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Paris *vs.* Murchison: Impact of hydrothermal alteration on organic matter in CM chondrites

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Abstract

Unravelling the origin of organic compounds that were accreted into asteroids requires better constraining the impact of asteroidal hydrothermal alteration on their isotopic signatures, molecular structures, and spatial distribution. Here, we conducted a multi-scale/multi-technique comparative study of the organic matter (OM) from two CM chondrites (that originate from the same parent body or from identical parent bodies that accreted the same mixture of precursors) and underwent a different degree of hydrothermal alteration: Paris (a weakly altered CM chondrite – CM 2.8) and Murchison (a more altered one – CM 2.5). The Paris insoluble organic matter (IOM) shows a higher aliphatic/aromatic carbon ratio, a higher radical abundance and a lower oxygen content than the Murchison IOM. Analysis of the OM *in situ* shows that two texturally distinct populations of organic compounds are present within the Paris matrix: sub-micrometric individual OM particles and diffuse OM finely distributed within phyllosilicates and amorphous silicates. These results indicate that hydrothermal alteration on the CM parent body induced aromatization and oxidation of the IOM, as well as a decrease in radical and nitrogen contents. Some of these observations were also reported by studies of variably altered fragment of Tagish Lake (C2), although the hydrothermal alteration of the OM in Tagish Lake was apparently much more severe. Finally, comparison with data available in the literature suggests that the parent bodies of other chondrite petrologic groups could have accreted a mixture of organic precursors different from that accreted by the parent body of CMs.

Keywords: Carbon; Meteorites; IOM; Pyrolysis; Raman; EPR; NMR; XANES

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1. INTRODUCTION

Carbonaceous chondrites (CC) are fragments of primitive asteroids that contain up to 4 wt.% of organic matter (OM). The molecular and isotopic signatures of these organic compounds carry information about their formation and evolution within the asteroidal parent bodies (Martins and Sephton, 2009; Remusat et al., 2010; Alexander et al., 2011; Caselli and Ceccarelli, 2012). Two types of OM are typically defined in CC depending on their solubility: insoluble organic matter (IOM) and soluble organic matter (SOM) (Pizzarello et al., 2006; Remusat, 2015). The IOM represents

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the major organic component of CCs (75–95 wt.% of the total organic content). This complex macromolecular assemblage shows variations among CCs in its elemental, molecular and isotopic compositions, as well as in its degree of aromatization. The IOM elemental composition is approximately $C_{100}H_{60-80}O_{16-18}N_3S_{2-7}$ (average of Orgueil (CI), Murchison (CM2) and Al Rais (CR2) - Alexander et al., 2007; Derenne and Robert, 2010). The SOM (5–25 wt.% of the total organic content) comprises numerous compounds showing a huge diversity (up to 46,000 compounds - Schmitt-Kopplin et al., 2010), with an average composition consistent with $C_{100}H_{155-170}O_{10-30}N_{3-7}S_{3-6}$. Identified soluble compounds include carboxylic acids, amino acids, sugars, amines, aliphatic carbons, polyaromatic hydrocarbons (3,4 ring-PAHs), alcohols, ketones, and sulfonic acids (e.g., Pizzarello et al., 2006 or Remusat, 2015). The origin of the variations in OM composition and structure in CCs and the relation between SOM and IOM remain the subjects of intense debates.

The main difficulty arises from the secondary processes (hydrothermal alteration, e.g. aqueous alteration and/or metamorphism) that occurred after their accretion into asteroids parent bodies and impact both their organic and inorganic constituents. It is widely recognized that thermal metamorphism at temperature higher than 300 °C induces aromatization of OM, loss of heteroatoms and isotopic modification (Bonal et al., 2006; Yabuta et al., 2007; Cody et al., 2008; Remusat et al., 2008, 2016; Oba and Naraoka, 2009; Quirico et al., 2014). However, no consensus has been reached regarding the possible impact of hydrothermal alteration that occurred at lower temperatures on OM molecular and isotopic signatures (Alexander et al., 2007, 2014; Glavin et al., 2010; Remusat et al., 2009, 2010; Burton et al., 2012; Le Guillou et al., 2014). Two end-member scenarios have been proposed: (i) all chondrite groups accreted similar OM and the presently observed chemical differences are only related to secondary processes (see Alexander et al., 2007, 2013) or (ii) hydrothermal alteration had a limited impact and the differences are inherited from processes that formed or modified OM prior to asteroidal accretion (Remusat et al., 2009, 2010; Orthous-Daunay et al., 2010, 2013). The truth likely lies between these two scenarios.

