# Origin and abundance of water in carbonaceous asteroids

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A B S T R A C T

The origin and abundance of water accreted by carbonaceous asteroids remains underconstrained, but would provide important information on the dynamic of the protoplanetary disk. Here we report the *in situ* oxygen isotopic compositions of aqueously formed fayalite grains in the Kaba and Mokoia CV chondrites. CV chondrite bulk, matrix and fayalite O-isotopic compositions define the mass-independent continuous trend ($\delta^{17}O = 0.84 \pm 0.03 \times \delta^{18}O - 4.25 \pm 0.1$), which shows that the main process controlling the O-isotopic composition of the CV chondrite parent body is related to isotopic exchange between $^{16}O$-rich anhydrous silicates and $^{17}$- and $^{18}O$-rich fluid. Similar isotopic behaviors observed in CM, CR and CO chondrites demonstrate the ubiquitous nature of O-isotopic exchange as the main physical process in establishing the O-isotopic features of carbonaceous chondrites, regardless of their alteration degree. Based on these results, we developed a new approach to estimate the abundance of water accreted by carbonaceous chondrites (quantified by the water/rock ratio) with CM (0.3–0.4) ≥ CR (0.1–0.4) ≥ CV (0.1–0.2) > CO (0.01–0.10). The low water/rock ratios and the O-isotopic characteristics of secondary minerals in carbonaceous chondrites indicate they (i) formed in the main asteroid belt and (ii) accreted a locally derived (inner Solar System) water formed near the snowline by condensation from the gas phase. Such results imply low influx of D- and $^{17}O$- and $^{18}O$-rich water ice grains from the outer part of the Solar System. The latter is likely due to the presence of a Jupiter-induced gap in the protoplanetary disk that limited the inward drift of outer Solar System material at the exception of particles with size lower than 150 μm such as presolar grains. Among carbonaceous chondrites, CV chondrites show O-isotopic features suggesting potential contribution of $^{17-18}O$-rich water that may be related to their older accretion relative to other hydrated carbonaceous chondrites.

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## 1. Introduction

Water played a key role in shaping the Solar System as it account for about 50% by mass of all condensable species in a gas of cosmic composition (Lodders, 2003). Water vapor controls oxygen fugacity, affecting the chemistry of sub-millimeter materials formed during the evolution of the solar protoplanetary disk. As bouncing and fragmentation limit the coagulation of dust particles, the growth processes from dust to planetesimals are not fully understood (Güttler et al., 2010). Water-ice mantling grain surfaces is believed to enhance their adhesion and promote particle coagulation processes (Gundlach and Blum, 2015). Thus, condensed water ices can locally increase the abundance of solids, favoring conditions that trigger streaming instabilities, and allowing the growth of decimeter-sized pebbles that can accrete to form planetesimals (Ros and Johansen, 2013). Water ice is thus fundamental

to the evolution of the Solar System, and, alongside oxides, silicates and metal, likely represented a significant fraction of the building blocks of planets. Ice-free chondrite accretion likely took place during the evolution of the protoplanetary disk as attested by enstatite chondrites, which show really limited traces of water (Brearley, 2006; Piani et al., 2011).

Within the solar protoplanetary disk, the formation of water ice is mainly controlled by the snowline, i.e., the distance from the Sun at which temperature is low enough for water to condense (about 150–170 K). The location of the snowline in the protoplanetary disk is a direct function of the stellar accretion rate and is expected to move inward as the accretion rate decreases with time (Bitsch et al., 2015). Based on astronomical observations, stellar accretion rates are estimated to have decreased on average from $10^{-8}$ M$_\odot$/y at 1 My to 1–5 × $10^{-9}$ M$_\odot$/y at 3 My (M$_\odot$ = the solar mass ∼2 × $10^{30}$ kg) (Hartmann et al., 1998), inducing the snowline to drift from 3 AU to 1 AU (astronomical unit AU = 150 × $10^6$ km, the distance from Earth to the Sun) (Bitsch et al., 2015). Such a snowline drift implies that water ice grains were ubiquitous in the inner Solar System, and formed abundant ice-

