

I–Xe systematics of the impact plume produced chondrules from the CB carbonaceous chondrites: Implications for the half-life value of ^{129}I and absolute age normalization of ^{129}I – ^{129}Xe chronometer

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Abstract

It is inferred that magnesian non-porphyritic chondrules in the CB (Bencubbin-type) carbonaceous chondrites formed in an impact generated plume of gas and melt at 4562.49 ± 0.21 Ma (Bollard et al., 2015) and could be suitable for the absolute age normalization of relative chronometers. Here xenon isotopic compositions of neutron irradiated chondrules from the CB chondrites Gujba and Hammadah al Hamra (HH) 237 have been analyzed in an attempt to determine closure time of their I–Xe isotope systematics. One of the HH 237 chondrules, #1, yielded a well-defined I–Xe isochron that corresponds to a closure time of 0.29 ± 0.16 Ma after the Shallowater aubrite standard. Release profiles and diffusion properties of radiogenic ^{129}Xe and ^{128}Xe , extracted from this chondrule by step-wise pyrolysis, indicate presence of two iodine host phases with distinct activation energies of 73 and 120 kcal/mol. In spite of the activation energy differences, the I–Xe isotope systematics of these two phases closed simultaneously, suggesting rapid heating and cooling (possibly quenching) of the CB chondrules. The release profiles of U-fission Xe and I-derived Xe correlate in the high temperature host phase supporting simultaneous closure of ^{129}I – ^{129}Xe and ^{207}Pb – ^{206}Pb systematics.

The absolute I–Xe age of Shallowater standard is derived from the observed correlation between I–Xe and Pb–Pb ages in a number of samples. It is re-evaluated here using Pb–Pb ages adjusted for an updated $^{238}\text{U}/^{235}\text{U}$ ratio of 137.794 and meteorite specific U-isotope ratios. With the addition of the new data for HH 237 chondrule #1, the re-evaluated absolute I–Xe age of Shallowater is 4562.4 ± 0.2 Ma. The absolute I–Xe age of the HH 237 chondrule #1 is 4562.1 ± 0.3 Ma, in good agreement with U-corrected Pb–Pb ages of the Gujba chondrules (Bollard et al., 2015) and HH 237 silicates (Krot et al., 2005).

All I–Xe data used here, and in previous estimates of the absolute age of Shallowater, are calculated using 15.7 ± 0.6 Ma value for ^{129}I half-life. The slopes of I–Xe – Pb–Pb correlation lines plotted for different sets of samples for Shallowater normalization are always ≤ 1 . Assuming uranium half-life values are correct; this restricts the half-life of ^{129}I to ≤ 15.7 Ma. © 2016 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

The CB (Bencubbin-type) carbonaceous chondrites differ from other chondrite groups by high metal content (up to 80 vol%), large depletion in volatile elements, and nearly a complete lack of interchondrule matrix material

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(Weisberg et al., 2001). Chondrules in CB chondrites have exclusively magnesium-rich compositions and non-porphyritic textures (skeletal olivine, SO, and cryptocrystalline, CC); relict grains or coarse-grained igneous rims, indicative of multiple chondrule melting events, are absent. Based on these observations and the young Pb–Pb age of CB chondrules, it was proposed that they formed during a single-stage highly-energetic event in a late-stage protoplanetary disk, most likely in an impact-generated plume (Wasson and Kallemeyn, 1990; Campbell et al., 2002; Rubin et al., 2003; Krot et al., 2005, 2010). According to this model, SO chondrules, rich in refractory lithophile elements (Ca, Al, REEs), represent melt fraction of the plume, whereas CC chondrules, highly depleted in these elements, represent gas–liquid condensates (Krot et al., 2010). Such an event, followed by rapid cooling, is capable of complete resetting short-lived and long-lived chronometers. As a result, the impact plume produced chondrules and metal grains in CB chondrites are potential candidates for anchoring short-lived relative chronometers [e.g., ^{26}Al – ^{26}Mg ($T_{1/2} \sim 0.705$ Ma), ^{53}Mn – ^{53}Cr ($T_{1/2} \sim 3.7$ Ma), ^{182}Hf – ^{182}W ($T_{1/2} \sim 8.9$ Ma), and ^{129}I – ^{129}Xe ($T_{1/2} \sim 15.7$ Ma)] to absolute (U-corrected) Pb–Pb chronology.

Recently, Bollard et al. (2015) reported U-corrected Pb–Pb ages of the magnesian SO chondrules in Gujba (CB_a), 4562.49 ± 0.21 Ma. High-precision bulk Mg-isotope measurements of the magnesian SO chondrules from Hammadah al Hamra 237 (HH 237, CB_b) showed no resolvable ^{26}Mg excess [$(^{26}\text{Al}/^{27}\text{Al}) = (4.5 \pm 8.3) \times 10^{-7}$], consistent with their late-stage origin, but due to the relatively short half-life of ^{26}Al not very useful for testing heterogeneity of ^{26}Al distribution in the disk (Olsen et al., 2013). Gujba metal nodules yield a ^{182}Hf – ^{182}W age of 4562.2 ± 2.4 Ma (Kleine et al., 2005) when anchored by U-corrected Pb–Pb age of the CV CAIs reported by Connelly et al. (2012), consistent with their U-corrected Pb–Pb age (Bollard et al., 2015).

The absolute age of I–Xe standard Shallowater was never measured directly due to the low U content, instead it is derived from the relationship between I–Xe and Pb–Pb systems (Gilmour et al., 2009). This approach allows to fine tune the absolute age normalization when the new data become available. The CB chondrules appear to be suitable for re-evaluation of the absolute I–Xe age of Shallowater, since the proposed formation scenario implies that I–Xe and Pb–Pb systems in these chondrules closed simultaneously. Previous I–Xe studies of chondrules from Gujba and HH 237 by Gilmour et al. (2009) yielded a closure time for Gujba 1.87 ± 0.4 Ma before the Shallowater aubrite standard, corresponding to an absolute age of 4564.2 ± 0.6 Ma. This value appears to be inconsistent with the absolute age reported by Krot et al. (2005) and Bollard et al. (2015), and it lead to a conclusion that “the Pb–Pb age of chondrules from CB chondrites is not representative of chondrule formation” (Gilmour et al., 2009). Thus the I–Xe age of Gujba chondrule and the corresponding Pb–Pb age cannot be used for the absolute age normalization of I–Xe chronometer. However, only 1 of the 7 chondrules measured in this work yielded an I–Xe isochron. This may be due to intense shock metamor-

phism experienced by the CB chondrites (e.g., Weisberg and Kimura, 2010; Garvie et al., 2011), which could have disturbed I–Xe isotope systematics in their chondrules to various degrees. In addition, chondrule formation scenario in an impact-generated plume itself infers some variations in heating and cooling conditions. In order to better understand the formation environment of CB chondrules as recorded by their I–Xe systematics, we focused our study on the skeletal olivine Gujba and HH 237 chondrules, believed to be representative of melt fraction of the impact-generated plume.

