

NOTICE: This is the author's version of a work that was accepted for publication in *Geochimica et Cosmochimica Acta*. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in *Geochimica et Cosmochimica Acta* [74, 2, 2010] DOI [10.1016/j.gca.2009.10.012](https://doi.org/10.1016/j.gca.2009.10.012)

Isotopic fractionation of Cu in tektites

Frederic Moynier^{1*}, Christian Koeberl², Pierre Beck³, and Fred Jourdan⁴

¹Department of Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University in St Louis, One Brookings Drive, St Louis, MO 63130, USA

²Department of Lithospheric Research, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria

³Laboratoire de Planetologie, Universite Joseph Fourier, CNRS/INSU, Bat. Physique D, BP 53, 38041 Grenoble cedex 9, France

⁴Western Australian Argon Isotope Facility, Department of Applied Geology & JdL-CMS, Curtin university of Technology, GPO Box U1987, Perth, WA 6845; Australia.

*Corresponding author: moynier@levee.wustl.edu, Tel: +1 314-935-8634, Fax: +1 314-935-7361

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 ($1.99 < \delta^{65}\text{Cu} < 6.98$) in comparison to the terrestrial crust ($\delta^{65}\text{Cu} \approx 0$) with

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

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

1 **1. Introduction:**

2
3 Tektites are terrestrial natural glasses of up to a few cm diameter size that are produced during
4 the early phases of a hypervelocity impact of an asteroid or a comet into terrestrial rock (Blum et
5 al., 1992; Glass, 1990; Koeberl, 1986; Koeberl, 1990; Koeberl, 1992). Tektites have been found
6 in only four geographically extended strewn fields (Glass et al., 1991): the North American
7 strewn field of age ~35 Ma (associated with the Chesapeake Bay impact structure, east of the
8 USA (Koeberl et al., 1996; Poag et al., 2004)); the Central European strewn field (associated
9 with the Ries crater in Bavaria, Germany, Engelhardt et al. (1987)) of age ~14.4 Ma, the Ivory
10 Coast tektites strewn field of age ~1.07 Ma (the Bosumtwi impact structure in Ghana is
11 recognized as the source for the IVC, based on similar geochemistry and ages of tektites and
12 crater-based impact melt (Koeberl et al., 1997; Koeberl et al., 1998)) and Australasian strewn
13 field of age ~0.8 Ma for which no impact structure has not yet been identified. The tektites from
14 these four strewn fields are characterized by different chemical compositions, petrologies, and
15 ages.

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

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

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 °C for 5-10 minutes or >3000 °C 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 $\text{Fe}^{3+}/\text{Fe}^{2+}$
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

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 ($\delta^{66/64}\text{Zn} = 0.61 \pm 0.30$ ‰); North
21 American bediasites ($\delta^{66/64}\text{Zn} = 1.61 \pm 0.49$ ‰); Ivory Coast tektites ($\delta^{66/64}\text{Zn} = 1.66 \pm 0.18$ ‰); the
22 Australasian tektites (others than the Muong Nong-type indochinites) ($\delta^{66/64}\text{Zn} = 1.84 \pm 0.42$ ‰);
23 and Central European moldavites ($\delta^{66/64}\text{Zn} = 2.04 \pm 0.19$ ‰). These results were contrasted with a

1 narrow range of $\delta^{66/64}\text{Zn}=0-0.7\text{‰}$ 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 $T_c(\text{Cu})$ of $\sim 1037\text{K}$ (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 $\delta^{65}\text{Cu} \sim 0 \pm 0.1 \text{‰}$ 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 $\delta^{65}\text{Cu}$ values of MORB and OIB scatter around
15 zero and Archer and Vance (2004) who found $\delta^{65}\text{Cu} = 0.07 \pm 0.08$ in the BCR-1 (basalt Colombia
16 River) geostandard and Herzog et al. (in press) which did not found any isotopic variations
17 ($\delta^{65}\text{Cu} = 0.00$ 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 $\delta^{65}\text{Cu}$ which
19 cluster around zero, with mean values of $0.03 \pm 0.15\text{‰}$ for I-type granites and $-0.03 \pm 0.42 \text{‰}$ 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

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).

