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Natural variations detected in the isotopic composition of copper: possible applications to archaeology and geochemistry

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Abstract

Copper isotopic compositions have been measured both in natural copper minerals from supergene/oxidation zones and in some ancient metal artefacts using two different instruments. Measurements were first made using a low temperature thermal ionisation technique with a thermal ionisation mass spectrometer (TIMS); independent data was obtained using a commercial inductively coupled plasma (ICP) magnetic sector multiple collector mass spectrometer. Significant variations of isotopic composition were found in both types of material, suggesting that there may be considerable potential for copper isotope analyses in metal provenance studies, at the least as a supplement to lead isotope studies. For minerals, δ values ranging from -1.63 to $+7.71$ were obtained, whilst archaeological artefacts had δ values from $+0.22$ to $+4.32$. This study also made a preliminary examination which suggests that fractionation of the isotopic composition of copper does not occur during smelting and fire refining processes thought to have been used in ancient times. (Int J Mass Spectrom 184 (1999) 1–9) © 1999 Elsevier Science B.V.

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1. Introduction

This work was motivated by the possibility that natural variations in the isotopic composition of copper, if they exist, might be of use to archaeological science in providing a direct method to provenance copper in ancient artefacts, at the least as a supplement to the indirect method of lead isotope provenancing [1]. Walker et al. [2] had also made suggestions about the application of variations in the isotopic composition of copper to questions of ore genesis.

Significant variations in the isotopic composition of copper in natural minerals were first suggested by Walker et al. [2] in 1957. In 1965, Shields et al. [3] made a more extensive examination, having previously established the isotopic composition of a National Bureau of Statistics/National Institute of Standards and Technology (NBS/NIST) copper isotope standard, SRM 976, as 2.2440 ± 0.0021, calibrated against highly enriched copper isotopes [4]. In their work on copper minerals Shields et al. [3] did not use enriched copper isotopes but, using the TIMS procedure devised in their earlier work, they reported variations in the copper isotope ratio in some minerals, beyond the limit of their experimental error.

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No further work on the isotopic composition of copper seems to have been done for 30 years. This may be in part have been because of scepticism on the part of isotope geochemists about the reality of the claimed isotopic variations, and in part because of the considerable difficulty of obtaining reproducible data for the isotopic composition of copper using thermal ionisation mass spectrometers (TIMS). Shields et al. [3,4] obtained relatively precise ^{63}Cu/^{65}Cu data only by adhering to a very rigorous time/ion beam regime. They found that ratios 1 to 2% away from the correct value, thus, completely obscuring natural variations, easily resulted by simply overheating the filament or changing the time/signal relationship. It seemed apposite to investigate this subject again, using the higher precision of isotopic compositional data afforded by modern multicollector TIMS and the new inductively coupled plasma mass spectrometry (ICP-MS) instruments fitted with magnetic sector mass dispersion and multicollectors [5], together with recent critical evaluation of the corrections for mass discrimination necessary for both techniques [5,6]. Currently both TIMS and magnetic sector/multicollector ICP-MS can typically attain precisions for isotope ratio measurements at the level of 0.005 to 0.01% RSD (relative standard deviation) [5].

2. New investigations of the isotopic composition of copper using TIMS

Hosoe et al. [7] had developed in 1988 a new low temperature TIMS method for the determination of the isotopic composition of copper which yielded more precise measurements of the ratio ^{63}Cu/^{65}Cu than previous techniques. For the certified NBS/NIST SRM 976 copper isotopic standard Hosoe et al. [7] determined $^{63}\mathrm{Cu}/^{65}\mathrm{Cu} = 2.2448 \pm 0.0007$ (standard deviation, 1σ) as the average uncorrected value for eight measurements; this is to be compared with the certified value [4] of 2.2440 ± 0.0021 (95% confidence interval). Other methods developed to measure copper isotope ratios were reviewed by Hosoe et al. [7] but all have too low precision to investigate possible isotopic anomalies, though some are useful for isotope dilution concentration measurements of copper in various matrices. Platzner [8] gave summary data for copper isotope ratios of good run-to-run reproducibility ($\pm$0.06% at the 2σ level) using TIMS but gave absolutely no description of the method used. None of these investigations included examination of possible natural variations of the isotopic composition of copper.

