The Meteoritical Society

Meteoritics & Planetary Science 47, Nr 2, 268–276 (2012)
doi: 10.1111/j.1945-5100.2011.01326.x

The Cu isotopic composition of iron meteorites

Matthew Cole BISHOP*, Frederic MOYNIER, Charlotte WEINSTEIN, Jean-Gabriel FRABOULET, Kun WANG, and Julien FORIEL

Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University, St. Louis, Missouri 63130, USA
*Corresponding author. E-mail: m.c.bishop@wustl.edu

(Received 29 July 2011; revision accepted 05 December 2011)

Abstract–High-precision Cu isotopic compositions have been measured for the metal phase of 29 iron meteorites from various groups and for four terrestrial standards. The data are reported as the δ^{65}Cu permil deviation of the ^{65}Cu/^{63}Cu ratio relative to the NIST SRM 976 standard. Terrestrial mantle rocks have a very narrow range of variations and scatter around zero. In contrast, iron meteorites show δ^{65}Cu approximately 2.3‰ variations. Different groups of iron meteorites have distinct δ^{65}Cu values. Nonmagmatic IAB-IIICD iron meteorites have similar δ^{65}Cu (0.03 ± 0.08 and 0.12 ± 0.10, respectively), close to terrestrial values (approximately 0). The other group of nonmagmatic irons, IIE, is isotopically distinct (−0.69 ± 0.15). IVB is the iron meteorite group with the strongest elemental depletion in Cu and samples in this group are enriched in the lighter isotope (δ^{65}Cu down to −2.26‰). Evaporation should have produced an enrichment in ^{65}Cu over ^{63}Cu (δ^{65}Cu > 0) and can therefore be ruled out as a mechanism for volatile loss in IVB meteorites. In silicate-bearing iron meteorites, Δ^{17}O correlates with δ^{65}Cu. This correlation between nonmass-dependent and mass-dependent parameters suggests that the Cu isotopic composition of iron meteorites has not been modified by planetary differentiation to a large extent. Therefore, Cu isotopic ratios can be used to confirm genetic links. Cu isotopes thus confirm genetic relationships between groups of iron meteorites (e.g., IAB and IIICD; IIIE and IIIAB); and between iron meteorites and chondrites (e.g., IIE and H chondrites). Several genetic connections between iron meteorites groups are confirmed by Cu isotopes, (e.g., IAB and IIICD; IIIE and IIIAB); and between iron meteorites and chondrites (e.g., IIE and H chondrites).

INTRODUCTION

Multiple-collector inductively coupled plasma–mass spectrometry (MC-ICP-MS) has allowed high precision isotopic measurements of transition metals and permitted the discovery of small isotopic variations in meteorites for elements such as: Fe (Zhu et al. 2001; Poitrasson et al. 2004; Williams et al. 2006), Cu (Luck et al. 2003; Williams and Archer 2011), Ge (Luais 2008), Zn (Luck et al. 2005; Moynier et al. 2007, 2010b), Cd (Wombacher et al. 2008), Ni (Cook et al. 2007; Moynier et al. 2007), and Sr (Moynier et al. 2010a). These isotopic variations provide a new outlook on metal/silicate/sulfide/vapor separation during nebular and planetary processes.

Copper is a moderately volatile element (Tc = 1037 K, Lodders [2003]), which behaves as a chalcophile/siderophile element. The abundance of Cu is greater than 100 ppm in most groups (Kracher et al. 1980; Malvin et al. 1984; Sutton et al. 1987; Wasson et al. 1998; Wasson and Huber 2006). Malvin et al. (1984) reported that some groups of iron meteorites show distinct Cu concentration values, and proposed the use of Cu to find genetic links among iron meteorites. One of the most striking observations is a large depletion in Cu (and other moderately volatile elements) in IVB (< 9 ppm) and to a smaller extent in IVA group meteorites (Wasson and Richardson 2001; Haack and McCoy 2003).

Copper isotopic fractionation in high temperature systems seems to be limited to volatilization from impact processes in terrestrial, lunar, and meteoritic materials (Moynier et al. 2006, 2010c; Herzog et al. 2009) and metal/silicate/sulfide segregation (Moynier et al. 2005; Williams and Archer 2011). In terrestrial rocks, Cu shows a narrow range of isotopic variations (Albarede

2004). Ben Othman et al. (2006), Archer and Vance (2004), Herzog et al. (2009) and Moynier et al. (2010c) showed that the δ^{65}Cu (permil deviation of the ^{65}Cu/^{63}Cu ratio from the standard NIST 976) of a variety of terrestrial basalts scatter around zero at $\pm 0.05‰$ amu^{-1} (atomic mass unit). On the other hand, lunar soils and tektites could be enriched in the heavy isotope up to 3‰ per amu (Moynier et al. 2006, 2010c; Herzog et al. 2009). These isotopic effects were ascribed to vaporization due to impact by meteorites or micrometeorites.

A noticeable feature is the correlation between the ^{65}Cu/^{63}Cu ratio and Δ^{17}O in carbonaceous chondrites (Luck et al. 2003), which has been interpreted as the result of a mixing of two or three different Cu and O reservoirs in the early solar nebula. This correlation also suggests that Cu isotopes could be used as a means to trace genetic links among meteorites.

