Highlights on Spanish Astrophysics IX, Proceedings of the XII Scientific Meeting of the Spanish Astronomical Society held on July 18 – 22, 2016, in Bilbao, Spain. S. Arribas, A. Alonso-Herrero, F. Figueras, C. Hernández-Monteagudo, A. Sánchez-Lavega, S. Pérez-Hoyos (eds.)

Murchison CM2 chondrite at nanoscale: evidence for hydrated minerals in the protoplanetary disk

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Abstract

The most pristine chondrites are undifferentiated meteorites with highly unequilibrated mineral grains that accreted from the protoplanetary disk about 4.6 Gyrs ago. Here we focus our attention in the study of Murchison, one of the most primitive carbonaceous chondrites belonging to the CM2 group. Despite of being aqueously altered, Murchison matrix is extraordinarily complex at nanoscale, and its study can hold clues to understand the origin of the water incorporated in the parent bodies of carbonaceous chondrites. Murchison comes from an undifferentiated carbon-rich asteroid which formed from the accretion of solid particles formed in the outer protoplanetary disk. Their rock-forming materials felt into the plane of the system where they mixed with organics, and probably with hydrated minerals. Our UHRTEM (ultra-high resolution transmission electron microscopy) data demonstrate that Murchison fine-grained matrix consists of a complex mixture of many ingredients, including chondrule and CAI fragments, stellar grains, phyllosilicates and organic compounds. We describe here some mineral and textural features that exemplify how pristine, and diverse is Murchison matrix. Our results indicate that the study of carbonaceous chondrites at nanoscale can provide a significant progress in our understanding of the accretion of materials and the preservation of presolar grains in the outer regions of the protoplanetary disk.

1 Introduction

The undifferentiated meteorites called chondrites contain the sediments of Solar System creation, the first solid particles available around the Sun about 4.6 Gyrs ago. Long-lived radioactive isotopes allow us dating the formation of chondritic components. For example, the lead-lead isotopic chronometer indicates that the first solids preserved in chondrites, the so-called Ca-Al rich inclusions (CAIs), formed ~ 4.567 million years ago (hereafter, Ma) [3, 5]. At this time the Solar System comprised a young star surrounded by a flattened cloud of billions of particles that constituted the protoplanetary disk (Fig. 1). Rock-forming minerals, well condensed from the vapour phase or accreted from nearby stars, felt into the plane of the rotating system. At the first stages the particles collided progressively to generate aggregates that were orbiting the Sun during timescales of thousands of years due to gas-drag, collisions and non-gravitational processes [28]. In the inner disk most of these particles were finally evaporated or heated to the extreme until being melted and producing refractory aggregates as a residue [18, 19]. This scenario is consistent with the fact that CAIs are composed of mineral phases that formed at very high temperatures within a gas of solar composition [10, 16].

The rocky aggregates formed the chondrites, named after the igneous silicate spheres that dominate their structure, so-called chondrules. The chondrites can be considered accretionary rocks mostly formed by mm-sized chondrules, CAIs, metal grains, sulphides and other accessory minerals. These components are sometimes surrounded by a fine-grained matrix, which is a complex mixture of many ingredients, including chondrule and CAI fragments, hydrous minerals and organic compounds, the later only present in some carbonaceous groups. Three main chondrite classes are the ordinary, enstatite and the carbonaceous ones (hereafter CCs, see e.g. [36]. The CCs come from outer regions of the disk where they incorporated organics, hydrous phases and ices. Every chondrite group probably represents a quite different formation environment [35, 36]. In fact, the CI1 carbonaceous chondrites have been considered as pure matrix material [13], that have the closest elemental compositional to the Sun [4]. Such chemical similitude comes from the fact that they are aqueously altered and incorporated some volatile elements into their structure.

