HIGH-PRECISION RESONANCE IONIZATION MASS SPECTROMETRY: APPLICABILITY TO PRESOLAR GRAINS.

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Introduction: The extremely high sensitivity and elemental selectivity afforded by resonance ionization mass spectrometry makes the technique uniquely suitable for isotopic analysis of trace elements in individual presolar grains. Our group has previously measured Sr, Zr, Mo, Ru, and Ba isotopes in presolar SiC grains [1–6], finding anomalous abundances that are characteristic of nucleosynthesis in asymptotic giant branch stars [7,8]. Most of these isotopic effects cannot be measured in individual presolar grains by secondary ion mass spectrometry (SIMS), because of the very low concentration of these elements (~10 ppm), or because of isobaric interferences (e.g., ^{96}Zr, ^{96}Mo, and ^{96}Ru) unresolvable by present-day SIMS instruments. In resonance ionization mass spectrometry, sputtered or desorbed neutral atoms are selectively ionized by lasers tuned to excite electronic transitions in an element of interest. Potentially interfering isobars are nearly transparent to the laser radiation, and therefore are scarcely ionized and detected. On the other hand, secondary neutral atoms of the element of interest (which typically outnumber secondary ions by orders of magnitude) can be ionized and detected very efficiently.

We are improving the isotopic precision achievable by resonance ionization mass spectrometry of presolar SiC grains, to enable much finer tests of stellar nucleosynthesis models. The deficits of p- and r-process isotopes in mainstream SiC grains relative to isotopes made only by the s-process are so extreme that only modest precision is required to detect them. For example, [1] reported δ^{96}Zr values between −432‰ and −983‰ for 10 SiC grains from the Murchson meteorite. However, high precision and reproducibility are necessary to study Cr and Fe isotopes, which, except for >100‰ enrichments in the most neutron-rich species, are thought to vary by only ~10‰ from their Solar System abundances [7,8]. We anticipate making the first ever high-precision, low-interference isotopic measurements of trace elements in individual presolar grains.

Resonance Ionization of Iron-Peak Elements. The largest nucleosynthetic signatures among Cr and Fe isotopes occur on ^{54}Cr and ^{58}Fe, neither of which can be resolved by SIMS instruments from their respective isobars ^{54}Fe and ^{58}Ni. The SIMS-accessible

Fe isotopes have been studied by [9]; however, resonance ionization enables the measurement of all the stable Cr and Fe isotopes because isobaric interferences are effectively suppressed. Figure 1 shows a mass spectrum we obtained by resonance ionization of Cr from NIST SRM 1264a steel. Though the Cr/Fe ratio in the sample is only 6.8×10^{-4}, the selectivity of our resonance ionization scheme is such that we detect ~100 Cr ions for every Fe ion. The suppression of Fe counts by a factor of 10^5 will render this interference negligible when we measure Cr isotopes in a non-ferrous material, such as presolar SiC. Similarly, we expect negligible interference from ^{58}Ni when we measure Fe isotopes in presolar SiC.

Molecular interferences from SiC are also negligible, provided that all our lasers operate at wavelengths longer than ~300 nm, so that non-resonant ionization of species such as SiC_2 and Si_2 is unimportant. We have therefore adopted a three-step resonance ionization scheme for Cr. The first step (427.600 nm) excites atoms in the **a** $^7S_3$ ground state to the **z** $^7P_3^o$ state at 23,386 cm^{-1}. A second step (449.296 nm) raises atoms in this excited level to the **f** $^7S_3$ state 45,643 cm^{-1} above the ground state. These two transitions are induced by frequency-doubled Ti:sapphire lasers. A final step uses a Nd:YAG laser at 1064 nm to raise the twice-excited atoms above the ionization threshold at 54,575 cm^{-1}.
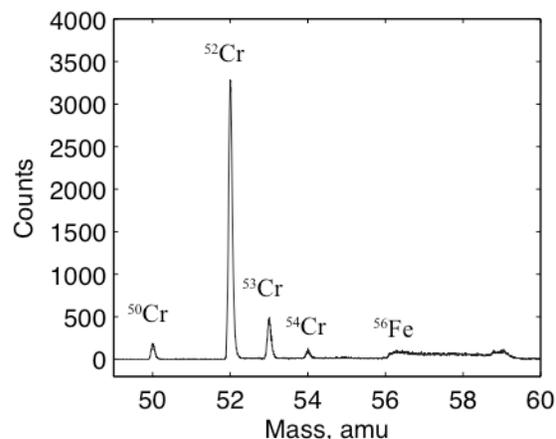

Figure 1: Mass spectrum of resonantly ionized Cr from NIST SRM 1264a shows little interference from Fe.

