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# **Cosmogenic Effects on Cu Isotopes in IVB Iron Meteorites**

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## Abstract

We measured Cu isotope compositions of 12 out of the 14 known IVB iron meteorites. Our results show that IVB iron meteorites display a very large range of  $\delta^{65}\text{Cu}$  values ( $-5.84\text{‰} < \delta^{65}\text{Cu} < -0.24\text{‰}$ ; defined as per mil deviation of the  $^{65}\text{Cu}/^{63}\text{Cu}$  ratio from the NIST-976 standard). These Cu isotopic data display clear correlations with W, Pt, and Os isotope ratios, which are very sensitive to secondary neutron capture due to galactic cosmic ray (GCR) irradiation. This demonstrates that  $\delta^{65}\text{Cu}$  in IVB irons is majorly modified by neutron capture by the reaction  $^{62}\text{Ni}(n,\gamma)^{63}\text{Ni}$  followed by beta decay to  $^{63}\text{Cu}$ . Using correlations with Pt and Os neutron dosimeters, we calculated a pre-exposure  $\delta^{65}\text{Cu}$  of  $-0.3 \pm 0.8\text{‰}$  (95% conf.) of IVB irons that agrees well with the Cu isotopic compositions of other iron meteorite groups and falls within the range of chondrites. This shows that the volatile depletion of the IVB parent body is not due to evaporation that should have enriched IVB irons in the heavy Cu isotopes.

**Keywords:** IVB iron meteorites; Copper isotopes; Cosmic ray exposure; Neutron capture

## 1. Introduction

Copper is a moderately volatile element ( $T_c=1037$  K; Lodders, 2003), and follows a chalcophile /siderophile behavior during planetary differentiation processes (Righter et al., 2010). It has two stable isotopes:  $^{63}\text{Cu}$  (69.17%) and  $^{65}\text{Cu}$  (30.83%) and even though few data have been published on the natural fractionation of Cu isotopes in terrestrial rocks, it seems that Cu has a very limited isotopic fractionation during igneous processes (Savage et al., 2015). In a survey of the Cu isotope compositions of iron meteorites, Bishop et al. (2012) observed that IVB irons ( $n=3$ ) had distinctly negative  $\delta^{65}\text{Cu}$  ( $\sim -2\text{‰}$ ;  $\delta^{65}\text{Cu}$  defined as the per mille deviation of a sample's  $^{65}\text{Cu}/^{63}\text{Cu}$  compositional ratio from that of the NIST-976 standard), which deviates from the values of chondrites ( $-1.51 \text{‰} < \delta^{65}\text{Cu} < 0.07 \text{‰}$ ; Luck et al., 2003; Barrat et al., 2012) and other iron meteorite groups ( $-1.83 \text{‰} < \delta^{65}\text{Cu} < 0.99 \text{‰}$ ; Luck et al., 2005; Bishop et al., 2012). Magmatic iron meteorites are believed to represent samples of the metallic cores of small planetary bodies (Scott, 1972). Among iron meteorite groups, the IVB group is the most volatile depleted with low concentrations of moderately volatile elements (*e.g.* Ga, Ge, and Cu) coupled with high concentrations of Ni (16 – 18 wt.%) and other refractory elements (*e.g.* Ir, Re; Campbell and Humayun, 2005; Walker et al., 2008). Bishop et al. (2012) proposed a precursor with a non-chondritic Cu isotopic composition for the IVB parent body to explain their uniquely light Cu isotopic composition. This explanation contradicts the prediction that angrites may represent the silicate portion of the IVB parent body (Campbell and Humayun, 2005).

The  $^{182}\text{Hf}$ – $^{182}\text{W}$  system ( $t_{1/2} = 8.9 \pm 0.1$  Myr; Vockenhuber et al., 2004) has proven to be a very important short-lived chronometer for dating metal-silicate differentiation events that occurred in the first 60 Myrs of the Solar System's history (Kleine et al., 2002; Schoenberg et al., 2002; Yin et al., 2002; Kleine et al., 2004; Jacobsen, 2005; Moynier et al., 2010a). However, some of the iron meteorites were found to have lower  $\epsilon^{182}\text{W}$  values (relative deviation of the ratio of  $^{182}\text{W}$  to a stable W isotope from a terrestrial standard in parts per  $10^4$ ; Kleine et al., 2005; Lee, 2005; Markowski et al., 2006a; Schersten et al., 2006; Qin et al., 2008) than the initial  $\epsilon^{182}\text{W}$  value ( $-3.51 \pm 0.10$ ) of the calcium-aluminum-rich

inclusions (CAIs; Burkhardt et al., 2012). The abnormally low  $\epsilon^{182}\text{W}$  values in these iron meteorites reflect superimposed neutron capture effects that result from long-duration exposure to galactic cosmic rays (GCR; Masarik, 1997; Leya et al., 2003; Markowski et al., 2006a, 2006b; Qin et al., 2008). When subjected to intense GCR irradiation, particles with energies of several MeV or more may induce nuclear reactions, including spallation and secondary neutron capture reactions in meteorites. Most iron meteorites have cosmic-ray exposure ages of several hundred Myrs, much larger than stony meteorites (Voshage and Feldmann, 1979; Voshage, 1984). Recent studies have found that neutron capture effects also modify the isotopic compositions of some other siderophile elements (e.g., Os, Ir, Pt, Rh, Pd) in iron meteorites (Walker, 2012; Wittig et al., 2013; Kruijer et al., 2013; Kruijer et al., 2014; Mayer et al., 2015); for example, neutron capture reactions create detectable  $^{192}\text{Pt}$  and  $^{190}\text{Os}$  excesses coupled with  $^{189}\text{Os}$  deficits (Walker, 2012; Wittig et al., 2013; Kruijer et al., 2013; Kruijer et al., 2014). These siderophile elements have comparable cross sections for secondary neutrons to W, so cosmogenic Pt and Os isotopic anomalies have been applied as *in situ* neutron dosimeters for  $^{182}\text{W}$  correction (Kruijer et al., 2013; Wittig et al., 2013; Kruijer et al., 2014).

