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Microstructural investigations on strongly stained olivines of the chassignite NWA 2737 and implications for its shock history

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ABSTRACT

Olivines from the meteorite Northwest Africa 2737 (NWA 2737) show unique characteristics such as strong brownish staining, the occurrence of perpendicular sets of bright lamellae and the exsolution of metallic nanoparticles. These features were investigated by transmission electron microscopy and spectroscopic techniques to understand their formation and consequent implications for the shock history of NWA 2737. Areas showing optically an intense brown staining are characterised by the occurrence of finely dispersed metallic nanoparticles, an extreme high density (10^{16} m^{-2}) of polygonised dislocations with Burgers vector [001] and a high abundance of trivalent iron (16%) as determined by electron energy loss spectroscopy. In contrast, the bright lamellae contain individual dislocation lines with Burgers vector [001] of a slightly lower density (10^{14} m^{-2}), almost no metallic nanoparticles and significantly lower trivalent iron content. Model mass balance calculations suggest that the high content of trivalent iron can be incorporated as a laihunite component into the cores of polygonised dislocations. This is charge balanced by the formation of metallic nanoparticles. Trivalent iron is likely responsible for the intense brown colour, whereas nanoparticles darken these areas considerably and cause an intense red slope in the infrared range. The proposed diffusion of trivalent iron into the cores of polygonised dislocations and the associated exsolution of metallic iron nanoparticles are likely fundamental processes for intense olivine staining during meteoritic impacts in general. Detailed analyses of variously stained regions suggest that the bright lamellae have experienced slightly higher shock-induced strain causing a recrystallisation of olivine, which occurred simultaneously with the polygonisation and exsolution processes resulting in the olivine staining of adjacent areas. The existence of individual dislocations can be interpreted as the result of a two-stage shock history for NWA 2737. After a first impact, the material of NWA 2737 was likely embedded in a hot ejecta blanket. This would ensure sufficient time at elevated temperatures for the polygonisation of dislocations and the recrystallisation of bright lamellae. A second impact resulted in the emission of individual dislocations into recrystallised olivine and the ejection of that meteorite from Mars.

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1. Introduction

The Martian achondrite Northwest Africa 2737 (NWA 2737) is an exceptional meteorite among the shergottite–nakhlite–chassignite (SNC) group. It represents the second known member of dunitic cumulates beside Chassigny, called together the chassignite subgroup. Due to their magmatic petrology, unique oxygen isotope and noble gas signatures, SNC meteorites are supposed to originate from Mars (Franchi et al., 1999; McSween, 1994) and gained a lot of attention as the only directly available material from the Red Planet up to now. In comparison with Chassigny, NWA 2737 has important implications for understanding magma formation and impact ejection conditions on Mars. Since its recovery from the Moroccan desert in 2000, its petrology, geochemistry, isotope and noble gas signatures have been intensely studied (e.g., Beck et al., 2006; Marty et al., 2006; Misawa et al., 2005). It has been nicknamed Diderot during these investigations, after the French encyclopedist born in Langres, just a few kilometres away from the French village Chassigny.

Unlike its counterpart Chassigny, NWA 2737 shows a dark colour in hand specimen due to strongly stained olivines. Noble gas analyses revealed a nearly complete depletion in xenon isotopes characteristic of the Martian mantle. Its noble gas signature is dominated by a trapped Martian atmospheric component comparable to shergottite impact glasses (Marty et al., 2006), whereas its petrology is very similar to Chassigny. These differences indicate a different shock history of a similar source material.

As shown by Beck et al. (2006), the mineralogy of NWA 2737 is dominated by cumulus phases of olivine (89.7 wt%) and minor

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amounts of a chromite-rich spinel (4.6 wt%), whereas in magmatic melt inclusions, a few percent of augite, orthopyroxene–pigeonite, analbitic maskelynite and traces of phosphates, sulfides and possibly a kaersutitic amphibole (Mikouchi, 2005) occur. Compared to Chassigny, the higher forsterite content of $Fo_{78.7}$ in NWA 2737 olivines and the lower plagioclase content of maskelynite indicate a less differentiated and more aluminium restricted parent magma (Floran et al., 1978; Langenhorst and Greshake, 1999). However, slightly different REE patterns do not imply that both rocks were formed from unrelated parental melts (Beck et al., 2006). Carbonates occurring on olivine grain boundaries and in vein fillings are supposed to be, to some extent, of Martian origin. Trace element analyses point to negligible terrestrial contamination of this desert find (Beck et al., 2006). Misawa et al. (2005) determined the Sm–Nd crystallisation age to be 1.38 Ga and cosmic ray exposure ages to be around 10–11 Ma, values quite similar to those known from Chassigny and the Nakhlites.

NWA 2737 shows unique microstructural characteristics such as strongly stained and mosaic olivine, characteristic sets of perpendicular bright lamellae hosted in a dark olivine matrix and the precipitation of finely dispersed iron metallic nanoparticles as first published by Van de Moortèle et al. (2007b). The examination of these shock-induced changes not only provides information on its shock history but is also important for interpreting spectra from orbital remote sensing (e.g., Treiman et al., 2007). Several studies coeval to ours have addressed these topics up to now; however, the formation of these features is still controversially discussed.

