EARLY HISTORY OF ACAPULCO AND LODRAN CONSTRAINED BY THE NANOSTRUCTURE AND C, N ISOTOPIC COMPOSITION OF THEIR CARBONS.

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Introduction: Primitive achondrites such as acapulcoites and lodranites (A-L) come from partially differentiated parent-bodies. Petrographic and chemical similarities with both chondrites and achondrites indicate that they form from chondrites, which underwent high grade metamorphism, partial melting (metal only or silicates and metal) and possibly shocks followed by post-shock annealing [1-2-3 e.g.]. In order to better understand the history of these meteorites and to unravel the first stages of planetary differentiation, we initiated a multiscale study of carbons in several acapulcoites and lodranites. The chemical and structural characteristics of carbons are indeed fingerprints of their conditions of formation and thermal history, while their isotopic composition can be used to trace their source materials. To reach this goal, we coupled Raman microspectrometry to quantify their degree of graphitization at the μm scale, in-situ C and N isotopic analysis by secondary ion mass spectrometry (SIMS) and high resolution transmission electron microscopy (HR-TEM) to visualize their organization at the nanometer scale (nanostructure) [4-5]. Our first results have shown that carbons of A-L are usually more graphitized than those of chondrites with petrologic type lower than at least 3.6. They can be highly graphitized in Acapulco, in agreement with previous studies [6-7]. They are systematically associated with metal grains, suggesting possible carbon-metal interactions and catalytic graphitization in a good agreement with the temperature expected in the A-L parent-body. No correlation has been found between C and N isotopes, nor with the degree of graphitization within a single meteorite, but both C and N isotopes are suggestive of a precursor similar to the acid-insoluble organic matter (IOM) of chondrites [5]. In order to show the possible catalytic role of iron on the graphitization, experimental analogs have been produced using blends of 10% saccharose-based chars analogous to chondritic IOMs and 90% iron powder heated between 650 and 1600°C and compared to natural carbons in Acapulco and Lodran [8]. Here, we report additional analyses of C and N isotopes in carbon veins from Acapulco, in experimental products from catalytic and non-catalytic graphitization experiments by SIMS, NanoSIMS and conventional gas-source mass spectrometry, as well as detailed HR-TEM examination of 10 thin sections prepared by Focused Ion Beam (FIB) sectioning of carbons from Acapulco and Lodran allowing us to propose a new model of carbon formation and thermal history in the A-L parent-body.

Results: *Structural studies*: Carbons present as grains (including "Rosettes") in Acapulco are very graphitized (Fig. 1a) and have a fabric similar to the "grey cast iron" from blast furnace [9], but "filamentous"-shaped carbons filling veins are more disordered (Fig 1b). HR-TEM images are well correlated with Raman analyses, as expected. Furthermore, they show that the graphitic layers in the highly graphitized carbons from Acapulco often form a shell around metal particles or spring out from metal particles, in favor of a catalytic effect of iron during graphitization as demonstrated in our experiments, which reproduce these nanostructures. By contrast carbons in Lodran occur systematically as veins within metal grains or at grain boundaries and have a systematically more disordered turbostratic structure and a mesoporous nanostructure (Fig 1b), despite numerous indicators including the nanoscale morphology of metal grains indicate that Lodran underwent a higher peak temperature than Acapulco (1200°C vs 1000°C, [10-11]). *Sensu stricto* graphite was never observed and thus the absence of clear catalysis by iron in this sample, which indicates that carbon was absent from Lodran during its thermal peak and has been emplaced later after a significant cooling. In this context, their occurrence as veins only is suggestive of carbon migration.

Isotopes : The C isotopic composition of the run products of catalytic graphitization experiments as well as that of chars from both graphitizable (anthracene based coke) and non-graphitizable (saccharose-based coke) precursor heated up to 2900°C do not show any evidence for fractionation during graphitization, suggesting that the large C isotopic variations in A-L carbons "predate" their graphitization s.s.

N isotopes show (Fig. 2) that the only carbonized turbostratic carbons in Lodran contain an mixture of a heavy N akin to that in chondritic IOM and a light N component. Whereas graphitized carbons in Acapulco contain only the light component, disordered carbon veins also point toward the heavy chondritic N component.