3. Experimental methods in Oxford

The VG IsoLab thermal ionisation mass spectrometer installed in the Isotrace Laboratory was used to develop a method for the isotopic analysis of copper, based closely on the Japanese technique [7]. A two-filament, low-temperature, static double collector TIMS procedure for copper (loaded in nitrate form) was employed, which was found empirically considerably to increase the precision and reduce mass spectrometric fractionation. The Oxford technique used Cross zone refined rhenium flat ribbon filaments (H. Cross, Milwaukee, WI) (0.030×0.0012) for both the evaporation and ionisation filaments. The ribbon filaments were arranged parallel to each other, 0.75 mm apart. All rhenium filaments were prebaked at 5 A current in a vacuum of 10^{-8} Torr with 1 kV applied voltage. At the usual operating temperature such prebaked filaments were found, using an ion counting Daly detector, to give rise to no observable Cu ion currents above 10^{-17} A. 200 μg of $\mathrm{Cu(NO_3)_2}$ in solution was loaded solely on the evaporation filament, and dried down gently in about 5 min in air by passing a current of about 1.3 A through the filament. In the spectrometer a strictly controlled filament heating procedure was used, in which the current through the ionisation filament alone was increased linearly with time in three steps: first to 1 A in 4 min, then to 1.5 A in an additional 7 min, then to 1.8 A in an additional 5 min. This resulted in a final temperature of the ionising filament between 880 and 920 °C; no current was passed through the evaporating filament. After the 16 min warm-up procedure, automatic focussing and beam centering operations were made during a further 10 min before static data

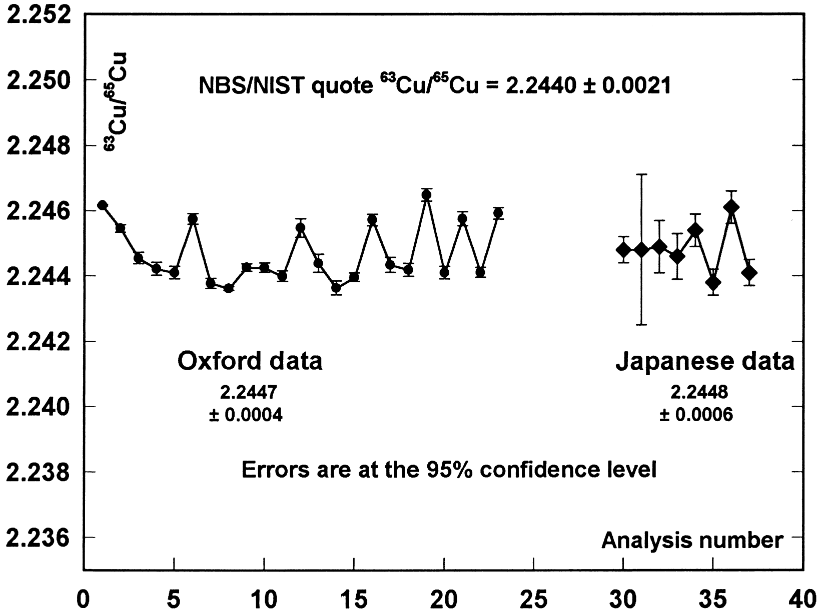

Fig. 1. Comparison of measurements of the isotopic composition of the SRM 976 copper isotope standard, using low temperature thermal ionisation mass spectrometry, in the Isotrace Laboratory Oxford and the Tokyo Institute of Technology.

taking began. This method resulted in very stable ^{63}Cu metal ion beams of from 2–5 pA. Static two-collector data gathering, in three blocks of 20 ratios each, with automatic beam focussing and centering between each block, took an additional 30 min. Hosoe et al. [7] commented that "the mechanism of ionisation at such a low temperature is not clear"; equally we have no certain explanation for it.