Van de Moortèle et al. (2007a,b) proposed the transition to a newly discovered and metastable high-pressure polymorph of olivine (ζ-phase) to explain additional Raman bands and a few percent of trivalent iron hosted in the dark matrix. In contrast, Treiman et al. (2007) and, later, Pieters et al. (2008) argued that measured values of trivalent iron are mostly due to accompanying phases such as chromite and the trivalent iron content in olivine is rather below 3%. Spectroscopic analyses by Pieters et al. (2008) have shown that all spectral features in the mid-infrared indicate normal crystalline olivine. Moreover the strong staining obvious in extremely low reflectance of visible to near infrared spectra could not be an effect of such a low abundance of trivalent iron but should be caused by finely dispersed iron nanoparticles. The bright lamellae were originally attributed to partial melting during an intense shock event (Beck et al., 2006). Based on their crystallographic orientation, Treiman et al. (2007) suggested a recrystallisation during postshock deformation at low strain rates, whereas fractures inside these lamellae are interpreted as evidence for a second shock event. Pieters et al. (2008) and Van de Moortèle et al. (2007b) concluded, however, that these observations do not unambiguously require a second shock event and proposed a single shock history, in which the bright lamellae experienced just slightly lower shock temperatures.

Independent of these studies, we have thoroughly investigated the microstructural characteristics of NWA 2737 olivine (Bläß et al., 2006) by transmission electron microscopy (TEM) and Mössbauer milliprobe spectroscopy. The observations of variously stained olivine regions resulted in an alternative explanation for the formation of all microstructural features, which not only eliminate the inconsistencies described above but also provide crucial constraints on the shock history of that unique meteorite.

2. Sample and analytical techniques

Small chips of strongly stained olivines from NWA 2737 have been carefully prepared as polished thin sections of 28 µm thickness for optical microscopy, Raman spectroscopy and Mössbauer spectroscopy. Raman spectra were collected using both UV-wavelength and visible light of a green laser. The UV-spectra were obtained by a Jobin–Yvon HR800 LabRam setup fitted to a UV sensitive microscope at the Institut für Physikalische Chemie, Friedrich-Schiller-Universität Jena, Germany. An excitation wavelength of 244 nm was derived from a Coherent Innova 300 frequency doubled argon laser; the setup resulted in a spectral resolution of 5 cm^{-1}. Raman spectra using visible light were collected on the same sample areas using a Jobin–Yvon HR VIS LabRam spectrometer at IPHT, Jena, Germany, equipped with a Coherent Innova 302 C Krypton laser of 568 nm wavelength and a grating of 1800 lines/mm provided a spectral resolution of around 0.5 cm^{-1}.

For Mössbauer spectroscopy, pieces of 28 µm thick olivine were separated from the thin section and mounted between a Mylar sheet and a 25 µm thick Ta foil drilled with a 500 µm hole. The Mössbauer spectrum was recorded at room temperature in transmission mode on a constant acceleration milliprobe Mössbauer spectrometer at Bayerisches Geoinstitut, University of Bayreuth, Germany, with a nominal 370 MBq^{57}Co high specific activity source in a 12 µm thick Rh matrix. The velocity scale was calibrated relative to a 25 µm thick α-Fe foil using the positions certified for the (former) National Bureau of Standards reference material no. 1541; line widths of 0.36 mm/s for the outer lines of α-Fe were obtained at room temperature. The spectrum was collected over 12 days and was fitted using the commercially available fitting program NORMOS written by R.A. Brand (distributed by Wissenschaftliche Elektronik GmbH, Germany). The conventional constraints of Lorentzian lineshapes with equal widths and areas were applied to the components of each doublet.

Subsequently, characteristically stained olivine areas were selected and mounted on molybdenum grids and thinned to electron transparency through argon ion bombardment using a Gatan DuoMill machine and 4.5 kV acceleration voltage. Transmission electron microscopy (TEM) studies were performed on a LEO 922 Omega microscope using a LaB_6 cathode and 200 kV accelerating voltage. The microscope is equipped with a high resolution objective lens, a ThermoNoran EDX-detector and an in-column Omega filter for electron spectroscopic images.

In order to determine locally the valence state of iron in olivine, electron energy loss spectra (EELS) of the iron $L_{2,3}$-edges were recorded on a Philips CM20 FEG at Bayerisches Geoinstitut, University of Bayreuth, Germany, using a Gatan PEELS 666 parallel spectrometer (cf. Frost and Langenhorst, 2002). The resulting energy resolution of 0.9 eV has been determined by the width of the zero-loss peak at half maximum. All spectra were preprocessed according to dark current and channel-to-channel gain variation and the subtraction of an inverse power law background. Plural inelastic scattering effects were removed by deconvolution of the spectra with the low-loss spectra (Egerton, 1996).

3. Results

3.1. Optical microscopy

Thin sections of NWA 2737 olivine show an intense brown colour, various sets of severe cracks and characteristic sets of bright lamellae in plane polarised light (Fig. 1), hereafter termed bright lamellae in this study. Under crossed Nicols, the variation in interference colours from first order red to second order green indicates a strong mosaicism, whereas uniform interference colours of the bright lamellae denote their equal crystallographic orientation, independent of their propagation direction in the thin section. The lamellae are usually a few microns wide and both sets of directions are oriented exactly orthogonal to each other, as shown by tilting the thin section on a 4-axis universal stage. Comparison of these tilt angles with electron diffraction data revealed that the bright lamellae are in fact parallel to either (100) or (001) olivine lattice planes. Major cracks are oriented either parallel to the same planes or close to {101}. These orientations of lamellae differ essentially from {021} as determined by Treiman et al. (2007) using conoscopic examination of interference figures under crossed Nicols. In contrast to diffraction methods,

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