17

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

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 HNO₃/HF at 130°C for several days

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:

11

$$12 \quad \delta^{65}\text{Cu} (\text{‰}) = \left(\frac{\left(\frac{{}^6\text{Cu}}{{}^65\text{Cu}} \right)_{\text{sample}}}{\left(\frac{{}^6\text{Cu}}{{}^65\text{Cu}} \right)_{\text{standard}}} - 1 \right) \times 1000 \quad (1)$$

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 ($\delta^{65}\text{Cu} = 0.06$); BHVO-2 ($\delta^{65}\text{Cu} = +0.10 \pm 0.07 \text{ ‰}$) and AGV-2 ($\delta^{65}\text{Cu} = +0.10 \pm 0.10 \text{ ‰}$) are
 20 almost not fractionated and show a typical terrestrial composition. These results confirm

1 previous founding on another geostandard by Archer and Vance (2004): $\delta^{65}\text{Cu} = 0.07 \pm 0.08$ ‰ 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 $\delta^{65}\text{Cu}$ 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 $\delta^{65}\text{Cu}$ 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 ($\delta^{65}\text{Cu}$
8 $= 4.60 \pm 2.06$ ‰; 2 standard error, $n=4$); the Australasian tektites (others than the Muong Nong-
9 type indochinites) ($\delta^{65}\text{Cu} = 4.25 \pm 0.70$ ‰; $n=8$) and the Ivory Coast tektites ($\delta^{65}\text{Cu} = 4.20$ ‰; $n=1$)
10 are indistinguishable while the North American bediasites ($\delta^{65}\text{Cu} = 2.61 \pm 0.02$ ‰; $n=2$) and
11 Muong-Nong type indochinites ($\delta^{65}\text{Cu} = 0.02 \pm 0.02$ ‰; $n=6$) 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 ($\delta^{65}\text{Cu} = 0.02 \pm 0.02$ ‰; $n=6$) and fall in the typical range of the
14 terrestrial crust..

15 The rim ($\delta^{65}\text{Cu} = 5.37$ ‰) of the flanged australite 5572 is slightly heavier isotopically
16 than the core ($\delta^{65}\text{Cu} = 4.03$ ‰). 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 $\delta^{65}\text{Cu}$ of
22 0.05 ‰ comparable to the mean value of the Muong Nong-type tektites. These values fall into
23 the typical terrestrial range.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22

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. Their constant Cu isotopic composition ($0.06\text{‰} < \delta^{65}\text{Cu} < 0.10\text{‰}$) 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 $\delta^{65}\text{Cu} = 0.31 \pm 0.23\text{‰}$ 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 $\delta^{65}\text{Cu} = -0.09\text{‰}$ (Luck et al., 2003). Most chondrite groups are enriched in ^{63}Cu with $\delta^{65}\text{Cu}$ varying between -1.50‰ to -0.09‰ in carbonaceous chondrites, -0.51‰ to $+0.10\text{‰}$ in ordinary chondrites. Iron meteorites demonstrate more variations around zero with $\delta^{65}\text{Cu}$ range between -0.50‰ to $+0.40\text{‰}$ (Luck et al., 2003; Luck et al., 2005). High-Ti lunar basalts are enriched in Cu heavy isotopes ($\delta^{65}\text{Cu} = +0.50 \pm 0.10\text{‰}$) (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 ($-1.5\text{‰} < \delta^{65}\text{Cu} < +0.50\text{‰}$), 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

1 isotope of Cu ($+1.99\text{‰} < \delta^{65}\text{Cu} < +6.98\text{‰}$). 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 $\delta^{65}\text{Cu}=0.49\text{‰}$, (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 ($6\text{ ppm} < [\text{Cu}] < 22\text{ ppm}$) than in the other types of tektites ($0.1\text{ ppm} < [\text{Cu}] < 6.5\text{ ppm}$). 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 ($\delta^{65}\text{Cu} = 0.02 \pm 0.02\text{‰}$) 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, $T_c \sim 1037$ 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 ($\delta^{66}\text{Zn}$ up to 2.49 ‰ and $\delta^{65}\text{Cu}$ 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 ± 1 ppm 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 ($\delta^{65}\text{Cu} = 0.02 \pm 0.02$).