From cosmochemical grounds, first chondritic planetesimals ended their growth being km-sized undifferentiated bodies that, colliding with each other and over longer timescales, became larger planetary embryos. This was a continuous process marked by energetic collisions that left their chemical fingerprints in the surviving bodies. Finally, tens of millions of years after the formation of CAIs, the terrestrial planets were formed from these building blocks, and inherited their peculiar chemical patterns (see e.g. [15]). From these undifferentiated bodies come the chondrites, authentic cosmic aggregates containing protoplanetary disk components at the particular heliocentric distance and time where they accreted [21]. Chemical differentiation occurred for bodies larger than few hundred kilometres in diameter, but exact figures depending on their exact initial rock:ice ratios (see e.g. [37]).

It is really fascinating that some highly unequilibrated chondrites are extremely pristine rocks exhibiting tiny fractions of stellar grains with isotopic anomalies inherited from the galactic chemical evolution and the stellar gas enrichment in the solar neighbourhood (see

Figure 1: A scheme of the protoplanetary disk with ring structures from which the different chondrite groups were formed (Adapted from [32]).

e.g. [38, 31]). In the outer disk undifferentiated bodies accreted far away from the Sun incorporated organics, ices and probably hydrous mineral phases, and formed C- and water-rich asteroids and comets ([33]). The study of highly unequilibrated chondrites allows us to infer clues on the complex astrophysical environment in which first planetesimals formed. We recently found that CR chondrites can host C-rich clasts with isotopic signatures of unsampled bodies, probably comets [23].

This chapter is focused in describing the evidence of aqueous alteration in Murchison CM2 chondrite, and the astrophysical relevance of studying the mineral components host in its pristine nanostructure. In the next sections we will present evidence supporting that Murchison is exceptionally complex at nanoscale and showing aqueously altered minerals in contact with anhydrous ones. It supports wet accretion in the outer disk region where Murchison parent body formed.

2 Experimental procedure

To study and characterize Murchisons composition at nanoscale and to see how their minerals suffered aqueous alteration, we have used a Transmission Electron Microscope (TEM) and a Scanning electron Microscope (SEM), which allow the study of chondrites minerals at 10-9 metres, letting us to interpret the nature of its components. The SEM that we used was a FEI Quanta 650 FEG working in low vacuum BSED mode at CIN2. The EDS detector used to perform elemental analyses is an Inca 250 SSD XMax20 with Peltier cooling with an active area of 20 mm^2. Some selected areas were explored at different magnification, and SEM elemental mapping together with EDS spectra were obtained. In order to study Murchison mineral structure at nanoscale we selected a chip that was thinned in a ring as usually made for TEM studies using a Fischione 1050 model ion mill at CIC (Granada University). The sample was bombarded with energetic ions or neutral atoms (Ar), removing sample material until the film was sufficiently thin to study by TEM. The result is a thinned ring that is cleaned to remove away the remaining amorphous materials and then analyzed by UHRTEM (ultra-high resolution transmission electron microscopy). The study was performed using a FEI Titan G2 60-300 microscope available at CIC with a high brightness electron gun (X-FEG) operated at 300 kV and equipped with a Cs image corrector (CEOS) and for analytical electron microscopy (AEM) a SUPER-X silicon-drift windowless EDX detector. The AEM spectra were collected in STEM (Scaning Transmission Electron Microscopy) mode using a HAADF (High Angle Annular Dark Field) detector. Digital X-Ray maps were also collected on selected areas of the samples. For quantitative micro-analyses, EDX data were corrected by the thin-film method [8, 17]. The K-factors were determined using mineral standards: Albite (Na, Al), Anorthite (Al, Ca), Anorthoclase (Na, Al), Augite (Mg, Al, Ca & Fe), Biotite (Mg, Al, K, Fe), Scapolite (Na, Al, Ca), Spesartine (Al, Mn), Hemimorphite (Zn), Microcline (Al, K), Muscovite (Al, K), Olivine (Mg, Fe), Rhodonite (Mn, Fe), Titanite (Ca, Ti), and Osumilite (Mg, Al, K, Fe). The resulting KAB factors were: Na 1.18 (0.03), Mg 1.10 (0.03), Al 1.00 (0.02),m Si 1.00, K 1.12 (0.04), Ca 1.03 (0.03), Ti 1.28 (0.04), Mn 1.33 (0.01), Fe 1.37 (0.03), & Zn 1.53 (0.01). Atomic concentration ratios were converted into formulae according to stoichiometry (number of O atoms in theoretical formulae).

