Isotopic fractionation of Cu in tektites

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Abstract: Tektites are terrestrial natural glasses of up to a few centimeters in size produced during a hypervelocity impact of an extraterrestrial projectile onto the Earth's surface. It is well established that the chemical and isotopic composition of tektites in general is identical to the composition of the upper terrestrial continental crust. Tektites typically have very low water content which has generally been explained by volatilization at high temperature; however the exact mechanism is still debated. Because volatilization can fractionate isotopes, comparing the isotope composition of volatile elements in tektites with that of their source rocks may help to understand the physical conditions during tektite formation.

Interestingly, volatile chalcophile elements (Cd and Zn) seem to be the only element isotopically fractionated in tektites. Here, we extend this study to Cu, another volatile chalcophile element. We have measured copper isotopic composition for 20 tektites originating from the four different strewn fields. All the tektites (but the Muong-Nong type) are enriched in the heavy isotopes of Cu ($1.99 < \delta^{65}Cu < 6.98$) in comparison to the terrestrial crust ($\delta^{65}Cu \approx 0$) with

no clear distinction between the different groups. Muong-Nong type tektites and a Libyan desert glass are not fractionated at all ($\delta^{65}Cu \approx 0$) in comparison to the terrestrial crust. To refine the Cu isotopic composition of the terrestrial crust we also present data for 3 geological reference materials ($\delta^{65}Cu \approx 0$).

The correlation of $\delta^{65}Cu$ with the abundance of Cu probably reflects that the isotopic fractionation occurred by evaporation during heating. A simple Rayleigh distillation cannot explain the Cu isotopic data and we suggest that the isotopic fractionation is governed by a diffusion-limited regime. Cu ($1.99 < \delta^{65}Cu < 6.98$) is isotopically more fractionated than the more volatile element Zn ($\delta^{66/64}Zn$ up to 2.49 ‰). This difference of behavior between Cu and Zn is predicted in a diffusion-limited regime where the magnitude of the isotopic fractionation is regulated by the balance between the evaporative flux and the diffusive flux at the diffusion boundary layer. Due to the difference of ionic charge in silicates (Zn^{2+} vs Cu^+), Cu has a coefficient of diffusion larger than Zn by at least two orders of magnitude. Therefore the larger isotopic fractionation in Cu than in Zn in tektites is due to the significant difference in their respective chemical diffusivity

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1. Introduction:

Tektites are terrestrial natural glasses of up to a few cm diameter size that are produced during the early phases of a hypervelocity impact of an asteroid or a comet into terrestrial rock (Blum et al., 1992; Glass, 1990; Koeberl, 1986; Koeberl, 1990; Koeberl, 1992). Tektites have been found in only four geographically extended strewn fields (Glass et al., 1991): the North American strewn field of age ~35 Ma (associated with the Chesapeake Bay impact structure, east of the USA (Koeberl et al., 1996; Poag et al., 2004)); the Central European strewn field (associated with the Ries crater in Bavaria, Germany, Engelhardt et al. (1987)) of age ~14.4 Ma, the Ivory Coast tektites strewn field of age ~1.07 Ma (the Bosumtwi impact structure in Ghana is recognized as the source for the IVC, based on similar geochemistry and ages of tektites and crater-based impact melt (Koeberl et al., 1997; Koeberl et al., 1998)) and Australasian strewn field of age ~0.8 Ma for which no impact structure has not yet been identified. The tektites from these four strewn fields are characterized by different chemical compositions, petrologies, and ages.

Tektites have a similar chemical and isotopic composition to that of terrestrial upper continental crust (Koeberl, 1986), as such, tektites must have formed by fusion of such target rock and do not appear to preserve material from the impactor. In addition, studies of cosmogenic radioisotopes (e.g., [10]Be) have shown that tektites derived from the top of the impacted target lithologies (see (Koeberl, 2007; Ma et al., 2004; Serefiddin et al., 2007)). However, osmium isotope studies have shown that a small, but measurable extraterrestrial signature can be detected in at least some Ivory Coast tektites (Koeberl and Shirey, 1993).

In addition to their different geographical origin, the tektites found on land (as opposed to the microtektites found in deep-sea cores) are classified into three groups: (1) normal or splash-

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1 form tektites. Their shapes are not aerodynamic forms, but result mostly from the solidification

2 of rotating liquids. (2) Aerodynamically shaped tektites which are formed from partial re-melting

3 of the tektite glass during atmospheric re-entry, after the initial melt had been ejected outside the

4 terrestrial atmosphere and solidified through quenching. These tektites are only found in the

5 Australasian strewn field, primarily in the form of flanged-button australites. (3) Muong Nong-

6 type (or layered) tektites which are usually considerably larger than normal tektites and are of

7 chunky or blocky appearance. The aerodynamically shaped tektites and the Muong Nong tektites

8 are predominantly found in the Australasian strewn fields.

9 The extreme water depletion of tektites (≤ 0.02 wt%), in comparison to their inferred

10 precursor rocks (typically sedimentary rocks have >1 wt% of water) is still not well understood.

11 Vapor fractionation at very high temperature (>2800 ºC for 5-10 minutes or >3000 ºC for less

12 than a minute) and under oxidizing conditions (Walter, 1967) is a possible origin for the water

13 loss of tektites. However, this model has some flaws (e.g., how to preserve the low Fe^{3+}/Fe^{2+}

14 ratio, as observed in tektites, under these temperature and oxidation state conditions – although

15 atomic bomb glass shows the same behavior; (Glass et al., 1988)) and, therefore, the behavior of

16 volatile elements and molecules during tektite formation is still debated.