Prior to mass spectrometry, copper was separated from solutions of natural copper minerals by a combined anion exchange/electrodeposition technique. The major impurity, Fe, was removed by passing the solution in 8.5 M HCl through an ion exchange column of Dowex AG1 X8, 200–400 mesh, which retains the Fe whilst allowing Cu to pass through. Following conversion of copper to nitrate form, further purification was effected by cathodic electrodeposition onto a platinum electrode at 1.8 V in 0.01 M HNO_3. The yield of these combined procedures was found to be greater than 98%. Direct proof that this separation technique did not fractionate copper isotopes was obtained by passing samples of SRM 976, mixed with ultrapure iron in solution, through the procedure. The deviation from the ^{63}Cu/^{65}Cu ratios measured after separation from those measured with no chemical separation was always less than 0.03%.

4. Data for the SRM 976 copper isotopic standard

Using this special TIMS technique data for the NBS (NIST) copper, isotopic standard SRM 976 were obtained. Within a run, precision of better than ±0.004% standard error for a single sample analysis is relatively easy to obtain, but it is difficult to achieve good run-to-run reproducibility. For this reason, the approach taken throughout was to make many repeat analyses for each unknown sample, each involving a newly loaded sample on a new filament bead; the mean of such sets of data was taken. A total of 23 separate repeat measurements were made of the SRM 976 standard, over the period of 6 months occupied by measurements of minerals and archaeological artefacts. Fig. 1 compares, for SRM 976, this Oxford data

Table 1
Comparison of data for the isotopic composition of the NBS/NIST SRM 976 copper isotope standard, using different methods

Method	$^{63}Cu/^{65}Cu$	Standard deviation	Number of analyses
Low temperature TIMS	2.244 70	0.000 89	23
MC-ICP-MS	2.244 27	0.000 17	6
NBS/NIST certified value	2.24 40	±0.0021[a]	

[a] The error for the NBS/NIST data is an overall limit of error based on the sum of the 95% confidence limit for the mean and upper bounds for the effects of known sources of possible systematic error.

with that reported by Hosoe et al. [7]. The overall mean of the Oxford data is $^{63}Cu/^{65}Cu = 2.2447 \pm 0.0008$, where the error is the 95% confidence interval computed in the standard way, and no correction for instrumental fractionation has been applied. This value is in complete agreement with the NBS/NIST certified value of 2.2440 ± 0.0021, and is to be compared with the figure of 2.2448 ± 0.007 [1σ] obtained by Hosoe et al. [7]. The standard deviation of the 23 repeat Oxford analyses is 0.000 894.

5. Natural variations in the isotopic composition of copper

Using this low temperature TIMS technique, an investigation was made in 1995 into possible isotopic differences in a number of copper minerals. Minerals (azurite, cuprite, atacamite, and bornite) from the University Museum, Oxford, were chosen from mines from which Shields et al. [3] had claimed fairly large isotopic anomalies. The term "isotopic anomaly" is used in this article to describe copper isotopic compositions that are different from that of the NIST SRM 976 copper isotope standard.

Table 2 summarises the copper isotope data obtained using low temperature TIMS in Oxford for these minerals, comparing it with data reported by NBS in 1965 [3] for other samples of the same minerals from the same mines. In this table, a delta value (δ) is quoted which is defined, as is conventional in isotope geochemistry, as:

$$\delta = 1000 \times \left(\frac{63\mathrm{Cu}/65\mathrm{Cu}}{2.2440} - 1 \right)$$

and measures the departure of a measured copper isotope ratio from the certified value for the SRM 976 copper isotope standard.

