



# I-Xe dating of aqueous alteration in the CI chondrite Orgueil: I. Magnetite and ferromagnetic separates

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## Abstract

The I-Xe system was studied in a ferromagnetic sample separated from the Orgueil CI carbonaceous chondrite with a hand-held magnet and in two magnetite samples, one chemically separated before and the other one after neutron irradiation. This work was done in order to investigate the effects of chemical separation by LiCl and NaOH on the I-Xe system in magnetite. Our test demonstrated that the chemical separation of magnetite before irradiation using either LiCl or NaOH, or both, does not contaminate the sample with iodine and thus cannot lead to erroneous I-Xe ages due to introduction of uncorrelated <sup>128</sup>Xe.

The I-Xe ages of two Orgueil magnetite samples are mutually consistent within experimental uncertainties and, when normalized to an absolute time scale with the reevaluated Shallowater aubrite standard, place the onset of aqueous alteration on the CI parent body at  $4564.3 \pm 0.3$  Ma,  $2.9 \pm 0.3$  Ma after formation of the CV Ca-Al-rich inclusions (CAIs). The I-Xe age of the ferromagnetic Orgueil separate is 3.4 Ma younger, corresponding to a closure of the I-Xe system at  $4560.9 \pm 0.2$  Ma. These and previously published I-Xe data for Orgueil (Hohenberg et al., 2000) indicate that aqueous alteration on the CI parent body lasted for at least 5 Ma.

Although the two magnetite samples gave indistinguishable I-Xe ages, their temperature release profiles differed. One of the two Orgueil magnetites released less radiogenic Xe than the other, 80% of it corresponding to the low-temperature peak of the release profile, compared to only 6% in case of the second Orgueil magnetite sample. This could be due to the difference in iodine trapping efficiencies for magnetite grains of different morphologies. Alternatively, the magnetite grains with the lower radiogenic Xe concentrations may have formed at a later stage of alteration when iodine in an aqueous solution was depleted. © 2018 Elsevier Ltd. All rights reserved.

**Keywords:** I-Xe systematics; Orgueil; Aqueous alteration; Magnetite

## 1. INTRODUCTION

CI chondrites, being among the most chemically primitive meteorites, provide the best compositional match to the solar photosphere (Anders and Grevesse, 1989; Palme and Jones, 2003). Yet, their primary mineralogy and pet-

rography were erased by extensive low-temperature aqueous alteration at  $\sim 50$ – $150$  °C on the CI parent body (Richardson, 1978; McSween, 1979; Kerridge et al., 1979a,b; Bunch and Chang, 1980; Clayton and Mayeda, 1984; Zolensky et al., 1989; Endress and Bischoff, 1996; Endress et al., 1996; Leshin et al., 1997) and subsequently, some CI chondrites experienced significant thermal metamorphism (e.g., Tonui et al., 2003). All known CI chondrites are regolith breccias consisting of various types of heavily-hydrated lithic fragments composed of a fine-

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grained phyllosilicate-rich matrix containing magnetite, sulfides, carbonates, and sulfates. In each CI chondrite, magnetite is out of oxygen isotopic equilibrium with the phyllosilicates ( $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O} = 1.3\text{‰}$  to  $1.8\text{‰}$  and  $-0.3\text{‰}$  to  $0.3\text{‰}$ , respectively), suggesting that, as anhydrous silicates were progressively altered to phyllosilicates, the latter continued to equilibrate with water, whereas magnetite did not (Rowe et al., 1994). As secondary minerals, magnetites can provide a window to view the progression of aqueous alteration. The I-Xe chronometry has been shown to be a promising technique for dating secondary alteration processes and it is capable of resolving age differences of a few hundred thousand years between closure times of different mineral phases from the same meteorite (e. g., Swindle et al., 1998; Brazzle et al., 1999; Pravdivtseva et al., 2001; 2003a, 2003b; Krot et al., 2006).

The I-Xe ages of magnetites from Murchison (CM) and Orgueil (CI) reported by Lewis and Anders (1975) were the oldest known and were initially interpreted as formation ages of magnetite by condensation in the solar nebula. Subsequent studies (Hohenberg and Kennedy, 1981) pointed out the problems associated with using pure KI as a monitor (as in Lewis and Anders, 1975) due to epi-thermal neutrons and neutron self-shielding. Because it was demonstrated that the trapped Xe resided mostly in the hydrated silicates and the radiogenic  $^{129}\text{Xe}$  in the magnetite (Herzog et al., 1973), Lewis and Anders (1975) paid special attention to the purity of the analyzed material. The Orgueil sample was finely ground and stirred with a saturated LiCl solution for 8 days at  $60\text{ °C}$  to remove the silicate-magnetite intergrowth. Although this procedure yields magnetic fractions that are more than 80% pure (Lewis and Anders, 1975), it could potentially contaminate the magnetite with iodine, which after irradiation will introduce non-correlated  $^{128}\text{Xe}$ , resulting in spurious I-Xe ages.

To avoid contamination problems, in our previous work with Orgueil (Hohenberg et al., 2000), we prepared two samples: the first sample was separated following the wet-chemical procedure described in Lewis and Anders (1975), whereas the second, highly-magnetic sample was separated with a hand magnet from a finely-ground powder. Only the hand-separated highly-magnetic sample was irradiated for the I-Xe dating, yielding an I-Xe age that was about 10 Ma younger than the age reported by Lewis and Anders (1975). Comparison of the radiogenic  $^{129}\text{Xe}$  concentrations in these two separates suggested presence of a second, minor iodine host phase, probably silicate, in the sample separated with a hand magnet. If the I-Xe systems in these two phases closed at different times, then the resulting apparent I-Xe age reported by Hohenberg et al. (2000) would not represent a single event in the alteration history of Orgueil. Thus simple separation of highly-magnetic sample with a hand magnet may not be sufficient for the I-Xe studies of magnetites.

The results presented here were obtained in order to define the I-Xe age of the relatively pure magnetite separated from Orgueil by the wet-chemical procedure and to investigate the possible effects of chemical separation by LiCl and NaOH on the I-Xe system in magnetite. A clear understanding of the effects of this chemical separation is

crucial for our future I-Xe studies of alteration in carbonaceous chondrites.