rich planetesimals. This point is not insignificant as geochemical constraints and numerical simulations suggest that inner planetesimals should have grown "dry" with only a small contribution of ice-rich planetesimals originating from larger heliocentric distances (Albarède, 2009; Marty, 2012). Yet, the accretion of chondrites occurred ∼2–4 My after the formation of Calcium–Aluminum-rich Inclusions (CAIs; Sugiura and Fujiya, 2014), when the snowline should have been closer to the Sun than the inner edge of the asteroid belt (Morbidelli et al., 2016). Such a conundrum, referred as the snowline problem (Oka et al., 2011), could be linked to inhibited water ice condensation due to the slower drift of the snowline than that of gas in the protoplanetary disk (Morbidelli et al., 2016). This would bring "dry" gas (from which water had already condensed farther out in the disk) in the vicinity of the snowline (Morbidelli et al., 2016). However, chondrites have been affected by variable but widespread water alteration processes, suggesting they accreted a significant amount of water ice (Doyle et al., 2015; Garenne et al., 2014; Vacher et al., 2017). Thus, the origin and the abundance of water accreted by different group of chondrites are not yet fully understood (Alexander, 2017; Vacher et al., 2016). Additionally, the oxygen isotopic evolution of water during secondary alteration processes has not been fully investigated, and could provide invaluable information on the physico-chemical processes occurring during the geological evolution of carbonaceous asteroids (Clayton and Mayeda, 1999, 1984).

Oxygen isotopic compositions are expressed in delta units (‰) relative to Standard Mean Ocean Water (SMOM) as $\delta^x O = [(^xO/^{16}O)_{sample}/(^xO/^{16}O)_{SMOW} - 1] \times 1000$ with $x$ being $^{17}O$ or $^{18}O$; mass-independent oxygen isotope fractionation are described by the parameter $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$. Among meteorites, carbonaceous chondrites present the most widespread evidences of fluid–rock interactions, in that the contain important diversity of aqueously formed minerals such as phyllosilicates, carbonates and magnetite (Brearley, 2006). Oxygen isotopic compositions of these secondary minerals can be used to decipher the origin of water in the chondrite-forming region as outer water ices are expected to exhibit significant $^{17}O$ and $^{18}O$ enrichment ($\Delta^{17}O \gg 0$) relative to inner Solar System values ($\Delta^{17}O \approx 0$) due to the self-shielding of $^{16}O$-rich nebular CO gas by UV light (Yurimoto and Kuramoto, 2004). In addition, oxygen isotopic compositions at both the bulk and mineral scales can be used to quantify (i) the abundance of water accreted by carbonaceous parent bodies (Clayton and Mayeda, 1984; Young et al., 1999) and (ii) the prevailing conditions during subsequent fluid–rock (Verdier-Paoletti et al., 2017). Among secondary minerals, fayalite ($Fe_2SiO_4$) is of primary importance as it represents a proxy of the fluid from which it formed due to its low fractionation factor $\alpha_{Fa-water}$ (Zheng, 1993) at the temperature range estimated for fayalite formation (i.e., 100–300 °C) (Doyle et al., 2015; Zolotov et al., 2006). In this contribution, we report the oxygen isotopic compositions of fayalite in the CV chondrites Kaba and Mokoia. We compute the amount of water ice accreted by combining these results with the bulk O-isotopic compositions of CV chondrites (Clayton and Mayeda, 1999). We also compare the O-isotopic composition at both the bulk and (secondary) mineral scales for CO, CM and CR chondrites to propose a quantitative view of the origin, abundance and O-isotopic evolution of water in the carbonaceous asteroids.

## 2. Materials and methods

We surveyed a thin section each of Kaba (Kaba N4075) and Mokoia (Mokoia N1185; both from the National Museum History, Vienna, Austria). Sections were examined microscopically in transmitted and reflected light. Scanning electron microscope (SEM) and Energy Dispersive X-ray (EDX) spectral analyses were performed

at Centre de Recherches Pétrographiques et Géochimiques (CRPG-CNRS, Nancy, France) using a JEOL JSM-6510 equipped with an EDX Genesis X-ray detector, using a 3 nA primary beam at 15 kV. Quantitative compositional analyses of fayalite were made with a CAMECA SX-100 electron microprobe at the University of Paris VI. Electron microprobe analyses of silicates were performed with a 40 nA focused beam, 15 kV accelerating potential, and 20 on-peak and background analysis times. Detection limits in silicates were 0.02 wt% for $SiO_2$, $Al_2O_3$, CaO and MgO, 0.01 wt% for $Na_2O$, $K_2O$, and $TiO_2$, and 0.04 wt% for $Cr_2O_3$ and FeO.

