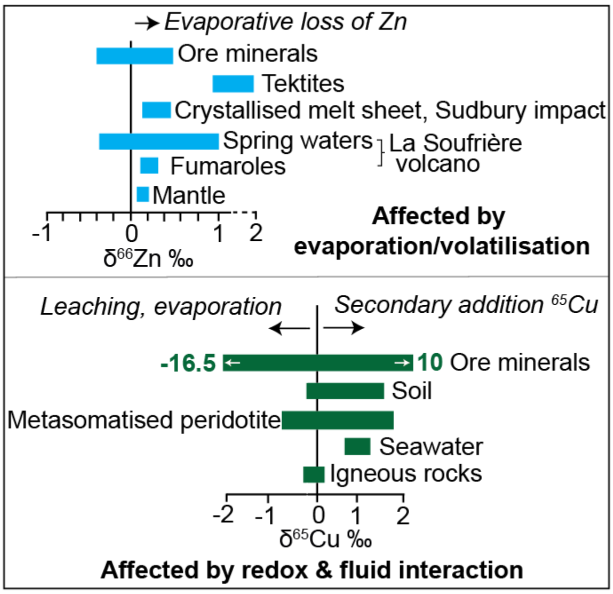
Cu and Zn stable isotope analyses

What it tells us



Both Cu and Zn occur together at similar crustal abundances (c. 70 ppm). The power of combining the stable isotope signatures of these two transition metals is that copper has one of the largest ranges of fractionation of any of the transition elements (δ^{65}Cu ‰ ranges from -16.5 to 10.0 ± c. 0.05) while Zn has a much narrower range (δ^{66}Zn ‰ ranges from -1 to 1 ± c. 0.05). Both metals are fractioned in magmatic and hydrothermal domains, although neither Cu nor Zn isotopes are typically thought to be strongly affected by high temperature processes such as melting or crystallisation of major rock forming minerals. Cu isotopes are redox sensitive and strongly affected by interaction with fluids. Zn isotopes are not redox sensitive and recent studies have shown strong fractionations by volatilisation/evaporation, and transport in hydrothermal waters. This means that remobilisation, transport and deposition of Cu and Zn by magmatic volatiles and hydrothermal fluids will be recorded by their isotope signatures.

Description of Analytical Method

For silicate samples rock powders are digested in concentrated HF and HNO_3 after which a dilution in HCl is created. If Cu and Zn concentration is not known, an aliquot of this solution is analysed by ICP-MS to obtain this, as it is important to know how much sample to load onto the columns. A minimum of about 5ppm Cu and 20 ppm Zn is needed for a successful analysis. Note that we are still developing Zn isotope analyses so this method is not finalized – we anticipate processing and analysing Cu and Zn separately, although the two aliquots could be taken from the same sample solution.

For Cu: An aliquot of the sample in solution containing approximately 5-10µg of Cu is eluted through a column containing 1.5 mL of a general cation exchange resin. The matrix elements are removed from the sample through washing the resin with an elution acid. The fraction containing Cu is collected and dried down. If the samples contain large amounts of matrix elements such as Fe, Sr, Ba, the column is repeated. For sulphide analysis, the process is the same, except that the digestion uses *aqua regia* (HNO_3 + HCl) instead of HF, and the concentration of Cu is assumed based on the mineral formula (e.g. Chalcopyrite = approx. 33% Cu). The resultant Cu fraction is diluted to 200 ppb to run on the multi collector ICP-MS. Samples are bracketed by a synthetic standard (NIST976) for mass bias and drift correction, and are spiked with 200 ppb Ga prior to analyses to aid drift correction. Each sample is run at least twice to calculate a 2SD error. Cu isotopes are reported as δ^{65}Cu in ‰, relative to the standard NIST976.

For Zn: An aliquot of the sample is spiked with a ^{67}Zn/^{70}Zn solution before loading onto the column. The column resin is cleaned multiple times to keep blank contributions low, and the procedure takes place in a metal-free, ultra clean laminar flow fume hood. The matrix elements, Cu and Fe are removed using half-concentration HCl acid, then a weaker HCl acid, then Zn is removed using 3M HNO_3. This may be repeated if a lot of matrix elements are present. This fraction is dried down, and diluted to

200 ppb for analysis by multi-collector ICP-MS. Samples are bracketed with a synthetic standard (JMC-Lyon) and this is used to obtain the δ^{64}Zn and δ^{66}Zn in ‰. Note that this method is still being set up and is subject to change (October 2022).

Type of Sample Material/Media

Rock and mineral powders. Depending on Cu and Zn concentration, approximately 0.1-0.3g of rock sample is digested (greater than 0.3g is problematic due to larger amounts of HF being required, and the production of fluorides which can retain certain elements). For sulphides, much less is required (0.01g), and these samples can be obtained by drilling out clean surfaces from rock samples, polished slabs, probe mounts etc.

Instrumentation/Costs

	Chemical preparation	**Analysis**
Cu	\$35 per sample	\$100
Zn	\$35 per sample	\$100
Cu + Zn	\$50 per sample	\$170

Chemical preparation involves sample digestion and column work. The cost is lower for Cu and Zn combined as in most cases both isotopes can be obtained from one digestion. Note that if trace element analysis is required this is an additional cost for time on the ICP-MS, but no additional cost for chemical prep.

Analysis by Neptune Multi Collector ICP-MS is charged by the hour of argon use (\$42.05 per hour). The cost here includes machine calibration, USGS and in-house rock and mineral standards, and running each sample at least twice. The slightly lower cost of combined Cu and Zn analysis is due to less calibration being required if the machine is already on and tuned.

Key references

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