17 Volatilization is one of the few mechanisms able to fractionate the isotopes of heavy

18 elements, thus comparing the isotope compositions of volatile heavy elements in tektites with

19 those of their source rocks may help to understand the conditions of evaporation. Variability in

20 the isotope composition of the source rocks is usually a problem for many "light" elements (H,

21 O…), which are fractionated by several mechanisms other than evaporation. "Heavy stable"

22 isotopes, which show no or little variability in terrestrial upper crustal rocks, are more suitable to

23 study the condition of evaporation in tektites. Humayun and Koeberl (2004) measured the K

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1   isotope composition in four tektites from the Australasian strewn field; without finding any

2   variations between the tektites and the related terrestrial rocks. The absence of K isotope

3   fractionation is a surprise because K is a moderately volatile element with a 50 % condensation

4   temperature (Tc) of ~1000K (Lodders, 2003), and K isotopes are fractionated strongly in lunar

5   regolith (Humayun and Clayton, 1995). Based on the absence of K isotopic fractionation in

6   tektites, Humayun and Koeberl (2004) placed an upper limit of loss of K at <2 % and concluded

7   that any other, less volatile elements should not be fractionated during the heating events

8   experienced by tektites. More recently, Herzog et al. (2008)observed that micro-tektites are

9   isotopically fractionated in K, with some micro-tektites being enriched in light isotopes (up to -

10   10.6 ±1.4 ‰) and others in heavy isotopes (up to 13.8±1.5 ‰). However, on average, the micro-

11   tektites were isotopically normal (1.1±1.7 ‰). This implies that, in contrast to tektites, micro-

12   tektites experienced both evaporative loss of isotopically light K and re-condensation of

13   isotopically heavy K. Wombacher et al. (2003) measured enrichment in heavy isotope of Cd in

14   one Muong-Nong tektite in comparison to typical terrestrial rocks. Cd is supposedly more

15   volatile than K, with a 50% condensation temperature of 652 K and this isotopic fractionation

16   may reflect the preferential loss of light Cd isotopes by evaporation during tektite formation.

17   In a previous study, Moynier et al. (2009) analyzed the Zn isotopic composition of 20

18   tektites from the four different strewn fields. Almost all samples were enriched in heavy isotopes

19   of Zn compared to the upper continental crust and on average, the different groups of tektites

20   were isotopically distinct: Muong-Nong type indochinites ($\delta^{66/64}$Zn=0.61±0.30 ‰); North

21   American bediasites ($\delta^{66/64}$Zn=1.61±0.49 ‰); Ivory Coast tektites ($\delta^{66/64}$Zn=1.66±0.18 ‰); the

22   Australasian tektites (others than the Muong Nong-type indochinites) ($\delta^{66/64}$Zn=1.84±0.42 ‰);

23   and Central European moldavites ($\delta^{66/64}$Zn=2.04±0.19 ‰). These results were contrasted with a

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1 narrow range of $\delta^{66/64}$Zn=0-0.7‰ for a diverse spectrum of upper continental crust materials. A

2 Simple Rayleigh distillation predicts isotopic fractionations much larger than what was actually

3 observed and Moynier et al. (2009) have developed a model of evaporation of Zn from a molten

4 sphere which proved that both the Zn isotopic composition and the chemical abundances

5 measured in tektites can be produced by evaporation in a diffusion-limited regime.

6   In the present paper we extend this study to Cu. Copper is a moderately volatile element,

7 with a condensation temperature Tc(Cu) of ~1037K (Lodders, 2003)). Cu is a chalcophile (sulfur

8 loving) element, which means that it bonds preferentially with S. All the elements in which

9 isotopic fractionation have been found in tektites so far (Cd and Zn) are both chalcophile

10 elements. Even if few data have been published so far on the natural fractionation of Cu isotopes

11 in terrestrial rocks, it seems that it has a very limited isotopic variation. The pioneer studies of

12 Marechal (1998) } report values of δ^{65}Cu ~ 0 ± 0.1 ‰ on one basalt from the active Piton de la

13 Fournaise volcano (Réunion Island, Indian Ocean). These results has been further confirmed by

14 Ben Othman et al.'s (2003) which show that the δ^{65}Cu values of MORB and OIB scatter around

15 zero and Archer and Vance (2004) who found δ^{65}Cu =0.07±0.08 in the BCR-1 (basalt Colombia

16 River) geostandard and Herzog et al. (in press) which did not found any isotopic variations

17 (δ^{65}Cu = 0.00 and -0.10) in Pele's hairs from the Nyiragongo volcano (Democratic Republic of

18 Congo). More recently, Li et al. (2009) found that most granitic rocks have a δ^{65}Cu which

19 cluster around zero, with mean values of 0.03±0.15‰ for I-type granites and -0.03±0.42 ‰ for

20 S-type granites. Li et al. (2009) concluded that the Cu isotopic composition of the crystalline part

21 of upper continental crust is close to zero.

22   On the other hand, it has been recently shown that isotope fractionation of Cu in lunar

23 soils (Herzog et al., in press; Moynier et al., 2006) is very large (variations larger than 2 ‰ per

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1 amu). These fractionations have been attributed to vaporization due to impact by

2 micrometeorites and/or sputtering onto the Moon surface. In addition, Albarede et al. (2007)

3 extended the study of isotopic fractionation of Zn and Cu to shocked rocks from a terrestrial

4 impact site, Meteor Crater. Both Cu and Zn are isotopically heavy in these rocks, Cu being

5 slightly more fractionated than Zn (up to 0.8 ‰ for Cu versus up to 0.4‰ for Zn).

6   Because Cu is a chalcophile and moderately volatile element that shows no or little

7 fractionation in most terrestrial rocks on one hand, and large isotopic fractionations have been

8 found in lunar soils and in impacted rocks from a terrestrial impact crater on the other, Cu is a

9 very suitable element to study volatile processes in tektites by means of stable isotope

10 fractionation.