Among all the Ni isotopes,  $^{62}\text{Ni}$  has the largest thermal neutron capture cross section (14.5 barns) and epithermal resonance integral (6.6 barns; Mughabghab, 2003), so a potential neutron capture reaction,  $^{62}\text{Ni}(n,\gamma)^{63}\text{Ni}(\beta^-)^{63}\text{Cu}$  might have produced excessive  $^{63}\text{Cu}$  in these IVB irons due to extremely high Ni/Cu ratio ( $\sim 1.1 \times 10^5$ ; 3 orders of magnitude higher than the ratios in CI chondrites), leading to some very low  $\delta^{65}\text{Cu}$  values as observed by Bishop et al. (2012). Thus, studying Cu isotopic variations among IVB irons is essential to constrain the magnitude of cosmogenic neutron capture to Cu isotopes.

In the present study, we measured Cu isotope compositions of 12 IVB iron meteorites from the same samples analyzed for W, Os, and Pt isotope compositions (Wittig et al., 2013) and found a good correlation between Cu isotopes and recently published W, Os, and Pt data, which are known to be modified by GCR neutron capture processes. We suggest that the Cu isotopic compositions of IVB meteorites are controlled by neutron capture effects on  $^{62}\text{Ni}$ . We further correct for the neutron capture

effect on Cu isotopes by coupling our data with previously measured Pt and Os isotopes to obtain a pre-irradiation value of  $\delta^{65}\text{Cu}$  for IVB irons.

## 2. Samples

In order to test our assumption that Cu isotopes of IVB iron meteorites have been modified by GCR, the Cu isotopic compositions of 12 of the 14 known IVB iron meteorites were measured by high-precision Multiple-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS). Since neutron capture effects vary with depth within a meteorite body, these samples were taken within 2 mm from the samples for which Pd, Os, Pt, and W isotopic compositions have been reported by Wittig et al. (2013) and Mayer et al. (2015). This sample set, based on previously reported cosmic ray exposure age data (Voshage and Feldmann, 1979) and W isotope compositions (Kleine et al., 2005; Markowski et al., 2006a; Qin et al., 2008; Wittig et al., 2013; Kruijer et al., 2013, 2014) is likely to cover a wide range in degrees of GCR irradiation.

In addition, we also report Cu isotopic compositions of 7 USGS geostandards (dunite DTS-1, peridotite PCC-1, andesite AGV-2, and basalts BCR-1, BCR-2, BIR-1, and BHVO-2) in order to test the reproducibility of our analytical technique, as well as to provide more data on the Cu isotopic composition of the Earth.

## 3. Analytical methods

Based on estimated Cu concentrations, 0.5 – 1 g of metal was cut and polished for isotopic analysis. Metallic chips were first cleaned in diluted HCl, and then rinsed with deionized water in an ultrasonic bath to get rid of surface contamination. Cleaned samples were digested in aqua regia in PTFE containers under hot lamps for > 48 hours until complete dissolution was observed. Purification of Cu was achieved

by anion exchange chromatography following the procedure described in Marechal et al. (1999) and Bishop et al. (2012). The samples were loaded in 1 ml of 7 mol/L HCl on 1.6 mL of anion-exchange resin (AGMP1). Matrix elements were eluted by 7 ml of 7 mol/L HCl and Cu was extracted by further addition of 19 ml of 7 mol/L HCl. This process was repeated twice to further purify Cu.

Copper isotopic compositions were measured on a Thermo-Finnigan Neptune Plus™ MC-ICP-MS at Washington University in St. Louis following the procedure described in Weinstein et al. (2011) and Bishop et al. (2012). Samples were introduced into the mass spectrometer in 0.1 mol/L HNO<sub>3</sub> via a CPI™ PFA nebulizer attached to a glass spray chamber. All samples and standards were adjusted to the same concentration (150 ± 10 ppm) for mass spectrometer analysis. Isotope intensities were collected simultaneously in static mode using a multiple faraday collector array. Twenty-five integrations of 5 s duration were acquired during one sample measurement with an associated internal error on the <sup>65</sup>Cu/<sup>63</sup>Cu of about 2-4 × 10<sup>-6</sup>.

Isotope measurements were performed using standard-sample bracketing to correct for any instrumental drift over time. Copper isotopic ratio is expressed in δ per mil units with respect to the standard NIST-976 as:

$$\delta^{65}\text{Cu} = [({}^{65}\text{Cu} / {}^{63}\text{Cu}_{\text{sample}}) / ({}^{65}\text{Cu} / {}^{63}\text{Cu}_{\text{NIST-976}}) - 1] \times 1000$$

Each sample was measured at least twice and the average is reported. The blank of the total procedure (dissolution and chemical purification) is < 5 ng, which is negligible compared with the total amount of Cu present in the samples (> 300 ng). The external reproducibility (2 s.d.) of the δ<sup>65</sup>Cu is 0.10 ‰ for iron meteorites (see Bishop et al., 2012).

The Ni and Cu concentrations were determined by laser ablation ICP-MS at Florida State University following the method described in Humayun (2012) and Williams and Humayun (2013).

#### 4. Results

The Cu isotopic compositions of well-characterized USGS standards (DTS-1, PCC-1, AGV-2, BCR-1, BCR-2, BIR-1, and BHVO-2) are listed in Table 1 together with some previously reported analyses. The good agreement between our data and literature values demonstrates the robustness of the methods and of our analyses. These igneous geostandard samples have very similar Cu isotopic compositions within the errors, showing a typical terrestrial composition, which scatters around 0 ‰ (Albarède, 2004; Ben Othman et al., 2006).

The Ni and Cu concentration and Cu isotopic composition for each of the 12 IVB iron meteorites are listed in Table 2, together with corresponding W, Pt, and Os isotope data from Wittig et al. (2013). The IVB irons display relatively small variations in Ni (15.68 – 17.87 wt.%) and Cu (1.26 – 1.79 ppm) contents, with Ni/Cu ratio ranging from 9.9 -  $12.9 \times 10^4$ ,  $\sim 10^2$  higher than in IVA iron meteorites.

Although a small nucleosynthetic anomaly in  $\epsilon^{184}\text{W}$  has been confirmed in IVB irons, the nucleosynthetic anomalies are negligible on  $\epsilon^{182}\text{W}$  (Qin et al., 2008; Wittig et al., 2013; Kruijer et al., 2013). The  $\delta^{65}\text{Cu}$  values of IVB irons are widely scattered between -0.24 and -5.84 ‰. Compared with chondrites and other groups of iron meteorites, IVB irons have a much larger  $\delta^{65}\text{Cu}$  span, and most of them display significant enrichment in  $^{63}\text{Cu}$  isotopes (or depletion in  $^{65}\text{Cu}$ ). Of the IVB iron meteorites, Weaver Mountains is the least modified by GCR-induced  $^{182}\text{W}$  burn-out and has the highest  $\delta^{65}\text{Cu}$  value, falling within the range of chondrites and other iron meteorites. In contrast, Tlacotepec, one of the most cosmic ray-irradiated samples, has the lowest  $\delta^{65}\text{Cu}$  measured in this study, of -5.84 ‰, which deviates the most from the average composition of chondrites.