It is clear that these data establish that there are natural variations of the isotopic composition of copper in at least some copper minerals. The data for the azurite and bornite samples are very similar to those measured earlier [3] for different samples of the same minerals from the same mines. This is not so for the cuprite from the Morenci mine, where the Oxford data shows an anomaly of $\delta = +2.41$ whereas the NBS [3] data gives $\delta = -3.6$. Nor is the agreement good for the atacamite samples, where the Oxford anomaly is $\delta = +7.71$ compared with $\delta = +1.6$ for the NBS [3] data for a different sample. There can always be some doubt about the true source localities of mineral samples from museum collections; the discrepancies between Oxford and NBS data may be due to this factor, or may indicate significant variations of copper isotope composition within some ore deposits.

Table 2
Comparison of copper isotope compositions obtained, using low temperature TIMS at the Isotrace Laboratory, Oxford and high temperature TIMS at the U.S. National Bureau of Standards (3), for copper minerals from various mines. The errors quoted are at the 95% confidence level; also is given the δ value expressing the departure from the certified $^{63}Cu/^{65}Cu$ ratio of 2.2440 ± 0.0021 for the SRM 976 copper isotope standard

Mineral	Mine	$^{63}Cu/^{65}Cu$ (Oxford)	δ	$^{63}Cu/^{65}Cu$ (NBS, 3)
Azurite	Chessy mine, France	2.240 33 ± 0.000 72	−1.63	2.2407
Bornite	Mufulira mine, Rhodesia	2.248 87 ± 0.000 74	+2.17	2.2513
Cuprite	Morenci mine, Arizona	2.249 40 ± 0.000 77	+2.41	2.2358
Atacamite	Atacama mine, Chile	2.261 30 ± 0.000 88	+7.71	2.2477

6. The use of MC-ICP-MS for copper isotope analyses: standard and minerals

Confirmation of substantial natural variations in the isotopic composition of copper opens up the possibility of a new field of isotope geochemistry. It also suggests that there may be a possibility that variations of the isotopic composition of copper might be useful for provenancing copper in ancient metal artefacts, at least as an additional tool to lead isotope analyses. This would depend on the copper isotope compositions of the ores passing unchanged into metal smelted from them to produce copper metal, or in subsequent operations such as the fire refining of copper. That changes in the ^{63}Cu/^{65}Cu ratio are easily produced by such a simple process as ion exchange electromigration has been shown by the work of Fujii et al. [9]. The work of Bamberger et al. [10] has shown that losses of copper metal can occur in the smelting of copper at a level that might allow accompanying fractionation of the isotopic composition of copper, a matter investigated later in this article.

TIMS is not an easy technique for the precise measurement of copper isotopic compositions. In contrast to the difficulty of thermally ionising copper, this element is easily ionised in a plasma, so that MC-ICP-MS [11] should in principle be applicable, a technique that has recently been developed by the firm VG Elemental [12–14]. MC-ICP-MS has a large but fixed bias which is claimed to be time independent and independent of the chemical properties of the element or admixing of other elements [13–15]. This allows mass fractionation to be corrected out, for Cu, in terms of the fixed isotopic ratio, ^{66}Zn/^{68}Zn, of additions of an in-house standard of Zn, in a way similar to the use of additions of Tl for the MC-ICP-MS measurement of the isotopic composition of Pb [11,12,15,16].

