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Coupled ^{63}Cu and ^{16}O excesses in chondritesJ. M. LUCK,¹ D. BEN OTHMAN,¹ J. A. BARRAT,² and F. ALBARÈDE^{3,*}¹G.T.S. CC 060, USTL, 34095 Montpellier, France²Laboratoire de Minéralogie, Université d'Angers, 49045 Angers, France³Ecole Normale Supérieure, 69007 Lyon, France

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Abstract—Recent developments in multiple-collector magnetic-sector ICP-MS (inductively coupled plasma-mass spectrometry) have permitted the relative abundances of the two isotopes 63 and 65 of copper to be measured with unprecedented precision (40 ppm). Here, we report Cu isotopic variations among eight carbonaceous chondrites (CCs) from the CI, CM, CO, and CV groups and the presently ungrouped Tagish Lake, and 10 ordinary chondrites (OCs) from the H, L, and LL groups. The widest isotopic range of $\sim 0.8\%$ per a.m.u. is observed for the carbonaceous chondrites. Copper in carbonaceous chondrites becomes isotopically lighter with petrologic type in the order 1 to 3 but seems extremely homogeneous for each type. The Cu isotopic composition of Tagish Lake confirms its other characteristics that are intermediate between CI and CM. In three of the groups (CI-CM-CO), as well as for Tagish Lake, ^{63}Cu excess over terrestrial mantle abundances correlates well with ^{16}O excess. For all four groups, ^{63}Cu excess also correlates remarkably well with elemental refractory/volatile ratios (e.g., Ca/Mn). For ordinary chondrites, small differences exist between the H, L, and LL groups, with Cu becoming isotopically heavier in that order. Equilibrated and unequilibrated samples, however, exhibit the same Cu isotopic signature within each group. Although the range of Cu isotopic compositions in ordinary chondrites is smaller than in carbonaceous chondrites, ^{63}Cu excesses still correlate with ^{16}O excesses. The observed trends of isotopic variation seem incompatible with a single-stage fractionation process by either volatilization or low-temperature metamorphism. The correlations between ^{63}Cu excesses and ^{16}O excesses suggest the presence of at least two and perhaps three isotopically distinct Cu reservoirs in the early Solar System: (1) an Earth-like reservoir common to the CI and LL probably representing the main Cu stock of the inner Solar System, (2) a reservoir present in all carbonaceous chondrites, but most abundant in CV, with large ^{63}Cu and ^{16}O excesses (this reservoir is probably hosted in refractory material), and (3) possibly a third reservoir present in ordinary chondrites. The OC trend may also be explained as a mixture of the first two Cu reservoirs if its oxygen was first equilibrated with nebular gas. The coexistence of ^{63}Cu and ^{16}O excesses in the same component raises the issue of how volatile Cu was preserved in refractory material. A strong correlation between $^{63}\text{Cu}/^{65}\text{Cu}$ and Ni/Cu ratios suggests that ^{63}Cu excess may have originated as more refractory ^{63}Ni ($T_{1/2} = 100$ yr) upon irradiation of refractory grains by electromagnetic flares and particle bursts during the T-Tauri phase of the Sun. *Copyright © 2003 Elsevier Science Ltd*

1. INTRODUCTION

Recent advances in multiple-collection inductively coupled plasma mass spectrometry (MC-ICP-MS) have opened up the field of stable isotope geochemistry of elements such as Cu, Zn (Maréchal et al., 1999, 2000; Zhu et al., 2000), Fe (Anbar et al., 2000; Zhu et al., 2001), Mg (Galy et al., 2000) and Ge (Hirata, 1997). A distinct additional advantage of this technique over TIMS or SIMS is an excellent control of the analytical mass bias, which makes it possible to determine the stable isotope abundances with a precision better than 0.1%. This excellent precision is obtained even for elements that possess only two isotopes and for which double-spike techniques therefore cannot be employed.

Mass-dependent isotopic fractionation in nature may be the result of temperature, coordination, or kinetic effects. For any given element, an essential piece of information is whether the material that formed the primordial Solar System was isotopically homogeneous. Oxygen isotopes for most terrestrial and

lunar samples (Clayton, 1993; Clayton et al., 1977), Fe (Zhu et al., 2001), and Zn isotopes (Luck et al., 2000) for all the planetary bodies studied so far meet this requirement. Oxygen isotopes in meteorites show both mass-independent and mass-dependent fractionation effects: The former may reflect interaction of refractory minerals with liquid water in the parent bodies (Clayton and Mayeda, 1984, 1999), whereas the latter may be accounted for by volatilization upon collisions of planetary objects, metal-silicate fractionation, or metamorphic and low-temperature processes, such as reaction of hydrous fluids with rocks within meteorite parent bodies. Mass-independent isotopic variations may also reflect the presence of presolar or circumsolar material inefficiently mixed in the Solar Nebula such as observed for the refractory inclusions of Allende and some ordinary chondrites (Clayton et al., 1977). A different interpretation holds that these mass-independent variations indicate kinetic effects during reactions in the gaseous state between components with particular symmetry properties (Thiemens, 1996, 1999).

The present report evaluates the extent of Cu isotopic variability in meteorites using the newly developed technique of MC-ICP-MS (Maréchal et al., 1999; Anbar et al., 2000; Zhu et

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al., 2000). Copper is a transition element with three oxidation states (0, I, and II) and is both chalcophile and siderophile. In meteorites, it enters FeNi metal (60%) and sulfides (20–25%) and forms tiny metallic Cu nuggets (4–5%) (Rubin, 1994). To a limited extent, it also enters silicates (olivine, pyroxene). Copper is considered a moderately volatile element with a condensation temperature of ~1050 to 1100 K (Wasson, 1985; Palme et al., 1988; Cassen, 1996). We focus here on samples from two main meteorite groups, carbonaceous (CC) and ordinary (OC) chondrites, and describe an unexpected correlation between their O and Cu isotopic properties.