## 2. EXPERIMENTAL

Our sample preparation schematic is shown in Fig. 1. Two grams of Orgueil was first ground to a fine powder in a mortar with the ferromagnetic fraction then separated with a hand magnet and split into two aliquots. Following the procedure described by Herzog et al. (1973), one 450 mg aliquot was constantly stirred in a saturated LiCl solution for 8 days at  $60\text{ °C}$ . The magnetic stirring bar, with particles of magnetic material stuck to it, was then removed, washed with ultrasonically agitated water and placed in a saturated NaOH solution where it was stirred for two more days. The magnetic bar was finally washed three times with ultrasonically agitated deionized water. The remaining material was then removed from the magnetic stirring bar, washed with acetone and dried, yielding 18.56 mg as a magnetite separate. The purity of this separate was confirmed by X-ray diffraction which showed only magnetite lines. Secondary electron images of this sample are shown in Fig. 2.

18.56 mg of the chemically separated magnetite, 90 mg aliquot of the parent ferromagnetic fraction and 27.91 mg of the absolute age standard Shallowater aubrite were individually sealed under vacuum in fused quartz ampoules and irradiated with thermal neutrons as part of the SLC-15 capsule in the Missouri University Research Reactor (MURR), receiving  $\approx 2 \times 10^{19}\text{ n/cm}^2$ . The samples were placed in a fixed horizontal plane at the center of the vertical neutron profile in the flooded reflector area of the reactor to minimize any vertical gradient and the capsule was continuously rotated to eliminate any x-y non-uniformity of the neutron flux. The irradiated ferromagnetic separate was then split into two parts. One of these was processed only in LiCl according to the procedure described above, yielding pure magnetite. As a result we had three irradiated Orgueil samples: one simple ferromagnetic (Fm; 11.08 mg)

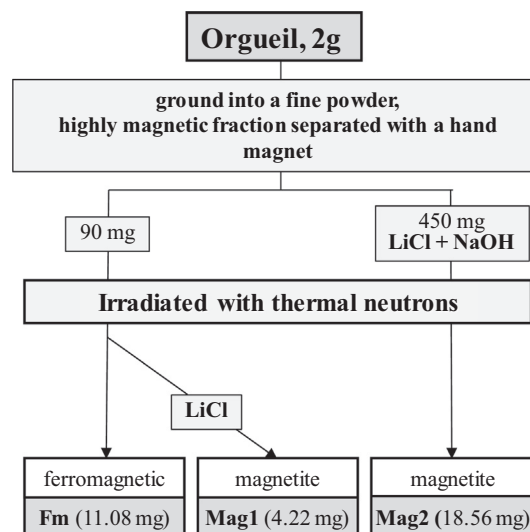


Fig. 1. Schematic samples separation procedure.

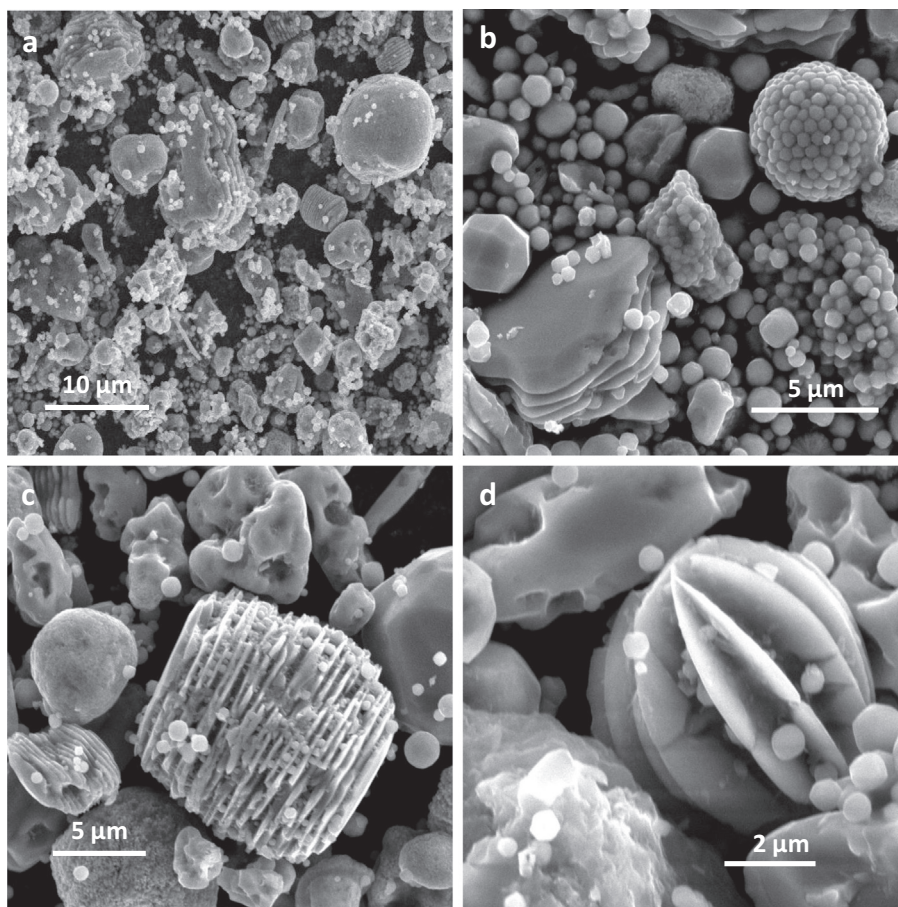


Fig. 2. The secondary electron images of Mag2 separate; a – general view. The sample mostly consists of barrel-shaped stacks of platelets and their fragments (c, d) and 0.1–1 μm framboidal magnetite spherules (b); larger framboids are rare (b).

and two magnetite separates, one separated in LiCl + NaOH prior to irradiation (Mag2; 18.56 mg) to examine possible effects of potential iodine contamination, the other separated after irradiation (Mag1; 4.22 mg) with no possibility, therefore, of contamination due to the activation of iodine that might have been introduced during the wet-chemical separation procedure (Fig. 1).