19 Assuming that the different target rocks have the composition of the average upper
20 terrestrial crust, $[\text{Cu}] = 28$ ppm, $[\text{Zn}] = 67$ ppm, and $[\text{K}] = 2.8\%$ (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 ($[\text{Cu}]_{\text{tektites}}/[\text{Cu}]_{\text{continental}}$
23 $\text{crust} = 0.06 \pm 0.04$) than in Zn ($[\text{Zn}]_{\text{tektites}}/[\text{Zn}]_{\text{continental crust}} = 0.28 \pm 0.06$) or K ($[\text{K}]_{\text{tektites}}/[\text{K}]_{\text{continental}}$

1 $\text{crust}=0.70\pm 0.12$) . 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 $\delta^{65}\text{Cu}$ 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 $\delta^{65}\text{Cu}$ as a function of the remaining fraction of Cu is plotted in Fig. 3.

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

15 with $[\text{Cu}]_0$ 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 $\sqrt{\frac{M^{63}\text{Cu}}{M^{65}\text{Cu}}}$ where $M^{65}\text{Cu}$ and $M^{63}\text{Cu}$ 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

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} m²/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} m²/s, which suggest even slower
18 diffusion than 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,

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 $\sim 10^{-10} \text{ m}^2/\text{s}$. 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 ($+1.99 \text{ ‰} < \delta^{65}\text{Cu} < +6.98 \text{ ‰}$). 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 ($\delta^{65}\text{Cu} \approx 0$). 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

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.

9

10 **Acknowledgments:** We thank Francis Albarede and Janne Blichert-Toft for providing access
11 to the MC-ICP-MS facility in Lyon. Joyce Brannon is thanked for the day to day maintenance of
12 the clean lab in St Louis. CK was supported by the Austrian Science Foundation (grant P18862-
13 N10).

