

Towards an Efficient Coupled Cu and Zn Purification Technique Adapted to Precious Terrestrial and Meteorite Materials. W. Debouge¹, N. Mattielli¹ and V. Debaille¹, ¹Laboratoire G-Time, Université Libre de Bruxelles, ULB, Brussels, Belgium (wdebouge@ulb.ac.be).

Introduction and study interests:

Copper is an important tracer for reconstruction of geochemical cycling in terrestrial or extraterrestrial environments. It is a transition element with three oxidation states (0, I, and II) and two isotopes (⁶³Cu and ⁶⁵Cu). With a condensation temperature of ~1050° to 1100° K, Cu is considered as a relatively volatile element [1-3]. In meteorites, this element is both chalcophile and siderophile as it enters in FeNi metals (60%) and sulfides (20–25%) and forms tiny metallic Cu nuggets (4–5%) [4]. To a limited extent, it also enters in silicate minerals (olivine, pyroxene). Specifically, in magmatic and non-magmatic iron meteorites (IM), Cu can provide information on primordial processes that affected the meteorite parent bodies: core formation [5] [6] and fractional crystallization [7]. These processes induce metal-silicate-sulphide segregation that might produce mass dependent fractionation recorded by the Cu isotopes. Accordingly, the study of Luck et al. [8] on carbonaceous and ordinary chondrites shows that Cu is isotopically heterogeneous in the solar nebula. In addition, Cu isotopic variations observed in chondrites suggest the existence of two isotopically distinct reservoirs [8]. As Cu is moderately volatile, some other processes like accretion and shock metamorphism can also produce Cu isotope fractionation and hence can be traced by the variations in Cu isotope ratios [5, 9]. Consequently, Cu isotopes can be a sensitive and powerful tracer for understanding primordial nebular and planetary processes.

The continuous development of the HR-MC-ICP-MS (high resolution multi-collector inductively coupled plasma- mass spectrometry) renews interest in heavy stable isotope systems, whose subtle natural isotopic variations require high precision, accuracy and reproducibility. However, significant inaccuracy in MC-ICP-MS measurements of Cu or Zn isotopic composition may be caused by inorganic and organic resin-derived components added to samples during column chemistry or/and to incomplete separation of the analyte from the sample matrix [10, 11]. In addition, previous studies [12] have shown that mass bias corrections, using sample-standard bracketing and external normalization (Zn as dopant for Cu isotope measurements, and Cu as dopant for Zn isotope measurements), may fail to accurately correct for these matrix effects.

Therefore, special attention is paid to the total recovery of Cu or Zn analyte during the chemical purification, and optimal elimination of potentially interfering matrix elements.

Analyses of Cu, as well as Zn, are important for understanding early planetary differentiation processes, and efficient purification procedure is required to ensure high-precision measurements. In this study, we present a new anion exchange chromatography procedure developed at Laboratoire G-Time (ULB) for Zn and Cu separation.

Analytical procedure and Results:

Compared to Zn or Fe, Cu is much more difficult to purify and to recover totally. In order to purify and collect Cu and Zn from a single aliquot of a sample, previous studies have been mainly using AG-MP1. This macroporous resin has a high level of crosslinkage but is very difficult to wash and has relatively poor blank levels (J.C.J. Petit, PhD thesis). Therefore a two passages column separation method on Bio Rad AG[®]1-X8 has been considered. The first column separates Zn from Cu, while the second column refines the purification of the Cu cut.

First for digestion of the samples, about 100 mg of finely ground powdered sample is dissolved with concentrated HF and HNO₃ (3:2) in PFA beaker. All reagents (hydrobromic acid, hydrochloric acid, nitric acid and hydrofluoric acid) that were used for this study were subboiled in PFA bottleneck systems. The necessary dilutions were performed with Milli-Q water (18.2 MΩcm) (Millipore system). After 48 hours on a hot plate at 120°C, samples are dried and dissolved again with 6M HCl on a hot plate at 100°C for 8h. Evaporation temperature is never higher than 100 C in order to avoid burnt crust.

The distribution coefficients on anion-exchange resin (Bio Rad AG[®]1-X8) (determined by [13]) for many elements at various concentrations of nitric acid, hydrochloric acid and hydrobromic acid have been used to determine the optimal combination. Copper is first separated from Zn using 2 ml Bio Rad AG[®]1-X8 100–200 mesh in HCl. Digested samples are redissolved in 1 ml 8 M HCl, centrifuged and loaded on the resin. Copper is recovered with 8 M HCl. Iron is subsequently discarded by rinsing with 1 M HCl. Zn is then eluted with a mixture of 1 M HNO₃/0.1 M HBr. If needed, Cd can also be recovered by using HNO₃. The procedure is detailed in Fig. 1a.

Elemental concentrations were determined by ICP-MS Agilent 7700 at Laboratoire G-Time for each sample before purification and Cu cut to monitor both Cu recovery and the presence of potential matrix interferences. Calibration curves (Fig. 1a) indicate a recovery close of 100 % for both Zn and Cu (Fig. 1b).

The second column to refine the purification of the Cu fraction of this first column is in development. Several tests have been performed using hydrobromic acid in order to purify the Cu cut from the presence of Ti that generates an important isobaric interference with Cu. However, despite promising experimental data [14], the results were deceptive. Copper should be purified on a micro column of 0.2 ml Bio Rad AG[®] 1-X8 using a similar procedure.

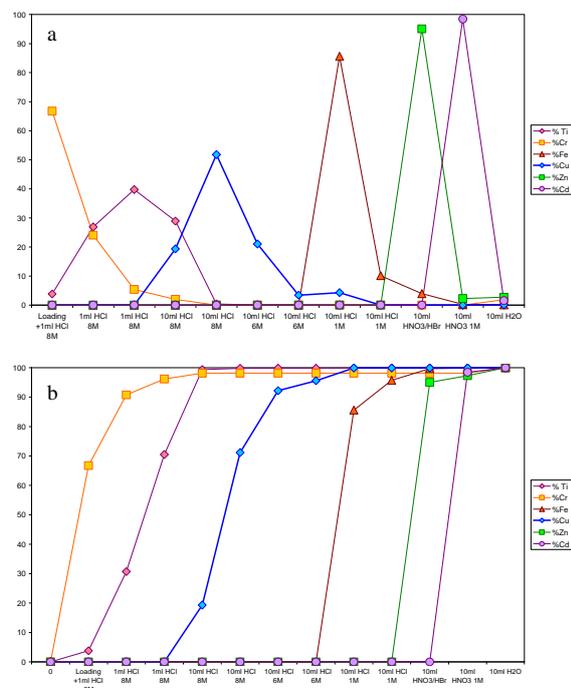


Fig. 1: a) Elution curve in percent, b) cumulative elution curve in percent, for Ti, Cr, Fe, Cu, Zn and Cd.

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