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Abstract

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}O- 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 $^{17\text{-}18}$O-rich water that may be related to their older accretion relative to other hydrated carbonaceous chondrites.

Highlights

Bulk, matrix and fayalite grains of CV chondrites define a continuous trend.

O-isotopic compositions of C-rich asteroids are established by isotopic exchange.

We estimated the abundance of water accreted by carbonaceous chondrites.

Carbonaceous asteroids formed in the asteroid belt and accreted local water.

Our results support low influx of ^{17}O- and ^{18}O-rich water ice from the outer Solar System.

Keywords: carbonaceous asteroids, water, oxygen isotopes, protoplanetary disk, Jupiter.

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 $\delta^{x}O = [(^{x}O/^{16}O)_{sample}/(^{x}O/^{16}O)_{SMOW} - 1] \times 1000)$ 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 ($\Delta^{17}O >> 0$) 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 $\alpha_{Fa\text{-}water}$ (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

158 microprobe at the University of Paris VI. Electron microprobe analyses of silicates were
159 performed with a 40 nA focused beam, 15 kV accelerating potential, and 20 on-peak and
160 background analysis times. Detection limits in silicates were 0.02 wt% for SiO_2, Al_2O_3, CaO
161 and MgO, 0.01 wt% for Na_2O, K_2O, and TiO_2, and 0.04 wt% for Cr_2O_3 and FeO.

162 Oxygen isotopic compositions were measured with a CAMECA IMS 1280 at CRPG-
163 CNRS. $^{16}O^-$, $^{17}O^-$, and $^{18}O^-$ ions produced by a 5 nA Cs^+ primary ion beam were measured in
164 multi-collection mode with three Faraday cup (FC). To avoid interference of $^{16}OH^-$ and $^{17}O^-$
165 signals at mass 17, and to maximize the flatness of the $^{16}O^-$ and $^{18}O^-$ peaks, entrance and exit
166 slits were adjusted to achieve a Mass Resolving Power of ~7000 for $^{17}O^-$ on the central FC
167 and ~2500 on the off-axis FC. Total measurement time was 240 s (180 s measurement + 60 s
168 pre-sputtering). We used four terrestrial standard materials (San Carlos olivine, magnetite,
169 diopside, and fayalite) to: (i) define the mass fractionation line (TFL) and (ii) correct the
170 matrix effects on instrumental mass fractionation for fayalite. Typical count rates obtained on
171 fayalite grains were 3×10^9 cps for ^{16}O, 1×10^6 cps for ^{17}O, and 4.5×10^6 cps for ^{18}O. Typical
172 2σ errors were ~ 0.7 ‰ for $\delta^{18}O$, ~ 0.8 ‰ for $\delta^{17}O$, and ~ 1 ‰ for $\Delta^{17}O$.

173
174 **3-Results**
175
176
177 Fayalite grains in Kaba and Mokoia occur in peripheral portions of type I chondrules,
178 in fine-grained chondrule rims, and in matrix (Fig. 1). Fayalite are large, subhedral-to-
179 anhedral grains, and sometimes associated with magnetite and sulfide grains (Fig. 1A),
180 although sulfide- and magnetite-free fayalite grains are commonly observed in the matrix
181 (Fig. 1B). Fayalite are chemically homogeneous (Fa_{97} to Fa_{100}; Table 1) with compositions
182 similar to those previously reported fayalite-bearing assemblages (Choi et al., 2000; Hua and
183 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 [$\delta^{17}O = (0.94\pm0.01) \times \delta^{18}O - 4.2$], 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 $\delta^{17}O = (0.83 \pm 0.02) \times \delta^{18}O - (4.18 \pm 0.13)$ (2σ, $r^2 = 0.99$, 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 $\delta^{17}O$ (2σ), respectively) (Choi et al., 2000). However, recent measurements in the Kaba chondrite aligns perfectly along the line of slope 0.83 (Fig. 2A; Krot and Nagashima, 2016). The continuous trend defined by bulk, matrix and fayalite compositions does not follow a mass-dependent fractionation relationship (Fig. 2A), implying that fayalite O-isotopic compositions did not result from fluid circulation along a temperature gradient, which would produce a trend with slope 0.52. Instead, this implies that

213 the main process controlling the O-isotopic composition of the CV chondrite parent body is
214 related to isotopic equilibrium between ^{16}O-rich anhydrous silicates and ^{17}O- and ^{18}O-rich
215 fluid as recently reported in CM chondrites (Verdier-Paoletti et al., 2017). In such a scheme,
216 ^{17}O- and ^{18}O-rich fayalite correspond to early precipitates from primitive fluids that did not
217 suffer significant O-isotopic exchange with ^{16}O-rich anhydrous silicates (Yurimoto et al.,
218 2014; Zolensky et al., 2017). Conversely, lighter isotopic compositions indicate that fayalite
219 formed only after significant alteration, as fluid O-isotopic compositions converge toward the
220 typical ^{16}O-rich values of anhydrous silicates. Both bulk and mineral phase data (Fig. 2) thus
221 identify O-isotopic exchange between ^{16}O-rich silicates and ^{17}O- and ^{18}O-rich fluid as the key
222 process controlling the O-isotopic composition of the alteration fluids from which fayalite
223 precipitated.

224 Thermodynamic calculations suggest that nearly pure fayalite grains (Fa > 90) as
225 observed in $CV3_{OxB}$ chondrites are stable at temperatures below 350°C (Zolotov et al., 2006),
226 and likely down to 100-200°C (Doyle et al., 2015). Considering the low $\alpha_{Fa\text{-}water}$ at this
227 temperature range (i.e., $1000\,ln\alpha_{Fa-water} = -3.4$ ‰ at 100°C and -1.1 ‰ at 200°C,
228 (Zheng, 1993), fayalite O-isotopic compositions represent a direct record of the oxygen
229 isotopic compositions of the fluid from which they precipitated. Additionally, fayalite and
230 magnetite from chondrite A-881317 lie on a mass-dependent fractionation line with Δ^{17}O =
231 - 0.3‰, consistent with equilibrium crystallization from the same fluid reservoir (Fig. 3B)
232 (Doyle et al., 2015). The -8.4 ‰ difference between δ^{18}O values of fayalite and magnetite
233 (Doyle et al., 2015) corresponds to fayalite crystallization at ≈ 150°C (Zheng, 1993), at which
234 temperature the fractionation factor α is minimal with 1000 $\ln\alpha_{Fa\text{-}water}$□□□0.6□‰.
235 Considering then that fayalite formation likely occurred in a very narrow range of
236 temperatures (i.e., 150-200°C), their parent fluids are characterized by near terrestrial values
237 with Δ^{17}O from -1 to +3.5‰ (Fig. 2A). However, these values do not necessarily correspond

to the initial O-isotopic composition of water accreted by CV chondrites as protracted fluid-rock interactions likely occurred before the precipitation of the rare, nearly pure, fayalite grains.

There is a lively debate on the conditions of secondary alteration processes that have affected chondrites, which is basically divided into open-system (Young et al., 1999) versus closed-system models (Clayton and Mayeda, 1999). Although the O-isotopic compositions of secondary minerals have been used to argue for both models, petrographic observations appear more consistent with closed-system alteration. For instance, there is little evidence for the redistribution of soluble elements within chondrites at scale greater than 100 μm (Brearley, 2006), thus suggesting that aqueous alteration processes are mostly isochemical. This is consistent with the estimated low permeability of chondrites (Bland et al., 2009) and the lack of variations in bulk chemical compositions between meteorites with different degrees of aqueous alteration (Brearley, 2006). Based on these observations, we thus considered a closed-system model to discuss the alteration conditions of carbonaceous asteroids.

In a closed system, the difference between the final (f) oxygen isotopic composition of rock *r* and water *w* can be described as:

$$\Delta = \delta_r^f - \delta_w^f \qquad (1)$$

The amount of water accreted by CV chondrites can be estimated by the water/rock ratio (Young et al., 1999)

$$\frac{N_w}{N_r} = \frac{\left(\delta_r^f - \delta_r^0\right)}{\delta_w^0 - \left(\delta_r^f - \Delta\right)} \qquad (2)$$

where N corresponds to the number of oxygen atoms in the reacting water (w) or rock (r), δ^0 their initial isotopic compositions, δ^f their final isotopic compositions and Δ represent the difference between rock and water at equilibrium. Such a formalism does not include the final isotopic composition of the water, which is generally not known. However, in the case where this parameter can be calculated, Eqn. 2 simplifies to:

$$\frac{N_w}{N_r} = \frac{\left(\delta_r^f - \delta_r^0\right)}{\left(\delta_w^0 - \delta_w^f\right)} \qquad (3)$$

Considering the bulk O-isotopic composition of Kaba ($\delta^{18}O$ = 2.18‰, (Clayton and Mayeda, 1999) and a more ^{16}O-rich bulk CV chondrite as a plausible CV protolith ($\delta^{18}O$ = -4.22‰; (Clayton and Mayeda, 1999), we calculate the water/rock ratio by assuming that the lowest $\delta^{18}O$ value of fayalite represent the final O-isotopic composition of CV water, after weighting by the fractionation factor at 150°C (i.e., 17.4 - 0.6 = 16.8‰; Table 2). Although the initial composition of water accreted by CV chondrite is unknown, it must be (i) located on the trend defined by both bulk CV and fayalite (Fig. 2A) and (ii) characterized by $\delta^{18}O$ value higher than the highest fayalie $\delta^{18}O$ value. Assuming an initial water with $\delta^{18}O$ = 30‰ (as estimated for CM chondrites; (Clayton and Mayeda, 1984) leads to an estimated water/rock ratio of 0.48 for Kaba; the same calculation giving a result of 0.74 for Mokoia. These values are slightly lower than those estimated on the basis of mineral assemblages and thermodynamic modeling (i.e., 0.8–1.1; (Zolensky et al., 1993) However, it is noted that our estimations represent maximum water/rock ratios, as increasing the $\delta^{18}O$ of the initial water or decreasing $\delta^{18}O$ of

final water lowers the water/rock ratio. For instance, an initial water with $\delta^{18}O$ = 45‰ gives estimated water/rock ratios for Kaba and Mokoia of 0.30 and 0.22, respectively. Considering the range of water/rock ratios modeled for the formation of near pure fayalite (i.e., 0.1-0.2; (Zolotov et al., 2006) provides $\delta^{18}O \geq +60$ ‰ (i.e., $\Delta^{17}O > 15$ ‰) for the initial CV water, suggesting a potential contribution of water ice from the outer Solar System (Sakamoto et al., 2007; Seto et al., 2008).

Kaba is considered the least altered oxidized CV chondrite with a petrographic grade of 3.1-3.4 (Bonal et al., 2006). Interestingly, Kaba fayalite grains are not in isotopic equilibrium with sulfide-associated magnetite (SAMs) poikilitically enclosed in low-Ca pyroxenes of chondrules (Fig. 3; (Marrocchi et al., 2016). Based on petrographic and isotopic characteristics, SAMs have been interpreted as magmatic minerals, resulting from the crystallization of FeS melts containing variable amounts of dissolved oxygen (Marrocchi et al., 2016; Marrocchi and Libourel, 2013). The fact that the $\Delta^{17}O$ of SAMs and fayalite grains from Kaba do not overlap (Fig. 3B) confirms that chondrule SAMs could be primary mineral formed during the high-temperature chondrule-forming event (Marrocchi et al., 2016). This does not exclude the potential occurrence of low-temperature aqueously formed magnetite in CV chondrites, but rather suggests that both processes occurred at different settings and under different physico-chemical conditions.

