W, HF, BA ISOTOPE MEASUREMENTS IN LARGE PRESOLAR SIC GRAINS. E. E. Groopman[1], L. R. Nittler[2], M. Verdier-Paoletti[2], D. G. Willingham[1], C. M. O'D. Alexander[2], and S. Amari[3] [1]Materials Science and Technology Division, U.S. Naval Research Laboratory, Washington, DC 20375, USA (evan.groopman@nrl.navy.mil), [2]Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, DC, 20015, USA, [3]Department of Physics, Washington University in St. Louis, St. Louis, MO 63130, USA

Introduction: SiC is the best studied presolar phase, with >17,000 grains studied by ion microprobe (see [1] and references therein), and 100s more by electron microscopy. Ample presolar SiC grain data exists for major and minor isotopes (e.g., Si, C, N, Mg, Al, Ti) to separate grains into classes matched to presumed progenitor star types. Roughly 95% of SiC grains are believed to have formed in the outflows of asymptotic giant branch (AGB) stars, with 2-3% thought to be from supernovae (SNe). More exotic progenitors, such as novae, born-again AGB stars, and Wolf-Rayet stars, have been proposed to account for other highly anomalous grains. While the major and minor elements allow grains to be categorized, the trace elements, such as Mo, Ba, Nd, and W are useful for investigating the properties of neutron-capture processes in these evolved stars and may help discriminate between grain subgroups, e.g., [2]. Trace analyses in atom-limited samples are challenging, however, and the vast majority of presolar SiC grains have only had their major and sometimes minor isotopes measured. Only 110 presolar SiC grains have been measured to have at least one anomalous Ba isotope at the 2σ level (out of 122) [3-8], though this makes Ba the best-studied trace element by far. By comparison, only two individual presolar SiC grains have been found to have anomalous W and Hf isotopes to date (out of 5 measured) [9]. There remains a clear need to acquire more trace element data to inform astrophysical models, and therefore ever more sensitive analyses.

Methods: We used the NAval Ultra-Trace isotope Laboratory's Universal Spectrometer (NAUTILUS) [10-11], a combination secondary ion mass spectrometer (SIMS) and single-stage accelerator mass spectrometer (SSAMS) to measure Ba, W, and Hf isotopes from large (>5µm) individual presolar SiC grains from the LS+LU acid separation from Murchison [12]. The NAUTILUS uses the SSAMS with its gas stripping cell to dissociate molecular ions from the SIMS (in lieu of high mass resolving power), which greatly reduces the SIMS measurement background. Seven grains (LU-3, LS-6, LU-9, LU-11, LU-19b, LU-23, LU-27) were selected for analysis, having previously been measured for C, Si, N, Mg, and Al [13]. In one session, a 3-5 nA O_2^- primary beam was used to measure $^{134\text{-}138}Ba^+$ isotopes (5 grains). In a separate session, $^{179,180}Hf^+$ and $^{182,183,184,186}W^+$ isotopes were measured by injecting

