Mem. S.A.It. Suppl. Vol. 20, 74

Memorie della
Supplementi

SEM exploration of carbonaceus chondrites

C. Guaita

GAT-Milano Planetarium, Via Mameli 13, I-21049 Tradate (VA), Italy e-mail: c.guaita@libero.it

Abstract. Some Carbonaceus Chondrites (CC) were studied by a last generation SEM microscope (Scanning Electron Microscope), equipped with an EDS probe. Pictures taken by the BSE detector shown a complex internal morphology, in which big gray chondrules, small white spots of metallic oxides and, above all, a number of black inclusions of Carbon material were present. In particular, the aspect of the Carbon inclusions was very suggestive, being sometimes similar to tar drops. This work demonstrates that the SEM, a normal instrument in the study of meteoritic rocks, is strongly useful also in the case of CC, the most interesting of all meteorites, being rich of thousands of the same Carbon molecules from which the Earth life arose.

Key words. Meteorites – Carbonaceous Chondrites – Organic Material – Scanning Electron Microscopy

1. Introduction

A scanning electron microscope (SEM) is an equipment able to take images by scanning a sample with a high-energy electrons beam, in a vacuum chamber. The interaction of the electrons with the atoms of the sample produces signals that contain information about the surface topography (emission of Secondary Electrons, SE) and composition (emission of Backscattered electrons, BSE). Backscattered electrons (BSE) consist of high-energy electrons of the beam, that are reflected or backscattered by the interaction with the atoms of the specimen. Heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), and so appear brighter in BSE image. In other words, the lighter is an element, the darker is the BSE response. A powerful SEM fitting is the EDS (Energy-dispersive X-ray spectroscopy) probe. When the incident beam hits an atom within the sample, a fluorescence-like process produces an emission of X-rays, strictly characteristic of that atom. The EDS probe is able to detects these characteristic X-rays: so it can singles out, in any point of the sample, the presence of any kind of atoms, starting from Carbon. The final result is an X-rays spectrum of all elements that are present in a specific point of the specimen. But the EDS probe can also be tuned in the X-rays emitted by a specific atom: the result is a 'map' of the distribution of that atom all over the sample. In general, EDS-maps are a further great analytical instrument of the SEM microscopy. Today SEM microscopy is applied in a number of scientific fields, such as Biology, Paleontology, Mineralogy, Metallography, Polymer Science. But SEM microscopy is a fundamental tool also for the study of all kind of meteoric rocks

Send offprint requests to: C. Guaita

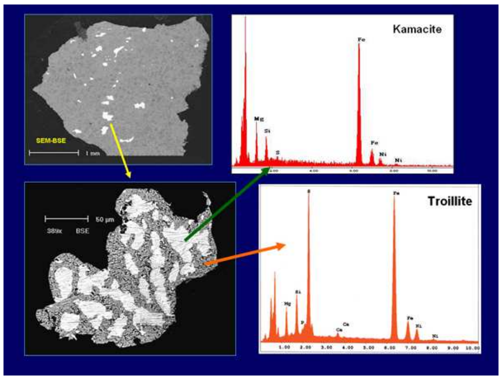

Fig. 1. This SEM-BSE pictures of a polished section of an ordinary chondrite shows a number of metallic inclusions of Fe-Ni and FeS, sometimes (as in this case) linked together.

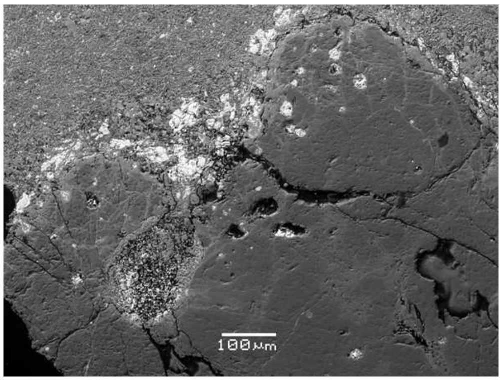

Fig. 3. SEM-BSE picture of a polished section of the Vigarano CC, in which black Carbon material is visible inside a fracture that crosses a big chondrule.