4.2 Comparison of CV to CM, CR and CO chondrites

4.2.1 CM chondrites

In a oxygen three-isotope plot, the continuous trend observed between whole rocks and secondary minerals is not unique to CV chondrites. In CM chondrites, Ca-carbonates replace fayalite as aqueously formed minerals defining the trend $\delta^{17}O = (0.66 \pm 0.05) \times \delta^{18}O$ -

(4.7 ± 1.5) (Verdier-Paoletti et al., 2017). This implies that isotopic equilibrium between ^{16}O-rich anhydrous silicates and ^{17}O- and ^{18}O-rich water controls the O-isotopic evolution of bulk CM chondrites and their secondary alteration mineral. To the first order, isotopic equilibrium dominates, with temperature gradients having a lesser effect in establishing the isotopic composition of CV and CM chondrites. Consequently, the isotopic compositions of secondary minerals are mainly controlled by the extent of isotopic exchange between water of initial composition and anhydrous silicates (Clayton and Mayeda, 1984; Verdier-Paoletti et al., 2017). In such a scheme, ^{17}O- and ^{18}O-rich secondary minerals correspond to early precipitates from primitive fluids that had not yet suffered significant O-isotopic exchange with anhydrous silicates.

In CM chondrites, the O-isotopic compositions of alteration water inferred from direct measurements and mass balance calculations define a continuous trend, parallel within errors to that of bulk CMs and Ca-carbonates, but with a different intercept ($\delta^{17}O = (0.69 \pm 0.02) \times \delta^{18}O - (2.12 \pm 0.30)$; (Verdier-Paoletti et al., 2017). This difference in intercepts is directly related to the isotopic fractionation factor, reflecting an average calculated precipitation temperature of 110°C for CM Ca-carbonates (Verdier-Paoletti et al., 2017). Similarly, Ca-carbonates of the Murchison and Mighei CM chondrites define a trend parallel to the CM water line, but with an intercept in good agreement, within errors, to that reported for 9 different CM chondrites ($\delta^{17}O = (0.70 \pm 0.03) \times \delta^{18}O - (5.65 \pm 1.25)$ (Fig. 4A: (Lindgren et al., 2017; Verdier-Paoletti et al., 2017). Such results allow calculation of the O-isotopic composition of the fluid from which a given carbonate precipitated by connecting the Ca-carbonate trend to the CM water line by a mass-dependent line (see (Verdier-Paoletti et al., 2017) for further details). Using the bulk O-isotopic composition of Murchison and Mighei (i.e., 7.3 and 7.6‰, respectively; (Clayton and Mayeda, 1999) and the O-isotopic composition of anhydrous CM silicates as plausible CM protolith (i.e., $\delta^{18}O$ = -4.2‰; (Clayton and

335 Mayeda, 1999), we calculate the water/rock ratio (Eqn. 3) assuming that the lowest Ca-
336 carbonate $\delta^{18}O$ value in a given CM chondrite represent the final $\delta^{18}O$ value of water
337 (weighted by 14.6‰, representing 1000 $\ln\alpha_{calcite\text{-}water}$ at 110°C). Murchison and Mighei thus
338 show water/rock ratios of 0.32 and 0.36, respectively, in good agreement with previous
339 estimates for CM2 chondrites (i.e., 0.3-0.6; (Clayton and Mayeda, 1984; Zolensky et al.,
340 1997).

341 With the exception of few Ca-carbonates enriched in ^{17}O- and ^{18}O relative to the main
342 carbonate trend (Vacher et al., 2016), the O-isotopic characteristics of secondary mineral in
343 CM chondrites indicate a dominant local origin of water during accretion (Alexander et al.,
344 2012). Near terrestrial $\Delta^{17}O$ values of the CM water line (-1 to + 4 ‰; Fig. 4B) confirm a
345 local water origin. Consequently, the contribution in CM chondrites of water coming from
346 large heliocentric distances is probably limited to few %. Such contributions could have been
347 overprinted by water inherited from the inner Solar System, as indicated by the hydrogen
348 isotopic composition of CM chondrites (Piani et al., 2017).

349
350 *4.2.2 CR chondrites*
351

352 Of the carbonaceous chondrites, CR chondrites are of primary importance because
353 they exhibit low degree of aqueous alteration and thermal metamorphism (Le Guillou and
354 Brearley, 2014). Nonetheless, they experienced significant alteration as attested by the
355 corrosion of Fe-Ni metal beads (Morlok and Libourel, 2013) and the presence of Ca-
356 carbonates (Brearley, 2006). Interestingly, CR chondrites show similar O-isotopic
357 characteristics as CV and CM chondrites, with bulk and Ca-carbonates O-isotopic
358 compositions defining the trend with $\delta^{17}O = (0.63 \pm 0.02) \times \delta^{18}O - (2.22 \pm 0.26)$ (Fig. 5A;
359 (Clayton and Mayeda, 1984; Jilly, 2015; Schrader et al., 2011). This similarity attests the

ubiquitous nature of O-isotopic exchange as the main physical process controlling the O-isotopic compositions of carbonaceous chondrites, whatever the extent of alteration.

Magnetite in CR chondrites is sometimes in close association with Ca-carbonates (Brearley, 2006; Jilly, 2015). Within a given CR chondrite, the two fall on a mass-dependent line (e.g., GRO 95577; Fig. 5B) with $\Delta^{17}O \sim 0$ ‰ (Jilly, 2015; Jilly et al., 2014), indicating that they probably formed at isotopic equilibrium from the same fluid reservoir. Assuming such equilibrium, the fractionation factor between carbonates (cc) and magnetite (mt) $\Delta^{18}O_{mt\text{-}cc}$ (i.e., $\delta^{18}O_{mt} - \delta^{18}O_{cc}$) is a function of their formation temperature (Chacko et al., 2001):

$$\Delta^{18}O_{mt\text{-}CC} = (-2.10 \times 10^{-4}\ T^{-2}) + (0.12\ T) - 34.46 \qquad (4)$$

Based on data from different CR chondrites (Jilly, 2015), this calculation provides a formation temperature estimate of 15–110°C, in good agreement with previous estimations of 50–150°C (Zolensky et al., 1993). At those temperature, we compute the O-isotopic compositions of water from which carbonates and magnetite formed in the different CR chondrites (Jilly, 2015; Jilly et al., 2014). CR water thus (i) defines a trend with $\delta^{17}O = (0.61 \pm 0.03) \times \delta^{18}O + (0.42 \pm 0.15)$ (Fig. 6A) and (ii) is characterized by $\Delta^{17}O \sim 0$ ‰, consistent with water originating from the inner Solar System. Interestingly, the CR water trend estimated from the O-isotopic compositions of Ca-carbonates and magnetite perfectly aligns with the estimation of the O-isotopic composition of water accreted by CM chondrites (Clayton and Mayeda, 1999; 1984) (Fig. 5A). This suggests that both types of chondrites could have accreted similar water, implying that the $\delta^{17}O$ and $\delta^{18}O$ values of initial CM water could be used to estimate the CR chondrite W/R ratios.

Definition of the CR water line allows calculation of the O-isotopic composition of the specific fluid from which a given CR carbonate precipitated, as their respective O-isotopic

compositions are related by a mass-dependent relationship. This further allows estimation of the water/rock ratio by assuming that (i) the lowest O-isotopic composition of bulk CR chondrites represent the $\delta^{18}O$ of the CR protolith (i.e., -2.29‰; Fig. 5A; (Schrader et al., 2011) and (ii) the initial CR water is similar to that accreted by CM chondrites (i.e., 30‰; (Clayton and Mayeda, 1984). This leads to a maximum estimation of the CR water/rock ratio in the range 0.10 to 0.40, lower than previous values of 0.4-1.1 (Zolensky et al., 1993).

4.2.3 CO chondrites

The case of CO chondrites is more complex than other carbonaceous chondrites. First, CO chondrites have experienced minimal fluid alteration; some show no evidence of alteration, whereas others exhibit alteration features at the sub-micrometer scale (Brearley, 2006). Rare secondary phases (phyllosilicates, fine-grained serpentine and saponite) are mainly located within the CO matrices (Brearley, 2006). Secondly, the bulk O-isotopic compositions of CO chondrite finds could have been affected by terrestrial weathering, inducing a shift toward ^{17}O- and ^{18}O-rich values (Greenwood and Franchi, 2004). Finally, a recent report of the bulk O-isotopic composition of CO chondrite falls show they are slightly shifted toward the CCAM line (Alexander et al., 2017) relative to previous measurements (Clayton and Mayeda, 1999; Greenwood and Franchi, 2004) (Fig. S1). The reason for such a shift remains unclear but could be linked to incomplete fluorination in previous measurements (Alexander et al., 2017). However, several observations can be used to improve our understanding of CO chondrites. (i) Considering the data reported by (Clayton and Mayeda, 1999; Greenwood and Franchi, 2004), the bulk O-isotopic compositions of CO chondrite falls show a significant deviation from the primordial slope 1 with $\delta^{17}O = (0.65 \pm 0.12) \times \delta^{18}O - (4.19 \pm 0.27)$ (Fig. 6A; $r^2 = 0.89$, MSWD = 7.6). (ii) This trend is similar to the one defined by CM chondrites (Fig. 6A). Although recent report suggest that CM and CO chondrites

could originate from distinct parent bodies (Schrader and Davidson, 2017), they probably formed in a common region within the accretion disk; the anhydrous precursors of CM2 were CO3-like, but CM accreted more water (Hewins et al., 2014). (iii) Taken together, the CM and CO falls define a trend with $\delta^{17}O = (0.69 \pm 0.04) \times \delta^{18}O - (4.05 \pm 0.18)$ (Fig. 6A; r^2 = 0.98, MSWD = 15). Although the bulk O-isotopic compositions of CO chondrites are more restricted than those of CM chondrites (Fig. 6a), they might have recorded fluid alteration processes. (iv) The absence of secondary phases that could be targeted by ion probe measurements precludes the possibility of combining bulk and mineral data (as reported for CV, CM and CR chondrites). However, MacAlpine Hills (MAC) 88107, a CO-like chondrite, shows abundant near-pure fayalite and magnetite (Krot et al., 2000) that can be used to estimate the isotopic characteristics of CO water. The O-isotopic compositions of fayalite from MAC 88107 fall along the trend defined by the bulk CM and CO chondrites, $\delta^{17}O = (0.69 \pm 0.03) \times \delta^{18}O - (4.01 \pm 0.21)$ (Fig. 6A; r^2 = 0.98, MSWD = 15). These observations suggest that the O-isotopic characteristics of CO chondrites were established by O-isotopic exchange between anhydrous silicates and significantly less water than the other groups of carbonaceous chondrites.

