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Analyzing Raman – Infrared spectral correlation in the recently found meteorite Csátalja

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ABSTRACT

Correlating the Raman and infrared spectra of shocked minerals in Csátalja ordinary chondrite (H4, S2, W2) with controlling the composition by EPMA measurements, we identified and improved various shock indicators, as infrared spectro-microscopic analysis has been poorly used for shock impact alteration studies of meteorites to date. We also provide reference spectra as SOM for the community with local mineralogical and shock alteration related context to support further standardization of the IR ATR based measurements.

Raman band positions shifted in conjunction with the increase in full width half maximum (FWHM) with shock stage in olivine minerals while in the infrared spectra when comparing the IR band positions and IR maximal absorbance, increasing correlation was found as a function of increasing shock effects. This is the first observational confirmation with the ATR method of the already expected shock related disordering. In the case of shocked pyroxenes the well-known peak broadening and peak shift was confirmed by Raman method, beyond the level that could have been produced by only chemical changes. With increasing shock level the 852–864 cm^{-1} and 1055–1071 cm^{-1} FTIR bands finally disappeared. From the shock effect occasionally mixed mineral structures formed, especially feldspars together with pyroxene. Feldspars were only present in the shock melted volumes, thus produced by the shock effect itself.

Based on the above mentioned observations in Csátalja meteorite the less shocked (only fractured) part witnessed 2–6 GPa shock pressure with temperature below 100 °C. The moderately shocked parts (minerals with mosaicism and mechanical twins) witnessed 5–10 GPa pressure and 900 °C temperature. The strongly shocked area (many olivine and pyroxene grains) was subject to 10–15 GPa and 1000 °C. The existence of broad peak near 510 cm^{-1} and disappearance of other peaks of feldspar at 480 and 570 cm^{-1} indicate the presence of maskelynite, which proposes that the peak shock pressure could reach 20 GPa at certain locations. We identified higher shock levels than earlier works in this meteorite and provided examples how heterogeneous the shock effect and level could be at small spatial scale. The provided reference spectra support the future improvement for the standardization of infrared ATR based methods and the understanding of shock-related mineral alterations beyond the optical appearance.

1. Introduction

Shock alterations play an important role in many meteorites [1,2,3,4,5] and they help to reconstruct the geological history of the given specimen and also its parent body [6]. In this work we analyzed the shock driven alteration of a recently found meteorite to identify how such alteration look like with comparing Raman and infrared spectral methods to improve our knowledge on the joint usage of these two spectroscopic methods – especially to provide controlled IR ATR measurements, as this later methods is poorly tested for meteorite minerals. The survey targeted the main mineral components of a chondrite meteorite: olivine, pyroxene and feldspar. The result may help to better understand the consequences of shock effects, and also to extrapolate using these findings of resemble alterations in other chondrites. We also aim to provide infrared spectroscopy based data as references and standards to further analyze the connection between infrared and Raman spectroscopic methods.

The analyzed meteorite called Csátalja is a H chondrite (H4, S2, W2), and based on the differences between its certain parts, probably is a

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breccia. The meteorite was found in August of 2012, some km east of the village of Csatalja (46.006° N, 18.991°) in Hungary by Karoly Kiss a tractor driver. The area is a fluvial plain formed in the last 10–40 thousand years and is under agricultural cultivation now, thus the meteorite was affected by weathering on the Earth, probable mainly producing iron-oxide vein fillings. The meteorite shows high iron abundance (25–31%), its main minerals are: orthopyroxene, olivine (fayalite content 16–20 mol%), 15–19% reduced Ni—Fe metal and 5% troilite. These minerals are partly metamorphosed to petrographic grade 3–7 (usually 5). The analyzed thin section (called "Csátalja 002") is a highly shocked one with up to 300 μm thick shock veins, chondrule fragments and mineral clasts.

2. Methods

The analyzed sample was a 15 × 20 mm sized, well prepared thin section with almost constant thickness. No substantial sample mass was lost during the polishing process, the meteorite was relatively hard. During the analysis three different methods were used and correlated: optical, Raman and IR microscopy based results.

A polarization microscope NICON Eclipse E600 POL was used for textural analysis and basic mineral determination. For infrared spectroscopy and microscopy a Vertex 70 FTIR spectrometer and Hyperion 2000 microscope was used with Attenuated Total Reflectance (ATR) method [7,8,9] where a high refractive index crystal is in physical contact with the target [10,11]. During the infrared analysis the minerals the thin section was contacted by the tip of the germanium (Ge) crystal of 100 μm in diameter. The infrared wave from the crystal 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 to the vibration mode and overtones of the sample crystals [12]. All measurements were performed for 30 s at 4 cm^{-1} resolution. Bruker Optics' Opus 5.5. software was used for manipulation of the gained spectra (e.g. baseline correction, atmospheric compensation etc.). The maximal absorbance (or IR intensity, or IR maximal intensity) used in this work refers to the position in wavenumber of the strongest v1 SiO vibration. Absorbance intensity variations can result from the simultaneous reorientation of a pair of dipole-transition moments responsible for the absorption bands, its value was measured by the ATR after standardization, subtracting the background at good signal/noise ratio. Although such measurements were not the focus of this work, but as this parameter changed with the shock produced crystalline lattice deformation, we measured and discussed it, despite its value being influenced by several parameters and the effects being relatively poorly known. The absorbance is influenced by the grain size, where the smaller grains decrease the intensity [13,14]. The absorbance also decreases by the incorporation of various "other" elements into the crystalline lattice, which distort it [15]. For feldspars the decrease of absorbance along with the shock deformation was already observed [16,17,18], here our new measurements could also provide some insight.