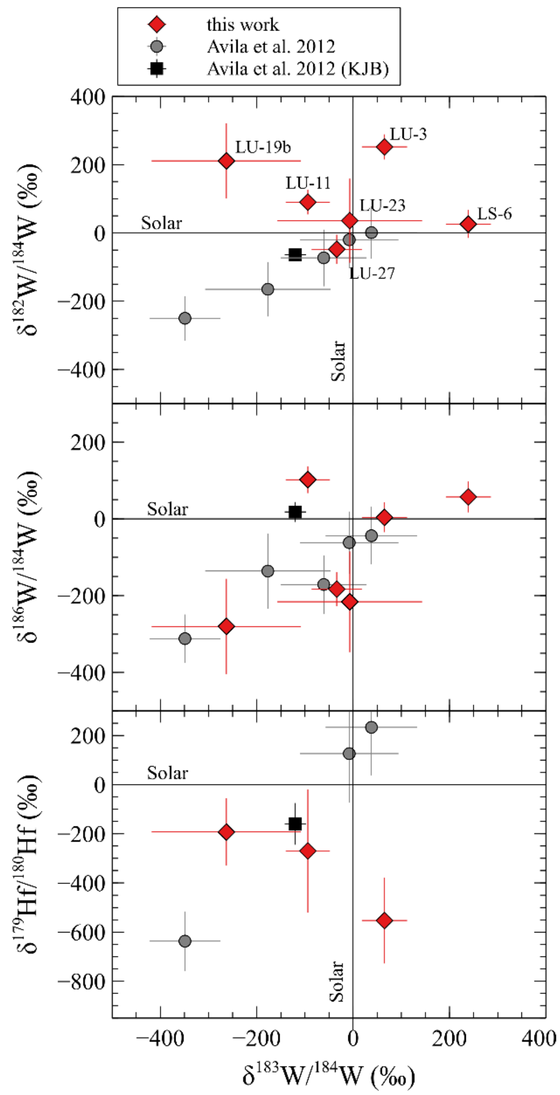

Figure 1: W isotopes in LS+LU SiC grains.

HfO^+ and WO^+ molecules into the SSAMS and dissociating them to measure the Hf^+ or W^+ fragment (6 grains). Previous work found that HfO^+ and WO^+ had higher SIMS yields than Hf^+ and W^+ [9]. NF_3 was used as a flood gas, since it is a good oxidizer and increased WO^+ yields from W metal. Flood gas was run at a pressure of 3×10^{-7} torr in the sample chamber (non-flooding pressure 3×10^{-9} torr). Counting times of 10s/isotope/cycle were used, with electrostatic peak switching used to jump between peaks [11]. Aggregates of small (<1µm) presolar SiC were measured for Ba isotopes.

Results: Barium isotope count rates on the LS+LU grains and aggregates were typically on the order of 0.1-

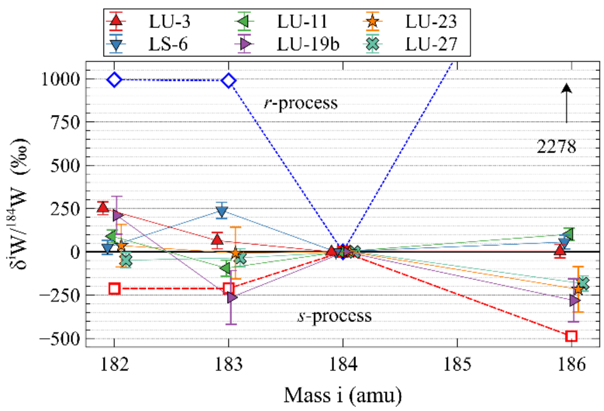

Figure 3: LS+LU W grain data (this work) vs. *r*- and *s*-process models from [14].

2 counts/s (cps) for $^{134}Ba^{+}$ up to 3-22 cps for $^{138}Ba^{+}$, though the count rates for LU-23 were 5-10× higher. Hafnium- and tungsten-oxide count rates were typically between 0.01 and 7 cps. It was difficult to assess the impact of NF_3 flooding on the presolar SiC given low count rates and no matrix-matched standard.

Three grains (LU-19b, LU-23, LU-27) show clear *s*-process W and/or Ba isotopic signatures (Figures 1-3) [14]. Grains LU-3 and LU-11 have excess ^{182}W. While ^{182}W production has generally been attributed to the *r*-process, it has also been suggested that AGB stars can produce ^{182}Hf ($t_{1/2}$ = 8.9 Ma) via the *s*-process, despite its *n*-capture parent, ^{181}Hf ($t_{1/2}$ = 43 d), having a short half-life [15]. Grain LU-3 has a larger excess of ^{182}W coupled with an excess of ^{183}W, which could also be possible under this *s*-process scenario with a further *n*-capture on longer-lived ^{182}Hf to ^{183}Hf ($t_{1/2}$ = 64 m). As stated in [15], an *s*-process pathway to create ^{182}Hf would help resolve a disagreement between the inferred initial solar system abundances of it and ^{129}I ($t_{1/2}$ = 15.7 Ma), an *r*-process isotope. Grain LU-11 contains both excess ^{186}W and depleted ^{183}W, signatures of opposite processes, though it does contain an *s*-process Ba signature (Figure 3). The source of LU-11's overabundance in ^{186}W remains unclear.