2. SAMPLES AND EXPERIMENTAL

Most samples were obtained by courtesy of the Muséum National d'Histoire Naturelle in Paris and the Museum of Copenhagen (courtesy J. Blichert-Toft) as small cm/mm-sized chunks free of fusion crust. Mike Zolensky provided the Tagish Lake chondrite (carbonate-poor lithology). The samples Orgueil (CI), Murchison and Cold Bokkeveld (CM2), Lancé and Ornans (CO3), and Allende and Efremovka (CV3) correspond to the four main groups of carbonaceous chondrites and account for a substantial part of the major and trace element and oxygen isotope variability in the inner Solar System. Tagish Lake is a carbonaceous chondrite considered to be intermediate between CI and CM (Brown et al., 2000). We also analyzed whole-rock samples of ordinary chondrites with different degrees of metamorphic equilibration from the H, L, and LL groups.

Chunks were leached for 1 min in 0.2 N HCl and then gently ground in a boron-carbide mortar before dissolution in HF/HNO₃ in PFA containers at 150°C for several days. Cu was first separated from Zn on Biorad AG1X4 ion exchange resin in HBr and was further purified on AGMP1 using 7N HCl following Maréchal et al. (1999). Because ion-exchange resins fractionate Cu isotopes (Maréchal et al., 1999), the full yield requested for the elution was routinely tested. For the entire separation procedure, this yield, checked on both standard solutions and rock samples by quadrupole ICP-MS analysis of all column fractions, was > 99.7%. Duplicate and triplicate analyses involving both the chemical isolation and mass spectrometry analysis of different aliquots of a sample solution established the external reproducibility of the method. Replicates from a same solution were found to be in excellent agreement (Table 1). All reagents were subboiled in PFA bottleneck systems. Total blanks are ~1 ng and represent 0.1 to 0.3% of the amount of element analyzed.

Mass spectrometry techniques are described in Maréchal et al. (1999). Good precision is achieved through correction for mass fractionation by adding an in-house stock Zn solution to the sample and using an exponential law of mass discrimination. Bracketing the sample with a standard solution every third sample further narrows down precision on isotopic ratios. As for light elements, variations are expressed as relative deviations from the standard in δ units (‰; $\delta^{65}\text{Cu}$ for $^{65}\text{Cu}/^{63}\text{Cu}$) with respect to NIST 976 (Shields et al., 1964) for which a $^{65}\text{Cu}/^{63}\text{Cu}$ ratio of 2.244 is assumed. The precision on a typical analysis (200 ratios) of the $^{65}\text{Cu}/^{63}\text{Cu}$ ratio for a ~500-ng sample is $\pm 0.02\%$ (2σ). The external reproducibility obtained through replicate measurements of the same sample in different

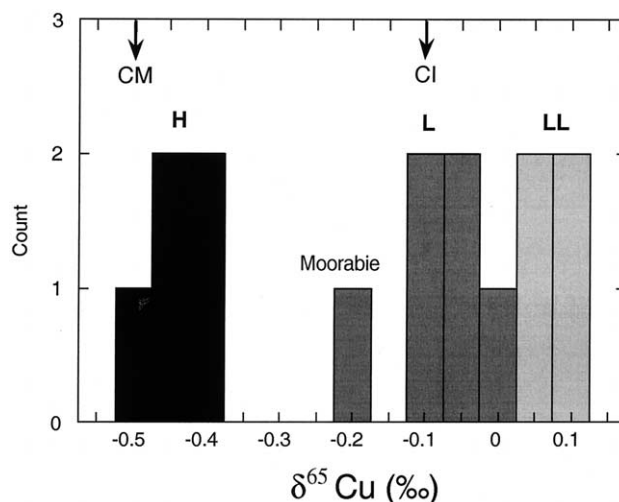


Fig. 1. Histogram of $\delta^{65}\text{Cu}$ for groups of ordinary chondrites (all duplicates are shown). The particular value for Moorabie, an extremely reduced and marginal L-chondrite is indicated. Also highlighted are mean values for CI and CM carbonaceous chondrites.

sessions is about $\pm 0.02\%$. An overall precision of $\pm 0.04\%$ holds for the mass-fractionation corrected ratios. The isotopic composition of blanks cannot be adequately measured because of too small signals. The effect of blank compositions on the data may be estimated through a simple calculation: Contamination of the sample with 0.3% blank, for which an extreme $\delta^{65}\text{Cu}$ of +6‰ (Maréchal, 1998) is assumed, would shift sample compositions by a barely detectable +0.02‰.