2. EXPERIMENTAL

Chondrules in Gujba and HH 237 have magnesium-rich compositions and non-porphyritic (SO and CC) textures (Fig. 1). Cryptocrystalline chondrules, commonly observed only in HH 237, are about 20–100 μm in diameter and have olivine-pyroxene normative compositions. Skeletal olivine chondrules are common in both HH 237 and Gujba. In HH 237, they are generally larger than CC chondrules, about 25–250 μm in diameter, and consist of forsteritic olivine (Fa_{2–4}), low-Ca pyroxene (Fs_{1–5}Wo_{4–7}), high-Ca pyroxene (Fs_{2–4}Wo_{40–50}), and anorthitic mesostasis. Skeletal olivine chondrules in Gujba are texturally and mineralogically similar to those in HH 237, but are significantly larger, up to 15 mm in diameter. Because of large sizes and enrichment in refractory lithophile elements, SO chondrules are better choice for the intercalibration of Pb–Pb and I–Xe chronometers than CC chondrules. For this study we separated 4 Gujba and 2 HH 237 SO chondrules. Each chondrule was split into fragments to allow combined I–Xe (this study) and potential Pb–Pb isotope measurements. Samples were weighed, loaded into the fused quartz ampules and sealed under vacuum.

Samples, along with a Shallowater enstatite irradiation standard, were irradiated with thermal neutrons as part of the SLC-16 capsule in the pool area of the Missouri University Research Reactor (MURR), receiving $\approx 2 \times 10^{19}$ n/cm². The samples were placed in a fixed horizontal plane at the center of the vertical neutron profile in the pool of the reactor to minimize any vertical gradient and the capsule was continuously rotated to eliminate any x – y gradient. To monitor the neutron density during the irradiation, four pieces of Co-doped aluminum monitor wire were placed among the samples in the middle and around the perimeter of the irradiation capsule. After cooling, samples were removed from the quartz ampoules, wrapped in platinum foil, and placed in the extraction system of the mass-spectrometer.

Xenon was released in stepwise extractions in a W-coil; 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 helium, neon, and argon using activated charcoal at a temperature of –90 °C for adsorption of xenon (the light gases were pumped away) and +165 °C for xenon desorption. The isotopic composition of the released xenon was measured by high transmission ion-counting mass-spectrometry (Hohenberg, 1980).