3 Results

In this section, SEM-EDX and HR-TEM analyses of two Murchison samples are presented. We wish to understand this meteorite at different scales in order to get clues on the formation of its parent body. For this reason, we have used different techniques, working at different scales. Most CM2 chondrites are breccias, and it has been also proposed that the collapse of matrix pore spaces occurred due to shock propagation associated with impact compaction of the CM parent body [30, 26].

First of all we discuss the evidence for parent body aqueous alteration in a thin section of this meteorite, 30 m in thickness. Aqueous alteration was not complete and pervasive as well exemplifies the rounded chondrule shown in Fig. 2a provides interesting clues. Originally the chondrule contained multiple metal grains that remained intact in the chondrule interior since it cooled down in the protoplanetary disk. Once compacted, the parent body was soaked in water that went through the matrix pores and reached the outer borders of chondrules and inclusions.

Most of the aqueous alteration observed in carbonaceous chondrites seems to be static [6], probably associated with short-time heating events that produced distinctive features like e.g. the famous Murchison aureoles formed around native metal grains by oxidation [11]. Fig. 2 suggests localized metallic corrosion penetrating in the chondrule, and forming secondary minerals precipitated in the silicate structure. We suggested that this could be explained by parent body compaction under impacts [30], but water availability was probably very heterogeneous and depending of its presence in the chondrule mantle o nearby matrix. To better understand the composition of this characteristic chondrule, EDX analyses are shown in figure 3, and reveal what could be a CAI relic in the chondrule interior. Chondrules probably