3. RESULTS

The data for whole-rock carbonaceous and ordinary chondrites are presented in Table 1. The overall range in isotopic compositions is ~0.8‰ per a.m.u., i.e., ~1.6‰ on $\delta^{65}\text{Cu}$, which compares with 0.7‰ per a.m.u. for Fe (Zhu et al., 2001) for the same sort of material. The range of $\delta^{65}\text{Cu}$ in meteorites is smaller than that reported for terrestrial samples ($\approx 10\%$) (Maréchal, 1998). Most of the $\delta^{65}\text{Cu}$ values are negative with LL ordinary chondrites being consistently slightly positive. The range of $\delta^{65}\text{Cu}$ is smaller for ordinary (+0.1 to -0.5‰) than for carbonaceous chondrites (-0.1 to -1.5‰). Cu becomes heavier in the order CV ($\delta^{65}\text{Cu} = -1.45\%$), CO (-0.86‰), CM (-0.50‰), Tagish Lake (-0.25‰), and CI (-0.09‰) for the CC, and in the order H, L, and LL for the OC. For carbonaceous chondrites, the $\delta^{65}\text{Cu}$ values increase with degree of low-temperature metamorphism, from petrologic grade 3 to 1. As expected from the petrologic description (Brown et al., 2000), the value for Tagish Lake is intermediate between those of CI and CM. The $\delta^{65}\text{Cu}$ values are remarkably consistent within each meteorite group, even in the CV3 group for the more reduced Efremovka and the more oxidized Allende. For ordinary chondrites, a histogram (Fig. 1) shows two main modes with the H chondrites plotting significantly apart (ca. -0.44‰) from the L-LL groups (ca. -0.08 and +0.08‰, respectively). This distribution is reminiscent of the oxygen isotope patterns in meteorites (Clayton, 1993). The values do not seem to vary as a function of whether samples are falls or

Table 1. Cu isotopic compositions in meteorites (whole rocks) expressed as $\delta^{65}\text{Cu}$ (relative variation, in permil, of $^{65}\text{Cu}/^{63}\text{Cu}$ from the NIST 976 standard). Quoted uncertainty is the two-sigma in-run error, expressed in $\delta^{65}\text{Cu}$ unit. Literature Cu concentrations are from Wasson et al. (1993) for CC and OC, and Brown et al. (2000) for Tagish Lake.

Carbonaceous chondrites	group & petr. Type	1	$\delta^{65}\text{Cu}^2$	$2\sigma_n$ run (%)	Cu (ppm) (this work)	Cu (ppm) (literature)
Orgueil (aliquot 1)	CI1	Fall	-0.09	0.02	108	121
Orgueil (aliquot 2)	CI1	Fall	-0.03	0.02		
Orgueil (aliquot 3)	CI1	Fall	-0.14	0.03		
Tagish Lake (C-poor)	?	Fall	-0.25	0.03	116	116
Murchison	CM2	Fall	-0.52	0.01	111	115
Cold Bokkeveld	CM2	Fall	-0.48	0.05	118	115
Lancé (aliquot 1)	CO3	Fall	-0.84	0.02	116	125
Lancé (aliquot 2)	CO3	Fall	-0.88	0.01		
Ornans (aliquot 1)	CO3	Fall	-0.89	0.02	121	125
Ornans (aliquot 2)	CO3	Fall	-0.82	0.02		
Allende (aliquot 1)	CV3	Fall	-1.40	0.03	99	100
Allende (aliquot 2)	CV3	Fall	-1.45	0.01		
Allende (aliquot 3)	CV3	Fall	-1.51	0.02		
Allende (aliquot 4)	CV3	Fall	-1.47	0.01		
Efremovka	CV3	Find	-1.44	0.04		100

Ordinary chondrites	group & petr. Type		$\delta^{65}\text{Cu}$	$2\sigma_n$ run (%)	Cu (ppm) (this work)	Cu (ppm) (literature)	
Brownfield	H3.7	Find	UOC	-0.51	0.03	85	82
Charsonville (aliquot 1)	H6	Fall	EOC	-0.41	0.02	83	82
Charsonville (aliquot 2)	H6	Fall	EOC	-0.47	0.03		
Kernouvé (aliquot 1)	H6	Fall	EOC	-0.42	0.03	73	82
Kernouvé (aliquot 2)	H6	Fall	EOC	-0.46	0.03		
Kernouvé 1 (unleached)	H6	Fall	EOC	-0.35	0.02		
Moorabie	L3	Find	UOC	-0.18	0.02		90
Julesburg	L3.6	Find	UOC	0.01	0.01	74	90
Khohar (aliquot 1)	L3.6	Fall	UOC	-0.09	0.02		90
Khohar (aliquot 2)	L3.6	Fall	UOC	-0.07	0.02		90
Bjurböle	L/LL4	Fall	EOC	-0.11	0.02	109	90
Mocs	L6	Fall	EOC	-0.03	0.02	73	90
KrymKa (aliquot 1)	LL3.1	Fall	UOC	0.10	0.01		80
KrymKa (aliquot 2)	LL3.1	Fall	UOC	0.10	0.02		80
St Séverin (aliquot 1)	LL6	Fall	EOC	0.04	0.02		80
St Séverin (aliquot 2)	LL6	Fall	EOC	0.06	0.02		80

¹ UOC: Unequilibrated ordinary chondrites. EOC: Equilibrated ordinary chondrites.

² Calculated with respect to $^{65}\text{Cu}/^{63}\text{Cu}$ ratio = 2.244 in NIST 976.

finds (Table 1). One meteorite, Moorabie, considered to be intermediate between groups, also displays an intermediate Cu isotopic composition. Moorabie is an extremely reduced L and only marginally in the L group for a variety of parameters such as the forsterite content, oxygen isotopes, and volatile element contents (Clayton et al., 1991; Wasson et al., 1993) and has the lowest $\delta^{65}\text{Cu}$ at -0.18% . The value for our Bjurböle sample, sometimes classified as L-LL, fits best within the L group.