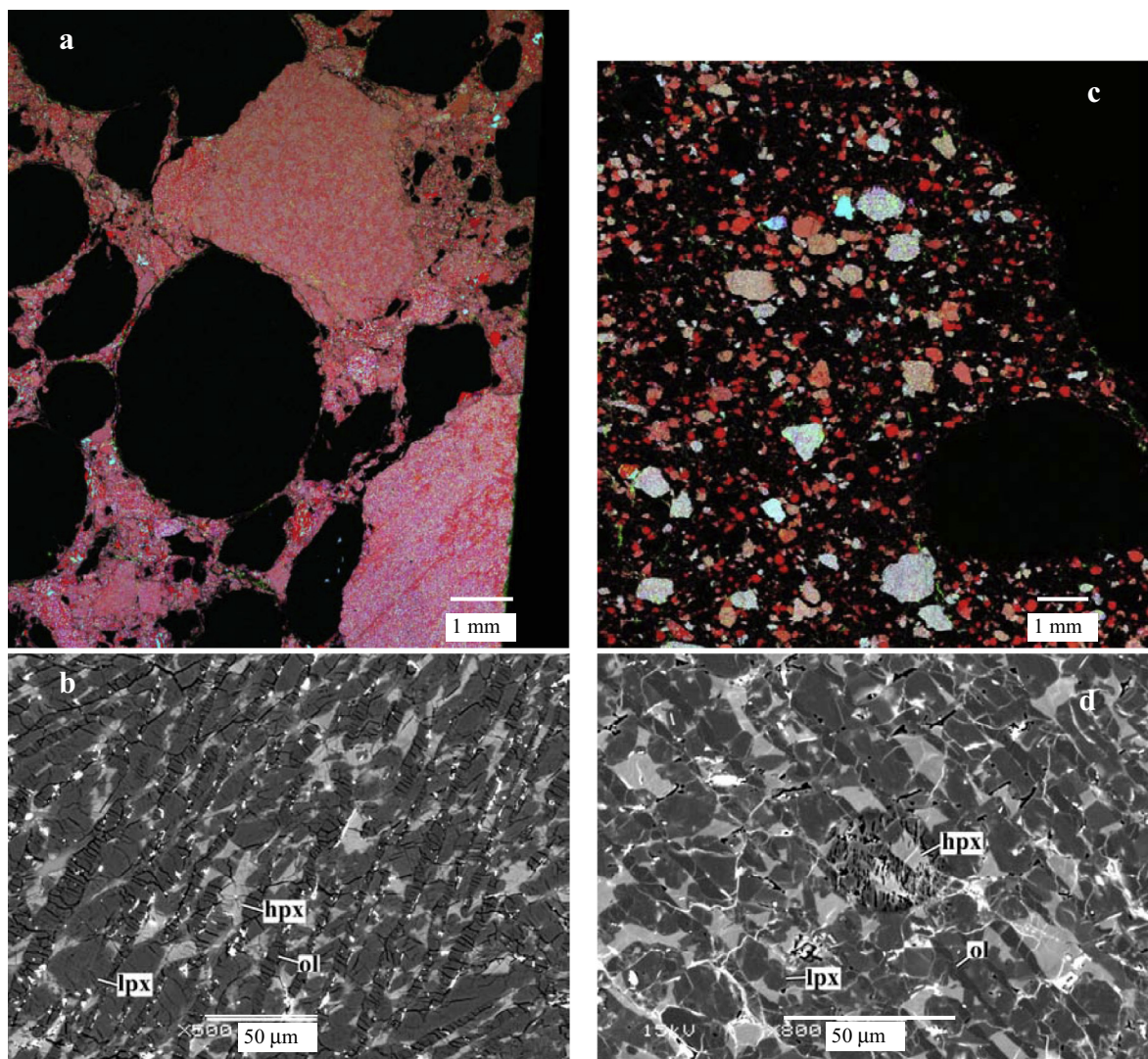


Fig. 1. The CB carbonaceous chondrites Hammadah al Hamra 237 (HH 237) and Gujba. a, c – combined elemental maps in Mg (red), Ca (green), and Al K α (blue) X-rays. b, d – elemental maps in Ni K α X-rays. Gujba consists of large chondrule fragments with skeletal olivine (SO) textures and compositionally uniform Fe,Ni-metal \pm sulfide nodules. HH 237 contains abundant, small Fe,Ni-metal grains, chondrules, and Ca,Al-rich inclusions (CAIs), and rare, large Fe,Ni sulfide nodules. Chondrules have cryptocrystalline (CC, reddish colors) and SO (bluish colors) textures.

Hot blanks were measured with an empty coil at 1500 °C (15 min) following standard analytical procedures and were about 2×10^{-15} $^{132}\text{Xe cm}^3$ STP and approximately atmospheric in composition. We do not measure extraction temperatures directly during the analysis, instead we determine them indirectly via the heating coil current. The heating coil temperature as a function of heating coil current was calibrated using an optical pyrometer, and the double-walled radiation shield around the heating coil insures good agreement between actual extraction temperatures within the coil and the coil temperatures established by the calibration. Since the samples are routinely wrapped in platinum foil for the analyses, the heating coil current, recorded for each studied sample at the melting of platinum, provide an independent internal calibration. After the stepwise heating analysis of each sample, the coil was kept for 10 min at a

temperature higher than the platinum melting temperature (~ 2000 °C), and a new hot blank was measured at 1500 °C before analyzing a new sample to assure that no sample memory effects exist.

3. RESULTS

The measured xenon isotopic compositions for the Gujba and HH 237 chondrules and the Shallowater standard are given in [Table 1 \(Supplement\)](#). Concentrations of radiogenic ^{129}Xe , ^{131}Xe and ^{128}Xe are calculated as excesses over trapped Q-Xe composition. These values as well as trapped ^{132}Xe , and U-fission ^{132}Xe are listed in [Table 1](#). Concentrations for ^{128}Xe shown for all extraction steps, minus the first one (800 °C), to minimize contributions from ^{128}Xe associated with the superficial iodine contamination.

Table 1

Concentrations of radiogenic ^{129}Xe , ^{131}Xe and ^{128}Xe , trapped ^{132}Xe , and U-fission ^{132}Xe in Gujba and HH 237 chondrules.

| | | ^{129}Xe | $^{128}\text{Xe}^{\text{b}}$ | ^{131}Xe | ^{132}Xe | |
|-------|----|--|------------------------------|-------------------|-------------------|-----------|
| | | $\times 10^{-10} \text{ cm}^3 \text{STP/g}^{\text{a}}$ | | | | |
| | | | | | Trapped | U-fission |
| Gujba | C1 | <0.001 | 0.54 | 8.0 | 7.8 | 0.02 |
| | C2 | <0.002 | 8.7 | 1.6 | 0.16 | 0.03 |
| | C4 | <0.001 | 0.28 | 0.39 | 0.10 | 0.01 |
| | C5 | <0.001 | 2.30 | 2.84 | 0.9 | 0.12 |
| HH237 | C1 | 31.1 | 57.4 | 8.6 | 9.8 | 0.1 |
| | C3 | 0.013 | 2.6 | 2.6 | 0.7 | 0.1 |

^a All concentrations should be considered lower limits since iodine- and uranium-bearing phases most probably constitute for only a part of the each studied chondrule fragment.

^b Concentrations for ^{128}Xe shown for all extraction steps, with an exception of the first one (800 °C), to minimize contributions from ^{128}Xe associated with the superficial iodine contamination.

Concentrations of ^{129}Xe in all of the Gujba chondrules studied here are below the detection limit. Although concentrations of ^{128}Xe in two Gujba chondrules are comparable with those in HH 237 chondrules, the remaining Gujba chondrules have ^{128}Xe concentrations that are about one order of magnitude lower. All analyzed samples contained small amounts of fission xenon, most likely a product of reactor neutron-induced fission of ^{235}U (Table 1).

Little evidence for ^{129}Xe was found in the HH 237 chondrule #3 which has a composition within 1σ of the Q-Xe trapped component (Busemann et al., 2000; Ott, 2014). Only HH 237 chondrule #1 was rich in ^{129}Xe . It yielded a high precision isochron defined by 7 experimental points in the temperature interval from 1300 °C up to the melting temperature of platinum (~1770 °C). The data obtained for this chondrule are illustrated on a three-isotope diagram, where $^{129}\text{Xe}/^{132}\text{Xe}$ is plotted versus $^{128}\text{Xe}/^{132}\text{Xe}$ after correction for fission Xe component (Fig. 2). Fission corrections are generally of negligible impact on I-Xe systematics with an alternative normalization to ^{130}Xe , which requires no fission correction. The larger uncertainties from the less abundant ^{130}Xe are all correlated so they do not significantly affect isochron slopes. Both are routinely utilized as redundancy checks and to verify any fission corrections. In all cases, slopes of the isochrons using both normalizations agree well within the stated uncertainties. In HH 237 chondrule #1, the isochron corresponds to closure of the I-Xe system 0.29 ± 0.16 Ma after Shallowater, i.e. about 2 Ma later than in a previously studied Gujba chondrule (1.87 ± 0.4 Ma before Shallowater, Gilmour et al., 2009).

