THE ^{53}Mn-^{53}Cr SYSTEM IN CAIs: AN UPDATE. D. A. Papanastassiou[1,2], G. J. Wasserburg[2], and O. Bogdanovski[2,3], [1]Div. Earth and Space Sci., Jet Propulsion Laboratory, MS 183-335, Pasadena, CA 91109-8099, [2]Div. Geol. Planet. Sci., Caltech, MC 170-25, Pasadena, CA 91125, [3]Current address, MPI-Chemie, Cosmochemie, PO 3060, 55020 Mainz, Germany (Dimitri.A.Papanastassiou@jpl.nasa.gov).

High precision techniques have been developed for the measurement of Cr isotopes on the Triton mass spectrometer, at JPL. It is clear that multiple Faraday cup, simultaneous ion collection may reduce the uncertainty of isotope ratios relative to single Faraday cup ion collection, by the elimination of uncertainties from ion beam instabilities (since ion beam intensities for single cup collection are interpolated in time to calculate isotope ratios), and due to a greatly increased data collection duty cycle, for simultaneous ion collection. Efforts to measure Cr by simultaneous ion collection have not been successful in the past. Determinations on $^{50-54}$Cr, by simultaneous ion collection on the Finnigan/MAT 262 instrument at Caltech, resulted in large variations in extrinsic precision, for normal Cr, of up to 1‰ in ^{53}Cr/^{52}Cr (data corrected for mass fractionation, using ^{50}Cr/^{52}Cr). We attributed these variations to the large relative mass difference of Cr isotopes (~8%) and to effects of z-focusing in instruments, with non-normal ion beam entry and exit, and possibly due to trimming of outer ion beams, by the vacuum envelope. These effects are expected to be dependent on variations in the position of the sample filament and on ion source focusing conditions. For samples without ^{54}Cr/^{52}Cr anomalies, techniques were attempted, on the F/MAT 262, for the measurement of ^{53}Cr/^{52}Cr by simultaneous data collection, over only half the mass range, for ^{52,53,54}Cr, and using ^{54}Cr/^{52}Cr for normalization. Given the lower abundance (by ~×2) of ^{54}Cr relative to ^{50}Cr, higher intensity ion beams were used (~8×10^{-11} A, for ^{52}Cr^{+}). However, the resulting data still showed variations between repeat analyses of normal Cr (extrinsic precision) by up to 1εu. This was much larger than the intrinsic precision of each run and is inadequate for measurement of the small effects in ^{53}Cr (at the level of 1.5εu due to ^{53}Mn decay, for the observed range in Mn/Cr). The F/MAT 262 has a mass dispersion acceptance of 10%, while the Triton has an increased mass acceptance of 15%. This suggested that static measurements, on the Triton for $^{50-54}$Cr would be an improvement over the F/MAT 262 instrument. Initial efforts at simultaneous ion collection for $^{50-54}$Cr on the Triton, yielded variations in ^{53}Cr/^{52}Cr of 1εu, which was a clear improvement, but still not satisfactory. With the ion beam zoom capability of the Triton, a peak-jumping technique for the measurement of Cr was developed using two "configurations", corresponding to ^{52,53,54}Cr (1st configuration)