11   Here, we investigate the degree of isotopic fractionation of Cu in 20 different tektites

12 from the four different strewn fields. The Cu isotopic composition of a non-tektite impact glass,

13 Libyan Desert Glass (LDG) from southwestern Egypt (Weeks et al., 1984), has also been

14 measured for comparison. To complete the knowledge of the Cu isotopic composition of the

15 Earth as well as to test the reproducibility of our technique we measure the isotopic composition

16 of Cu in three standard geological reference materials (BHVO-2, AGV-2 and NIST SRM 278).

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18 **2. Samples and analytical methods:**

19 **2.1. Sample description:**

20   Most of all the samples presented in this study have been previously studied for their Zn

21 isotopic fractionation (Moynier et al. 2009). We analyzed the following samples:

22   1) The Ivory Coast (IVC) tektites: IVC-3395 which was previously analyzed for their

23 major and trace element composition by Koeberl et al. (1997) and Zn isotopic composition

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1 (Moynier et al. 2009). 2) Nine Australiasan tektites: Seven Muong Nong-type tektites (MN 8301,

2 MN 8309, MN 8314, MN X102, MN X103, a large Muong Nong tektite and Hainan HFS1); two

3 Australites (5772 and T8205). Australite 5772 is a typical flanged-button australite, for which the

4 rim and the core have been separately been analyzed for Cu isotopic and chemical compositions,

5 whereas T8205 was only analyzed in bulk; two philippinites (1995 and 9201) and two thailandite

6 (8204, 9201). All these samples were already analyzed for their major and trace element

7 compositions by Koeberl (1992) or Moynier et al. (2009) 3) Four Central European tektites: one

8 moldavite from Clum (MC), and three moldavites from Jankov (Jankov 2, 3, and 4).The major

9 and trace element compositions of these samples have been previously reported by Moynier et al.

10 (2009).

11   4) Two North American tektites: Bediasites BED8401 and BED8402 that had been

12 described in Weinke and Koeberl (1985).

13   5) In order to compare the isotopic composition of tektites with an impact glass, we

14 analyzed the Zn isotope composition and the major and trace element composition of a Libyan

15 Desert Glass specimen, LDG 8501. This glass had already been described by Koeberl (1985).

16   6) Three standard geological reference materials: USGS BHVO-2, an ocean island

17 basalt from Hawaii, USA; USGS AGV-2, an andesite from the Guano Valley, in Lake County,

18 Oregon, USA and NIST SRM 278, an obsidian standard.

19   **2.2 Analytical methods:**

20   For all the tektites and the LDG, we retrieved the samples that have been previously

21 processed for Zn isotopic composition (Moynier et al., 2009). For these, fragments of tektites or

22 powders of ~150 mg were cleaned in water for 5 minutes in an ultrasonic bath; the leaching

23 solution was removed, and then the residue was dissolved in HNO_3/HF at 130°C for several days

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1   in closed Teflon beakers. The final sample have been run through an anion exchange resin (AG-

2   1X8 200-400 mesh) in HBr, which absorb Zn, while Cu and major elements pass straight

3   through. The combined major element and Cu fraction was collected and subsequently processed

4   for Cu separation. Cu is further purified from major elements on AGMP1 anion-exchange resin

5   in 7N HCl as described in Maréchal et al. (1999).

6   Copper isotopic compositions were measured on a Nu Plasma High Resolution Multi

7   Collection-Inductively Coupled Plasma-Mass Spectrometer (MC-ICP-MS) at the Ecole normale

8   superieure de Lyon, France, following the procedure described in Maréchal et al. (1999) and

9   Moynier et al. (2006). Isotope ratios are expressed as parts per 1,000 deviations relative to a

10   standard:

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12   $$\delta^{65}\text{Cu (‰)} = \left(\frac{\left(^{65}\text{Cu}/_{63}\text{Cu} \right)_{sample}}{\left(^{65}\text{Cu}/_{63}\text{Cu} \right)_{standard}} - 1 \right) \times 10 \qquad (1)$$

13   The reference material used is the NIST 976 (Maréchal et al., 1999).

14

15   **3. Results:**

16   The Cu isotopic compositions of the geostandards are reported in table 1. The Cu

17   isotopic measurement of BHVO-2 and AGV-2 has been replicated several times to test the

18   reproducibility of the measurement. In average, the three geostandards, obsidian NIST SRM 278

19   (δ^{65}Cu = 0.06); BHVO-2 (δ^{65}Cu =+0.10 ± 0.07 ‰) and AGV-2 (δ^{65}Cu =+0.10 ± 0.10 ‰) are

20   almost not fractionated and show a typical terrestrial composition. These results confirm

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1   previous founding on another geostandard by Archer and Vance (2004): $\delta^{65}Cu$ =0.07±0.08 ‰ in

2   the BCR-1 and confirms the homogeneous distribution of Cu within the silicate Earth.

3   From the replicated measurements of BHVO-2 and AGV-2 we obtain a 2σ external

4   reproducibility ±0.10 ‰ for $\delta^{65}Cu$ that we will use as our error bar in the rest of the paper.

5   The Cu isotopic composition and elemental abundances are reported in the table 2. The

6   full range of $\delta^{65}Cu$ values is about 7 ‰ from -0.06 ‰ (the Muong-Nong tektite 8314) to

7   +6.94 ‰ (the moldavite Jankov 3). On average, the Central European moldavites ($\delta^{65}Cu$

8   =4.60±2.06 ‰; 2 standard error, n=4); the Australasian tektites (others than the Muong Nong-

9   type indochinites) ($\delta^{65}Cu$=4.25±0.70 ‰; n=8) and the Ivory Coast tektites ($\delta^{65}Cu$=4.20 ‰; n=1)

10   are indistinguishable while the North American bediasites ($\delta^{65}Cu$=2.61±0.02 ‰; n=2) and

11   Muong-Nong type indochinites ($\delta^{65}Cu$=0.02±0.02 ‰; n=6) are lighter. When error bars are taken

12   into accounts almost all the groups overlapped at the exception of the Muong-Nong indochinites

13   which are not fractionated ($\delta^{65}Cu$=0.02±0.02 ‰; n=6) and fall in the typical range of the

14   terrestrial crust..