The isotopic composition of xenon released during stepwise heating analysis of the HH 237 chondrule #1 strongly supports simultaneous closure of the I-Xe and Pb-Pb systematics. Although the release profiles of trapped ^{132}Xe and I-derived xenon (^{129}Xe and ^{128}Xe) do not correlate (Fig. 3), the release profiles of ^{129}Xe , ^{128}Xe and U-fission ^{132}Xe do seem to correlate at the two higher temperatures peaks 1300–1400 °C and 1550–1600 °C, suggesting a common host. The concentration of radiogenic ^{129}Xe increases from the low temperature to high temperature with each extraction step as the composition gradu-

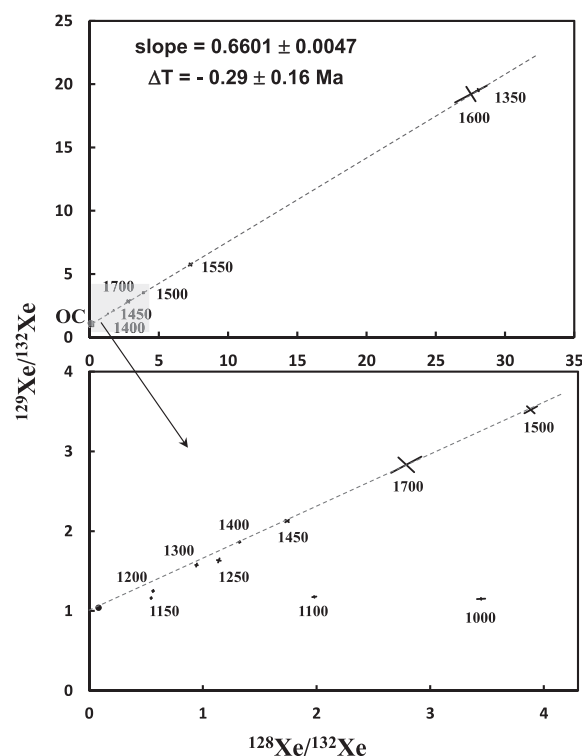


Fig. 2. ^{129}I – ^{129}Xe isochron for the HH237 chondrule #1. $^{129}\text{Xe}/^{132}\text{Xe} = 0.98 \pm 0.13$ at OC $^{128}\text{Xe}/^{132}\text{Xe}$ value (0.083). The I-Xe age is calculated relative to the slope of the Shallowater correlation line of 0.6686 ± 0.0036 . Numbers are extraction temperatures.

ally approaches the isochron beginning at 1300 °C. This systematic behavior of I-derived xenon also allows studying its diffusion properties. When presented in form of an Arrhenius plot, the low temperature extractions (1100–1300 °C) approaching major release peak of ^{129}Xe and ^{128}Xe indicate host phase with a Xe diffusion activation energy $E = 70$ kcal/mol (Fig. 4). The extraction steps approaching the high-temperature release peak (1500–1700 °C) fall on a steeper correlation line, consistent with the diffusion from a more refractory phase with a

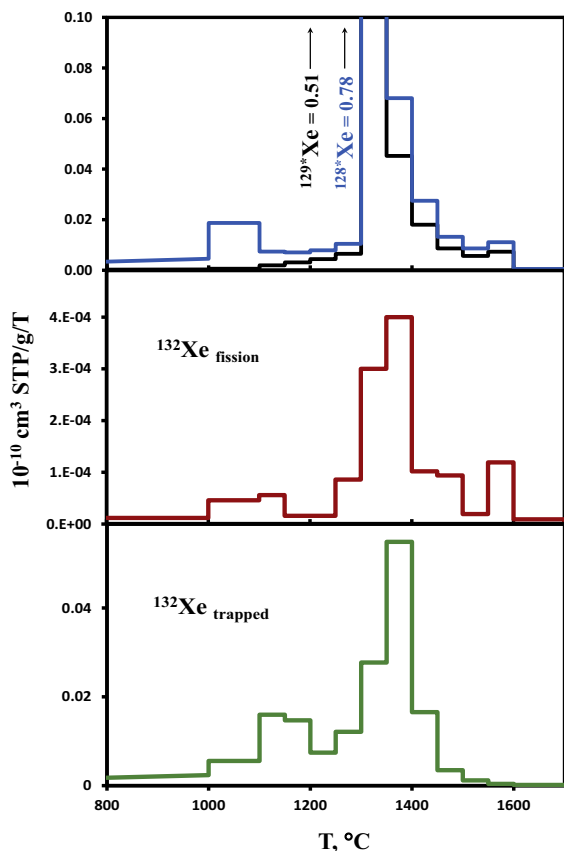


Fig. 3. Release profiles of the radiogenic $^{128*}\text{Xe}$, $^{129*}\text{Xe}$, trapped ^{132}Xe and U-fission ^{132}Xe as a function of temperature for the HH 237 chondrule #1.

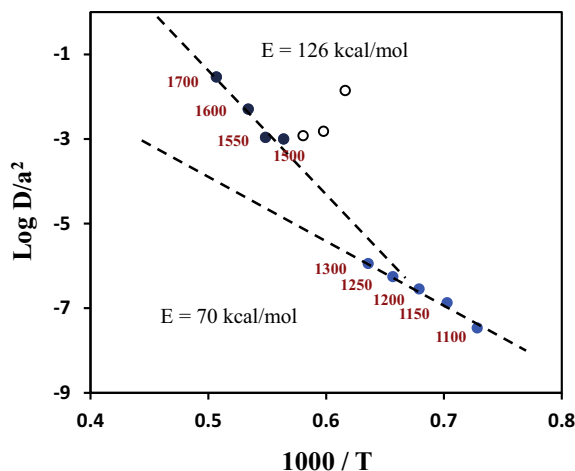


Fig. 4. Arrhenius plot, $\log D/a^2$ vs. $1000/T$, for radiogenic $^{129*}\text{Xe}$ from HH237 chondrule #1. Low temperature and high temperature release peaks (solid symbols) define distinct linear trends with activation energies of ~ 70 and ~ 126 kcal mole $^{-1}$, respectively. Open symbols correspond to the extractions where two peaks are unresolved.

corresponding activation energy of $E = 126$ kcal/mol. Open symbols on the Arrhenius plot represent extractions in 1350–1450 °C temperature range where the two release

peaks overlap, the corresponding concentrations of radiogenic $^{129*}\text{Xe}$ are sums of $^{129*}\text{Xe}$ released from both low and high temperature carrier phases (Fig. 3). It is possible to resolve these concentrations, but Bogard et al. (2005) demonstrated that this would result in an even steeper slope of the higher temperature correlation line on the Arrhenius plot and correspondingly higher Xe diffusion activation energy for a refractory phase. In case of HH 237 chondrule #1, the concentration of $^{129*}\text{Xe}$ in the high temperature peak is ~ 50 times less than that in 1300–1400 °C extractions, so an attempt to resolve these two peaks will result in high uncertainties.

