

## $^{57}\text{Fe}$ Mössbauer study of orthopyroxene of metamorphic origin

A FEW Mössbauer studies on orthopyroxene of different geneses have been reported in the literature with a view to ascertaining the distribution of iron in the two non-equivalent octahedral coordination sites  $M_1$  and  $M_2$ . The samples, of igneous origin, collected from ultramafic plutons in Sukinda showed (Mitra, 1961, 1973) mostly a single doublet while one contact sample showed the presence of two doublets. The valence states and the distribution of iron indicated that the temperature of crystallization of one of the orthopyroxene-bearing rocks was over  $800^\circ\text{C}$  (Saxena, 1971; Mitra, 1976). On the basis of this it was concluded that either the crystallization temperature (non-equilibrated) of some parts of the composite ultramafic intrusives was above  $800^\circ\text{C}$  or the rock mass was locally affected above this temperature by later thermal events leading to  $\text{Mg}^{2+}$ - $\text{Fe}^{2+}$  disordering in orthopyroxene. In this paper some results of a Mössbauer investigation on the orthopyroxene (enstatite) in pyroxenites of Mysore (India) are discussed. The chemical analysis of this sample indicated the presence of 2.91% of  $\text{Fe}^{3+}$ , 4.26%  $\text{Fe}^{2+}$ , 17.57% Mg and no trace of Ti.

*Experimental.* A constant acceleration electromagnetic drive (Gupta, 1975) was used to observe the Mössbauer spectrum. Gamma rays were detected by a 1 mm thick NaI (Tl) scintillator coupled to a Harshaw photomultiplier tube. A thin beryllium window was used in front of NaI crystal to cut off 6.3 keV X-rays from  $^{57}\text{Co}:\text{Cu}$  of 5 mC strength. The pulses corresponding to the desired 14.4 keV energy were selected using a single channel analyser and fed to a 400-multichannel analyser operated in a time sequence storage mode. The channel width was 0.2249 mm/sec per channel. Calibration of the spectrometer was done using a standard iron foil, a stainless-steel '310' foil, and sodium nitroprusside powder. The observed data with an off-resonance count of the order of 0.37 million were fed to the computer to fit absorption peaks (assumed Lorentzian) superimposed on the base line parabola by the method of minimizing the value of the sum of the squared residuals of the deviations using an iteration process to keep the convergence criterion to less than  $1 \times 10^{-7}$ . The spectrum in fig. 1. shows the computer fit corrected for the parabolic effect.

*Results and discussion.* The Mössbauer spectrum of pyroxenite shown in fig. 1 exhibits two well-resolved lines each of width about 0.4355 mm/sec. The observed lines being broad efforts were made

