PALLADIUM-SILVER AGES OF THE ORDINARY CHONDRITE ALLEGAN (H5) AND ACAPULCOITE DHOFAR 125 AND RELATED STABLE ISOTOPE FRACTIONATION.

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Introduction: The short-lived ^{107}Pd-^{107}Ag chronometer (half-life 6.5 Myr) is a useful tool for dating early solar system processes and has recently been applied to a range of iron meteorites and carbonaceous chondrites [1-6]. Silver is a moderately volatile element with a half-mass condensation temperature of ~993 K [7] and an affinity for sulphide phases. In contrast, Pd is a relatively refractory, siderophile element with a half-mass condensation temperature of ~1320 K [7]. This implies that the decay system can be used to date the crystallisation process of iron meteorites, whilst it also provides constraints on the timing of volatile depletion events that occurred during early solar system formation.

In order to tie the relative ages obtained from the short-lived Pd-Ag chronometer to an absolute timescale, the initial ^{107}Pd abundance of our solar system must be known. Current values for the initial ^{107}Pd/^{108}Pd ratio range from 2.2×10^{-5} to 8.9×10^{-5} [4,5] and, as such, is not well defined. This severely limits the precision of the absolute ages obtained from the Pd-Ag data.

To address this issue, we aim to determine internal isochrons for two meteorites: Allegan (H5 ordinary chondrite) and Dhofar 125 (a volatile rich acapulcoite) with the intention to better define the initial ^{107}Pd abundance of our solar system.

Samples: Allegan has a shock category S1 and our fragment (Fig. 1a) showed no evidence of weathering. Previous studies report a Re-Os age of 4568 ± 11 Myr [8] and a Pb-Pb age of 4556.3 ± 0.8 Myr, whereby the latter is thought to reflect a metamorphic event [9].

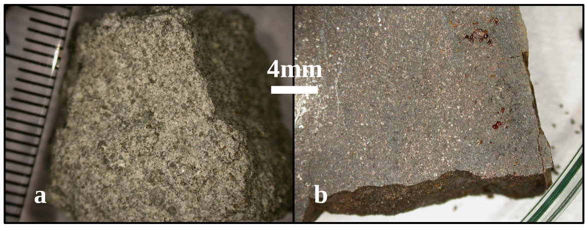

Figure 1a) Allegan and b) Dhofar 125.

The acapulcoite Dhofar 125 (Fig. 1b) has a chemical composition similar to that of ordinary chondrites but is more volatile enriched. It also belongs to the S1 shock category, but shows clear evidence for weathering. Dhofar 125 has a well-defined Hf-W age of 4563.1 ± 0.8 Myr [10] and a Pb-Pb age of 4555.9 ± 0.6 Myr [11].

Analytical Techniques: The samples were cleaned, crushed and separated by grain size. The different cuts were then split into magnetic and non-magnetic fractions. For Allegan five silicate fractions, two bulk samples and two metal fractions were separated. The Dhofar 125 fractions include four silicate fractions, a bulk sample and five metal fractions. Purification and isolation of Ag was achieved by ion exchange chromatography [3]. The samples were analysed on a Nu Plasma multi-collector ICPMS [6]. The Ag isotope composition of each sample is given as $\varepsilon^{107}\mathrm{Ag} = ((^{107}\mathrm{Ag}/^{109}\mathrm{Ag}_{\mathrm{sample}} - {}^{107}\mathrm{Ag}/^{109}\mathrm{Ag}_{\mathrm{standard}}) / {}^{107}\mathrm{Ag}/^{109}\mathrm{Ag}_{\mathrm{standard}}) \times 10^4$ using a ^{107}Ag/^{109}Ag value of 1.079760 for the NIST SRM978a Ag standard. Palladium and Ag concentrations were acquired by isotope dilution [2].

Reproducibility: The external reproducibility (2 sd; n = 10) obtained for Cody Shale of ± 0.5 ε was applied to the results of this study as a conservative estimate for the total external reproducibility of a sample passed through the analytical procedure.

Results: Eight fractions of Allegan were analysed and yielded ε^{107}Ag values of +1.4 to -5.9 and ^{108}Pd/^{109}Ag ratios varying from 1.6 to 276 (Fig. 2).

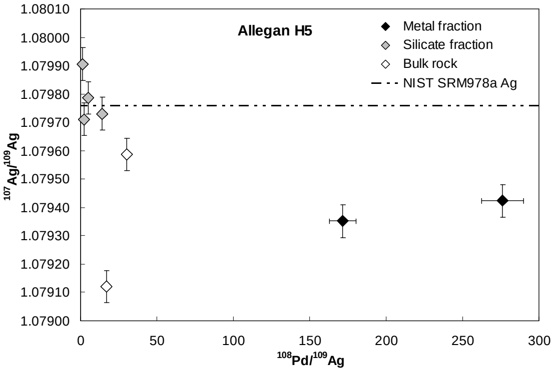

Figure 2 - Pd-Ag isochron diagram for Allegan.

The four Dhofar 125 fractions analysed so far show a much smaller range in ^{108}Pd/^{109}Ag ratios from 2.1 to 3.7 and ε^{107}Ag values from -0.6 to -1.3 (Fig. 3). Six further fractions of Dhofar 125 are currently being processed.