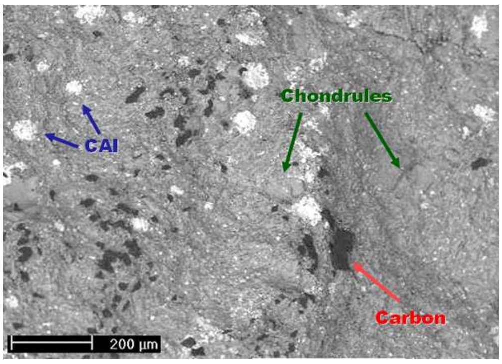

Fig. 2. This SEM-BSE picture of a polished section of a carbonaceous chondrite (CC) shows three main features: grey chondrules, white inclusion of metallic oxides and black deposits of Carbon material.

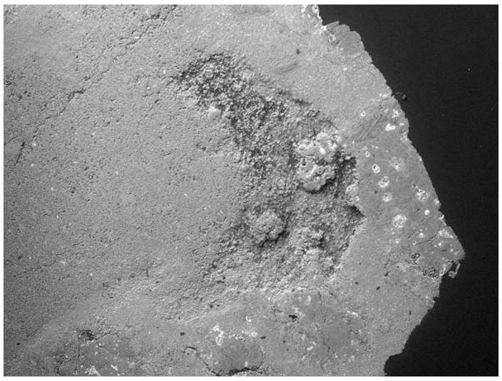

Fig. 4. SEM-BSE picture of a polished section of Allende CC, in which black Carbon material is present inside a porous part of the matrix.

(Klaus & Fredriksson 1964). The purpose of his work is to demonstrate the utility of the SEM in the case of rare and precious meteorites such as the Carbonaceous Chondrites (CC).

There are three main classes of meteorites (Graham et al. 1985): stony meteorites or aerolites (more than 90 % of fallen meteorites), iron meteorites or siderites (7 % of fallen meteorites), stony-iron meteorites or siderolites (about 1 % of the total), composed of similar amount of metal and stone. Stony meteorites are traditionally divided into two categories: chondrites (85 % of the fallen meteorites) and achondrites (about 8 % of the fallen meteorites). Chondrites are groups of meteorites that have undergone little change since their parent bodies originally formed and are characterized by the presence of chondrules, some kind of millimetric or submillimetric sferules (composed of Fe and Mg silicates), that were produced by a sudden (even if not well understood) melting of protoplanetary material. Achondrites are groups of meteorites of quite homogeneous basaltic composition that have a complex origin involving asteroidal or planetary differentiation (SNC martian meteorites are part of them).

Sometimes even more primordial inclusions, named CAI (Calcium, Alluminium Inclusions) are present. Composed mainly of metal oxides, CAI formed almost a couple of million years before chondrules (Bizzarro et al. 2004). Ordinary chondrites are caracterized by the presence of a number of light micrometric islands, composed of Fe-Ni (Kamacite) and FeS (troillite). Sometimes inclusion of Kamacite are enclosed in a Troillite matrix (Fig. 1), a material well known inside the proto-planetary discs (Guaita 2006). Optical or electronic microscopy can easily single out them.

There is a small amount of chondrites (3−5 % of the total) characterized by unusual properties: they are very dark (and sometimes brittle) and contain up to 5 % of organic matter (that's Carbon linked to H, O, N, S, P). That's why they are named Carbonaceus Chondrites (CC). Being composed of Carbon, the CC organic material shows a dark color to SEM-BSE detector and a plastic/shapeless look: in the best BSE images the CC Carbon material could simulate 'tar' drops located between all other morphological structures (metallic islands, CAI, chondrules) (Fig. 2). In general, the organic material is embedded in fractures (Fig. 3) or porous parts (Fig. 4) of the matrix. At the moment, about 50 different CC are known, often broken in a number of fragments, because of the intrinsic brittleness of the matrix.

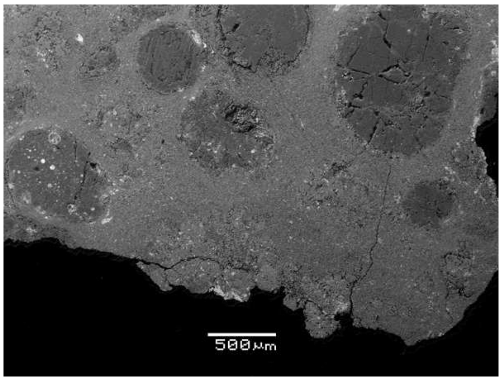

Fig. 5. SEM-BSE picture of big chondrules inside a polished section of the Vigarano CC.