What is important here is, independent of the exact Xe-diffusion activation energies, the values are clearly different, pointing to presence of at least two distinct iodine host phases in HH 237 chondrule #1. Nevertheless, the I–Xe systems in these distinct mineral phases closed simultaneously. The $^{129*}\text{Xe}/^{128*}\text{Xe}$ ratio (corresponding to the $^{129}\text{I}/^{127}\text{I}$ ratio at closure) is constant in temperature range 1300–1600 °C, overlapping the step-wise heating and melting of both iodine-carrier phases. This indicates rapid heating and cooling, or rather quenching, of HH 237 chondrules in an environment which is consistent with the high-energy impact model (Wasson and Kallemeyn, 1990; Campbell et al., 2002; Rubin et al., 2003; Krot et al., 2005, 2010).

Release profiles of I-derived $^{129*}\text{Xe}$ and U-fission ^{132}Xe also seem to correlate (Fig. 3). In the case of HH 237 chondrule #1, we do not have sufficient temperature resolution to definitely conclude that I- and U-derived xenon were released from the same mineral phase in 1300–1400 °C release. A majority of samples we analyzed over the years (Hohenberg and Pravdivtseva, 2008) tend to form isochrons in the temperature range starting from ~ 1250 °C. It is possible that iodine and xenon reside in two different mineral phases which happen to release xenon at similar temperatures during the step-wise heating of this chondrule. In contrast, the 1550–1600 °C release peak is highly unusual. It is the first time we have observed a $\sim 32\%$ $^{129*}\text{Xe}$ spike over the previous extraction step at such a high temperature. A similar release profile pattern for Gujba CB chondrule was reported by Gilmour et al. (2009). In their case, the I–Xe isochron was defined only by these high temperature extractions and corresponded to a closure of the I–Xe system at 1.87 ± 0.4 Ma before Shallowater. This age is consistent with the relative I–Xe ages of the oldest chondrules from ordinary chondrites 1.8 ± 1.8 Ma before Shallowater (Hohenberg and Pravdivtseva, 2008), suggesting that the I–Xe age of this Gujba chondrule corresponds to the highly refractory iodine-carrier phase that survived a catastrophic impact between the planetary embryos.

4. DISCUSSION

4.1. Implications for absolute age normalization of I–Xe chronometer

^{129}I – $^{129*}\text{Xe}$ is a relative chronometer that can be made into an absolute chronometer by proper normalization, typically through intercalibration with Pb–Pb absolute

chronology. Ideally, to normalize it to an absolute time scale, the relative I–Xe age and the absolute Pb–Pb age should be measured in the same sample, with the implicit assumption that both chronometers closed at the same time and date the same event. Even if such a sample is a pure mineral phase, this does not necessarily insure that I–Xe and U–Pb systems would have closed simultaneously. To complicate the situation further, these two chronometers could have been affected by secondary processes, such as alteration, shock, thermal metamorphism, and weathering, to different degrees. To make the search for suitable samples even harder, minerals rich in iodine (hence radiogenic ^{129}Xe) usually have concentrations of uranium too low for high precision Pb–Pb dating, and *vice versa*. Very few meteoritic materials fit the requirement for both good Pb–Pb and good I–Xe ages.

During a reactor irradiation stable ^{127}I is converted into ^{128}Xe which is measured along with radiogenic ^{129}Xe produced by ^{129}I decay in I–Xe dating. To obtain an ^{129}I – ^{129}Xe age, this ratio must be related to the $^{129}\text{I}/^{127}\text{I}$ that existed at closure. This is a difficult task since the neutron capture probability must be known, a quantity extremely difficult to monitor and one that varies from irradiation to irradiation due to the importance of resonance neutron capture in ^{127}I (Hohenberg and Kennedy, 1981). However, the use of a meteorite standard, irradiated along with the sample, avoids all these problems since the I–Xe age of the sample *relative* to the standard (relative ages) is easily determined, without any assumptions, simply from differences in their isochron slopes.

The first successful normalization of I–Xe and Pb–Pb ages was obtained from pure Acapulco phosphate separates, one of the few minerals with sufficient iodine and uranium for both techniques (Nichols et al., 1994). However, one sample is not enough to normalize a whole dating scheme and this material, in itself, cannot qualify as an irradiation standard. A more comprehensive comparison between the I–Xe and Pb–Pb systems was required. Brazzle et al. (1999) confirmed the broader correlation between I–Xe and Pb–Pb ages, establishing ^{129}I – ^{129}Xe as an effective chronometer and inferring a more solid absolute age for the Shallowater standard of 4566 ± 2 Ma relative to the Pb–Pb age of Acapulco phosphate. As long as we know its absolute age with a high precision, Shallowater is exceptionally suitable as an absolute ^{129}I – ^{129}Xe age standard: (i) it is available, (ii) it does not require any special sample preparation procedures, and (iii) its I–Xe age is highly reproducible. However, systematic I–Xe and Pb–Pb age differences for Richardton chondrules and pyroxenes suggested that the absolute I–Xe age estimated in this way for the Shallowater I–Xe standard was probably ~ 2 Ma too old if we assume that both Pb–Pb and I–Xe systems in these Richardton samples closed at the same time (Pravdivtseva et al., 1998). A better anchor for the effective Pb–Pb age of Shallowater enstatite was needed.

Gilmour et al. (2006) tied the effective Pb–Pb age of Shallowater, not to a single Acapulco phosphate, but to a group of 9 samples where both I–Xe and Pb–Pb ages were determined, deriving a new absolute value of 4563.3 ± 0.4 Ma, consistent with the earlier observations

(Pravdivtseva et al., 1998). It was refined later to exclude data points that were statistically improbable, resulting in even younger I–Xe absolute Shallowater age of 4562.3 ± 0.4 Ma (Gilmour et al., 2009). That value was derived from a correlation based on the Pb–Pb ages calculated using an old canonical $^{238}\text{U}/^{235}\text{U}$ value of 137.88. A more recent study (Goldmann et al., 2015) of 27 bulk meteorites, combined with previous $^{238}\text{U}/^{235}\text{U}$ data (Brennecka et al., 2010; Bouvier et al., 2011; Connelly et al., 2012; Brennecka and Wadhwa, 2012), led to a revised estimate for the current $^{238}\text{U}/^{235}\text{U}$ value for the Earth and Solar System of 137.794 ± 0.027 , a value which would result in a Pb–Pb age adjustment of -0.9 Ma. Although U-isotope ratios agree within analytical uncertainties for most bulk achondrites and carbonaceous chondrites studied so far, for ordinary chondrites the observed U-isotope ratios range between 137.711 ± 0.008 and 137.891 ± 0.025 . In such cases, if Pb–Pb dating is combined with precise $^{238}\text{U}/^{235}\text{U}$ analyses on the same sample, the accuracy of Pb–Pb ages improves significantly.

