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► To cite this version:

Zuzana Rodovská, Tomáš Magna, Karel Žák, Chizu Kato, Paul Savage, et al.. Implications for behavior of volatile elements during impacts - Zinc and copper systematics in sediments from the Ries impact structure and central European tektites. *Meteoritics and Planetary Science*, 2017, 52 (10), pp.2178-2192. 10.1111/maps.12922 . insu-02917363

HAL Id: insu-02917363

<https://insu.hal.science/insu-02917363>

Submitted on 20 Aug 2020

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1 **Implications for behavior of volatile elements during**
2 **impacts – zinc and copper systematics in sediments from**
3 **the Ries impact structure and central European tektites**

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19 Re-submitted to *Meteoritics and Planetary Science*

20	Word count abstract (incl. Keywords):	307
21	Word count main text:	6802
22	Characters w/spaces (abstract, main text,	
23	acknowledgement):	46217
24	Figures:	4
25	Tables:	2
26		

Abstract

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Moldavites are tektites genetically related to the Ries impact structure, located in Central Europe, but the source materials and the processes related to the chemical fractionation of moldavites are not fully constrained. To further understand moldavite genesis, the Cu and Zn abundances and isotope compositions were measured in a suite of tektites from four different sub-strewn fields (South Bohemia, Moravia, Cheb Basin, Lusatia) and chemically diverse sediments from the surroundings of the Ries impact structure. Moldavites are slightly depleted in Zn (~10–20%) and distinctly depleted in Cu (>90%) relative to supposed sedimentary precursors. Moreover, the moldavites show a wide range in $\delta^{66}\text{Zn}$ values between 1.7 and 3.7‰ (relative to JMC 3-0749 Lyon) and $\delta^{65}\text{Cu}$ values between 1.6 and 12.5‰ (relative to NIST SRM 976) and are thus enriched in heavy isotopes relative to their possible parent sedimentary sources ($\delta^{66}\text{Zn} = -0.07$ to $+0.64$ ‰; $\delta^{65}\text{Cu} = -0.4$ to $+0.7$ ‰). In particular, the Cheb Basin moldavites show some of the highest $\delta^{65}\text{Cu}$ values (up to 12.5‰) ever observed in natural samples. The relative magnitude of isotope fractionation for Cu and Zn seen here is opposite to oxygen-poor environments such as Moon where Zn is significantly more isotopically fractionated than Cu. One possibility is that monovalent Cu diffuses faster than divalent Zn in the reduced melt and diffusion will not affect extent of Zn isotope fractionation. These observations imply that the capability of forming redox environment may aid in volatilizing some elements, accompanied by isotope fractionation, during the impact process. The larger extent of elemental depletion, coupled with isotope fractionation of more refractory Cu relative to Zn, may also hinge on the presence of carbonyl species of transition metals and electromagnetic charge, which could exist in the impact-induced high-velocity jet of vapor and melts.

52 Keywords: zinc isotopes; copper isotopes; tektites; Ries crater; Ries area sediments; isotope

53 fractionation; impact; volatile loss

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1. Introduction

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Tektites are terrestrial silica-rich glasses produced during hypervelocity impacts of an extraterrestrial projectile onto the Earth's surface (Koeberl, 1994, 2014; Artemieva, 2008) and as such, they represent a unique source of information about conditions and processes occurring during early phases of the impact process. The close similarity between the chemical composition of the Earth's surface sediments and tektites implies that tektites were formed by reworking of such target materials, mostly from the uppermost unconsolidated strata (e.g., Shaw and Wasserburg, 1982; Koeberl and Fredriksson, 1986; Blum et al., 1992; Dressler and Reimold, 2001; Řanda et al., 2008; Skála et al., 2009; Stöffler et al., 2013; Žák et al., 2016). At present, four major geographically distinct tektite strewn fields are recognized: North American, Central European, Ivory Coast and Australasian. The Central European tektites (moldavites) are assumed to have been formed by reworking of the chemically and mineralogically variable sediments of the Upper Freshwater Molasse (Obere Süßwassermolasse, OSM; e.g., Luft, 1983; von Engelhardt et al., 1987, 2005; Žák et al., 2016). The Ries impact structure (centered close to Nördlingen, south-eastern Germany) is accepted as the parent crater to moldavites, based on the excellent concordance of their ages at ca. 14.75 ± 0.20 Ma (e.g., Buchner et al., 2010; Schwarz and Lippolt, 2014). However, the agreement between the chemical composition of the OSM sediments and moldavites is not excellent, which was explained as a result of chemical modifications during the process of tektite formation (von Engelhardt et al., 2005; Žák et al., 2016).

Zinc (lithophile) and Cu (chalcophile) both are volatile/moderately volatile elements (Lodders, 2003). Chondrites are significantly enriched in Zn compared with the Bulk Silicate Earth (BSE) and Mars (McDonough and Sun, 1995; Barrat et al., 2012; Paniello et al., 2012a) while both the Moon and the howardite–eucrite–diogenite (HED) meteorites from asteroid 4-

80 Vesta are depleted in Zn (Paniello et al., 2012a; Paniello et al., 2012b), implying planetary-
81 scale processes leading to sizeable loss of Zn, perhaps caused by giant collisions, thermal
82 metamorphism and/or cataclysmic bombardment (Day and Moynier, 2014). Previously
83 published Zn concentrations in tektites revealed a significant range with a particular
84 difference among individual strewn fields (7–283 ppm; Koeberl, 1992; Koeberl et al., 1997;
85 Moynier et al., 2009a; Skála et al., 2009) and high $\delta^{66/64}\text{Zn}$ values from 0.2‰ to 2.5‰ (per
86 mil deviation of the $^{66}\text{Zn}/^{64}\text{Zn}$ ratio from the JMC 3-0749L standard), when compared to the
87 average upper continental crust ($\delta^{66/64}\text{Zn}$ from 0‰ to 0.7‰; Albarède, 2004; Chen et al.,
88 2013) and Bulk Silicate Earth ($\delta^{66/64}\text{Zn}_{\text{BSE}} = 0.30 \pm 0.03\text{‰}$; Moynier et al., 2011; Chen et al.,
89 2013; Doucet et al., 2016; Wang et al., 2017). Most tektites analyzed previously show an
90 average Cu content of only 2 ± 1 ppm and are significantly enriched in heavy Cu ($\delta^{65}\text{Cu}$
91 values between 2 and 7‰, relative to NIST 976; Moynier et al., 2010) which is in contrast to
92 the results of Li et al. (2009), Liu et al. (2015) and Savage et al. (2015) which, in general,
93 attest to a homogeneous Cu isotope composition of terrestrial igneous lithologies
94 ($0.08 \pm 0.17\text{‰}$; Moynier et al., 2017) as well as clastic sediments ($0.08 \pm 0.20\text{‰}$; Moynier et al.,
95 2017). Because tektites suffer from minor Zn loss but significant Cu depletion (Moynier et al.,
96 2009a; Moynier et al., 2010; Žák et al., 2016), the impact processes can potentially be used as
97 a proxy for the loss of volatile species during planetary formation.