After cooling, samples were removed from quartz ampoules, wrapped in platinum foil and placed in the extraction system of our mass spectrometer. Xenon was released in stepwise heating extractions in a W coil of the resistance furnace starting with 800 °C. The released gases were cleaned sequentially by first exposing them to SAES St707 getter pellets, maintained at 275 °C, and then to freshly deposited Ti-film getters. The heavy noble gases were separated from He, Ne and Ar using activated charcoal at a temperature of –90 °C for adsorption of the Xe, with the light gases pumped away, and then elevated to 165 °C for Xe desorption. The isotopic composition of the released Xe was measured by high transmission ion-counting mass spectrometry (Hohenberg 1980). Hot blanks were measured with an empty coil at 1500 °C (15 min), following the standard analysis procedure, and were typically  $2 \times 10^{-15}$   $^{132}\text{Xe}$  cm<sup>3</sup> STP. After the stepwise heating program for each sample, and before a new sample was intro-

duced, the coil was kept for 10 min at ~2000 °C for cleaning and a new hot blank was then measured at 1500 °C. This assures that no memory or cross sample effects exist.

### 3. RESULTS

Data are given in [Supplementary Table 1](#). We present the Xe isotopic data in three-isotope plots as  $^{129}\text{Xe}/^{132}\text{Xe}$  vs.  $^{128}\text{Xe}/^{132}\text{Xe}$  or  $^{129}\text{Xe}/^{130}\text{Xe}$  vs.  $^{128}\text{Xe}/^{130}\text{Xe}$ . All isotopes here are dominated by iodine-derived  $^{128*}\text{Xe}$ ,  $^{129*}\text{Xe}$  and trapped Q-Xe component (Busemann et al., 2000). Three-isotope plot for Shallowater is shown in Fig. 3 as  $^{129}\text{Xe}/^{132}\text{Xe}$  vs.  $^{128}\text{Xe}/^{132}\text{Xe}$  after correction for 0.3% contribution for  $^{132}\text{Xe}$  from neutron-induced fission of  $^{235}\text{U}$ . The correction was done based on  $1.840 \pm 0.076$   $^{134}\text{Xe}/^{132}\text{Xe}$  value for  $^{235}\text{U}$ -fission (Ozima and Podosek, 2002). The low temperature extractions 800°, 1000° and 1200 °C demonstrate typical behavior observed during step-wise pyrolysis when uncorrelated  $^{128*}\text{Xe}$  is present. The experimental points at these lower temperatures usually reflect the partial losses of  $^{129*}\text{Xe}$  from the low retention sites or the addition of extraneous  $^{128*}\text{Xe}$  due to superficial iodine contamination. With each increasing temperature step, the experimental points gradually approach the isochron, a two-component

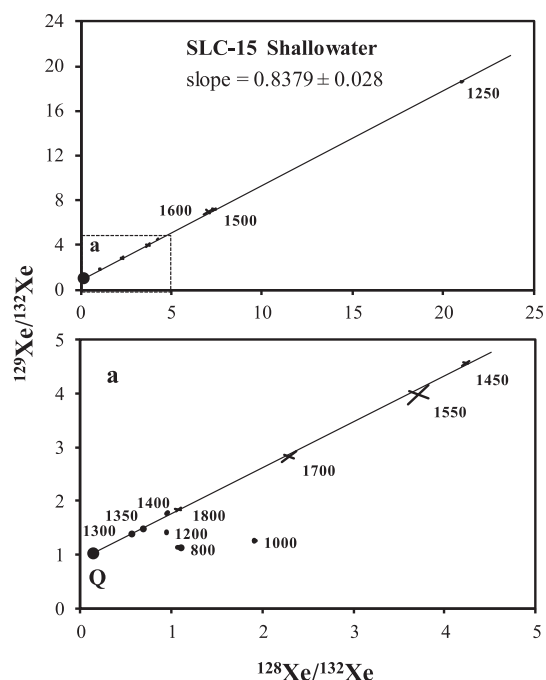


Fig. 3. I-Xe isochron for the Shallowater aubrite absolute age standard. SLC-15 stands for the irradiation package. Numbers represent extraction temperatures. 800, 100 and 1200 °C extraction points on a lower panel (a) correspond to the uncorrelated releases of radiogenic Xe. Free fit correlation line (not forced through Q-Xe end-member) is defined by 10 points starting from 1250 °C;  $^{129}\text{Xe}/^{132}\text{Xe} = 0.966 \pm 0.004$  at Q  $^{128}\text{Xe}/^{132}\text{Xe}$  value (0.082).

mixing line between iodine-derived and trapped Q-Xe. The slope of this line gives the  $^{129}\text{Xe}/^{128}\text{Xe}$ , which provides the relative I-Xe age. Here, for Shallowater, it is defined by 10 experimental points. Since the absolute age standard Shallowater is always irradiated with the samples, we do not need to know the  $^{127}\text{I}$  ( $n, \gamma\beta$ )  $^{128}\text{Xe}$  conversion factor specific to each particular irradiation. The relative I-Xe age of a sample is derived from a difference in the isochrons slopes for each sample and Shallowater.

Three-isotope plots for the Orgueil separates are shown in Fig. 4. Release profiles for the trapped  $^{132}\text{Xe}$  and radiogenic  $^{129}\text{Xe}$  and  $^{128}\text{Xe}$  are shown in Fig. 5. Concentrations of trapped and radiogenic iodine-derived Xe for the Orgueil samples are presented in Table 1. None of the chemically separated Orgueil samples contained detectable  $^{235}\text{U}$ -fission xenon. For the ferromagnetic separate contribution from  $^{235}\text{U}$ -fission Xe was 0.4% of the total  $^{132}\text{Xe}$  concentration and was limited to the first extraction steps where uncorrelated radiogenic Xe was released. Since only the extraction points representing correlated  $^{128}\text{Xe}$  and  $^{129}\text{Xe}$  define the isochron, we did not correct for  $^{235}\text{U}$ -fission contribution for the ferromagnetic sample three-isotope plot.