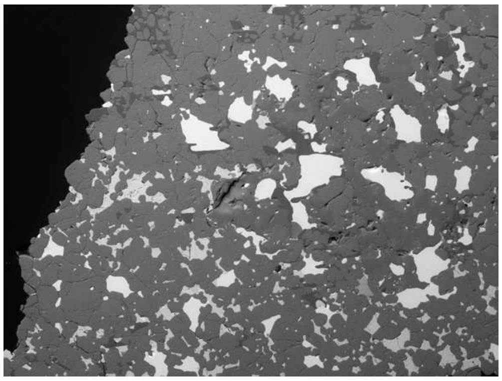

Fig. 6. SEM-BSE picture of abundant inclusions of Ni-Fe (white) and FeS (dark grey) inside a polished section of Tafassasset CC.

2. Carbonaceous Chondrites

The CC classification is very complex and depends on the % of Fe-Ni content (1-50 %), on the dimensions and number of chondrules (sometimes so small than are not visible), on the amount of water present (up to 20%) and, obviously, on the amount of Carbon (up to 5%) and on the ratio between low molecular weight and polymeric Carbon. Because of the great variability between the different CC, subclasses are very numerous and, generally, the names came from the first characteristic specimen. Here a summary of the main sub-classes.

<u>CI chondrites</u>, only a handful of which are known, are named for the Ivuna meteorite, fallen in Tanzania in 1938. They have very few chondrules and Fe-Ni inclusions and are composed mostly of crumbly, fine-grained material that has been changed a lot by exposure to water on the parent asteroid. As a result of this aqueous alteration, CI chondrites contain up to 20% water in addition to various minerals altered in the presence of water, such as clay-like hydrous phyllosilicates and iron oxide in the form of magnetite. They also harbour organic matter, including polycyclic aromatic hydrocarbons (PAHs) and racemic amino acids. This group encloses the famous Orguel meteorite, that fell in France on May 14, 1864. It contains 3% of C and 20% of water. In 2001 D.P. Glavin (Ames Research Center) discovered, inside the organic part, traces of glycine and β-alanine

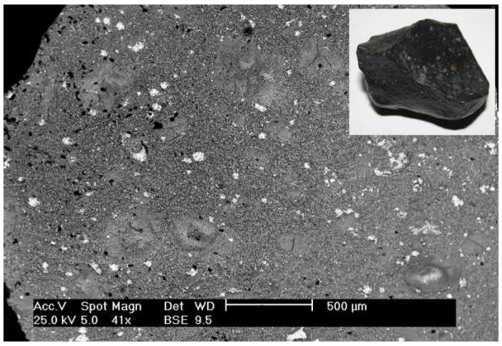

Fig. 7. This SEM-BSE picture demonstrates that this rock is a CC Chondrite, because of the presence of a number of black islands (Carbon material), many irregular white islands (Metallic oxides) and some big grey inclusions (chondrules).

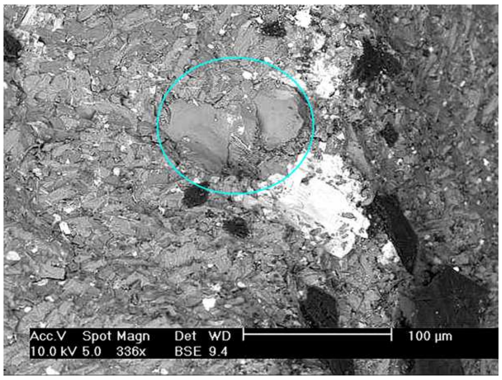

Fig. 8. This SEM-BSE picture of a polished section of a CC chondrite shows a big chondrule (grey color), near some inclusions of white metallic oxides and black Carbon material.

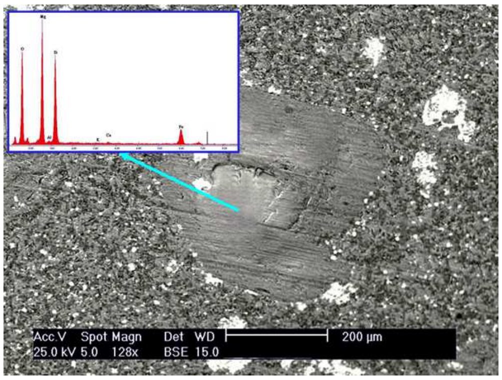

Fig. 9. The SEM-EDS spectrum proves that this big chondrule in made of quite pure olivine.

clearly of cosmic origin, being their Carbon unbalanced in C13 (Glavin, 2001).

