159. *Order-disorder of Ferric Iron and Aluminum in Ca-rich Clinopyroxene*

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(Comm. by Seitarō TSUBOI, M. J. A., Sept. 12, 1970)

Determination of the distribution of cations and the detection of order-disorder phenomena in crystal structure have been obtained from crystal structure analyses by x-ray diffraction method. Recently, Mössbauer spectroscopy provides a rapid method for characterizing the oxidation state, co-ordination number and estimating site populations in iron-bearing minerals. This method has been used to measure the degree of order-disorder between ferrous iron and magnesium in the orthopyroxene series.²⁾⁻⁵⁾

The present study was aimed to investigate the chemical shift and quadrupole splitting with change in electron configuration, oxidation state, and co-ordination symmetry of iron in ferric iron-bearing clinopyroxenes. Measurements of Mössbauer spectra were made at room temperature of five synthetic pyroxenes and one natural pyroxene.

In the diopside structure cations occupy two positions, M_1 and M_2 . The M_2 position which is filled by Ca^{2+} ions is an eight co-ordination site. The M_1 position which is filled by Mg ions is a six co-ordination site, and M_1 octahedron is more distorted in diopside than that in orthopyroxene. Cations in the M_1 positions are in octahedral co-ordination with six oxygen ions each linked to one silicon atom. Cations in the M_2 positions are surrounded by four oxygen ions which are linked to one silicon atom, and four bridging oxygen ions which are shared by two silicon atoms.

We have synthesized the solid solution of diopside with other iron-bearing compounds such as $NaFeSi_2O_6$, $CaFe_2SiO_6$, $CaFeAlSiO_6$ and hematite.

The binary system acmite-diopside has been studied by Yagi (1966).⁶⁾ At lower temperature there is a complete series of solid solution between the two end members. The Mössbauer spectra of acmite show a simple one line characteristic of Fe^{3+} . This ferric iron must be located at the M_1 site in acmite structure which is similar to that of diopside. The solid solutions of acmite-diopside also show the same parameter of Mössbauer spectra as that of acmite end member.

Fig. 1. Mössbauer spectra of ferric iron-bearing clinopyroxene solid solutions.

I.S.: Chemical shift, ΔE : Quadrupole splitting, M₁: Octahedral site (six co-ordination), T: Tetrahedral site (four co-ordination).

The system of diopside-ferri-Tschermak's molecule has been studied by Huckenholz *et al.* (1967).⁷⁾ They observed that the maximum degree of solid solution of ferri-Tschermak's molecule in the stable diopside is greater than 31.1 and less than 35.0 wt% and is believed to be close to 33% at 1157°C. We have synthesized the solid solution which has a composition of (diopside)₈₀-(ferric-Tschermak's molecule)₂₀. The Mössbauer spectra of this clinopyroxene show characteristic peaks of Fe³⁺ which occupies the different sites, M₁ and tetrahedral site. The presence of a ferri-Tschermak's molecule CaFe³⁺Fe³⁺SiO₆ is inferred, in which Fe³⁺ ions occupy Mg and Si sites of the standard diopside structure. The quadrupole splitting gives an information that the symmetry of tetrahedral site is slightly distorted. This may be caused by the interaction between Fe³⁺ ion in the six co-ordination site and Fe³⁺ ion in the four co-ordination site.

Segnit (1951)⁸⁾ studied the incorporation of ferric iron in diopside in the subsolidus region. He reported that a maximum of 10 wt% Fe₂O₃ was present in the diopside. This clinopyroxene solid solution is formed by a reaction of CaMgSi₂O₆+Fe₂O₃→CaFeFeSiO₆+MgSiO₃. Mössbauer spectra of this clinopyroxene solid solution show a similar pattern which is characteristic to Fe³⁺ of octahedral and tetrahedral sites in that of the diopside-ferri-Tschermak's solid solution.

Clinopyroxene of CaFeAlSiO₆ composition was synthesized by Hijikata and the phase diagram for the CaMgSi₂O₆-CaFeAlSiO₆ has been determined in air by Hijikata and Onuma (1969).⁹⁾ The system has complete solid solutions up to 1250°C. The Mössbauer spectra of CaFeAlSiO₆ clinopyroxene and solid solution of (diopside)₈₀-(CaFeAlSiO₆)₂₀ shows simple two lines. One of the chemical shift of the Fe³⁺ in these pyroxenes is closed to M₁ position in the acmite. The other shift of the Fe³⁺ must be located at the tetrahedral position of clinopyroxene structure and the chemical shift is close to the four co-ordinated Fe³⁺ in the ferri-Tschermak's molecule. Judging from the Mössbauer spectra the Fe³⁺ occupies both the M₁ octahedral position and tetrahedral position. This phenomenon is related to the order-disorder of Fe³⁺ and Al. It is estimated that Fe³⁺ and Al are included in two sites of six co-ordination and four co-ordination. So the CaFeAlSiO₆ clinopyroxene should be expressed as Ca(Fe_{1-x}Al_x)(Al_{1-x}Fe_x)SiO₆.

We also measured Mössbauer spectra of natural augite from Eifel, Germany. The chemical composition of this mineral is shown in Table I. The peaks noticed in the Mössbauer spectra of this pyroxene may be assigned as follows: Fe²⁺ ions in the M₁ position, Fe³⁺ ions in both the M₁ site and four co-ordination tetrahedral site.

Table I. Chemical analysis of augite from
apatite-magnetite-clinopyroxenite¹⁾
(Eifel, Germany)

	wt%
SiO ₂	46.20
Al ₂ O ₃	7.38
TiO ₂	1.70
Fe ₂ O ₃	6.94
FeO	5.97
MnO	0.26
MgO	8.96
CaO	19.85
Na ₂ O	1.91
K ₂ O	0.06
H ₂ O	0.67
Total	99.90*

(Analyst K. Aoki)

*) The total is given as 99.86 in the original paper.

The Fe³⁺ and Al exchange between the octahedral sites and tetrahedral sites in clinopyroxenes has been recognized in natural and synthetic pyroxenes. The detection of order-disorder phenomena in these pyroxenes may provide a potential means of determining the temperature and pressure of formation of these minerals.

The writers wish to express their sincere thanks to Professor S. Tsuboi, M. J. A., and Professor K. Yagi for the critical reading of the manuscript, and to Dr. K. Aoki for the gift of the augite from Eifel. The authors also wish to thank Mr. Y. Fujio for Mössbauer analyses.

References

- 1) Aoki, K., and Kushiro, I. (1968): Contr. Miner. and Petr., **18**, 326-337.
- 2) Bancroft, G. M., and Burns, R. G. (1967): Earth and Planetary Sci. Letters, **3**, 125-127.
- 3) Bancroft, G. M., Burns, R. G., and Howie, R. A. (1967): Nature, **213**, 1221-1223.
- 4) Dundon, R. W., and Walter, L. S. (1967): Earth and Planetary Sci. Letters, **2**, 372-376.
- 5) Evans, B. J., Ghose, S., and Hafner, S., (1967): Jour. Geol., **75**, 306-322.
- 6) Yagi, K. (1966): Amer. Miner., **51**, 976-1000.
- 7) Huckenholz, H. G., Schairer, J. F., and Yoder, H. S., Jr. (1968): Yb. Carnegie Inst. Wash., **66**, 336-341.
- 8) Segnit, E. R. (1951): Miner. Mag., **30**, 218-226.
- 9) Hijikata, K., and Onuma, K. (1969): Jour. Japan. Assoc. Min. Petr. Econ. Geol., **62**, 209-217.