98 Here, we present new Cu–Zn isotope data for the set of well-characterized moldavites
99 from the Czech Republic and Germany, and chemically diverse sediments from the close
100 surroundings of the Ries impact structure (Žák et al., 2016) in order to provide further
101 constraints on (i) Zn and Cu elemental and isotope variability in possible tektite source
102 materials that could be linked to the heterogeneity of their bulk chemistry, and (ii) the extent
103 of Zn and Cu isotope fractionation between the plausible source sediments and tektites. The
104 latter has been only marginally studied for Zn, with the Ivory Coast strewn field displaying a

105 $\delta^{66/64}\text{Zn}$ offset $>1\text{‰}$ between the Bosumtwi crater rocks, having crustal Zn isotope signature,
106 and isotopically heavier Ivory Coast tektites (Moynier et al., 2009a). Moreover, there may be
107 a difference between Bosumtwi and Ries in the quantity of volatiles (in particular water) in
108 the surface layer of the target materials (crystalline versus loosely bound; Koeberl et al., 1998;
109 Žák et al., 2016) which may play a key role in effective fragmentation of molten tektite glass
110 due to the escape of volatile species (see recent model of Žák et al., 2016) and the attainment
111 of conditions suitable for Zn and Cu loss and related isotope fractionation.

112

113 **2. Samples and analytical techniques**

114

115 In this study, 13 samples of moldavites from four distinct sub-strewn fields of the Central
116 European tektite field and 16 samples of sediments from surrounding of the Ries,
117 characterized previously with respect to their major and trace element chemistry, physical
118 properties (shape, color and sculpture) and Li elemental/isotope systematics (Řanda et al.,
119 2008; Skála et al., 2009; Skála et al., 2010; Řanda et al., 2014; Rodovská et al., 2016; Žák et
120 al., 2016), were analyzed for Zn and Cu abundance and isotope compositions. Details on the
121 general chemistry of moldavites can be found elsewhere (e.g., Bouška et al., 1973; von
122 Engelhardt et al., 1987, 2005; Meisel et al., 1997; Trnka and Houzar, 2002; Řanda et al.,
123 2008; Skála et al., 2009; Magna et al., 2011; Žák et al., 2016). The studied sediment samples
124 were previously characterized with respect to their chemistry and mineralogy (Žák et al.,
125 2016). They comprise OSM sediments with variable proportions of fine-grained (clay)
126 fraction and sand fraction, and with variable proportions of quartz and other minerals in the
127 sand fraction (**Table 1**). Several samples which could have been also present at the surface
128 during the impact were also included (sedimentary fill of paleokarst depressions rich in
129 limestone weathering residual minerals; freshwater Oligocene limestone). Sediment sample

130 locations, descriptions, chemical and mineralogical characteristics are given in Žák et al.
131 (2016). It should be noted that the exact morphology and sedimentary cover conditions of the
132 target area itself are unknown, because they were completely destroyed by the impact.
133 Therefore, the studied sediments represent only an approximation of the conditions and
134 materials of the intrinsic target area. In addition, three samples of clay-size fractions, isolated
135 from sedimentary samples using a common sedimentation method in distilled water were
136 measured (we note that these fractions are not completely pure clay fractions but may contain
137 a small proportion of other minerals including secondary phases, such as secondary Fe and
138 Mn oxides/hydroxides). The procedure to prepare samples for clay minerals identification
139 involved extensive washing in distilled water and separation of the clay fraction in the
140 Andreasen cylinder. To determine bulk mineral composition X-ray diffraction patterns have
141 been acquired from untreated bulk specimens between 3 and 70° 2 Θ (CuK α_1 radiation). The
142 specimens have been scanned with a diffractometer between 2 and 40° 2 Θ and then saturated
143 with ethylenglycol for 4 hours at 80°C. Following saturation the new set of X-ray diffraction
144 data has been acquired. After that, the glass sample wafers with specimens have been heated
145 at 550°C under ambient atmosphere for 1 hour. In general, clay mineral composition is similar
146 in all samples with subtle differences among individual sediments. Identified clay minerals
147 include kaolinite, illite, chlorite, montmorillonite and interstratified illite/montmorillonite.

148 The analytical procedures for Zn and Cu purification were performed in the CAGE
149 laboratories, the Institut de Physique du Globe de Paris (IPGP). Zinc was isolated and purified
150 by a two-stage HBr-based anion exchange chromatography following methods given
151 elsewhere (Moynier et al., 2006; Moynier and Le Borgne, 2015). A single-stage anion
152 exchange chromatography for Cu purification using AG-MP1 resin was employed (Maréchal
153 et al., 1999; Savage et al., 2015) with 95–100% recovery; the total procedural blank for Cu
154 was ~4 ng. The Zn and Cu concentrations and isotope compositions were measured by

155 standard–sample bracketing (Maréchal et al., 1999; Moynier et al., 2006, 2009a, 2010; Savage
156 et al., 2015) using a *Neptune Plus* multiple-collector inductively-coupled-plasma mass
157 spectrometer (MC-ICPMS; ThermoFisher, Bremen, Germany), housed at IPGP. The 2SD on
158 repeated measurements of the bracketing standard was $\pm 0.06\%$; for multiple dissolutions and
159 purifications of BHVO-2, the 2SD uncertainty was $\pm 0.08\%$. Zinc and Cu concentrations were
160 determined against a 100 ppb Zn reference solution (JMC 3-0749 Lyon) and a 50 ppb NIST
161 SRM 976 reference solution, respectively. Zinc isotope compositions were calculated as $\delta^x\text{Zn}$
162 ($\%$) = $[(^x\text{Zn}/^{64}\text{Zn})_{\text{sample}} / (^x\text{Zn}/^{64}\text{Zn})_{\text{standard}} - 1] \times 1000$, where ^xZn denotes ^{66}Zn , ^{67}Zn and ^{68}Zn ,
163 respectively. Potential interferences from $^{23}\text{Na}^{40}\text{Ar}^+$ and $^{25}\text{Mg}^{40}\text{Ar}^+$ on ^{63}Cu and ^{65}Cu ,
164 respectively, were ruled out by measuring Na/Cu and Mg/Cu ratios in the samples prior to the
165 isotope analysis. Isotope ratios of Cu are expressed as $\delta^{65}\text{Cu}$ ($\%$) =
166 $[(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}} / (^{65}\text{Cu}/^{63}\text{Cu})_{\text{standard}} - 1] \times 1000$. Reference rock standards BCR-2 and BHVO-
167 2 (US Geol. Surv.) were processed and analyzed along with the unknown samples to monitor
168 the accuracy and reproducibility of the analytical procedures and spectrometry routines; their
169 Zn and Cu isotope compositions were consistent with previous studies (**Table 1** and Archer
170 and Vance, 2004; Moynier et al., 2010; Moeller et al., 2012; Chen et al., 2013; Sossi et al.,
171 2014; Savage et al., 2015; Lv et al., 2016).

173 **3. Results**

175 **3.1 Zinc abundance and isotope compositions**

176
177 The Zn concentrations and isotope ratios in moldavites, sediments and clay fractions are
178 reported in **Table 1** and plotted in **Fig. 1**. The moldavites show a wide range in Zn abundance
179 (1.9–108 ppm), extending to both lower and higher Zn contents compared with data from

180 Moynier et al. (2009a), which may reflect the wider chemical range of moldavites selected for
181 this study (see Skála et al., 2009). Moldavites from South Bohemia have 1.9–34.5 ppm Zn,
182 those from Moravia have 7.3–18.8 ppm Zn and those from the Cheb Basin contain 20.6–108
183 ppm Zn (with three out of four samples having [Zn] >58 ppm); a single moldavite from
184 Lusatia has 16.7 ppm Zn. These results attest to modest differences between the Cheb Basin
185 moldavites and those from the other sub-strewn fields, noted by Řanda et al. (2008) and Skála
186 et al. (2009). The Ries sediments show a remarkable range in Zn abundances from 4.6 to 186
187 ppm Zn. Zinc contents in sediments correlate with Al₂O₃ contents (**Fig. 2**) and FeO (not
188 shown). Zinc contents obtained in this study are broadly consistent with those reported by Žák
189 et al. (2016) for different aliquots of the same samples of moldavites and sediments, with the
190 exception of slightly lower Zn contents in high-Zn samples reported in this study. The clay
191 fractions from three sediments (1 UTZ, 10 GLM, 13 BMB) have from 94 to 161 ppm Zn; this
192 is, in all three cases, higher than Zn abundance in the respective bulk sample, in case of
193 sample 13 BMB by a factor of three (**Table 1**).