## 5. Discussion

### *5.1 Mechanisms of Cu isotopic fractionation*

Compared with chondrites and terrestrial igneous rocks, iron meteorites as a whole display larger Cu isotopic fractionation, however, Cu isotopic compositions among most individual iron groups are



relatively homogeneous ( $\leq 1\%$ ). The IVB iron meteorites show a much larger range of variability ( $\sim 6\%$ ), and the IVB is the only group that does not fall within the chondritic range. It was suggested that mass-dependent processes such as evaporation-condensation and fractional crystallization could account for the small variations within the group (Bishop et al., 2012), but it is unclear that such processes could fractionate Cu isotopes to the magnitude observed in the IVB group. In the following sections we will consider the different possible mechanisms of Cu isotopic fractionation.

#### *5.1.1 Copper isotope fractionation during low-temperature alteration processes*

Low-temperature alteration and biological processes could generate significant Cu isotopic fractionations (Albarède, 2004). For example, iron and copper minerals from supergene profile of the Bayugo porphyry copper-gold deposit yielded  $\delta^{65}\text{Cu}$  values between  $-3.4$  and  $+6.9\%$  (Braxton and Mathur, 2011). However, any low-temperature fractionation process (e.g. aqueous alteration) that occurred on the IVB parent body prior to the core formation would have been homogenized in the melt from which all IVB irons crystallized, and would not be expected to create large isotopic variations among individual IVB irons. Previous studies on Re–Os isotopic systematics (Walker et al., 2008) and siderophile element concentrations in IVB irons (Campbell and Humayun, 2005; Walker et al., 2008) both confirmed that their parent body remained a chemically closed system after crystallization. In addition, our samples were specifically selected from polished interior slices, free from fusion crust or from oxidation products. Each sample was polished to remove sawn surfaces. Therefore, Cu isotopic variations in these samples should not be the result of alteration that occurred after crystallization either.

#### *5.1.2 Copper isotope fractionation during evaporation processes*

Copper is a moderately volatile element, with a 50 % condensation temperature ( $T_c$ ) of 1037 K (Lodders, 2003). Previous studies have observed that Cu isotopes are substantially fractionated during evaporation-condensation processes (Herzog et al., 2009; Moynier et al., 2010b). The IVB group contains the lowest concentrations of moderately volatile elements among all iron meteorite groups, which either reflects high nebular temperatures when their parent body accreted or volatile loss during one or more impacts

(Rasmussen et al., 1984; Campbell and Humayun, 2005). During the process of evaporation, light isotopes of an element are preferentially lost into vapor, leaving the residual phase enriched in heavier isotopes (Humayun and Clayton, 1995; Humayun and Cassen, 2000). This has been observed in shock-melted rocks (Albarede et al., 2004), especially in the tektites (hypervelocity impact glasses) that are among the terrestrial samples with the heaviest Cu isotopic composition ( $\delta^{65}\text{Cu}$  up to 6.99 ‰; Moynier et al., 2010b), although no such fractionation of potassium ( $T_c = 1006\text{ K}$ ) isotopes is observed in tektites or in impact melts (Humayun and Clayton, 1995; Humayun and Koeberl, 2004). Since IVB irons are significantly depleted in heavier Cu isotopes, which is opposite to what is expected from an evaporation process (Fig. 1), our new data agree with the conclusions by Bishop et al. (2012) that partial vaporization did not modify Cu isotopes in IVB irons, and that the severe depletions of Cu and other moderately volatile elements in IVB irons must have been induced by other mechanisms.

### *5.1.3 Copper isotope fractionation during igneous processes*

Although the volatile history and accretion processes of IVB parent body are still under debate (Campbell and Humayun, 2005; Walker et al., 2008; Yang et al., 2010; Williams and Humayun, 2013), the variations of chemical compositions within the IVB group can be successfully modeled as the result of simple crystallization of the metallic liquid in a closed system (Walker et al., 2008). Previous studies have suggested that isotopic fractionations observed in iron meteorites might have been created during the partitioning of Cu between metal and silicates (Luck et al., 2003; Moynier et al., 2007). Metal-silicate fractionation could give rise to a small isotope shift of the parental IVB metallic liquid relative to any plausible chondritic starting composition, and Savage et al. (2015) showed that this was  $< 0.1\text{‰}$ . The magmatic differentiation is unlikely to account for the Cu isotopic variations observed in IVB irons for the following reasons:

First, no such large span of  $\delta^{65}\text{Cu}$  has been found in any other group of magmatic iron meteorites, which exhibits similar or even larger ranges of fractional crystallization (Goldstein et al., 2009). Current studies have shown that most of the iron groups have relatively homogeneous Cu isotopic composition ( $\delta^{65}\text{Cu}$

variation  $< 1$  ‰) within each group (Bishop et al., 2012). Among all the major iron meteorite systems, IVB group has the simplest chemical evolution that resulted from crystallization of a metallic liquid (Walker et al., 2008), so it is unlikely that magmatic differentiation could induce  $\delta^{65}\text{Cu}$  fractionation up to 5.6 ‰ in IVB irons.

Second,  $\delta^{65}\text{Cu}$  variation is independent of magmatic evolution among IVB irons. Rhenium (Re) is a highly compatible element, whose concentration decreases with increasing degree of fractional crystallization, and thus it has been applied as an indicator of magmatic differentiation in iron meteorites (Walker et al., 2008). During fractional crystallization, Cu isotope fractionation between solid metal and the residual liquid may give rise to Cu isotope differences that are a function of the extent of fractional crystallization. Since Cu isotopes do not correlate with Re abundances (Fig. 2,  $R^2 = 0.16$ ), this effect is not important in controlling the Cu isotope composition of individual IVB irons.