For carbonaceous chondrites, $\delta^{65}\text{Cu}$ shows an excellent ($R \sim 0.99$) negative correlation with Al/Mn and Ca/Mn ratios, with these ratios increasing in the order CI-Tagish Lake-CM-CO-CV (Fig. 2). The ordinary chondrite samples plot on the same trend but with little dispersion around CI. As most of the copper in OC is in the metal phase, Cu isotopes suggest the derivation of the metal of OC from a CI-like parent body (e.g., Kong and Ebihara, 1997). Although $\delta^{65}\text{Cu}$ varies smoothly with $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ for both CC and OC, the most remarkable correlation is with $\Delta^{17}\text{O}$, a parameter that represents the departure of $\delta^{17}\text{O}$ from the terrestrial fractionation line at the same value of $\delta^{18}\text{O}$. In a $\delta^{65}\text{Cu}$ vs. $\Delta^{17}\text{O}$ plot (Fig. 3), carbonaceous

chondrites on the one hand, and ordinary chondrites on the other, form two distinct correlations.

4. DISCUSSION

In the present section, we will consider the possible origins for the Cu isotopic variations in chondrites. We will first consider simple phase equilibrium processes such as silicate-vapor fractionation and fluid-rock interaction. We will subsequently suggest that Cu and O components with distinct isotopic signatures coexist in chondrites and consider which nucleosynthetic processes may account for their existence.

4.1. Silicate-Vapor Fractionation

The correlation between $\delta^{65}\text{Cu}$ and $\Delta^{17}\text{O}$, a parameter that cannot be changed by mass-dependent fractionation effects such as phase change, precludes simple thermodynamic fractionation between the gas from the solar nebula and condensed materials (metal, silicates). In addition, it is expected that, as for other stable isotopes, the lighter ^{63}Cu should be more

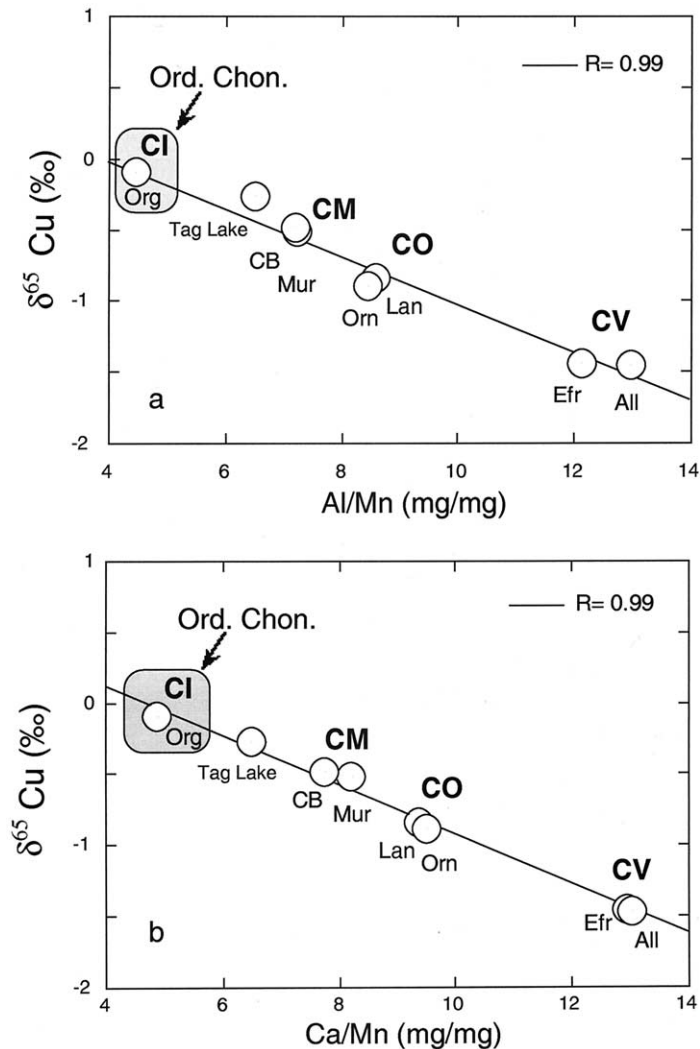


Fig. 2. Correlation between $\delta^{65}\text{Cu}$ and the Al/Mn (top) and Ca/Mn (bottom) ratios. (Sources of major element data: Kallemeyn and Wasson, 1981; Kallemeyn et al., 1989; Jarosewich, 1990; Wasson et al., 1993; Brown et al., 2000.) Al and Ca being more refractory than Mn, volatilization would be expected to deplete both Mn and the lighter ^{63}Cu and, therefore, to produce a positive correlation. The error bar ($\pm 0.04\%$) on $\delta^{65}\text{Cu}$ is smaller than the size of the symbols in all figures. Abbreviations: Org (Orgueil), Tag Lake (Tagish Lake), CB (Cold Bokkeveld), Mur (Murchison), Lan (Lancé), Orn (Ornans), All (Allende), Efr (Efremovka).

volatile than the heavier ^{65}Cu (e.g., Criss, 1999). The order of $\delta^{65}\text{Cu}$ values observed in carbonaceous chondrites do not conform to the order of element volatility (Kallemeyn and Wasson, 1981; Wasson, 1985; Larimer, 1988): If it did, Cu in the volatile element-depleted CV meteorites should be isotopically heavier than in the volatile-rich CM and CI. This is particularly well illustrated with the relative behavior of Mn, an element of moderate volatility similar to that of Cu, and two refractory elements, Al and Ca. Mn is slightly less volatile than Cu (1150–1200 K vs. 1050–1100 K condensation temperatures) but more volatile than both Al and Ca. The negative correlation (Fig. 2) between $\delta^{65}\text{Cu}$ and the Al/Mn and Ca/Mn ratios strongly argues against isotopic fractionation at high temperature (Humayun and Clayton, 1995). Volatilization is expected to leave a solid residue enriched in the heavy isotope. Isotopic enrichment can be either enhanced by Rayleigh distillation or

weakened if the solid material back-reacts with the vapor phase. Only in extreme situations could solid-gas back-reaction produce a solid phase enriched in the light ^{63}Cu isotope. A conservative interpretation of the present Cu isotopic data is mixing between two types of reservoirs, a volatile-rich (CI) reservoir with the highest $\delta^{65}\text{Cu}$ and a volatile-poor (CV) reservoir with the lowest $\delta^{65}\text{Cu}$.