CM chondrites are named for the Mighei meteorite that fell in Mykolaiv province, Ukraine, in 1889. They contain small chondrules (typically 0.1 to 0.3 mm in diameter) and similar-sized refractory inclusions. They also show less aqueous alteration than CI chondrites, and about half the water content. Comparisons of reflectance spectra point to the asteroid 19 Fortuna or, possibly, the largest asteroid, 1 Ceres, as candidate parent bodies. This group encloses two famous meteorites. The first one is the Murray meteorite, a rock of 3.5 kg fallen in Kentucky (USA) on September 20, 1950: inside 17 NON terrestrial amino-acids (6 racemic and 11 unknown in proteins) were singled out (Lawless, 1971). The second one is the Murchison meteorite, fallen 200 km from Melbourne (Australia) on September 28, 1968. Thanks to a recovery of an amount of 82 kg, the Murchison organic material is the best studied to date (hundreds of different amino acids were found inside).

CV chondites are named for the Vigarano meteorite that fell in Italy in 1910. They resemble ordinary chondrites and have large, well-defined millimetric chondrules (Fig. 5) of magnesium-rich olivine (Fosterite), in a dark-gray matrix of mainly iron-rich olivine (Fayalite). They also contain FeS and up to 5% of calcium-aluminium inclusions (CAIs), the most ancient minerals known in the solar system. This group encloses the famous Allende meteorite, that fell in Mexico on February 8, 1969. It is the most heavy cosmic rock ever fallen (more than 2000 kg), even if the Carbon content doesn't exceed 0.4%. In the soluble part of this organic material many amino-acids were found; the insoluble part released, after pyrolysis, many kinds of PAH (Zenobi 1989).

CO chondrites are named for the Ornans meteorite that fell in France in 1868. They show some similarities in composition and chemistry to the CV chondrites and may have formed with them in the same region of the early solar system. As in the CV group, CAIs are present but are commonly much smaller

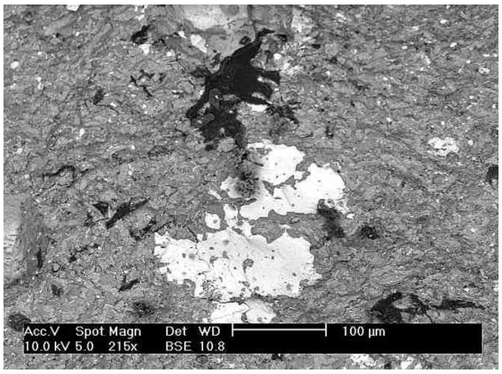

Fig. 10. This SEM-BSE picture of a polished section of a CC chondrite shows a white inclusion of metallic oxides, near a black deposit of Carbon material.

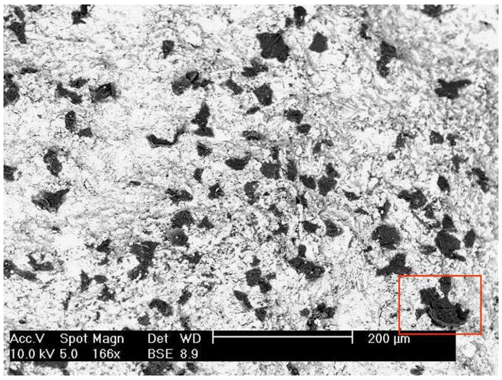

Fig. 12. This SEM-BSE picture of a polished section of a CC chondrite shows a large number of black deposits of Carbon material.

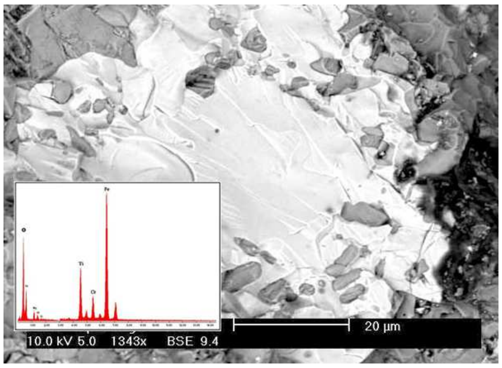

Fig. 11. This SEM-EDS spectrum proves that this white inclusion is a mixture of Fe, Ti and Cr oxides.

and spread more sparsely in the matrix. Also typical of COs are small inclusions of free metal, mostly Nichel-Iron, that appear as tiny flakes on the polished surfaces.

