

## Mineralogy of meteorite Chelyabinsk as determined by Raman spectroscopy.

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**Introduction:** Using Raman spectroscopy that we anticipate will be used in future planetary surface exploration, we have identified and characterized the major, minor and trace mineral phases in rock chips and dust of meteorite Chelyabinsk, fall 15 February 2013, over Chelyabinsk, Russia. Raman spectra are shown for olivine, pyroxene, feldspar, magnetite, pyrrhotite (an Fe sulfide group), calcite and, possibly, parasite. The variations in composition of the silicate minerals represent different stages of crystallization at dust/gas clouds of solar nebula heating by shock events and the following evolution of the asteroidal parent body.

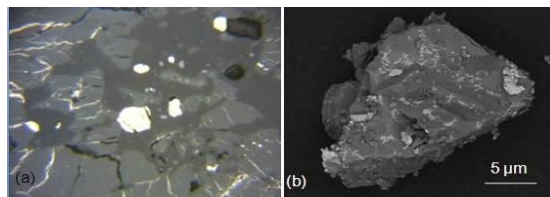
**Samples:** On 19 February 2013, GEOKHI RAS sent an expedition from staff of the laboratory of meteoritic for the collection of the substance of the meteorite in the region of settlements the Deputy, Pervomaisky and Emangelinka, about 40 km to the South West from Chelyabinsk. It was first found about 3.5 kg fragments of the meteorite, and mineralogical, chemical and isotopes compositions were analyzed [1]. Main result is that meteorite Chelyabinsk is ordinary chondrite, type LL5-S4 W0 according international classification [2]. Preliminary analysis of trajectory and orbit established that the Chelyabinsk superbolide was fragment of an Apollo asteroid, specific group of near-Earth objects. Special issue of *Geochemistry International* journal under edition of academician Galimov E.M., MAIK "Nauka/Interperiodica" (Russia), July 2013, will be devoted to the detailed review of the investigations conducted. Here we will concentrate on the results concerning compositional and structural information that can be obtained on key mineral groups using *in situ* Raman measurements, only [3].

**Procedure:** Renishaw InVia Reflect Spectrometer System was used for all of the Raman measurements reported here. High power near infrared diode laser, 300 mW at 785 nm, was used as the excitation source for most measurements; DPSS laser radiation, 100 mW at 532 nm, was used for a few. The Raman spectrometer has a spectral resolution of 1–2 cm<sup>-1</sup>. The wavelength calibration was done by least-squares fitting to a set of standard Ne lines. The wavenumber accuracy is better than 0.5 cm<sup>-1</sup> in the spectral region of interest; wavenumber reproducibility was checked using the Raman peak of an Si wafer each working day, and was better than 0.3 cm<sup>-1</sup> over several months. Extremely high efficiency 250 mm focal length spectrograph (>30% throughput in spectrograph) was used for all Raman measurements. It provides a laser spot size

continuously variable from 1 to 300 μm in diameter at the focal plane (objective and excitation wavelength dependent) with fully optimized beam path.

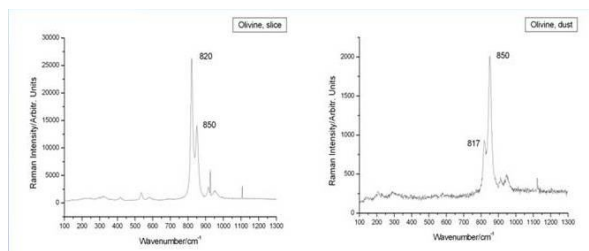
Also, Scanning Electron Microscopy (SEM) and energy dispersive X-Ray microanalyses (EDX) were performed on a Leo Supra 50VP microscope equipped with Oxford-Instruments X-Max detector. Measurement parameters of the microscope system during analysis were: low vacuum (N<sub>2</sub>, 40 Pa), 15 kV electron beam, working distance 7 nm.

**Results:** Raman measurements were made on rough, broken surface of the rock chip with surface relief on the order of about 0.1-0.3 mm, thin polished rock slice and rock dust (see Fig.1). The S/N ratios of the spectra vary from excellent to poor, but >90% of the points yielded spectra adequate for mineral identification.



**Fig.1** Samples: (a) polished slice; (b) dust particle

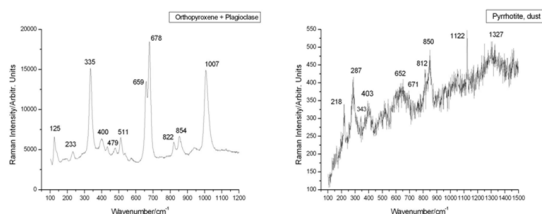
At the Raman spectra of **olivine**, the band position and the relative intensities of the characteristic SiO<sub>4</sub> stretching doublet are sensitive to the cation substitution. For the our samples, these components appear near 820 and 850 cm<sup>-1</sup>, respectively (see Fig.2). Using the correlation chart established by [4] between the band position of the doublet and the Mg/Fe ratio in the forsterite–fayalite series, a high Mg content – Mg/(Mg+Fe) = 0.6-0.7 is obtained. This result is also confirmed by EDX analysis.