Finally, the published Cu isotopic data of igneous rocks showed that Cu isotopic fractionation induced by magmatic differentiation is rather limited (Savage et al. 2015). The  $\delta^{65}\text{Cu}$  values of igneous standards derived from different geological settings (see table 1) and unaltered igneous rocks acquired by previous studies are narrowly distributed between -0.1 and 0.3 ‰ (Albarède, 2004; Ben Othman et al., 2006; Li et al., 2009; Savage et al., 2015). Although these igneous rocks went through different degrees of fractional crystallization, the variations of Cu isotopes are much smaller than what was measured in IVB irons (5.6 ‰). Therefore we conclude that it is unlikely that high-temperature magmatic processes could induce  $\delta^{65}\text{Cu}$  fractionation up to the scale of 5.6 ‰ as observed in IVB irons.

#### *5.1.4 Nucleosynthetic Effects and short-lived radionuclides in Iron Meteorites*

Copper has only two stable isotopes, and thus it is impossible to differentiate between mass-dependent and mass-independent fractionation (*e.g.* nucleosynthetic effect and radioactive decay). However, from the discussion above, we exclude mass-dependent fractionation processes such as low-temperature alteration, high-temperature volatilization, and magmatic differentiation as the major processes that fractionate Cu isotopes in IVB irons. For some metal elements, mass-independent effects have been observed in iron meteorites. *e.g.* Ni (Regelous et al. 2008), Cr (Trinquier et al. 2007), Mo (Dauphas et al.

2002; Burkhardt et al., 2011), Ru (Chen et al. 2010; Fischer-Gödde et al., 2015) and Pd (Mayer et al., 2015). These isotopic anomalies most likely result from heterogeneous distribution of isotopically diverse presolar dust in the Solar System at the time when iron meteorite parent bodies formed (Trinquier et al., 2007; Burkhardt et al., 2011). However, the magnitudes of nucleosynthetic effects in these elements are rather small ( $< 0.1\text{‰ amu}^{-1}$ ). For example, the total ranges of  $\epsilon^{60}\text{Ni}_{58/61}$ ,  $\epsilon^{62}\text{Ni}_{58/61}$ , and  $\epsilon^{64}\text{Ni}_{58/61}$  in iron meteorites (including IC, IIAB, IIIAB, IVA, IVB) are only 0.14, 0.36, and 0.69 per ten thousand, respectively (Steele et al., 2011). In addition, any nucleosynthetic anomalies should be present in all IVB irons equally after the melting and differentiation of parent body. Therefore, even if Cu isotopes were not well mixed in the Solar System by the time of IVB parent body formation, the magnitude of nucleosynthetic effect on  $\delta^{65}\text{Cu}$  is very unlikely to be more than 0.1 ‰, which is negligible compared to the range of Cu isotopes in IVB irons.

The radioactive decay of some short-lived radionuclides, which were synthesized in stars or by irradiation in the early Solar System, could also create isotopic anomalies in meteorites and their components (e.g. Lee et al., 1976; Lugmair and Shukolyukov, 1998). The decay of the short-lived nuclide  $^{63}\text{Ni}$  produces  $^{63}\text{Cu}$  by beta decay. The presence of  $^{63}\text{Ni}$  at the time of fractional crystallization in the IVB iron parent body could potentially lead to variation of  $\delta^{65}\text{Cu}$  among individual irons, which is due to different parent/daughter ( $^{63}\text{Ni}/^{63}\text{Cu}$ ) ratios created by chemical differentiation.

After melting and mixing inside the IVB parent body, the short-lived  $^{63}\text{Ni}$  is expected to be homogeneously distributed throughout the melt from which all IVB irons crystallized. The radiogenic ingrowth model is shown in Figure 3, assuming a  $^{63}\text{Ni}/^{60}\text{Ni}$  of  $1 \times 10^{-5}$  at the birth of the Solar System and a  $\delta^{65}\text{Cu}$  of 0 at the time of fractional crystallization. All the variations of  $\delta^{65}\text{Cu}$  and Ni/Cu reflect the growth with time of radiogenic  $^{63}\text{Cu}$  excesses due to decay of short lived  $^{63}\text{Ni}$ . The four isochron lines (with a solidification age of 500, 750, 1000, 1250, and 2000 years respectively) display linearly negative correlation between  $\delta^{65}\text{Cu}$  and the Ni/Cu ratio. Had the IVB irons crystallized very quickly after the birth of the Solar System (e.g.  $< 1000$  years after the synthesis of  $^{63}\text{Ni}$  nuclide), resolvable  $\delta^{65}\text{Cu}$  differences

could be detected between individual IVB irons due to different Ni/Cu ratios. However, as the half-life of  $^{63}\text{Ni}$  is only 100.1 years, which is thousand times shorter than the shortest known isotope chronometers found in meteorites, *e.g.*,  $^{41}\text{Ca}$  ( $1.02 \times 10^5$  years),  $^{26}\text{Al}$  ( $7.17 \times 10^5$  years), etc., it is too short-lived to have been present in the early Solar System. Even though we used a higher initial  $^{63}\text{Ni}/^{60}\text{Ni}$  ratio ( $1 \times 10^{-5}$ ) than the estimation ( $\sim 5 \times 10^{-6}$ ) by Luck et al. (2003), as the model predicted, no resolvable  $\delta^{65}\text{Cu}$  fractionation due to the radioactive decay of  $^{63}\text{Ni}$  would exist if fractional crystallization occurred 2000 years after the production of  $^{63}\text{Ni}$  nuclides. The IVB irons formed about  $\sim 1$  Ma after CAIs (Wittig et al., 2013; Kruijer et al., 2013), so it is inconceivable that nucleosynthetic  $^{63}\text{Ni}$  could have been present in the parental liquid from which IVBs formed.

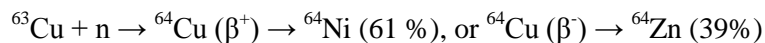
If  $^{63}\text{Ni}$  was present at the time of crystallization of the IVB iron meteorites, a linear anti-correlation between the Ni/Cu ratio of individual irons and their  $\delta^{65}\text{Cu}$  would be expected. However, there is no clear correlation between  $\delta^{65}\text{Cu}$  and Ni/Cu ratio observed in the IVB irons (Fig. 3), therefore, the  $\delta^{65}\text{Cu}$  variation is unlikely the result of radioactive decay of nucleosynthetic  $^{63}\text{Ni}$ .