Separation in strong electrolytes reduced the amounts of trapped Xe in the magnetite samples (Table 1, Fig. 5). This is consistent with the previously published observation (Jeffery and Anders, 1970) that trapped Xe in Orgueil mostly resides in silicates, while the iodine-derived radio-

genic Xe resides mainly in the magnetite. Presence of the trapped Xe component in the magnetite separates by itself does not create any problems for the I-Xe dating of these samples. Here it rather serves as an indicator of the amount of silicates still present in the magnetite separate. These silicates, or/and possibly other mineral phases associated with them, may carry their own preserved I-Xe systematics, resulting in a superposition of the I-Xe ages, as was observed for the ferromagnetic samples in our earlier work (Hohenberg et al., 2000) and here. Having a magnetite separate as close to a mono-mineral phase as possible insures that the resulting I-Xe datum is meaningful and could be interpreted as the time of magnetite formation. In this work we chose two different separation procedures to compare their effects on the I-Xe systems of the resulting samples, separation in LiCl + NaOH serving as a proxy for separation in NaOH only. It was suggested that separation in NaOH may etch the minerals and cause gas loss (Herzog et al., 1973). Separation of Mag2 was done in two steps to preserve silicates during the first step LiCl treatment in a failed attempt to recover them for the I-Xe studies. The NaOH treatment followed to make sure that magnetite/silicate intergrowths are removed efficiently.

As was expected based on the earlier works (Jeffery and Anders, 1970; Herzog et al., 1973; Lewis and Anders, 1975), separation of magnetite in LiCl solution was less effective than separation in LiCl + NaOH in removing the trapped Xe component. More gentle LiCl treatment resulted in 50× reduction in the trapped Xe concentration in Mag1, and LiCl + NaOH cut the trapped Xe concentration in Mag2 by 100. Trapped  $^{132}\text{Xe}$  in all samples is released in two major peaks which, in the case of the ferromagnetic sample, overlap somewhat. Chemical separation in LiCl effectively removed most of the trapped component associated with the high temperature release in Mag1, and the harsher treatment in LiCl + NaOH resulted in a complete loss of the high temperature host of the trapped Xe component in Mag2. Apparently, both treatments were equally effective in removing the trapped Xe carrier phase associated with the low temperature release.

The ratio of radiogenic iodine-derived xenon isotopes  $^{129}\text{Xe}/^{128}\text{Xe}$  is the same for both magnetite samples, indicating that chemical separation in LiCl or/and NaOH does not contaminate magnetite with iodine. If present, such contamination would result in a higher  $^{128}\text{Xe}$  concentration in Mag2, which was irradiated after the chemical separation. As previously observed by Hohenberg et al. (2000; see Introduction), this ratio is lower for the ferromagnetic sample indicating the presence of at least one more iodine-carrier phase, probably silicate, with a younger I-Xe age. Surprisingly, concentrations of  $^{128}\text{Xe}$  and  $^{129}\text{Xe}$  in Mag2 are 6× higher than in Mag1. This could be due to a higher heterogeneity of the smaller Mag1 sample determined by the unique morphology of CIs magnetite, first described by Jedwab as “groupements de plaquettes” in his paper published in French (1967). In the later English-language publications this magnetite morphology was referred to as “platy” (Lewis and Anders, 1975) or “stacks of platelets” (Hua and Buseck, 1998). Both terms are essentially the same; we used the English transcription in our