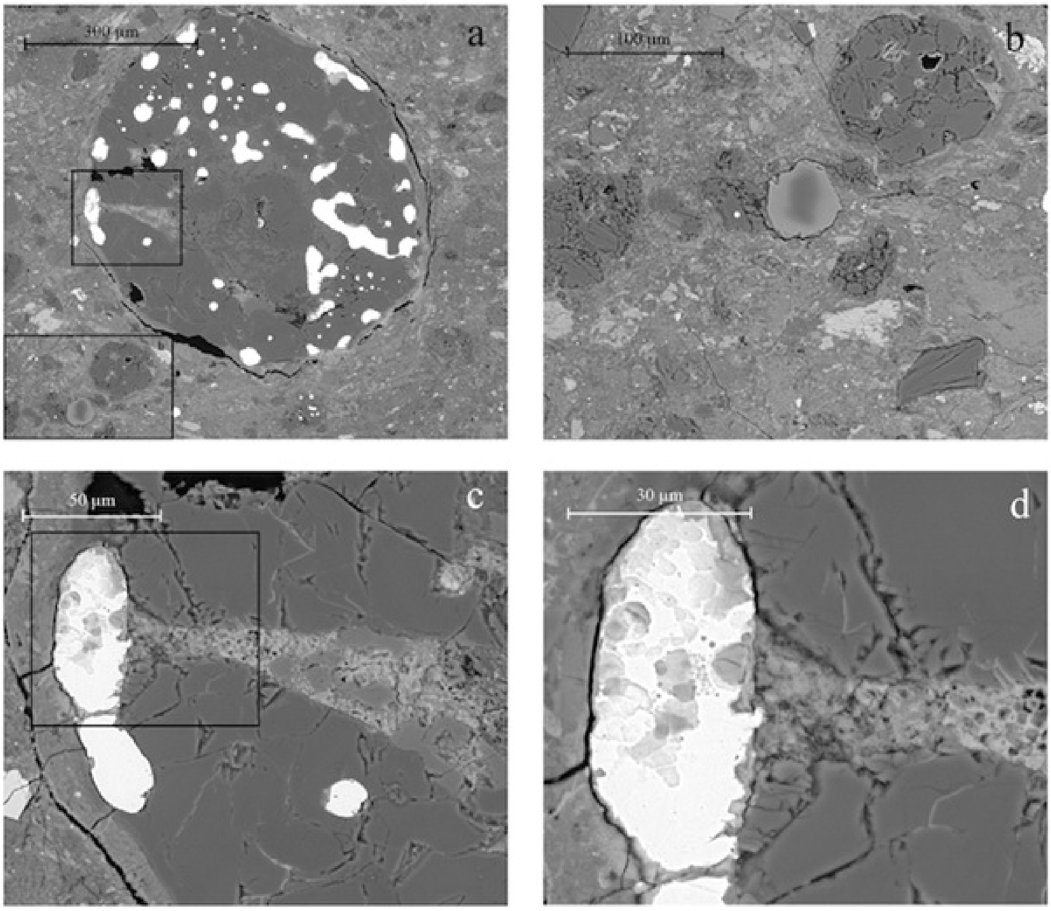

Figure 2: a) BSE image of a Murchisons mafic chondrule in our section, b) and c) show two framed areas of first image. In (b) there is a relict grain marked in a), while in (c) and (d), the metallic grain has been magnified to see how aqueous alteration penetrated inside the chondrule.

were able to absorb metal grains, sulphides and other particles while molten in the disk, before their final cooling, so the chondrule interior reveals a process clearly pre-accretionary. Refractory melt inclusions have been also hypothesized to represent direct condensates from the nebula (see e.g. [25]). The X-ray mapping images indicate the proportion of each element based on the relative brightness. The elements in figure 3 were chosen to show the major chondrule-forming constituents of this chondrule.

So far we have described the localized action of aqueous alteration at microscopic scale, but the appearance of Murchison at nanoscale changes drastically. As it has been mentioned before, it exhibits a heterogeneous matrix composed by highly unequilibrated mineral phases and dominated by phyllosilicates, sulphides, carbonates and other minerals. In order to study the nature of the matrix at nanoscale, we used HRTEM of a chip thinned in a ring as explained before. EDX spectra were obtained to identify the main forming minerals and decipher the way they interact with each other.

Murchison seen at nanoscale shows clear evidence of having a chemically unequilibrated matrix, and it is not so homogeneous as seems under microscopic examination. From the study of different imagery obtained we have selected some examples to illustrate the level of complexity found. Figure 4 shows a 1 μm window of the Murchison matrix where the center includes an elephant-shaped aggregate with the characteristic layering of phyllosilicates oriented perpendicularly to the line of sight. This figure includes small numbered boxes where several EDX spectra were taken. Serpentine in its variety of lizardite is representative of boxes #1 and 4, but in #2 and 3 (forming the elephants trunk) we found a mixture of serpentine with cronstedtite. Other minerals tentatively identified from their EDX spectra are: #5 and #6 pentlandite, #8 carbonate, #11 pyrrhotite, and #12 pyroxene. In general the presence of these minerals exemplifies an extraordinary diversity in CM2 chondrite Murchison. We think this complexity at nanoscale might be indicative of the formation conditions of this meteorite, and the little thermal processing occurred in its parent asteroid. The heterogeneity at nanoscale, and the phyllosilicates found in the matrix indicates that Murchison parent body accreted hydrated minerals from the outer disk. Pre-accretionary aqueous alteration was also invoked by Bischoff et al. (1998), among other authors.

4 Discussion

The astrobiological significance of studying hydrated chondrites is exemplified by the fact that isotopic heritage on the volatile elements (H, C, N and noble gases) in the atmospheres of terrestrial planets has been recently established [1, 22]. Current evidence indicates that the role of comets is probably marginal, while transitional water-rich asteroids could be a dominant source of such volatiles. In that sense, the CI and CM groups of carbonaceous chondrites are among the envisioned products of these transitional bodies that during eons could have efficiently delivered volatiles to Earth.