194 The moldavites in this study show a range in $\delta^{66}\text{Zn} = 1.7\text{--}3.7\text{‰}$, which is significantly
195 larger compared to data reported by Moynier et al. (2009a) for four south Bohemian
196 specimens ($\delta^{66}\text{Zn} = 1.9\text{--}2.3\text{‰}$). The moldavites from different sub-strewn fields do not show
197 distinct Zn isotope compositions (Moravia: $\delta^{66}\text{Zn} = 2.1\text{--}2.7\text{‰}$; Lusatia: $\delta^{66}\text{Zn} = 2.5\text{‰}$; South
198 Bohemia: $\delta^{66}\text{Zn} = 1.7\text{--}3.3\text{‰}$; the Cheb Basin: $\delta^{66}\text{Zn} = 2.0\text{--}3.7\text{‰}$). The sediments from the
199 Ries surroundings show little variability in $\delta^{66}\text{Zn}$ values (-0.07‰ to 0.64‰), which is
200 consistent with global data for sediments (see recent review by Moynier et al., 2017). The clay
201 fractions always have lighter Zn isotope compositions than the corresponding bulk sediments,
202 and define a narrow range of $\Delta^{66}\text{Zn}_{\text{clay-bulk sediment}}$ values ($\delta^{66}\text{Zn}_{\text{clay}} - \delta^{66}\text{Zn}_{\text{bulk sediment}}$) between
203 -0.5 and -0.7‰ , indicating preferential incorporation of light Zn isotopes into clay.

204

205 **3.2 Copper abundance and isotope compositions**

206

207 The Cu contents and isotope compositions are listed in **Table 1** and plotted in **Fig. 1**. The
208 moldavites show a range in Cu abundance from 0.2 to 2.9 ppm (the values were taken from
209 Žák et al., 2016), much lower than the canonical abundance of the upper continental crust at
210 ~28 ppm (Rudnick and Gao, 2014). Moldavites from South Bohemia have 0.2–1.4 ppm Cu,
211 those from Moravia have 0.6–0.8 ppm Cu and those from the Cheb Basin have 0.4–2.9 ppm
212 Cu; a single Lusatian moldavite has 1.1 ppm Cu. These values are consistent with those found
213 by Skála et al. (2009) for the Cheb Basin moldavites (0.9 to 4.7 ppm) as well as for other
214 tektite fields, with the exception of low Cu contents for moldavites (<0.4 ppm) reported by
215 Moynier et al. (2010). The Ries sediments show a range in Cu concentrations from 0.8 to 58
216 ppm Cu; these values are consistent with those reported by Žák et al. (2016). The clay
217 fractions from three sediments have from 21.4 to 42.2 ppm Cu which is in all three cases
218 higher than Cu content in the respective bulk sediment, and is consistent with the findings for
219 Zn.

220 The moldavites from South Bohemia have $\delta^{65}\text{Cu}$ values from 2.2 to 5.4‰, those from
221 Moravia between 5.8 and 8.8‰ and those from the Cheb Basin between 1.6 and 12.5‰; a
222 single Lusatian moldavite has $\delta^{65}\text{Cu}$ of 6.1‰. The new $\delta^{65}\text{Cu}$ values measured for moldavites
223 extend towards significantly heavier values than those reported previously (Moynier et al.,
224 2010), with the Cheb Basin moldavites showing some of the highest $\delta^{65}\text{Cu}$ values (up to
225 12.5‰) ever observed in natural high-temperature modified samples. The largest previously
226 reported natural ^{65}Cu enrichments were observed in strongly weathered shales from central
227 China (up to 19.7‰; Lv et al., 2016) and secondary Cu minerals associated with ore body
228 formation, where $\delta^{65}\text{Cu}$ values are typically positive in the supergene, and can reach ~10‰
229 (e.g., Rouxel et al., 2004; Mathur et al., 2009). The $\delta^{65}\text{Cu}$ values in the Ries area sediments

230 show a narrow variation (-0.4 to 0.7%) and are in the range of common crustal lithologies
231 (Luck et al., 2003; Li et al., 2009). The clay fractions show a range in $\delta^{65}\text{Cu}$ values between
232 -0.1 and $+0.2\%$ and are, contrary to Zn, isotopically heavier than the respective bulk
233 sediments ($\Delta^{65}\text{Cu}_{\text{clay-bulk sediment}}$ values between 0.01 and 0.21%).

234

235

4. Discussion

236

237 **4.1.1 Statistical evaluation of Zn isotope data – implications for isotope fractionation in** 238 **natural processes**

239

240 It has been discussed that kinetic effects may become an important factor in forming
241 measurable isotope fractionation effects. For example, (Young and Galy, 2004) raised this
242 possibility for Mg isotopes although the resolution of equilibrium and kinetic fractionation
243 processes in the three-isotope Mg plot seems to be barely outside of the statistical resolution.
244 Applying the approach of (Young and Galy, 2004) to Zn, the calculated theoretical slopes $\beta =$
245 1.942 and 1.972 for equilibrium and kinetic fractionation, respectively, suggest that these two
246 different mechanisms of Zn isotope fractionation could be resolved in nature. With the given
247 data set we were able to test this hypothesis for Zn isotopes. In the triple-Zn isotope plot (**Fig.**
248 **3**), both x - y variables (i.e., $\delta^{66}\text{Zn}$ and $\delta^{68}\text{Zn}$) can be considered as random, containing
249 measurement errors and other variability. Such cases are referred to as structural or model II
250 regression. A very simple structural relationship is assumed to be hidden in our data in the
251 form of a line with theoretically known slope. The SMATR package (Falster et al., 2006;
252 Warton et al., 2006) provides the possibility of fitting bivariate lines using the major axis
253 (MA) or standardized major axis (SMA).

254 In the present study, we defined three separate groups, sediments (S), moldavites from
255 this study (M), and other published tektites (T). The results of fitting MA lines, paralleled by
256 95% confidence intervals, are listed in **Table 2**. Because the basic assumption for MA
257 regression is the bivariate normality, we have inspected whether the S, M and T group data
258 are approximately bivariate normal, and applied the normality tests. For the group M, the
259 normality assumption was violated and two samples SBM-192 and SBM-44 were excluded
260 from further statistical evaluation. The former sample represents only a single measurement
261 and averaging of several independent measurements was therefore not possible, while the
262 latter is an average of three measurements all of which deviated outside the pattern of the
263 individual measurements of the other samples in this study. The cleaned data were denoted as
264 M1 (SBM-192 excluded) and M2 (both SBM-192 and SBM-44 excluded), and the results for
265 all the three variants of moldavite data (M, M1, and M2) are listed in **Table 2**. Furthermore, a
266 bootstrap (by resampling residuals) was applied to compute confidence intervals for the
267 slopes and elevations for comparison. A good agreement of the computed slopes b with the
268 theoretical ones ($\beta = 1.942$ for sediments, and 1.972 for moldavites and other tektites), is
269 observed with all confidence intervals containing the theoretical values. In case of groups M1
270 and M2 the confidence intervals are narrower. The computed intercepts a are close to zero
271 with a larger difference for the group M.