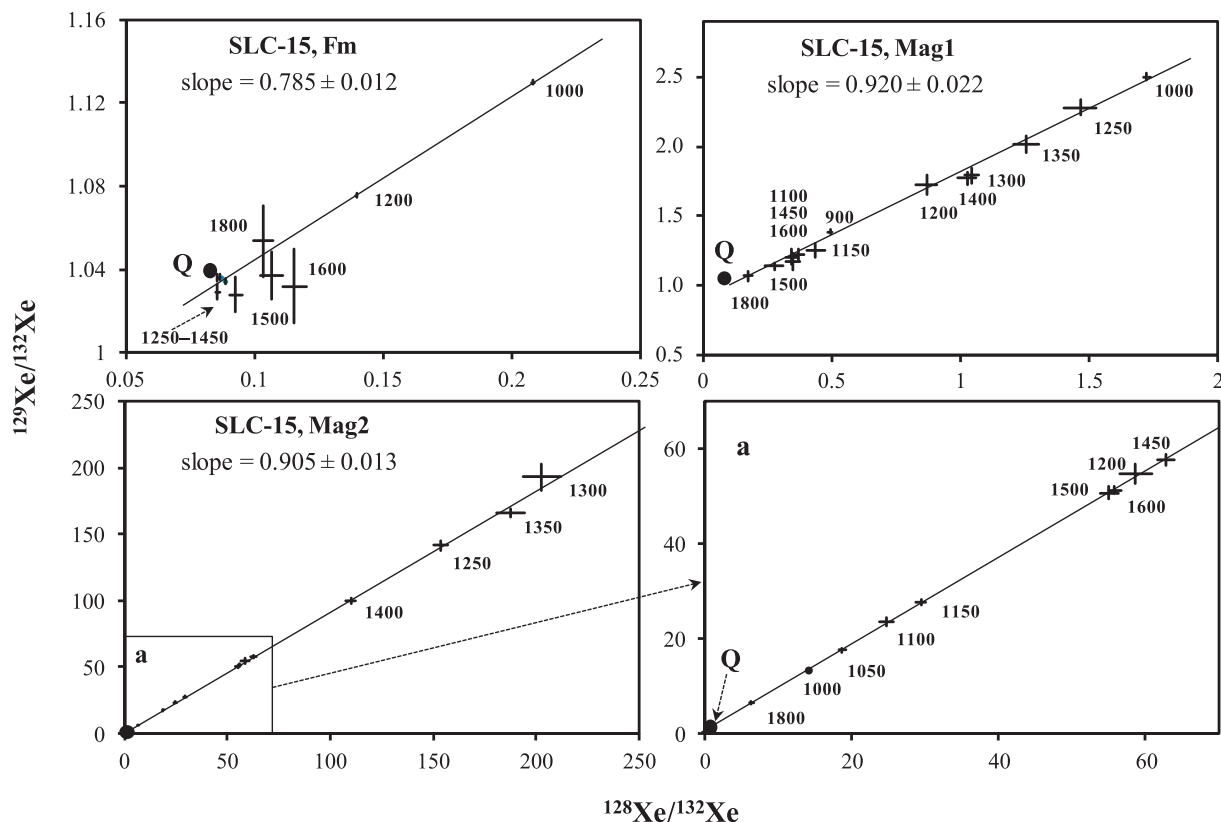


Fig. 4. Three-isotope plots for the Orgueil ferromagnetic sample (Fm) and magnetite separates (Mag1 and Mag2). Mag1 – magnetite separated in LiCl solution after irradiation; Mag2 – magnetite separated in LiCl + NaOH solution before irradiation; SLC-15 stands for the irradiation package; numbers represent extraction temperatures. Only the extractions that define the isochrons are shown on the plots. The free fit correlation line (not forced through Q-Xe end-member) correspond to  $^{129}\text{Xe}/^{132}\text{Xe} = 0.966 \pm 0.001$  for ferromagnetic sample; and to  $^{129}\text{Xe}/^{132}\text{Xe} = 0.90 \pm 0.02$  and  $^{129}\text{Xe}/^{132}\text{Xe} = 0.9 \pm 0.4$  for Mag1 and Mag2 respectively at Q  $^{128}\text{Xe}/^{132}\text{Xe}$  value (0.082).

earlier publication (Hohenberg et al., 2000) and here as well. The SEM images of the Mag2 sample are shown in Fig. 2. The sample mostly consists of barrel-shaped stacks of platelets and their fragments and 0.1–1  $\mu\text{m}$  framboidal magnetite spherules stuck to them. The release profiles of  $^{128}\text{Xe}$ ,  $^{129}\text{Xe}$  in magnetites (Fig. 5) are characterized by two major peaks that could be associated with these different morphologies, and it is possible that the population of grains in the smaller Mag1 sample is dominated by the stack of platelets morphology (Fig. 2a and c), which have trapped iodine less efficiently than framboids. It is also possible that the magnetite grains with lower radiogenic Xe concentrations have formed later, when iodine in an aqueous solution was depleted, although this age difference cannot be resolved here.

Alternatively, neutron irradiation in the reactor could have resulted in micro damage to the crystalline structure of the magnetite grains due to the neutron capture reactions on iron and, to a lesser degree, due to reactions on chromium and nickel (Greenwood, 1983). The post-irradiation chemical treatment of Mag1 could have potentially resulted in the loss of radiogenic Xe from these weakened areas, but would have equally affected both magnetite morphologies, resulting in similar radiogenic Xe release profiles for Mag1 and Mag2 (Fig. 5). In reality, the concentrations of

radiogenic Xe in the low temperature peak, defined by 800–1000  $^{\circ}\text{C}$  and 900–1050  $^{\circ}\text{C}$  extractions for Mag2 and Mag1, respectively, are compatible, but for the high temperature peak these concentrations differ by a factor of 5. In fact, 72% of  $^{129}\text{Xe}$  and  $^{128}\text{Xe}$  in Mag2 is associated with the high temperature peak compared with 15% in Mag1. This behavior supports the higher heterogeneity explanation for the lower radiogenic Xe content in Mag1. Although we cannot completely exclude the possibility of radiogenic Xe losses due to thermal neutron damage of the sample, these losses will only result in lower concentrations of radiogenic Xe isotopes, and would not affect their ratio. The I-Xe isochron is defined by the extractions from the sites in the crystalline structure of the sample where the I-Xe system was closed to Xe loss. After conversion of  $^{127}\text{I}$  to  $^{128}\text{Xe}$ , both  $^{128}\text{Xe}$  and  $^{129}\text{Xe}$  would be equally affected by the chemical treatment, thus none of them can be lost preferentially.

Independent of whether the differences are due to sample heterogeneity or some losses occurred, the important point here is that chemical separation of magnetite in LiCl or/and NaOH does not contaminate the samples with iodine and thus does not lead to erroneous I-Xe ages. Since chemical separation of magnetite from an already irradiated sample is much more difficult considering the safety