Murchison is a very relevant meteorite because it fell in Sept. 28th, 1969 and was quickly recovered in NASA clean rooms created to study the lunar samples returned by Apollo missions. Its study demonstrated to contain indigenous organic matter of fascinating

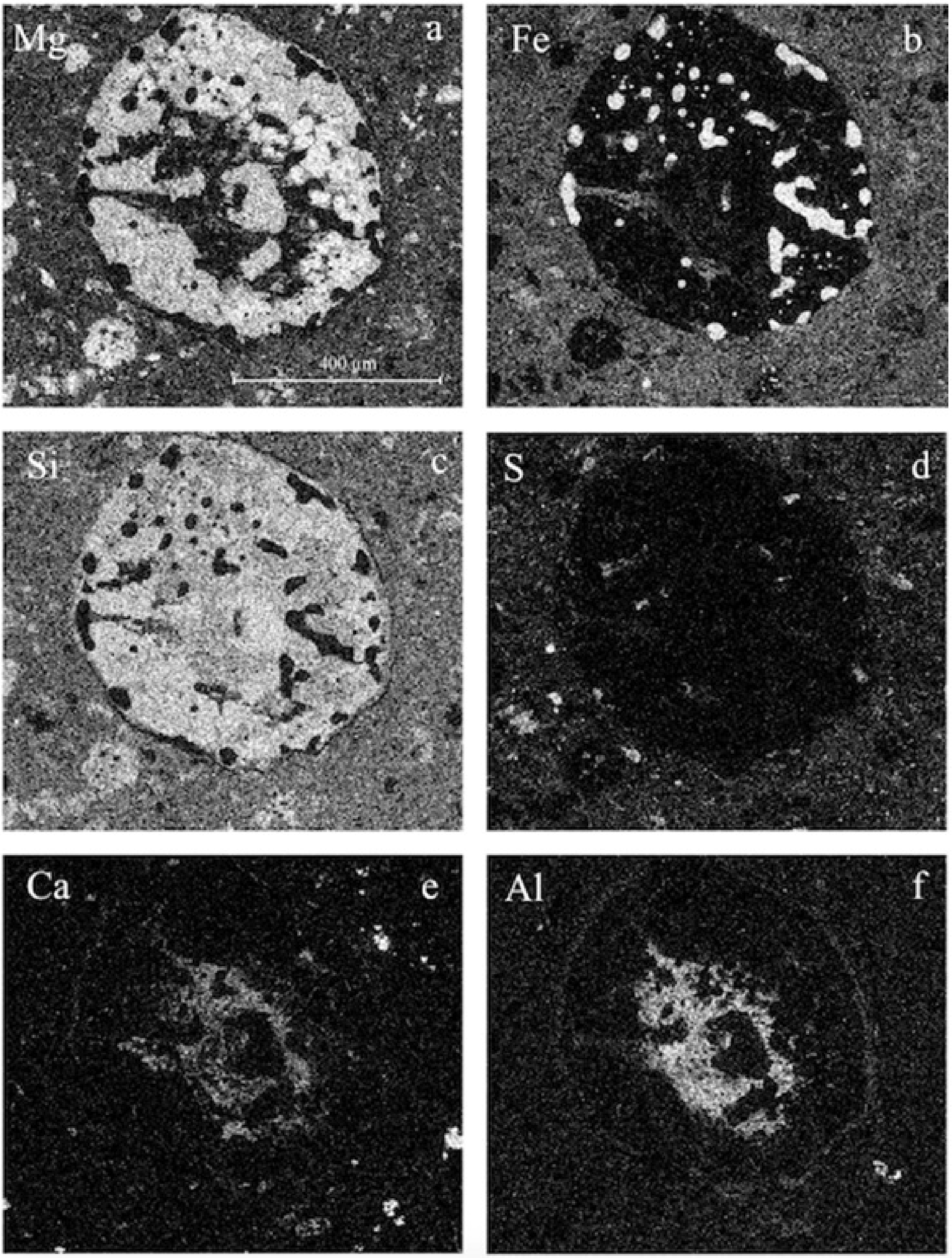

Figure 3: X-Ray elemental mapping of the Murchisons chondrule seen in Fig. 2. It contains an amoeboidal-shaped refractory interior, rich by Ca and Al, that we hypothesize could be interpreted as a relic of a mixing between a CAI and a chondrule.

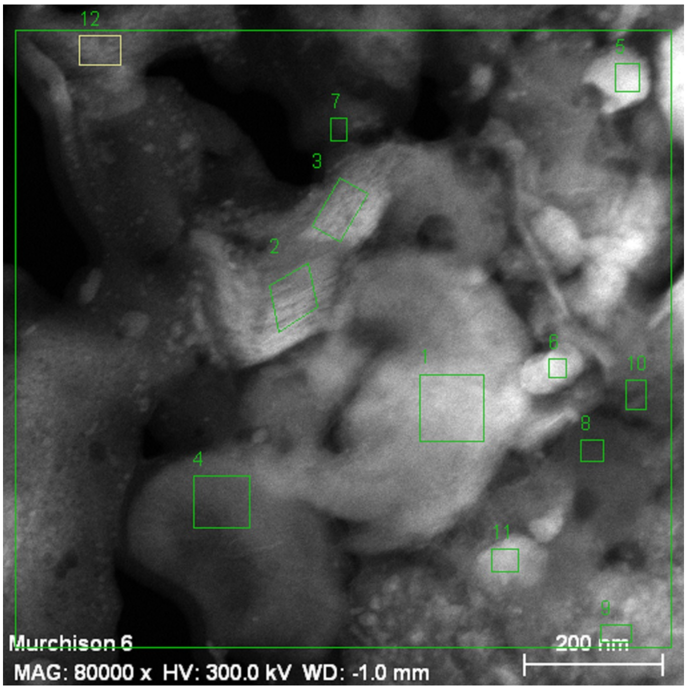

Figure 4: HR-TEM X-Ray mapping of a selected region of Murchison. X-Ray maps for the main rock-forming elements are given in Fig. 5.

complexity [24]. On the other hand, Murchison is so far the most massive CM2 fall with about 100 kg recovered in short time so it does not suffered significant terrestrial alteration. Despite of little terrestrial alteration, this carbonaceous chondrite was proved to be partially altered and its textural, mineralogical, and petrological properties can be related with parent body (not terrestrial) aqueous alteration [7, 12].

The brecciated nature and the distinctive alteration of the specimens coming from the CM chondrite group points towards a plausible disruption of the parent body that produced many fragments. Many CM chondrites are breccias that exhibit different aqueous alteration stages [30, 27]. This is not surprising, as a natural outcome of the collisional processing of chondritic asteroids. Asteroid families are common and formed by separated fragments that exhibit distinguishable spectral properties and evolve separately [34]. The smallest fragments are affected by non-gravitational forces, including the Yarkovsky effect that produce a progressive loss of energy and an inward migration of their orbits. When they cross resonances can be transformed into Earth-crossers, and delivered as meteorites to Earth [9].

Highly hydrated meteorites (e.g. CI and CM chondrites) are associated with a parent body that has experienced significant aqueous processing. These non-differentiated asteroids need to be fragile bodies, experiencing significant microporosity because they are formed by fine-grained minerals embedded in a nanometric matrix preserving chemical clues of the forming environment [33]. The study of the mineral phases of CM chondrites at nanoscale can provide important information about their origins and textural relationship [34]. Besides,