So far, only three studies have reported the Cu stable isotopic composition of iron meteorites (Luck et al. 2005; Moynier et al. 2007; Williams and Archer 2011). The pioneering work of Luck et al. (2005) reported the ^{65}Cu/^{63}Cu ratio (as permil deviation from the NIST SRM 976, δ^{65}Cu) for five different iron meteorites: Canyon Diablo (IA), Campo del Cielo (IA), Nantan (IIICD), Casas Grandes (IIIA), and Charcas (IIIA). The three nonmagmatic iron meteorites show small isotopic enrichments in ^{65}Cu that were interpreted as evidence for evaporation due to impact at the surface of the IAB-IIICD parent body. The two magmatic iron meteorites show a narrow range of variations due to equilibrium isotopic fractionation between metal and silicate. Williams and Archer (2011) expanded this limited set of data to 11 other magmatic iron meteorites (2 IIA, 2 IIB, 1 IIIA, 2 IIIB, 2 IVA, 1 IVB, and one IIE) and four nonmagmatic iron meteorites (3 IAB and 1 IIICD) as well as troilites (FeS) from some of these samples. They observed that the fractionation factor (difference in δ^{65}Cu) between metal and troilite is variable, which implies a kinetic origin for the isotopic variations in troilites due to the preferential diffusion of ^{63}Cu from metal to sulfide during sulfide exsolution from crystallizing metal.

These two initial studies of Cu isotopic composition of iron meteorites showed that Cu isotopic ratio (1) might reveal genetic relationships among iron meteorites (2) could be used as a tracer of evaporation effect and thus help us understand the origin of volatile depletion of iron meteorites (3) could yield new insights into the origin of sulfide nodules found in some iron meteorites.

There are only a dozen different iron meteorites from eight different groups for which the Cu isotopic composition has been reported. This paucity of data has so far prevented interpreting the Cu isotopic ratio in terms of group average and genetic relations between samples.

The main goal of this work is to document stable Cu isotope composition in complete sets of magmatic iron meteorites from the groups: IIB, IIC, IID, IIE, IIIB, IIIE, IIIF, IVA, IVB and the ungrouped Piñon. We also report additional data for the nonmagmatic irons group IAB and IIE.

SAMPLES AND ANALYTICAL METHOD

Samples

Twenty-nine iron meteorites (22 magmatic and 7 nonmagmatic) were measured by MC-ICP-MS (see Table 1). The nonmagmatic iron meteorites analyzed here are composed of six IAB and two IIE. The magmatic iron meteorites are composed of one IIB, three IIC, three IID, one IIF, one IIIB, one IIIE, one IIIF, six IVA, three IVB, and one ungrouped (Piñon). For all the iron meteorites studied, large chips (0.5–1 g) with no visible sulfides were selected. However, the presence of microscopic sulfides, which would contribute to some isotopic heterogeneity, cannot be excluded. To test this possible isotopic heterogeneity, two different chips of Toluca (IAB), Weekoroo Station (IIE), La Grange (IVA), and Piñon (ungrouped) were analyzed. We also independently processed six different aliquots from homogeneous dissolutions of La Grange (IVA) chip #2 and five aliquots of Odessa (IAB) through chemistry and MC-ICP-MS measurements to test the reproducibility of the full experiment (see Table 1).

Finally, we processed four terrestrial standards to better constrain the Cu isotopic composition of the bulk silicate Earth. This also allowed us to make sure that our chemical preparation and analytical procedures were working correctly by comparing our data with those of previous studies. AGV-1 is a terrestrial andesite from the Guano Valley in Oregon, USA; BE-N is a terrestrial basalt from Essey-la-Cote, France; UB-N is a serpentinite; and ISH-R is a terrestrial trachyte.

Analytical Techniques

From iron meteorites, 0.5–1 g of metal was dissolved in aqua regia at 130 °C for several days in closed Teflon beakers. From the initial dissolution, 10% was used for the chemical purification of Cu on an AGMP1 anion-exchange resin in 7 N HCl as described in Maréchal et al. (1999).

Copper isotopic compositions were measured on a Thermo-Finnigan Neptune MC-ICP-MS at Washington University in St. Louis following the procedure described in Maréchal et al. (1999). ^{65}Cu/^{63}Cu ratio is expressed in δ permil units with respect to the standard NIST 976 as:

Table 1. Cu isotopic composition and elemental abundance for iron meteorites and terrestrial standards. The isotopic composition is represented using the δ notation (parts per 1000 deviation of the $^{65}Cu/^{63}Cu$ ratio from a terrestrial Cu standard NIST SRM 976). The Cu concentration values are from the literature (see reference in the footnotes of the table) and are reported in ppm. The external reproducibility (2σ) of $\delta^{65}Cu$ is $\pm 0.10‰$.

Sample names	Museum code	Type	$\delta^{65/63}$Cu	Cu (ppm)	Ref.
AGV-1		Terrestrial andesite	0.01		
UB-N		Terrestrial serpentinite	0.06		
ISH-R		Terrestrial trachyte	0.12		
BE-N		Terrestrial basalt	−0.10		
Deport	M 1.25	IAB	0.02	177	4
Anoka	ME 980	IAB	−0.26	223	4
Seelasgen	BM 2005 M 238	IAB	−0.20	159	4
Seelasgen[1]		IAB	−0.07	159	4
Toluca chip 1	ASU 128.845	IAB	−0.06	170	4
Toluca chip 2		IAB	−0.08	170	4
Toluca A[1]		IAB	0.03		
Toluca B[1]		IAB	−0.02		
Carlton	ME 880	IAB	−0.30	260	4
Odessa[1]		IAB	0.15	260	4
Odessa 1	ME 2388.1	IAB	0.28		
Odessa 2		IAB	0.18		
Odessa 3		IAB	0.16		
Odessa 4		IAB	0.13		
Odessa 5		IAB	0.16		
Canyon Diablo[2]		IAB	0.06	149	4
Canyon Diablo[3]		IAB	0.06	149	4
Campo del Cielo chip 1[2]	M 522.2	IAB	0.00	174	4
Campo del Cielo chip 2[2]		IAB	0.28	174	4
Nantan[2]		IIICD	0.12	132	2
Watson	ME 3195	IIE	−0.52		
Watson[1]		IIE	−0.62		
Weekeroo Station chip 1	ASU 133a	IIE	−0.78	217	5
Weekeroo Station chip 2		IIE	−0.84	217	5
Coahuila[1]		IIA	0.04		6
					6
Carbo	USNM 838	IIB	−1.49		
Mount Joy[1]		IIB	−0.18	133	6
Sao Juliao de Moreira[1]		IIB	−0.66	94	6
Ballinoo	ME 980	IIC	−0.44		
Perryville	USNM 428	IIC	−1.06	334	
Wiley	BM 1859,914	IIC	−1.23	274	
Arltunga	MET 43 AD	IID	−0.40	264	7
Needles	USNM 3533	IID	−1.26	249	7
Wallapai	USNM 788	IID	−1.47	241	7
Monahans	ASU 256.3	IIF	−1.34	309	8
Merceditas chip 1[1]		IIIA	0.97	100	1
Merceditas chip 2[1]		IIIA	0.99		
Casas Grandes chip 1[2]		IIIA	−0.42	166	2
Casas Grandes chip 2[2]		IIIA	−0.49		
Casas Grandes[3]		IIIA	−0.44		
Charcas chip 1[2]		IIIA	−0.30	490	2
Charcas chip 2[2]		IIIA	−0.40		
Charcas chip 3[2]		IIIA	−0.29		
Henbury	ASU 193.156	IIIB	−0.11	181	9
Grant[1]		IIIB	0.23	75	1
Bear Creek[1]		IIIB	−0.15	119.00	1
Aliskerovo	M649.1	IIIE	−0.23		