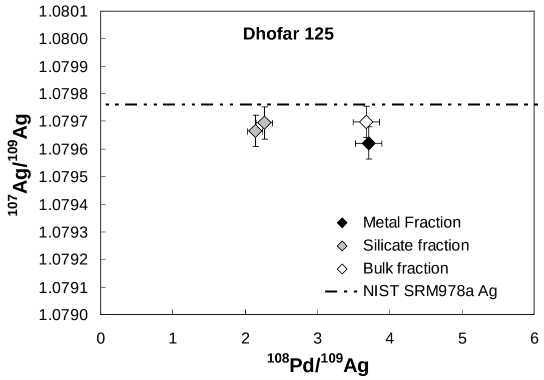

Figure 3 - Pd-Ag isochron diagram for Dhofar 125.

Discussion: The data for Allegan and Dhofar 125 exhibit considerable scatter (Fig. 2 and 3) and do not define internal isochrons. They display disturbed Pd-Ag systematics and thus an initial ^{107}Pd abundance cannot be determined. However, based on the radioactive decay of ^{107}Pd and assumptions about Pd/Ag ratio of the reservoir from which Allegan and Dhofar formed, it is possible to model the Ag isotope evolution of each meteorite and compare the results to the measured data. Following model assumptions were used: (i) an initial chondritic Pd/Ag reservoir with a value of 2.8; (ii) a solar system initial ^{107}Pd/^{108}Pd ratio of 5.9 x 10^{-5} [4]; and (iii) closure of the Pd/Ag decay system at the same time as the Pb-Pb chronometers for both samples [8,10] i.e. ~12 Myr after CAI formation.

Allegan. The metal fractions display measured Pd/Ag ratios of 320 and 510. Using the lower value results in a minimum ε^{107}Ag model value of +24.6 for metal. The measured ε^{107}Ag, however, is -3.4. This suggests a late (~60 Myr) thermal event that reset the Ag isotope composition of the reservoir and prevented further ^{107}Ag in-growth. Otherwise, the metal fraction would be much more radiogenic. However, preferential ^{107}Ag loss from the metal - involving stable isotope fractionation - is also required, because the metal value (-3.4 ε) is slightly lower, although identical within uncertainty, to the solar system initial ε^{107}Ag of – 3.1 ± 0.6 [4]. The silicates (Pd/Ag = 10) have a predicted ε^{107}Ag of -1.5 and a measured value of +0.2 ε. Thus, their Ag isotope composition is too radiogenic. This is consistent with excess ^{107}Ag from the metal diffusing into the silicates. It is important to note that Cd, which is more volatile than Ag, shows large mass-dependent isotope effects in ordinary chondrites [12]. It was suggested that this fractionation occurred during open system thermal metamorphism [12] and this is also most likely the case for Ag isotopes.

Dhofar 125. The metal (Pd/Ag = 7) has a predicted ε^{107}Ag of -1.9. The actual value is -1.3 ε indicating more radiogenic ^{107}Ag in-growth than predicted. Assuming that the system closed at 3.3 Myr (instead of 12 Myr) after CAI, in accordance with the Hf-W data [10], the model value is in agreement with the measurement (-1.3 ε). The Pd/Ag ratio of 4 for the silicates yields a model ε^{107}Ag of -1.9 (system closure at 3.3 Myr). The measured value (-0.8 ε) is more radiogenic than any model prediction for metal or silicates. Hence, stable Ag isotope fractionation is required to explain this data. Additional data is on the way to shed further light on this issue.

Conclusion: The Pd-Ag data of Allegan indicate a resetting event that took place ~60 Myr after CAI formation. The Dhofar 125 data is consistent with an early closure at 3.3 Myr after CAI proposed from the Hf-W decay system for acapulcoites [10]. These events were accompanied or followed by stable isotope fractionation and for Allegan this occurred during transport of Ag from the metal into silicates/sulphides. The resetting event recorded by Allegan was most likely the same event that lead to mass-dependent Cd isotope fractionation on the ordinary chondrite parent body. Thus the Pd-Ag age of ~60 Myr dates the protracted duration of open system metamorphism. It is a minimum age and metamorphism could have lasted for more than 60 Myr because ^{107}Pd became extinct at that time and is not sensitive to later resetting.

References: [1] Carlson R.W. & Hauri E.H. (2001) *GCA, 65*, 1837-1848. [2] Woodland S.J. et al. (2005) *GCA, 69*, 2153-2163. [3] Schönbächler M. et al. 2007. *Int. J of Mass Spec. 261*, 183-191. [4] Schönbächler M. et al., (2008) *GCA, 72*, 5330-5341. [5] Horan M.F. et al. (2012) *EPSL, 351-352*, 215-222. [6] Theis K.J. et al. (2012) *EPSL*, in press. [7] Lodders K. (2003) *Astrophys. J. 591*, 1220-1247 [8] Smoliar M.I. et al. (2006) *LPS XXXVII*, Abstract #1468. [9] Göpel C. et al. (1994). *EPSL, 121*, 153-171. [10] Touboul M. et al. (2009) *EPSL*, *284*, 168-178. [11] Göpel C. & Manhès G. (2010) *Comptes Rendus Geoscience, 342*, 53-59. [12] Wombacher F. et al. (2008) *GCA*, *72*, 646-667.