## 5.2 Neutron capture effects on Cu isotopes during GCR-exposure

IVB iron meteorites have large GCR exposure ages of 200-950 Myrs (Voshage and Feldmann, 1979; Herzog, 2007). When exposed to GCR irradiation, secondary neutrons produced by cosmic ray spallation in iron meteorites are captured by siderophile element nuclei. These neutrons are dominantly captured by the most abundant nuclides in iron meteorites, including Fe, Ni, and Co (Leya and Masarik, 2013). Among the Ni isotopes,  $^{62}\text{Ni}$  has a thermal neutron capture cross section an order of magnitude larger than for other Ni isotopes or for Fe isotopes (Mughabghab, 2003). For  $^{62}\text{Ni}$ , there is the following reaction:



$^{62}\text{Ni}$  captures a neutron to produce  $^{63}\text{Ni}$ ; since  $^{63}\text{Ni}$  ( $t_{1/2}$ : 100.1 y) is unstable, it quickly decays to  $^{63}\text{Cu}$ . Similarly, for Cu isotopes (note the branching beta decay):



Although both  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  can also be burned out by capturing secondary neutrons, the direct effect is negligible compared to the production of cosmogenic  $^{63}\text{Cu}$  from  $^{62}\text{Ni}$ , because  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  have smaller neutron capture cross sections (4.5 and 2.2 barns, respectively) than  $^{62}\text{Ni}$ , and the  $^{62}\text{Ni}/^{63}\text{Cu}$  ratio is as high as  $5 \times 10^3$  in IVB irons. Given the long exposure to GCR, the accumulated  $^{63}\text{Cu}$  from  $^{62}\text{Ni}$  burn-out leads to a resolvable decrease in  $^{65}\text{Cu}/^{63}\text{Cu}$  value in IVB iron meteorites. It should be pointed out that the total burn-out on  $^{62}\text{Ni}$  is too small ( $<0.001\%$ ; calculated from  $\delta^{65}\text{Cu}$  deviation) to be detected by measuring Ni isotopic ratios under current analytical precisions ( $\sim 0.05\%$ ; Moynier et al. 2007; Regelous et al. 2008), even in the most irradiated sample, Tlacotepec. Similarly, variations in  $\delta^{65}\text{Cu}$  are not affected measurably by direct GCR burning of the Cu isotopes.

The deviation of  $\delta^{65}\text{Cu}$  from its pre-exposure value depends on the Ni/Cu ratio and the dosage of secondary neutrons. The higher the Ni/Cu ratio and longer the galactic cosmic ray exposure is, the larger the deviation from the pre-exposure value would be. In IVB iron meteorites,  $\delta^{65}\text{Cu}$  values display an apparent positive correlation with  $\epsilon^{189}\text{Os}$  and negative correlations with  $\epsilon^{190}\text{Os}$  and  $\epsilon^{192}\text{Pt}$  that were measured on a sample taken within 2 mm from our samples (Fig. 4), with Weaver Mountain and Tlacotepec representing the least and most irradiated samples. This implies that  $\delta^{65}\text{Cu}$  of IVB irons was modified by neutron capture effects.

The IVB irons contain exceptionally low concentrations of moderately volatile elements (*e.g.* Ga, Ge, and Cu) and high Ni contents (16 – 18 wt.%). The Cu concentrations of IVB irons measured in this study are 1.26-1.77 ppm (Table 2), while most of samples from other groups studied by Bishop et al. (2012) have Cu concentrations higher than 100 ppm. The Ni/Cu ratios of IVB group members are generally  $\sim 100$  times higher than in other groups of iron meteorites, indicating the deviations of  $\delta^{65}\text{Cu}$  induced by GCR irradiation for IVB irons are expected to be 2 orders of magnitude larger than in other iron meteorite groups, given the same cosmic-ray exposure history. For example, given the  $\delta^{65}\text{Cu}$  difference (5.6‰) between the most (Tlacotepec) and the least cosmic ray damaged sample (Weaver Mountains) in IVB group, it is possible to estimate from the Ni/Cu ratios that for other iron meteorites with equally long

exposure-ages as Tlacotepec ( $945 \pm 55$  ma; Voshage and Feldmann, 1979), the  $\delta^{65}\text{Cu}$  shift induced by neutron capture effects on  $^{62}\text{Ni}$  is expected to be no more than 0.1 ‰, which is barely beyond our current analytical uncertainties. This explains why significantly negative  $\delta^{65}\text{Cu}$  only appears in the IVB group and why Cu isotope variations of other iron meteorite groups (except IVBs) are close to the range defined by chondrites. However, several volatile-depleted ungrouped irons with long exposure ages, e.g., Deep Springs (Scott, 1978; Qin et al. 2008) might also exhibit large  $\delta^{65}\text{Cu}$  deviations. Neutron capture reactions will need to be considered for other irons in the future.

### 5.3 Pre-exposure $\delta^{65}\text{Cu}$ value derived from correlated Cu–Os–Pt isotope systematics

The pre-exposure  $\delta^{65}\text{Cu}$  can be obtained from the linear correlation between Cu and Pt, as well as Os isotopes. As cosmogenic  $\epsilon^{192}\text{Pt}$  anomalies are dependent on Ir/Pt ratios, which display a relatively large variation in the IVB group (0.46-1.00 with an average of 0.74; Walker et al., 2008), it is necessary to eliminate the  $\epsilon^{192}\text{Pt}$  bias from chemical differences (Kruijer et al., 2013; Wittig et al., 2013). In  $\delta^{65}\text{Cu}$  vs.  $\epsilon^{192}\text{Pt}$  space (Fig. 4c), all  $\epsilon^{192}\text{Pt}$  values were normalized to a common Ir/Pt value (average value 0.74) based on the neutron capture reaction. Like  $\epsilon^{192}\text{Pt}$ ,  $\delta^{65}\text{Cu}$  deviation induced by GCR also depends on chemical composition (Ni/Cu ratios) and, therefore, should also be normalized to a common Ni/Cu value. But due to the relatively limited Ni/Cu variations in IVB irons and possibly larger uncertainties arising from a pre-exposure  $\delta^{65}\text{Cu}$  assumption for normalization,  $\delta^{65}\text{Cu}$  is not normalized in this study. In contrast,  $\epsilon^{189}\text{Os}$  and  $\epsilon^{190}\text{Os}$  show anti-correlation (Wittig et al., 2013), with little dependence on the chemical composition, therefore, no normalizations are needed.