15   The rim ($\delta^{65}Cu$ = 5.37 ‰) of the flanged australite 5572 is slightly heavier isotopically

16   than the core ($\delta^{65}Cu$= 4.03 ‰). Australites are supposed to be formed in two steps: first the high

17   velocity impact of an asteroid into the target rock produces a melt droplet (the future core of the

18   australite), which is ejected above the Earth's atmosphere; second, during its re-entry into the

19   atmosphere the core is heated and re-melted at its surface. The re-melted surface forms the rim

20   (Taylor, 1961).

21   Despite coming from different target rocks, the Libyan Desert Glass 8501 has a $\delta^{65}Cu$ of

22   0.05 ‰ comparable to the mean value of the Muong Nong-type tektites. These values fall into

23   the typical terrestrial range.

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4. Discussion

4. 1. Homogeneous isotopic composition of terrestrial igneous rocks

BHVO-2 (ocean island basalt), BCR-1 (andesite) and NIST SRM 278 (obsidian) are all derived from terrestrial igneous rocks. There constant Cu isotopic composition (0.06 ‰<δ^{65}Cu<0.10 ‰) confirms the previous results from Marechal et al. (1998), (Ben Othman et al., 2006) and (Li et al., 2009) that terrestrial igneous rocks have a nearly homogeneous Cu isotopic composition which scatter around zero. Sedimentary rocks seem to be slightly more fractionated in Cu isotopes. Maréchal et al. (2000) demonstrate that Mn-nodules have a δ^{65}Cu = 0.31 ± 0.23 ‰ but there are still very few data available, and the largest isotopic effects seem to be limited to ores and hydrothermal systems (Zhu et al., 2000). In comparison, meteorites are more fractionated than terrestrial igneous rocks. For example the CI chondrite Orgueil has a δ^{65}Cu = -0.09 ‰ (Luck et al., 2003). Most chondrite groups are enriched in ^{63}Cu with δ^{65}Cu varying between -1.50 ‰ to -0.09 ‰ in carbonaceous chondrites, -0.51 ‰ to +0.10 ‰ in ordinary chondrites. Iron meteorites demonstrate more variations around zero with δ^{65}Cu range between -0.50 ‰ to +0.40 ‰ (Luck et al., 2003; Luck et al., 2005). High-Ti lunar basalts are enriched in Cu heavy isotopes (δ^{65}Cu=+0.50±0.10 ‰) (Herzog et al., in press).

4.2 Cu isotopic fractionation in tektites

In comparison to the homogeneous Cu isotopic composition of most terrestrial and extra-terrestrial rocks (-1.5 ‰<δ^{65}Cu<+0.50 ‰), all the tektites (with exception of the Muong Nong-type tektites and also the Libyan Desert Glass LDG 8501) are greatly enriched in the heavy

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1   isotope of Cu (+1.99 ‰<δ^{65}Cu <+6.98 ‰). This isotopic fractionation has a magnitude

2   comparable to what is observed in lunar regolith samples (up to 4.51 ‰, (Moynier et al., 2006)).

3   We do not know the exact Cu isotope compositions of the target rocks and of the

4   impactor for the different tektites. Therefore we cannot totally rule out that the Cu isotopic

5   fractionations are due to 1) either mixing between a meteoritic component and terrestrial rocks or

6   2) by secondary alteration. Since the heaviest meteoritic samples analyzed so far (Brenham

7   pallasite with δ^{65}Cu=0.49 ‰, (Luck et al., 2005)) is isotopically lighter than most of the tektites,

8   the hypothesis 1) is very improbable. Very little is known about the isotopic fractionation of Cu

9   during alteration. However, the isotopic composition of most terrestrial rocks analyzed so far is

10 very homogeneous and it would, thus, be unlikely that the isotopic fractionation observed in

11 tektites would be the first observation of alteration effects. Therefore, as for Zn, the enrichment

12 in heavy isotopes of Cu in tektites is more likely explained by the loss of isotopically light Cu

13 that was concentrated in the vapor fraction during the heating events experienced by tektites.

14 In addition, the Muong Nong-type tektites are known to be less depleted in volatile

15 elements than splash-form tektites (Koeberl, 1992; Koeberl, 1994). This is confirmed by the

16 elemental concentrations of our tektites where Cu is more abundant in Muong Nong-type tektites

17 (6 ppm<[Cu]<22 ppm) than in the other types of tektites (0.1 ppm<[Cu]<6.5 ppm).   Muong

18 Nong-type tektites are also the ones that remain closest to the site of impact (Koeberl, 1994; Ma

19 et al., 2004). As expected from vapor fractionation, Muong Nong-type tektites are not

20 fractionated at all (δ^{65}Cu =0.02±0.02 ‰) and therefore behave differently than any other kind of

21 tektites. Therefore the Muong-Nong tektites seem to have recorded the typical continental crust

22 isotopic composition.