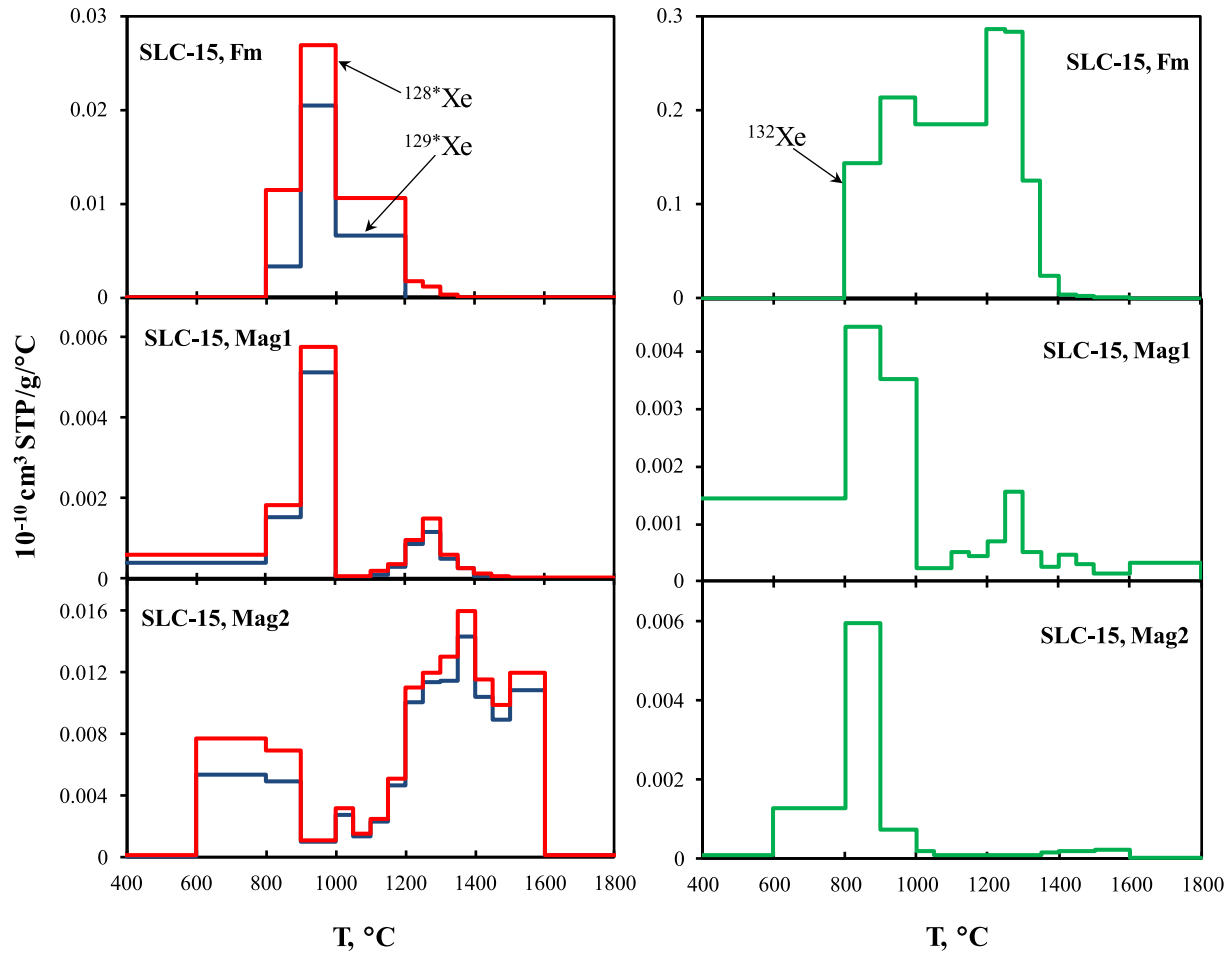


Fig. 5. Release profiles of the radiogenic  $^{128*}\text{Xe}$ ,  $^{129*}\text{Xe}$  and trapped  $^{132}\text{Xe}$  as functions of temperature for the Orgueil ferromagnetic sample and magnetite separates. The concentrations of the Xe components at  $n$  temperature step are divided by  $\Delta T = n - (n - 1)$ .

Table 1

Concentrations of trapped and radiogenic iodine-derived Xe and I-Xe ages (relative to Shallowater) for the analyzed Orgueil samples.

Orgueil separates	Weight, mg	Separation	$\times 10^{-10} \text{ cm}^3 \text{ STP/g}$			$\Delta T$ , Ma
			$^{132}\text{Xe}_{\text{trapped}}$	$^{129*}\text{Xe}$	$^{128*}\text{Xe}$	
<i>SLC-15 irradiation, slope of the Shallowater isochron <math>0.8379 \pm 0.0029 \equiv 0 \text{ Ma}</math></i>						
Fm	11.08	Hand magnet	$109 \pm 6$	$3.6 \pm 0.3$	$6.5 \pm 0.7$	$-1.5 \pm 0.3$
Mag1	-4.22	LiCl after irradiation	$2.0 \pm 0.1$	$1.1 \pm 0.1$	$1.3 \pm 0.1$	$-2.1 \pm 0.6$
Mag2	18.56	LiCl + NaOH before irradiation	$1.0 \pm 0.1$	$6.6 \pm 0.4$	$7.9 \pm 0.5$	$-1.8 \pm 0.3$

measures, the disposal of the radioactive solutions and handling problems in general, it is much more desirable to chemically treat the sample before irradiation. This is especially true now that the Mag1 data suggest that post-irradiation chemical treatment may cause the correlated loss of  $^{128*}\text{Xe}$  and  $^{129*}\text{Xe}$ . Nevertheless, it is reassuring that both Mag1 and Mag2 have the same  $^{129*}\text{Xe}/^{128*}\text{Xe}$  ratio indicating that, even if such losses have occurred, the I-Xe chronological record was not disturbed.

This is evident from the I-Xe ages of the Orgueil magnetite samples. The I-Xe isochron for Mag2 is well-defined by 13 experimental points, starting with the 1000 °C extraction (Fig. 4), and corresponds to the closure of

the I-Xe system in this sample at  $1.8 \pm 0.3 \text{ Ma}$  before Shallowater. The I-Xe isochron for Mag1 starts at 900 °C extraction, it is also defined by 13 experimental points, but with a lesser precision owing to the lower radiogenic Xe concentrations in this sample, in addition to Mag1 being more than 4 times smaller than Mag2. The slope of the Mag1 correlation corresponds to the I-Xe closure at  $2.1 \pm 0.6 \text{ Ma}$  before Shallowater. The I-Xe ages for magnetite samples agree within experimental uncertainty, the weighted average of the two is  $1.9 \pm 0.3 \text{ Ma}$  older than the Shallowater reference age of  $4562.4 \pm 0.2 \text{ Ma}$  (Pravdivtseva et al., 2017). When normalized to the absolute time scale, the I-Xe age of magnetites corresponds to

$4564.3 \pm 0.3$  Ma, 2.9 Ma after CV CAIs (Connelly et al., 2012). The ferromagnetic Orgueil separate is 3.4 Ma younger, corresponding to the closure of the I-Xe system at  $4560.9 \pm 0.2$  Ma.

#### 4. DISCUSSION

The CI carbonaceous chondrites experienced high degrees of aqueous alteration and consist almost entirely of aqueously-formed minerals, including magnetite (Kerridge et al., 1979a,b). Based on thermodynamic modeling (e.g., Berger et al., 2011; Zolotov, 2012), experimentally determined phase diagrams for the Fe-Ni-Co-S system (Bullock et al., 2005; Berger et al., 2011), and oxygen isotopic compositions of aqueously-formed minerals (e.g., Leshin et al., 1997; Clayton and Mayeda, 1999), it is inferred that the CIs experienced relatively low-temperature aqueous alteration ( $\sim 20$ – $150$  °C) under variable, but generally high water/rock (W/R) mass ratios of up to 0.6 or even higher.