Magnetite and fayalite in MAC 88107 plot along a mass-dependent fractionation line with $\delta^{17}O = (0.48 \pm 0.02) \times \delta^{18}O - (1.10 \pm 2.05)$ (Fig. 6B; r^2 = 0.84, MSWD = 0.56), interpreted as formation at isotopic equilibrium with the same fluid reservoir (Doyle et al., 2015). Based on O-isotopic compositions and mineralogical, petrographic and thermodynamic constraints, it has been proposed that fayalite and magnetite formed at low water/rock ratios (0.1–0.2) and relatively elevated temperature (100–200°C; (Doyle et al., 2015). However, considering the average $\delta^{18}O$ values of magnetite and fayalite (i.e., 10.2 ± 1.3‰ and 14.1 ± 0.6‰, respectively), the observed $\Delta^{18}O_{mt\text{-}Fa}$ (= $\delta^{18}O_{mt} - \delta^{18}O_{Fa}$) rather suggests a formation temperature of 480 ± 20°C (Chacko et al., 2001). Considering even the

larger $\Delta^{18}O_{mt\text{-}Fa}$ (Doyle et al., 2015) leads to an estimate temperature of ~250°C, significantly higher than that previously estimated for CO chondrites (i.e., 0–50°C) (Zolensky et al., 1993). Whatever the alteration temperature of MAC 88107, the fractionation factor $\alpha_{Fa\text{-}water}$ is relatively small (i.e., 3.4‰ at 100°C and -3.6‰ at 500°C) (Zheng, 1993), allowing the final O-isotopic composition of CO water to be computed at $\delta^{18}O$ of 15 ± 3.5‰. Although the bulk O-isotopic composition of MAC 88107 has not been determined, it is possible to estimate the water/rock ratio of CO chondrites by following some reasonable assumptions. Considering that MAC 88107 likely has a bulk O-isotopic composition falling in the lower range observed for CO chondrites (i.e., -4 to -2‰) and assuming that COs have similar initial water and anhydrous protolith as CMs (+30.3 and -4.2 ‰, respectively; (Clayton and Mayeda, 1984), the water/rock estimated for MAC 88107 range from 0.01 to 0.10. These values are consistent with previous estimates (Zolensky et al., 1993) and the limited alteration of CO chondrites relative to CV and CM. However, it should be kept in mind that the lack of secondary phases in CO chondrites makes this estimation less robust than those reported for CM, CR and CV chondrites.

4.3 Implications for the structure and evolution of the accretion disk

All carbonaceous chondrites show varying degrees of fluid alteration suggesting that water ice grains were significant components of their parent bodies. By combining bulk and mineral O-isotope data, we estimate the water/rock ratios of carbonaceous chondrites to be: CM (0.3-0.4) ≥ CR (0.1–0.4) ≥ CV (0.1–0.2) > CO (0.01–0.10) (Fig. 7). Our results suggest that water was heterogeneously distributed across the chondrite accretion regions. Current debate considers carbonaceous chondrites formation either in the main asteroid belt (Alexander et al., 2012) or in the outer Solar System (i.e., 5–15 UA) before subsequent implantation into the main belt during the dynamic evolution of the Solar System (the Grand

463 Tack model; (Walsh et al., 2011). The low water/rock ratios estimated in this study support
464 carbonaceous chondrite accretion close to the snowline as accretion at greater heliocentric
465 distances would have induced a solar water/rock ratio of 1.2 (Lodders, 2003). The low
466 carbonaceous chondrite water/rock ratios suggest that the snowline did not drift closer to the
467 Sun than the inner edge of the asteroid belt (Morbidelli et al., 2016) and was probably located
468 at 2–3 AU during the accretion of the carbonaceous asteroid, ~2–4 My after the formation of
469 CAIs (Krot et al., 2015).

470 The majority of secondary minerals in carbonaceous chondrites show O-isotopic
471 signatures that are consistent with accretion of locally derived water from the inner Solar
472 System. Such water presents minimal mass-independent O-isotopic variations (i.e., $\Delta^{17}O \sim$
473 0‰), contrary to outer water ices enriched in ^{17}O- and ^{18}O ($\Delta^{17}O >> 0\%$), implying that water
474 ice originating from the outer Solar System was not the main source for water in
475 carbonaceous chondrites (Yurimoto and Kuramoto, 2004). This conclusion is consistent with
476 D-poor compositions of carbonaceous chondrite waters (Alexander 2012, Piani 2017). Based
477 on the expected heliocentric D/H gradient ratio in the accretion disk (Jacquet and Robert,
478 2013), both H and O isotopes suggest an inner Solar System origin of water accreted into
479 carbonaceous chondrite, probably where carbonaceous asteroids are located today (Alexander,
480 2017).

481 The low influx of ^{17}O- and ^{18}O-rich and D-rich water ice from the outer part of the
482 Solar System may be due to the early growth of Jupiter (≈ 1My after the start of the Solar
483 System), which would have prevented inward radial drift in the protoplanetary disk (Walsh et
484 al., 2011). An inner Solar System origin of carbonaceous chondrites is consistent wit their
485 type I chondrules containing olivines with Mg#>90, suggesting formation at relatively low
486 oxygen fugacity, whereas formation beyond the orbit of Jupiter should have occurred under
487 more oxidizing conditions. Contrary to these conclusions, (Kruijer et al., 2017) attribute the

molybdenum and tungsten isotopic compositions of iron meteorites derived from a carbonaceous meteorite reservoir to a late addition of W- and Mo-bearing presolar material to the outer Solar System. However, presolar grains (generally < 20 μm in size), being tightly coupled to gas motions (i.e., particles < 150 μm in size; Fig. 8C) might have crossed Jupiter's orbit and reached the inner Solar System (Zhu et al., 2012). As the carrier phases of Mo and W isotope anomalies (Kruijer et al., 2017), presolar grains could have thus been preferentially incorporated into asteroids accreting near the snow line, i.e. carbonaceous chondrites (Fig. 8D). Chondrites forming at smaller heliocentric distances and/or earlier in the history of the protoplanetary disk would have incorporated a different population of presolar grains. Ordinary chondrites are consistent with such an origin, as their potential earlier onset of aqueous activity (Krot et al., 2015; Sugiura and Fujiya, 2014) as well as D-rich water and organic matter relative to carbonaceous chondrites (Piani et al., 2015) could have resulted from accretion before the Jupiter-induced gap in the protoplanetary disk. Additionally, ordinary chondrites contain more type II chondrules characterized by low Mg# olivines (i.e., Mg# < 90) than carbonaceous chondrites, indicating their formation in more oxidizing environments.

Carbonaceous chondrites and their water are thus by-products of the evolution of the inner Solar System. The O-isotopic composition of water produced via self-shielding photodissociation decreases with time and increasing heliocentric distance in the accretion disk, becoming similar to that observed in carbonaceous chondrites after 1 My (Yang et al., 2011). Consequently, the O-isotopic of water upon the accretion of hydrated carbonaceous parent bodies (i.e., 2–4 Ma; (Sugiura and Fujiya, 2014) should have been smoothed toward Earth-like values, potentially via re-equilibration with silicates in the disk (Alexander, 2017; Yurimoto and Kuramoto, 2004). Inner solar water accreted by hydrated carbonaceous asteroids may be ice condensed at the snow line and/or liquid water adsorbed at the grain

surfaces. The increasing water/rock ratios of CO, CV, CR, and CM reflects that these classes of carbonaceous asteroids accreted near to the snow line, but at increasing heliocentric distances. We note that some Ca-carbonates of the least altered CM chondrite Paris have peculiar O-isotopic compositions suggesting accretion of few percent water ice grains originating 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). These results suggest limited but significant contribution of outer Solar System materials to the chondrite-forming regions. Interestingly, CV chondrites may have accreted ^{17}O- and ^{18}O-rich water (i.e., $\Delta^{17}O > 15‰$) during their formation ≈ 1My before the more hydrated carbonaceous chondrites (Sugiura and Fujiya, 2014). It is possible that inward radial mixing was more efficient at the time of CV chondrite accretion but significantly decreased upon the formation of Jupiter, which limited later contribution of outer water ices in favor of locally derived water in the accretion zones of carbonaceous asteroids.

5- Concluding remarks

We report the oxygen isotopic composition of sulfide- and magnetite-free, nearly pure fayalite grains in CV chondrites Kaba and Mokoia. When combined with both the bulk and matrix O-isotopic compositions of CV chondrites, their O-isotopic composition define the continuous trend $\delta^{17}O = (0.84 \pm 0.03) \times \delta^{18}O - (4.25 \pm 0.1)$. This implies that the process controlling the O-isotopic composition of the CV chondrite parent body was related to isotopic equilibrium between ^{16}O-rich anhydrous silicates and ^{17}O- and ^{18}O-rich fluid. Similar behaviors are observed in CM, CR and CO chondrites, demonstrating the ubiquitous nature of O-isotopic exchange as the main physical process controlling the O-isotopic features of carbonaceous chondrites, regardless of the extent of alteration. Based on these results, we estimate the abundance of water accreted by carbonaceous chondrites (quantified by the

water/rock ratio) to be CM (0.4) ≥ CR (0.1–0.4) ≥ CV (0.1–0.2) > CO (0.01–0.10). This suggests a heterogeneous distribution of water in the accretion zone of carbonaceous asteroids. The relatively low water/rock ratios estimated for carbonaceous chondrites indicate their accretion near the snowline, in the inner Solar System, as accretion further out in the disk would have induced solar water/rock ratio of 1.2. Most of aqueously formed minerals in carbonaceous chondrites show O-isotopic characteristics consistent with accretion of local water, likely formed from the condensation of the gas near the snowline and/or liquid water adsorbed at the grain surfaces. These results provide no evidence of carbonaceous chondrite formation beyond the orbit of Jupiter and imply a limited influx of D- and ^{17}O- and ^{18}O-rich water ice grains from the outer part of the Solar System. Such a limited influx might result from a gap in the solar protoplanetary disk due to the early and rapid formation of Jupiter, which would limit the inward motion of particles with size higher than 150 µm. This model accounts for the O- and H-isotopic signatures of carbonaceous chondrites, and suggest their accretion in the inner Solar System, closer to Jupiter than non-carbonaceous chondrites. Hence, carbonaceous chondrites would have preferentially accreted W- and Mo-bearing presolar grains crossing the orbit of Jupiter, resulting in significant lower W- and Mo-anomalies in non-carbonaceous meteorites. Among carbonaceous chondrites, only CV chondrites show O-isotopic features compatible with accretion of $^{17\text{-}18}$O-rich water, possibly related to their older accretion age relative to other hydrated carbonaceous chondrites.

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Figure Caption

Fig. 1: Back-scattered electron micrographs of fayalite grains in the Kaba CV chondrite. (A) Fayalite grains located in the chondrule rim in association with iron sulfides and isolated in the matrix. OA = opaque assemblage. (B) Sulfide- and magnetite-free fayalite grain commonly observed in the Kaba and Mokoia matrices.

