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Non-destructive analyses on a meteorite fragment that fell in the Madrid city centre in 1896

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ABSTRACT

The historical Madrid meteorite chondrite fell in 1896 showing thin melt veins with a 65% of brecciated forsterite fragments surrounded by a fine grained matrix formed by troilite, chromite and Fe–Ni blebs. It exhibits a delicate iron infill, neo-formation of troilite in pockets and shock veins and neo-formation of Na-feldspar formed at high temperature and fast quenching. The semi-quantitative mineral determinations were performed with IMAGEJ freeware and chemical mappings resulting in the following approximated compositions: olivine (~55%); augite (~10%); enstatite (~10%); plagioclase (~10%); chromite (~2%); troilite (~4%), kamacite–taenite α–γ-(Fe, Ni) (~7%) and merrillite (~7%). The specimen was also studied by computer tomography, micro-Raman spectroscopy and spectral cathodoluminescence. X-ray diffraction patterns were also recorded in non-destructive way on a polished surface because of the small size of the specimen. This combination of non-destructive techniques provides an improved knowledge on the Madrid-1896 meteorite compared to the previous study performed on the same specimen carried out twenty years ago by electron probe microanalysis and optical microscopy in destructive way. Limits of these techniques are the specimen's size in the analytical chambers and the threshold resolution of the microscopes analyzing shock veins micro-crystals.

1. Introduction

Historical meteorites kept in Museums are valuable stones that traditionally have been sliced to perform polished petrographic sections for their study under polarizing microscopes and by electron probe micro-analysis. Furthermore, at the present time, many different kinds of non-destructive techniques are being developed to analyze different valuable materials [1,2] by different facilities. Non-destructive evaluation methods usually include some kinds of microscopy and spectroscopy techniques to examine external surfaces of solids in detail [3]. The Madrid L6 chondrite historical fragment fallen in the Madrid downtown in 1896 was here studied only by non-destructive techniques together with measurements of electron probe microanalysis and X-ray diffraction (XRD) recorded in non-destructive way operating on the main polished plane of the meteorite. Madrid meteorite fragments were analyzed and studied in the same year of the fall (1896) [4,5]. It was a very important daylight fireball witnessed by hundreds of Madrid inhabitants together with their audible booms. The geological event was extensively reported allowing to outline nowadays a strewn field of fragments inside the Madrid city centre [6]. The Madrid meteorite was classified in 1985 [7] as a veined L6 chondrite and confirmed in 1990 [8] assuming the mineralogical composition of olivine (Fo_{76}), low-Ca pyroxene (Fs_{24}), metallic Fe, Ni (6%) veins and troilite (5 wt%) previously analyzed by Mason (1963) [9]. The Madrid meteorite was described in the 90s [10] under the polarizing microscope, as a severely shocked specimen, highly veined, i.e., with light-colored portions of the rock made up of silicates with undulated extinction being crossed by black shock veins. These veins consist of extremely fine-grained, shock-melted silicates and opaque minerals. The fine grain size is responsible for the dark appearance of the veins. The authors in [11] conclude that the Madrid meteorite is an impact-melt breccia exposed to at least two impact events: the first produced the melt (dark) portions from light material and was mixed with residual, unmelted, light material, i.e., formed the impact-melt breccia. The second impact event took place after the impact-melt breccia was assembled and solidified and resulted in the formation of the shock veins. Currently, the main Museums of Natural Science are setting new facilities to prevent irreversible damages to their main type specimens. Typically, they are micro-focus X-ray computer tomography (μCT), environmental scanning electron microscopes (ESEM) with large chambers to hold large specimens with analytical probes which provide different types of information such as (i) chemical data, i.e. wavelength dispersive spectroscopy (WDS), electron probe micro-analysis (EPMA), etc.; (ii) elemental analysis by energy dispersive spectroscopy (EDS), backscattering (BS), (iii) morphological, i.e., electronic, optical and X-ray imaging, (iv) molecular, i.e., micro-

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Raman (Raman) and Infrared Transmission (FTIR) spectrometers in optical microscopes with large holders, (v) structural defects producing cathodoluminescence (CL) emission. These facilities provide a useful characterization of meteorite microstructural features good enough to infer crucial geological formation; in many cases much better than the simple observation performed under the traditional petrographic microscope. Operating with BS, EDS and WDS probes on poly-mineral specimens, such as a meteorite, it is important to state the chemical and elemental analyses accuracy adequately. For different metals such as iron–nickel alloys, or oxides, e.g., chromite, the EDS probe accuracy could be adequately compared to those provided by WDS or EPMA. Other interesting spectral comparison can be achieved with the cathodoluminescence (CL) and photoluminescence (PL) probes, the electron-beam excitation sources provide subtle different luminescence spectra compared with those provided from the most penetrative laser sources. The molecular information offered by the micro-Raman spectroscopy and integrated into an optical microscope provides a unique spectrum for each meteorite mineral grain of sub-micrometer dimensions. Meteorites encode important information on shock metamorphism which is a fundamental process in the evolution of the planetary bodies. They are materials particularly complex with long-time geological histories formed in the outer space which are studied with special emphasis on their micro-structures and micro-textures [12].