Preliminary isotopic composition measurements for copper were made with this technique using a P54 MC-ICP-MS instrument in 1997, first to verify the anomalies found by TIMS in 1995 for the copper isotope composition of copper minerals. All copper samples for MC-ICP-MS in solution were doped with a Johnson Matthey ultrapure zinc solution; the concentrations of the samples in the solution aspirated into the ICP source were about 4 ppm for both Cu and Zn. The isotopes ^{66}Zn, ^{68}Zn, ^{63}Cu, and ^{65}Cu were measured. ^{64}Zn was not used to avoid any possible isobaric interference from ^{64}Ni, though it was found for all samples studied that Ni was not present in significant amount. For each sample checks were also made for the presence of Ti, V, and Cr, in case these might cause oxide polyatomic interferences, but no significant amount of these elements was found in any sample. Analysis times of 10 min per sample were employed, measuring three blocks of 20 ratios each with 5 s integration times for each isotope, and measuring baselines at $\pm 0.5\ \mu$ at the beginning of each block. Because Luais et al. [17] refer to mass bias in MC-ICP-MS as being very dependent on the ion source conditions, we kept the ion source conditions constant, having first adjusted the source to achieve maximum ion beam. The mass bias was monitored for each analysis and shown to be quite constant throughout the 10 h of measurements, at $1.036\,90 \pm 0.000\,40$ (1σ).

Initially the NBS SRM 976 copper isotope standard was analysed. The ^{63}Cu/^{65}Cu ratio was measured and referenced to the NBS/NIST certified value of 2.2440. This allowed a mass bias figure to be computed, from which the measured ^{66}Zn/^{68}Zn ratio was exponentially corrected for mass bias to give a mean corrected value of ^{66}Zn/^{68}Zn $= 1.512\,680$ [1 standard deviation $= 0.000\,085$] for the internal laboratory zinc standard. This is significantly higher than the value of ^{66}Zn/^{68}Zn $= 1.484\,04$ reported by Rosman [18] as the average for terrestrial samples of zinc. It is presently uncertain whether this is because of natural variations in the isotopic composition of zinc (which were not observed in Rosman's work) or because of isotopic fractionation resulting from some of the procedures used by Johnson Matthey in purifying their ultrapure zinc sample. The mean value for ^{66}Zn/^{68}Zn in the internal laboratory standard, corrected as earlier, was then entered into the P54 computer analysis programme for the correction of mass bias, using an exponential correction rather than a power law, so that all further measurements of copper isotope ratios could be referred to it. This

