A NEW APPROACH TO Pb DATING OF WHOLE METEORITIC PHASES BY THERMAL EXTRACTION AND THERMAL IONIZATION IN SILICA MELT. Christopher R.J. Charles and Donald W. Davis, Jack Satterly Geochronology Laboratory, Department of Geology, University of Toronto (22 Russell Street, Toronto, Ontario, CANADA, M5S3B1. christopher.charles@utoronto.ca & dond@geology.utoronto.ca).

Introduction: A significant challenge to precise $^{207}Pb/^{206}Pb$ meteorite chronometry remains the removal of terrestrial lead. Presently this is done by leaching, dissolution and chromatographic separation in clean-lab environments followed by ID-TIMS [1,2] or MC-ICP-MS [3,4]. Here a novel thermal extraction (TE) procedure followed by thermal ionization mass spectrometry (TIMS) is described, where chemically untreated whole meteoritic phases are embedded in a silicate glass ionization enhancer (Figure 1). Radiogenic Pb from whole-samples is thermally extracted into the silicate melt and thermally ionized during TIMS analysis. $^{207}Pb/^{206}Pb$ ages for whole fragments of calcium-aluminum-rich inclusions (CAIs) from the Allende CV3 chondrite and for a pyroxene crystal from angrite SAH99555 were resolvable by this approach.

Method: Three CAI fragments ca. 200 µm in diameter (~0.01 mg) were obtained from Allende (#M29173; Royal Ontario Museum) by freeze thaw disaggregation and hand picking. One different Allende CAI fragment (#316/39) [5,6] of approximately the same weight and size was obtained by hand picking. One euhedral pyroxene crystal (800 µm diameter; 0.1 mg) from angrite SAH99555 was also obtained by crushing and hand picking. After rinsing with 3-4 cycles of clean acetone and MQ-H2O, all grains were washed several times with sub-boiling distilled HCl (0.1–3.0N) and HNO_3 (0.1–3.0N) under cleanroom conditions. Whole grains were covered with of clean Merck silicic acid "silica gel" & 9N H_3PO_4 emitter similar to [7]. All reagent blanks were ca. 0.1 pg Pb/mL as measured by ID-TIMS. The gel-fragment mixture for each individual sample was loaded in troughs (800 µm width) on separate zone-refined rhenium filaments (12 µm-thick × 1200 µm-wide; c.f. Figure 1). Filaments were previously moulded to this trough-shape and were spot-welded to standard Cathoedon #519 filament assemblies. Before sample loading all filaments were vacuum outgassed at 2000ºC for 1 hour. After loading each sample was fused to a glass in vacuum at 1400ºC over 30 min taking care to fully embed each fragment inside the glass. A VG354 thermal ionization mass spectrometer was used to measure all ratios in Daly-counting mode. Temperatures were recorded by a wire-pyrometer on the hottest part of each filament (typically around the folds of the trough). Mass fractionation corrections and data reductions were made under the UTILAGE software package (v060703; D.W. Davis). Results were fitted by IsoPlot/Ex (v3; K. Ludwig).

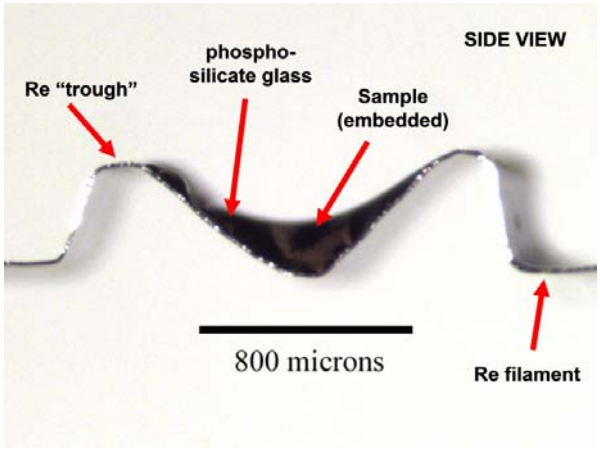

Figure 1: Trough-shaped Re filament showing a whole-sample fused into the phospho-silicate glass.