CK chondrites are named for the Karoonda meteorite that fell in Australia in 1930. Their dark gray or black coloration is due to a high percentage of magnetite dispersed in a matrix of dark silicates consisting of iron-rich olivine and pyroxene. Most CK chondrites contain large CAIs and some show shock veins that point to a violent impact history.

CR chondrites are named for the Renazzo meteorite that fell in Italy in 1824. They are similar to CMs in that they contain hydrosilicates, traces of water, and magnetite. Up to 50% of the black matrix is composed of large chondrules; abundant inclusions of Nichel-Iron and iron sulfide are also present (Fig. 6). A possible parent body is Pallas, the second largest asteroid. The CH and CB chondrites are so closely related to the CRs that all three groups may have come from the same parent or at least from the same region of the solar nebula.

CH chondrites are named for their High metal content in the form of nickel-iron that can reach up to 15% by weight. They also show many fragmented chondrules, most of which, along with the less abundant CAIs, are very small. As with the CRs, the CHs contain some phyllosilicates and other traces of alteration by water. Their high metal content has suggested, as a possible source, Mercury, the planet with the larger metal core in the Solar System.

CB chondrites, are named for the prototype found near Bencubbin, Australia, in 1930. Only a handful of these unusual meteorites are known. All are composed of more than 50% nickel-iron, together with highly reduced silicates and chondrules similar to those found in members of the CR group. Chondrites CH, CR and CB could have a common origin.

C-U chondrites (Ungrouped) are so named because fall outside all other groups. This group encloses the famous Tagish meteorite, that fell into the Canadian Tagish Lake on January 18, 2000 (Pizzarello et al. 2001).

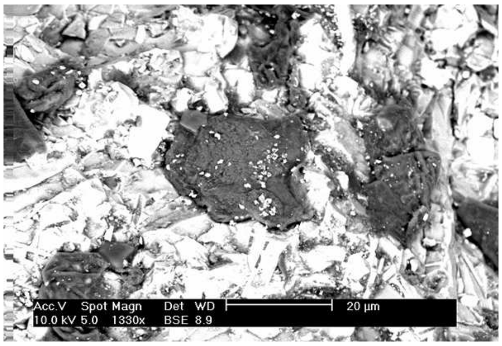

Fig. 13. In this SEM-BSE picture of a polished section of the same CC chondrite of Fig. 12, the internal morphology of some Carbon deposits is clearly visible.

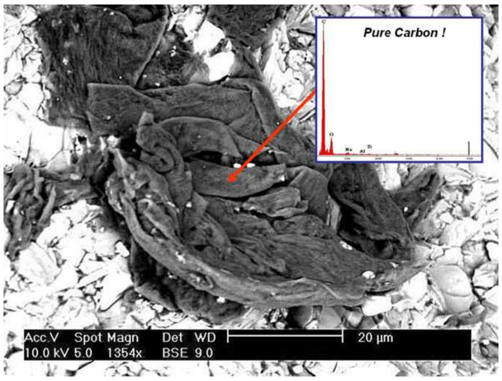

Fig. 14. The SEM-EDS spectrum proves that this black deposit is made of quite pure Carbon material.

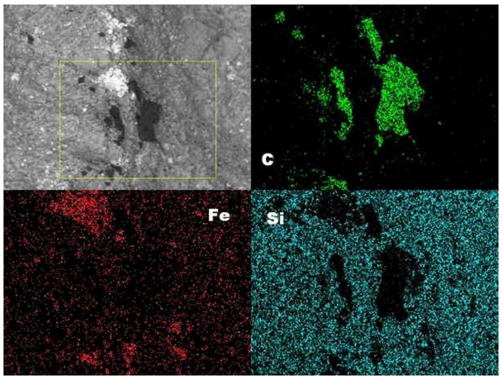

Fig. 15. These EDS maps give a further demonstration that the white inclusion of this CC chondrite is made of metallic oxides (Fe rich, red color) and that the black deposit is made of Carbon material (green color), inside a silicate matrix.

The composition of the organic material of CC is very complexe. Normaly, it consists of a low molecular weight part (20-30%), easily extractable with non polar solvents and a polymeric part of very low solubility. All CC groups show qualitative and quantitative differences in the kind of organic molecules. In general, CC are richer in compounds with some prebiological purport than the material arising from classical Miller experiments (that's obtained in totally reducing condition). A short summary is useful, taking in account the Murchison meteorite, undoubtedly the most studied CC. On February 2010 P. Schmitt-Kopplin (Helmholtz Research Center of Munich) published an impressive research that increased of a couple of order the number of the before known organic molecules (from about 500 to more than 50.000!). This result was obtained applying a new kind of high resolution Mass spectrometry (FTICR/MS) to the extractable organic part (Schmitt-Kopplin et al. 2010).