**Fig.2** Raman spectra of olivine.

The **orthopyroxenes** are the major mineral phases identified in meteorite Chelyabinsk, followed by oli-

vines. The Raman spectra was obtained for enstatite, which is magnesium endmember of the pyroxene silicate mineral series enstatite ( $\text{Mg}_2[\text{SiO}_3]_2$ ) - ferrosilite ( $\text{Fe}_2[\text{SiO}_3]_2$ ). The orthopyroxenes show, in general, fairly quite homogeneous spectra with few exceptions (see Fig.3). The most intense bands at 1007, 659 and 678  $\text{cm}^{-1}$  have been assigned to the stretching  $\nu(\text{Si}-\text{O}_{\text{nb}})$  and  $\nu(\text{Si}-\text{O}_{\text{b}}-\text{Si})$ , respectively, where  $\text{O}_{\text{nb}}$  and  $\text{O}_{\text{b}}$  mean non-bonded oxygen and the chain-bonded oxygen of the  $\text{SiO}_4$  tetrahedron, respectively, in the two oxygen-shared  $\text{SiO}_4$  tetrahedra of inosilicates. Also, it is accepted that the 335  $\text{cm}^{-1}$  band arises mainly from translations of the cations.



**Fig.3** Raman spectra of pyroxenes and pyrrhotite.

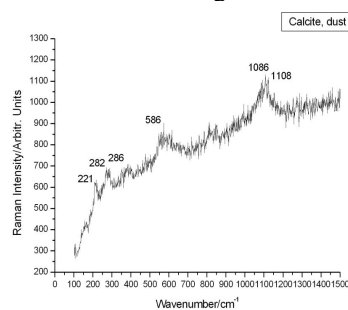
All the **plagioclase** feldspars exhibit a characteristic  $A_g$  vibrational mode between 500 and 510  $\text{cm}^{-1}$  which is the strongest feature in each spectrum. A second strong band is observed between 478 and 488  $\text{cm}^{-1}$  and both of these bands have been assigned to a mixed Si-O-Si (or Si-O-Al) band/stretch [5]. The spectra also show that, unlike most other silicates, the feldspars have very weak Si-O stretching modes, probably because the feldspars contain a continuous three-dimensional network of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra with no non-bonded oxygen or isolated  $\text{SiO}_4$  groups. The Raman spectrum of the plagioclase series  $\text{NaAlSi}_3\text{O}_8 - \text{CaAl}_2\text{Si}_2\text{O}_8$  (see Fig. 3) closely resembles previously published spectra of albite. This is sodium-rich feldspar has triclinic symmetry, with space group  $C^1_i$  ( $P\bar{1}$ ), and factor group analysis predicts that the modes near 507 and 478  $\text{cm}^{-1}$  should be observed as very strong. The Raman spectra obtained for the meteorite Chelyabinsk are consistent with this description for albite,  $\text{Ab}_{91}\text{An}_9$ , and contains modes near 511 and 479  $\text{cm}^{-1}$ .

**Iron-bearing sulfide** was not detected in the Raman measurements of the thin slice. An Fe sulfide phase was, however, found by our Raman spectroscopic examination of several locations at the dust. It has a central peak near 287  $\text{cm}^{-1}$  and weak shoulder near 218  $\text{cm}^{-1}$  (see Fig. 3). The position of its Raman peak near 343  $\text{cm}^{-1}$  suggests a solid solution of pyrite ( $\text{FeS}_2$ ), pyrrhotite and troilite [4], but detailed characterization would require a systematic Raman study of sulfides first. Among the Raman spectra of pyrrhotite obtained from our traverses on dust of the rock samples, it contains identifiable spectral peaks of Fe-Ti-Cr oxides,

including magnetite ( $\text{Fe}_3\text{O}_4$ ) near 671  $\text{cm}^{-1}$  and titanomagnetite ( $\text{FeTiO}_3 + \text{Fe}_3\text{O}_4$ ) near 812  $\text{cm}^{-1}$ , most of them are solid solutions. Typical Raman spectra obtained from Fe-Ti-Cr oxides in the measurements on dust of the rock chips are shown in Fig. 3. Among them, Fe and Cr has a coarse grain size, as shown by its EDX analysis.

**Calcite** and aragonite were observed before in Vaca Muerta meteorite (assumed that it originated on Vesta) as small globules 5–10  $\mu\text{m}$  in diameter generally situated in the interior of the eucrite inclusions, results and obtained Raman spectra were presented in [6].

Calcite and aragonite show similar spectral positions for the totally symmetrical carbonate stretching mode, 1086 and 1084  $\text{cm}^{-1}$ , respectively. For identification purposes the librational modes of carbonate at 282  $\text{cm}^{-1}$  in calcite and 207  $\text{cm}^{-1}$  in aragonite are most useful. A calcite phase was found by our Raman spectroscopic examination of several locations at the dust (see Fig. 4). Raman spectra contain peaks near 1086  $\text{cm}^{-1}$  and 282  $\text{cm}^{-1}$  clearly indicate the presence of calcite, while no trace of aragonite was found.



**Fig.4** Raman spectra of calcite.

**Discussion:** In addition to calcite modes Raman spectra contains identifiable spectral peaks near 286, 586 and 1108  $\text{cm}^{-1}$ , presumably of **parisite** (see Fig.4). It is a rare mineral comprising of cerium (Ce), lanthanum (La) and calcium fluoro-carbonate –  $\text{Ca}(\text{Ce}, \text{La})_2(\text{CO}_3)_3\text{F}_2$ . The likely origin of calcite and parisite is the metasomatism of the calcium oxide (CaO) bearing rocks with carbonated water originating from the cometary ice.

#### References:

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