4.2. Mixing between Multiple Sources of Cu

Clayton and his co-workers (e.g., Clayton and Mayeda, 1999) showed that the oxygen isotopic compositions of carbonaceous chondrites may be accounted for by interaction between two primordial oxygen reservoirs, ^{16}O -rich refractory silicates and a high- $\delta^{18}\text{O}$ gas. This interaction was followed by hydrous reactions at low temperature (0–25°C) within the

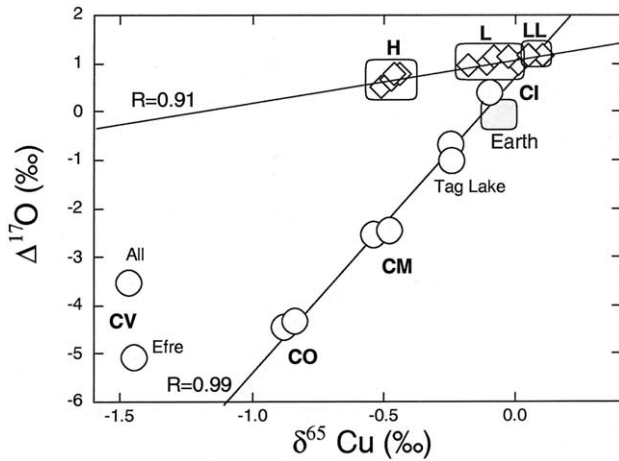


Fig. 3. Correlation between $\delta^{65}\text{Cu}$ and $\Delta^{17}\text{O}$ for carbonaceous chondrites (open circles) and ordinary chondrites (open diamonds). The oxygen data are from Clayton and Mayeda (1999) and Clayton et al. (1991) and the two different oxygen isotopic compositions of Tagish Lake (Brown et al., 2000) are shown. The domain labeled Earth refers to Cu data on basalts (Maréchal, 1998; Luck et al., 1999) and $\Delta^{17}\text{O} = 0$ is assumed (see Franchi et al., 1999). Mixing curves in these diagrams are not straight lines, but the range of Cu/O ratios in chondrites remains small enough ($<$ factor of 2) to use a linear approximation. We consider that the present diagram supports the presence of three components: an Earth-like component (next to LL and CI), a refractory component in the lower left corner, and an additional component falling to the left on the ordinary chondrite correlation that may represent the reaction of the second component with Solar Nebula gas. Note that, in this model, the CV have been severely affected by this reaction.

meteorite parent bodies, which account in multi-isotopic plots for the internal arrays with a slope of ~ 0.5 controlled by mass-dependent isotopic fractionation.

The parameter $\Delta^{17}\text{O}$ is essentially a measure of the ^{16}O excess. Likewise, $\delta^{65}\text{Cu}$ is a measure of the ^{63}Cu excess with respect to a terrestrial reference represented, for instance, by basalts from Réunion Island, with $\delta^{65}\text{Cu} = -0.03\text{‰}$ (Maréchal, 1998), and from Iceland, with $\delta^{65}\text{Cu} = -0.10\text{‰}$ (Ben Othman et al., 2001). The excellent correlation (Fig. 3) observed between $\Delta^{17}\text{O}$ and the $\delta^{65}\text{Cu}$ of CO-CM-Tagish Lake-CI carbonaceous chondrites on the one hand and of ordinary chondrites on the other can be understood by concluding that Cu in the Solar System was derived from genetically unrelated sources. Mixing curves in this diagram are not straight lines, but the relatively narrow range of variation of the Cu/O ratio (less than a factor of 2; Wasson and Kallemeyn, 1988) among chondrites makes the linear approximation reasonable. A simple account of the $\Delta^{17}\text{O}$ vs. $\delta^{65}\text{Cu}$ linear relationships involves three components (Fig. 4):

1. A first component, referred to as MC (main component), whose Cu and O isotopic signatures lie at the intersection of the CO-CM-Tagish Lake-CI trend and of the ordinary chondrite trend. The isotopic values of this component are close to those of LL and CI chondrites ($\Delta^{17}\text{O} \approx 0-1\text{‰}$, $\delta^{65}\text{Cu} \approx 0\text{‰}$) and to the values of terrestrial basalts.
2. A second component with $\Delta^{17}\text{O} \leq -9\text{‰}$ and $\delta^{65}\text{Cu} \leq -1.5\text{‰}$, referred to as RC (refractory component), whose mixing with MC may account for the CO-CM-Tagish

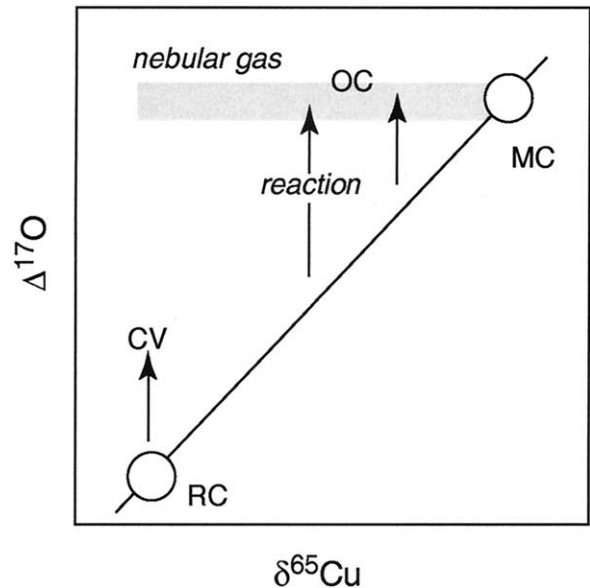


Fig. 4. Possible origin of the $\delta^{65}\text{Cu}$ and $\Delta^{17}\text{O}$ relationships among chondrites in a two-component system. Mixing of the main component (MC) with the refractory component (RC) is followed by reaction with nebular gas oxygen (shaded pattern).