Fig. 2: Oxygen three-isotope plot for bulk and matrix CV chondrites (Clayton and Mayeda, 1999; 1984; Greenwood et al., 2010) and sulfide- and magnetite-free fayalite grains from Mokoia and Kaba. Oxygen isotopic variations are expressed in delta units as deviations of the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ isotopic ratios relative to the V-SMOW international standard ($\delta^{X}O=(^{X}O/^{16}O/^{X}O^{16}O_{V\text{-}SMOW}\text{-}1)\times1000$; x=$^{18}O$ or ^{17}O). Two different lines (PCM = Primary Chondrules Minerals and TFL) are shown (see text). The O-isotopic compositions of fayalite in CV chondrite A-881317 (Doyle et al., 2015) and Kaba ((Krot and Nagashima, 2016), corresponding to * in the figure caption) are also represented. CV water corresponds to the O-isotopic composition from which fayalite grains have precipitated according to the fractionation factor α (Zheng, 1993). Uncertainties shown are 2σ. (B) $\Delta^{17}O$ values (see text) of bulk, matrix and fayalite in CV chondrites. The data are plotted arbitrarily along the x-axis. Uncertainties shown are 2σ.

Fig. 3: (A) Oxygen three-isotope plot for bulk and matrix CV chondrites ((Clayton and Mayeda, 1999; 1984)) and fayalite grains from Mokoia, Kaba and A-881317 (Doyle et al., 2015). The O-isotopic composition of magnetite in Kaba chondrules (Marrocchi et al., 2016) and in the matrix of A-881317 (Doyle et al., 2015) and Kaba (Krot and Nagashima, 2016) are also represented. Uncertainties shown are 2σ. (B) $\Delta^{17}O$ values of bulk, matrix, fayalite and magnetite in the CV chondrites Kaba, Mokoia and A881317. The similar $\Delta^{17}O$ observed between fayalite and magnetite in A-881317 indicate that they probably formed at isotopic equilibrium from the same fluid reservoir. To the contrary, fayalite and magnetite in Kaba show significantly different $\Delta^{17}O$ that could be linked to the formation of magnetite during the high-temperature chondrule-forming event (Marrocchi et al., 2016). Uncertainties shown are 2σ.

Fig. 4: (A) Oxygen three-isotope plot of Ca-carbonates in CM chondrites Murchison and Mighei (Lindgren et al., 2017). The O-isotopic compositions of Ca-carbonates define the trend $\delta^{17}O = (0.70 \pm 0.03) \times \delta^{18}O - (5.65 \pm 1.25)$, similar, within errors, to that reported for 9 different CM chondrites (Verdier-Paoletti et al., 2017). The O-isotopic compositions of CM alteration water inferred from direct measurements and mass balance calculations define a continuous trend, parallel within errors to that shown by bulk CMs and Ca-carbonates, but with a different intercept ($\delta^{17}O = (0.69 \pm 0.02) \times \delta^{18}O - (2.12 \pm 0.30)$). As both trends are parallel, the temperature of carbonate precipitation can be determined (see text). Uncertainties shown are 2σ. (B) $\Delta^{17}O$ values of inferred CM water showing the near terrestrial values of water accreted by CM chondrites. Uncertainties shown are 2σ

Fig. 5: (A) Oxygen three-isotope plot of bulk, matrix and Ca-carbonates of CR chondrites (Clayton and Mayeda, 1999; Jilly, 2015; Jilly et al., 2014; Schrader et al., 2011). The O-

isotopic compositions of CR alteration water from which Ca-carbonates precipitated are also represented. CR water O-isotopic compositions were calculated based on the isotopic equilibrium between Ca-carbonates and magnetite per CR chondrite (represented in panel (B); data from Jilly, 2015). Uncertainties shown are 2σ.

Fig. 6: (A) Oxygen three-isotope plot of bulk and matrix in CO chondrites (Clayton and Mayeda, 1999). The O-isotopic compositions of fayalite grains in CO-like MacAlpine Hills 88107 are also represented (Doyle et al., 2015). Together, the data define the continuous trend with $\delta^{17}O = (0.68 \pm 0.08) \times \delta^{18}O - (4.08 \pm 0.14)$. CO water corresponds to the O-isotopic composition from which fayalite grains precipitated according to the fractionation factor α between fayalite and water (Zheng, 1993). Uncertainties shown are 2σ. (B) Oxygen isotopic compositions of magnetite and fayalite in CO-like chondrite MacAlpine Hills 88107 (Doyle et al., 2015) plot on a mass-dependent fractionation line, allowing the alteration temperature and the O-isotopic composition of the alteration water of this chondrite to be determined (CO water; see text for details). Uncertainties shown are 2σ.

Fig. 7: Schematic representation of the water/rock ratio estimated for the CO, CV, CR and CM chondrites.

Fig. 8: A) Coexistence and spatial separation of non-carbonaceous chondrite (NCC) and carbonaceous chondrite (CC) reservoirs as depicted by (Kruijer et al., 2017). The early formation of Jupiter (~1 Ma after the formation of the Solar System) would have acted as a barrier against inward transport of solids across the disk, and thus mixing of the CC and NCC reservoirs. (B) Key observables of the oxygen and hydrogen isotopic compositions in the protoplanetary disk are at odds with the model proposed by (Kruijer et al., 2017).

(C) Scenario proposed herein for the preservation of ^{16}O-rich and D-poor water in the inner solar system. Jupiter would have acted as a barrier precluding significant inward transport of outer Solar System water toward the inner Solar System. (D) Scenario proposed in this study for the accretion of ^{16}O-rich and D-poor water by hydrated carbonaceous asteroids. The increasing water/rock ratios of CO, CV, CR and CM chondrites reflect that these different types of carbonaceous asteroids accreted close to the snow line, at increasing heliocentric distances.