Considering the proposed formation scenario (Krot et al., 2005), and the strong xenon isotopic evidence for the simultaneous closure of the I–Xe and Pb–Pb systems, the HH 237 chondrule #1 data seem to be suitable for the absolute age normalization of I–Xe chronometer. Because of nearly a complete lack of interchondrule matrix material in CB chondrites, the Pb–Pb age of HH 237 silicates (Krot et al., 2005) in fact is the age of silicates separated from the HH 237 chondrules. In addition, Bollard et al. (2015) reported U-corrected weighted average Pb–Pb age of 4562.49 ± 0.21 Ma for three magnesian skeletal Gujba (CB_a) chondrules. For the absolute age normalization plot we use both, HH 237 and Gujba Pb–Pb ages as corresponding absolute age values for the relative I–Xe age of HH 237 chondrule #1 reported here.

The Pb–Pb ages are corrected using latest U-isotope ratio for the Earth and Solar System of 137.794 ± 0.027 and meteorite specific U-isotope ratios for Richardton (137.711 ± 0.008) and Acapulco (137.796 ± 0.013). An average of two Allende bulk U-isotope ratios (Connelly et al., 2012; Goldmann et al., 2015) was applied for the correction of the Pb–Pb ages of the earliest chondrules. The U-isotope ratio of 137.794 ± 0.014 for Gujba (Connelly et al., 2012) used here as a proxy for HH 237 U-isotope ratio value.

When considering the set of samples for the I–Xe – Pb–Pb correlation plot, as reported by Gilmour et al. (2009), but using U-ratio corrected Pb–Pb age values, the slope of the correlation line is 0.98 ± 0.11 . An addition of the HH237 chondrule #1 data point to the compilation brings the slope to 1.01 ± 0.11 (Fig. 5a), both consistent with a value of 1, thus supporting simultaneous closure of the I–Xe and Pb–Pb systems in HH 237 chondrules. Derived from the 1.01 ± 0.11 correlation line the absolute age of Shallowater now seems to be 4562.2 ± 0.2 Ma, 0.1 Ma younger than the previous value reported by Gilmour et al. (2009).

In fact, HH237 chondrule #1 is the only sample in this compilation with strong evidence for the simultaneous closure of the I–Xe and Pb–Pb systems. According

