

**Fe<sup>2+</sup> PARTITIONING BETWEEN THE M1 AND M2 SITES IN SILICATE PHASES FROM SOME STONY AND STONY-IRON METEORITES STUDIED USING X-RAY DIFFRACTION AND MÖSSBAUER SPECTROSCOPY.** A. A. Maksimova, A. V. Chukin, E. V. Petrova and M. I. Oshtrakh, Institute of Physics and Technology, Ural Federal University, Ekaterinburg, 620002, Russian Federation. E-Mail: [oshtrakh@gmail.com](mailto:oshtrakh@gmail.com).

**Introduction:** Stony and stony-iron meteorites consist of various iron-bearing phases with the main content of silicate phases. These phases are olivine (Fe, Mg)<sub>2</sub>SiO<sub>4</sub>, orthopyroxene (Fe, Mg)SiO<sub>3</sub> and clinopyroxene (Fe, Mg, Ca)SiO<sub>3</sub> which have two crystallographically non-equivalent positions for Fe<sup>2+</sup> and Mg<sup>2+</sup> cations denoted as M1 and M2. The information about the Fe<sup>2+</sup> and Mg<sup>2+</sup> partitioning between the M1 and M2 sites in silicate crystals is important for estimation of their thermal history. Therefore, evaluation of the Fe<sup>2+</sup> and Mg<sup>2+</sup> occupancies in silicate phases in stony and stony-iron meteorites could be useful for analysis of their thermal history.

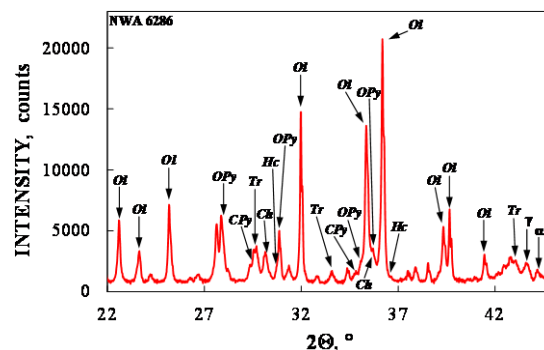
X-ray diffraction (XRD) and Mössbauer spectroscopy are very useful techniques for the study of various meteorites including the Fe<sup>2+</sup> partitioning between the M1 and M2 sites in silicate phases. In this work we present the results of our approach to estimate the Fe<sup>2+</sup> cations distribution between two nonequivalent sites in silicates using XRD and Mössbauer spectroscopy with a high velocity resolution. The latter technique has much more precise reaching the resonance and much better sensitivity to the absorption lines features than conventional Mössbauer spectroscopy (see [1, 2]).

**Materials and Methods:** Samples of powdered matter from ordinary chondrites (several fragments of Chelyabinsk LL5, Northwest Africa (NWA) 6286 and 7857 LL6, Annama H5) and stony part from Seymchan main group pallasite (PMG) were prepared for the study. After measurement of XRD patterns samples powders were glued on Fe-free Al foil with a thickness of ~8 mg Fe/cm<sup>2</sup> or less for Mössbauer spectra measurements.

XRD patterns were measured using XRD-7000 (Shimadzu) operated at 40 kV and 30 mA with CuK<sub>α</sub> radiation using a monochromator on the secondary beam, scanned over 2 $\Theta$  from 12° to 80° with a step of 0.03° per 10 s, and PANalytical X'Pert PRO MPD diffractometer (The Netherlands) with CuK<sub>α</sub> radiation and Ni filter in the 2 $\Theta$  range of 10–90° with a step of 0.013° per 300 s. Mössbauer spectra of meteorites were measured using an automated precision Mössbauer spectrometric system built on the base of the SM-2201 spectrometer with a saw-tooth shape velocity reference signal formed by the digital-analog converter using discretization of 2<sup>12</sup> (quantification using 4096 steps). Details and characteristics of this spectrometer

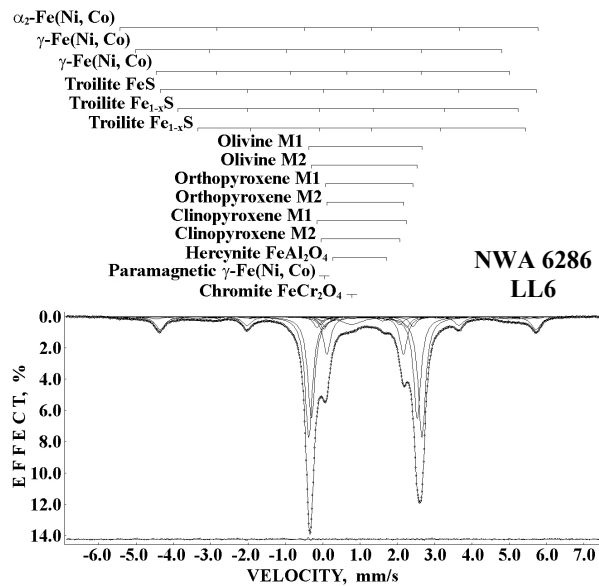
and the system were given elsewhere [1–4]. The 1.8×10<sup>9</sup> Bq <sup>57</sup>Co(Rh) source (Ritverc GmbH, St. Petersburg) was used at room temperature. The Mössbauer spectra were measured in transmission geometry with moving absorber at 295 K and recorded in 4096 channels. Then spectra were converted into 1024 channels. The Mössbauer spectra of meteorites were computer fitted with the least squares procedure using UNIVEM-MS program with a Lorentzian line shape. The spectral parameters such as: isomer shift,  $\delta$ , quadrupole splitting,  $\Delta E_Q$ , line width,  $\Gamma$ , relative subspectrum area,  $A$ , and statistical quality of the fit,  $\chi^2$ , were determined. Criteria for the best fits were differential spectrum (the difference between experimental and calculated spectral points),  $\chi^2$  and a physical meaning of the spectral parameters. Values of  $\delta$  are given relative to  $\alpha$ -Fe at 295 K.