In each systematics (Fig. 4), the dashed line is the best-fit regression to the correlation, calculated using Isoplot (Ludwig, 2003). The intercepts to the pre-exposure  $\epsilon^{189}\text{Os}$ ,  $\epsilon^{190}\text{Os}$ , and  $\epsilon^{192}\text{Pt}$  values (by definition 0) represent the pre-exposure  $\delta^{65}\text{Cu}$  value. The  $\delta^{65}\text{Cu}$  vs.  $\epsilon^{189}\text{Os}$  (Fig. 4A),  $\delta^{65}\text{Cu}$  vs.  $\epsilon^{190}\text{Os}$  (Fig. 4B), and  $\delta^{65}\text{Cu}$  vs.  $\epsilon^{192}\text{Pt}$  (Fig. 4C) correlations yield pre-exposure  $\delta^{65}\text{Cu}$  values of  $-0.3 \pm 1.8$  (95% conf.),  $-0.5 \pm 1.2$  (95% conf.),  $-0.1 \pm 1.2$  (95% conf.), respectively. Since the  $\epsilon^{189}\text{Os}$  and the  $\epsilon^{190}\text{Os}$  both measure the same neutron capture reaction, an error-weighted average of these two yielded  $\delta^{65}\text{Cu}$  values of  $-0.4 \pm 1.0$

(95% conf.). This value was then averaged with that from Fig. 4C to obtain  $\delta^{65}\text{Cu}$  values of  $-0.3 \pm 0.8$  (95% conf.). This corrected Cu isotopic composition for the IVB iron meteorites falls in the range defined by other iron meteorite groups as well as chondrites (Fig. 5). Therefore, our results imply that volatile depletion in IVB meteorites did not fractionate Cu isotopes by a magnitude greater than that of the range in chondritic Cu isotope values. Recent measurements of nucleosynthetic anomalies in Ni (Regelous et al., 2008), Mo (Burkhardt et al., 2011), Ru (Chen et al., 2010; Fischer-Gödde et al., 2015), Pd (Mayer et al., 2015) and W (Qin et al., 2008; Kruijer et al., 2012; Wittig et al., 2013) isotopes show that IVB irons have the largest isotopic anomalies among iron meteorites, similar to the scales observed in chondrites. The IVB irons also show a chondritic pre-exposure Cu isotope composition within our current analytical precision (Fig. 5).

## 6. Conclusions

This study presents Cu isotopic compositions for 12 of the 14 known IVB iron meteorites. IVB magmatic iron meteorites show significant Cu isotopic variations ( $-5.84\text{‰} < \delta^{65}\text{Cu} < -0.24\text{‰}$ ) that resulted from neutron capture on  $^{62}\text{Ni}$  induced by cosmic ray exposure. The  $\delta^{65}\text{Cu}$  displays clear negative correlations with  $\epsilon^{192}\text{Pt}$  and  $\epsilon^{190}\text{Os}$  and positive correlations with  $\epsilon^{189}\text{Os}$  and  $\epsilon^{182}\text{W}$ , with Weaver Mountains representing the least and Tlacotepec representing the most radiation-damaged samples. The  $\delta^{65}\text{Cu}$ - $\epsilon^{192}\text{Pt}$ ,  $\delta^{65}\text{Cu}$ - $\epsilon^{190}\text{Os}$ ,  $\delta^{65}\text{Cu}$ - $\epsilon^{189}\text{Os}$  correlations defined by the IVB irons yield an average pre-exposure  $\delta^{65}\text{Cu}$  of  $-0.3 \pm 0.8\text{‰}$  (95% conf.), which agrees well with the Cu isotopic compositions of other iron meteorite groups and falls within the range of chondrites. The pre-irradiation Cu isotope composition of IVB irons ( $-0.3 \pm 0.8\text{‰}$ ) provides no support for an evaporative loss of Cu as the cause of the low Cu/Ni ratio of the IVB parental liquid (Campbell and Humayun, 2005). Despite the large uncertainty of the pre-irradiation  $\delta^{65}\text{Cu}$  for IVBs, it is clear that the extreme volatile Cu depletion in IVB irons was not accompanied by enough  $\delta^{65}\text{Cu}$  variation to set it apart from other iron meteorite groups. The large neutron capture effect observed in IVB irons is due to the high Ni/Cu ratios of these meteorites. Thus, this effect may not be



apparent in most other irons, but may affect some other irons that have undergone significant GCR exposure with lower Ni/Cu ratios than IVBs.

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## Figure Captions

**Fig.1.**  $\delta^{65}\text{Cu}$  range for the bulk Silicate Earth (BSE), tektites, lunar basalts and soils, chondrites, IVB and other group iron meteorites. The dashed line represents the average Cu isotopic composition of BSE:  $\delta^{65}\text{Cu} = 0.07 \pm 0.10 \text{ ‰}$  (2 s.d.; Savage et al., 2015). tektite data are from Moynier et al. (2010b); Lunar soil and basalt data are from Moynier et al. (2006) and Herzog et al. (2009); chondrite data are from Luck et al. (2003) and Barrat et al. (2012); and iron meteorite data are from Bishop et al. (2012). The IVB iron data (before cosmogenic neutron capture corrections) are from this study.

**Fig.2.**  $\delta^{65}\text{Cu}$  versus the degree of crystal-liquid differentiation as represented by the Re concentration for IVB iron meteorites. The external uncertainty is  $\pm 0.10$  (2 s.d.) for  $\delta^{65}\text{Cu}$ . Re data are from Walker et al. (2008), except for Dumont which were determined by Campbell and Humayun (2012).

**Fig.3.**  $\delta^{65}\text{Cu}$  versus the Ni/Cu ratio of IVB iron meteorites. The five red dashed lines represent modeled  $^{63}\text{Ni}$ - $^{63}\text{Cu}$  evolution diagrams (isochron lines), which assume the initial  $^{63}\text{Ni}/^{60}\text{Ni}$  of  $1 \times 10^{-5}$  and  $\delta^{65}\text{Cu}$  of 0. The differences in the slopes of the four correlation lines correspond to the differences in times of crystallization.

**Fig.4.** Correlation of  $\delta^{65}\text{Cu}$  (this study) with GCR-modified isotopes (Wittig et al., 2013) (A)  $\varepsilon^{189}\text{Os}$ , (B)  $\varepsilon^{190}\text{Os}$ , and (C)  $\varepsilon^{192}\text{Pt}$  in IVB iron meteorites. In each panel, the dashed line represents the best-fit linear regression line calculated using Isoplot (Ludwig, 2003) and projection to the x-axis intercept of 0 yields the pre-GCR irradiation  $\delta^{65}\text{Cu}$  of the IVB iron meteorite group (black bar, 2 s.d.). Error bars on symbols represent the uncertainties (see Table 2). Uncertainty of  $\delta^{65}\text{Cu}$  is 0.10‰, which is not resolvable in this figure set due to large span of Cu variation.

