

## Accretion and accredited anomalies

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The time-scales for the accretion of objects in the inner solar system have been determined using short-lived nuclides with half-lives in the range  $10^5$  to  $10^8$  years. Recently MC-ICPMS has been used to study the following isotope systems (covering a range of half-lives):  $^{97}\text{Tc}$ - $^{97}\text{Mo}$  (2.6 Myrs),  $^{92}\text{Nb}$ - $^{92}\text{Zr}$  (36 Myrs),  $^{107}\text{Pd}$ - $^{107}\text{Ag}$  (6.5 Myrs),  $^{126}\text{Sn}$ - $^{126}\text{Te}$  (0.235 Myrs),  $^{182}\text{Hf}$ - $^{182}\text{W}$  (9 Myrs) and  $^{247}\text{Cm}$ - $^{235}\text{U}$  (16 Myrs). Caution is required when making some of these measurements by MC-ICPMS. Although the sensitivity and precision can be excellent, artefacts can compromise the accuracy. It appears that the cone design is critical. For example, we have found that more sensitive cone designs can yield deviations in isotope ratios of Mo and Te in samples separated from certain meteorite matrices. These anomalies are not found or are not as extreme with standard cone designs. The measurement of Ag isotopes is also very sensitive to small matrix differences. There are differences in the magnitude of reported Mo and Zr isotopic anomalies measured by MC-ICPMS and the degree to which these are analytical artefacts is currently unclear.

The most extensively used chronometer in recent years has been Hf-W. It provides strong constraints on the early history of the solar system. However, the acquisition of higher quality data by MC-ICPMS is revealing new complexities. Most of the data have been produced on a Plasma 54 for which superior reproducibility is achieved by normalising to  $^{184}\text{W}$ , rather than by using the smaller (and sometimes apparently anomalous)  $^{183}\text{W}$ . It has been shown that the  $^{182}\text{W}/^{184}\text{W}$  of the silicate Earth (or standards) and carbonaceous chondrites are identical. As such, terrestrial accretion and core formation must be somewhat protracted as predicted from dynamic modelling. However, more modern MC-ICPMS instruments achieve very good data for  $^{183}\text{W}$ . The  $^{183}\text{W}/^{184}\text{W}$  when normalised with  $^{186}\text{W}/^{184}\text{W}$  appears to be roughly 100 ppm higher in Allende than in the Earth as measured by MC-ICPMS. This offset is not caused by interferences from Os as some have suggested. This means that, unlike with  $^{182}\text{W}/^{184}\text{W}$ , there is a roughly 200 ppm difference in  $^{182}\text{W}/^{183}\text{W}$  between Allende and the Earth. A similar effect is found for Murchison and using  $^{184}\text{W}/^{183}\text{W}$  as opposed to  $^{186}\text{W}/^{183}\text{W}$  for normalisation does not eliminate it. These effects are not well understood at present. Equilibrated metals from bencubbinites yield both  $^{182}\text{W}/^{184}\text{W}$  and  $^{183}\text{W}/^{184}\text{W}$  that are identical to the silicate Earth. However, if the relative proportion of radiogenic  $^{182}\text{W}$  differs between the silicate Earth and average solar system, terrestrial accretion and core formation may have been slightly faster than previously suggested. The mean life for accretion would be more like 17 Myrs as opposed to 25 Myrs.

## Sulfide melts and the origin of Cu/Au ratios in porphyry deposits

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Experimental data and earlier analyses of Cu, Au, Sn and W in fluid inclusions by LA-ICPMS indicate that bulk metal ratios of magmatic-hydrothermal ore deposits are primarily controlled by the composition of the magmatic volatile phase focused into veins and fractured porphyry stocks. To elucidate the origin of this volatile phase, we are reconstructing the evolution of an ore-forming andesitic complex by systematic study of magmatic melt inclusions.

Melt inclusions (MI) commonly record silicate liquid, but sulfide liquids were also discovered in certain rocks. Following extensive petrographic study, we used laser-ablation ICPMS to analyze the major to trace element content of entire unexposed MI. This allows an integrated analysis of inclusions, essential in the case of sulfide melts that never quench to a homogeneous glass. Both types of inclusions were quantified using a silicate glass standard. Calibration tests on chalcopyrite standards yielded Cu concentrations within 5 wt.-% of the certified value (Halter et al., 2002).

Analyses were conducted on volcanic and intrusive rocks from the Farallón Negro Volcanic Complex (Argentina), hosting the world-class Bajo de la Alumbrera porphyry Cu-Au deposit. Sulfide MI were found in amphibole of subvolcanic intrusions, co-existing with Cu-poor silicate MI. Sulfide melts contain as much as 9 wt.-% Cu and 4 ppm Au.

The mean Au/Cu ratio of sulfide MI overlaps with the average Au/Cu ratio in fluid inclusions of the earliest hydrothermal brine in the Alumbrera deposit, which in turn is identical to the Au/Cu ratio of the entire ore body. We conclude that the ore-forming hydrothermal fluid acquired its high metal content and characteristic Au/Cu ratio by bulk de-stabilization of magmatic sulfides. Bulk resorption of the sulfide liquid is expected to result from the exsolution of a volatile phase, which causes oxidation through  $\text{H}_2$  loss and removal of sulfur as  $\text{SO}_2$  and  $\text{H}_2\text{S}$ . A link between wholesale de-stabilization of sulfide melts and the generation of the ore fluid is substantiated by similar Fe/Cu ratios, despite contrasting chemical behavior of these two elements.

Our data indicate that magmatic sulfide melts can act as intermediate metal hosts contributing to metal enrichment in large hydrothermal porphyry-Cu-Au deposits, by pre-concentrating Cu and Au prior to volatile saturation. Sulfide melts have previously been proposed as a key factor in the genesis of the giant porphyry deposit at Bingham (Utah). It remains to be tested whether the exsolution of sulfide liquid is an essential prerequisite for the formation of large Cu-Au ore deposits (cf. Audétat et al., this issue).

Halter, W.E., Pettke, T. and Heinrich, C.A., (2002), *Science*, in press.

Audétat A., Pettke, T., Dolejs, D. and Bodnar, R. (2002) this issue.