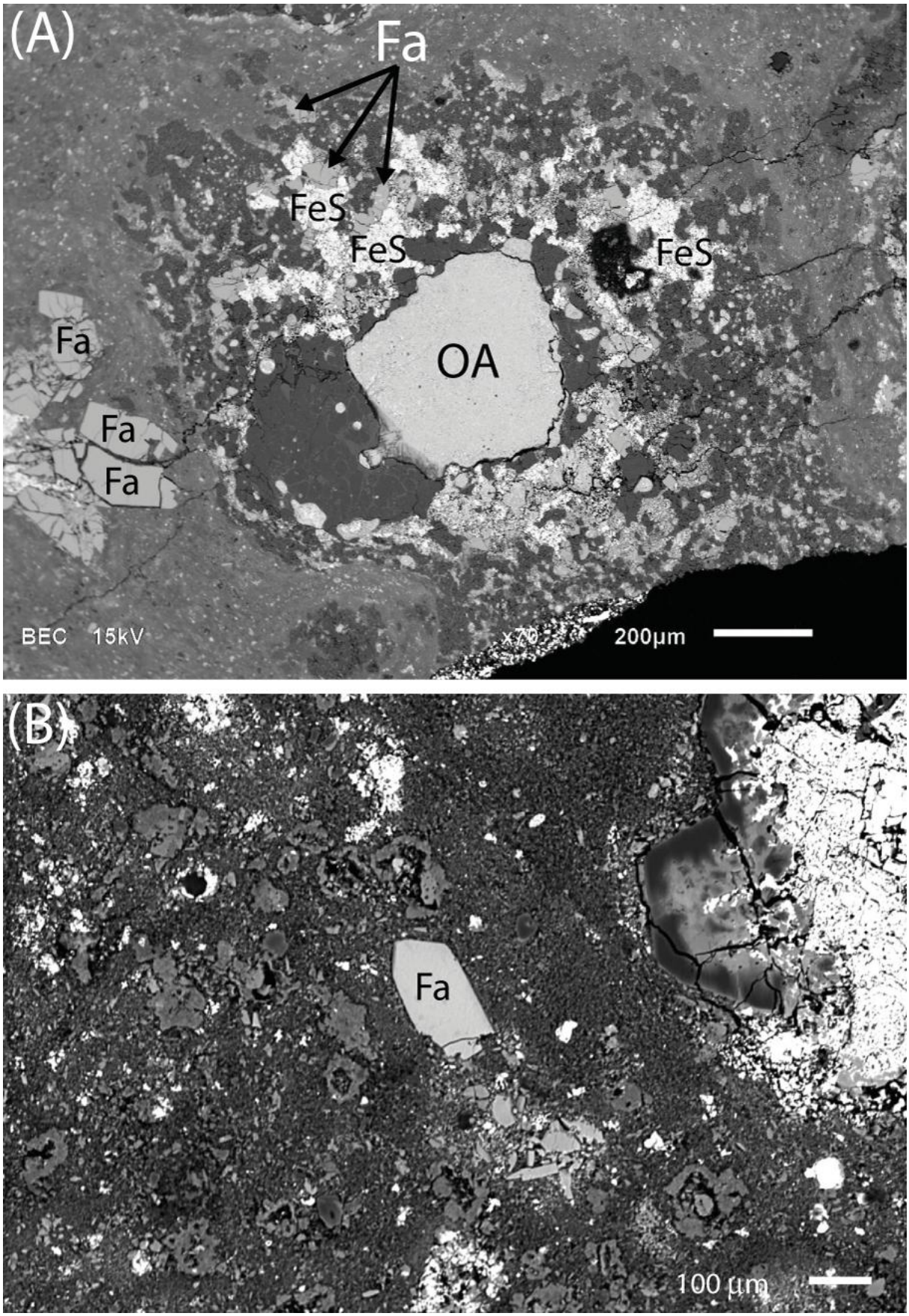


Fig. 1

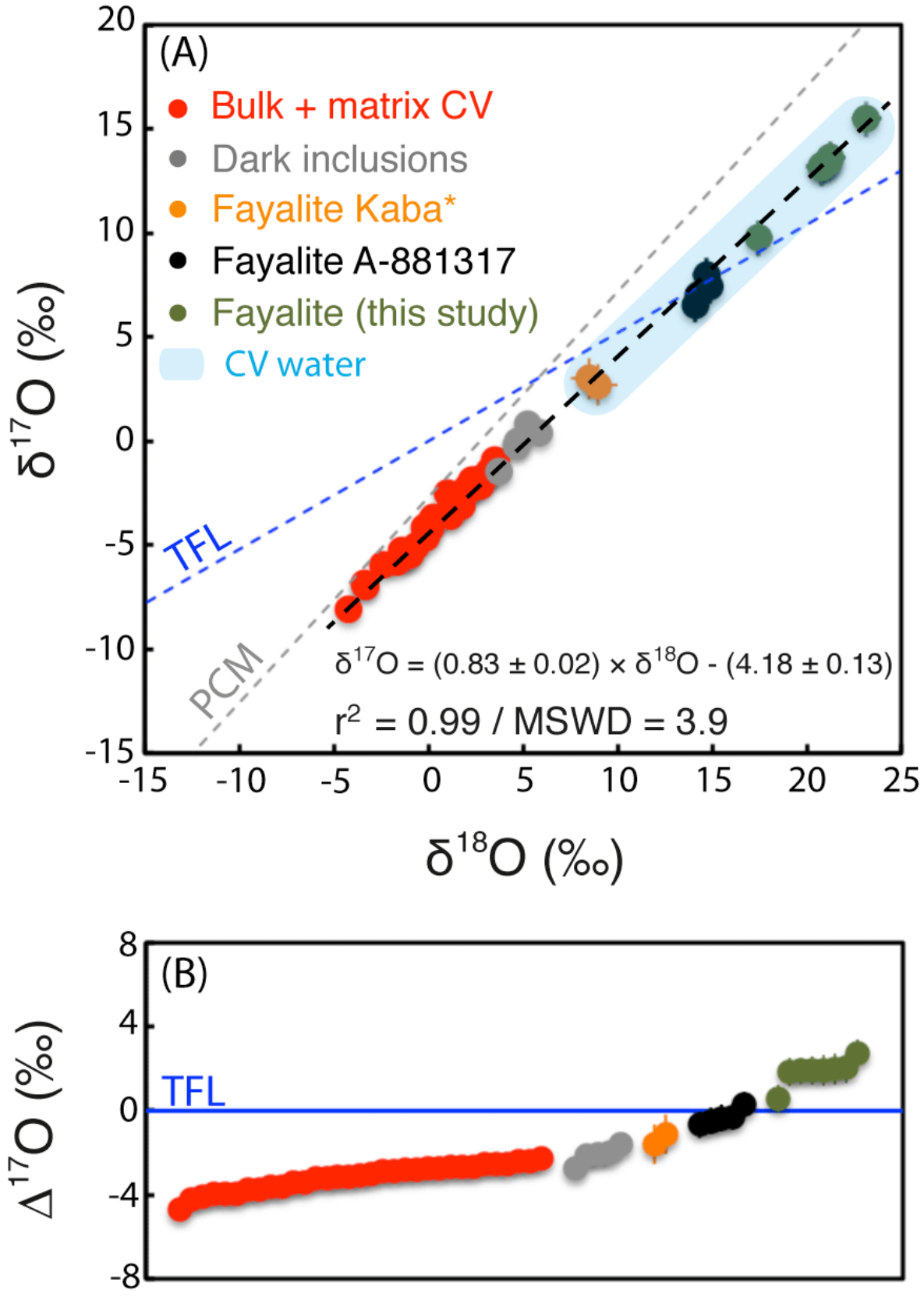

(A)
Bulk + matrix CV
Dark inclusions
Fayalite Kaba*
Fayalite A-881317
Fayalite (this study)
CV water
TFL
PCM
δ17O = (0.83 ± 0.02) × δ18O - (4.18 ± 0.13)
r2 = 0.99 / MSWD = 3.9
δ17O (‰)
δ18O (‰)
(B)
TFL
Δ17O (‰)

Fig. 2

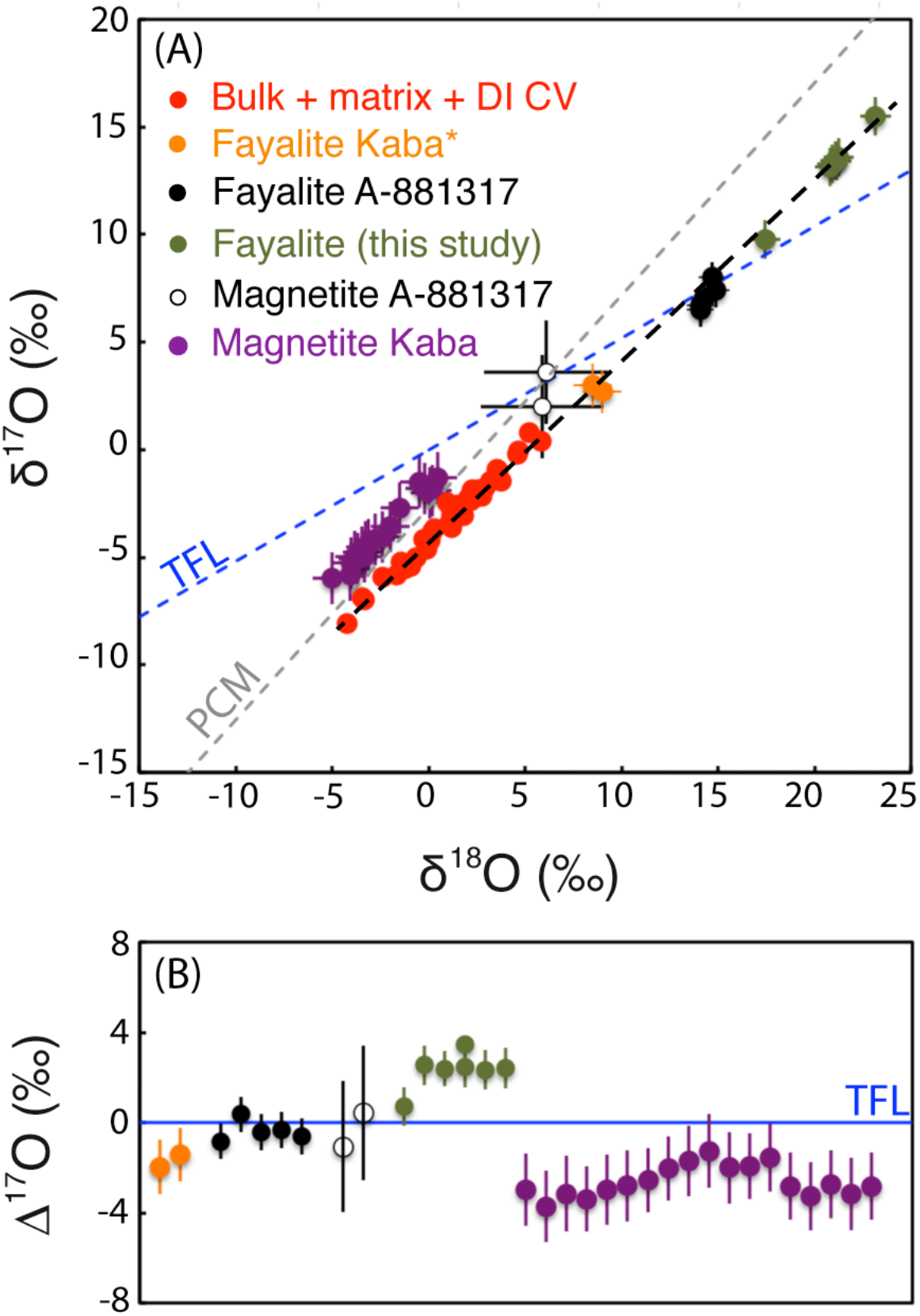

(A)
Bulk + matrix + DI CV
Fayalite Kaba*
Fayalite A-881317
Fayalite (this study)
Magnetite A-881317
Magnetite Kaba
TFL
PCM
δ17O (‰)
δ18O (‰)
(B)
TFL
Δ17O (‰)

Fig. 3

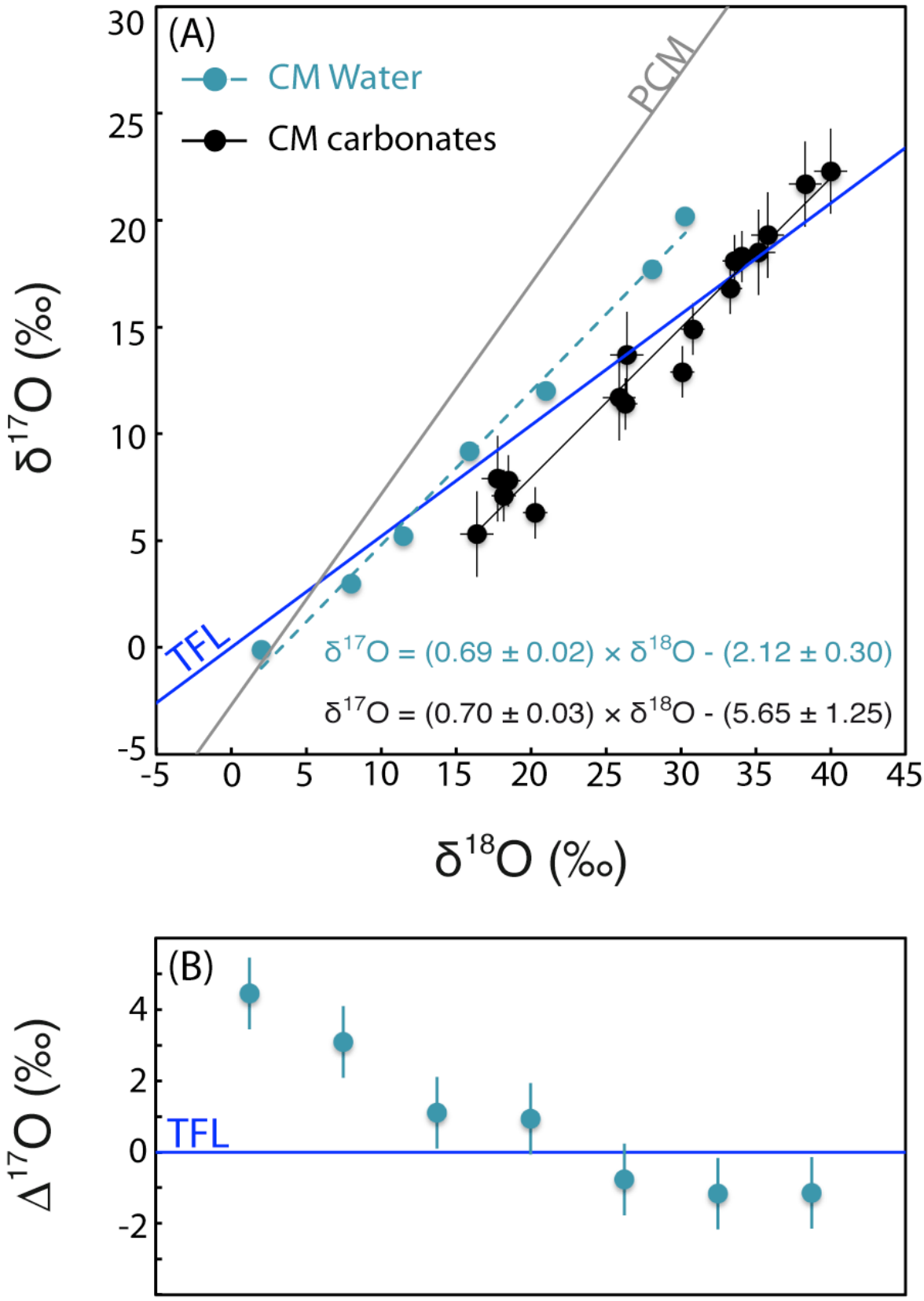

(A)
CM Water
CM carbonates
PCM
TFL
δ17O = (0.69 ± 0.02) × δ18O - (2.12 ± 0.30)
δ17O = (0.70 ± 0.03) × δ18O - (5.65 ± 1.25)
δ17O (‰)
δ18O (‰)
(B)
TFL
Δ17O (‰)

