THE SMOKING GUN: ^{44}Ti IN AN ^{16}O-RICH PRESOLAR SPINEL GRAIN F. Gyngard[1,2], L. R. Nittler[2], F. J. Stadermann[1], E. Zinner[1], [1]Laboratory for Space Sciences and Department of Physics, Washington University, One Brookings Drive, St. Louis, MO 63130, USA, [2]Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, DC 20015, USA, fgyngard@dtm.ciw.edu.

Introduction: Presolar grains are condensates from various stellar sources that predated the formation of the solar system [1]. These tiny dust particles formed in the stellar outflows of Asymptotic Giant Branch (AGB) stars, supernovae (SNe), and novae, spent tens to hundreds of millions of years traversing the interstellar medium [2, 3], and were subsequently incorporated into their meteoritic parent bodies.

While the majority of presolar oxide, silicate, and SiC grains most likely condensed in low-mass, close-to-solar metallicity AGB stars, a minor fraction – ~1% for SiC [4] and ~10% for oxides and silicates [5] – have isotopic compositions indicative of an origin in type II SN ejecta. For presolar SiC grains of type X, large enrichments in ^{28}Si indicate contributions from the inner Si/S zone of a SN. In addition, observations of large overabundances of ^{44}Ca, thought to be from the decay of radioactive ^{44}Ti, in a portion of both SiC X grains and presolar graphite grains [6-8] have been purported to be the so-called "smoking gun" for a true SN origin. Titanium-44 is primarily produced by α-rich freeze-out in the Si and Ni rich core of type II SNe [9, 10].

In contrast to carbonaceous SN grains, which clearly contain isotopic signatures originating from the deep interiors of the SN, group 4 oxide grains have been hypothesized to have condensed mostly from a mixture of the H-envelope and He/C zone material in the outer SN layers [11]. The He/C zone is enriched in ^{18}O and contribution from this zone is required to explain the ^{18}O excesses observed in group 4 grains; however, it remains unclear why so few ^{16}O rich presolar grains have been found, as SN are prodigious at synthesizing this isotope. Here we report the discovery of a presolar spinel grain highly enriched in ^{16}O which also has radiogenic ^{44}Ca from the decay of ^{44}Ti, unequivocal evidence for a SN origin.

Experimental: A residue (termed "CG") of the Murray CM2 chondrite, prepared by physical and chemical separation [12] and mostly consisting of spinel grains (average diameter ~0.5 μm), was automatically analyzed in the Washington University NanoSIMS as described in [13]. For this work, 312 20x20 μm^2 areas were presputtered with a high current (several 100 pA) Cs$^+$ primary beam to remove surface contamination and implant Cs; an ~1pA, 100nm Cs$^+$ beam was then rastered over the area and secondary ion images of ^{16,17,18}O$^-$, ^{24}MgO$^-$, and AlO$^-$ were simultaneously obtained; discrete grains were automatically identi-

fied and sorted by a particle definition algorithm; individual grain isotopic measurements were taken by deflecting the primary beam and rastering over each grain. The sample stage was then moved and the entire process repeated on a new area. In this manner, ~ 4000 individual measurements were performed. A unique advantage of our technique when compared to previous automated systems developed for the NanoSIMS [14] is full integration into the instrument's acquisition software, in principle allowing for greater measurement flexibility.

Auger spectra and high-resolution SEM images of the grains identified as presolar were taken with the Washington University Auger Nanoprobe, in order to document their elemental composition and mineralogy, as well as to relocate them. For roughly a quarter of the automatically measured presolar grains, the SEM images indicated that the actual particles identified and measured by the system were composites of multiple grains. Removal of the surrounding isotopically normal particles with the NanoSIMS Cs$^+$ beam, as described by [15], revealed at least 2 of the grains to be significantly more anomalous in their O isotopic compositions than the automated measurement indicated.