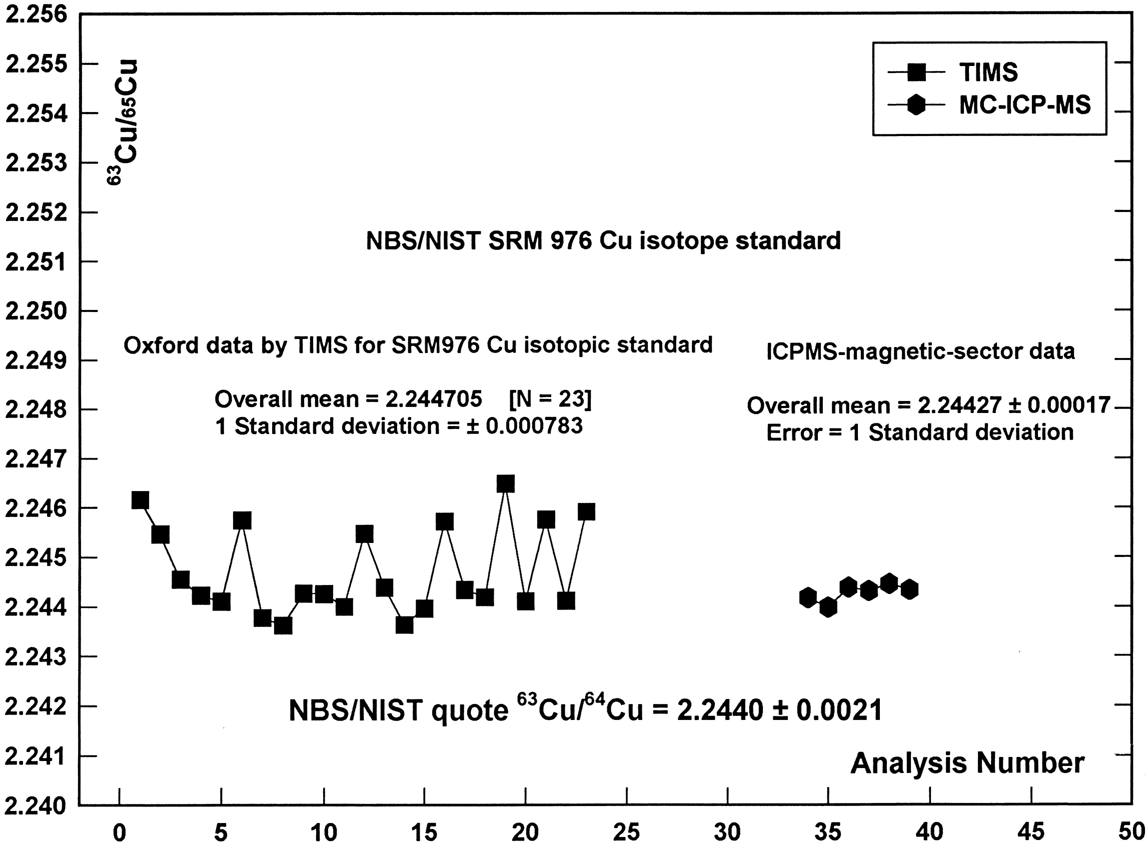

Fig. 2. Comparison of measurements of the isotopic composition of the SRM 976 copper isotope standard, using low temperature thermal ionisation mass spectrometry in the Isotrace Laboratory Oxford, and using ICP mass spectrometry with magnetic sector mass dispersion and multicollectors at VG Elemental, Cheshire.

procedure effectively references back to the SRM 976 standard all measurements of copper isotope ratios in unknown samples. It is accepted that the large mass fractionation introduced into MC-ICP-MS by jet separation associated with the exit orifice of the plume and first cone of the source is not yet well understood from the theoretical and numerical point of view. Moreover Heumann et al. [5] have demonstrated that, for a quadrupole ICP-MS instrument, the ^{63}Cu/^{65}Cu ratio is sensitively dependent on source potentials. Nevertheless we have demonstrated for the VG P-54 MC-ICP-MS instrument that, with source potentials held constant, mass bias is time independent over at least 10 h, yielding very precise ^{63}Cu/^{65}Cu data for repeated measurements of the SRM 976 standard.

In TIMS, and also occasionally in MC-ICP-MS [17], normalisation is accomplished by well proven mass bias corrections (linear, power law, exponential) using a “spike” of the *same* element. In MC-ICP-MS the practise has evolved of making such mass bias corrections on the basis of a purely empirical correction formula even when a “spike” of a different element has been introduced to make the corrections, as for example for Pb isotopes where added Tl is used for normalisation [11,12,15,16]. Some mass spectrometrists remain unconvinced of the applicability of instrumental fractionation correction laws, derived from the use of the same element for internal correction, to the case of “external” correction in MC-ICP-MS using a different element. However Hirata [11] made an empirical investigation of mass fractionation in MC-ICP-MS for the elements Rb, Sr, Ru, Nd,

Table 3
Comparison of copper isotope compositions obtained for copper minerals from various mines, using TIMS, and MC-ICP-MS with internal bias corrected in terms of $^{66}Zn/^{68}Zn = 1.512680$ for an internal laboratory Zn standard. The errors quoted for the TIMS data are at the 95% confidence level, whilst those for MC-ICP-MS are 1 standard deviation

Mineral	Mine	$^{63}Cu/^{65}Cu$ (TIMS, Oxford)	$^{63}Cu/^{65}Cu$ (MC-ICP-MS)
Azurite	Chessy mine, France	2.24033 ± 0.00072	2.24056; 0.00011
Atacamite	Atacama mine, Chile	2.26130 ± 0.00088	2.26296; 0.00015