272 As the lines for all groups should pass through the origin, we have also used MA
273 regression with zero intercept (i.e., with the line forced through the origin). For the group M
274 the theoretical slope (1.972) is not in the 95% confidence interval, implying statistically
275 significant difference. Due to violation of the normality assumption for the group M, the
276 cleaned data M1 and M2 reveal an agreement with the theoretical slope. For the group T, the
277 regression with zero intercept shows a significant difference from the theoretical slope. The
278 reasons for this difference are unknown but some inter-laboratory differences could perhaps

279 be involved. We tested several inter-group comparison hypotheses using SMATR. (i) By
280 comparing S and M (M1, M2) groups only (i.e., data from this study measured in the same
281 laboratory), the test for common slope did not reject the hypothesis that slopes are equal ($p =$
282 0.082, 0.226, 0.384). (ii) The test for particular slope did not reject the hypothesis that the
283 common slope of other tektites (T) and moldavites M (M1, M2) is equal to 1.97 ($p = 0.071,$
284 0.141, 0.165). (iii) The test for common slope did not reject the hypothesis that slopes of all S,
285 M (M1, M2), and T are equal ($p = 0.066, 0.092, 0.085$). Collectively, the detailed statistical
286 treatment indicates that a significant statistical difference between sediments and tektites was
287 not proven (**Fig. 3**) but in some cases, this hypothesis was close to rejection (**Table 2**). Such a
288 conclusion leaves the question of possible resolution of Zn isotope fractionation during
289 kinetic and equilibrium processes unsolved. It may be that this subtle difference may only
290 become apparent at Zn isotope compositions that are much beyond the range of common
291 terrestrial as well extra-terrestrial values.

292

293 **4.2 Zinc and copper systematics in the Ries area sediments**

294

295 The $\delta^{66}\text{Zn}$ variation in common terrestrial crustal igneous rocks is, in general, limited to
296 between ~ 0 and 0.6‰ (Maréchal et al., 1999; Chen et al., 2013), and can be up to 0.7‰ in
297 sedimentary rocks (Pichat et al., 2003; Albarède, 2004; Mason et al., 2005). This is paralleled
298 by moderately high Zn abundance in the upper continental crust (67 ± 6 ppm; Rudnick and
299 Gao, 2014) compared with ~ 55 ppm in the primitive upper mantle (McDonough and Sun,
300 1995), and between ~ 20 and 200 ppm in different granite types (I, S, A; (Hall, 1975; Chappell
301 and White, 1992; King et al., 1997). These findings are consistent with uniform Zn isotope
302 composition of the bulk Ries sediments in this study (**Fig. 1**) with $\delta^{66}\text{Zn}$ constrained between
303 -0.07 and 0.64‰. On the other hand, Zn contents in sediments from the Ries vary

304 significantly by a factor of ~40 which, together with the variability of Zn contents of
305 moldavites, attests to a compositional variability of the target materials and incorporation of
306 chemically distinct sedimentary lithologies that ultimately led to the formation of moldavites
307 (e.g., von Engelhardt et al., 1987; Rodovská et al., 2016; Žák et al., 2016). The apparently
308 higher Zn contents in the Cheb Basin moldavites suggest that specific sediments must have
309 been sourced which also have higher Fe and Al abundances (**Fig. 2**). The paleogeography
310 indicates that the northern boundary of the OSM sediments occurred in the target area (e.g.,
311 Pohl et al., 1977; Hörz et al., 1983). Uneven karst surface with residual karst sediments could
312 have been present in the northern part of the target area. This type of material, represented by
313 the samples 14 BMB, 24 RTS and 25 RTS, shows distinctly higher Zn contents (>118 ppm),
314 paralleled by elevated abundances of Cu, Al, and Fe. Their participation in the ultimate source
315 of materials for moldavites of the Cheb Basin area, carrying elevated Zn contents, is therefore
316 probable (see also Rodovská et al., 2016).

317 Typical Cu contents in continental crustal lithologies vary greatly (~28 ppm in the bulk
318 continental crust, ~118 ppm in shales, ~20 ppm in soils; Jeng, 1992; McDonough and Sun,
319 1995; Bigalke et al., 2011; Rudnick and Gao, 2014) while ultramafic mantle rocks have 20–30
320 ppm Cu (McDonough and Sun, 1995; Palme and O'Neill, 2014). The effusive and intrusive
321 igneous rocks from the Earth's mantle and crust, such as basalts and granites, typically have
322 invariant $\delta^{65}\text{Cu}$ values of ~0‰ (Luck et al., 2003; Archer and Vance, 2004; Li et al., 2009;
323 Savage et al., 2015), and the weighted mean $\delta^{65}\text{Cu}$ of continental sediments of ~0‰ attests to
324 insignificant Cu isotope fractionation during weathering (note a restricted range in $\delta^{65}\text{Cu}$
325 between -0.57‰ and 0.44‰ found for different soil horizons; Bigalke et al., 2011). In
326 contrast, recent data of Lv et al. (2016) reveals extreme fractionation of Cu isotopes during
327 chemical weathering, with $\delta^{65}\text{Cu}$ values ranging between -6.4 and 19.7‰. This is
328 underscored by significant Cu isotope fractionations reported for oxidative weathering of

329 primary sulphides (0.0 to +2.0‰ $\delta^{65}\text{Cu}_{\text{solution-chalcopyrite rock}}$; Fernandez and Borrok, 2009;
330 Mathur et al., 2012), as well as during sorption on Fe-oxides and organic complexation
331 (Fernandez and Borrok, 2009). Lithologically diverse sediments in this study show a range in
332 Cu concentrations between 0.9 and 58 ppm (**Table 1**) that are well correlated with Zn
333 contents (only the sample 15 HRD shows elevated Cu abundance at a given Zn content; **Fig.**
334 **1a**). The broad Zn–Cu isotope co-variation observed for sediments from surroundings of the
335 Ries (**Fig. 1b**) also indicates a similar sense of stable isotope fractionation of chalcophile
336 elements during weathering of common silicate lithologies despite the possibility that Zn and
337 Cu might be accommodated in different phases in the source rocks of sediments and in the
338 secondary minerals. The contents of Cu in sediments correlate with FeO, Al₂O₃ and suggest
339 higher FeO and Al₂O₃ content in possible parent sediments. This would indicate somewhat
340 different behavior of Zn and Cu during weathering in the sense that these elements would be
341 isotopically fractionated in the opposite direction during formation of clay minerals. This
342 means that (i) the formation of unconsolidated materials through weathering imparts rather
343 minor isotope effects to both Zn and Cu, (ii) the behavior of Cu and Zn during tektite
344 formation is not completely identical, and (iii) strong isotope effects observed for tektites (see
345 Section 4.3) must solely be linked to conditions existing during or shortly after the impact.

