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Petrographic and C & O isotopic characteristics of the earliest stages of aqueous alteration of CM chondrites

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Abstract

CM chondrites form the largest group of hydrated meteorites and span a wide range of alteration states, with the Paris meteorite being the least altered CM described to date. Ca-Carbonates are powerful proxies for the alteration conditions of CMs because they are direct snapshots of the chemical and isotopic compositions of the parent fluids. Here, we report a petrographic and a C isotope and O isotope survey of Ca-carbonates in Paris in order to better characterize the earliest stages of aqueous alteration. Petrographic observations show that Paris contains two distinct populations of Ca-carbonates: Type 1a Ca-carbonates, which are surrounded by rims of tochilinite/cronstedtite intergrowths (TCIs), and new Type 0 Ca-carbonates, which do not exhibit the TCI rims. The TCI rims of Type 1a Ca-carbonates commonly outline euhedral crystal faces, demonstrating that these Ca-carbonates were (i) partially or totally pseudomorphosed by TCI and (ii) precipitated at the earliest stages of aqueous alteration, before Type 0 Ca-carbonates. Isotopic measurements show that Paris' Ca-carbonates have δ^{13}C values that range from 19 to 80‰ (PDB), δ^{18}O values that range from 29 to 41%, and δ^{17}O values that range from 13 to 24‰ (SMOW). According to the δ^{13}C–δ^{18}O values of Paris' Ca-carbonates, we developed a new alteration model that involves (i) the equilibration of a primordial ^{17,18}O-rich water (PW) with ^{16}O-rich anhydrous silicates and (ii) varying contribution of ^{12}C- and ^{13}C-rich soluble organic matter (SOMs). It also suggests that many parameters control the C and O isotopic composition of Ca-carbonates, the principles being the degree of isotopic equilibration between the PW and the anhydrous silicates, the respective contribution of ^{12}C and ^{13}C-rich SOMs as well as the thermal evolution of CM parent bodies. Consequently, we suggest that CM Ca-carbonates could record both positive and negative δ^{13}C–δ^{18}O relationships, but a systematic correspondence is probably absent in CM chondrites due to the large number of factors involved in generating the isotopic characteristics of Ca-carbonates. From recent reports of the C-isotopic compositions of SOM in CM chondrites, we propose that water-soluble organic compounds were the most probable source of ^{13}C enrichment in the majority of CM carbonates.

Keywords: Chondrites; Secondary alteration; Calcite; Aragonite; Pseudomorphism; Oxygen and carbon isotopes

1. INTRODUCTION

The solar system formed 4.567 billion years ago (Connelly et al., 2012) *via* the collapse of a dense molecular cloud leading to the creation of a protoplanetary disk (Safronov, 1969; Boss and Goswami, 2006). The physico-

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chemical evolution of the disk led to the formation of several mineral assemblages: calcium- and aluminum-rich refractory inclusions (CAIs), chondrules, Fe-Ni metal and sulphide beads, and a suite of very fine-grained crystalline and amorphous materials. These components accreted to form the asteroidal parent bodies that are the sources of unequilibrated meteorites (i.e., chondrites). Depending on the radial distance to the early Sun and the turbulence within the disk (Johansen et al., 2015), sub-millimeter-sized water ice grains of solar system (Alexander et al., 2012) and interstellar origin (Piani et al., 2015; Vacher et al., 2016) may have comprised a significant proportion of asteroids and comets (Brearley, 2006; Alexander et al., 2015). Heat released from the decay of ^{26}Al led to melting of the water ice, resulting in the establishment of significant fluid alteration processes within asteroids and shortly after their accretion (Grimm and Mcsween, 1989; Wilson et al., 1999; Petitat et al., 2009; Dyl et al., 2012; Doyle et al., 2015)

The physicochemical conditions under which hydrated chondrites were aqueously altered are poorly constrained (Brearley, 2006), in particular the length scale of liquid water flow. Numerical simulations of asteroidal aqueous alteration in an open system have predicted large-scale flow over tens of km (Grimm and Mcsween, 1989; Young et al., 1999, 2003; Cohen and Coker, 2000; Coker and Cohen, 2001; Young, 2001a, 2001b, 2004; McSween et al., 2002; Travis and Schubert, 2005; Grimm, 2007). Nevertheless, these results are difficult to reconcile with petrographic and geochemical observations of meteorites. There is little evidence for the redistribution of soluble elements within chondrites at scale greater than 100 μm, thus suggesting that aqueous alteration processes are mostly isochemical (Kerridge et al., 1979; McSween, 1979; Grossman et al., 2000, 2002; Grossman and Alexander, 2004). Moreover, CI chondrites, whose average compositions are similar to that of the solar photosphere (Palme et al., 2014), show the higher degree of alteration. The apparent paradox between the numerical models of fluid and thermal alteration of asteroids and petro-geochemical observations might be due to a significant overestimation of the permeability of chondrites (Bland et al., 2009). Bland et al. (2009) argued that numerical simulations strongly depend on the permeability of chondrites, which is four to eight orders of magnitude lower than previously estimated (Grimm and Mcsween, 1989; Bland et al., 2009). Taking this re-evaluation into account, the revised numerical simulations suggest that liquid water was transported in the range of 10–100 s of μm (Bland et al., 2009), a finding which is consistent with the small-scale of alteration observed within the least altered chondrites (Pignatelli et al., 2016). Nevertheless, the early stages of alteration remain poorly understood (Le Guillou et al., 2015) especially in terms of (i) the order of appearance of secondary minerals and the relationships between them, and (ii) the isotopic compositions of the altering fluids.