The new molecules enclose amino-acid, sugars (or their precursor) and, even, purinic and pyrimidinic bases. More that 70 amino-acids were discovered: the largest part (90%) is quite unknown inside the terrestrial proteins, the remaining 10%, even if well known inside the terrestrial material, is present as racemic mixture, so it is not biological. A further confirmation of their non biological origin is demonstrated by a clear excess of C13 compared to C12 (δ^{13}C $\sim$ +30‰ against a terrestrial value between −5 and −30‰) and by a similar excess of N14 compared to N15 (δ^{15}N $\sim$ +60‰ against a terrestrial value between −5 and +20‰). At the end of 2001, G. Cooper (Ames Research Center) singled out, inside the water extract of two CC (Murchison and Murray) a score of poly-alcohols (carbon compounds with more that a single OH group), containing up to 6 Carbon atoms: between them sugars, sugar alcohols, sugar acids (Cooper et al. 2011). The prevailing opinion is that the starting compounds could be formaldehyde (HCHO) and glicol-aldeyde (OHCH2-CHO), two molecules well known in the interstellar space (Hollis et al. 2004). Possibly, the compounds found by Cooper could be degradation products from real sugars of biological significance (glucose, ribose). Lastly, in 2008, Zita Martins (Leiden University) made the most surprising discovery: the presence of Uracile (a purinic base) and xanthine, adenine, guanine (pyrimidinic bases) in the formic acid extract of the organic portion of Murchison, Murray and Orgueil meteorites. A sharp excess of C13 ($\delta^{13}C \sim +40‰$) was a clear demonstration of extraterrestrial origin (Martin et al. 2008).

The deepest studies about the poor extractable (being polymeric) carbonaceous part of CC were performed by M. Sephton (Open University) at the end of 90's years (Sephton 2002). He used a pyrolytic thermal decomposition followed by a mass spectrometry. The result was very clear: a polymer of aromatic nature was found, the main monomers of which (released by pyrolysis) are single aromatic rings (main) or more or less substituted double rings (toluene, xilene, fenols, naftalenes). The differences in composition (between different CC) are small: this could be an indication of a common origin, possibly linked to the catalytic action (on the starting aromatic monomers) of the strong UV radiation that permeated the primordial solar nebula.

But the CC polymeric material could be present also in poly-peptidic form (amino-acids linked together in something similar to protein chains). The demonstration could be found in a work of E. Bandusky (Arizona University), who pyrolyzed up to 600°C the insoluble organic material of Orguel meteorite. Between the decomposition products, the same kind of ciano-compounds normally released during the pyrolysis of proteins (aceto-CN, acrilo-CN, benzo-CN) were found (Bandursky et al. 1976). Also in this case, the catalytic action of UV radiation could be very important, above all where the temperature of the primordial nebula was higher.

After all, the great scientific interest about the CC organic material is linked to the presence of all the Carbon molecules typical of the life. Isotopic ratio of C and N demonstrates that the synthesis of CC organic molecules, far from being of biological origin, is linked to natural processes inside the interstellar space, with a quantitative and qualitative yield (thanks to the long time available) even better than the classical Miller reactions (that failed to account for the aromatic polymeric material and for purinic and pyrimidinic bases). The understanding of these interstellar processes is very important. Indeed, if they should be quite simple as it seems, the interstellar space could be the primary source of the basic molecules of life. This kind of study was yet performed in the 70's years by the E. Anders group (Chicago University), who tried to simulate the behaviour of H2 and CO (the two most abundant interstellar molecules) at the estimated temperature (100-250°C) and the low pressure of the primordial solar nebula (Anders et al. 1973). E. Anders, as a chemist, took in account the well known industrial reaction of Fisher-Tropsch, by which light hydrocarbons are produced, starting from H2 and CO in presence of suitable catalyzing agents (such as magnetite, a ferric oxide often present inside CC). The result of these so called FIT (Fisher-Tropsch-Type) experiments was surprising: all aromatic and aliphatic hydrocarbons normally found in the extractable fraction of Murchison CC, were produced!