Fig. 4

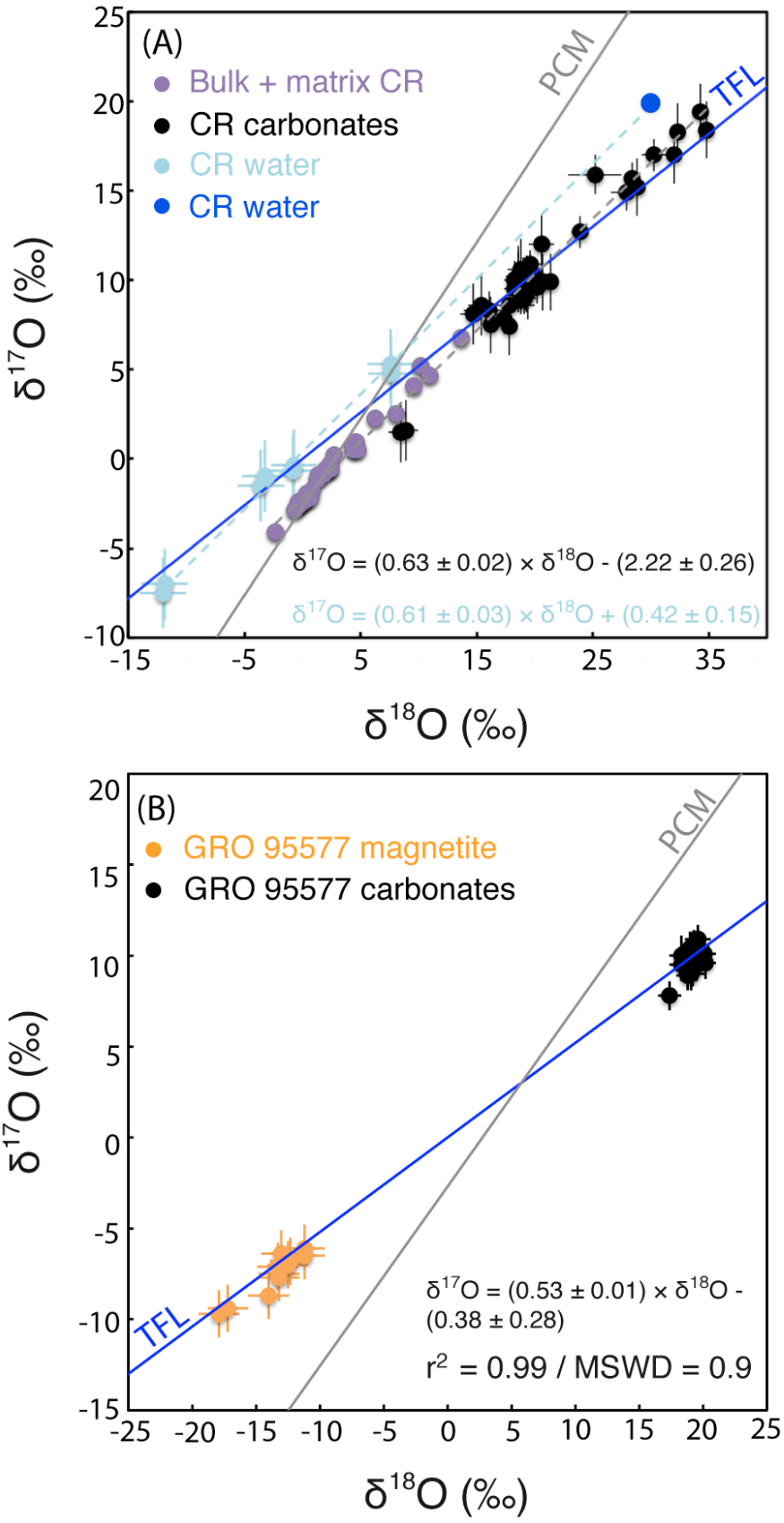
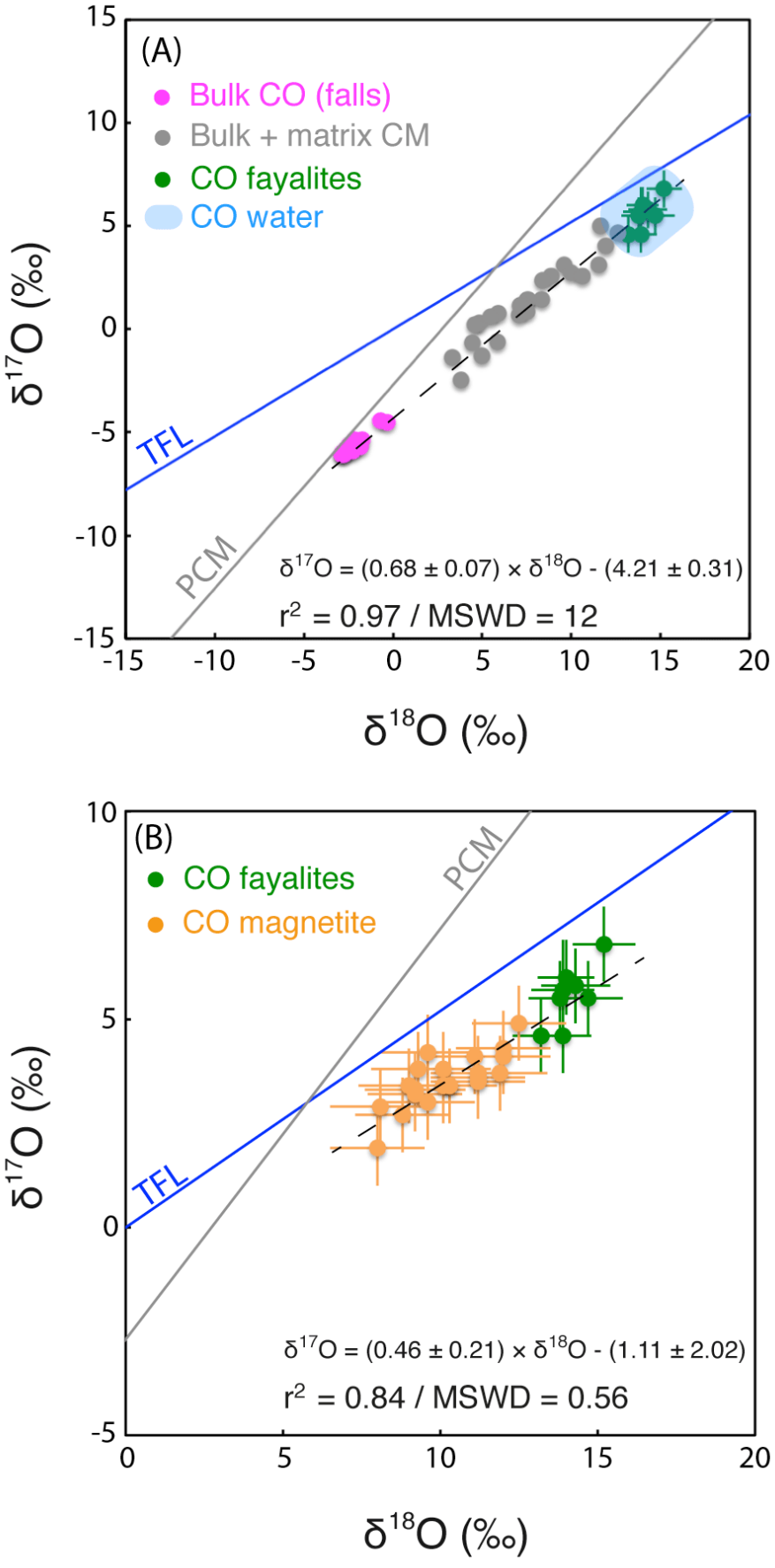

(A)
Bulk + matrix CR
CR carbonates
CR water
CR water
PCM
TFL
δ17O = (0.63 ± 0.02) × δ18O - (2.22 ± 0.26)
δ17O = (0.61 ± 0.03) × δ18O + (0.42 ± 0.15)
δ17O (‰)
δ18O (‰)
(B)
GRO 95577 magnetite
GRO 95577 carbonates
PCM
TFL
δ17O = (0.53 ± 0.01) × δ18O - (0.38 ± 0.28)
r2 = 0.99 / MSWD = 0.9
δ17O (‰)
δ18O (‰)

Fig. 5


(A)
Bulk CO (falls)
Bulk + matrix CM
CO fayalites
CO water
TFL
PCM
δ17O = (0.68 ± 0.07) × δ18O - (4.21 ± 0.31)
r2 = 0.97 / MSWD = 12
δ17O (‰)
δ18O (‰)
(B)
CO fayalites
CO magnetite
TFL
PCM
δ17O = (0.46 ± 0.21) × δ18O - (1.11 ± 2.02)
r2 = 0.84 / MSWD = 0.56
δ17O (‰)
δ18O (‰)

669
670

Fig. 6

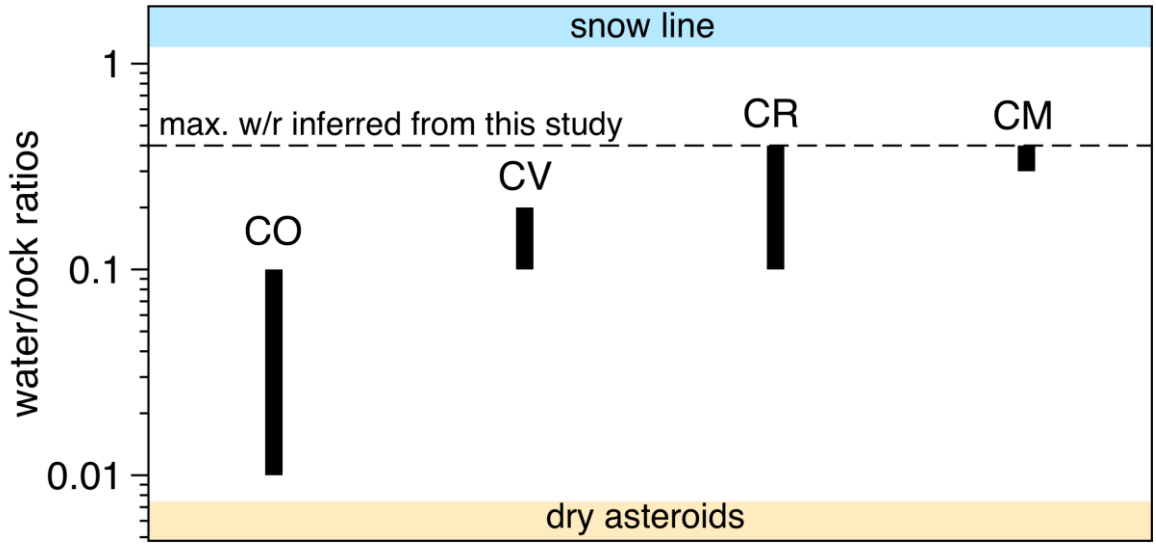
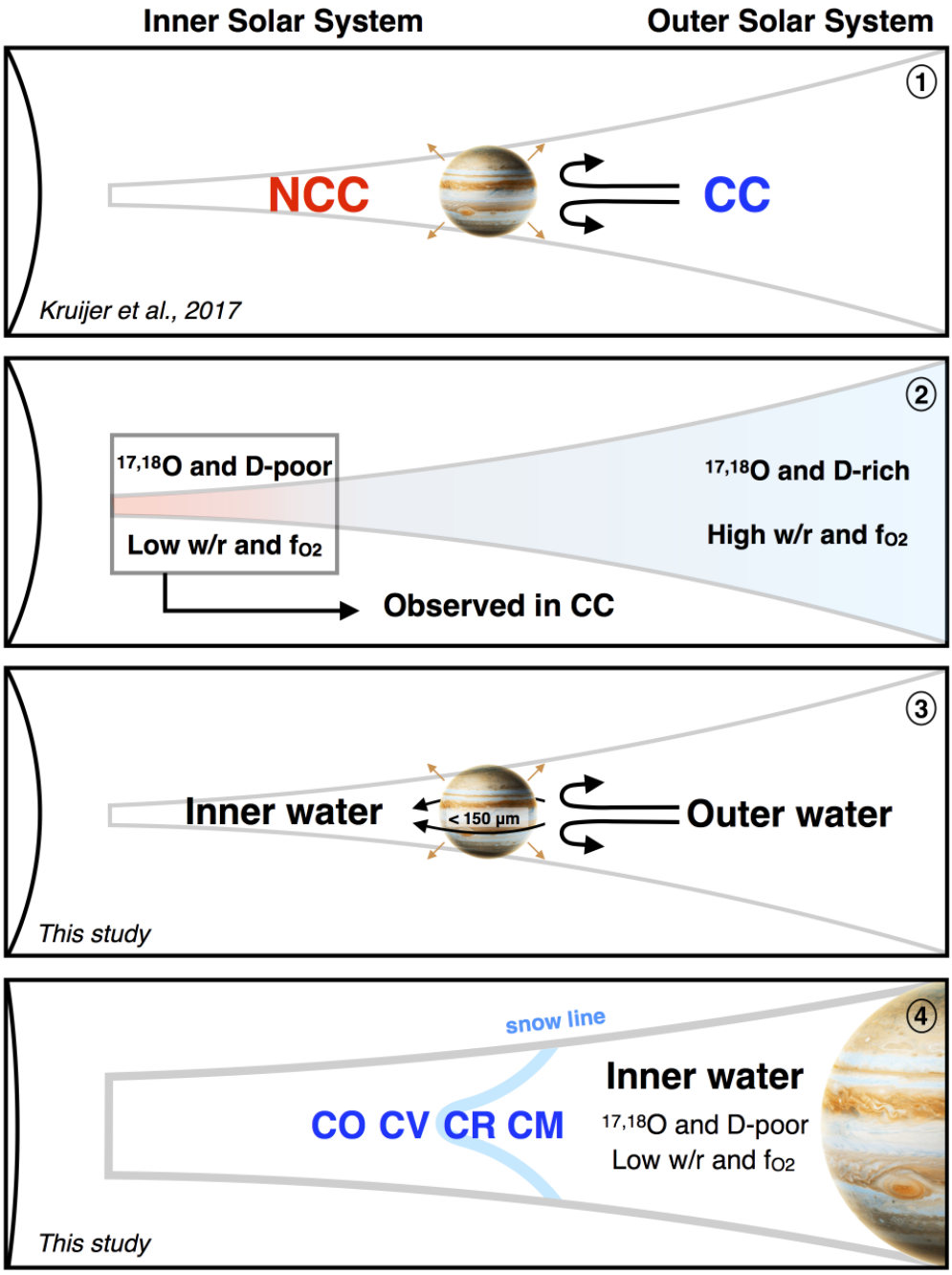

