CATION DISTRIBUTION IN PYROXENES FROM MARTIAN METEORITE.

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Introduction: Clinopyroxenes from the martian meteorite NWA856 were studied by means of single crystal diffractometry with synchrotron radiation at ID13/ESRF and D3/DESY. A structure refinement with Bragg data from martian pyroxene single crystals was performed and the cation distribution determined. In pyroxenes, the Mg and Fe2+ cations fractionate between the non-equivalent M1 and M2 sites. The fractionation value KD (Fe2+M1 MgM2)/(Fe2+M2 MgM1) is sensitive to temperature and thus serves as a recorder for the cooling rate of the host rock.

Experimental: (a) Selection of sample material. Pyroxene samples from martian meteorites have previously been considered as a hybrid between single crystals and textured powder in literature [1]. In the course of several preliminary experiments with synchrotron radiation we found that well ordered crystals exist, which are suitable for data collection and subsequent structure refinement. The crystal size seems to be the most important factor for determining the crystal quality. Crystals with edge lengths of <1µm - to 10 µm were examined and only smallest crystals exhibit reflection profiles suitable for data collection and, most importantly, extraction of integrated intensity. Due to the very similar lattice constants of the intergrown pigeonite and augite lamellae an overlap of reflections from both phases occurs and the separation of reflections belonging to the two phases is difficult, especially if the mosaicity of the crystals is high. In practice, powdered sample material is placed on a kapton foil, which was scanned for good quality single grains. Data was collected at λ = 0.731Å and 0.976 Å and varying distances. The best sample was a crystal of 7*3*5 µm, mainly pigeonite, with lattice constants a:9.73Å, b: 8.96 Å, c:5.26 Å, ß: 108.60°.

(b) Composition: Microprobe analysis revealed that the sample material is non-homogeneous, the composition varying from augite En31-36Wo32-35Fs29-37 and pigeonite En27-54Wo13-16Fs30-61. The composition of the microcrystal used for structure refinement could not determined by microprobe measurement. A rough estimate of the composition of the selected single crystal En60:50Wo10:10Fs80:20 was therefore made by taking the b and b lattice parameters as a guide. The volume of augite was estimated at 15% from the intensity ratios of several reflections.

(c) Reconstructed reciprocal layers. The low degree of shock, as indicated by sharp reflections and absence of (mechanical) twinning is apparent in Fig. 1. No streaking along a* of c* directions was found. The FWHM of h+k = odd or even type reflections were determined with Gaussian profiles, results see [2]. The other crystals investigated showed a much higher degree of  mosaicity, streaking along a* and in one case (001) twinning affecting both augite and pigeonite.

Structure refinement: Data collection was carried out at the beamline ID13/ ESRF with CCD camera recording. Integral intensities were derived from data processing with XDS program package [3]. The refinement was carried out only for the major pigeonite phase in the low-clino space group P2_1/c using the Jana2000 software [4]. About 800 independent reflections were used for structure refinement. Starting atomic parameters were taken from [5]. Due to the unknown starting composition, the En/Fs ratio was varied. The best Rwp value of 5.0, GoF of 2.25, was achieved with a starting composition En30, W019, F85. The data set had a high Rint of 5.4, due to some overlap of augite and pigeonite reflections. The reflections overlapping the strongest augite reflections at low 2

Fig.2 Reconstructed [h0l] layer of G1 sample.
were excluded from the refinement. Integrated intensities and, in consequence, structure refinement may also be affected by diffuse contributions due to antiphase domains and exsolution textures, cf. [6]. The decrease in displacement parameters for O3A and B using only h+k = odd reflections was not remarkable, this is another indication that the sample may consist of rather coarse antiphase domains.

X-ray diffraction methods have been used to calibrate the KD values of pigeonite as intracrystalline thermometer [7]. The closure temperature of the exchange was calculated from the experimentally determined geothermometric equation. The refinements taking into account all non-equivalent reflections give a KD value ≈ 0.05, corresponding to a closure temperature ≈ 550°C.

The results of the refinement have to be considered preliminary, further analysis, taking both phases into account, is in progress.

**Mössbauer Spectroscopy:** Mössbauer spectra were taken with a 512-multichannel analyzer and a constant acceleration drive (γ-source~10mCi 57Co/Rh). All isomer shift data are given with reference to metallic Fe. The absorber thickness was < 4 mg Fe/cm². The powder under study was glued onto a thin plastic foil. A cryostat was available for low-temperature measurements. Fitting of the spectra was accomplished applying Rancourt's Recoil fitting procedure and using Lorentzian fits; i.e. equal line width and intensity for the two partner lines of a given doublet. The 85K spectrum showed that at least three doublets are necessary for a reasonable fit (χ²~1.2). A still better fit was possible with a four doublet fit (χ²~0.88) (Fig.2). A four doublet fit appears to be adequate considering the two intergrown phases (Table 1).

![Fig. 1 Mössbauer spectra of NWA856 at 85 K, four doublet fit.](image)

<table>
<thead>
<tr>
<th>IS (mm/s)</th>
<th>QS(mm/s)</th>
<th>B(mm/s)</th>
<th>F</th>
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<tr>
<td>1</td>
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<tr>
<td>4</td>
<td>1.22</td>
<td>2.76</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Table 1: Parameters obtained by fitting the 85 K spectra of a Fig.1; QS= quadrupole splitting, IS = isomer shift (with respect to metallic iron), B = line width (FWHM); error for fitted parameters ± 0.02 mm/s; F = area fractions of subspectra (referred to the total area).

The spectra yield average values for Fe²⁺ distribution, due to the overlap, the relative volumes of augite and pigeonite can not be separated. The site occupancy indicates a rather pronounced order, with approximately 70% fraction of Fe²⁺ on the M₂ site, similar to the cation distribution in a lunar pigeonite [8] with an equilibrium temperature close to 600°C. This result seems to be the upper limit of the intracrystalline partitioning coefficient, with results from structure refinement at around 550°C. The closure temperature for the Ca-Fe, Mg interdiffusion as estimated from a result of TEM/EDS measurements [9], was given as 700°C. The width and periodicity of lamellae indicated a cooling rate <0.1°C/h [9]. The Mössbauer and structure refinement results indicate possibly even lower cooling rates for temperatures down to 500°C.

**References:**


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