The elemental composition of the measured locations was determined by EPMA with 1–2 μm spatial resolution 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. Olivine, albite, plagioclase and wollastonite were standards; we estimated the detection limit for main element identification below 0.5% based on experiences from earlier measurements with various samples.

The thin section was divided to a matrix of units for target identification, each measurement point was identified by the zone code (A1, A2) and a number (see Fig. 1), while the acronyms of measurement locations do not have any meaning. The observed targets were selected from strongly shocked areas (shock melt with clasts showing mosaicism) at D1 zone, and along a shock vein with clasts from A7-A8 area. Altogether at 109 measuring points were infrared spectroscopic data obtained, and 75 of them were selected for Raman spectroscopy.

Raman spectroscopy also applied to determine the mineralogical characteristics with Morphologi G3-ID produced by Malvern Instruments [19] The Raman spectra were detected by Kaiser Optical Systems Inc. Raman Rxn1 Spectrometer with NIR Laser Diode at 785 nm wavelength, using exposure time of 30 s at 10 mW laser power, while the size of the laser spot was 3 μm at 50× magnification. The spectral resolution was 4 cm^{-1}, the focal depth 1.82 μm. For the identification of Raman spectra, Bio-Rad's KnowItAll ID Expert software and Morphologi software were used. Comparative spectra of the minerals were imported from RUFF database by Lafuente et al. [20].

2.1. Analyzing Chemical Versus Shock Changes

An important point in the interpretation of Raman and IR peak positions is that chemical changes could also produce peak position shifts beside the shock effects. To take into account this aspect, we compared our results to unshocked reference Raman and IR peak positions of olivine and pyroxene with various observed compositions. The reference Raman spectra demonstrated the dependence of peak positions on the composition of olivines, using the following range of compositions: Fo% = 1, 8, 34, 40, 62, 65, 89, 91, 100 [21]. For Fe-Mg-Ca pyroxenes the following reference measurements were used with different compositions: $En_{.975}Fs_{.025}$, $En_{.90}Fs_{.10}$, $En_{.87}Fs_{.13}$, $En_{.80}Fs_{.20}$, $En_{.78}Fs_{.22}$, $En_{.72}Fs_{.26}Wo_{.03}$, $En_{.52}Fs_{.44}Wo_{.04}$, $En_{.47}Fs_{.27}Wo_{.26}$, $En_{.44}Fs_{.29}Wo_{.27}$, $En_{.50}Wo_{.50}$, $En_{.49}Fs_{.01}Wo_{.50}$, $En_{.45}Fs_{.04}Wo_{.50}$, $En_{.42}Fs_{.08}Wo_{.50}$, $En_{.34}Fs_{.16}Wo_{.50}$, En.09Fs.39Wo.52, $En_{.46}Fs_{.09}Wo_{.44}$, $Wo_{1.0}$, $En_{.10}Fs_{.90}$, $En_{.17}Fs_{.83}$ [22]. Peak positions from these measurements were compared to our data (see in SOM Table 1). In the case of ATR-FTIR reference the following compositions were available for olivine: Fo% = 0, 10, 20, 30, 40, 50, 55, 65, 70, 75, 80, 89.5, 100 [23].

The unshocked feldspar reference Raman band data came from Freeman et al. [24] on: andesine ($Or_2Ab_{56}An_{42}$ (510.5 cm^{-1}), oligoclase ($Or_1Ab_{76}An_{23}$ (510.6 cm^{-1}), labradorite $Or_1Ab_{37}An_{62}$ (508.7), which were used for identification of the shock induced shift of peak positions. The unshocked ATR-FTIR reference spectra of RUFF database [20] for plagioclase (oligoclase, labradorite) were used to separate shock induced from chemical changes related peak shift.

3. Results

The analyzed thin section is a highly shocked meteorite with up to 300 μm thick shock veins, chondrule fragments and shocked mineral clasts. There are different units in the meteorite, regarding their shock level, and as these units have different geological history, the sample could be termed breccia. The minerals show nice interference colour in polarized optical light, and they were relatively transparent because the sample's thickness is constant and around 30 μm, while the melted zones are dark. The sample shows heterogeneous structure at cm scale, with eroded but still observable chondrules and heavily crushed, as well as melted units modified by different level of shock driven alteration.

We investigated two areas of the sample (Fig. 1): a strongly shocked area at D1 zone and a less shocked area at A7-A8 zones. The optical appearance provides context for the interpretation of the shock event. The **D1 zone** is near to a hematite-bearing amoeboid patch, with kamacite, troilite, and mineral clasts (olivines with strong mosaicism, eroded rims, there are also shock annealed and highly amorphized pyroxenes with subgrained structures and isotropic patches) in the dark melt. The **A7-A8 zone** is a less shocked area where the veins are filled by iron oxide (possibly secondary mineral by terrestrial alteration) and embedded mineral clasts. The measurements made in the opaque vein (thickness 0.1–1 mm) of less shocked with fractured olivines (A7a-f, A8a-c, Table 1, columns 3–5), which contain embedded olivine and pyroxene grains.