snow line
max. w/r inferred from this study
CO
CV
CR
CM
water/rock ratios
1
0.1
0.01
dry asteroids

Fig. 7


Inner Solar System
Outer Solar System
①
NCC
CC
Kruijer et al., 2017
②
17,18O and D-poor
Low w/r and fO2
17,18O and D-rich
High w/r and fO2
Observed in CC
③
Inner water
< 150 μm
Outer water
This study
④
snow line
CO CV CR CM
Inner water
17,18O and D-poor
Low w/r and fO2
This study

686
687

Fig. 8

chondrite	point	SiO_2	K_2O	FeO	Na_2O	Al_2O_3	CaO	MnO	MgO	Cr_2O_3	TiO_2	Total	Fa
Kaba	Fa-1	29.3	bdl	69.1	bdl	bdl	bdl	0.7	0.8	bdl	bdl	99.9	98.9
	Fa-2	29.4	bdl	69.4	bdl	bdl	bdl	0.4	0.6	bdl	bdl	99.7	99.2
	Fa-3	29.2	bdl	69.2	bdl	bdl	bdl	0.7	0.5	bdl	bdl	99.7	99.2
	Fa-4	29.0	bdl	69.6	bdl	bdl	bdl	0.7	0.0	bdl	bdl	99.4	100.0
	Fa-5	29.8	bdl	67.1	bdl	bdl	bdl	0.8	2.1	bdl	bdl	99.7	97.0
	Fa-6	29.5	bdl	68.2	bdl	bdl	bdl	1.2	0.8	bdl	bdl	99.6	98.9
Mokoia	Fa-7	29.2	bdl	68.8	bdl	bdl	bdl	0.6	1.2	bdl	bdl	99.8	98.3
	Fa-8	28.9	bdl	68.1	bdl	bdl	bdl	0.9	1.8	bdl	bdl	99.7	97.4

Table 1: Chemical composition and Fa# of fayalite grains observed in the Kaba and Mokoia CV chondrites

chondrite	point	$d^{18}O$	2s	$d^{17}O$	2s	$D^{17}O$	2s
Kaba	Fa-1	17.4	0.8	9.8	0.9	0.7	0.9
	Fa-2	21.3	0.8	13.6	0.9	2.5	0.9
	Fa-3	20.9	0.8	13.3	0.9	2.4	0.8
	Fa-4	21.1	0.8	13.4	0.9	2.5	0.9
	Fa-5	20.8	0.8	13.2	0.9	2.3	0.9
	Fa-6	21.2	0.8	13.4	0.9	2.4	0.9
Mokoia	Fa-7	23.2	0.8	15.5	0.9	3.5	0.8
	Fa-8	20.8	0.8	13.2	0.9	2.4	0.9

Table 2: Oxygen isotopic composition of fayalite grains in the Kaba and Mokoia CV chondrites. Uncertainties reported are 2σ.

References

Albarède, F., 2009. Volatile accretion history of the terrestrial planets and dynamic implications. Nature 461, 1227–1233. doi:10.1038/nature08477

Alexander, C.M.O., 2017. The origin of inner Solar System water. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 375, 20150384–20. doi:10.1098/rsta.2015.0384

Alexander, C.M.O'D, Bowden, R., Fogel, M.L., Howard, K.T., Herd, C.D.K., Nittler, L.R., 2012. The Provenances of Asteroids, and Their Contributions to the Volatile Inventories of the Terrestrial Planets. Science 337, 721–723. doi:10.1126/science.1223474

Alexander, C.M.O'D, Greenwood, R.C., Bowden, R., Gibson, J.M., Howard, K.T., Franchi, I.A., 2017. A mutli-technique search for the most primitive CO chondrites. Geochim. Cosmochim. Acta 1–15. doi:10.1016/j.gca.2017.04.021

Bitsch, B., Johansen, A., Lambrechts, M., Morbidelli, A., 2015. The structure of protoplanetary discs around evolving young stars. A&A 575, A28–17. doi:10.1051/0004-6361/201424964

Bland, P.A., Jackson, M.D., Coker, R.F., Cohen, B.A., Webber, J.B.W., Lee, M.R., Duffy, C.M., Chater, R.J., Ardakani, M.G., McPhail, D.S., McComb, D.W., Benedix, G.K., 2009. Why aqueous alteration in asteroids was isochemical: High porosity≠high permeability. Earth Planet. Sci. Lett. 287, 559–568. doi:10.1016/j.epsl.2009.09.004

Bonal, L., Quirico, E., Bourot-Denise, M., Montagnac, G., 2006. Determination of the petrologic type of CV3 chondrites by Raman spectroscopy of included organic matter. Geochim. Cosmochim. Acta 70, 1849–1863. doi:10.1016/j.gca.2005.12.004

Brearley, A.J., 2006. The action of water. Meteorites and the early solar system II. Edited by Lauretta D. S. and McSween H. Y. Tucson, Arizona: The University of Arizona Press. pp. 587–624.

Chacko, T., Cole, D.R., Horita, J., 2001. Equilibrium Oxygen, Hydrogen and Carbon Isotope Fractionation Factors Applicable to Geologic Systems. Reviews in Mineralogy and Geochemistry 43, 1–81. doi:10.2138/gsrmg.43.1.1

Choi, B.-G., Krot, A.N., Wasson, J.T., 2000. Oxygen isotopes in magnetite and fayalite in CV chondrites Kaba and Mokoia. Meteoritics & Planetary Science 35, 1239–1248. doi:10.1111/j.1945-5100.2000.tb01512.x

Clayton, R.N., Grossman, L., Mayeda, T.K., 1973. A Component of Primitive Nuclear Composition in Carbonaceous Meteorites. Science 182, 485–488. doi:10.1126/science.182.4111.485

Clayton, R.N., Mayeda, T.K., 1999. Oxygen isotope studies of carbonaceous chondrites. Geochim. Cosmochim. Acta 63, 2089–2104. doi:10.1016/s0016-7037(99)00090-3

Clayton, R.N., Mayeda, T.K., 1984. The oxygen isotope record in Murchison and other carbonaceous chondrites. Earth and Planetary Science Letters 67, 151–161. doi:10.1016/0012-821x(84)90110-9

Doyle, P.M., Jogo, K., Nagashima, K., Krot, A.N., Wakita, S., Ciesla, F.J., Hutcheon, I.D., 2015. Early aqueous activity on the ordinary and carbonaceous chondrite parent bodies recorded by fayalite. Nat Comms 6, 7444. doi:10.1038/ncomms8444

Garenne, A., Beck, P., Montes-Hernandez, G., Chiriac, R., Toche, F., Quirico, E., Bonal, L., Schmitt, B., 2014. The abundance and stability of "water" in type 1 and 2 carbonaceous chondrites (CI, CM and CR). Geochim. Cosmochim. Acta 137, 93–112. doi:10.1016/j.gca.2014.03.034

Greenwood, R.C., Franchi, I.A., 2004. Alteration and metamorphism of CO3 chondrites: Evidence from oxygen and carbon isotopes. Meteoritics & Planetary Science 39, 1823–1838. doi:10.1111/j.1945-5100.2004.tb00078.x

Greenwood, R.C., Franchi, I.A., Kearsley, A.T., Alard, O., 2010. The relationship between CK and CV chondrites. Geochim. Cosmochim. Acta 74, 1684–1705. doi:10.1016/j.gca.2009.11.029

Gundlach, B., Blum, J., 2015. The stickiness of micrometer-sied water-ce particles. The Astrophys. J. 798, 34–12. doi:10.1088/0004-637X/798/1/34

Güttler, C., Blum, J., Zsom, A., Ormel, C.W., Dullemond, C.P., 2010. The outcome of protoplanetary dust growth: pebbles, boulders, or planetesimals? A&A 513, A56–16. doi:10.1051/0004-6361/200912852

Hartmann, L., Calvet, N., Gullbring, E., D'Alessio, P., 1998. Accretion and the Evolution of T-Tauri Disks. The Astrophysical Journal. 495, 385–400. doi:10.1086/305277

Hewins, R.H., Bourot-Denise, M., Zanda, B., Leroux, H., Barrat, J.-A., Humayun, M., Göpel, C., Greenwood, R.C., Franchi, I.A., Pont, S., Lorand, J.-P., Cournède, C., Gattacceca, J., Rochette, P., Kuga, M., Marrocchi, Y., Marty, B., 2014. The Paris meteorite, the least altered CM chondrite so far. Geochim. Cosmochim. Acta 124, 190–222. doi:10.1016/j.gca.2013.09.014

Hua, X., Buseck, P.R., 1995. Fayalite in the Kaba and Mokoia carbonaceous chondrites. Geochim. Cosmochim. Acta 59, 563–578. doi:10.1016/0016-7037(94)00383-w

Jacquet, E., Robert, F., 2013. Water transport in protoplanetary disks and the hydrogen isotopic composition of chondrites. Icarus 223, 722–732. doi:10.1016/j.icarus.2013.01.022

Jilly, C.E., 2015. Timescales and conditions for the aqueous alteration of chondrites. Dissertation of the university of hawai‘i.

