Introduction: Interstellar and circumstellar silicate grains are thought to be Mg-rich and Fe-poor, based on astronomical observations and equilibrium condensation models of silicate dust formation in stellar outflows [1-3]. On the other hand, presolar silicates isolated from meteorites have surprisingly high Fe contents and few Mg-rich grains are observed [4 and references therein]. The high Fe contents in meteoritic presolar silicates may indicate they formed by a non-equilibrium condensation process [1]. Alternatively, the Fe in the stardust grains could have been acquired during parent body alteration [5].

The origin of Fe in presolar silicates may be deduced from its isotopic composition. Thus far, Fe isotopic measurements of presolar silicates are limited to the $^{54}$Fe/$^{56}$Fe ratios of 14 grains [6,7]. Only two slight anomalies (albeit solar within error) were observed. However, these measurements suffered from contamination of Fe from the adjacent meteorite matrix, which diluted any isotopic anomalies. We have isolated four presolar silicates having unusual O isotopic compositions by focused ion beam (FIB) milling and obtained their undiluted Mg and Fe isotopic compositions. These compositions help to identify the grains’ stellar sources and to determine the source of Fe in the grains.

Experimental: Silicate matrix grains separated from the Acfer 094 meteorite were analyzed by raster ion imaging on the NanoSIMS 50L ion probe. Anomalous grains were identified by simultaneous ion imaging of O and Si isotopes, and $^{24}$Mg/$^{18}$O using a Cs$^+$ primary ion beam. Two grains having enrichments in $^{18}$O, one grain depleted in $^{17}$O and $^{18}$O, and one grain with an extremely large $^{17}$O enrichment were selected for further isotopic study. Based on the $^{28}$Si/$^{16}$O ratios, these grains are likely silicates.

While Fe isotopes can be measured as FeO using the Cs$^+$ primary beam, the same cannot be done for Mg isotopes due to mass interferences. Fe and Mg isotopes were measured as positive secondary ions using the O$^+$ primary ion beam. Two grains having enrichments in $^{18}$O, one grain depleted in $^{17}$O and $^{18}$O, and one grain with an extremely large $^{17}$O enrichment were selected for further isotopic study. Based on the $^{28}$Si/$^{16}$O ratios, these grains are likely silicates.

54Cr corrections were only ~1% for all grains. Matrix grains within the same image were used as isotopic standards. In a second measurement step, the Mg isotopes, $^{27}$Al, and $^{56}$Fe were analyzed by ion imaging.

Results and Discussion: Silicates enriched in $^{18}$O. Grains 6_5a and 6_16 are highly enriched in $^{18}$O and are classified as Group 4 grains [8] (Fig. 1). There is mounting evidence that most, if not all, Group 4 grains originated in supernovae (SNe). Grain 6_5a was found to be enriched in $^{26}$Mg and depleted in $^{25}$Mg, while 6_16 does not show any Mg anomalies (Fig. 2). These compositions are similar to those previously observed. The Si and Fe isotopic compositions for both grains are solar within error.

Figure 1. O isotopic ratios of presolar silicates from this study and presolar grains of likely SN or nova origins that have been measured for Mg isotopes [8-12].

The isotopic and elemental compositions of these grains constrain the mass and metallicity (Z) of their parent stars and the proportions of SN zones that must have been mixed to form each grain. The O, Mg, Si, and $^{54}$Fe/$^{56}$Fe isotopic ratios of 6_5a and 6_16 can be reproduced by mixing a small fraction of inner zone material with the outer zones of a 15M$_\odot$ SN [13], given the $^{29}$Si yield in the O/Ne and O/Si zones are doubled [14]. These mixes include material from the very $^{54}$Fe- and $^{56}$Si-rich Si/S zone, which is required to counter the elevated $^{28}$Si/$^{26}$Si from the O-rich zones. The lack of $^{54}$Fe enrichments in our grains is puzzling, but is consistent with SiC X grains from SN [15] that also have material from the Si/S zone, and with one
other Group 4 silicate [7]. Conversely, one $^{18}$O-rich, slightly $^{54}$Fe-rich silicate [6], and one $^{18}$O-rich, $^{54}$Fe-poor FeO grain [16] were argued to have AGB origins.