CM carbonaceous chondrites have clear evidence for the action of fluids and impact brecciation in the early Solar System (Metzler et al., 1992; Zolensky et al., 1997; Brearley, 2006). These chondrites are characterized by a large scale of aqueous alteration degrees (Rubin et al., 2007), from less altered (CM 2.7; Hewins et al., 2014; Marrocchi et al., 2014; Rubin, 2015) to heavily altered (i.e., CM 2.0). CMs commonly contain a wide range of secondary mineral phases that were likely produced through parent-body processes, for example phyllosilicates, magnetites, carbonates and Fe-Ni sulphides (Zolensky et al., 1997; Brearley, 2006). However, the secondary phases that are the most abundant of the CM chondrites are tochilinite ($6Fe_{0.9}S{\cdot}5(Mg,Fe^{2+}(OH)_2)$ – cronstedtite ($(Fe^{2+}_2Fe^{3+})_3(Fe^{3+}Si)O_5(OH)_4$) associations (hereafter referred as TCI for Tochilinite-Cronstedtite Intergrowths) (Pignatelli et al., 2016, 2017), which occur as complex, irregular-shaped intergrowths dispersed throughout the matrix (Tomeoka and Buseck, 1985; Rubin et al., 2007). TCIs are commonly observed in close association with grains of calcite, mostly as irregular rims surrounding or penetrating the carbonates (Browning and Bourcier, 1998; Benedix et al., 2003; Lee and Ellen, 2008; De Leuw et al., 2010; Lindgren et al., 2011; Lee et al., 2013, 2014; Fujiya et al., 2015). The textural relationship between TCIs and Ca-carbonates suggests that TCIs are Ca-carbonates pseudomorphs (Lee et al., 2014), but the opposite reaction is also thermodynamically possible (Browning and Bourcier, 1998). Thus, the chronology of the formation of secondary mineralogical assemblages remains largely un-constrained.

Over the last years, several studies have focused on the Paris chondrite, the least altered CM chondrite known to date (Bourot-Denise et al., 2010; Hewins et al., 2014; Marrocchi et al., 2014; Rubin, 2015; Leroux et al., 2015; Pignatelli et al., 2016; Vacher et al., 2016). Although Paris has been classified as a CM 2.7 (Marrocchi et al., 2014), relatively unaltered regions display characteristics corresponding to a subtype 2.9 with abundant proportions of Fe-Ni metal beads and pristine matrix (Hewins et al., 2014; Leroux et al., 2015; Rubin, 2015). Thus, Paris offers a unique opportunity to better characterize the early stages of fluid alteration in CM chondrites (Pignatelli et al., 2016, 2017). Paris contains a significant proportion of Ca-carbonates ($\approx 2 \pm 0.6$ vol.%; Marrocchi et al., 2014) whose O-isotopic compositions fall along the continuous trend defined by CM chondrites (Vacher et al., 2016; Verdier-Paoletti et al., 2017). However, some Ca-carbonates have peculiar O-isotopic compositions that suggest the accretion of few percent of water ice grains coming from the outer part of the solar system (Vacher et al., 2016). This is supported by the distinct C/H vs. D/H correlation reported for the Paris' matrix compared to the other CM chondrites (Piani et al., 2017). Taken together, these results support a dual origin of water ice grains in the CM-accretion region with contributions either from the inner and outer regions of the Solar System. The detection of interstellar water ices in Paris could be linked to its low H_2O concentration relative to other CMs (i.e., 4.8 wt.% vs. ≈9 wt.%; Rubin et al., 2007; Vacher et al., 2016) which would preclude the dilution of ^{17,18}O- and D-rich water ices by local water during the alteration processes. Consequently, Paris could also have kept the record of C-bearing inorganic ices from the outer part of the Solar System (Ciesla and Scott, 2012). However, the C isotopic composition of the Paris' carbonates has not been determined yet would bring important information on