Oxygen isotopic compositions were measured with a CAMECA IMS 1280 at CRPG-CNRS. $^{16}O^-$, $^{17}O^-$, and $^{18}O^-$ ions produced by a 5 nA $Cs^+$ primary ion beam were measured in multi-collection mode with three Faraday cup (FC). To avoid interference of $^{16}OH^-$ and $^{17}O^-$ signals at mass 17, and to maximize the flatness of the $^{16}O^-$ and $^{18}O^-$ peaks, entrance and exit slits were adjusted to achieve a Mass Resolving Power of ∼7000 for $^{17}O^-$ on the central FC and ∼2500 on the off-axis FC. Total measurement time was 240 s (180 s measurement + 60 s pre-sputtering). We used four terrestrial standard materials (San Carlos olivine, magnetite, diopside, and fayalite) to: (i) define the mass fractionation line (TFL) and (ii) correct the matrix effects on instrumental mass fractionation for fayalite. Typical count rates obtained on fayalite grains were $3 \times 10^9$ cps for $^{16}O$, $1 \times 10^6$ cps for $^{17}O$, and $4.5 \times 10^6$ cps for $^{18}O$. Typical $2\sigma$ errors were ∼0.7‰ for $\delta^{18}O$, ∼0.8‰ for $\delta^{17}O$, and ∼1‰ for $\Delta^{17}O$.

## 3. Results

Fayalite grains in Kaba and Mokoia occur in peripheral portions of type I chondrules, in fine-grained chondrule rims, and in matrix (Fig. 1). Fayalite are large, subhedral-to-anhedral grains, and sometimes associated with magnetite and sulfide grains (Fig. 1A), although sulfide- and magnetite-free fayalite grains are commonly observed in the matrix (Fig. 1B). Fayalite are chemically homogeneous ($Fa_{97}$ to $Fa_{100}$; Table 1) with compositions similar to those previously reported fayalite-bearing assemblages (Choi et al., 2000; Hua and Buseck, 1995; Jogo et al., 2009). Eight large (>40 μm) sulfide- and magnetite-free fayalite grains were selected for isotopic analyses. Their O-isotopic compositions fall above the TFL, with $\Delta^{17}O$ values ranging from 0.8 to 2.6‰ (Fig. 2, Table 2).

## 4. Discussion

### 4.1. Origin, abundance and O-isotopic evolution in CV chondrites

It is commonly accepted that bulk O-isotopic compositions of CV chondrites plot along the Carbonaceous Chondrite Anhydrous Mineral (CCAM) line [$\delta^{17}O = (0.94 \pm 0.01) \times \delta^{18}O - 4.2$], derived from $BrF_5$ analyses of anhydrous minerals from CAIs in carbonaceous chondrites (Clayton et al., 1973). In detail, it rather appears that bulk and matrix O-isotopic compositions of CV chondrites define the trend $\delta^{17}O = 0.84 \times \delta^{18}O - 4.25$ ($r^2 = 0.99$; Fig. 2A; Clayton and Mayeda, 1999; Greenwood et al., 2010), which likely corresponds to secondary alteration processes. The O-isotopic compositions of fayalite grains reported here do not fall on the TFL but show $\Delta^{17}O > 0$‰ (Fig. 2B). When plotted with the bulk, matrix and dark inclusions O-isotopic compositions of CV chondrites, the Kaba and Mokoia fayalite grains define the continuous trend $\delta^{17}O = (0.83 \pm 0.02) \times \delta^{18}O - (4.18 \pm 0.13)$ ($2\sigma$, $r^2 = 0.99$, and Mean Squared Weight Deviation, MSWD = 3.9; Fig. 2A). Fayalite grains reported in the CV3 chondrite A-881317 also fall on this trend (Fig. 2A) (Doyle et al., 2015). Comparison with other studies is difficult due to the large uncertainties associated with O-isotope measurements (e.g., 4.4 and 2.5‰ on $\delta^{18}O$ and $\delta^{17}O$