14

1 **References:**

- 2 Albarede, F., Bunch, T.E., Moynier, F. and Douchet, C., 2007. Isotope fractionation during
3 impact: Earth versus the moon (abstract). *Meteoritics & Planetary Science*, 42: A11-A11.
- 4 Behrens, H. and Hahn, M., 2009. Trace element diffusion and viscous flow in potassium-rich
5 trachytic and phonolitic melts. *Chemical Geology*, 259: 63-77.
- 6 Ben Othman, D., Luck, J.M., Bodinier, J.L., Arndt, N.T. and Albarede, F., 2006. Cu--Zn isotopic
7 variations in the Earth's mantle (abstract). *Geochimica et Cosmochimica Acta*
8 Supplement, 70: 46.
- 9 Blum, J.D., Papanastassiou, D.A., Wasserburg, G.J. and Koeberl, C., 1992. Neodymium and
10 strontium isotopic study of Australasian tektites - New constraints on the provenance and
11 age of target materials. *Geochim. Cosmochim. Acta*, 56: 483-492.
- 12 Chaussidon, M. and Koeberl, C., 1995. Boron content and isotopic composition of tektites and
13 impact glasses: Constraints on source regions. *Geochim. Cosmochim. Acta*, 59: 613-624.
- 14 Engelhardt, W.V., Luft, E., Arndt, J., Schock, H. and Weiskirchner, W., 1987. Origin of
15 moldavites. *Geochim. Cosmochim. Acta*, 51: 1425-1443.
- 16 Esat, T. and Taylor, S., 1986. Mg isotope composition of Ivory Coast Microtektites, Lunar Planet
17 Sci. Conf., 17, 210-211.
- 18 Glass, B.P., 1990. Tektites and microtektites: key facts and inferences. *Tectonophysics*, 171:
19 393-404.
- 20 Glass, B. and Koeberl, C., 1989. Trace elements of high and low refractive index Muong Nong
21 type tektites from Indochina. *Meteoritics*, 24: 143-146.
- 22 Glass, B., Senftle, F.E., Muenow, D.W., Aggrey, K.E. and Thorpe, A.N., 1988. Atomic bomb
23 glass beads: tektite and microtektite analogs. In: J. Konta (Editor), *Proceedings of the 2nd*
24 *International Conference on Natural Glasses*, Charles University, Prague, pp. 361-369.
- 25 Glass, B.P., Kent, D.V., Schneider, D.A. and Tauxe, L., 1991. Ivory Coast microtektite strewn
26 field - Description and relation to the Jaramillo geomagnetic event. *Earth Planet. Sci.*
27 *Lett.*, 107: 182-196.
- 28 Grasset, O. and Albarede, F., 1994. Hybridization of mingling magmas with different densities.
29 *Earth Planet. Sci. Lett.*, 121: 327-332.
- 30 Herzog, G.F., O'D. Alexander, C.M., Berger, E.L., Delaney, J.S. and Glass, B.P., 2008.
31 Potassium isotope abundances in Australasian tektites and microtektites. *Meteoritics*
32 *Planet. Sci.*, 43: 1641-1657.
- 33 Herzog, G.F., Moynier, F. and Albarède, F., in press. Isotopic and elemental abundances of
34 copper and zinc in: lunar basalts, glasses, and soils, a terrestrial basalt, Pelé's hairs, and
35 zagami, *Geochim. Cosmochim. Acta*.
- 36 Holzheid, A. and Lodders, K., 2001. Solubility of copper in silicate melts as function of oxygen
37 and sulfur fugacities temperature and silicate composition. *Geochim. Cosmochim. Acta.*,
38 65: 1933-1951.
- 39 Humayun, M. and Clayton, R.N., 1995. Potassium isotope cosmochemistry: Genetic implications
40 of volatile element depletion. *Geochim. Cosmochim. Acta*, 59: 2131-2148.
- 41 Humayun, M. and Koeberl, C., 2004. Potassium isotopic composition of Australian tektites.
42 *Meteoritics Planet. Sci.*, 39: 1509-1516.
- 43 Koeberl, C., 1985. Trace Element Chemistry of Libyan Desert Glass. *Meteoritics*, 20: 686.
- 44 Koeberl, C., 1986. Geochemistry of tektites and impact glasses. *Annual Review of Earth and*
45 *Planetary Sciences*, 14: 323-350.