346

347 ***4.2.1 Behavior of Zn and Cu at low temperatures***

348

349 Primary and secondary mineralogy can play a determining role in the stable isotope
350 systematics of sedimentary units although for many isotope systems the experimental data
351 and/or natural observations are insufficient or absent. Clay fractions isolated from bulk
352 sediments are uniformly enriched in Cu and Zn relative to the corresponding bulk sediments
353 despite the compositional diversity (clay-rich, quartz sand-rich, limestone weathering

354 residuum), attesting to similar behaviour of Cu and Zn at low temperatures, although
355 adsorption of heavy metals may differ upon variable chemical and physical conditions (e.g.,
356 Young Do and Park, 2011; Helios-Rybicka and Wójcik, 2012). The enrichment of Cu and Zn
357 is most apparent for the low-[Cu]–[Zn] sample 13 BMB with an enrichment factor in the clay
358 fraction of >2 and ~3 for Cu and Zn, respectively. Notable differences are, however, observed
359 for Zn and Cu isotope systematics in clay fractions. Zinc isotope compositions are
360 significantly lighter in clays relative to the corresponding bulk sediments which is in contrast
361 to the findings of Guinoiseau et al. (2016) who observed a systematic enrichment in heavy Zn
362 isotopes on the surface of kaolinite ($\Delta^{66}\text{Zn}_{\text{adsorbed-solution}}$ from 0.11‰ to 0.49‰).

363 Cu isotopes in clay fractions show zero to slight enrichments in ^{65}Cu . This indicates a
364 mineralogy-mediated dichotomy in generating intra-sample Zn–Cu isotope variations, which
365 may perhaps reflect occupation at different crystal sites for Zn and Cu. Still, $\delta^{66}\text{Zn}$ values in
366 clay fractions are similar to those reported for global clays (e.g., Maréchal et al., 2000).
367 Interestingly, the recent experimental study of Li et al. (2015) showed the opposite sense of
368 Cu isotope fractionation during adsorption onto kaolinite where the $\Delta^{65}\text{Cu}_{\text{kaolinite-solution}}$ of
369 $-0.17 \pm 0.10\text{‰}$ (2σ) appears to invoke preferential incorporation of isotopically light Cu into
370 clays, perhaps as a result of sorption of free Cu ion onto the surface of clay mineral. Li et al.
371 (2015) concluded that the isotope compositions of Cu adsorbed onto natural soils may vary
372 greatly at relatively low Cu concentrations of the soil solutions. This is underscored by a large
373 variation in $\delta^{65}\text{Cu}$ from -17 to $+10\text{‰}$ that was observed in secondary mineral phases which
374 typically develop during weathering of sulphides in the near-surface environment (Mathur et
375 al., 2009). These observations indicate that clay minerals of the OSM sediments cannot form a
376 major part of the moldavite melts because they are distinctly enriched in Zn, and, at the same
377 time, they carry a resolvedly light Zn isotope signature (**Fig. 1**). Moreover, they also have too
378 much Al and not enough Si so that their theoretically elevated proportion would violate major

379 element constraints because only the sands (containing abundant mica, feldspar, etc.) with a
380 moderate clay admixture and a very small content of clastic (mainly dolomitic) carbonates are
381 suitable for moldavite production (von Engelhardt et al., 1987; Žák et al., 2016).

382

383 **4.3 Zinc and copper systematics in moldavites – implications for the impact processes**

384

385 Several stable isotope systems have been studied previously (Humayun and Clayton,
386 1995; Wombacher et al., 2003; Moynier et al., 2009a, 2010; Magna et al., 2011; Rodovská et
387 al., 2016 in order to test the possible isotope fractionations related to extreme physical
388 conditions existing during the hypervelocity impact events. For example, Moynier et al.
389 (2009a) have found large variations for Zn isotopes ($\delta^{66}\text{Zn} = 0.3\text{--}2.5\text{‰}$), and the differences
390 in $\delta^{66}\text{Zn}$ among moldavites, Ivory Coast tektites, Australasian tektites (including Muong
391 Nong-type tektites), and bediasites (North American tektite field) were explained as a result
392 of evaporation in the context of shock heating. However, the p–T conditions of individual
393 impacts and the pre-impact chemical and lithological situation may be largely different, which
394 could perhaps be reflected in variable Zn isotope systematics of tektites from individual
395 strewn fields. In a follow-up study, Moynier et al. (2010) explored Cu elemental and isotope
396 systematics in tektites and have shown that (i) Cu in tektites was significantly more depleted
397 than Zn, and (ii) tektites displayed a significantly larger range in $\delta^{65}\text{Cu}$ than in $\delta^{66}\text{Zn}$
398 (reflected in larger ‰/amu variation) despite higher half mass condensation temperature of
399 Cu compared to Zn. Indeed, Albarede et al. (2007) noted that Cu is isotopically more
400 fractionated (up to 0.8‰) than Zn (up to 0.4‰) in shocked sandstones from the Meteor
401 Crater, USA. This could, in part, result from the differences in ionic radii of Zn^{2+} and Cu^+
402 which translates into different diffusion coefficients of these ions in silicate melts (see
403 discussion in Moynier et al., 2010). Highly reducing conditions of the impact systems have

404 been documented by the predominance of Fe^{2+} over Fe^{3+} in moldavites (e.g., Dunlap et al.,
405 1998; Skála et al., 2009) or reduced gaseous species (Žák et al., 2012), while in the source
406 sediments this relationship is opposite; the existence of Cu^+ rather than Cu^{2+} compositions is
407 therefore likely during tektite-forming events. Wombacher et al. (2003) have found significant
408 enrichments in heavy Cd isotopes in one investigated Muong Nong-type tektite caused
409 probably by evaporative loss whereas other terrestrial materials have shown no or very minor
410 variation in $\delta^{112/114}\text{Cd}$. Combined studies of Li systematics in central European tektites and
411 possible target sediments from the Ries (Magna et al., 2011; Rodovská et al., 2016) indicated
412 that neither is Li lost during the impact event nor are Li isotopes fractionated significantly by
413 shock heating and flash melting. Moreover, it appears that Li is homogenized effectively in
414 tektites despite a large range in Li contents and isotope compositions of target sediments.
415 Studies of somewhat more volatile potassium (Humayun and Clayton, 1995; Herzog et al.,
416 2008) are consistent with a limited loss of some elements from a molten glass into the
417 vapor/plasma although energetic collisions may fractionate K isotopes (Wang and Jacobsen,
418 2016).

419 In contrast to sediments (Section 4.2), all tektites measured in the present study are
420 distinctly enriched in the heavy isotopes of Zn and Cu (**Fig. 1b**), consistent with earlier results
421 (Moynier et al., 2009a, 2010). The only other natural samples known so far to have
422 comparably heavy Zn isotope compositions are lunar regolith samples ($\delta^{66}\text{Zn}$ up to 6.4‰;
423 Moynier et al., 2006; Paniello et al., 2012a; Kato et al., 2015), EL6 enstatite chondrites and
424 eucrites (Moynier et al., 2011; Paniello et al., 2012b) although not all of these high- $\delta^{66}\text{Zn}$
425 samples suffered from a resolvable Zn loss. In particular, Hvittis, Atlanta and North West
426 Forrest EL6 enstatite chondrites have $\delta^{66}\text{Zn}$ values up to 7.4‰, the highest observed so far for
427 Solar System materials, with very low Zn concentrations compared to enstatite chondrites of
428 lower metamorphic grades (Moynier et al. 2011). Recent studies have shown that Zn isotopes

429 are significantly fractionated during evaporation–condensation processes (Moynier et al.,
430 2011). For example, the $\delta^{66}\text{Zn}$ of lunar basalts is $\sim 1\%$ heavier than average terrestrial basalts
431 and this extent of fractionation is assumed to have occurred during an evaporation event
432 (Paniello et al., 2012a; Day and Moynier, 2014; Kato et al., 2015). A recent study of Day et
433 al. (2017) has shown that Zn isotopes are indeed fractionated by $\sim 0.5\%$ /a.m.u. at high
434 temperatures and pressures (locally $>8400\text{K}$ and $>8\text{ GPa}$) by evaporation during the nuclear
435 deronation at the Trinity test site, USA, following a Rayleigh distillation processes and that
436 Zn loss could be significant under some conditions. On the other hand, Zn loss during tektite
437 formation does not exceed $\sim 20\%$ (this study and Žák et al., 2016) and our Zn (and Cu)
438 elemental and isotope data do not fit a simple Rayleigh fractionation process suggesting that
439 evaporation processes taking place during formation of tektites are more complex than during
440 the nuclear detonation.