Hf, Re, Os, Tl, and Pb, and a special investigation of the external correction of Pb isotope ratios using Tl. Hirata concluded that the mass discrimination factors observed using MC-ICP-MS are a linear function of mass, so that the correction factors obtained with Tl isotopes should first be corrected for mass and then applied to Pb isotopes [11]. Habfast (personal communication, 1998) has suggested that such uncertainties might be avoided by using an automatic sample changer to alternate analyses of an unknown copper sample with those of the SRM 976 standard, normalising directly to the latter. This suggestion came after the work for this article was concluded; consequently we effected fractionation corrections in terms of an added Zn sample, in a way parallel to the methods used by Halliday et al. [13,19], Walder et al. [15,16], and Hirata [11] for precise lead isotope measurements. Our chief purpose was to arrive at an MC-ICP-MS method which yields highly precise reproducibility rather than, necessarily, accuracy, because it is precise reproducibility that allows discovery of variations in the isotopic composition of copper.

Table 4
Comparison of copper isotope compositions obtained for the products of smelting and fire refining experiments carried out by J. Merkel. MC-ICP-MS was used for JM1, JM2, and JM3, with internal bias corrected in terms of $^{66}Zn/^{68}Zn = 1.512\,680$ for an internal laboratory Zn standard. Low temperature TIMS was used for JM6 and JM7. The copper metal of samples JM6 and JM7 was smelted from an ore sample from a different mine from that involved in JM1, JM2, and JM3

Sample No.	Product	$^{63}Cu/^{65}Cu$	Standard deviation
JM1	Malachite ore from Zaire	2.245 05	0.000 24
JM2	Copper metal smelted from the above ore	2.245 13	0.000 06
JM3	Copper metal in slag from the above smelt	2.245 19	0.000 09
JM6	Copper metal; product of one fire refining step	2.244 26	0.000 60
JM7	Copper metal, fire refined from JM6	2.244 56	0.000 92

Fig. 2 illustrates, by a comparison of data for the isotopic standard SRM 976, the improvement in reproducibility obtained by the use in this way of MC-ICP-MS rather than low temperature TIMS. Independent analyses were made by MC-ICP-MS of the two copper minerals discussed above which show the largest anomalies; the copper isotope data obtained is presented in Table 3. The new MC-ICP-MS data is in full agreement with the earlier Oxford TIMS data.

7. Investigation using MC-ICP-MS of possible fractionation of copper isotope ratios because of anthropogenic processes

Direct experimental investigations using TIMS of possible metallurgically induced fractionation were first carried out in Oxford in 1995. In 1997 measurements were made by MC-ICP-MS to assess further whether smelting or fire refining processes produce changes in copper isotope compositions. Table 4 presents the results of these copper isotope measurements on the source material and smelting products of a smelting experiment carried out by Merkel using malachite ore originating from Zaire. The isotopic composition of copper was determined in the original malachite ore, in the copper metal smelted from this ore, and in copper extracted (by dissolution, ion exchange separation and electrodeposition) from the slag produced in this smelting process. The data presented in Table 3 show that, in this experiment, there are no statistically significant differences in the $^{63}Cu/^{65}Cu$ ratios between the starting malachite ore,

Table 5
Comparison of copper isotope compositions obtained for a number of Late Bronze Age copper oxhide ingots from sites in Cyprus, Crete, and Sardinia. MC-ICP-MS was used, with internal bias corrected in terms of $^{66}Zn/^{68}Zn = 1.512\ 680$ for an internal laboratory Zn standard calibrated against the SRM 976 copper isotope standard. The errors quoted are 1 standard deviation. The δ values quoted express the departure from the certified $^{63}Cu/^{65}Cu$ ratio of 2.2440 ± 0.0021 for the SRM 976 copper isotope standard