Disentangling the respective role of interstellar, protoplanetary disk and asteroidal processes requires the impact of hydrothermal alteration on OM in CCs to be carefully investigated. Laboratory experiments may provide key information in that respect, but extrapolation to typical timescales of asteroidal hydrothermal alteration remains difficult. Several recent studies have investigated the chemical evolution of IOM and SOM in different CCs showing increasing hydrothermal alteration (IOM: Gardinier et al., 2000; Sephton et al., 2000, 2004; Cody and Alexander, 2005; Yabuta et al., 2005; Alexander et al., 2007, 2014; Remusat et al., 2009; Orthous-Daunay et al., 2013; Quirico et al., 2014; SOM: Martins and Sephton, 2009; Glavin et al., 2010; Burton et al., 2012; Elsila et al., 2012). For instance, recent studies of IOM from fragments of Tagish Lake (ungrouped C2) with variable alteration histories (Blinova et al., 2014) have shown that hydrothermal alteration is mainly responsible for the aromatization of IOM coupled with a decrease of its H/C ratio and δD signatures (Herd et al., 2011; Alexander et al., 2014).

In this study, we characterize in detail the OM of the Paris meteorite (one of the least altered CM chondrite classified as unmetamorphosed - CM 2.7–2.9; Marrocchi et al., 2014; Hewins et al., 2014) and compare the results with those obtained for the OM of Murchison (a more altered chondrite of the same group - CM 2.5; Rubin et al., 2007). Paris and Murchison belong to the same petrologic group according to their oxygen isotope compositions, chondrule/matrix ratios and bulk compositions (Hewins et al., 2014; Marrocchi et al., 2014). It is commonly assumed that chondrites of the same petrologic group originate from the same parent body (or identical parent bodies) and hence accreted the same components. Comparing Paris and Murchison OM thus allows documenting the impact of hydrothermal alteration processes that occurred secondarily, i.e. after the accretion.

The mineralogical heterogeneities, the significant porosity, and the persistence of Fe-Ni metal (usually absent in CMs), amorphous silicates and nanosulfides in the matrix have led to the conclusion that the Paris CM chondrite only experienced mild/gentle hydrothermal alteration (Marrocchi et al., 2014; Hewins et al., 2014; Leroux et al., 2015), in agreement with similar observations made on other very pristine chondrites (Brearley, 1993; Chizmadia and Brearley, 2008; Abreu and Brearley, 2010; Le Guillou and Brearley, 2014). Paris itself hosts two different lithologies showing different alteration degrees (Fig. 1; Hewins et al., 2014). Therefore, both organic and inorganic phases constituting the least altered regions of the Paris matrix may represent the closest available material to the precursors of any currently known CM chondrite. In contrast, Murchison only hosts one lithology showing an intermediate alteration degree among CMs (2.5; Rubin et al., 2007). Amorphous silicates and Fe-Ni metal are absent, while typical products of aqueous alteration, i.e., Mg and Fe-rich phyllosilicates, oxides, carbonates and sulfides can be observed (Rubin et al., 2007). Hence, while Paris has remained quite pristine, as indicated by the presence of metal and amorphous silicates (Hewins et al., 2014; Marrocchi et al., 2014), Murchison has suffered from larger extent of hydrothermal alteration and likely carries an evolved organic component (Rubin et al., 2007; Le Guillou et al., 2014). While Murchison OM has been extensively studied (Cronin et al., 1988; Cronin and Chang, 1993; Cody and Alexander, 2005; Pizzarello et al., 2006; Derenne and Robert, 2010; Le Guillou et al., 2014), the nature of Paris OM has only been scarcely documented (Merouane et al., 2012; Martins et al., 2015).

Here, we report results of a multi-scale/multi-technique comparative study that relied on a combination of complementary spectroscopic and analytical techniques to determine the elemental, isotopic, structural and molecular properties of Paris OM at different scales. We compare these results to available data on Murchison OM and discuss the impact of hydrothermal alteration processes and the possible nature of the organic precursors accreted into the CM parent body.