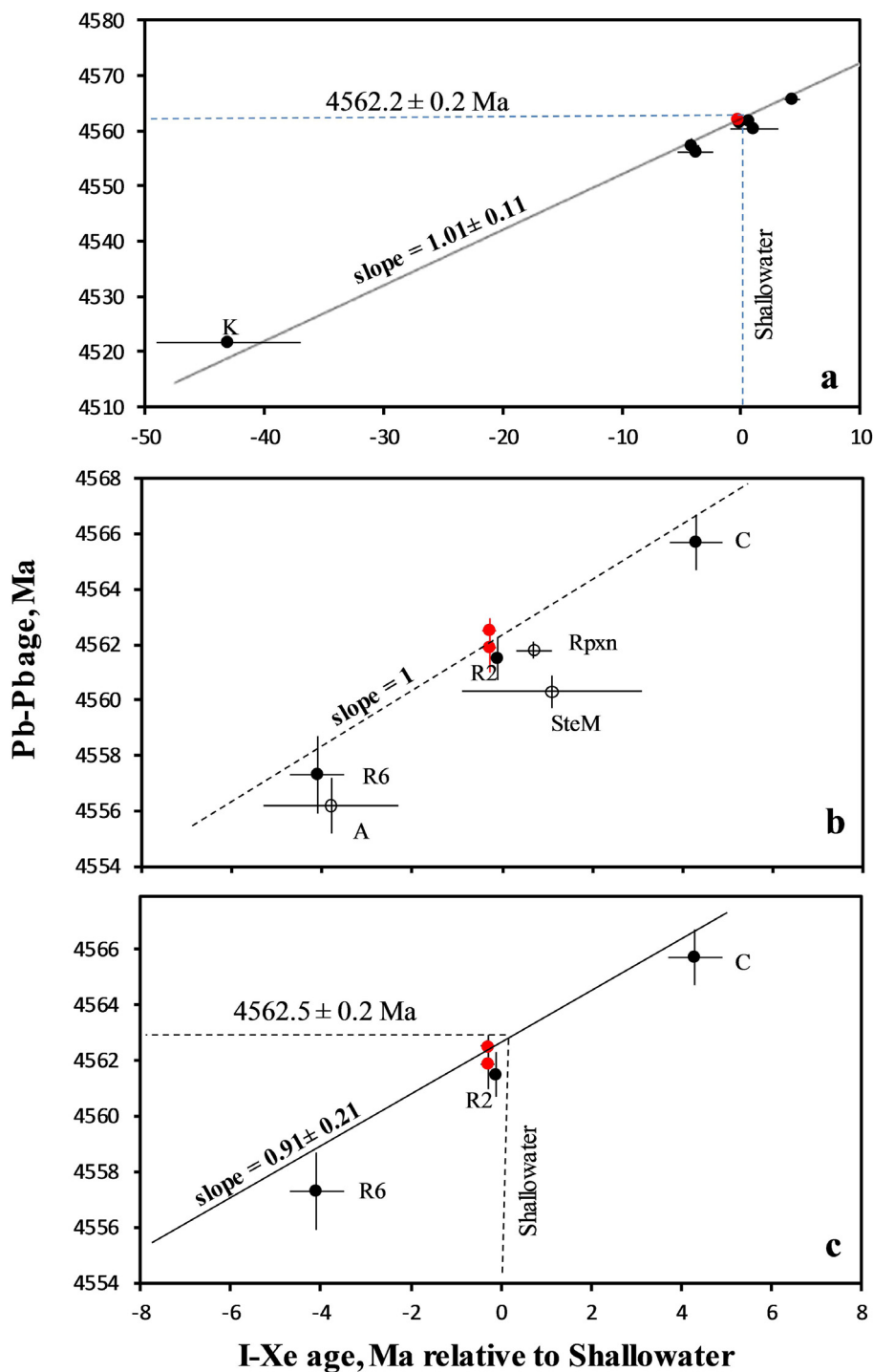


Fig. 5. Comparison of I-Xe and U-corrected P-Pb ages in a range of materials from the early Solar System (Table 2). *Abbreviations:* K – Kernouve; A – Acapulco; R – Richardton; C – earliest chondrules; SteM – Ste Marguerite. HH 237 chondrule #1 data shown as red symbols. (a). Free-fit correlation line based on all available data including HH 237 chondrule #1 (data point for Richardton chondrule #2 and 2 data points for HH 237 chondrule #1 overlap). (b). The gradient of the dotted line, drawn through HH 237 chondrule #1 data (red solid symbols), defined to be 1, as required for concordant evolution of Pb-Pb and I-Xe systematics. Solid symbols are for the Richardton and earliest chondrules. (c). Free fit normalization correlation based on chondrules data only.

proposed single-stage highly energetic event formation scenario for CB chondrules, HH 237 skeletal olivine chondrule #1 represents melt fraction of the impact-generated plume. I-Xe systematics in HH 237 chondrule #1 is unusual, diffu-

sion properties of ^{129}Xe indicate presence of two distinct iodine-carrier mineral phases, one of them highly refractory. Nevertheless I-Xe system in both iodine-carrier phases closed simultaneously, consistent with rapid melting

and cooling due to the highly energetic impact and it was not affected by secondary processing. Thermal metamorphism would have affected major I-carrier phase only or to a higher degree than minor high temperature carrier phase, resulting in a difference in I–Xe closure. That is not what we observe in HH 237 chondrule #1; $^{129}\text{Xe}/^{128}\text{Xe}$ ratio in this sample is constant for both iodine carrier phases. In comparison, the data point for the earliest chondrules is based on the I–Xe ages for two ordinary chondrites Chainpur and Semarkona and the Pb–Pb age of the carbonaceous chondrite Allende. In the cases of Acapulco and Ste Marguerite, the I–Xe ages were measured in feldspars, while Pb–Pb ages in phosphates. The I–Xe age of Kernouve, -43 ± 6 Ma, has an uncertainty that undermines the usefulness of its data point, since the correlation line is strongly weighted by errors on both axes and the older ages on the correlation plot have much lower uncertainties. The exclusion of the Kernouve data from the correlation plot changes neither the absolute age of Shallowater value nor its uncertainty. I–Xe and Pb–Pb ages of the Richardton chondrules were measured in the same chondrules, split for these analyses. Nevertheless, Richardton is H4 and it is possible that the I–Xe and Pb–Pb systems could have been affected by thermal metamorphism to a different degrees.

Assuming HH237 chondrule #1 is indeed the only sample where I–Xe and Pb–Pb systems closed simultaneously, the absolute I–Xe age of Shallowater could be derived from the line with a slope of 1 (slope 1 assumes all half-lives are correct), drawn through HH237 data point (dotted line in Fig. 5b). The data points for 2 Richardton chondrules and earlier chondrules (solid symbols, Fig. 5b) fall closest to this line, suggesting that within this set of samples chondrules are probably better candidates for the absolute age normalization of the I–Xe chronometer than pure mineral separates from Richardton, Acapulco and Ste Marguerite (open symbols, Fig. 5b). The Acapulco and Ste Marguerite points then both fall below the chondrule correlation line, indicating that Pb–Pb system in their phosphate separates closed within 2 Ma after I–Xe closure in respective feldspars.

Although evidence for the simultaneous closure of Pb–Pb and I–Xe systems in HH 237 chondrule #1 is convincing, we cannot rely on one sample to derive an absolute age of Shallowater. The relative I–Xe age of HH 237 chondrule #1 is defined with high precision, but corresponding Pb–Pb ages used in our calculations have been measured in different CB chondrules, not in HH 237 chondrule #1. CB chondrites experienced intense shock metamorphism (e.g., Weisberg and Kimura, 2010; Garvie et al., 2011), which could have disturbed I–Xe and Pb–Pb isotope systems in their chondrules to various degrees. In any case, the correlation between I–Xe and corresponding Pb–Pb ages in a number of samples is a proof that two systems experienced concordant evolution, as shown by the slope 1.0 correlation line in Fig. 5, thus absolute age of the Shallowater standard can be derived with confidence.

The absolute I–Xe age of Shallowater derived from the correlation based on all available data (Table 2, Fig. 5a) is 4562.2 ± 0.2 Ma. Nevertheless, there seems to be stronger correlation for the chondrule data within this available

Table 2

| Samples used in Gilmour et al. (2009) absolute age normalization of the I–Xe chronometer and their respective I–Xe (relative to Shallowater) and U-ratio corrected Pb–Pb ages. I–Xe age of HH 237 chondrule #1 studied here and respective Pb–Pb ages for HH 237 silicates and Gijba chondrules are shown in a last row. | | | | | |
|--|---|--------------------------------------|---------------|---|--------------------------------------|
| | I–Xe age, Ma | | Pb–Pb age, Ma | | |
| Earliest chondrules | Swindle et al. (1991a) Swindle et al. (1991b) | Chainpur, LL3.4 Semarkona, LL 3.0 | 4.3 ± 0.6 | Amelin and Krot (2007) | Allende, CV3 |
| Richardton, H4 | Pravdivtseva et al. (1998) Gilmour et al. (2006) | Pyroxene | 1.1 ± 2.0 | Amelin (2001) | Pyroxene |
| | | Chondrule 2 | −0.1 ± 0.1 | Gilmour et al. (2006) | Chondrule 2 |
| | | Chondrule 6 | −4.1 ± 0.6 | | Chondrule 6 |
| Acapulco | Brazzle et al. (1999) | Feldspar | −3.8 ± 1.5 | Göpel et al. (1994) | Phosphate |
| Ste Marguerite, H4 | Brazzle et al. (1999) | Feldspar | 0.7 ± 0.4 | Göpel et al. (1994) | Phosphate |
| Kernouve, H6 | Brazzle et al. (1999) | Phosphate | −43 ± 6 | Göpel et al. (1994) | Phosphate |
| HH 237, CB | This work | Chondrule | −0.29 ± 0.16 | Krot et al. (2005) Bollard et al. (2015) | HH 237 silicates Gijba chondrules |
| | | | | | 4562.5 ± 0.2 |

data set. The absolute age of Shallowater, derived from the correlation line based only on the chondrule data (Fig. 5c), is 4562.5 ± 0.2 Ma, although the slope of the line correlating Pb–Pb and I–Xe is 0.91 ± 0.21 , less than if all 9 data points are considered (1.01 ± 0.11). The slopes of the both correlation lines, based on only chondrule data (Fig. 5c) and based on the full data set from Table 2 (Fig. 5a), are weighted heavily by data points for Richardton chondrule #2 and HH 237 chondrule #1, they cluster close to the relative I–Xe age of 0, so 10% change in the slope value results in the difference between two Shallowater absolute age estimations of only 0.3 Ma, within their uncertainties. We suggest a median value of 4562.4 ± 0.2 Ma as the new absolute age of Shallowater. This value should be considered as the best current estimate, and could be further evaluated and fine-tuned when new suitable data became available.

