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## EARTH PANFAR SEACO LEMAS

### A systematic for oxygen isotopic variation in meteoritic chondrules



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#### A R T I C L E I N F O

#### ABSTRACT

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Keywords: chondrites chondrules oxygen isotopes evaporation gas-melt interactions Primitive meteorites are characteristically formed from an aggregation of sub-millimeter silicate spherules called chondrules. Chondrules are known to present large three-isotope oxygen variations, much larger than shown by any planetary body. We show here that the systematic of these oxygen isotopic variations results from open-system gas-melt exchanges during the formation of chondrules, a conclusion that has not been fully assessed up to now. We have considered Mg-rich porphyritic chondrules and have modeled the oxygen isotopic effects that would result from high-temperature interactions in the disk between precursor silicate dust and a gas enriched in SiO during the partial melting and evaporation of this dust. This formation process predicts: (i) a range of oxygen isotopic composition for bulk chondrules in agreement with that observed in Mg-rich porphyritic chondrules, and (ii) variable oxygen isotopic disequilibrium between chondrule pyroxene and olivine, which can be used as a proxy of the dust enrichment in the chondrule-forming region(s). Such enrichments are expected during shock waves that produce transient evaporation of dust concentrated in the mid-plane of the accretion disk or in the impact plumes generated during collisions between planetesimals. According to the present model, gas-melt interactions under high PSiO<sub>(gas)</sub> left strong imprints on the major petrographic, chemical and isotopic characteristics of Mg-rich porphyritic chondrules.

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#### 1. Introduction

Chondrites are complex aggregates of high temperature components formed in the solar nebula 4.56 billion years ago: chondrules, refractory inclusions (hereafter CAIs) and Fe-Ni metal beads. They provide a direct glimpse into the astrophysical conditions under which the Sun was formed and the dynamics and evolution of the accretion disk. Since the discovery of large massindependent oxygen isotopic variations in CAIs from primitive meteorites (Clayton et al., 1973), many studies have demonstrated that the oxygen isotopic compositions provide key constraints on the origin and evolution of the first solids in the Solar protoplanetary disk (Yurimoto et al., 2008).

CAIs and chondrules present large non-mass-dependent oxygen isotopic variations that are thought to reflect the existence in the accretion disk of at least two reservoirs with very different isotopic compositions (i.e., <sup>16</sup>O-rich and <sup>16</sup>O-poor, respectively) (Yurimoto et al., 2008; Clayton, 2002). The <sup>16</sup>O-rich reservoir (i.e.,  $\Delta^{17}O = -29\%$ ) identified to be Solar oxygen, from the

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analysis of present day Solar Wind in NASA Genesis collectors (McKeegan et al., 2011) and Gyr-old Solar Wind in lunar soils (Hashizume and Chaussidon, 2005), represents the bulk oxygen isotopic composition of the mixture of gas and dust from which the Sun formed. The <sup>16</sup>O-poor reservoir (i.e.,  $\Delta^{17}$ O up to +90%) is evidenced by rare oxide phases in the matrix of carbonaceous chondrites, which are considered to be by-products of metal- and sulfide-oxidation by <sup>16</sup>O-poor water (Sakamoto et al., 2007). The presence of large oxygen isotopic variations in the regions of the accretion disk where the first planetesimals and planets formed is demonstrated by the variable <sup>16</sup>O depletion observed in meteoritic chondrules relative to the Sun (Clayton et al., 1983). The origin of these <sup>16</sup>O variations within chondrites is not yet fully understood and open questions remain as to what are these reservoirs, their origin and evolution over time. Two different models have been proposed: (i) self-shielding of UV light by CO gas that would produce a <sup>16</sup>O-poor water from <sup>16</sup>O-rich nebular CO (Clayton, 2002; Thiemens and Heidenreich, 1983; Yurimoto and Kuramoto, 2004) and (ii) non mass-dependent reactions akin those involved in the production of ozone from molecular oxygen (Thiemens and Heidenreich, 1983), which would produce a <sup>16</sup>O-rich reservoir and its <sup>16</sup>O-poor counterpart from a nebular gas having initially an oxygen isotopic composition close to that of the terrestrial planets. The re-



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cent determination of the <sup>16</sup>O-rich composition of the Sun can be taken as a strong argument in favor of the self-shielding scenario (McKeegan et al., 2011; Hashizume and Chaussidon, 2005). Whatever the origin of the <sup>16</sup>O variations, they were present very early in the disk. <sup>26</sup>Al-dated CAIs present oxygen isotopic variations suggesting the occurrence of a <sup>16</sup>O-poor gas reservoir within the first 10<sup>5</sup> years of the solar system history (MacPherson, 2007). Furthermore, chondrule silicates have variable but <sup>16</sup>O-depleted isotopic compositions that confirm the existence of a <sup>16</sup>O-poor reservoir in the chondrule-forming region (Krot et al., 2006). The <sup>16</sup>O variability in chondrules can result either from: (i) physical mixing within the solid chondrules' precursors of grains having different origins and  $\Delta^{17}$ O values, (ii) high temperature exchanges between the chondrule melt and the surrounding nebular gas (having different  $\Delta^{17}$ O values), or (iii) a combination of both processes. Because of that, it has always been difficult to use this <sup>16</sup>O variability to infer unequivocally the key physico-chemical processes at play during the formation of chondrules, and by consequence the origin of chondrules.

