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Case study of chondrule alteration with IR spectroscopy in NWA 2086 CV3 meteorite

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ABSTRACT

Analyzing the alteration in an olivine chondrule of the NWA 2086 CV3 meteorite, infrared spectral, electron microprobe and optical microscopic observations were correlated to each other. The intensity and wavelength positions of olivine peaks changed characteristically with the progression of alteration and related Fe/Mg substitution inward of the chondrule. Moderate to good correlations were identified between Fo% composition and positions of 830 and 860 cm^{-1} IR peaks. The disappearance of 1020 cm^{-1} peak by structural change happens already at a low level alteration without changing the optical appearance of the mineral. The existence of the 980 cm^{-1} peak is found to be an indicator of the intact phase of olivine. While profiles perpendicular to the chondrule's perimeter showed that the alteration progressed 15–20 μm distance inward without observable fractures (probablly by some diffusion related process), the "alteration distance" from various obvious fractures inside the chondrule was only 3–5 μm distance. These observations suggest that the substitution was more effective close to the matrix, and also related to some fluids that although were able to circulate along the large internal fractures too, did not produce such strong substitution there, like what happened close to the matrix. It was also demonstrated that the poorly exploited contact mode observations with ATR based reflection method in infrared spectroscopy provide a useful tool to analyze the alteration at micrometer scale without much sample preparation, and enable identifying alterations already at such a low level where the olivines still look optically intact.

1. Introduction

The aim of this work is to analyze the alteration of a chondrule in the NWA 2086 CV3 type chondrite with a special method: contact measurements with ATR detector on a Fourier Transform Infrared Spectrometer; the findings might have implications on other carbonaceous chondrites, including their alterations (Fintor et al., 2013). Although being an often analyzed meteorite type, several questions are unanswered in this group. Alteration in CV chondrites occasionally happened at high water/rock ratios (Zolensky et al., 1993), and while most CV meteorites belong to the petrographic type 3 (McSween, 1977) with little or no metamorphic and water related alteration, some signatures could also be present there related to hydration and interaction with water (Beck et al., 2010; Fintor et al., 2014). Thermal metamorphism happening at very low level in this type (Bonal et al., 2006), as well as their potential connection to CK chondrites (Weisberg et al., 2006) should be analyzed, with emphasis on the formation conditions (Quirico et al., 2011) that also requires more detailed work. Below the analysis of a chondrule from NWA 2086 is presented, which was selected to be an "average" one with large enough ingredients to observe them firmly. This chondrule exhibits mainly intact olivines, altered units, and it is surrounded by the matrix of the meteorite. Among the aims the comparison of optical and IR methods was also addressed, especially focusing on alteration signatures.

The measurements were made by the IR contact method with ATR specific reflectance measurement mode, which is sensitive only to the topmost layer of the sample (Dyar et al., 2011). These measurements were completed by electron microprobe (EMPA) and polarization microscope analysis. Optical microscopy was utilized for identification of "bulk" optical properties along the line of sight, and used only for rough characterization of the sample. The EMPA is able to detect only the thin top layer with down to 1 μm depth providing comparable data to IR ATR measurements that are also sensitive for the thin surface layer. The reason for the selection of this unique method was to get information on how mineral alterations could be characterized in this way and also provide a somewhat non-traditional look at alterations happening in the meteorite.

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2. Methods

For textural analysis a polarization microscope NICON Eclipse E600 POL was used with magnifications of 40, 100, 200, and 400 times. Elemental composition of certain sections of the sample was determined by 1–2 μm spatial resolution with EPMA on the sample covered in vacuum deposited thin amorphous carbon layer, using a JEOL Superprobe 733 electron microprobe with an INCA Energy 200 Oxford Instrument Energy Dispersive Spectrometer. The analytical circumstances were 20 keV acceleration voltage, 6 nA beam current and count time of 60 s for the spot measurement and 5 min for linescan analysis. Olivine, albite, plagioclase and wollastonite were standards; we estimated the detection limit for main element identification below 0.5% based on earlier measurements with various samples.

The Attenuated Total Reflectance (ATR) method is getting widely used in laboratories as it provides easy analysis of solid and liquid targets, mainly applied for organics and polymers (Harrick, 1967; Urban, 1996) but recently in Earth and planetary science too (Chemtob et al., 2010; Morlok et al., 2004; Johnston and Premachandra, 2001). Here a crystal with high refractive index is in physical contact with the target (Koji and Reikichi, 1985a, b); the wave penetrates only a few micrometer below the surface as an evanescent wave and rapidly decays from the interface. The reflected beam is attenuated with corresponding frequencies of the vibration mode and overtones of the sample crystals (Ferguson, 2010).

This ATR based method gives information only on the very top, thin surface layer of the sample, where it provides useful information of the structural properties of the crystals. Although it is not useful to characterize such phases that dominate in volume (along the cross section visible with optical microscopy) of the sample, still it could provide interesting information. Based on the published results this specific method has been poorly exploited yet for the analysis of chondrules, and as it provides accurate information on the crystalline structure of material, it is rational to use for the characterization of the alteration process (together with other methods).