I-Xe ages of the Orgueil magnetites studied here (red symbols, Fig. 6) are the same within experimental uncertainty and place the onset of aqueous alteration on the CI parent body at  $4564.3 \pm 0.3$  Ma,  $2.9 \pm 0.3$  Ma after CV CAIs (Fig. 6; Connelly et al., 2012). Simple ferromagnetic separates (black symbols, Fig. 6), as reported here and in our previous work with Orgueil (Hohenberg et al., 2000), are not sufficient to define the I-Xe age of pure magnetite since there are clearly other iodine host minerals present in these separates. The ferromagnetic samples have been characterized by correlated radiogenic Xe releases and well-defined isochrons, suggesting dominance of the I-Xe system by one of these hosts. The resolvable difference in

the I-Xe closure times in the ferromagnetic samples,  $-1.5 \pm 0.3$  Ma here and  $-3.0 \pm 0.4$  in Hohenberg et al. (2000) (both younger than Shallowater) could be due to a difference in the separates magnetite content. For two iodine carriers, with comparable radiogenic xenon concentrations in the range observed here for the Orgueil magnetites Mag1 and Mag2, the 35–65% mixture of magnetite (2.0 Ma older than Shallowater) and a hypothetical second carrier phase ( $-3.5$  Ma younger than Shallowater), may result in an apparent isochron corresponding to closure at  $-1.5$  Ma. Then the younger  $-3.0$  Ma relative I-Xe age of the ferromagnetic separate (Hohenberg et al., 2000) will require 10% magnetite + 90% of this hypothetical iodine carrier phase mixture. We also cannot rule out more complex scenario where more than two iodine carrier phases with variable radiogenic xenon concentrations contribute to the apparent I-Xe ages of the ferromagnetic samples. However, with the exception of magnetite, the exact iodine carrier phase or phases in the ferromagnetic separates and their corresponding I-Xe ages are unknown. Based on our previous results (Hohenberg et al., 2000) and the I-Xe data presented here, the alteration in Orgueil started at  $\sim 2.9$  Ma after CV CAIs and lasted for at least 5 Ma.

This is consistent with the observations by other short-lived chronometers, although the comparison is not straightforward. Our I-Xe ages and Mn-Cr data for Orgueil dolomites and breunnerites by other authors (Endress et al., 1996; Hoppe et al., 2007; Fujiya et al., 2013) are shown together in Fig. 6, relative to the formation time of the CV CAIs (Connelly et al., 2012). When considered together, the Mn-Cr data by three different groups are consistent with the early onset of the alteration at  $\sim 4.56$  Ga but show systematic shifts between groups most probably due to the Mn/Cr relative sensitivity factor (RSF) differences – *i.e.*, differences in the overall sensitivity of the mass spectrometer to ions of different elements. For ion microprobe analyses the RSFs are obtained using a synthetic standard, which so far was limited to only one end-member of the carbonate group. A large range in the RSFs of other carbonates was suggested (Steele and McKeegan, 2014), and efforts are under way to prepare the appropriate synthetic dolomite standard (Ichimura and Sugiura, 2015).

The I-Xe chronometer is immune to the relative sensitivity factor problems. The proxy for the  $^{129}\text{I}$  mother isotope is stable  $^{127}\text{I}$ , which is converted to  $^{128*}\text{Xe}$  by neutron irradiation. Since the daughter product of  $^{129}\text{I}$  decay is  $^{129*}\text{Xe}$ , only the measurements of Xe isotopic composition of the sample are required. The typical irradiation fluence of  $\sim 2 \times 10^{19}$  thermal neutrons/cm<sup>2</sup> ensures that the resulting  $^{128*}\text{Xe}/^{129*}\text{Xe}$  ratio will be in 0.6–1.0 range and thus can be measured with a high precision. Variations in fluences between the irradiations due to the differences in the neutron flux spectra or the durations of the irradiations are not important, since the I-Xe absolute age standard Shallowater is always irradiated with the samples and its  $^{129*}\text{Xe}/^{128*}\text{Xe}$  ratio or rather the slope of its isochron is determined for each irradiation. It was demonstrated by Gilmour et al. (2006) that Shallowater is reproducible and thus superior to the prior absolute age standards used for the I-Xe dating over the years. The absolute I-Xe age of the Shallowater

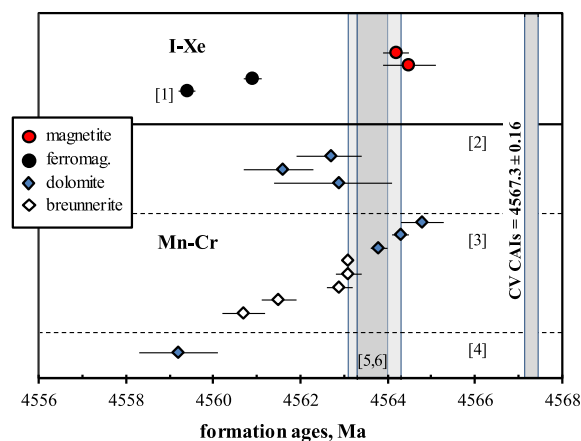


Fig. 6. Comparison of I-Xe ages for Orgueil ferromagnetic sample and magnetite separates and Mn-Cr ages for dolomite and breunnerites separates relative to the Pb-Pb age of CV CAIs (Connelly et al., 2012). Two overlapping grey areas represent accretion ages estimated for a CI-like parent body 50 km in diameter with a water-to-rock ratio of 0.56 (left panel) and 1 (right panel). (1) – Hohenberg et al. (2000); (2) – Fujiya et al. (2013); (3) – Hoppe et al. (2007); (4) – Endress et al. (1996); (5) – Sugiura and Fujiya (2014); (6) – Krot et al. (2017).

standard is derived from the observed correlation between I-Xe and Pb-Pb ages in a number of samples. It was recently re-evaluated with the addition of the new I-Xe data for the Hammadah al Hamra 237 CB chondrule and using Pb-Pb ages adjusted for an updated  $^{238}\text{U}/^{235}\text{U}$  ratio of 137.794 and meteorite specific U-isotope ratios (Brennecka et al., 2010; Bouvier et al., 2011; Brennecka and Wadhwa; 2012; Connelly et al., 2012; Goldmann et al., 2015; Pravdivtseva et al., 2017). The Shallowater aubrite is now the universally accepted absolute age standard; it provides a convenient comparison of the I-Xe data by different laboratories and serves as the much needed bridge to other chronometries.