4.2. Implications for the ^{129}I half-life value

The slopes of I–Xe – Pb–Pb correlation lines range from 1.01 ± 0.11 for the whole set of data points to 0.91 ± 0.21 , when only chondrule data are considered. Moreover, the slope of the correlation line was always ≤ 1 when we investigated how inclusion of various data points from Table 2 affects the slope value, suggesting that the half-life of ^{129}I used in our I–Xe age calculations is close to the correct value. When Holden (1990) proposed to use 17 Ma, the unweighted average of all available data (Katcoff et al., 1951; Russell, 1957; Emery et al., 1972; Kuhry and Bontems, 1973), as a value for ^{129}I half-life, the most accurately quoted results for ^{129}I half-lives were either unpublished or contain insufficient detail for inclusion. Since the earlier published values of 15.6 ± 0.6 Ma (Russell, 1957) and 15.7 ± 0.6 Ma (Emery et al., 1972) were in good agreement with each other, we historically used an average of these two numbers as the ^{129}I half-life value in our calculations (15.7 ± 0.8 Ma). All I–Xe data used here and in previous estimation of the absolute age of Shallowater (Gilmour et al., 2009) are acquired in our laboratory and calculated using this value, consistent with the Oak Ridge National Lab report by Russell (1957). In fact, in order to bring the slope of 0.91 ± 0.21 for the chondrules I–Xe and Pb–Pb ages correlation to 1, the half-life of ^{129}I should be even lower, about 14.6 Ma. However, since the ^{129}I half-life only affects the relative I–Xe ages, the few Ma relative to Shallowater, the absolute I–Xe ages are almost immune to this uncertainty in the ^{129}I half-life. Therefore, although our data favor the shorter ^{129}I half-life of 15.7 ± 0.8 Ma, either half-life value, 17 Ma or 15.7 Ma, would give almost the same absolute I–Xe ages for these samples.

It worth noticing that the Pb–Pb age of Allende chondrules, used as an ordinate value for the earliest chondrules data point, was corrected using 137.78 ± 0.016 U-isotope ratio, an average of two values measured in bulk Allende samples. U-isotope ratio for Allende CAIs is lower 137.29 ± 0.026 (average of two values, Goldmann et al., 2015) pointing to the heterogeneity of U-isotope ratios among the Allende components. It is possible that U-isotope ratio in Allende chondrules is yet different from

the bulk and CAI values, affecting the slope of the correlation line between I–Xe and Pb–Pb ages. This change would be more significant for the correlation based on only chondrule data. We cannot set the low limit for the half-life of ^{129}I based on our observations. But since the slopes of I–Xe – Pb–Pb correlation lines are ≤ 1 , the half-life of ^{129}I most probably is ≤ 15.7 Ma, not 17 Ma as was proposed by Holden (1990). This value is in a good agreement with half-life of ^{129}I 16.1 ± 0.7 Ma listed in Table de Radionucléides (BNM-LNHB/CEA, 2004) and based on the same data (Katcoff et al., 1951; Russell, 1957; Emery et al., 1972; Kuhry and Bontems, 1973) but now calculated as the weighted average.

5. CONCLUSIONS

The absolute age normalization of the Shallowater I–Xe standard should be based not on a single measurement but on a range of samples dated by both I–Xe and Pb–Pb techniques. The underlying problems here are the divergence of minerals suitable for dating by both chronometers and the evaluation of the data sets for a diverse set of samples. When refined, using updated list of samples and Pb–Pb ages which are corrected using latest U-isotope ratio for the Earth and Solar System and meteorite specific U ratios, a self-consistent value for the absolute age of Shallowater aubrite is 4562.4 ± 0.2 Ma, only 0.1 Ma older than the previous estimation. This gives us confidence that the absolute age normalization of I–Xe system is now robust. Calculated relative to Shallowater, the I–Xe age of HH 237 chondrule #1 of -0.29 ± 0.16 Ma corresponds to an absolute age of 4562.1 ± 0.3 Ma, in agreement with the Pb–Pb ages of HH 237 silicates of 4561.9 ± 0.9 Ma (Krot et al., 2005) and Gujba chondrules 4562.49 ± 0.21 Ma (Bollard et al., 2015). This age supports a simultaneous reset of the I–Xe and Pb–Pb systems after the high-energy impact and following rapid cooling at the chondrule formation time (Krot et al., 2005).

HH237 appears to be more suitable for the I–Xe studies than Gujba. One in four HH 237 chondrules yielded a high precision I–Xe age compared with one in nine for Gujba (Gilmour et al., 2009; this study). Although radiogenic xenon in the earlier Gujba work, and reported here for HH237, follows a similar release pattern, in the case of HH 237 the experimental points corresponding to both release peaks fall on the same isochron. In addition, the HH 237 chondrule #1 has higher concentrations of radiogenic ^{129}Xe and ^{128}Xe than the Gujba chondrules studied here and by Gilmour et al. (2009). Given the impact-plume model for the formation of CB chondrules (Krot et al., 2005) and the inferred simultaneous closure of the I–Xe and Pb–Pb systems [this study], an even more refined inter calibration of I–Xe and Pb–Pb might be possible by a direct comparison of common host Pb–Pb and I–Xe ages of additional CB chondrules.

Independent of the choice of data for the absolute age normalization plot, the slopes of I–Xe – Pb–Pb correlation lines are consistently ≤ 1 . Assuming that the U half-life values are correct, the half-life of ^{129}I most probably is ≤ 15.7 Ma.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.gca.2016.01.012>.

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