And, what's more, when NH3 was added to CO and H2, FIT experiments gave rise to the main amino-acids discovered in the extractable fraction of the Murchison CC and to a number of purinic and pyramidinic bases.

Taking in account all this, the research of 'drops' of organic material inside a CC meteorite appears as a very fascinating work. The SEM microscope (Scanning Electron Microscope) is the ideal instrument for this kind of study, creating 'extraterrestrial' landscapes of incredible suggestion. This work refers for the study of a set of 'black' rocks from China of anonymous origin: under the SEM scrutiny, these 'chinise' rocks exhibited some extraordinary features typical of a CC meteorite, very rich in Carbon content.

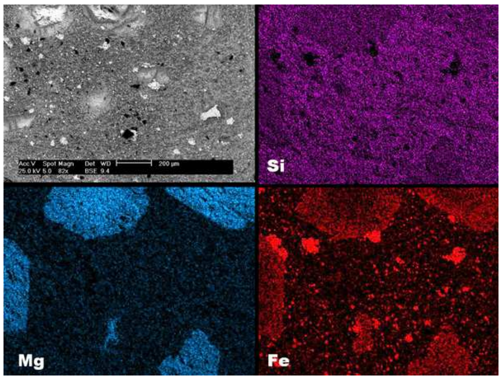

Fig. 16. These EDS maps of a polished section of a CC chondrite exhibit very well big chondrules (Mg rich, blue color) and metallic inclusions (Fe rich, red color), inside a Silicate matrix (Cyan color).

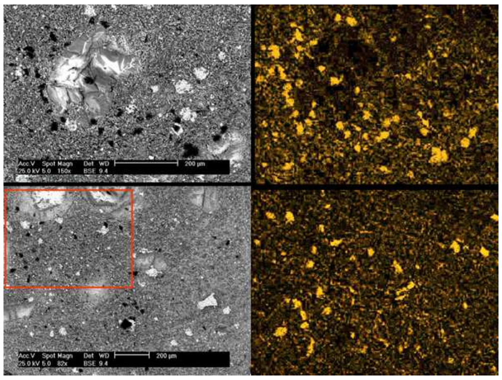

Fig. 18. These EDS Carbon maps (right, yellow color)) exhibit very well the Carbon inclusions present in the same CC polished sections of Fig. 16 and Fig. 17.

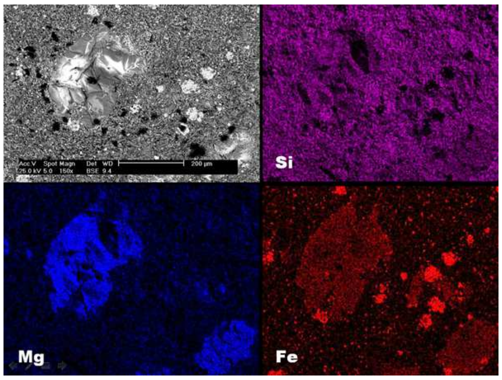

Fig. 17. EDS maps of an other polished section of the same CC chondrite of Fig. 16.

3. Results and discussion

Normally, the Carbon enclosed in CC meteorites produces a typical back colouring. So, the external colouring is yet a preliminary indication for a precious CC meteorite. For SEM scrutinizing, a small amount of sample (2-4 mm^2 well polished is enough) is needed. To avoid external pollutions, the drawing has to be done well inside the matrix (remember that each spurious carbonaceous trace will be strongly exhibited in the very small SEM field). Furthermore, the polishing of the surface should be done in absence of every laboratory Carbon sources, such as the support of a polymeric resin (araldite) and the help of a lubricating agent (paraffinic oil): this to be sure that the Carbon eventually found in the meteoritic matrix is surely of cosmic origin. For the SEM imaging, BSE detector has to be use: BSE electrons (that's back-scattered electrons), being very penetrative, give useful and quick (even if coarse!) information about the composition (because of the low atomic weight of Carbon, organic material looks black; on the contrary, metallic material looks white because its high atomic weight confers good scattering properties). For more precise inquiry about composition (global or local), EDS probe (Energy Dispersion X-Rays Spectrometry) is indispensable.

The nature and the source of the samples here tested were doubtful (they were part of a large number of pieces coming from China...): they showed very sharp edges (possibly an indication of an intrinsic brittleness) and a dark grey colouring inside and outside (possibly an indication of the presence of Carbon compounds). Results of the SEM investigation were similar for all samples: a demonstration of a common origin from a larger object (probably a CK carbonaceous meteorite).