Lake-CI trend. The maximum values for the RC component correspond (Fig. 3) to the intercept of the CI-CM-CO trend with a vertical line passing through the CVs. Such low isotopic values have been observed for oxygen in refractory materials from CVs, and leaching experiments on Allende (unpubl. data from the authors).

3. A third, oxygen-rich component, referred to as SNG (solar nebula gas) has a higher $\Delta^{17}\text{O}$ and interacted with the RC component to give rise eventually to both the CVs (more so for Allende than for Efremovka) and to the second endmember of the ordinary chondrite trend. As in Clayton's original model, this ^{16}O -depleted component, most likely Cu-poor as expected for a vapor, may simply correspond to the ambient gas of the Solar Nebula. In this model, the Cu isotopic heterogeneities predated the mixing events and the low-temperature metamorphism on the chondrite parent bodies did not change $\delta^{65}\text{Cu}$ significantly (see below). Alternatively, one may simply envisage that OC parent material, after mixing between RC and MC, further interacted with nebular oxygen gas, thereby increasing its $\Delta^{17}\text{O}$ with no change in $\delta^{65}\text{Cu}$, since Cu is not highly volatile and hence not abundant in the gas phase.

It remains in principle possible to restrict the number of components to two: the main component (MC) and the refractory component (RC). Copper evaporation from RC-MC mixtures with preferential loss of ^{63}Cu is unlikely because the most refractory samples, CV and ordinary chondrites, are enriched and not depleted in ^{63}Cu . In contrast, exchange of the oxygen from such mixtures with nebular gas oxygen to produce CV and ordinary chondrites is an acceptable alternative (Fig. 4).

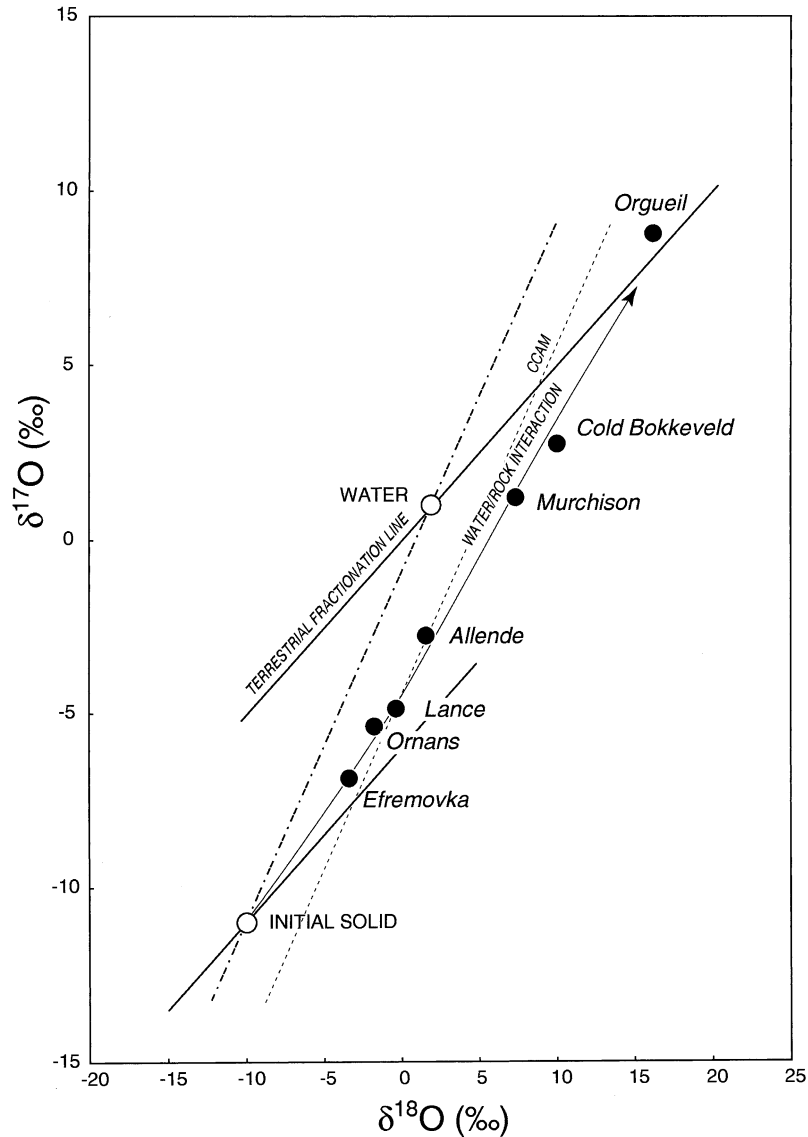


Fig. 5. Open-system water-rock interaction between an aqueous fluid with an initial isotopic composition represented by the open circle and an initial Allende CAI-like solid. The dashed line is the CCAM (carbonaceous chondrite anhydrous minerals) reference line (Clayton, 1993). The dot-dashed line with a slope of 1 goes through the extreme composition of the CAI inclusion analyzed by Young and Russell (1998) and, for the sake of illustration, is used as the unaltered initial solid. Although the present calculation does not capture all the complexities of the model presented by these authors, it does reproduce the oxygen isotope patterns of the carbonaceous chondrites. In contrast, this model does not explain the correlated O and Cu isotopic properties.