- 1 Koeberl, C., 1990. The geochemistry of tektites: an overview. *Tectonophysics*, 171: 405-422.
- 2 Koeberl, C., 1992. Geochemistry and origin of Muong-Nong-type tektites. *Geochim.*
3 *Cosmochim. Acta*, 56: 1033-1064.
- 4 Koeberl, C., 1994. Tektite origin by hypervelocity asteroidal or cometary impact: target rocks,
5 source craters, and mechanisms. In: B.O. Dressler, R.A.F. Grieve and V.L. Sharpton
6 (Editors), *Large Meteorite Impacts and Planetary Evolution*. Geological Society of
7 America Special Papers, pp. 133-152.
- 8 Koeberl, C., 2007. The geochemistry and cosmochemistry of impacts. In: A.M. Davis (Editor),
9 *Treatise of Geochemistry*. Elsevier, pp. 1.28.1-1.28.52.
- 10 Koeberl, C. and Shirey, S.B., 1993. Detection of a meteoritic component in Ivory Coast tektites
11 with rhenium-osmium isotopes. *Science*, 261: 595-598.
- 12 Koeberl, C., Poag, C.W., Reimold, W.U. and Brandt, D., 1996. Impact origin of the Chesapeake
13 bay structure and the source of the north american tektites. *Science*, 271: 1263-1266.
- 14 Koeberl, C., Bottomley, R., Glass, B. and Storzer, D., 1997. Geochemistry and age of Ivory
15 Coast tektites and microtektites. *Geochim. Cosmochim. Acta*, 61: 1745-1772.
- 16 Koeberl, C., Reimold, W.U., Blum, J. and Chamberlain, C., 1998. Petrology and geochemistry of
17 target rocks from the bosumtwi impact structure, Ghana, and comparison with Ivory
18 Coast tektites. *Geochim. Cosmochim. Acta*, 62: 2179-2196.
- 19 Levich, V.G., 1962. *Physicochemical Hydrodynamics*. Prentice-Hall, Englewood Cliffs, 700 pp
20 pp.
- 21 Li, W., Jackson, S., Pearson, N.J., Alard, O. and Chappell, B.W., 2009. The Cunext term isotopic
22 signature of granites from the Lachlan Fold Belt, SE Australia *Chemical Geology*, 258:
23 38-49.
- 24 Lodders, K., 2003. Solar System abundances and condensation temperatures of the elements.
25 *Astrophys. J.*, 591: 1220-1247.
- 26 Luck, J.M., Othman, D.B., Barrat, J.A. and Albarede, F., 2003. Coupled ^{63}Cu and ^{16}O excesses
27 in chondrites. *Geochim. Cosmochim. Acta*, 67: 143-151.
- 28 Luck, J.M., Othman, D.B. and Albarede, F., 2005. Zn and Cu isotopic variations in chondrites
29 and iron meteorites: Early solar nebula reservoirs and parent-body processes. *Geochim.*
30 *Cosmochim. Acta*, 69: 5351-5363.
- 31 Ma, P., Aggrey, K., Tonzola, C., Schnabel, C., de Nicolas, P., Herzog, G., Wasson, J.T., Glass,
32 B., Brown, L., Tera, F., Middleton, R. and Kleine, T., 2004. Beryllium-10 in Australasian
33 tektites: constraints on the location of the source crater. *Geochim. Cosmochim. Acta.*, 68:
34 3883-3896.
- 35 Marechal, C., 1998. *Géochimie des isotopes du Cuivre et du Zinc. Méthode, variabilités*
36 *naturelles, et application océanographique*. PhD Thesis, Ecole Normale Supérieure de
37 Lyon, 253 pp.
- 38 Maréchal, C., Télouk, P. and Albarède, F., 1999. Precise analysis of copper and zinc isotopic
39 compositions by plasma-source mass spectrometry. *Chem. Geol.*, 156: 251-273.
- 40 Maréchal, C.N., Douchet, C., Nicolas, E. and Albarède, F., 2000. The abundance of zinc isotopes
41 as a marine biogeochemical tracer. *Geochem., Geophys., Geosyst.*, 1: 1999GC-000029.
- 42 Moynier, F., Albarede, F. and Herzog, G., 2006. Isotopic composition of zinc, copper, and iron
43 in lunar samples. *Geochim. Cosmochim. Acta*, 70: 6103-6117
- 44 Moynier, F., Beck, P., Jourdan, F., Yin, Q.-Z., Reimold, U. and Koeberl, C., 2009. Isotopic
45 fractionation of zinc in tektites. *Earth Planet. Sci. Lett.*, 277: 482-489.

- 1 Mungall, J.E., 2002. Empirical models relating viscosity and trace diffusion in magmatic silicate
2 melts. *Geochim. Cosmochim. Acta.*, 66: 125-143.
- 3 Poag, C.W., Koeberl, C. and Reimold, U., 2004. Chesapeake Bay Crater: geology, and
4 geophysics of a late Eocene submarine impact structure.
- 5 Rudnick, R.L. and Gao, S., 2003. Composition of the continental crust. In: H.D. Holland and
6 K.K. Turekian (Editors), *Treatise on Geochemistry*, pp. 1-64.
- 7 Serefiddin, F., Herzog, G.F. and Koeberl, C., 2007. Beryllium-10 concentrations of tektites from
8 the Ivory Coast and from Central Europe: Evidence for near-surface residence of
9 precursor materials. *Geochim. Cosmochim. Acta.*, 71.
- 10 Walter, L.S., 1967. Tektite compositional trends and experimental vapor fractionation of silicates.
11 *Geochim. Cosmochim. Acta.*, 31: 2043-2063.
- 12 Weeks, R.A., Underwood, J.R. and Giegengack, R., 1984 Libyan Desert Glass: A review. *J.*
13 *Non-Cryst. Solids*, 67: 593-619.
- 14 Weinke, H.H. and Koeberl, C., 1985. Trace elements in two bediasite tektites. *Meteoritics*, 20:
15 783.
- 16 Wombacher, F., Rehkamper, M., Mezger, K. and Munker, H., 2003. Stable isotopes composition
17 of Cadmium in geological materials and meteorites determined by multiple-collector
18 ICPMS. *Geochim. Cosmochim. Acta.*, 76: 4639-4664.
- 19 Zhu, X.K., O'Nions, R.K., Guo, Y., Belshaw, N.S. and Rickard, D., 2000. Determination of Cu-
20 isotope variation by plasma source mass spectrometry: implications for use as
21 geochemical tracers. *Chem. Geol.*, 163: 139-149.