For the grains in which enough material remained, we measured ^{24,25,26}Mg$^+$ and ^{27}Al$^+$ in multicollection with an ~10 pA, 0.5 – 1.0 μm O$^-$ primary beam. A particularly interesting grain, discussed below, was further characterized in a separate measurement of ^{39,41}K$^+$, ^{40,42,43,44}Ca$^+$, and ^{47,48}Ti$^+$ with a combination of multidetection and magnetic peak switching. Although beam blanking was used, the larger spot size of the O$^-$ primary beam compared to the Cs$^+$ beam made contamination due to beam overlap difficult to eliminate during this analysis. A perovskite standard was used for normalization of the Ca-Ti isotopic compositions and a relative sensitivity factor of 2.83 between Ca and Ti (determined from a NBS 610 glass) was assumed.

Results and Discussion: SEM and NanoSIMS images showed grain 7-5-7 to be an ~400nm in diameter grain directly touching an isotopically normal grain, and remeasurement of its O isotopes after removal of the nearby grain revealed 7-5-7 to be extremely ^{16}O-rich (Fig. 1). Out of the ~1000 presolar O-rich grains discovered to date, only 2 other grains have comparable O isotopic compositions: another ^{16}O-rich grain, T84 [16], and a unique ^{17}O-depleted and ^{18}O-enriched grain, B10A [17]. For the sake of comparison, the O isotopic ratios of presolar hibonite grain KH2 [5], the

only O-rich grain before this study with evidence for [44]Ti, are also displayed. Grain 7-5-7 has a large depletion in [25]Mg (δ^{25}Mg-value of -276 ± 10‰) and essentially solar [26]Mg (δ^{26}Mg-value of 13 ± 12‰). Due to the small size of this grain, very little material remained after the Mg-Al measurement, and analytical uncertainties for subsequent measurements are large. In addition, K, Ca, and Ti are present only as trace elements, and minor element abundances are lower in presolar oxides than in other phases, such as SiC. No counts of [42]Ca and [43]Ca were recorded, and the calculated [41]K/[39]K and [47]Ti/[48]Ti ratios are normal within errors; however, the grain has a [44]Ca/[40]Ca ratio of 1.3, corresponding to a [44]Ca excess of ~58,000‰. This leads to an inferred [44]Ti/[48]Ti ratio of (3.6 ± 0.8) x 10^{-3}, comparable (albeit somewhat lower) to what has been observed for many presolar SiC and graphite grains. The inferred [44]Ti/[48]Ti ratio of KH2 is 0.13, significantly higher than that of grain 7-5-7; however, although we tried to avoid nearby contamination, any terrestrial Ti would reduce the calculated [44]Ti/[48]Ti ratio. Such dilution of the grain's true [44]Ti/[48]Ti ratio likely occurred, as we observed an unexpectedly high [48]Ti^{+}/[40]Ca^{+} ratio, perhaps from material leftover from the nearby grain. However, an explanation for why there would be much more Ti than Ca contamination is unknown. Regardless, the inferred [44]Ti/[48]Ti ratio reported above is likely a lower limit.

Simple two component mixing of variable amounts of material from the He/C zone with the O-rich inner zones from a 15M$_\odot$ SN model [18] can reproduce the O isotopic composition of both grains 7-5-7 and T84 (Fig. 1). Not surprising, however, is that granular mixing of more SN layers is required to fit the multiple element isotope data of 7-5-7. Mixing of variable amounts of SN ejecta from 5 individual layers of the same SN model of [18] can match the grain's O and Mg isotopic compositions to about 5-15%, but overproduce the [44]Ti/[48]Ti ratio by at least a factor of 2.7 (Fig 2). New model simulations of a 15M$_\odot$ SN by [19] yield much better agreement between the predictions and grain data, and, although the fit is slightly worse for the O isotopic composition, the measured and calculated [44]Ti/[48]Ti ratios agree within the one sigma analytical uncertainty. The dearth of ^{16}O-rich grains from SNe must indicate a fundamental difference in formation history from that of the group 4 grains. Perhaps dust condensing from inner zone material is predominately smaller (< 50nm) in size and more efficiently destroyed by sputtering in reverse shocks [20] or less efficiently detected. Future searches, aided by automated techniques, will hopefully uncover more such grains.