4.3. Interaction with an Exotic Aqueous Fluid

Young et al. (1999) proposed an alternative model based on variable amounts of hydrous fluids percolating through the parent bodies of the various carbonaceous chondrites. This mechanism combines in a single stage mixing between sources that are not related through mass-dependent fractionation and aqueous alteration. The oxygen isotopic composition of the initial material is chosen at the intersection of the $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$ trends of altered and unaltered refractory inclusions in the Allende chondrite. The amount of water having percolated through the surface (Q = water/rock ratio) increases in the order CO-CM-Tagish Lake-CI, as does the extent of alteration.

In this model, the CIs represent the end product of the alteration process. A simpler model, but essentially similar to that of Young et al. (1999), has been reproduced in Figure 5 using the open-system exchange equations of Taylor (1978) (see also equations in Albarède, 1995, pp. 48–49) for a fluid percolating through a porous rock. Refractory material such as that found in a particular CAI, considered by Young et al. (1999) as representing unaltered starting material ($\delta^{18}\text{O} = -10\text{‰}$, $\delta^{17}\text{O} = -11\text{‰}$), interacts with an isotopically unrelated aqueous fluid ($\delta^{18}\text{O} = 2.0\text{‰}$, $\delta^{17}\text{O} = 1.0\text{‰}$), both lying on a line with a slope of 1. To represent the progressive heating of the percolating fluid, rock-water $\delta^{18}\text{O}$ fractionation is assumed to decrease with the water/rock ratio from a low-temperature

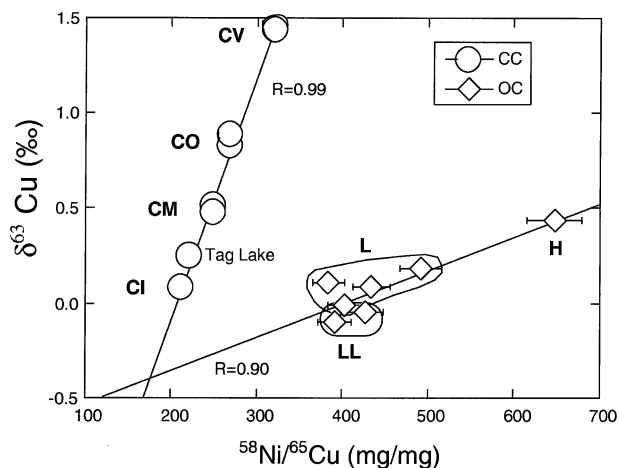


Fig. 6. Correlation between the $^{63}\text{Cu}/^{65}\text{Cu}$ ratio and $^{58}\text{Ni}/^{65}\text{Cu}$ ratios of chondrites. Because the small sample size would not make the Cu and Ni concentration analyses of an aliquot of the very same sample significant, the Ni and Cu contents were simply taken as their literature mean values (Wasson and Kallemeyn, 1988). For reasons presented in the “Results” section, the value for Moorabie was not included. This diagram supports mixing between components that differ by some amount of ^{63}Ni decay ($T_{1/2} = 100$ yr). The values of the $^{58}\text{Ni}/^{65}\text{Cu}$ ratios are those derived from the literature mean Ni/Cu ratios (Wasson and Kallemeyn, 1988). This plot suggests that the ^{63}Cu excess accompanying the ^{16}O excess in the refractory component may have actually originated as a more refractory ^{63}Ni anomaly.

value of 50‰ to a warmer-temperature value of 15‰. As found by Young et al. (1999), this type of model reproduces the oxygen isotope values of most carbonaceous chondrites (Fig. 5). We assume that, upon solid/liquid equilibration, heavy isotopes concentrate in the solid, which is a common observation for a number of other elements. Preferential leaching of the light ^{63}Cu isotope upon aqueous alteration should leave increasingly heavier Cu in the solid in the order CO-CM-Tagish Lake-CI. In this model, $\delta^{65}\text{Cu}$ should correlate with the increasing volatile content, i.e., with decreasing Ca/Mn and Al/Mn ratios (Fig. 2) and with $\Delta^{17}\text{O}$, just as observed for chondrites. Unfortunately, this model fails to explain three critical features:

1. The comparable $\Delta^{17}\text{O}$ of CI, L, and LL require that carbonaceous chondrites and ordinary chondrites should have very similar end points for the hydrous alteration processes. These meteorites should have reacted with similar proportions (same Q) of the same fluid, which seems unlikely.
2. Chondrites and the terrestrial mantle should have been formed from a material that happened to have been similarly altered: CI and two terrestrial basalts have similar $\Delta^{17}\text{O}$ and $\delta^{65}\text{Cu}$. Again, we consider that the O and Cu isotopic compositions of the terrestrial mantle, material clearly depleted in volatile elements, should be distinct from those of CI chondrites.
3. It seems unlikely that Cu isotopic fractionation of up to 1.5‰ can take place without significant loss of metal. The Cu contents of CI and CO are, however, up to 20% higher (Wasson and Kallemeyn, 1988) than the contents of the other groups, not lower. There is no indication, therefore, that Cu has been lost from CI and CO.