This question is of up most importance, and has gained renewed interest in the context of the growing evidences that the formation of chondrules took place under non-canonical conditions with enhanced partial pressures of alkali- and volatile-elements (Krot et al., 2006; Tissandier et al., 2002; Libourel et al., 2006; Alexander et al., 2008; Fedkin and Grossman, 2013; Marrocchi and Libourel, 2013). Partial melting of solids in such an environment must result in strong oxygen isotopic exchanges with the gas since O is abundant in the gas either as CO or SiO, thus leaving traces in the oxygen isotopic composition of chondrules. Laboratory experiments have shown that pyroxenes can form in chondrule melts by incorporation of SiO from the nebular gas, during the partial dissolution of olivine precursors (Tissandier et al., 2002). If taking place, such a process would control part of the bulk chemical and oxygen isotopic compositions of chondrules (Libourel et al., 2006). Evidence that this process was taking place was brought by ion probe measurements revealing that in some Mg-rich chondrules low-Ca pyroxenes are <sup>16</sup>O-depleted relative to relict olivines from the same chondrule (Chaussidon et al., 2008). However, such a difference is not systematic, olivine and coexisting low-Ca pyroxene having similar O-isotopic in many chondrules (Rudraswami et al., 2011; Ushikubo et al., 2012; Tenner et al., 2015). This has been used as an argument to rule out that most chondrules formed under high PSiO(gas) and thus that gas-melt interactions are key to control the composition of chondrules.

In the following, we explore and re-evaluate the constraints that can be brought on gas-melt interactions during the formation of chondrules from their oxygen isotopic compositions. To do so, a model has been developed to study the systematic of oxygen isotopes during the formation of chondrules by partial melting and evaporation of solid precursors in a nebula gas. The model takes into account: (i) all existing high-precision oxygen isotopic data of chondrules and (ii) the latest oxygen isotopic fractionations determined between CO, SiO, H<sub>2</sub>O gas and solids of various compositions (olivine and pyroxene) (Javoy et al., 2012). Based on this isotopic survey and modeling, we re-evaluate the constraints that can be brought on gas-melt interactions during the formation of chondrules. We focus on chondrules from CV and CR chondrites as they present olivine with the most <sup>16</sup>O-rich isotopic compositions, making them a priori the most appropriate candidate to look for oxygen isotopic effects due to gas-melt interactions. A large set of data has recently been accrued for these chondrules from high-precision oxygen isotopic studies using multi-collector ion microprobes (Krot et al., 2006; Chaussidon et al., 2008; Rudraswami et al., 2011; Tenner et al., 2015). The chondrules considered here are all ferromagnesian chondrules and share the same general petrographic characteristics: low-FeO olivine of variable size ( $\approx$ 30–100 µm),



**Fig. 1.** Oxygen three-isotope plot for individual minerals (olivine and low-Ca pyroxene) in CV and CR chondrules excluding relict minerals (Chaussidon et al., 2008; Rudraswami et al., 2011; Tenner et al., 2015). Oxygen isotopic variations are described from the variations of the <sup>17</sup>O/<sup>16</sup>O and <sup>18</sup>O/<sup>16</sup>O isotopic ratios expressed in delta unit relative to the V-SMOW international standard ( $\delta^{x}O = (^{x}O/^{16}O/^{x}O^{16}O/_{x-SMOW} - 1) \times 1000; x = ^{18}O \text{ or }^{17}O$ ). Three different lines (CCAM, YR and TFL) are shown (see text). The individual minerals from chondrules together appear to define a single line referred to as the 'Primitive Chondrule Minerals' line (PCM, Ushikubo et al., 2012).

slightly larger low-Ca pyroxenes ( $\approx$  60–150 µm), glassy mesostasis and Fe–Ni metal beads (Hewins et al., 2005). The olivines present rounded to subhedral crystal shapes and are frequently associated with a glassy mesostasis while the low-Ca pyroxenes are in the form of euhedral crystals, with resorbed or poikilitically enclosed olivines and limited mesostasis. Most of these chondrules are radially zoned with olivines and mesostasis located towards the interior of the chondrules and an outer zone that is dominated by low-Ca pyroxenes.

### 2. Oxygen isotopic variations in chondrules at bulk and mineral scales

Since the discovery of <sup>16</sup>O variations in meteorites (Clayton et al., 1973), it has been recognized that these variations define a general array along a line of slope close to one in the three oxygen isotope diagram reporting  $\delta^{17}$ O relative to  $\delta^{18}$ O values (in ‰). In that diagram (Fig. 1), two lines play a fundamental role: (i) the CCAM (Carbonaceous Chondrites Anhydrous Minerals) line  $[\delta^{17}O = (0.94 \pm 0.01) \times \delta^{18}O - 4.2]$ , derived from BrF<sub>5</sub> analyses of anhydrous minerals from CAIs in carbonaceous chondrites (Clayton et al., 1977) and (ii) the YR (Young-Russell) line  $[\delta^{17}O = (1.00 \pm 0.03) \times \delta^{18}O - 1.04]$ , inferred from UV laser microprobe analyses of unaltered minerals from a CAI of the Allende CV3 chondrite (Young and Russell, 1998). These lines point to the existence in the disk of reservoirs variously enriched/depleted in <sup>16</sup>0. The YR line is proposed to represent the primitive oxygen isotope reservoirs of the early solar nebula. Minerals plotting to the right of this line are inferred to have their oxygen isotopic composition fractionated by partial isotopic exchanges with a gas or a fluid at various temperatures, either in a nebular setting or during parentbody processes (Young and Russell, 1998). In a general manner, low-temperature parent-body processes are expected to drive the oxygen isotopic composition to the right of the CCAM line because of the positive mineral-water oxygen isotopic fractionations (except for magnetite-water), which increase with decreasing temperature (Zhao and Zheng, 2003).

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