Table 1. *Continued.* Cu isotopic composition and elemental abundance for iron meteorites and terrestrial standards. The isotopic composition is represented using the δ notation (parts per 1000 deviation of the $^{65}Cu/^{63}Cu$ ratio from a terrestrial Cu standard NIST SRM 976). The Cu concentration values are from the literature (see reference in the footnotes of the table) and are reported in ppm. The external reproducibility (2σ) of $\delta^{65}Cu$ is ±0.10‰.

Sample names	Museum code	Type	$\delta^{65/63}Cu$	Cu (ppm)	Ref.
Clark County	USNM 1304	IIIF	−1.40		
Gibeon chip 1	NMW	IVA	−0.86	167	10
Gibeon chip 2		IVA	−1.12		
Gibeon[1]		IVA	−0.35		
La Grange chip 1	ASU 291a	IVA	−1.09	162	10
La Grange chip 2-1	ASU 291a	IVA	−0.85		
La Grange chip 2-2		IVA	−0.83		
La Grange chip 2-3		IVA	−0.80		
La Grange chip 2-4		IVA	−0.81		
La Grange chip 2-5		IVA	−0.83		
La Grange chip 2-6		IVA	−0.85		
Muonionalusta		IVA	−0.86	113	10
Obernkirchen		IVA	−0.91	146	10
Putman County	ASU 246.2	IVA	−0.72		
Yanhuitlan	M861.1	IVA	−0.69	150	10
Yanhuitlan[1]		IVA	−1.83		
Santa Clara	ASU 1060	IVB	−1.80	1.54	11
Cape of Good Hope	USNM 985	IVB	−1.70	1	11
Warburton Range	WAM 12285.7	IVB	−2.26	2	
Chinga[1]		IVB	−0.21	14	9
Piñon	ASU 147.3x	Ungrouped	−0.89		
Piñon		Ungrouped	−1.45		

1 (Williams and Archer 2011) 2 (Luck et al. 2005) 3 (Moynier et al. 2007) 4 (Wasson and Kallemeyn 2002) 5 (Wasson and Wang 1986) 6 (Wasson et al. 2007) 7 (Wasson and Huber 2006) 8 (Kracher et al. 1980) 9 (Malvin et al. 1984) 10 (Wasson and Richardson 2001) 11 (Campbell and Humayun 2005).

Notes: USNM = United States National Museum, Washington, DC; NHM = The National History Museum, London; ASU = Arizona State University, Tempe; ME = The Field Museum, Chicago; NMW = Naturhistorisches Museum, Vienna; WAM = Western Australia Museum, Perth; M = Oscar Monnig Meteorite Collection, Texas Christian University.

$$\delta^{65}Cu = \left[\frac{(^{65}Cu/^{63}Cu)_{sample}}{(^{65}Cu/^{63}Cu)_{NIST976}} - 1\right] \times 1000 \quad (1)$$

The 2σ sample external reproducibility of the $\delta^{65}Cu$ is 0.10‰ (see Herzog et al. 2009; Weinstein et al. 2011). The blank of the total procedure (dissolution and chemical purification) is <10 ng, which is negligible compared with the total amount of Cu present in the samples (several μg).

RESULTS

The four geostandards, AGV-1 ($\delta^{65}Cu$ = 0.01), BE-N ($\delta^{65}Cu$ = −0.10), UB-N ($\delta^{65}Cu$ = 0.06), and ISH-R ($\delta^{65}Cu$ = 0.12), are essentially unfractionated between each other and show a typical terrestrial composition, which scatters around zero (Albarede 2004; Ben Othman et al. 2006). The results support the isotopic homogeneity of terrestrial rocks (Albarede 2004; Ben Othman et al. 2006). For the iron meteorites, the IVA La Grange and IAB Odessa, replicated (6 and 5 times, respectively) chemical purification and mass-spectrometer give an external reproducibility of 0.04 and 0.12‰ (2σ), respectively. This precision is comparable to the value from Herzog et al. (2009) and shows that our full procedure does not fractionate Cu isotopes. For the rest of the article, and to be conservative with our interpretation, we will assume the larger uncertainty (0.12) as representative of our entire data set. The average of five different measurements of Odessa ($\delta^{65}Cu$ = 0.18 ± 0.12) is in agreement with the data from Williams and Archer (2011) ($\delta^{65}Cu$ = 0.15 ± 0.25).