**Fig.5.** Comparison of Cu isotopic composition between primitive meteorites and pre-exposure IVB iron meteorites. The yellow band represents the  $\delta^{65}\text{Cu}$  value of Bulk Silicate Earth, i.e.  $0.07 \pm 0.10 \text{ ‰}$  (2 s.d.; Savage et al., 2015). Carbonaceous and ordinary chondrites data are from Luck et al. (2003) and Barrat et al. (2012).

**Table 1.** Copper isotopic compositions of USGS geostandards.

Geostandard	$\delta^{65}\text{Cu}$	2s.d.	Reference
BCR-1	0.21	0.09	This study
	0.07	0.08	Archer and Vance (2004)
BCR-2	0.20	0.09	This study
	0.22	0.08	Bigalke et al., (2010)
	0.18	0.08	Bigalke et al., (2011)
BIR-1	0.04	0.09	This study
	-0.02	0.10	Li et al., (2009)
BHVO-2	0.13	0.09	This study
	0.10	0.07	Moynier et al., (2010b)
AGV-2	-0.02	0.09	This study
	0.10	0.11	Moynier et al., (2010b)
PCC-1	0.17	0.09	This study
DTS-1	0.08	0.09	This study

**Table 2.** Cu, W, Os, and Pt isotope data of IVB iron meteorites

	$\delta^{65}\text{Cu}^{\text{a}}$	$n^{\text{b}}$	Ni (wt.%)	Cu (ppm)	Ni/Cu ( $10^4$ )	Re (ppm) <sup>c</sup>	$\epsilon^{182}\text{W}^{\text{d}}$	$2\text{se}_m$	$\epsilon^{189}\text{Os}^{\text{d}}$	$2\text{se}_m^{\text{e}}$	$\epsilon^{190}\text{Os}^{\text{d}}$	$2\text{se}_m$	$\epsilon^{192}\text{Pt}^{\text{d}}$	$2\text{s.d.}^{\text{f}}$
Cape of Good Hope	-2.40	2	15.68	1.30	12.0	3.06	-3.6	0.18	-0.32	0.11	0.11	0.06	24.6	0.8
Dumont	-4.53	2	16.30 <sup>g</sup>	1.27	12.9	2.63 <sup>g</sup>	-3.85	0.06	-0.23	0.07	0.26	0.01	23.6	0.3
Hoba	-1.53	3	16.43	1.31	12.6	2.43	-3.61	0.09	-0.06	0.03	0.00	0.00	13.7	0.4
Iquique	-1.96	2	15.99	1.39	11.5	3.21	-3.55	0.03	-0.25	0.05	0.18	0.03	24.3	1.0
Kokomo	-4.30	2	16.29	1.27	12.9	3.15	-3.55	0.12	-0.25	0.06	0.15	0.03	31.8	0.8
Santa Clara	-2.26	3	17.64	1.68	10.5	1.81	-3.64	0.06	-0.34	0.01	0.14	0.10	13.8	0.4
Skookum	-3.47	3	17.83	1.63	11.0	1.37	-3.59	0.17	-0.16	0.00	0.19	0.03	6.3	0.6
Tawallah Valley	-2.89	2	17.66	1.77	10.0	1.37	-3.72	0.17	-0.24	0.10	0.06	0.05	8.6	0.5
Tinnie	-1.54	2	17.69	1.79	9.9	1.53	-3.57	0.07	-0.05	0.03	0.03	0.02	6.3	0.3
Tlacotepec	-5.84	3	16.06	1.26	12.7	3.10	-4.21	0.13	-0.64	0.06	0.39	0.07	52.8	0.4
Weaver Mountains	-0.24	3	17.87	1.65	10.9	1.40	-3.33	0.12	-0.03	0.01	0.06	0.03	4.4	0.3
Warburton Range	-2.42	2	17.84	1.77	10.1	1.23	-3.42	0.16	0.02	0.06	0.05	0.08	5.9	0.5

<sup>a</sup> External reproducibilities (2 s.d.) are estimated to be  $\pm 0.10$  ‰ for  $\delta^{65}\text{Cu}$

<sup>b</sup> n=number of repeat measurements by MC-ICP-MS

<sup>c</sup> Re data for IVB iron meteorites from Walker et al. (2008)

<sup>d</sup>  $\epsilon^{182}\text{W}$ ,  $\epsilon^{189}\text{Os}$ ,  $\epsilon^{190}\text{Os}$ , and  $\epsilon^{192}\text{Pt}$  data from Wittig et al. (2013)

<sup>e</sup> Uncertainties of W and Os isotope data are given as standard error of the mean ( $2\text{se}_m$ ) derived from replicate measurements of the same digestions

<sup>f</sup> Uncertainties of Pt isotopes are given as in-run standard deviation (2s.d.)

<sup>g</sup> data from Campbell and Humayun (2012)