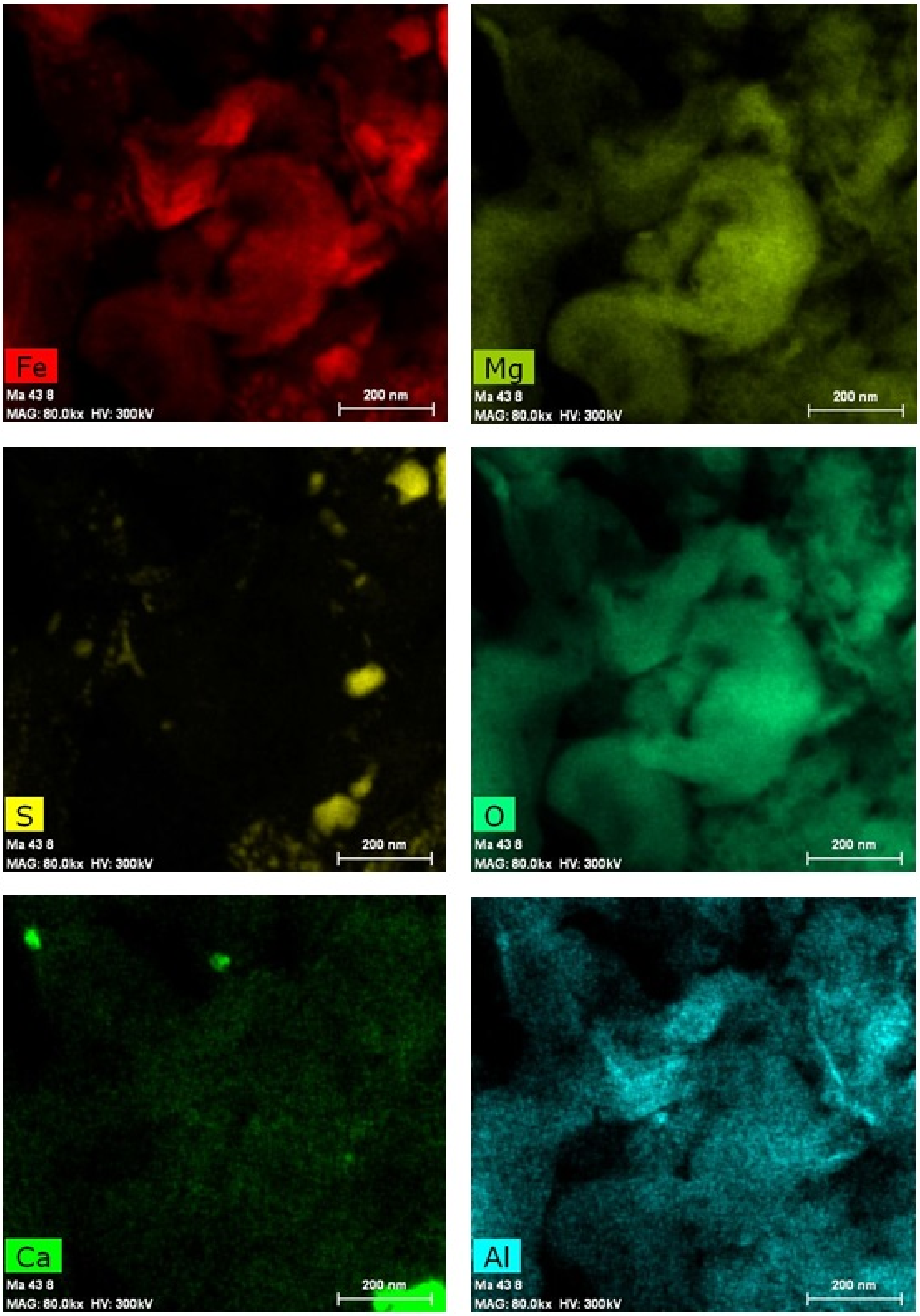

Figure 5: HR-TEM X-Ray elemental maps of Murchison matrix shown in Fig. 5.

their matrices are composed mostly by phyllosilicates and probably formed as a result of aqueous alteration [6, 30]. Phyllosilicates are approximately 10-100 nm in size and most of them are serpentines with diverse morphologies, degrees of crystallinity and compositions. One of the main roles that aqueous alteration has over chondrites is their capability of changing their reflectance properties and spectra depending on the degree of hydration.