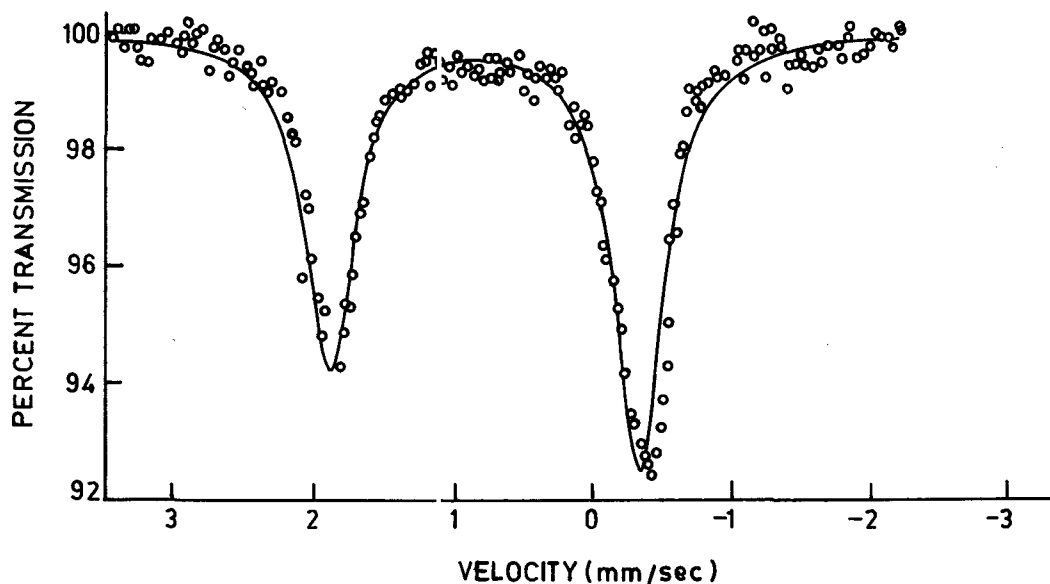


FIG. 1. Mössbauer spectrum of orthopyroxene at room temperature.

to fit more than two lines to the observed data. The attempts however proved unsuccessful.

It is known that iron in minerals of the type being investigated exists, in general, in the divalent and the trivalent charge states. It is also known that iron goes to two non-equivalent sites,  $M_1$  and  $M_2$ , both of which have non-cubic site symmetry. Since in the present studies we have observed only two lines in the Mössbauer spectrum it is concluded that iron exists either in the  $Fe^{2+}$  or in the  $Fe^{3+}$  state. From the isomer shift value ( $1.2660 \pm 0.0046$  mm/sec with respect to stainless steel) it is inferred that iron is in the divalent state. In addition the difference in the quadrupole splitting values due to  $M_1$  and  $M_2$  sites reported by earlier workers being significantly large ( $\approx 0.3$  mm/sec), the Mössbauer spectrometer in the present investigations would have distinguished  $Fe^{2+}$  at the two sites by recording two quadrupole doublets. The appearance of only one quadrupole doublet in the observed Mössbauer spectrum indicates the existence of  $Fe^{2+}$  only at one of the two sites. A comparison of the observed quadrupole splitting ( $2.2030 \pm 0.0113$  mm/sec) with those reported earlier (Bancroft, 1967; Evans, 1967) in the literature suggests that  $Fe^{2+}$  exists only at the  $M_2$  sites. A slight asymmetry

in the intensity of the two lines and the large line widths observed may be due to the presence of an extremely small amount of iron at the  $M_1$  site.

As the  $Fe^{2+}$  is largely present in the  $M_2$  site it is inferred that ordering was nearly complete due to slow crystallization during metamorphism.

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## Distribution of lanthanum, europium, germanium, tin, phosphorus, and sulphur in nickeliferous lateritic profiles

GEOCHEMICAL distribution of several elements through three lateritic profiles on serpentinized peridotite has been ascertained by Ahmad and Morris (1978) and Gharib and Morris (1978). The deposits are in Guatemala, New Caledonia, and Indonesia; they are worked for Ni and could prove to be important sources of other elements, e.g. noble metals, Co, and Cr. In each case there is marked depletion of Si and Mg and sedentary concentration of iron (III) oxides and hydroxides. This is a typical result of the extensive weathering of ultrabasic rock under the tropical conditions where drainage is good (Krauskopf, 1967).

The present paper deals with the geochemistry of La, Eu, Ge, Sn, P, and S in the profiles. A description of most of the samples reported on here is given in the earlier article, Ahmad and Morris (1978).

#### Analytical methods

*Lanthanum and europium.* Instrumental neutron activation analysis (INAA) was used for the determination of these two elements. The 1.596 MeV gamma ray of  $^{140}\text{La}$  and the 0.963 MeV  $\gamma$ -ray of  $^{152}\text{Eu}^m$  were measured with a Ge(Li) semiconductor spectrometer. A comparison standard similar in composition to that described by Ahmad and Morris (1977), but doped with known additions of Specpure La(III) and Eu(III), was prepared. Samples of powdered laterite (0.4 g) were irradiated in the nuclear reactor HERALD together with similar weights of control. An irradiation was usually of 2 hours' duration in a thermal flux of  $1.6 \times 10^{12}$  neutrons  $\text{cm}^{-2} \text{s}^{-1}$ .

Counting was conveniently commenced about 24 hours after the end of irradiation. Repeat measurements were made over a period of 3 days to establish half-lives and confirm identification.