4.4. The Origin of the Refractory (RC) Cu Component

Copper nucleosynthesis has been reviewed with reference to its Solar System abundance by Matteucci et al. (1993). This element is produced by a combination of two nucleosynthetic processes: the “weak” s -process in massive stars and the explosive nucleosynthesis in Type-Ia supernova. Although a fraction of Cu may be produced in low-mass stars by the “main” s -processes, it is considered to be small. The negative correlation between $\Delta^{17}\text{O}$ and $\delta^{65}\text{Cu}$ may be viewed as a positive correlation between ^{16}O and ^{63}Cu excesses. The difficulty of explaining the present results is not so much the presence of isotopically anomalous Cu in the Solar System as it is the correlation between these excesses. It is broadly accepted that the ^{16}O excess is carried by CAIs (e.g., Clayton et al., 1977), and the correlation of Figure 3 strongly suggests that this should also be the case for the ^{63}Cu excess. Any interpretation, therefore, must account for the survival of significant proportions of the relatively volatile Cu under the extreme conditions prevailing during the formation of these unusual mineral assemblages.

Before we turn to possible explanations, let us first point out that one route to ^{63}Cu production is through the beta decay of ^{63}Ni , a nuclide with a 100-yr half-life. A plot (Fig. 6) of the $^{63}\text{Cu}/^{65}\text{Cu}$ ratio vs. $^{58}\text{Ni}/^{65}\text{Cu}$ (^{58}Ni is the most abundant isotope of Ni and is shielded from r -process input by ^{58}Fe) yields two good alignments that, were the half-life of the progenitor substantially longer, could be interpreted as an extinct radioactivity isochron. The correlation of the $^{63}\text{Cu}/^{65}\text{Cu}$ ratio with the Ni/Cu ratio does not simply reflect a binary mixing between a minor refractory component and the prevalent non-refractory composition of the Solar Nebula. When Ni is replaced by other siderophile elements such as Co and Ir, substantial scatter is observed with CV falling off any possible trend. With condensation temperature being some 350 K higher for Ni than for Cu (Wasson, 1985), we therefore suggest that excesses of the rather volatile ^{63}Cu originated as excesses of fairly refractory ^{63}Ni . The steeper slope of the CC alignment ($R = 0.98$) with respect to the OC alignment ($R = 0.93$) reflects different ^{63}Ni excesses in their refractory components. Because of the very short half-life of ^{63}Ni , however, we consider that the slope and intercept of these alignments have no simple significance and, in particular, should not be interpreted in terms of ages and production ratios.

In the following, we review the origins of the ^{63}Cu excess in the RC component.

4.4.1. Both the ^{63}Cu and ^{16}O excesses are presolar

There is no doubt that, if ^{63}Cu was produced by beta decay of ^{63}Ni , the progenitor must have been dead by the time this anomalous copper was incorporated into the meteorite. Variable ^{63}Cu excesses in meteorites may reflect variable contributions from the weak s -process and from statistical nuclear equilibrium (explosive nucleosynthesis or e -process) that, in particular, generates most Ni isotopes (e.g., Hainebach et al., 1974; Meyer, 1994). The weakness of this model is the persistence of an unknown but clearly significant concentration of volatile Cu in the refractory endmember.

4.4.2. Both the ^{63}Cu and ^{16}O excesses formed in the Solar System

Mass-independent fractionation processes in the nebular gas, possibly of kinetic origin, have been advocated to explain the ^{16}O excess in chondritic material. These processes probably result from the unusual symmetry properties of the species involved in the reaction (Thiemens, 1999). How these processes would generate excess ^{63}Cu remains unexplained.

Alternatively, we consider that during their early T-Tauri phase of gravitational collapse, young stellar objects (Shuh et al., 1997) produce highly energetic electromagnetic flares (x-rays, ultraviolet) and also protons and ^3He nuclei. Spallation reactions induced in the refractory inclusions by these particles when accelerated by the x-winds from the proto-Sun have been suggested to account for the production of several nuclides, including the short-lived ^{26}Al (Gounelle et al., 2001) and also major element fractionation (Hutchison, 2002). Self-shielding in the nebular cloud during irradiation by ultraviolet bursts has recently been revived as a plausible mechanism for producing mass-independent oxygen isotope fractionation (Clayton, 2002). Production of refractory ^{63}Ni upon irradiation of ^{16}O -rich refractory material by high-energy electromagnetic flares leaves enough time for isolated grains to cool down before ^{63}Ni decays into ^{63}Cu and therefore does not raise the problem of Cu volatility as for the presolar model. Re-injection of this material into the solar system away from the Sun and mixing with volatile-rich material (Shuh et al., 1997; Hutchison, 2002) could generate the observed correlations.

4.4.3. The ^{16}O excesses are presolar but ^{63}Ni excesses formed in the Solar System

In the inner Solar System, refractory material with trapped presolar ^{16}O is subjected to intense irradiation by energetic electromagnetic flares and particles. As in the previous case, irradiation generates refractory ^{63}Ni that rapidly decays into ^{63}Cu , but not before the temperature of refractory minerals cooled down below Cu condensation temperature.

5. CONCLUSIONS

Correlated excesses of ^{63}Cu and ^{16}O in carbonaceous and ordinary chondrites and the opposite relationship between $^{63}\text{Cu}/^{65}\text{Cu}$ and Al/Mn (or Ca/Mn) support the presence of isotopically distinct Cu components in the Solar System. At least one pre-solar or early solar Cu component seems to have existed that was 1.5‰ lighter than ordinary copper (i.e., CI-type). We suggest that the correlation between the ^{63}Cu and ^{16}O excesses cannot be explained by selective volatility or fluid/rock interaction within the chondrite parent bodies. The correlation between the $^{63}\text{Cu}/^{65}\text{Cu}$ and Ni/Cu ratios in chondrites may reflect that the very short-lived (100 yr) ^{63}Ni was the progenitor of excess ^{63}Cu . Presence of this excess may be related to irradiation of refractory material by the energetic radiations emitted by the nascent Sun.

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