441 It has been recognized that most chondrite groups are enriched in ^{63}Cu relative to BSE,
442 with $\delta^{65}\text{Cu}$ values varying from -1.5 to -0.1% in carbonaceous chondrites, -0.5 to $+0.1\%$ in
443 ordinary chondrites and -0.4 to -0.15% in enstatite chondrites (Luck et al., 2003; Savage et
444 al., 2015). This observation implies that impact events and accretion processes result in
445 distinct Cu isotope systematics of distal impact melt ejecta and planetesimals. Furthermore,
446 the new $\delta^{65}\text{Cu}$ values for tektites in this study (up to 12.5%) are, to our knowledge, some of
447 the highest ever measured in natural samples. These high values cannot originate from a
448 common natural process; for example, smelting is unable to fractionate Cu isotopes despite
449 high temperatures applied (Gale et al., 1999; Mattielli et al., 2006). While the new Zn and Cu
450 data for tektites may appear to support the evaporation-induced fractionation process (see
451 Moynier et al., 2009a, 2010), the lack of possible parental materials to tektites in these studies
452 did not enable a more exact assessment of alternative processes. The full complement of new
453 data for sediments from the Ries (**Table 1**) appears to put certain ambiguity on a purely

454 evaporative loss of chalcophile elements. This is illustrated in **Fig. 4** where Rayleigh
455 fractionation paths are plotted for several starting Zn and Cu concentrations in order to mimic
456 the large range in Zn and Cu contents of the sedimentary parentage. For Zn, all calculated
457 paths (elemental and binary species) cross-cut the field of moldavite data at a too
458 perpendicular angle, invoking the inability of the Rayleigh process to result in the observed
459 elemental and isotope systematics of Zn. The model also indicates that a singular initial Zn
460 abundance value may be at odds with natural systems. On the other hand, the Cu data can be
461 broadly anchored by a Rayleigh fractionation process if the starting Cu concentration is ~3–4
462 ppm. Such a low Cu content is not excluded from the current data set (**Table 1**) but we stress
463 that our data set only represents the best available proxy for Cu systematics of the
464 sedimentary parentage to moldavites and that moldavite melt represents a mixture of a
465 number of chemically diverse sediments.

466

467 **4.4 Implications for volatile loss during tektite formation**

468

469 The major observations of this study are two-fold: (i) Zn and Cu are lost to distinctively
470 different degrees from the assumed sedimentary materials with Cu loss being significantly
471 more pronounced (up to 95%) than Zn loss (~10–20%), calculated from the average Cu and
472 Zn contents of volatile loss-corrected OSM sediments (von Engelhardt et al., 2005; Žák et al.,
473 2016), and (ii) Cu isotopes in tektites are significantly more fractionated than Zn isotopes.
474 These findings are consistent with earlier observations made for tektites (Moynier et al.,
475 2009a, 2010) but are opposite to what has been found for lunar samples where Zn is
476 significantly more fractionated than Cu (Moynier et al., 2006). In the model of Moynier et al.
477 (2009a), a velocity field stirs the tektite, while differential evaporation of Zn isotopes occurs
478 at the surface. If the characteristic evaporation time is slow with regard to the diffusion

479 timescale, the system deviates from Rayleigh process because a diffusion-limited regime is
480 established. As a consequence, the magnitude of the Zn isotope fractionation is reduced for
481 the latter process at a given extent of Zn loss. The isotope fractionation in a diffusion-limited
482 regime is controlled by the balance between the evaporative flux and the diffusive flux at the
483 diffusion boundary layer.

484 The role of redox conditions has been suggested by Moynier et al. (2010) and recent
485 experimental study by (Ni and Zhang, 2016) provides evidence that monovalent Cu is
486 significantly more mobile than divalent Zn in silicate melts, most likely as a consequence of
487 higher chemical diffusivity. This would perhaps imply that oxidation state and chemical
488 makeup of the system prior to impact (which would control the mineralogical host and
489 chemical exchange in the impact plasma) may play a prominent role in fractionating these
490 elements during the impacts. In fact, the volatility of the elements is directly related to the
491 redox conditions (e.g., O'Neill and Palme, 2008). In the gas phase, both Cu and Zn will be
492 present as mono-atomic Cu_g and Zn_g at a large range of physical conditions (Moynier et al.,
493 2007). On the other hand, in the condensed phase Cu will be present as Cu^+ and, therefore,
494 associated to either 1/2 S atom or 1/2 O atom as $\text{CuS}_{1/2}$ or $\text{CuO}_{1/2}$ while Zn will be present at
495 Zn^{2+} and associated with one O atom as ZnO in silicate minerals. Following a similar
496 approach as applied by O'Neill and Palme (2008), this would indicate that Cu will become
497 relatively more volatile than Zn at higher f_{O_2} and would be consistent with observations from
498 this study. Moreover, significant redox-related diffusive loss of Cu from tektites can be
499 compared with conservative behaviour of Li which belongs to the fastest diffusing elements
500 with associated isotope effects (e.g., Richter et al., 2003) and yet, tektites do not show any
501 kinetic effects on Li (Magna et al., 2011; Rodovská et al., 2016).

502 In earlier studies, von Engelhardt et al. (1987, 2005) proposed that moldavites are early
503 condensates from the plasma of vaporized source materials in which the elements with larger

504 ions were preferentially trapped in the condensed silicate melt relative to those with small
505 ionic radii. However, this model of vaporization contradicts the presence of partly unmelted
506 inclusions (baddeleyite) and abundant domains of pure silica glass (lechatelierite in
507 moldavites; Trnka and Houzar, 2002). Korta and Mráz (1975) experimentally stepwise
508 melted a sample of sandy–silty clay and suggested that evaporation of the silicate material
509 caused a significant change in relations between the major oxides compared to the original
510 chemical–physical relations in the source rocks. They also concluded that direct melting of
511 source sediments is unlikely to form tektites and that evaporation–condensation process
512 should be taken into account. This would require a significant part of the tektite material to
513 have been converted to plasma and re-condensed during rapid cooling. The recent model of
514 moldavite formation (Žák et al., 2016) is based on fragmentation of tektite melt due to
515 separation of volatiles (i.e., H₂O, CO₂, CO) during adiabatic decompression of the ejected
516 matter, followed by coalescence of molten glass droplets to larger tektite bodies. The
517 temperature, at which the individual moldavite bodies were formed, was in the range between
518 the melting temperature of moldavite glass and the melting temperature of lechatelierite,
519 roughly between ~1100 and ~1713°C. However, this temperature range is too high for both
520 Zn and Cu to condense. Therefore, the process of element loss, instead of condensation,
521 should perhaps be considered for elements with T_c lower than that of potassium or rubidium,
522 both of which would unlikely to be condensed on a hot glass.

