agreement with the modelled values.

### References:

Matsumoto T, Tokonami M., Morimoto N. (1975) Am Mineral 60: 634-641.  
Poyer A., Dachs E., McCammon C. (2004) Contrib Miner Petr 147:305-318.