22
23

24

25

1 Figure Captions:

2

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

6

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

11

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

16

17

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	$\delta^{65}\text{Cu}$
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 $\pm 2\sigma$	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 $\pm 2\sigma$	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 $\delta^{65}\text{Cu}$ is 0.10 .

5

Sample name	$\delta^{65}\text{Cu}$	[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)

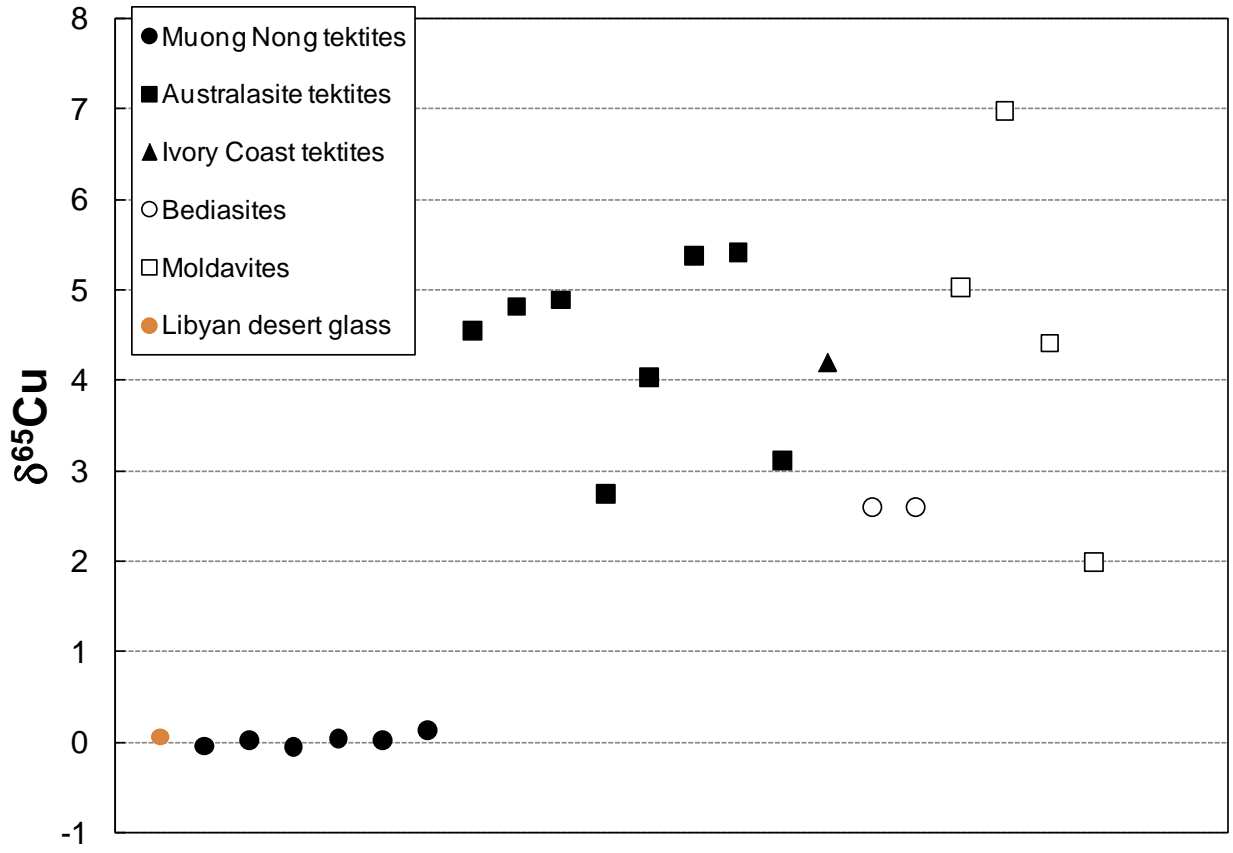
7 ^b(Moynier et al., 2009)