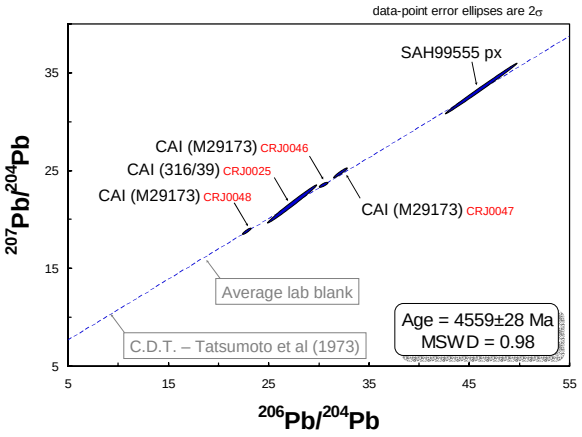

Figure 2: Pb-Pb plot of the four Allende CAIs and one px from angrite SAH99555. Primordial Canyon Diablo troilite & average lab blank are overlain but not included in this fit.

Observations – Allende CAIs: Interferences were seen on masses 204, 206, 207 and 208 for all fragments below 1590ºC. At 1630 – 1740ºC, lead ratios of the four fragments stabilized between $23 < {}^{206}Pb/^{204}Pb < 33$ (cf. Figure 2). Beam intensities ranged between 1.2 – 4 kcps on ^{206}Pb in this temperature interval showing the most radiogenic Pb. Three data blocks (30 ratios) were recorded for $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$.

Observations – SAH99555 px: Interferences were observed until 1750ºC for this sample. Between 1770 – 1820ºC a beam intensity of 2.5 kcps on ^{206}Pb

was obtained giving an average ratio $^{206}Pb/^{204}Pb = 46$. This was the most radiogenic of all samples analyzed (cf. Figure 2). Three data blocks (30 ratios) for $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ were recorded.

Results: The data define a linear array within error in Pb-Pb space (Fig. 2) corresponding to an age of 4559±28 Ma (2σ). about the common Pb component is likely a mixture of initial Canyon Diablo troilite (CDT) lead[8] and laboratory blank (Fig. 2). If we include primordial CDT Pb and laboratory blank in the fit, an indistinguishable age of 4563±23 Ma (2σ; MSWD=3.5) is obtained.

Discussion & Conclusions: Results on two 0.1 mg samples of Allende CAIs (M29173) yielded mostly thorogenic Pb ($^{208}Pb/^{204}Pb$ = 160 and 260) [9]. ^{208}Pb emission began to increase at 1580ºC and attained between 16 – 30 kcps over about about 40 min. Given the small sample sizes and low concentrations of primary Pb in Allende CAI's (typically 0.3 – 0.01 ppm), the presence of a whole CAI in the melt does not appear to have significantly reduced the ionization efficiency of the Pb. Since Allende CAIs are known to contain primary Pb that is highly radiogenic, precise ratios should be measureable if sufficient sample can be embedded on the filament (comparible to [1] for example).

Potential limitations of TE include (a) degree of suppression of ionization from large samples; (b) influence of loading blank; and (c) practicalities of sample handling and loading – particularly the amount of silicic acid gel used. These will be investigated using a ^{202}Pb spike that is in preparation.

Aside from initial washing of the specimens, no clean chemical separation is required. In addition, thermal pre-treatment of CAI and angrite px fragments may prove useful for differential evaporation of contaminant Pb from meteoritic materials, as shown with zircon [10].

References: [1] Amelin Y. et al. (2002) *Science, 297,* 1678-1683. [2] Chen J. & Wasserburg G. (1981) *EPSL 52*, 1-15. [3] Albarede F. et al. (2004) *Geochim. Cosmochim. Acta 68*, 2725-2744. [4] Baker J. et al. (2005) *Nature 436*, 1127-1131. [5] Bogdanovski O. & Jagoutz E. (1997) *LPSC XXVIII*, 129. [6] Bogdanovski O. & Jagoutz E. (1999) *LPSC XXX*, 1891. [7] Gerstenberger H. & Haase G. (1997) *Chem. Geol. 136*, 309-312. [8] Tatsumoto M. et al. (1973) *Science 180*, 1279-1283. [9] Charles C.R.J. & Davis D.W. (2007) *Goldschmidt XVII,* Abstract #A161. [10] Davis, D.W. (2007) *Goldschmidt XVII,* Abstract #A206.