523 In addition to these observations, we offer further additional physical factors that may
524 help elucidate the Cu–Zn elemental and isotope systematics during the impacts. We note,
525 however, that no experimental data exist for relevant impact and post-impact conditions. It
526 could be that electromagnetic properties of ejected particles may come into play. Monovalent
527 and divalent Cu differ in magnetic properties whereby Cu(I) is diamagnetic and Cu(II) is
528 paramagnetic. Electric charges are generated in particle clouds (Pähtz et al., 2010) but it is not

529 clear at present, whether such an effect may impart separation of Cu isotopes in the transient
530 plasma/overheated melt stage of the matter. Furthermore, Fe-group elements can readily form
531 carbonyls at extreme conditions which are relevant to tektite formation (Řanda et al., 2008).
532 Organic matter was present at the impact site and formation of these highly volatile
533 organometallic compounds cannot be excluded at some stages of the impact process and
534 subsequent p–T relaxation (Cody et al., 2000). Žák et al. (2016) noted that Fe and Cu belong
535 to the few elements that display a large extent of depletion in moldavites relative to possible
536 precursor materials and it remains to be tested whether organometallic compounds may
537 fractionate isotope systems of some other transitional metals to a resolved degree of
538 confidence. Preliminary experimental data of Wiesli et al. (2007) have hinted at marginal Fe
539 isotope fractionation of liquid and vapor Fe-pentacarbonyl. However, only further
540 experimental work can provide new limitations to the behavior of stable isotope systems at
541 extreme conditions.

542

543

5. Conclusions

544

545 The moldavites measured in this study are depleted in Zn and Cu contents, and are
546 distinctly enriched in the heavy Zn and Cu isotopes relative to their possible parent
547 sedimentary sources with Cu isotope fractionation in tektites being significantly more
548 pronounced than that of Zn. The origin of this is unclear at present but redox transition of
549 divalent to monovalent Cu appears to be the dominant factor, resulting in strikingly different
550 diffusivities of Cu^+ and Zn^{2+} in tektite melts. It could also be potentially related to formation
551 of volatile carbonyls, or perhaps to different electromagnetic properties of monovalent and
552 divalent Cu. Clay fractions isolated from bulk sediments are uniformly enriched in Cu and Zn
553 relative to the corresponding bulk sediments despite the compositional diversity of the latter.

554 The clay minerals of the Ries sediments cannot form a major part of the moldavite melts
555 because they are enriched in light Zn isotopes. The karst sediments show distinctly higher Zn
556 and Cu contents paralleled by elevated abundances of Al and Fe, and cannot thus be a major
557 lithological composition for moldavites, perhaps with the exception of the Cheb Basin
558 moldavites, where participation of karst-like residual soils in the ultimate source of
559 moldavites is probable. Rayleigh distillation process appears to be incapable of generating the
560 observed Zn and Cu isotope variability in tektites although no singular starting composition
561 should be applied, considering a possible range in chemistry of parent sediments of tektites.
562 From the Zn triple-isotope plot it follows that kinetic effects may become important for high-
563 temperature processed matter while equilibrium processes apply to low-temperature samples,
564 although sizeable difference could only become apparent at high values of $\delta^{66}\text{Zn}$ and $\delta^{68}\text{Zn}$.
565 The opposite sense of magnitudes of Zn and Cu isotope fractionation in tektites versus lunar
566 samples invokes an important role of oxygen and redox processes in general in inducing
567 isotope fractionation of some chalcophile elements whereas other processes apply for oxygen-
568 devoid environments.

569

570

571 **Acknowledgements** – We thank M. Trnka for some moldavite samples, Z. Řanda, J. Mizera,
572 L. Strnad and L. Dziková for chemical characterization, and M. Št'astný for isolation of clay
573 size fractions. Comments by Dominik Hezel, Yuri Amelin, and two anonymous persons on an
574 earlier version of the manuscript improved significantly the clarity of the text. We are grateful
575 to Sheng-Ao Liu and Asish Basu for reviews and Christian Koeberl for editorial handling.
576 This study has been funded through the Czech Science Foundation project 13-22351S. Paul
577 Savage was supported by the Marie Curie IOF 'Isovolc'. Frederic Moynier is grateful to the
578 European Research Council under the European Community's H2020 framework

579 program/ERC grant agreement # 637503 (Pristine) and the Agence Nationale de la Recherche
580 for a chaire d'Excellence Sorbonne Paris Cité (IDEX13C445), and for the UnivEarthS Labex
581 program (ANR-10-LABX-0023 and ANR-11-IDEX-0005-02). Parts of this work were
582 supported by IPGP multidisciplinary program PARI, and by Region Île-de-France SESAME
583 Grant no. 12015908. The authors declare no conflicts of interest.
584

Table 1: Zinc and copper abundances and isotope compositions of Ries sediments and central European moldavites