Analysis of two distinct chips of Weekeroo Station (IIE, $\delta^{65}Cu$ = −0.84 and −0.78) and Toluca (IAB, $\delta^{65}Cu$ = −0.06 and −0.08) yielded similar results, the latter being consistent with previously published data ($\delta^{65}Cu$ = −0.03 and +0.02, Williams and Archer 2011). The consistency with previous measurements suggests that the isotopic composition of Cu in these meteorites is homogenous. However, IVA meteorites seem to be slightly more heterogeneous than IIE and IAB, as chips from Gibeon ($\delta^{65}Cu$ = −0.86 and −1.12) and La Grange ($\delta^{65}Cu$ = −1.09 and −0.83) show significant discrepancies.

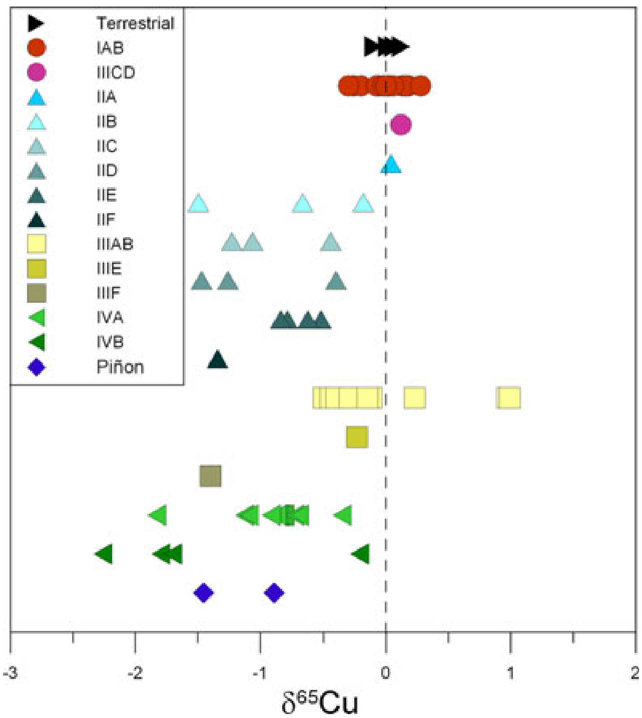

Fig. 1. Cu isotopic composition of iron meteorites and terrestrial standards. The isotopic composition is represented using the δ notation (parts per 1000 deviation from a terrestrial Cu standard NIST SRM 976).

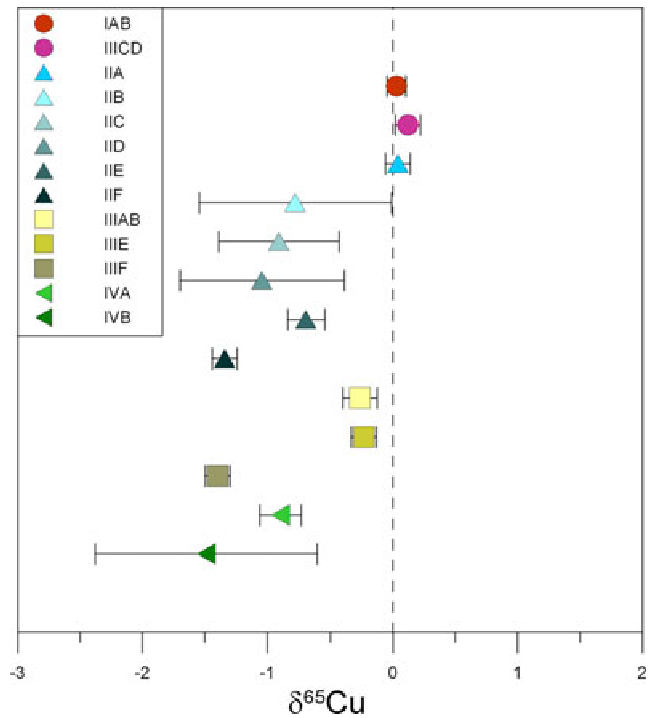

Fig. 2. Cu isotopic composition for the different groups of iron meteorites.

The ungrouped Piñon seems to be the most heterogeneous sample with δ^{65}Cu = −0.89 and −1.45 (Fig. 1).

The variations in the ratios of Cu stable isotopes between the different iron meteorite groups are small but significant (Table 1 and Fig. 2). The total range of isotopic fractionation is about 2.3 permil. The mean values for iron meteorites seem to be related to chemical group (Table 2 shows a compilation of our results with all the δ^{65}Cu published so far). The highly isotopically fractionated Mercidetas (data from Williams and Archer 2011) has been excluded from the average value of the IIIB group. This is the only IIIB sample reported by Williams and Archer (2011) and it differs by more than 1 permil from the 9 other IIIB samples analyzed by Luck et al. (2005), Moynier et al. (2007), and the present study. IAB–IIICD nonmagmatic iron meteorites are clearly enriched in ^{65}Cu compared with most other groups and members of group IVB are the most depleted in ^{65}Cu.

The only IIB sample analyzed in the present study is isotopically distinct from the two previous IIB meteorites and the one IIA sample analyzed by other groups.

As was observed by Luck et al. (2003) in chondrites, our data show that group-averages of δ^{65}Cu and Δ^{17}O are correlated in the four groups of iron meteorites containing silicate inclusions (IAB, IIICD, IIE, and IVA, see Fig. 3).

Table 2. Average Cu isotopic composition and Δ^{17}O for different iron meteorite groups.

Group	$\delta^{65/63}$Cu	2SE	Δ^{17}O [1]	2SE
IAB	0.03	0.08	−0.46	0.10
IIICD	0.12	0.10	−0.49	
IIE	−0.69	0.15	0.59	0.07
IIA	0.04	0.10		
IIB	−0.78	0.77		
IIC	−0.91	0.48		
IID	−1.04	0.65		
IIF	−1.34	0.10		
IIIAB	−0.26	0.14		
IIIE	−0.23	0.10		
IIIF	−1.40	0.10		
IVA	−0.89	0.17	1.17	0.11
IVB	−1.49	0.89		

[1] Clayton et al. 1983; Clayton and Mayeda 1996.