Isotopic Precision. We tested and rejected an alternative, two-step resonance scheme for Cr, in which atoms were excited by 236.663 nm radiation to the $x\ ^7P^o_3$ level at 42,254 cm^{-1}, and then were ionized by 807.2 nm photons. In addition to finding unacceptably large backgrounds from non-resonant ionization of SiC_2 and Si_2 from SiC, we also observed large fluctuations in measured ratios of Cr isotopes that were due to slight drifts in the wavelength of the 236.663 nm laser. Even at their most stable, the mean wavelengths of our lasers drifted by ~0.005 nm, possibly due to ~1 °C fluctuations in ambient temperature, and this was sufficient to change isotope ratios by 1000‰ (Figure 2, open symbols). We have observed even greater sensitivity to wavelength among Fe isotopes, when using a two-step resonance scheme with a 226.021 nm first step. Measurements made on standards using these resonance ionization schemes had χ^2 between 40 and 250 per degree of freedom; much greater reproducibility was clearly needed to determine the Cr and Fe isotopic composition of presolar SiC grains.

The root cause of this isotopic imprecision was insufficient luminosity at 236.663 nm to power-broaden the atomic transition, which occurs at very slightly different wavelengths for each isotope. We had generated the 236.663 nm laser beam by frequency-quadrupling a Ti:sapphire beam, an inherently inefficient process that provided, in our case, only ~30 µJ per laser pulse. This represents 2–3 times the power necessary to saturate the atomic transition, implying

that we could power-broaden the transition by a factor of only 2–3 relative to the inherent linewidth. Without enough power to smear out the isotope shifts in the atomic line, even small drifts in the laser wavelength produced intolerably large isotopic fractionation.

We have remedied this problem in two ways. First, the three-step resonance ionization scheme we have adopted for Cr requires frequency-doubled, rather than quadrupled, Ti:sapphire beams, in which we deliver 100–170 µJ per laser pulse. This appears to be 10–20 times the saturation power for the respective transitions, and we observe power-broadened line profiles ~0.015 nm wide. The spectral line broadening removes the wavelength sensitivity of the measured isotope ratios (Figure 2, closed symbols). Second, we have implemented a system of active feedback control on our tunable lasers, which keeps the mean wavelength constant within <0.001 nm. With these two improvements, we now make repeated measurements on standards in which we obtain <10‰ statistical uncertainties with $\chi^2 \approx 1$ per degree of freedom.

Conclusions. With Poisson-limited reproducibility and precision at the sub-percent level, we can attempt the first high-precision, four-isotope measurements of Cr and Fe in presolar SiC grains. The abundances of ^{54}Cr and ^{58}Fe will test stellar nucleosynthesis models [7,8], constrain neutron fluxes in thermally pulsing asymptotic giant branch stars, and ultimately help assess the extent of mixing in the solar nebula [10]. The abundances of the lighter isotopes, which are scarcely modified by nucleosynthesis in the asymptotic giant branch stars where the grains condensed, may allow us to glimpse nucleosynthetic signatures from an earlier generation of stars.

References: [1] Nicolussi G. K. et al. (1997) *Science 277*, 1281–1283. [2] Nicolussi G. K. et al. (1998) *Phys. Rev. Lett. 81*, 3583–3586. [3] Nicolussi G. K. et al. (1998) *Geochim. Cosmochim. Acta 62*, 1093-1104. [4] Savina M. R. et al. (2003) *Geochim. Cosmochim. Acta 67*, 3201–3214. [5] Savina M. R. et al. (2004) *Science 303*, 640–652. [6] Barzyk J. G. et al. (2006) *New Astron. Rev. 50*, 587–590. [7] Gallino R. et al. (1998) *Astrophys. J. 497*, 388–403. [8] Busso M. et al. (2001) *Astrophys. J. 557*, 802–821. [9] Marhas K. K. et al. (2007) *LPSC 38*, abstr. 2124. [10] Trinquier A. et al. (2007) *Astrophys. J. 655*, 1179-1185.

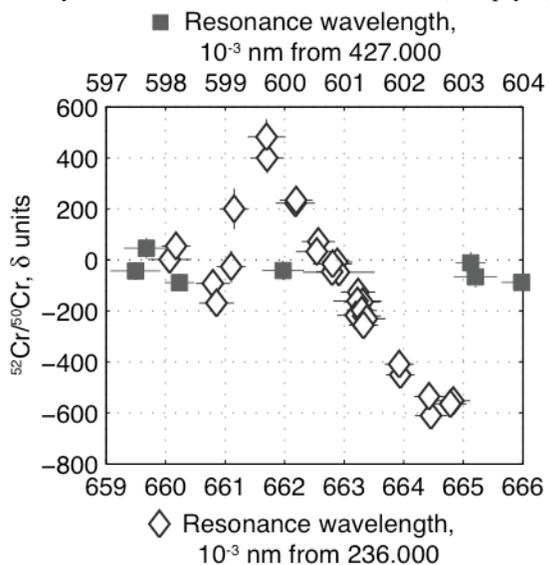**Figure 2:** Isotope ratios ($^{52}Cr/^{50}Cr$ ratio is shown) are much less sensitive to small fluctuations in laser wavelength when atomic transitions are effectively power-broadened (closed symbols, top axis) than when they are not (open symbols, bottom axis). Error bars 1σ.