	Petrographic description	Zn (ppm)	$\delta^{66}\text{Zn}$ (‰)	2SD	$\delta^{67}\text{Zn}$ (‰)	2SD	$\delta^{68}\text{Zn}$ (‰)	2SD	Cu (ppm)	$\delta^{65}\text{Cu}$ (‰)	2SD	Al_2O_3 (wt.%) ^a
<i>Ries area</i>												
1 UTZ	Untertzell; OSM, clay-rich ("bentonite clay")	81.8	0.31	0.08	0.40	0.36	0.57	0.11	17.4	0.00	0.03	13.8
	clay fraction	93.9	-0.52	0.08	-0.74	0.07	-1.01	0.16	26.9	0.21	0.01	-
2 UTZ	Untertzell; OSM, clay- and carbonate-rich	37.9	0.09	0.10	0.24	0.10	0.22	0.12	7.5	0.29	0.04	9.34
3 UTZ	Untertzell; OSM; quartz-dominated fine-grained sand	19.2	0.28	0.13	0.37	0.32	0.47	0.21	3.2	-0.33	0.02	5.07
4 UTZ	Untertzell; OSM, silty-sandy layer	42.0	0.11	0.07	0.26	0.12	0.25	0.14	5.5	-0.11	0.07	9.72
5 ZMTH	Ziemetshausen; OSM, sand with carbonate	18.2	0.17	0.16	0.21	0.34	0.33	0.25	2.1	0.11	0.03	5.79
9 GLM	Guldesmühle; OMM, carbonate and clay-rich sand	57.5	0.04	0.03	0.14	0.06	0.11	0.08	2.7	-0.15	0.02	7.79
	Guldesmühle; OSM, fine-grained sand with clay and carbonate	108	0.46	0.12	0.61	0.33	0.86	0.20	35.3	-0.01	0.04	18.8
10 GLM	clay fraction	161	-0.14	0.06	-0.16	0.08	-0.26	0.10	42.2	0.00	0.01	-
13 BMB	Burgmagerbein; paleokarst depression filled with Miocene sediments (mainly limestone weathering residuum)	44.6	0.27	0.11	0.38	0.33	0.54	0.15	9.4	-0.19	0.05	8.22
	clay fraction	137	-0.27	0.04	-0.32	0.05	-0.49	0.09	21.4	-0.10	0.02	-
14 BMB	Burgmagerbein; paleokarst channels filled with Oligocene sediments (mainly limestone weathering residuum)	180	0.26	0.14	0.28	0.27	0.42	0.22	32.7	0.03	0.04	24.3
15 HRD	Heroldingen; OSM?, clayish carbonate-rich silt to fine-grained sand	59.9	0.08	0.07	0.16	0.14	0.17	0.17	58.0	-0.30	0.03	11.5
16 HRD	Heroldingen; OSM?, white fine-grained quartz sand	4.6	-0.05	0.04	-0.04	0.07	-0.10	0.06	0.82	-0.44	0.02	0.95
23 MHR	Möhren; freshwater oligocene limestone	66.4	0.58	0.12	0.80	0.31	1.10	0.19	12.2	0.19	0.02	7.97
24 RTS	Rothenstein; clay-rich paleokarst depression fill	118	-0.07	0.03	-0.12	0.29	-0.19	0.03	33.1	-0.35	0.04	30.9
25 RTS	Rothenstein; quartz-rich red depression fill	186	0.32	0.03	0.43	0.29	0.56	0.09	40.0	-0.17	0.02	25.2
26 LMH	Lohrmanshoff; dolomitized limestone	8.7	0.64	0.05	0.87	0.41	1.24	0.03	1.8	0.68	0.02	0.68
28 ALT	Altisheim; OSM, quartz-dominated sand with minor clay and carbonate	33.2	0.07	0.06	0.18	0.05	0.19	0.09	3.0	-0.15	0.01	5.26
<i>Moldavites</i>												
SBM-11	South Bohemia	14.9	2.23	0.20	3.32	0.40	4.46	0.37	0.42	5.35	0.07	10.9
SBM-23	South Bohemia	30.7	1.66	0.11	2.35	0.41	3.23	0.19	1.23	5.10	0.04	9.47
SBM-35	South Bohemia	25.9	3.20	0.11	4.69	0.37	6.28	0.20	0.63	4.82	0.05	8.50
SBM-44	South Bohemia	6.9	2.94	0.28	4.65	0.49	6.18	0.30	0.17	3.92	0.08	7.79
SBM-88	South Bohemia	34.5	1.82	0.12	2.64	0.31	3.55	0.17	1.44	5.02	0.10	12.2
SBM-192	South Bohemia	1.85	3.30	-	5.27	-	6.95	-	0.19	2.19	0.08	8.70
MM-60	Moravia	18.8	2.74	0.16	4.05	0.39	5.40	0.25	0.62	8.81	0.06	11.2
MM-67	Moravia	7.3	2.11	0.05	3.08	0.63	4.22	0.26	0.75	5.77	0.04	10.5
CHBM-5	Cheb Basin	108	1.96	0.15	2.86	0.28	3.82	0.23	2.86	1.62	0.04	8.70
CHBM-6	Cheb Basin	71.3	3.65	0.10	5.38	0.26	7.16	0.14	1.27	4.21	0.18	10.2

CHBM-7	Cheb Basin	58.7	3.32	0.19	5.03	0.27	6.58	0.31	0.39	12.5	0.01	9.62
MCB-2	Cheb Basin	20.6	2.32	0.23	3.56	0.26	4.68	0.35	1.83	2.72	0.05	-
LM-1	Lusatia	16.7	2.47	0.08	3.69	0.32	4.95	0.14	1.13	6.08	0.04	11.8
<i>Reference materials</i>												
BHVO-2			0.31	0.03	0.53	0.07	0.63	0.07		0.10	0.04	
BCR-2			0.17	0.05	0.28	0.11	0.34	0.10				

A double-pass quartz spray chamber combined with a 100 $\mu\text{L}/\text{min}$ nebulizer was used. Typical signals of $\sim 3\text{V}$ for ^{64}Zn and $\sim 10\text{V}$ for ^{65}Cu were achieved. For Zn, isobaric interference at mass 64 from Ni was found negligible by monitoring ^{62}Ni signal ($< 8 \times 10^{-5}\text{ V}$) and assuming natural Ni isotope composition; levels of Ga and Cu were always lower than 2 mV and 20 mV, respectively.

A single measurement has only been performed for moldavite SBM-192 due to extremely low Zn content and a limited sample mass available for analysis.

^a Al_2O_3 contents from Žák et al. (2016), save for 26 LMH (this study; recalculated to volatile-free basis according to Žák et al., 2016).

Table 2: Statistical parameters for Zn isotope data						
	a	L	U	b	L	U
SMATR, major axis (MA) regression						
S	0.0029	-0.0296	0.0353	1.9077	1.8038	2.0214
M	-0.1620	-0.5788	0.2548	2.0658	1.9184	2.2325
M1	-0.0350	-0.3846	0.3147	2.0062	1.8788	2.1480
M2	0.0450	-0.1533	0.2433	1.9629	1.8882	2.0424
T	0.0486	-0.1732	0.2705	2.0934	1.9651	2.2360
SMATR, MA, zero intercept (line forced through origin)						
S	0			1.9149	1.8468	1.9870
M	0			2.0068	1.9727	2.0419
M1	0			1.9932	1.9642	2.0228
M2	0			1.9798	1.9622	1.9977
T	0			2.1208	2.0708	2.1728
Bootstrap, MA with resampled residuals						
S	0.0027	-0.0268	0.2840	1.9087	1.8171	2.0024
M	-0.1665	-0.4993	0.1716	2.0674	1.9462	2.2029
T	0.0468	-0.1506	0.2445	2.0946	1.9753	2.2190

Lines fitted to Zn isotope data. Intercepts (a), slopes (b) and their lower (L) and upper (U)

95% confidence limits, for sediments (S), moldavites (M) and other tektites (T). The groups

M1 and M2 are cleaned M data (see text for explanation).

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Figure captions

Figure 1

Copper vs. Zn concentrations (a) and isotope compositions (b) in central European tektites and sediments from the Ries area. Clay fractions are also plotted. Copper shows significantly larger scatter in isotope compositions relative to Zn. The Cu and Zn elemental and isotope data for other tektites (gray field) and moldavites (dashed area) are from Moynier et al. (2009a, 2010).

Figure 2

The Zn contents versus Al₂O₃ contents in moldavites and sediments from the Ries area. A broadly positive correlation is observed for sediments whereas tektites show rather uniform Al₂O₃ contents at a large range of Zn abundances. Zinc and Al data for other tektites and moldavites are given in Moynier et al. (2009a).

Figure 3

The plot of $\delta^{68}\text{Zn}$ versus $\delta^{66}\text{Zn}$ for moldavites, sediments and clay fractions. The slopes for different groups (sediments and moldavites – this study, tektites – Moynier et al., 2009a) imply similar processes of Zn isotope fractionation for samples modified at high temperatures (kinetic effects) and for those that underwent only low-temperature consolidation (equilibrium effects); see main text for further discussion. Dashed circle denotes australite 5772 core (Moynier et al., 2009a) which is clearly off the linear trend and also shows peculiar Zn enrichment (265 ppm). Samples SBM-44 and SBM-192 are marked and were discussed in terms of statistical evaluation (see Section 4.1).

Figure 4

The plot of Zn (a) and Cu (b) abundances and isotope compositions versus possible paths of a Rayleigh distillation process. Several starting points for Zn and Cu abundance were used to illustrate the concentration range of these elements in sedimentary materials of the Ries area.

Rayleigh distillation paths for Cu(I) species are nearly identical to Cu(II) species and a case for Cu₂O is only plotted. The primitive upper mantle and the upper continental crust values are from McDonough and Sun (1995) and Rudnick and Gao (2014).