2. Experimental

2.1. Fireball and meteorite fragments

Madrid meteorite fragments fell in Madrid City Centre on February 10th in 1896, few seconds before 9:30 a.m. Ten samples were recovered in Madrid city, just after a bright white-blue light and a strong explosion scared and advertised people of the fallen meteorite [5]. The heaviest one weighs 143.79 g and the lightest 1.3 g. The meteorite fragments distribution formed a characteristic strewn field ellipse, NW/SE orientated. The largest meteorites fell in the NW orientation [6]. The material was highly crystallized and brecciated with chondrules poorly defined and clearly visible feldspars [6]. The Madrid L6 chondrite fragment, weighting 18.5 g and sized approximately $18 \times 17 \times 9\ mm^3$, belongs to the MNCN historical collection (Fig. 1a and b).

2.2. X-ray tomography

Following recent non-destructive modus operandi for meteorite fragments [13] we performed quantitative tomography analysis (μCT) of the meteorite (Fig. 1c and d). The stone was scanned with a Scanco micro-tomographic system housed at the National Research Centre for Human Evolution in Burgos, Spain (μCT 80, Scanco Medical, Switzerland), using the following settings for each scan: voltage 70 kV, amperage 114 mA, angular increment 0.36 grades and 0.8 s of time for each exposure. The μCT analysis of the sample was recorded during 4 h of X-ray exploration producing 640 planes with isometric voxel size of $36\ \mu m^3$ and three-dimensional views. The images were analyzed with Voxblast 3D software (Vaytek, Inc.) following the Conebeam Conv./Backpr mathematical method.

2.3. Chemical and elemental analyses on a flat surface

The historical specimen analyzed in this study was held into a mold of $29 \times 29\ mm^2$ together with wet bassanite ($CaSO_4 \cdot 0.5H_2O$). It was linked to metallic conductive plate to consolidate a solid block that was placed in the EPMA samples holder (Fig. 1b). This gypsum plaster can be removed by just washing to recover the historical specimen. The re-polished surface of the meteorite was examined by a combination of non-destructive facilities such as ESEM–EDS, CL, Raman and XRD. Analyses of morphology, textures, crystal habits and crystals sizes as well as the composition of glasses and minerals were collected using physical–chemical facilities of the Museo Nacional de Ciencias Naturales and the National Centre of Electron Microscopy of the Universidad Complutense, Madrid (Spain). Compositions of maskelenite glasses and meteorite crystals were obtained by EPMA. These data were performed with a WDS, JEOL-Superprobe JXA-8900M, equipped with four spectrometers and TAP, LD2, PETJ, LIF and LIFH crystal analyzers. The EPMA spot analyses were performed on the polished surface later sputtered with graphite. Analytical routine included the following oxides: SiO_2, TiO_2, Al_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O, NiO and Cr_2O_3. The standards used were supplied by the Smithsonian Institute of Washington [1,11]. Measurement conditions for the meteorite minerals were 15 kV accelerating voltage and 20 nA beam current for mineral and 10 nA for the glass analyses in order to minimize sodium losses. This element was accordingly measured on the first position. The beam diameter used was 5 μm and the measurement times ranged from 10 to 60 s. Detection limits are in the order of 0.01 wt%. The environmental electron microscopy studies were performed using a FEI Inspect (5350 NE Dawson Creek Drive Hillsboro, Oregon 97124, USA) ESEM microscope. The ESEM in low vacuum mode admits hydrated samples to be studied in their original state, with the large field detector (LFD) to avoid electron losses. The samples were observed with the BS detector. The ESEM resolution at low-vacuum was at 4.0 nm at 30 kV (BS). The accelerating voltage was 200 V–30 kV and the probe current up to 2 μA was continuously adjusted; low vacuum was 0.45–0.55 Torr, with a working distance of 10 mm. Samples' EDS and mapping areas were studied with an energy dispersive X-ray spectrometer, Oxford Instruments INCA Energy 200 Energy Dispersive System.

2.4. X-ray diffraction on the flat surface

The XRD analyses of the Madrid meteorite surface were performed using XPOWDER software which also allows a full duplex control of the Philips PW-1710/00 diffractometer. The experimental conditions were set under CuKα radiation with a Ni filter and a setting of 40 kV and 40 mA. Performing background subtraction, Kα2 stripping and chemical elements were restrained to Si, Al, O, Ca, Mg, Ti, C, P; Fe, Mn, Ni, Cr, Cl, P, S, Na, K and Cr. These initial assumptions improve the Boolean search-matching on the ICDD-PDF2 and RRUFF databases.

2.5. Micro-Raman spectroscopy of meteorite minerals

The micro-Raman and photoluminescence spectra of the spot samples were performed in a Thermo-Fischer DXR Raman Microscope (West Palm Beach, FL 33407, USA). The system has Olympus BX-RLA2 Microscope and a CCD (1024×256 pixels) detector, motorized XY stage, auto-focus and microscope objectives Olympus UIS2 series (West Palm Beach, FL 33407, USA) all controlled through OMNIC 1.0 software. The light at 532 nm of a frequency doubled Nd:YVO_4 DPSS solid laser (maximum power 30 mW) was used for excitation. The DXR Raman has a point-and-shoot Raman capability of one micron spatial resolution. We used the 20 × objective of the confocal microscope together with the laser source at 532 nm and 6 mW in laser mode power at 100%. The average spectral resolution in the Raman shift ranging from 100 to 3600 cm^{-1} was 4 cm^{-1}, i.e., grating 900 lines/mm and 2 μm spot sizes. The system was operated under OMNIC 1.0 software fitting working conditions such as pinhole aperture of 25 μm, bleaching time 30 s; four exposures average timed 10 s each.