DISCUSSION

Our new data for four terrestrial standards derived from different geological settings support the idea that igneous terrestrial rocks are homogeneous with regard to Cu isotopes and that Cu isotopes are fractionated little or none by processes affecting igneous rocks. This supports previous results (see Ben Othman et al. [2006], Li et al. [2009] and Moynier et al. [2010c]). Large Cu isotopic fractionation is limited to biological activity,

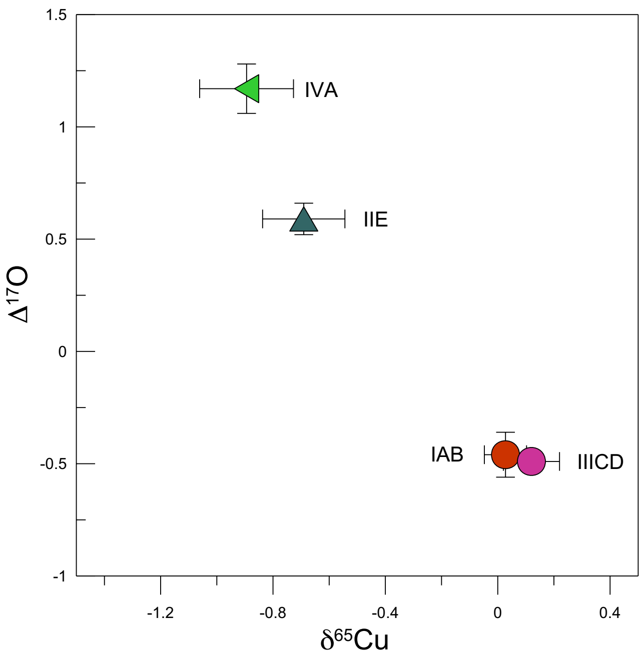

Fig. 3. $\Delta^{17}O$ versus $\delta^{65}Cu$ for silicate-bearing iron meteorites: IAB, IIICD, IIE, and IVA. Oxygen data from Clayton and Mayeda (1996) and Clayton et al. (1983).

ores, and hydrothermal systems where redox reactions or supergene recycling are taking place (Zhu et al. 2000; Larson et al. 2003; Rouxel et al. 2004; Mathur et al. 2005, 2009; Asael et al. 2007; Weinstein et al. 2011) or systems subjected to large evaporation (Moynier et al. 2010c). Chondrites are more fractionated than terrestrial rocks with $-1.51 < \delta^{65}Cu < -0.09$ for carbonaceous chondrites and $-0.51 < \delta^{65}Cu < 0.10$ for ordinary chondrites. Our new results for iron meteorite groups for which data were previously available (but usually for only one specimen), as well as for groups not analyzed before, show that most of the groups have homogeneous Cu isotopic composition.

The absence of correlation between the $\delta^{65}Cu$ and Cu concentration is an argument against secondary isotopic fractionation processes such as evaporation. IVB and to a greater extent IVA are depleted in Cu (and other volatile elements) compared with most iron groups; however, they exhibit the most ^{63}Cu-enriched isotopic composition (with the IVB Warburton Range being the isotopically lightest iron meteorite analyzed so far). This enrichment in the light isotope of the volatile-poor samples suggests that evaporation is not at the origin of the volatile depletion observed in IVA (Wasson and Richardson 2001), IVB (Campbell and Humayun 2005) or IIIF (Scott and Wasson 1976) as evaporation should remove the lighter isotope ^{63}Cu preferentially and leave in the meteorite and excess of the heavier isotope ^{65}Cu. On the contrary, a volatile-rich group like IID (Wasson and Huber 2006) is isotopically heavier than the volatile poor IVB. In addition, IVB is the only group that does not fall within the chondritic range for $\delta^{65}Cu$. This suggests a precursor with a nonchondritic Cu isotopic composition for the IVB parent body, which was already proposed based on highly siderophile elements (HSE) and Os isotopes due to a sub chondritic Re/Os and Pt/Os ratios (Walker et al. 2008).

The correlation between $\delta^{65}Cu$ and $\Delta^{17}O$ suggests a connection between oxygen and copper isotopes as already observed in carbonaceous chondrites by Luck et al. (2003). As Cu has only two isotopes, it is impossible to differentiate between mass-dependent and mass-independent isotopic fractionation. Some of the transition metals such as Zn (Moynier et al. 2009), Fe (Dauphas et al. 2008), and Ge (Luais 2008) were fractionated out of a common reservoir and any potential pre-existing nucleosynthetic anomalies had been averaged out by mixing in the solar nebula by the time of planetary body accretion. Some other elements, such as Ni (Regelous et al. 2008), Cr (Trinquier et al. 2007; Qin et al. 2008), Ti (Trinquier et al. 2009), Mo (Dauphas et al. 2002), and Ru (Chen et al. 2010) show some nonmass-dependent effects, which are due to a heterogeneous isotopic distribution, or mass-independent isotopic effects (Fujii et al. 2006). However, the magnitude of the isotopic effect in $\delta^{65}Cu$ (approximately 1‰) argues against nonmass-dependent effects that are usually limited to less than 0.1‰ amu^{-1} (Trinquier et al. 2007, 2009; Qin et al. 2008). Therefore, the correlation between $\delta^{65}Cu$ (mass-dependent effect) and $\Delta^{17}O$ (nonmass-dependent) must represent a mixing between at least two components: one endmember depleted in ^{63}Cu and depleted in ^{17}O and a second endmember enriched in ^{63}Cu and enriched in ^{17}O. This suggests that, at least in terms of Oxygen and Copper, the composition of the silicate-bearing iron meteorites originates from mixing in the presolar nebula rather than from planetary differentiation effects, such as volatilization. This is also likely to be true for other iron groups. Therefore, the Cu isotopic composition of the different groups of iron meteorites may be used to confirm genetic connection.