23

1 **4. 2. Isotopic fractionation of chalcophile elements in tektites**

2   Mg (Esat and Taylor, 1986), K (Humayun and Koeberl, 2004), and B (Chaussidon and

3 Koeberl, 1995) do not show any isotopic fractionation in tektites. In contrast, chalcophile

4 elements, (Zn (Moynier et al., 2009), Cd (Wombacher et al., 2003) and Cu (this study)) show

5 large enrichment in heavy isotopes.   Magnesium is a fairly refractory element and is not

6 isotopically fractionated in lunar regolith. It is, thus, not surprising that this element does not

7 show fractionation in tektites. Potassium, T_c of ~1006 K (Lodders, 2003), is slightly more

8 volatile than Cu, T_c ~1037 K, therefore the large isotopic fractionation of Cu in comparison to

9 the absence of isotopic fractionation of K is surprising. In addition, Zn is more volatile than Cu

10 but less isotopically fractionated in tektites (δ^{66}Zn up to 2.49 ‰ and δ^{65}Cu up to 6.98 ‰). We

11 conclude that the magnitude of the isotopic fractionation is either controlled by a mechanism

12 dependent on other parameters than volatility of the element (*e.g*. a diffusion-limited regime),,

13 and/or that in the condition of evaporation of the tektites Cu behaves as a more volatile element

14 than both Zn and K.

15   This conclusion is supported by the strong depletion of Cu in tektites compared to target

16 rocks. The tektite samples analyzed here have an average Cu content of 2±1ppm when Muong-

17 Nong tektites are excluded. Muong-Nong tektites are less depleted in Cu with an average content

18 of 14±4 ppm and do not show any Cu isotopic fractionations (δ^{65}Cu=0.02±0.02).

19   Assuming that the different target rocks have the composition of the average upper

20 terrestrial crust, [Cu]=28 ppm, [Zn]=67 ppm, and [K]=2.8% (Rudnick and Gao, 2003) one can

21 calculate the relative depletion of the tektites in Cu, Zn and K. It then appears that the tektites

22 (after exclusion of the Muong-Nong tektites) are more depleted in Cu ([Cu]$_{tektites}$/[Cu]$_{continental}$

23 $_{crust}$=0.06±0.04) than in Zn ([Zn]$_{tektites}$/[Zn]$_{continental\ crust}$=0.28±0.06) or K ([K]$_{tektites}$/[K]$_{continental}$

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1    $_{crust}$=0.70±0.12) . The larger depletion (and isotopic fractionation) of Cu in comparison to K is

2   most probably due to its stronger chalcophile behavior and that the evaporation of metal in

3   tektites may be controlled by the S content of the target rock and the impactor and the

4   evaporation of a sulfide phase more volatile than silicates. Interestingly, Albarede et al. (2007)

5   observed that Cu were isotopically more fractionated (up to +0.8 ‰) than Zn (up to +0.4 ‰) in

6   shocked rocks from the Meteor Crater and based on Cu and Zn isotopic composition Moynier et

7   al. (2006) already reached the conclusion that during the formation of lunar volcanic glass Cu

8   should be more volatile than Zn.

9   Figure 2 shows a slightly negative correlation between δ^{65}Cu and the Cu abundance for

10   all bulk tektites analyzed here. As anticipated, if the origin of the isotopic fractionation is

11   evaporation, the isotopic composition becomes heavier when the Cu content decreases.

12   Assuming that evaporation obeys a simple Rayleigh distillation law (Eq. 2), the evolution of the

13   expected δ^{65}Cu as a function of the remaining fraction of Cu is plotted in Fig. 3.

14
$$\delta^{65}Cu = 10^3 \times \left(\frac{[Cu]}{[Cu]_0}\right)^{\alpha-1} - 10^3 \qquad (2)$$

15   with [Cu]$_0$ being the Cu concentration before the evaporation (e.g. the average content of the

16   continental crust, 28 ppm (Rudnick and Gao, 2003)) and α the kinetic fractionation factor that

17   we approximate by $\sqrt{M^{63}Cu / M^{65}Cu}$ where M^{65}Cu and M^{63}Cu are the masses of ^{65}Cu and ^{63}Cu.

18   It can be seen from Fig. 3 that the observed isotopic composition cannot be explained by

19   a Rayleigh distillation of Cu (small dash curve), CuO (black curve) or CuS (large dash curve). A

20   much larger isotopic fractionation would result from a Rayleigh distillation. This result agrees

21   with previous conclusions from Moynier et al. (2009) and Wombacher et al. (2003) that the

22   enrichment in heavy isotopes of both Cd and Zn in tektites cannot be accounted by a Rayleigh

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1 distillation. Instead we recently proposed a model of isotopic fractionation by evaporation at the

2 surface of a molten sphere, the sphere being re-homogenized by diffusion and advection

3 (Moynier et al., 2009).

4

5 **4. 3. Fractionation in a diffusion-limited regime**

6 In a previous modeling of the isotopic fractionation of Zn in tektites, Moynier et al.

7 (2009), used the Rybczynski-Hadamard formulae (Grasset and Albarede, 1994; Levich, 1962),

8 which is a solution of the Navier-Stokes equation for the steady motion of a viscous sphere

9 within a viscous medium. In this model, a velocity field stirs the tektite, while differential

10 evaporation of Zn isotopes occurs at the surface. It was shown that if the characteristic

11 evaporation time is slow with regard to the diffusion timescale, the system deviates from

12 Rayleigh distillation as a diffusion-limited regime is installed, and for a same Zn elemental loss

13 the magnitude of the isotopic fractionation is reduced. One of the limitations of this modeling

14 was the lack of experimental measurements of the diffusion coefficient of Zn in silicate liquid,

15 and 10^{-8} m^2/s was used as likely upper value. Since then, Behrens and Hahn (2009) have reported

16 on extensive study of trace element diffusion in acidic melts, including Zn. At T=1150°C, the

17 diffusivity of Zn was found to range between 10^{-14} to 5.10^{-12} m^2/s, which suggest even slower

18 diffusion that the one modeled in Moynier et al. (2009), and confirms their suggestion that

19 evaporation should have occurred in a diffusion-limited regime.

20 Such a mechanism might also be proposed to explain the isotopic fractionation we have

21 measured for Cu. To our knowledge, the diffusivity of Cu has not been measured in silicate melts.