8 ^c(Koeberl, 1992)

9 ^d(Glass and Koeberl, 1989)

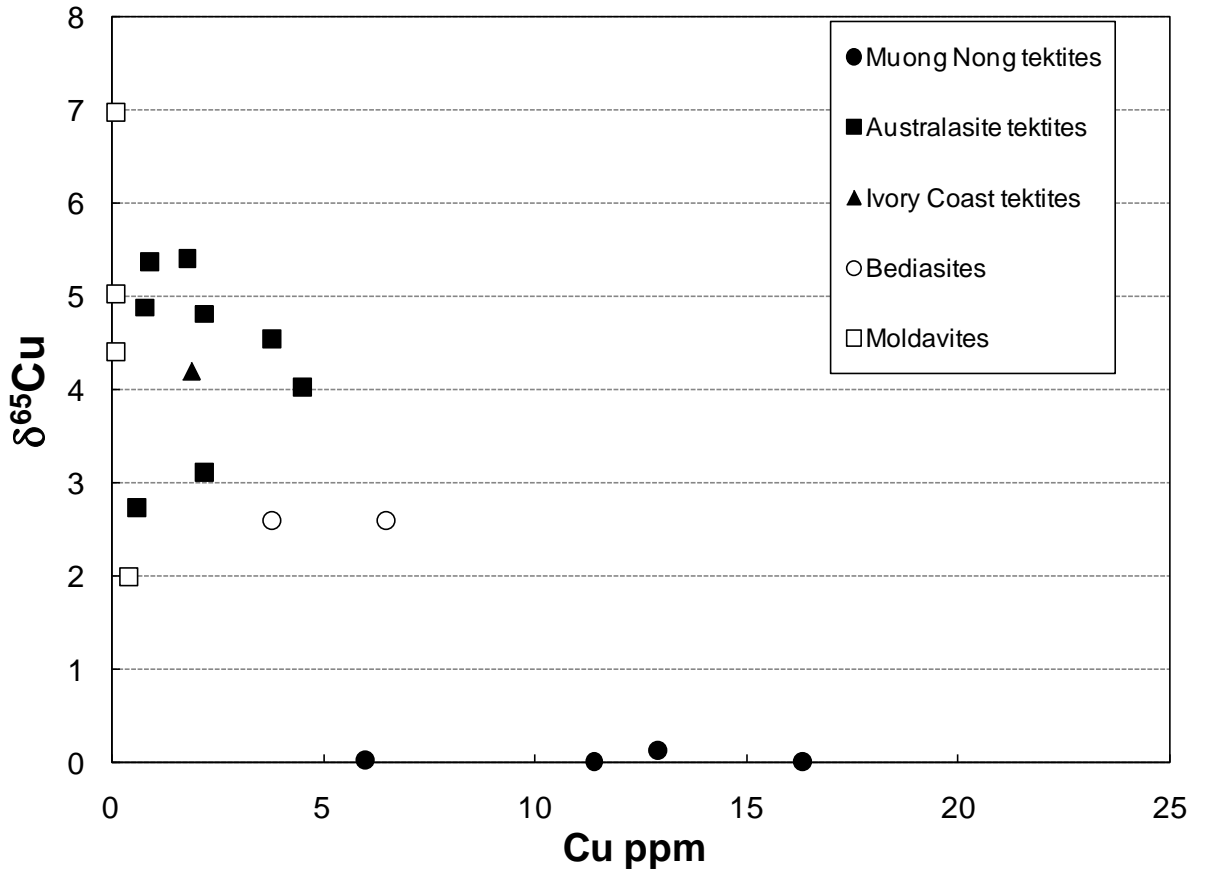
10

1
2 Fig.1



3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23