In this work spectra were collected with a Bruker VERTEX 70 Fourier Transform Infrared Spectrometer equipped with a HYPERION 2000 microscope with an ATR objective. To identify the region of interest in adjacent minerals, the ATR objective is used in the visual mode. During the infrared analysis the minerals in thin section are contacted by the tip of the germanium (Ge) crystal of 100 μm in diameter, after the ATR objective was switched to the infrared mode. With this approach, infrared spectral information is gathered only from the surface layer of the sample to about ~(1/2) μm depth. The spatial resolution with the used 20-time magnification was somewhat below 2 μm. All measurements were performed for 30 s at 4 cm^{-1} resolution. Bruker Optics' Opus 5.5. software was used for manipulation of the resultant spectra (e.g. baseline correction, atmospheric compensation, etc.).

During the work an important aim was to realize infrared based ATR and microprobe measurements for the same locations and along the same profiles. In reality the spatial coincidence between the infrared and microprobe measurement locations was not always below 1 μm; rarely it may reach up 15–20 μm. We used only those data points where the two locations' distance (measured by the two different detectors) was smaller than 10 μm, and finally the correlations were calculated for the "best selection" of measurement point pairs with distance below 2 μm. All of these results were used only for statistical purposes. The targeting of the measurements was identified by the help of coordinates (defined at the beginning of the measurements and measured from a given point of the sample), and also correlating BSE and infrared reflection images. It turned out that the best results (spatial coincidence) were given if one realized the microprobe profiling firstly, and the infrared profiling secondly, as it was easier to follow the profile by IR method indicated on a BSE image. After the two types of measurements, the map of data points were overlain on each other (and on an optical microscopic mosaic) in order to see the appearance and characteristics of a given mineral with different instruments. The overlay was made by the Photoshop software and the best spatially coinciding infrared and microprobe measurements points were selected by these multi-layer images.

3. Overview of current knowledge

As the main component of the analyzed chondrule was olivine, below we outline its properties focusing on its infrared behavior to provide a better context for the interpretation.

Olivines can be described with formula Me_2SiO_4 ($Me = Mg^{2+}$, Fe^{2+}, Mn^{2+}, and Ca^{2+}), Me has six-fold coordination with isolated silicate endmembers. The Mg-rich endmember is called fayalite, Fe-rich endmember is called forsterite. The cations of these major endmembers are substituted by Ca ($CaMgSiO_4$ monticellite, $CaFeSiO_4$ kirschsteinite). The manganese endmember is called tephroite. The metal ions occur in 2 positions in the crystalline structure (M1, M2) defining their symmetry. In general the Fe^{2+} ions prefer M1 site. Mg–Fe olivines have been identified from meteorites, planetary surfaces of Mars, and interstellar dusts, as well as from earth crust and mantle rocks.

The vibrational modes of olivines were described by Reynard (1991) and Hamilton (2010) as occurring in 3 **principal bands**. (1) 850–1000 cm^{-1} Si–O asymmetric stretching vibrations (v3 mode in SiO_4), (2) feature near 825 cm^{-1} v1 mode (symmetric stretch), and three or four features between 460–620 cm^{-1} region as v4. In general the **IR bands are shifted** by proportion of cations in olivines. The IR vibrations are determined by dipole moment (μ), ionic radius, and atomic mass of central cations (Nasdala et al., 2004). The IR active bands are asymmetric (u = ungerade) bands (Nasdala et al., 2004). If the iron content of olivine increases, the wavenumber of IR bands decreases, which is caused by increasing radius and mass of the substituting cation linking to SiO_4 tetrahedron, as the Mg is smaller than Fe. Consequently, the cation substitution induces IR band shifts and change in relative intensities (Burns and Huggins, 1972; Reynard, 1991). The cation size of Fe^{2+} is larger than that of Mn, thus distorting the octaeder in the silicate lattice. The peak around 955–960 (v3 mode) becomes stronger with increasing iron content of olivine (Hamilton, 2010). In Fe-rich olivines (forsterite), Fe cations can be substituted by Mn and Cr (Hamilton, 2010) too. The Mn content increases commonly with Fe content of olivines (Burns and Huggins, 1972; Hamilton, 2010). The Mn occupies M1 position of olivine lattice inducing better ordering of crystal structure (Burns and Huggins, 1972). The increasing Mn content drives to decrease v4 band positions (460–620) (Burns and Huggins, 1972), whereas vibration modes v1 and v3 are influenced by increase of iron content (Hamilton, 2010). The major band of v3 (in our spectra 859–865 cm^{-1}) specifies 4 composition groups: Fo0-25, Fo35-39, Fo54-68, and Fo90-92, whereas v1 mode (in our case 839–837 cm^{-1}) allows 2 composition groups Fo0-54 and Fo60-92 (Hamilton, 2010).

In our spectra the recorded wavenumber is between 600 and 4000; hence v4 mode is not detected here. We selected the following simple indicators to measure IR spectral properties. 1. peak position (according to wavenumber): that reflects some internal properties of crystalline structure related to bond distances, and affected by substitution, here especially Mg/Fe interchange; and 2. relative peak intensity: level of "crystallinity", e.g. ratio of amorphous (and poorly crystalline) to high level or regular crystalline structure. Only the same type of peaks could be compared to each other that represent the same crystalline position.