22 However, it can be estimated from Mungall (2002) empirical model if its speciation is known.

23 From the measurement of the dependence of Cu partition between silicate melt and metal,

15

1   Holzheid and Lodders (2001) have concluded that copper is present as Cu+ in silicate melts, and

2   will behave as a low field strength element. Using Mungall (2002) model with a temperature of

3   1150°C, we obtain a value for D_{Cu} of $\sim 10^{-10}$ m^2/s. This value is at least 2 orders of magnitude

4   higher than the diffusivity of Zn at similar temperature, which is physically explained by the

5   difference of ionic charge (Zn^{2+} vs Cu^+) which leads to a higher mobility of copper.

6   The magnitude of the isotopic fractionation in the case of a diffusion-limited regime will

7   be controlled by the balance between the evaporative flux and the diffusive flux at the diffusion

8   boundary layer. For a given evaporation flux, a higher diffusivity will lead to an increase of the

9   isotopic fractionation. As a consequence, the larger isotopic fractionation in Cu than in Zn in

10 tektites is due to the significant difference in their respective chemical diffusivity.

11

12 **5. Conclusions**

13 We measured the Cu isotopic composition of 20 tektites from the four different strewn fields,

14 one Libyan desert glass and 3 terrestrial reference materials All the tektites but the Muong-Nong

15 type Indochinites are enriched in heavy isotopes of Cu compared to the upper continental crust

16 ($+1.99$ ‰$<\delta^{65}$Cu $<+6.98$ ‰) On the other hand, the Libyan Desert Glass LDG8501, BHVO-2,

17 BCR-2 and NIST SRM 978 have all the same isotopic composition than our terrestrial standard

18 (δ^{65}Cu ≈ 0). This isotopic fractionation is most probably due to preferential evaporation of the

19 light isotopes of Cu during the heating event of the tektites. We remarked that Cu is isotopically

20 more fractionated than elements which are supposedly more volatile (e.g. K) and only

21 chalcophile elements (Cu, Zn and Cd) show large isotopic effects in tektites. We suggest that

22 this preferential isotopic fractionation of chalcophile element is due to their preferential

23 bounding with S and the evaporation of a sulfide phase more volatile than silicates. Among

16

1   chalcophile elements, Cu is isotopically more fractionated than the more volatile Zn. This

2   unexpected behavior is well explained if, as previously suggested (Moynier et al., 2009), isotopic

3   fractionation in tektites is controlled by a diffusion-limited regime. In a diffusion-limited regime,

4   the isotopic fractionation will be controlled by the balance between the evaporative flux and the

5   diffusive flux at the diffusion boundary layer.Due to the difference of ionic charge in silicates

6   (Zn^{2+} vs Cu^{+}), Cu is more mobile than Zn in silicate melt and have a coefficient of diffusion

7   larger than Zn by at least two orders of magnitude. Therefore for a constant evaporative flux and

8   temperature Cu isotopes are more fractionated than Zn in a diffusion-limited regime.

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Figure Captions:

Fig. 1: $\delta^{65}Cu$ for all the tektites analyzed in this study. All the tektites (at the exception of the Muong-Nong type Indochinites) are enriched in the heavy isotope ($\delta^{65}Cu>0$). In comparison the Libyan Desert Glass LDG 8501and the Muong-Nong type tektites have a $\delta^{65}Cu \approx 0$.

Fig. 2: $\delta^{65}Cu$ vs [Cu] for the different tektites analyzed in this study. This general negative correlation suggests that the isotopic fractionation occurred during evaporation of Cu ([Cu] decreases and $\delta^{65}Cu$ increases because of the preferential loss of light isotopes in the vapor phase).

Fig. 3:. The curves represent the evolution of the in the case of $\delta^{65}Cu$ in function of [Cu]for the residue during a Rayleigh distillation. For comparison the results on the tektites are represented by black dots. A much larger isotopic fractionation than the observations would result from a Rayleigh distillation whatever the Cu species evaporating (Cu, CuS or CuO).

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1 Table 1: Isotopic composition and concentration of Cu in the three geostandards BHVO-2, NIST
2 obsidian, and AGV-2. The isotopic composition is represented using the δ notation (parts per
3 1000 deviation from a terrestrial Cu standard NIST SRM 278).
4

Sample name	δ^{65}Cu
NIST SRM 278	0.06
BHVO-2 1	0.17
BHVO-2 2	0.09
BHVO-2 3	0.08
BHVO-2 4	0.09
BHVO-2 5	0.07
BHVO-2 6	0.08
Average ± 2σ	0.10 ± 0.07
AGV-2 1	0.09
AGV-2 2	0.12
AGV-2 3	0.16
AGV-2 4	0.11
AGV-2 5	0.09
AGV-2 6	0.13
AGV-2 7	-0.02
AGV-2 8	0.16
Average ± 2σ	0.10 ± 0.11

1   Table 2: Isotopic composition and concentration of Cu in tektites and in a Libyan desert glass.
2   The isotopic composition is represented using the δ notation (parts per 1000 deviation from a
3   terrestrial Cu standard NIST XX). The Cu concentrations are in ppm. The external
4   reproducibility (2σ) of δ^{65}Cu is 0.10 .
5

Sample name	δ^{65}Cu	[Cu] ppm
Ivory Coast 3395	4.20	1.9[a]
Bediasite 8402	2.60	6.5[b]
Bediasite 8401	2.60	3.8[b]
Moldavite Jankov 2	5.03	0.1[b]
Moldavite Jankov 3	6.98	0.1
Moldavite Jankov 4	4.41	0.1[b]
Moldavite Clum	1.99	0.4
Hainan HSF1	3.11	2.2[b]
Muong Nong 8301	-0.05	17.7[c]
Muong Nong 8309	0.02	11.4[c]
Muong Nong 8314	-0.06	20.2[c]
Muong Nong X102	0.04	6[d]
Muong Nong X103	0.02	16.3[d]
Large Muong Nong	0.13	12.9
Philippinite 1995	4.54	3.8[b]
Philippinite P9201	4.81	2.2[b]
Thailandite 8204	4.88	0.8[b]
Thailandite 9201	2.73	0.6
Australite 5772 Core	4.03	4.5
Australite 5772 Rim	5.37	0.9[b]
Australite T8205	5.41	1.8[b]
Libyan Desert Glass LDG8501	0.05	1.3[b]