Discussion: The apparent paradox between the higher peak temperature in Lodran and the lack of graphitized carbon associated with metal suggests that carbon was absent from the A-L parent-body and was added in a later event. We propose that carbon could have been

introduced in the parent-body by a late impact with a chondritic body. At this time, Acapulco was closer to the surface and to the impact location and was submitted to a heat wave raising temperature around 1000°C enough to carbonize and catalytically graphitize IOM whereas Lodran deeper in the parent-body underwent a lower temperature increase due to impact heating. Chondritic IOM could have been introduced in the A-L by the impact. Its carbonization in the Acapulco region would have produced both char residues and effluents. In this region, chars would have resulted in highly graphitic carbons, whereas carbon-rich effluents could have migrated along veins and fractures deeper in the parent-body to reach the Lodran region and to produce mesoporous turbostratic "pyrobitumens" by carbonization. Based on our experiments, the evaluated carbonization temperature (about 650°C) is too low to allow graphitization, even in presence of catalytic iron.

As recently showed, two main nitrogen speciations are present in chondritic IOM : nitrile and heterocyclic N (pyrrole) [12]. Pyrroles are thermally much more stable and stay in chars and to a lesser extent in graphite, whereas nitriles are more fragile and can be easily released with the effluents. Consequently, the negative $\delta^{15}N$ could be related to the persistence of pyrrole in the graphitized chars. Graphitization of pyrrole enriched chars would subsequently explain the lack of $\delta^{15}N$ variations as N content continue to decrease in Acapulco during the catalytic graphitization. By contrast, carbonization without catalytic graphitization of nitrile enriched effluents and mixture with secondary chars derived from effluents would explain the N isotopic systematics in Lodran.

Such a scenario potentially also explains the observed C isotopic variations, as large isotopic fractionations could have been produced during the release of effluents. Subsequent carbonization of the effluents and mixing with char residues would then results in a large range of $\delta^{13}C$ still centered around chondritic values.

Conclusion: The original scenario proposed here reconcile all structural and isotopic observations of carbons in Acapulco and Lodran with the expected thermal history of these meteorites, and provide new insights on their potential shock history and the proposed exogenous origin of their carbons [1-6-7].

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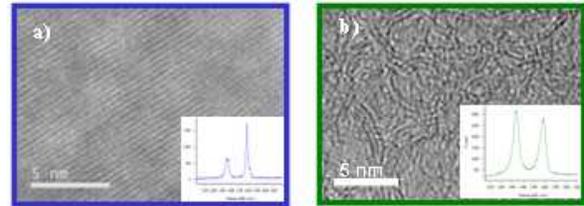

Fig. 1 : HRTEM images of Acapulco (in blue) and Lodran (in green) carbons with their Raman spectra (insets). In Acapulco, highly graphitized carbons are imaged, constituted by planar graphene layers and perfectly piled following a tri-periodic order, they correspond to the Raman spectra with a weak D band and a fine G band. In Lodran, carbons are more disordered than in Acapulco; their Raman spectra characterized by more intense D bands and by larger G bands, and appear as mesoporous turbostratic carbons with short and bended layers, few nanometers long, hardly stacked.
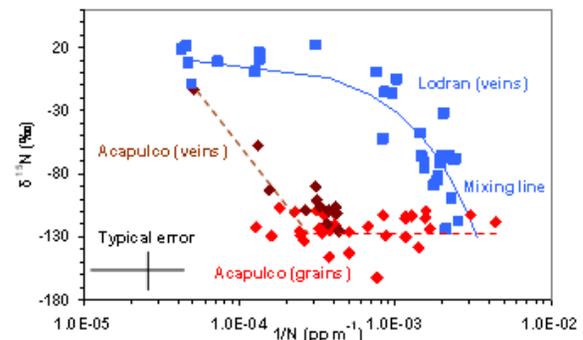

Fig. 2 : Nitrogen isotopic composition of carbons ($\delta15N$) vs. the inverse of N concentration (expressed by C-/CN- ratio). In Acapulco, carbons have globally the isotopic composition of metal ($\delta15N \sim -150‰$ [10]). A mixing line is observed in Lodran between nitrogen similar to those of Acapulco and nitrogen similar to those of the IOM of chondrites.