Grain LS-6 is another interesting case, given its *r*-process W isotopic signature, with a large excess in ^{183}W (Figures 1,2). Its $^{182}W/^{184}W$ and $^{186}W/^{184}W$ ratios were not clearly resolvable from solar. Based upon its major and minor isotopic composition ($^{12}C/^{13}C$ ~ 3, $^{14}N/^{15}N$ ~ 116, Si isotopes ~ solar, and inferred $^{26}Al/^{27}Al$ ~ 1.4×10^{-2} [13]), LS-6 would be classified as an AB1 grain [2]. The suspected *r*-process ^{183}W in LS-6 coupled with approximately solar Ba isotopic composition (Figure 3) may provide further evidence that some AB1 grains formed in SNe [2].

Grain LU-9 has highly depleted ^{134}Ba and enrichments in $^{135,137,138}Ba$. Other than the enrichment in ^{135}Ba, this is similar to the composition of an X1 grain in [16],

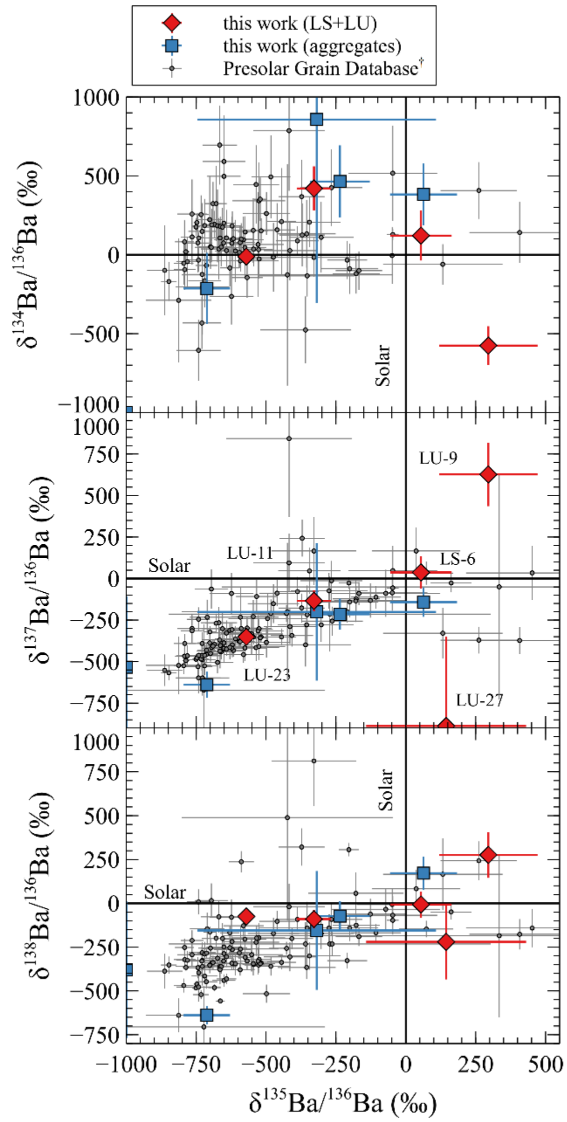

Figure 2: Barium isotopic composition of LS+LU grains and SiC aggregates. †Presolar grain database [1] references [3-8]

however LU-9's C, N, Si, and Mg-Al isotopes are indicative of being mainstream SiC [13]. The origin of these discrepancies is unclear.

References: [1] Stephan T. et al. (2020) *LPSC* (this conference) [2] Liu N. et al. (2018) *ApJ* 855, 144 [3] Jennings C.L. et al. (2002) *LPSC* abs. 1833 [4] Savina M.R. et al. (2003) *GCA* 67, 3215 [5] Pellin M.J. et al. (2006) *LPSC* abs. 2041 [6] Barzyk J.G. et al. (2007) *MAPS* 42, 1103 [7] Marhas K.K. et al. (2007) *MAPS* 42, 1077 [8] Liu N. et al. (2014) *ApJ* 786, 66 [9] Ávila J. et al. (2012) *ApJ* 744 [10] Groopman E.E. et al. (2018) *PNAS* 115, 8676 [11] Groopman E.E. et al. (2019) *arXiv* 1912.09494 [12] Amari S. et al. (1994) *GCA* 58, 459 [13] Gyngard F. et al. (2018) *GCA* 221, 60 [14] Bisterzo et al. (2015) *MNRAS* 449, 506 [15] Lugaro M. et al. (2014) *Science* 345, 650 [16] Stephan T. et al. (2018) *GCA* 221, 109