On the basis of similar $\Delta^{17}O$ values of the silicate inclusions found in a limited number of groups of iron meteorites (IAB, IICD, IIE, and IVA), some genetic connections between chondrites and iron meteorites were proposed (Clayton and Mayeda 1978, 1996; Clayton 1993, 2003). Some of these connections are confirmed with Cu isotopes, notably between the IIE group ($\delta^{65}Cu = -0.69 \pm 0.15$) and H chondrites ($\delta^{65}Cu = -0.51 \pm 0.10$ for unequilibrated H chondrites; Luck et al. 2003).

IAB and IIICD are closely related groups (Wasson et al. 1980; Choi et al. 1995; Wasson and Kallemeyn 2002). On average, Cu in IAB is isotopically very similar to

Cu in IIICD, which reflects the strong relationship between the two groups (Wasson and Kallemeyn 2002). In addition, a connection between IAB irons and chondrites was first proposed by Rambaldi et al. (1978). From its oxygen isotope composition, the IAB-IIICD group as a whole was proposed to be linked to carbonaceous chondrites and winnonaites (undifferentiated eucrites) by Clayton and Mayeda (1996) and Benedix et al. (2000). From our results, it seems that IAB-IIICD Cu isotopic composition falls within the range of CI carbonaceous chondrites confirming what was inferred from the oxygen isotopes.

We only analyzed one IIB sample (Carbo) and found it to be isotopically distinct from the two previous measurements on IIB irons. Furthermore, the only IIA sample analyzed for Cu isotopes by Williams and Archer (2011) is also isotopically distinct from the three IIB samples. The very limited set of data on IIAB samples (one sample from the present study and 2 from Williams and Archer 2011) prevent us from drawing any conclusions from these potential intra-group variations.

IIIE and IIIAB are very closely related groups, for which the main difference is the presence of carbides in IIIE (Scott et al. 1973). Sugiurai et al. (2000) showed that IIIE and IIIAB have the same N isotopic composition and only a very slightly different C isotopic composition. The δ^{65}Cu composition of these two groups is similar within uncertainty (−0.26 versus −0.23), which confirms the close relationship between IIIE and IIIAB.

CONCLUSIONS

Cu isotopic composition was measured in five IAB, two IIE, one IIB, three IIC, three IID, one IIF, one IIIB, one IIIE, one IIIF, six IVA, three IVB, and one ungrouped (Piñon) iron meteorites and four terrestrial standards. Terrestrial igneous rocks are little or not at all fractionated and scatter around δ^{65}Cu approximately 0. Iron meteorites are much more fractionated with a range of approximately 2.3 permil. Nonmagmatic IAB-IIICD iron meteorites have similar δ^{65}Cu, which is distinct from IIE. The volatile poor group IVB is enriched in the light isotope, and therefore evaporation fails to explain the depletion of IVB in volatiles.

In silicate-bearing iron meteorites, Δ^{17}O correlates with δ^{65}Cu, which suggests that the Cu isotopic composition of iron meteorites represents that of the parent body. Some genetic links between meteorites inferred from oxygen isotopes or siderophile element ratios are confirmed by Cu isotopes, notably between IAB and IIICD, IIIE and IIIAB, and IIE and H chondrites.

Acknowledgments—This manuscript greatly benefited from comments by Helen Williams, Osama Ghidan, and one anonymous reviewer. We are also indebted to Franz Brandstätter (Naturhistorisches Museum, Vienna), Alex Bevan (Western Australian Museum, Perth), Timothy McCoy (US National Museum of Natural History, Smithsonian Institution, Washington, DC), Caroline Smith (The Natural History Museum, London), Phillipp Heck and James Holstein (The Field Museum, Chicago), Meenakshi Wadhwa (Arizona State University, Tempe), Rhiannon Mayne (Oscar E. Monnig Meteorite Collection, TCU) for their generous donations of meteorite samples for this work and for their confidence in our analytical and scientific capabilities.

This work was supported by NASA Fund #NNX09AM64G. We also acknowledge the support of the Office of Undergraduate Research at Washington University (CB) and the Missouri space grant consortium (CW).

Editorial Handling—Dr. Nancy Chabot

REFERENCES

Albarede F. 2004. The stable isotope geochemistry of copper and zinc, edited by Johnson C. M., Beard B. L., and Albarede F. Reviews in Mineralogy and Geochemistry, vol. 55. Washington, D.C.: Mineralogical Society of America. pp. 409–427.

Archer C. and Vance D. 2004. Mass discrimination correction in multiple-collector plasma source mass spectrometry: An example using Cu and Zn isotopes. *Journal of Analytical Atomic Spectrometry* 19:656–665.

Asael D., Matthews A., Bar-Matthews M., and Halicz L. 2007. Copper isotope fractionation in sedimentary copper mineralization (Timna Valley, Israel). *Chemical Geology* 243:238–254.

Benedix G. K., McCoy T. J., Keil K., and Love S. G. 2000. A petrologic study of the IAB iron meteorites: Constraints on the formation of the IAB-Winonaite parent body. *Meteoritics & Planetary Science* 35:1127–1141.

Ben Othman D., Luck J. M., Bodinier J. L., Arndt N. T., and Albarede F. 2006. Cu-Zn isotopic variations in the Earth's mantle. *Geochimica et Cosmochimica Acta* 70:46.

Campbell A. and Humayun M. 2005. Compositions of group IVB iron meteorites and their parent melt. *Geochimica et Cosmochimica Acta* 69:4733–4744.

Chen J. H., Papanastassiou D. A., and Wasserburg G. J. 2010. Ruthenium endemic isotope effects in chondrites and differentiated meteorites. *Geochimica et Cosmochimica Acta* 74:3851–3862.

Choi B. G., Ouyang X., and Wasson J. T. 1995. Classification and origin of IAB and IIICD iron meteorites. *Geochimica et Cosmochimica Acta* 59:593–612.