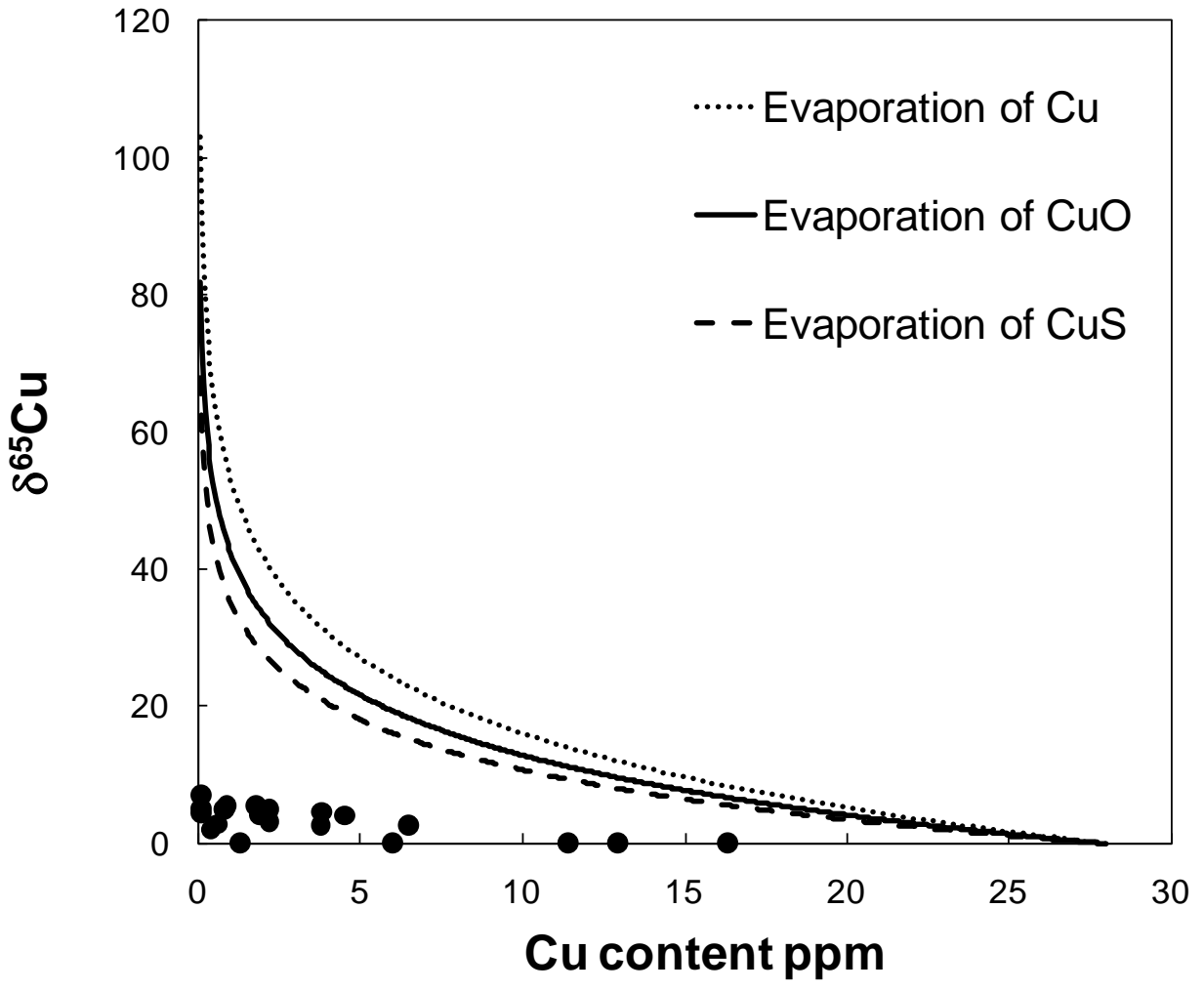
1 Fig. 2
2



3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22

1
2
3
4

Fig. 3



5
6
7