6   [a](Koeberl et al., 1997)
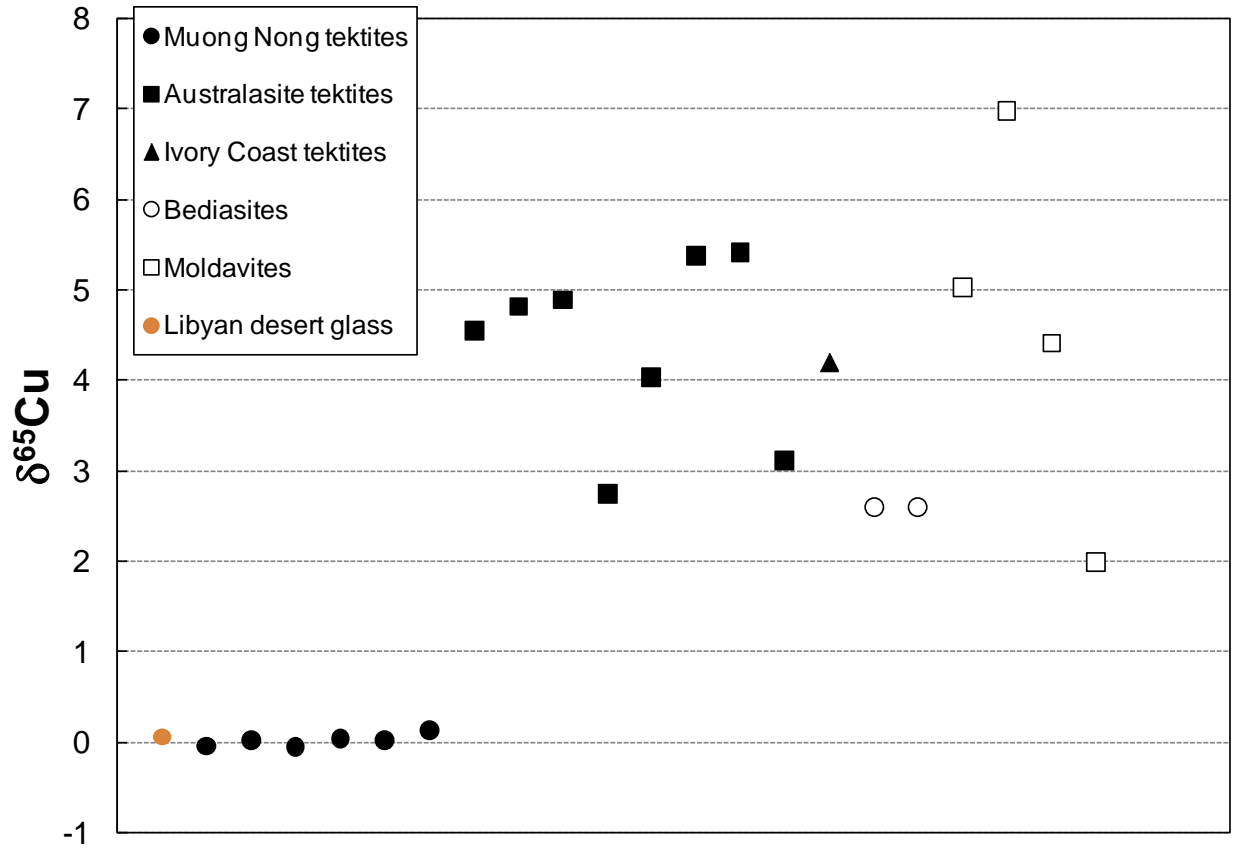7   [b](Moynier et al., 2009)
8   [c](Koeberl, 1992)
9   [d](Glass and Koeberl, 1989)
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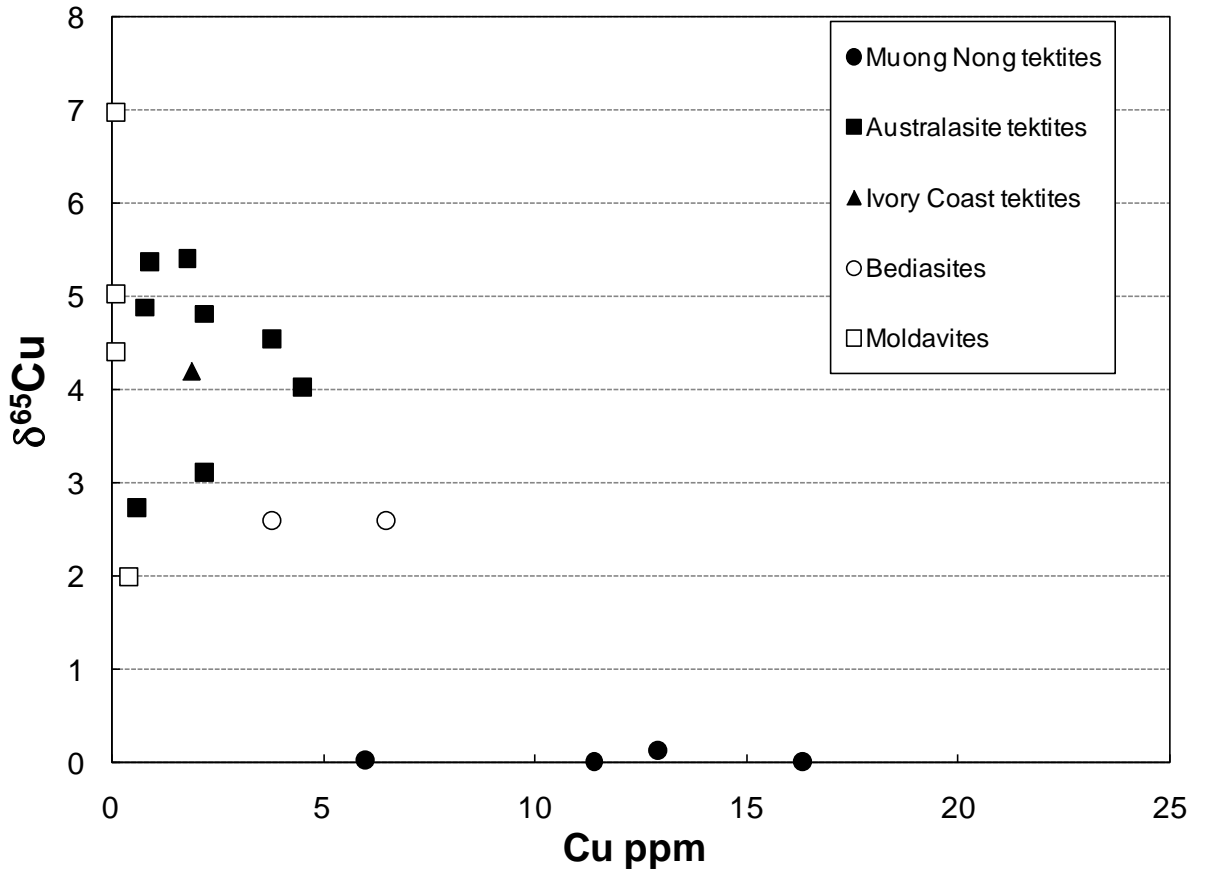