Clayton R. N. 1993. Oxygen isotopes in meteorites. *Annual Review of Earth and Planetary Science Letters* 21:115–149.

Clayton R. N. 2003. Oxygen isotopes in the solar system. *Space Science Reviews* 106:19–32.

Clayton R. N. and Mayeda T. K. 1978. Genetic relations between iron and stony meteorites. *Earth and Planetary Science Letters* 40:168–174.

Clayton R. N. and Mayeda T. K. 1996. Oxygen isotope studies of achondrites. *Geochimica et Cosmochimica Acta* 60:1999–2017.

Clayton R. N., Mayeda T. K., Olsen E. J., and Prinz M. 1983. Oxygen isotope relationships in iron meteorites. *Earth and Planetary Science Letters* 65:229–232.

Cook D. L., Wadhwa M., Clayton R. N., Dauphas N., Janney P. E., and Davis A. M. 2007. Mass-dependent fractionation of nickel isotopes in meteoritic metal. *Meteoritics & Planetary Science* 42:2067–2077.

Dauphas N., Marty B., and Reisberg L. 2002. Molybdenum evidence for inherited planetary scale isotope heterogeneity of the protosolar nebula. *The Astrophysical Journal* 565:640–644.

Dauphas N., Cook D. L., Sacarabany A., Frohlich C., Davis A. M., Wadhwa M., Pourmand A., Rauscher T., and Gallino R. 2008. Iron-60 evidence for early injection and efficient mixing of stellar debris in the protosolar nebula. *The Astrophysical Journal* 686:560–569.

Fujii T., Moynier F., and Albarède F. 2006. Nuclear field vs nucleosynthetic effects as cause of isotopic anomalies in the early solar system. *Earth and Planetary Science Letters* 247:1–9.

Haack H. and McCoy T. 2003. Iron and stony iron meteorites. In *Meteorites, comets, and planets*, edited by Holland H. D. and Turekian K. K. Treatise on Geochemistry, vol. 1. Amsterdam: Elsevier. pp. 41–61.

Herzog G. F., Moynier F., Albarede F., and Berezhnoy A. A. 2009. Isotopic and elemental abundances of copper and zinc in lunar samples, Zagami, Pele's hairs, and a terrestrial basalt. *Geochimica et Cosmochimica Acta* 73:5884–5904.

Kracher A., Willis J., and Wasson J. T. 1980. Chemical classification of iron-meteorites .9. A new group (IIF), revision of IAB and IIICD, and data on 57 additional irons. *Geochimica et Cosmochimica Acta* 44:773–787.

Larson P. B., Maher K., Ramos F. C., Chang Z., Gaspar M., and Meinert L. D. 2003. Copper isotope ratios in magmatic and hydrothermal ore forming environments. *Chemical Geology* 201:337–350.

Li W., Jackson S., Pearson N. J., Alard O., and Chappell B. W. 2009. The Cu isotopic signature of granites from the Lachlan Fold Belt, SE Australia. *Chemical Geology* 258:38–49.

Lodders K. 2003. Solar system abundances and condensation temperatures of the elements. *The Astrophysical Journal* 591:1220–1247.

Luais B. 2008. Isotopic fractionation of germanium in iron meteorites: Significance for nebular condensation, core formation and impact processes. *Earth and Planetary Science Letters* 273:400.

Luck J. M., Othman D. B., Barrat J. A., and Albarede F. 2003. Coupled ^{63}Cu and ^{16}O excesses in chondrites. *Geochimica et Cosmochimica Acta* 67:143–151.

Luck J. M., Othman D. B., and Albarede F. 2005. Zn and Cu isotopic variations in chondrites and iron meteorites: Early solar nebula reservoirs and parent-body processes. *Geochimica et Cosmochimica Acta* 69:5351–5363.

Malvin D. J., Wang D., and Wasson J. T. 1984. Chemical classification of iron-meteorites .10. Multielement studies of 43 irons, resolution of group-IIIE from group-IIIAB and evaluation of Cu as a taxonomic parameter. *Geochimica et Cosmochimica Acta* 48:785–804.

Maréchal C., Télouk P., and Albarède F. 1999. Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chemical Geology* 156:251–273.

Mathur R., Ruiz J., Titley S., Liermann L., Buss H., and Brantley S. 2005. Cu isotopic fractionation in the supergene environment with and without bacteria. *Geochimica et Cosmochimica Acta* 69:5233–5246.

Mathur R., Titley S., Barra F., Brantley S., Wilson M., Phillips A., Munizaga F., Maksaev V., Vervoort J., and Hart G. 2009. Exploration potential of Cu isotope fractionation in porphyry copper deposits. *Journal of Geochemical Exploration* 102:1–6.

Moynier F., Rushmer T., and Albarède F. 2005. Zn isotopic mass fractionation during high temperature segregation of metal from silicate (abstract 5223). *Meteoritics & Planetary Science* 40.

Moynier F., Albarede F., and Herzog G. 2006. Isotopic composition of zinc, copper, and iron in lunar samples. *Geochimica et Cosmochimica Acta* 70:6103–6117.

Moynier F., Blichert-Toft J., Telouk P., Luck J. M., and Albarede F. 2007. Comparative stable isotope geochemistry of Ni, Cu, Zn, and Fe in chondrites and iron meteorites. *Geochimica et Cosmochimica Acta* 71:4365–4379.

Moynier F., Dauphas N., and Podosek F. A. 2009. A search for 70Zn anomalies in meteorites. *The Astrophysical Journal* 700:L92–L95.

Moynier F., Agranier A., Hezel D. C., and Bouvier A. 2010a. Sr stable isotope composition of Earth, the Moon, Mars, Vesta, and meteorites. *Earth and Planetary Science Letters* 300:359–366.