References: [1] Zinner E., (2007) in: *Treatise on Geochemistry,* (eds. H.D. Holland and K. K. Turekian), pp. 1-33. [2] Gyngard F. et al. (2009) *ApJ 694*, 359. [3] Heck P.R. et al. (2009) *ApJ 698*, 1155. [4] Hoppe P. et al. (2000) *Meteoritics &. Planet. Sci. 35*, 1157. [5] Nittler L.R. et al. (2008) *ApJ 682*, 1450. [6] Amari S. et al. (1992) *ApJ 394*, L43. [7] Nittler L.R. et al. (1996) *ApJ 462*, L31. [8] Besmehn A. and Hoppe P. (2003) *GCA 67*, 4693. [9] Woosley S.E. and Weaver T.A. (1995) *ApJS 101*, 181. [10] Timmes F.X. et al. (1996) *Astrophys. J.* 464, 332. [11] Choi B.-G. et al. (1998) *Science* 282, 1284. [12] Tang M. et al. (1988) *GCA 52*, 1221. [13] Gyngard F. et al. (2009) *LPS XL*, Abstract #1386. [14] Gröner E. and Hoppe P. (2006) *Appl. Surf. Sci. 252*, 7148. [15] Zinner E. and Gyngard F. (2009) *LPS XL*, Abstract #1046 [16] Nittler L.R. et al. (1998) *Nature* 393, 222. [17] Messenger S. et al. (2005) *Science* 309, 737. [18] Rauscher T. et al. (2002) *ApJ 576*, 323. [19] Woosley S.E. and Heger A. (2007) *Phys. Rep. 442*, 269. [20] Nozawa T. et al. (2007) *ApJ 666*, 955.
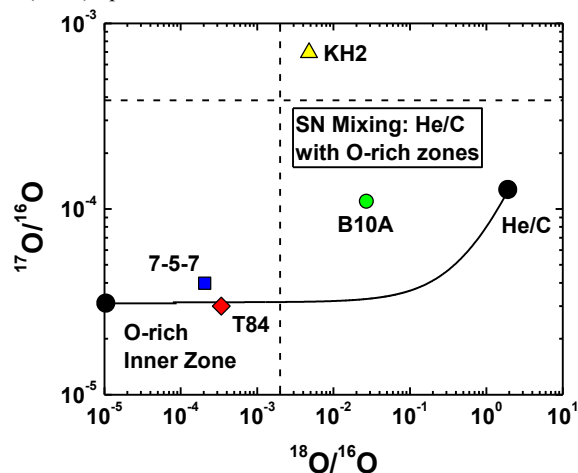
Figure 1. Oxygen 3-isotope plot of the composition of grain 7-5-7, along with the other ^{16}O-rich and [16,18]O-rich grains discovered so far [16, 17]. Also plotted is KH2, a group 4 presolar hibonite which has a [44]Ca excess from the decay of [44]Ti [5].
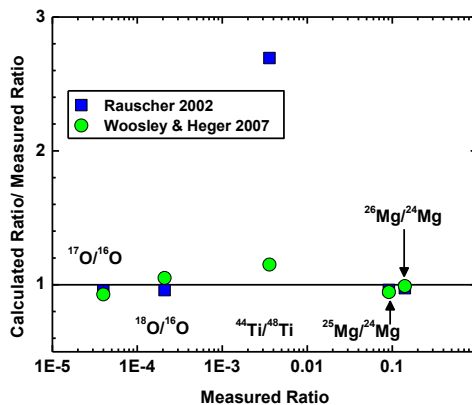
Figure 2. Plot of calculated isotopic ratios for mixtures of various SN zones for 15M$_\odot$ models from [18] and [19] relative to those of grain 7-5-7.