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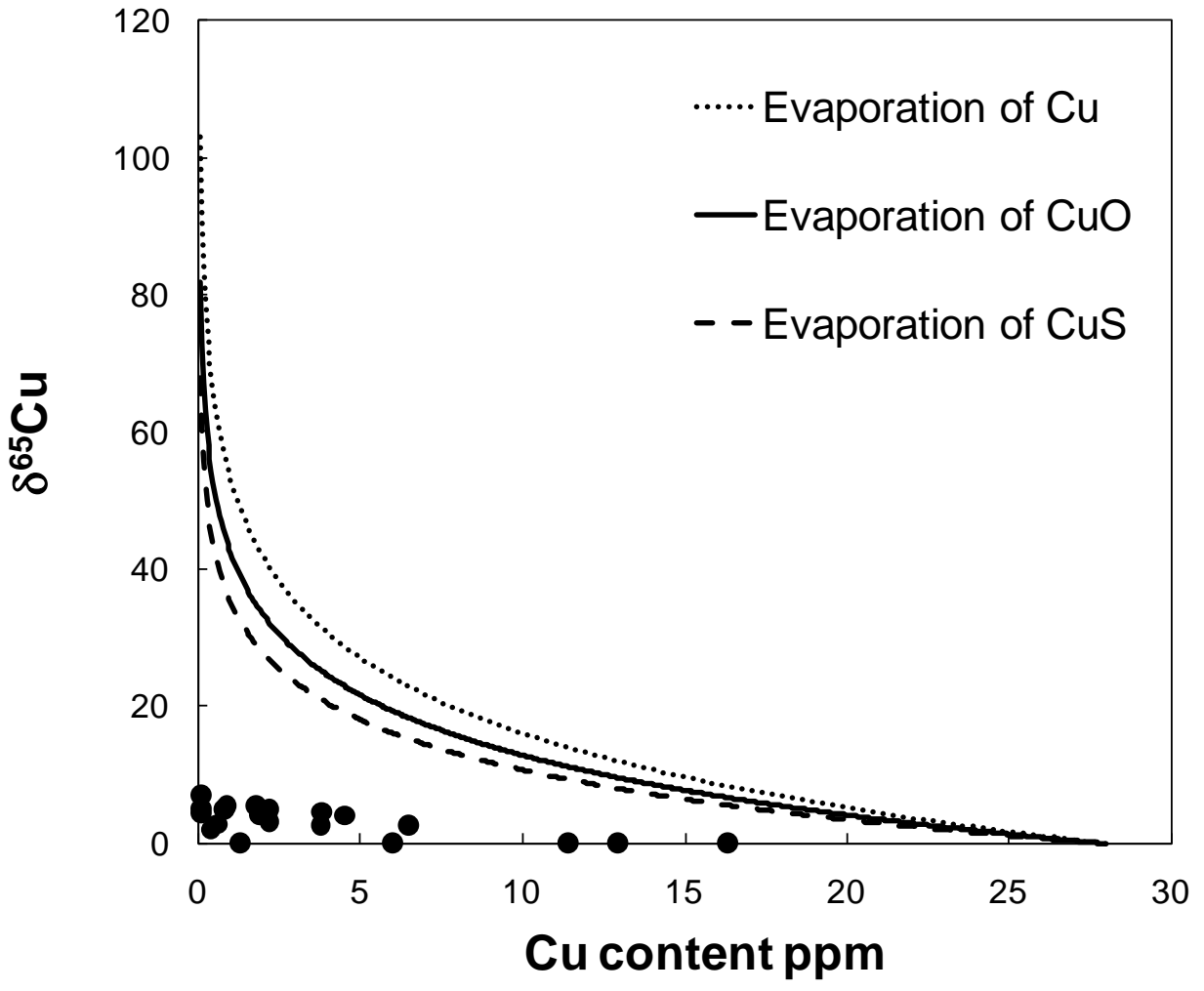

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1   Fig. 2
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Fig. **3**