**Results and Discussion:** Examples of XRD pattern and the Mössbauer spectrum of NWA 6286 ordinary chondrite are shown in Figs. 1 and 2. All XRD patterns were fitted using the Ritveld full profile analysis with revealing the Fe<sup>2+</sup> and Mg<sup>2+</sup> occupations of the M1 and M2 sites in silicates ( $X_{Fe}^{M1}$  and  $X_{Fe}^{M2}$  and  $X_{Mg}^{M1}$  and  $X_{Mg}^{M2}$ , respectively) shown in Table 1.



**Fig. 1.** XRD pattern of NWA 6286 LL6 ordinary chondrite shown in selected 2 $\Theta$  range. Ol – olivine, OPy – orthopyroxene, CPy – clinopyroxene, Tr – troilite, Ch – chromite, Hc – hercynite,  $\alpha$  –  $\alpha$ -Fe(Ni, Co) phase,  $\gamma$  –  $\gamma$ -Fe(Ni, Co) phase.

All Mössbauer spectra were better fitted with revealing of the main and minor spectral components. The components related to the <sup>57</sup>Fe in the M1 and M2 sites in all silicates were identified and their relative areas  $A^{M1}$  and  $A^{M2}$  were obtained for olivine, orthopyroxene and clinopyroxene (see Table 1).



**Fig. 2.** Mössbauer spectrum of NWA 6286 LL6 ordinary chondrite. Indicated components are the result of the best fit. The differential spectrum is shown below.

**Table 1.** The Fe<sup>2+</sup> partitioning between the M1 and M2 sites in silicates estimated using XRD and Mössbauer (MS) data.

Silicates	Method of estimation	
	XRD $X_{Fe}^{M1}/X_{Fe}^{M2}$	MS $A^{M1}/A^{M2}$
<b>Olivine</b>		
Chelyabinsk LL5 No 2	1.17	1.18
NWA 6286 LL6	1.23	1.19
NWA 7857 LL6	1.16	1.22
Annama H5	1.2	1.4
Seymchan PMG	1.38	1.31
<b>Orthopyroxene</b>		
Chelyabinsk LL5 No 2	0.20	0.25
NWA 6286 LL6	0.25	0.26
NWA 7857 LL6	0.33	0.34
Annama H5	0.1	0.2
Seymchan PMG	–	–
<b>Clinopyroxene</b>		
Chelyabinsk LL5 No 2	1.78	1.90
NWA 6286 LL6	1.33	1.30
NWA 7857 LL6	2.00	2.43
Annama H5	–	–
Seymchan PMG	1.6	1.67

A comparison of the Fe<sup>2+</sup> partitioning between the M1 and M2 sites in silicates obtained on the basis of two techniques appeared to be similar, i.e. indicated a good agreement between XRD and Mössbauer spec-

troscopy with a high velocity resolution. Furthermore, it is possible to estimate the distribution coefficient  $K_D$ :

$$K_D = \frac{X_{Fe}^{M1} \times X_{Mg}^{M2}}{X_{Fe}^{M2} \times X_{Mg}^{M1}}, \quad (1)$$

and the temperatures of equilibrium cations distribution  $T_{eq}$  using the following equations for olivine [5]:

$$-\Delta G = R \times T_{eq} \times \ln K_D, \quad (2)$$

where  $\Delta G$  is the Gibbs energy ( $\Delta G=20935$  J for olivine),  $R=8.31$  J·K<sup>-1</sup>·mol, and for orthopyroxene [6]:

$$\ln K_D = 0.391 - \frac{2205}{T_{eq}}. \quad (3)$$

However, in contrast to XRD which permits estimation of  $X_{Fe}^{M1}$  and  $X_{Fe}^{M2}$  and  $X_{Mg}^{M1}$  and  $X_{Mg}^{M2}$ , Mössbauer spectroscopy cannot estimate  $X_{Mg}^{M1}$  and  $X_{Mg}^{M2}$  without additional data. It takes to use fayalite Fa and ferrosilite Fs data to obtain  $X_{Mg}^{M1}$  and  $X_{Mg}^{M2}$  values from Mössbauer spectroscopy (see [7]). Some estimated values of  $T_{eq}$  for olivine are shown in Table 2. The results obtained using two techniques are consistent.

**Table 2.** Selected values of  $T_{eq}$  estimated for olivine using XRD and Mössbauer data.

Olivine	$T_{eq}$ , K	
	MS	XRD
Chelyabinsk LL5 No 2	1115	1179
NWA 6286 LL6	1052	1010
Seymchan PMG	835	684

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