Ingot no.	Site	$^{63}Cu/^{65}Cu$ (MC-ICP-MS)	δ value
MAT1	Mathiati, Cyprus	2.245 70 ± 0.000 11	+0.76
E13	Enkomi, Cyprus	2.248 52 ± 0.000 11	+2.01
SK1	Skouriotissa, Cyprus	2.244 75 ± 0.000 06	+0.33
LAN1	Lanusei, Sardinia	2.244 49 ± 0.000 01	+0.22
THB	Hagia Triadha, Crete	2.245 36 ± 0.000 05	+0.61
THE	Hagia Triadha, Crete	2.253 70 ± 0.000 08	+4.32
THG	Hagia Triadha, Crete	2.248 85 ± 0.000 06	+2.16
THI	Hagia Triadha, Crete	2.247 35 ± 0.000 02	+1.49
SRM 976	NBS/NIST Copper isotope standard	2.244 27 ± 0.000 17	

the copper smelted from it, or the traces of copper remaining in the slag. On the basis of this experiment there is at present no evidence that smelting changes the isotopic composition of copper in the smelted metal away from that in the copper ore which was smelted.

Table 3 also shows copper isotope data for fire refined copper; the copper metal used for these experiments is not related to the malachite ore from Zaire, or the metal smelted from it, which were discussed above. JM6 is a particular batch of copper metal which had been once fire refined by Merkel; JM7 is a batch of copper metal which was the direct product of fire refining batch JM6. The data show clearly that there is no statistically significant difference of the ratio $^{63}Cu/^{65}Cu$ between batch JM6 and JM7, so that fire refining does not, on this evidence, alter the isotopic composition of copper.

Though we do not doubt that further investigation of these matters is necessary, present evidence strongly suggests that smelting and fire refining do not alter the $^{63}Cu/^{65}Cu$ ratio away from that in the original copper ore, and that Cu isotopes might therefore make a contribution to provenancing archaeological objects made of copper based alloys.

8. Isotopic composition of copper in some Bronze Age archaeological copper ingots

The question clearly arises: are copper isotopic anomalies actually found in archaeological copper objects? Because we can find no evidence in the literature that this has ever been investigated, we have made a few analyses of copper oxhide ingots found in Crete, Cyprus, and Sardinia (see Bass [20] for an archaeological discussion of this widely traded form of copper in the Bronze Age Mediterranean region).

Table 5 presents MC-ICP-MS copper isotope data for three copper “oxhide” type ingots from Cyprus, one from Sardinia, and four from the earlier, LM IB, site of Hagia Triadha in Crete, in comparison with the data for the SRM 976 copper isotopic standard. There is essentially no difference in isotopic composition from the SRM 976 standard for ingots MAT1, SK1 and LAN1, though the Cypriot ingot E13 and the Cretan ingot THB seem to have a positive anomaly. On the other hand Table 4 shows that the other three ingots from Crete: THI, THG, and THE show clearly different isotopic compositions from each other and from the SRM 976 standard, with positive anomalies of $\delta = 1.5$, 2.2, and 4.3, respectively. These Minoan ingots are typologically different from (and some 300 years earlier in date) than the ingots from Cyprus and Sardinia. Moreover, they are from the group of oxhide ingots that also have Pb isotope compositions which do not match the isotopic compositions of any copper deposits so far analysed in the Mediterranean region, including Cyprus and Turkey [21].

9. Conclusions

(1) The suggestions from the 1965 work of Shields et al. [3] have been verified; natural variations of the

isotopic composition of copper do occur in natural copper ore minerals. A low temperature TIMS technique, using a multicollector and simultaneous measurement of both isotopes, has improved measurement precision. Results obtained using this technique have been confirmed by MC-ICP-MS isotopic analyses, a technique which provides data of the highest precision so far available.

(2) Processes of copper smelting or fire refining do not, on present evidence, alter the isotopic composition of copper; consequently copper isotope analyses may be a valuable addition to the lead isotope provenancing of copper metal.

(3) Copper isotope anomalies have been found in some late Bronze Age copper oxhide ingots.

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