Jilly, C.E., Huss, G.R., Nagashima, K., 2014. Oxygen isotope fractionation among secondary calcite and magnetite in CR chondrites. 45th Lunar and Planetary Science Conference, Houston, USA. Abstract # 1642.

Jogo, K., Nakamura, T., Noguchi, T., Zolotov, M.Y., 2009. Fayalite in the Vigarano CV3 carbonaceous chondrite: Occurrences, formation age and conditions. Earth and Planetary Science Letters 287, 320–328. doi:10.1016/j.epsl.2009.08.014

Krot, A.N., Brearley, A.J., Petaev, M.I., Kallemeyn, G.W., Sears, D.W.G., Benoit, P.H., Hutcheon, I.D., Zolensky, M.E., Keil, K., 2000. Evidence for low- temperature growth of fayalite and hedenbergite in MacAlpine Hills 88107, an ungrouped carbonaceous chondrite related to the CM- CO clan. Meteoritics & Planetary Science 35, 1365–1386. doi:10.1111/j.1945-5100.2000.tb01522.x

Krot, A.N., Nagashima, K., 2016. Evidence for oxygen-isotope exchange in chondrules and refractory inclusions during fluid-rock interaction on the CV chondrite parent body. 79th Annual Meeting of the Meteoritical Society, Berlin, Germany. LPI Contribution No. 1921, id.6014

Krot, A.N., Nagashima, K., Alexander, C.M.O'D, Ciesla, F.J., Fujiya, W., Bonal, L., 2015. Sources of Water and Aqueous Activity on the Chondrite Parent Asteroids, in: Asteroids IV. University of Arizona Press, pp. 1–27. doi:10.2458/azu_uapress_9780816532131-ch033

Kruijer, T.S., Burkhardt, C., Budde, G., Kleine, T., 2017. Age of Jupiter inferred from the distinct genetics and formation times of meteorites. Proceedings of the National Academy of Sciences 201704461. doi:10.1073/pnas.1704461114

Le Guillou, C., Brearley, A., 2014. Relationships between organics, water and early stages of aqueous alteration in the pristine CR3.0 chondrite MET 00426. Geochim. Cosmochim. Acta 131, 344–367. doi:10.1016/j.gca.2013.10.024

Lindgren, P., Lee, M.R., Starkey, N.A., Franchi, I.A., 2017. Fluid evolution in CM carbonaceous chondrites tracked through the oxygen isotopic compositions of carbonates.

Geochim. Cosmochim. Acta 204, 240–251. doi:10.1016/j.gca.2017.01.048
Lodders, K., 2003. Solar system abundances and condensation temperatures of the elements. Astrophys. J. 591, 1220–1247. doi:10.1086/375492
Marrocchi, Y., Chaussidon, M., Piani, L., Libourel, G., 2016. Early scattering of the solar protoplanetary disk recorded in meteoritic chondrules. Science Advances 2, e1601001–e1601001. doi:10.1126/sciadv.1601001
Marrocchi, Y., Libourel, G., 2013. Sulfur and sulfides in chondrules. Geochim. Cosmochim. Acta 119, 117–136. doi:10.1016/j.gca.2013.05.020
Marty, B., 2012. The origins and concentrations of water, carbon, nitrogen and noble gases on Earth. Earth Planet. Sci. Lett. 313-314, 56–66. doi:10.1016/j.epsl.2011.10.040
Morbidelli, A., Bitsch, B., CRIDA, A., Gounelle, M., Guillot, T., Jacobson, S., Johansen, A., Lambrechts, M., Lega, E., 2016. Fossilized condensation lines in the Solar System protoplanetary disk. Icarus 267, 368–376. doi:10.1016/j.icarus.2015.11.027
Morlok, A., Libourel, G., 2013. Aqueous alteration in CR chondrites: Meteorite parent body processes as analogue for long-term corrosion processes relevant for nuclear waste disposal. Geochim. Cosmochim. Acta 103, 76–103. doi:10.1016/j.gca.2012.10.030
Oka, A., Nakamoto, T., Ida, S., 2011. Evolution of snowline in optically thick protoplanetary disks: Effects of water ice opacity and dust grain size. Astrophys. J. 738, 141–11. doi:10.1088/0004-637X/738/2/141
Piani, L., Robert, F., Beyssac, O., Binet L., Bourot-Denise, M., Derenne, S., Guillou, C.L., Marrocchi, Y., Mostefaoui, S., Rouzaud, J.-N., Thomen, A., 2011. Structure, composition, and location of organic matter in the enstatite chondrite Sahara 97096 (EH3). Meteoritics & Planetary Science 47, 8–29. doi:10.1111/j.1945-5100.2011.01306.x
Piani, L., Robert, F., Remusat, L., 2015. Micron-scale D/H heterogeneity in chondrite matrices: A signature of the pristine solar system water? Earth Planet. Sci. Lett. 415, 154–164. doi:10.1016/j.epsl.2015.01.039
Piani, L., Yurimoto, H., Remusat, L., 2017. A Dual Origin for Water in the CM Carbonaceous Chondrites. 48th Lunar and Planetary Science Conference, Houston, USA. Abstract # 1203.
Ros, K., Johansen, A., 2013. Ice condensation as a planet formation mechanism. A&A 552, A137–14. doi:10.1051/0004-6361/201220536
Sakamoto, N., Seto, Y., Itoh, S., Kuramoto, K., Fujino, K., Nagashima, K., Krot, A.N., Yurimoto, H., 2007. Remnants of the Early Solar System Water Enriched in Heavy Oxygen Isotopes. Science 317, 231–233. doi:10.1126/science.1142021
Schrader, D.L., Davidson, J., 2017. CM and CO chondrites: A common parent body or asteroidal neighbors? Insights from chondrule silicates. Geochim. Cosmochim. Acta 214, 157–171. doi:10.1016/j.gca.2017.07.031
Schrader, D.L., Franchi, I.A., Connolly, H.C., Jr, Greenwood, R.C., Lauretta, D.S., Gibson, J.M., 2011. The formation and alteration of the Renazzo-like carbonaceous chondrites I: Implications of bulk-oxygen isotopic composition. Geochim. Cosmochim. Acta 75, 308–325. doi:10.1016/j.gca.2010.09.028
Seto, Y., Sakamoto, N., Fujino, K., Kaito, T., Oikawa, T., Yurimoto, H., 2008. Mineralogical characterization of a unique material having heavy oxygen isotope anomaly in matrix of the primitive carbonaceous chondrite Acfer 094. Geochim. Cosmochim. Acta 72, 2723–2734. doi:10.1016/j.gca.2008.03.010
Sugiura, N., Fujiya, W., 2014. Correlated accretion ages and ε 54Cr of meteorite parent bodies and the evolution of the solar nebula. Meteorit Planet Sci 49, 772–787. doi:10.1111/maps.12292
Vacher, L.G., Marrocchi, Y., Verdier-Paoletti, M.J., Villeneuve, J., Gounelle, M., 2016. Inward radial mixing of interstellar water ices in the Solar protoplanetary disk. The

Astrophysical Journal Letters 827, 1–6. doi:10.3847/2041-8205/827/1/L1
Vacher, L.G., Marrocchi, Y., Villeneuve, J., Verdier-Paoletti, M.J., Gounelle, M., 2017. Petrographic and C & O isotopic characteristics of the earliest stages of aqueous alteration of CM chondrites. Geochim. Cosmochim. Acta 213, 271–290. doi:10.1016/j.gca.2017.06.049
Verdier-Paoletti, M.J., Marrocchi, Y., Avice, G., Roskosz, M., Gurenko, A., Gounelle, M., 2017. Oxygen isotope constraints on the alteration temperatures of CM chondrites. Earth Planet. Sci. Lett. 458, 273–281. doi:10.1016/j.epsl.2016.10.055
Walsh, K.J., Morbidelli, A., Raymond, S.N., O'Brien, D.P., Mandell, A.M., 2011. A low mass for Mars from Jupiter's early gas-driven migration. Nature 475, 206–209. doi:10.1038/nature10201
Yang, L., Ciesla, F.J., Lyons, J.R., Lee, J.E., 2011. Oxygen isotope anomalies in the solar nebula inherited from the proto-solar cloud. 42th Lunar and Planetary Science Conference, Houston, USA. Abstract # 1602.
Young, E.D., Ash, R.D., England, P., Rumble, D., 1999. Fluid Flow in Chondritic Parent Bodies: Deciphering the Compositions of Planetesimals. Science 286, 1331–1335. doi:10.1126/science.286.5443.1331
Yurimoto, H., Itoh, S., Zolensky, M., Kusakabe, M., Karen, A., Bodnar, R., 2014. Isotopic compositions of asteroidal liquid water trapped in fluid inclusions of chondrites. GEOCHEMICAL JOURNAL 48, 549–560. doi:10.2343/geochemj.2.0335
Yurimoto, H., Kuramoto, K., 2004. Molecular cloud origin for the oxygen isotope heterogeneity in the solar system. Science 305, 1763–1766. doi:10.1126/science.1100989
Zheng, Y.F., 1993. Calculation of oxygen isotope fractionation in anhydrous silicate minerals. Geochim. Cosmochim. Acta 57, 1079–1091. doi:10.1016/0016-7037(93)90042-u
Zhu, Z., Nelson, R.P., Dong, R., Espaillat, C., Hartmann, L., 2012. Dust filtration by planet-induced gap edges: Implications for transitional disks. Astrophys. J. 755, 6–18. doi:10.1088/0004-637X/755/1/6
Zolensky, M., Barrett, R., Browning, L., 1993. Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites. Geochim. Cosmochim. Acta 57, 3123–3148. doi:10.1016/0016-7037(93)90298-b
Zolensky, M.E., Bodnar, R.J., Yurimoto, H., Itoh, S., Fries, M., Steele, A., Chan, Q.H.S., Tsuchiyama, A., Kebukawa, Y., Ito, M., 2017. The search for and analysis of direct samples of early Solar System aqueous fluids. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 375, 20150386. doi:10.1098/rsta.2015.0386
Zolensky, M.E., Mittlefehldt, D.W., Lipschutz, M.E., 1997. CM chondrites exhibit the complete petrologic range from type 2 to 1. Geochim. Cosmochim. Acta 61, 5099–5115. doi:10.1016/s0016-7037(97)00357-8
Zolotov, M.Y., Mironenko, M.V., Shock, E.L., 2006. Thermodynamic constraints on fayalite formation on parent bodies of chondrites. Meteoritics & Planetary Science 41, 1775–1796. doi:10.1111/j.1945-5100.2006.tb00451.x