Figure 1

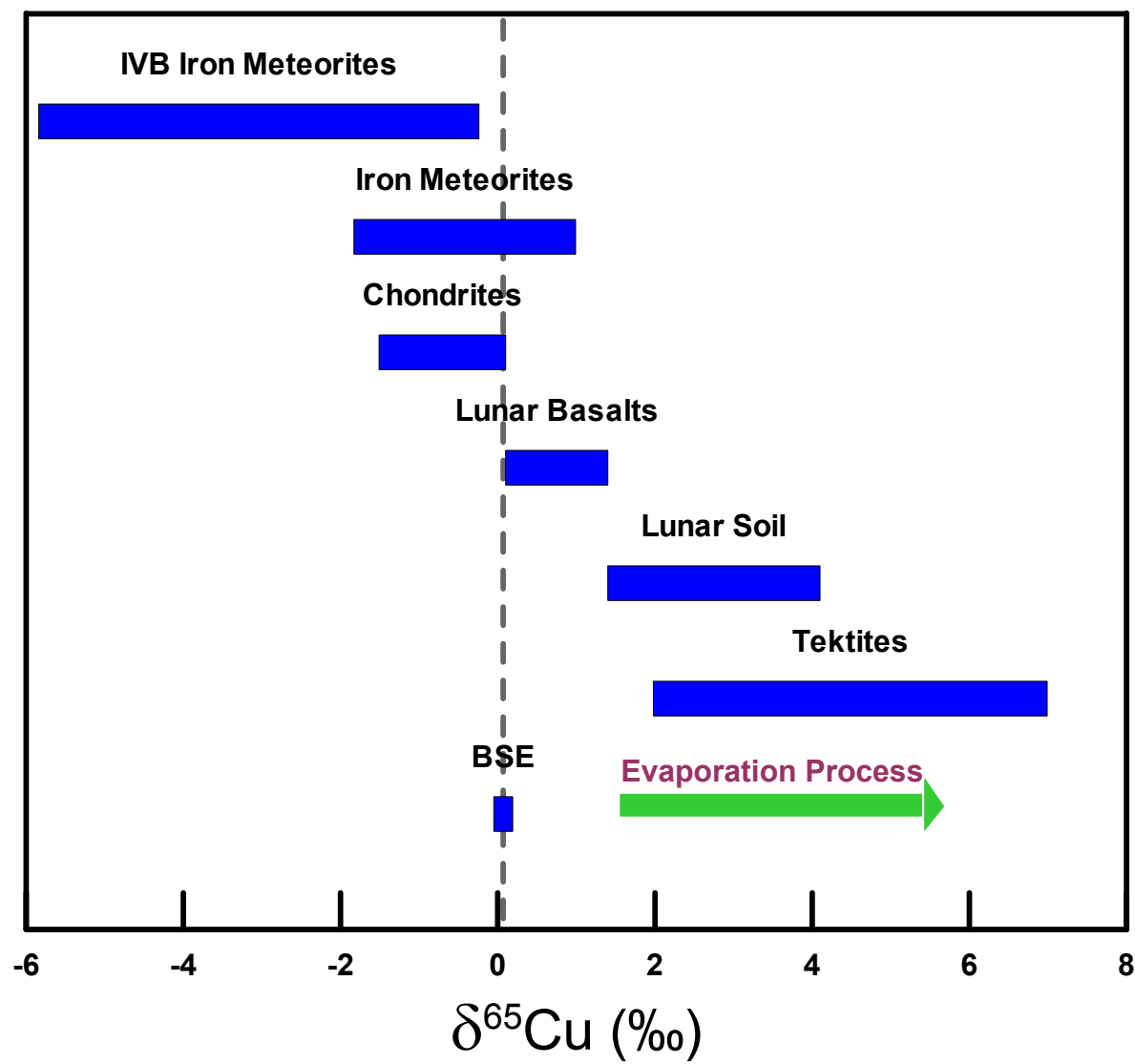


Figure 2

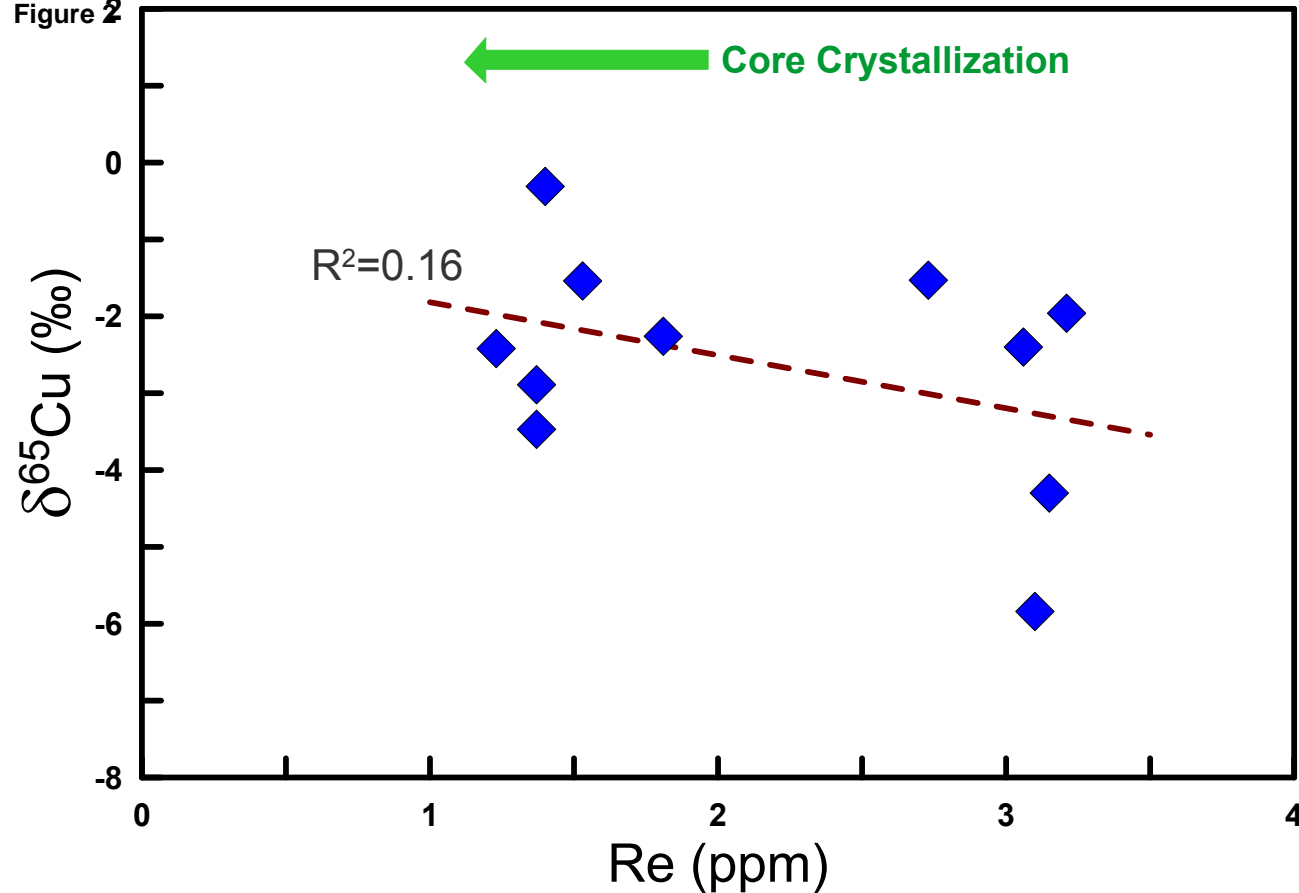


Figure 3