Wide field BSE images of the supposed CC chondrites coming from China have shown a morphology totally different compared to a normal chondrite (Fig. 7). A grey and brittle matrix was rich of a number of irregular black islands (material of a low atomic number), variable in form and geometry (dimension of 10-30 micron). Many irregular white islands (20-50 micron) were also present (material of high metal content). Some big grey inclusions (200-500 micron) were also easily visible as compact material inside the brittle matrix (possibly a basaltic material, derived from some primordial process of fusion and solidification). By the use of the EDS probe (spots and maps), the precise nature of these tree components was understood, so demonstrating the cosmic origin of these 'Chinise' rocks: they were precious CC chondrites, probably of CK class.

The grey compact inclusions (rare but so big to take up almost half of the volume) (Fig. 8) were chondrules of quite pure Olivine (Magnesium silicate+ trace of Iron silicate) (Fig. 9).

The smooth, irregular white islands were a mixture of metal oxides (Fig. 10). This was demonstrated by the EDS probe that detected the prevailing presence of Fe + minor amount of Ti, Mg, Al, the absence of Si and a strong peak of Oxigen (Fig. 11). The presence of metal oxides could be explained by a prolonged contact (at high temperature) with liquid water. Water that it is often present in quantity up to 20% inside the CC chondrites.

The black islands were surely the most interesting structure (Fig. 12). The BSE images at high magnification (Fig. 13) were astonishing: their amorphous and plastic aspect was similar to deposits of tar! An interpretation confirmed by the EDS probe, that detected the presence of only pure Carbon inside all the black islands examined (Fig. 14).

In some regions the EDS probe performed global 'maps' of all possible elements (Si, Mg, Ca, Al, Fe, Ti, C), so obtaining a further and clearer confirmation of all main morphological structures. (Figs. 15, 16, 17, 18).

EDS detected also the composition of the brittle CC matrix: it was a mixture of olivines and pyroxenes (Mg, Ca, Al, Fe silicates), quite typical of meteoric rocks, even if less compact and so more difficult to be polished.

4. Conclusions

SEM is a powerful tool for the investigation of the internal morphology of cosmic rocks in general, and of CC chondrites in particular. The BSE detector can locate very easily some of the typical CC feature such as small/big chondrules (gray color), CAI (white color) and, above all, Carbon inclusion (black color). This helps a lot in the classification of the sample. Sometimes the Carbon inclusions are similar to black islands of irregular shape, sometimes Carbon material is dispersed inside fractures or porous parts of the matrix, sometime it is so scattered that only an EDS Carbon map is able to give a correct global location. In any case a precise rule doesn't exist: every CC shows a peculiar morphology and this is one of the reasons of the great appeal of the SEM exploration. The Carbon maps are very useful also because (almost in theory) they can give some notion about the real amount of carbon material inside the matrix (up to 5%). On the contrary, the chemical composition of CC Carbon material is totally outside the SEM possibility. As described before, this fundamental problem needs micro-analytical techniques of new generation, well different from the SEM screening.

A systematic SEM study of the internal morphology of many different CC chondrites belonging to the historical collection of Milan's Museum of Natural History (Folco et al. 2002) is on going. One of the purpose of this screening is a search for a possible link between the Carbon material and some particular feature inside the meteoritic matrix.

References

Anders, E., et al. 1973, Science, 182, 781
Bandursky, E., et al. 1976, Geochimica and Cosmochimica Acta, 40, 1397
Bizzarro, M., et al. 2004, Nature, 431, 275
Cooper, G., et al. 2011, Nature, 414, 879
Folco, L., et al. 2002, MAPS, 37, B95
Glavin, D., et al. 2001, PNAS, 98, 2138
Guaita, C. 2006, UAI Astronomia, 3, 48
Graham, A., et al. 1985, Catalogue of Meteorites, Arizona University Press, Tucson
Hollis, J.M., et al. 2004, ApJ, 613, L45

Klaus, K., & Fredriksson, K. 1964, JGR, 69, 3487
Lawless, J., et al. 1971, Science, 173, 626
Martin, Z., et al. 2008, Earth and Planetary Science Letters, 270, 130
Pizzarello, S., et al. 2001, Science, 293, 2236
Sephton, M. 2002, NPR, 19, 292
Schmitt-Kopplin, P., et al. 2010, PNAS, 107, 2763
Zenobi, R. 1989, Science, 246, 1026