Two overlapping grey areas in Fig. 6 represent the accretion times of the CI-like asteroid with a 50 km radius (Sugiura and Fujiya, 2014; Krot et al., 2017) calculated for 0.56 (left panel) and 1 (right panel)  $\text{Water}/\text{Rock}$  volume ratios. Accretion times were estimated based on the peak temperatures experienced by the CIs, the Mn-Cr ages, and temperatures of secondary mineral formation, with the assumption that the  $^{26}\text{Al}$  was homogeneously distributed in the early solar system. The uncertain contribution to the peak temperature from heat generated by hydration (Sugiura and Fujiya, 2014) causes large uncertainties for the estimated accretion age. The I-Xe ages of Orgueil magnetites are more consistent with the higher W/R ratio of 1 for the CI-like asteroid and set a limit for the onset of accretion of the CI asteroid. Based on the I-Xe magnetite ages, and if the accretion time is correct, the alteration of CIs coincided with the accretion process. This implies that temperature on the CI asteroid at this time was sufficiently high for water ice to melt.

The I-Xe ages of Orgueil magnetites are in a good agreement with the I-Xe ages of the CV chondrite Allende dark inclusions (DIs) (Pravdivtseva et al., 2003b; Hohenberg et al., 2004) (Fig. 7), indicating near simultaneous onset

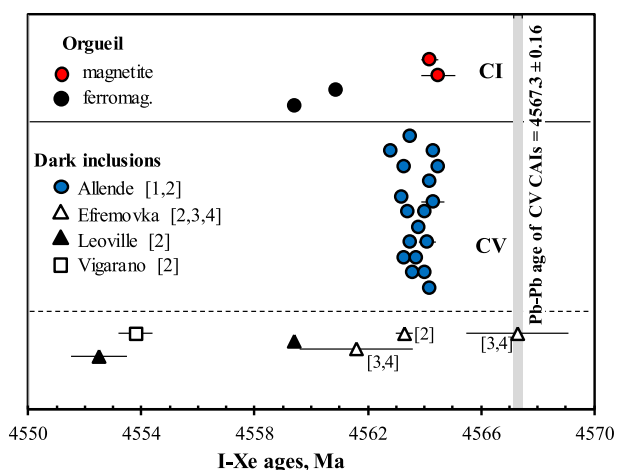


Fig. 7. Comparison of I-Xe ages for Orgueil ferromagnetic sample and magnetite separates and I-Xe ages for CV3 carbonaceous chondrites from Allende, Efremovka, Leoville and Vigarano relative to the Pb-Pb age of CV CAIs – Connelly et al. (2012). (1) – Pravdivtseva et al. (2003b); (2) – Hohenberg et al. (2004); (3) – Swindle et al. (1998); (4) – Krot et al. (1999).

of aqueous alteration in CIs and CVs, consistent with the Mn-Cr chronology (Fujiya et al., 2012, 2013; Krot et al., 2017). The I-Xe ages of the DIs from the reduced CV chondrites Efremovka, Leoville, and Vigarano are generally younger; these DIs experienced different types of aqueous alteration, which affected them to various degrees. For the Efremovka DIs, the I-Xe ages correlate with the degree of alteration (Krot et al., 2006); the least altered DI being as old as CV CAIs. The earlier I-Xe studies of two Efremovka DIs (Swindle et al., 1998; Krot et al., 1999) applied Bjurböle as an absolute age standard. Although Bjurböle was shown to produce inconsistent results (Hohenberg and Kennedy, 1981), no better alternative was established at the time. The plotted I-Xe ages of the Efremovka DIs (Fig. 7) are renormalized to Shallowater using  $0.46 \pm 0.15$  Ma relative I-Xe age for Bjurböle (Brazzle et al., 1999). It was later demonstrated that the I-Xe ages of 4 whole rock Bjurböle samples from the same irradiation varied from 0.5 Ma older to 3.5 Ma younger than Shallowater (Gilmour et al., 2006). Had the Efremovka data been renormalized to the Shallowater standard using a different relative I-Xe age for Bjurböle, the I-Xe ages of the Efremovka DIs would have been younger.

## 5. CONCLUSIONS

The I-Xe system was studied in a ferromagnetic sample separated from the CI Orgueil carbonaceous chondrite with a hand-held magnet and in two chemically separated magnetites, one before and the other after the irradiation. Chemical separation of magnetites using saturated electrolyte solutions of LiCl and LiCl + NaOH does not contaminate resulting sample with iodine and thus can be done in an easier and safer way, prior to the neutron irradiation of the sample. Separation in LiCl + NaOH was the more effective as it reduced the trapped xenon concentration in the sample by two orders of magnitude compared to a factor of 50 when sample was treated only in LiCl. The separation protocols investigated here resulted in the compatible  $^{128}\text{Xe}$  and  $^{129}\text{Xe}$  concentrations in two magnetite separates and revealed a possible heterogeneity of the I-Xe system within the magnetites. The difference in the distribution of radiogenic Xe between two release peaks for magnetite samples suggests that different morphologies of magnetite grains may have trapped iodine with different efficiencies. Alternatively, the magnetite grains with lower radiogenic Xe concentrations may have formed at a later stage of alteration when iodine in an aqueous solution was depleted.

I-Xe ages of the Orgueil magnetites studied here are mutually consistent within experimental uncertainties, placing the onset of aqueous alteration on the CI parent body at  $4564.3 \pm 0.3$  Ma, no later than  $2.9 \pm 0.3$  Ma after CV CAIs (Connelly et al., 2012). These ages are in a good agreement with the Allende DIs I-Xe record of aqueous alteration in CV3 carbonaceous chondrites (Pravdivtseva et al., 2003b; Hohenberg et al., 2004), suggesting that aqueous alteration in CIs and CVs started simultaneously.

The I-Xe system in Orgueil survived not only in magnetites but in the younger aqueous alteration products as



well. The resolvable difference in the I-Xe closure times in the ferromagnetic samples analyzed previously (Hohenberg et al., 2000) and studied here suggests that more than one iodine-carrier phase experienced alteration later than the Orgueil magnetites. Based on our previous results, and the I-Xe data presented here, the alteration in Orgueil lasted for at least 5 Ma.

The I-Xe data for Orgueil magnetites and ferromagnetic sample show good agreement with the Mn-Cr chronology of the CI alteration products (Hoppe et al., 2007; Fujiya et al., 2012, 2013) and are consistent with the estimated accretion age for the 50 km in diameter CI-like parent body with Water/Rock volume ratio of 1 (Krot et al., 2017).

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#### APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.gca.2018.02.004>.

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