Figure 2. Mg isotopic ratios of the presolar grains shown in Fig. 1. Two extremely $^{26}$Mg-rich oxides are not shown.

To explain the relatively small Fe anomalies in SiC X grains, it was suggested that Fe implantation from collisions with reverse shocked gas could dilute the $^{54}$Fe enrichment, perhaps to the initial abundance of the pre-supernova star [17]. However, this model also predicts implantation of $^{26}$Al, which is not observed in the presolar silicates or SiC X grains. Marhas et al. [16] instead suggested chemical fractionation of Fe and Si to explain the Fe isotopic ratios. Of course, SN silicates are observed to be Mg-rich [18] and it is possible that the Fe in our grains was acquired after grain condensation. This Fe diffusion likely would have occurred by thermal metamorphism [5]. Indeed, the Acfer 094 silicate matrix is rather Fe-rich. However, our current data do not unequivocally support primary or secondary origin of Fe.

Silicate depleted in $^{17}$O and $^{18}$O. Grain 2_3a is enriched in $^{16}$O and classified as a Group 3 grain. Such grains are proposed to originate either from low-Z stars, or in SN outflows. The O isotopic compositions of grains lying above the galactic chemical evolution (GCE) trend (Fig. 1) are well explained by low-Z stellar sources. Compositions falling below the trend, such as silicate 2_3a, cannot be similarly explained and may have SN origins. Group 3 grains are rare and this is the first Group 3 silicate to be measured for Mg or Fe isotopes. The Mg, Si, and Fe isotopic compositions of grain 2_3a are too low for a low-Z stellar source. For comparison, a very $^{16}$O-rich spinel grain has a $\sim$28% $^{26}$Mg depletion but normal $^{26}$Mg/$^{24}$Mg [13]. Performing the same SN mixing exercise for 2_3a as for the Group 4 silicates, we similarly find that all isotopic ratios can be replicated save for the $^{54}$Fe/$^{56}$Fe ratio. The inner $^{16}$O-rich zones have large $^{29,30}$Si enrichments, which again can be offset by material from the $^{54}$Fe-rich Si/S zone. Of course this zone mix is not a unique solution. Inclusion of material from the Ni core instead of the Si/S zone would also produce solar Si isotopic ratios, but this would generate $^{54}$Fe depletions and $^{53}$Fe enrichments. If Fe and Si are chemically fractionated in these zones, or if the Fe is secondary, then the results for 2_3a support the theory that similar Group 3 grains and Group 4 grains may have condensed in the outflow of a single SN [9].

Highly $^{17}$O-rich silicate. Grain 4_2 has one of the most extreme $^{17}$O enrichments observed among presolar silicate and oxide grains. The large $^{17}$O enrichments of these grains cannot be produced in AGB stars [19], but novae are potential sources. 4_2 was found to be very $^{25}$Mg-rich, similar to another potential nova oxide [13], and moderately $^{26}$Mg-rich. The Si and Fe isotopic ratios are solar within error. CO nova models [20] can explain the $^{17}$O enrichment and normal Si isotopic ratios of 4_2, but greater $^{25,26}$Mg enrichments, and much larger $^{16}$O depletions are expected. The nova models do not yet include predictions for Fe. The less extreme compositions of 4_2 could be explained by isotopic exchange in the circumstellar environment [10].

Overall, the Fe isotopic ratios of the presolar silicates are closer to solar composition than expected. In the case of SN grains, these data may be explained by either chemical fractionation in the Si/S or Ni zones, or Fe incorporation into the grain after condensation. Given the uncertainties in the SN mixing models and isotopic measurements we cannot distinguish between these possibilities at present and further studies must be conducted.