Moynier F., Beck P., Yin Q., Ferroir T., Barrat J. A., Paniello R. C., Telouk P., and Gillet P. 2010b. Volatilization induced by impacts recorded in Zn isotope composition of ureilites. *Chemical Geology* 276:374–379.

Moynier F., Koeberl C., Beck P., Jourdan F., and Telouk P. 2010c. Isotopic fractionation of Cu in tektites. *Geochimica et Cosmochimica Acta* 74:799–807.

Poitrasson F., Halliday A. N., Lee D.-C., Levasseur S., and Teutsch N. 2004. Iron isotope differences between Earth, Moon, Mars and Vesta as possible records of contrasted accretion mechanisms. *Earth and Planetary Science Letters* 223:253–266.

Qin L., Alexander C. M. O., Carlson R. W., and Horan M. F. 2008. Chromium nucleosynthetic anomalies in bulk and components of chondrites. *Geochimica et Cosmochimica Acta* 72:A769.

Rambaldi E. R., Cendales M., and Thacker R. 1978. Trace element distribution between magnetic and non-magnetic portions of ordinary chondrites. *Earth and Planetary Science Letters* 40:175–186.

Regelous M., Elliott T., and Coath C. D. 2008. Nickel isotope heterogeneity in the early solar system. *Earth and Planetary Science Letters* 272:330–338.

Rouxel O. D., Fouquet Y., and Ludden J. N. 2004. Copper isotope systematics of the Lucky Strike, Rainbow, and Logatchev hydrothermal fields on the Mid-Atlantic Ridge. *Economic Geology* 99:585–600.

Scott E. and Wasson J. T. 1976. Chemical classification of iron meteorites-VIII Groups IC, IIE, IIIF and 97 other irons. *Geochimica et Cosmochimica Acta* 40:103–115.

Scott E. R. D., Wasson J. T., and Buchwald V. F. 1973. Chemical classification of iron meteorites. 7. Reinvestigation of irons with Ge concentrations between 25 and 80 ppm. *Geochimica et Cosmochimica Acta* 37:1957–1983.

Sugiurai N., Ikeda Y., Zashu S., and Wasson J. T. 2000. Nitrogen-isotopic compositions of IIIE iron meteorites. *Meteoritics & Planetary Science* 35:749–756.

Sutton S. R., Delaney J. S., Smith J. V., and Prinz M. 1987. Copper and Nickel partitioning in iron-meteorites. *Geochimica et Cosmochimica Acta* 51:2653–2662.

Trinquier A., Birck J.-L., and Allègre C. J. 2007. Widespread 54Cr heterogeneity in the inner solar system. *The Astrophysical Journal* 655:1179–1185.

Trinquier A., Elliott T., Ulfbeck D., Coath C., Krot A. N., and Bizzarro M. 2009. Origin of nucleosynthetic isotope heterogeneity in the solar protoplanetary disk. *Science* 324:374–376.

Walker R. J., McDonough W. F., Honesto J., Chabot N. L., McCoy T., Ash R. D., and Bellucci J. J. 2008. Modeling fractional crystalisation of group IVB iron meteorites. *Geochimica et Cosmochimica Acta* 72:2198–2216.

Wasson J. T. and Huber H. 2006. Compositional trends among IID irons; their possible formation from the P-rich lower magma in a two-layer core. *Geochimica et Cosmochimica Acta* 70:6153–6167.

Wasson J. T. and Kallemeyn G. W. 2002. the IAB iron-meteorite complex: A group, five subgroups, numerous grouplets, closely related, mainly formed by crystal segregation in rapidly cooling melts. *Geochimica et Cosmochimica Acta* 66:2445–2473.

Wasson J. T. and Richardson J. W. 2001. Fractionation trends among IVA iron meteorites: Contrasts with IIIAB trends. *Geochimica et Cosmochimica Acta* 65:951–970.

Wasson J. T. and Wang J. M. 1986. A non magmatic origin of group-IIE iron-meteorites. *Geochimica et Cosmochimica Acta* 50:725–732.

Wasson J. T., Willis J., Wai C. M., and Kracher A. 1980. Origin of iron meteorite groups IAB and IIICD. *Zeitschrift für Naturforschung* 35a:781–795.

Wasson J. T., Choi B. G., Jerde E. A., and Ulff-Moller F. 1998. Chemical classification of iron meteorites: XII. New members of the magmatic groups. *Geochimica et Cosmochimica Acta* 62:715–724.

Wasson J. T., Huber H., and Malvin D. J. 2007. Formation of IIAB iron meteorites. *Geochimica et Cosmochimica Acta* 71:760–781.

Weinstein C., Moynier F., Wang K., Paniello R., Foriel J., Catalano J., and Foriel J. 2011. Cu isotopic fractionation in plants. *Chemical Geology* 22:266–271.

Williams H. M. and Archer C. 2011. Copper stable isotopes as tracers of metal-sulphide segregation and fractional crystallisation processes on iron meteorite parent bodies. *Geochimica et Cosmochimica Acta* 75:3166–3178.

Williams H. M., Markowski A., Quitte G., Halliday A. N., Teutsch N., and Levasseur S. 2006. Fe isotope fractionation in iron meteorites: New insights into metal-sulphide segregation and planetary accretion. *Earth and Planetary Science Letters* 250:486–500.

Wombacher F., Rehkämper M., Mezger K., Bischoff A., and Münker C. 2008. Cadmium stable isotope cosmochemistry. *Geochimica et Cosmochimica Acta* 72:646–667.

Zhu X. K., O'Nions R. K., Guo Y., Belshaw N. S., and Rickard D. 2000. Determination of Cu-isotope variation by plasma souce mass spectrometry: Implications for use as geochemical tracers. *Chemical Geology* 163:139–149.

Zhu X. K., Guo Y., O'Nions R. K., Young E. D., and Ash R. D. 2001. Iron isotope homogeneity in the early solar nebula. *Nature* 412:311–313.