A part from hydrous silicates, CM chondrites also contain up to 13 wt.% in water as hydroxyls inside the structure of phyllosilicates [27, 2]. Depending on the degree of aqueous alteration, these phyllosilicates vary in composition, being the Mg-rich phyllosilicates dominant and exhibiting higher hydration. Thus give rise to secondary minerals in its matrix, and make difficult the search for evidence of pre-accretionary hydration at microscopic scale. In any case, it is clear that such alteration was not pervasive and homogeneous. Murchison is not extensively altered like other CM chondrites and contains well-preserved metallic-Fe-Ni-bearing, olivine- and pyroxene-rich chondrules and a comminuted matrix with highly unequilibrated phases (Rubin et al., 2007). The low degree of alteration is shown by the abundance of metal grains and sulfides in a number of regions of the meteorite (Fig. 4). When water alteration started, porous minerals such as olivine and pyroxenes altered to phyllosilicates, but water availability was not extended. In our Murchison sample some amorphous to finely fibrous material (bearing sulfide grains, see the lower-left in our Fig. 4) are found in contact with coarse-fibrous material (without sulfides) as it was previously described in Paris CM chondrite by [14].

There is significant debate about the origin of aqueous alteration, the preferred vision concluded that alteration took place on the CM parent asteroid (e.g., [20, 29, 30]) rather than in the solar nebula (e.g., [10]). Alternatively, K. Metzler and co-workers made the alternative suggestion that alteration occurred in uncompacted precursor planetesimals. In view of the collected evidence we think that in some localized (less altered) regions of Murchison the distribution of hydrous and anhydrous minerals in the matrix could be primordial and predate the post-accretionary aqueous alteration occurred in Murchisons parent body.

5 Conclusions

The study of Murchison meteorite components has changed the view in which we look at primitive asteroids. First its organic content exemplified an amazing complexity, and now the study of its nanostructure reveals clues on the presence of hydrous minerals in the protoplanetary disk. Being a massive meteorite fall of a carbonaceous chondrite occurred at the time that the first clean laboratories were built by NASA to study lunar samples returned by Apollo. Our results indicate that this continues being a fascinating meteorite:

- The rock-forming minerals of Murchison seen at nanoscale are quite heterogeneous, very diverse and chemically unequilibrated. Being this CM2 chondrite a breccia probably exhibits different degrees of heating and aqueous alteration, but the region of the meteorite analyzed by UHRTEM seems to preserve its pristine nature. Murchison components preserve unique clues on the formation conditions in which accretion of undifferentiated bodies in the outer protoplanetary disk took place.

- Evidence of parent body aqueous alteration is remarkable at micro-scale by the localized presence of Murchison aureoles around metal grains, altered chondrule mantles and interiors. In any case, such evidence decreases at nanoscale in which tiny minerals have clearly preserved their primordial nature.
- When looking at nanoscale the fine-grained interstitial materials forming the chondrite matrix, i.e. at much higher magnification than conventional electronic microscopy, we found evidence for high complexity and the presence of amorphous materials. Metal grains, sulfides, and phyllosilicates are often in close contact despite of being reactive.
- Our observations support wet accretion because hydrated minerals incorporated from the protoplanetary disk into the fine-grained interstitial matrix of Murchison CM2 chondrite are not equilibrated with metal, and other reactive minerals. The matrix of this fascinating chondrite consists of highly diverse hydrous and anhydrous minerals, plus organic components that remain highly unequilibrated and essentially unaltered.

Acknowledgments

This work was financially supported by AYA2011-26522 and AYA2015-67175-P grants. Mike Zolensky (NASA) is also acknowledged for kindly providing the studied Murchison materials.

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