and to ^{50,52}Cr (2nd configuration). A data cycle consists of data collection with the 1st configuration followed by switching the B-field to the 2nd configuration. This technique reduces the effective mass dispersion range to 3.8%, for both configurations and utilizes the L1 and H1 cups, with ^{53}Cr or mass 51 (e. g., ^{51}V) in the Center cup, for the two configurations, respectively. The chemical separation for Cr eliminates V and Ti, so that there is no V^{+} or Ti^{+} ions during the Cr runs and no mass interference at mass 50 from from ^{50}Ti or ^{50}V (^{50}V/^{51}V~0.1%). Interference at mass 54 from Fe was eliminated through anion separation of Fe as the chloride complex and found to be negligible. Samples were analyzed with a cold trap in the ion source region to reduce hydrocarbons. For the Triton, the ion beam zoom is adjusted to center the ^{50}Cr and ^{52}Cr ion beams, in the L1 and H1 cups (those adjacent to the Center cup), while the cups remain stationary with their positions having been determined (with the zoom turned off) by centering of the ^{52}Cr and ^{54}Cr beams (with ^{53}Cr centered in the Center cup). An analysis consists of 180 data cycles, with the ion beams integrated for 64 seconds for each configuration for each data cycle, at an intensity for ^{52}Cr^{+} of (5-6)×10^{-11} A . The long ion beam integrations are consistent with the absence of the need for interpolation of ion beam intensities with time. Similarly, small instabilities inherent in ion emission from the borosilicate matrix (silica gel + boric acid) do not adversely effect the data precision. With this arrangement, we obtained extrinsic reproducibility for ^{53}Cr/^{52}Cr and for ^{54}Cr/^{52}Cr of 24 ppm and of 55 ppm, respectively (both 2σ), after normalization (within each data cycle) of ^{53}Cr/^{54}Cr and ^{54}Cr/^{52}Cr from the 1st configuration, for isotope fractionation using the ^{50}Cr/^{52}Cr from the 2nd configuration. The intrinsic precision for each run was typically a factor of three better, but not a sufficient determinant of reproducibility. The time sequence of the data on Cr normals are shown in Fig. 1 and 2, for ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr, respectively. We also show the sequence of analyses of Cr extracted from the Allende Egg-3, coarse-grained, Type B, CAI, with the analyses of Egg-3 interleaved with the sequence of analyses of normal Cr. The samples analyzed correspond to Cr extracted from a pyroxene mineral separate from Egg-3 and to the spinel-rich residue from dissolution of the pyroxene separate. The spinel was dissolved in a Teflon bomb, using standard procedures (HF+HNO$_3$). We

note that the data for each analysis require about 4 hours and that the extrinsic precision allows duplicate analyses to yield the same precision as obtained by ~20 analyses of data collected over many days using a single Faraday cup [1]. The scheme presented here represents a substantial improvement in sensitivity and in precision.

The Mn-Cr data for Egg-3 are shown in an evolution diagram in Fig. 3. There is good agreement between the data using the Triton and the data from earlier work at Caltech, on the Lunatic I, using a larger number of analyses [2]. If we interpret the Mn-Cr data on Egg-3 as an isochron, the data on Egg-3 yield an initial $(^{53}Mn/^{55}Mn)_0$ of 14.8×10^{-5} and an initial $(^{53}Cr/^{52}Cr)_0$ of -169 ppm. The presence of a deficit in $(^{53}Cr/^{52}Cr)_0$ is considered consistent with early formation and with the presence of live ^{53}Mn. The pioneering work of Birck and Allègre [3] on Mn-Cr also identified a negative $(^{53}Cr/^{52}Cr)_0$ for the Allende CAI, BR1 and a similar initial ^{53}Mn. Based on earlier work [2] and on [3], we have obtained a range in initial $(^{53}Mn/^{55}Mn)_0$ for Allende CAIs. Using the Mn-Cr data on Allende BR1 [3] as reference, the data on coarse inclusions Egg-2, Egg-3, Egg-6, and Big-Al (obtained using single Faraday cup data collection, on the Lunatic I, [2]) show a range of $^{53}Mn-^{53}Cr$ formation time intervals +7, +6, -3, and -7 Ma, respectively. These time intervals are not consistent with the data for the $^{26}Al-^{26}Mg$ system, available for Egg-3 and for Egg-6 [4, 5]. Our conclusion has been that, for Allende, alteration of the inclusions has resulted in disturbed Mn-Cr systematics, through diffusion of Mn. We note that the $^{54}Cr/^{52}Cr$ endemic effects for Egg-3 pyroxene and coexisting spinel (Fig. 2) are distinct and that the $^{54}Cr/^{52}Cr$ effects are correlated with Fe/Cr (lower $^{54}Cr/^{52}Cr$ for higher Fe/Cr). The current Mn-Cr data [2, 3] suggest the preservation of effects in Allende refractory inclusions, due to live ^{53}Mn in the early solar system, as well as the preservation of primitive initial $(^{53}Cr/^{52}Cr)_0$ values, significantly lower than for normal Cr and for diffrentiated meteorites [1]. The presence of only small ^{53}Cr effects in FUN inclusions, accompanying very large ^{54}Cr effects [6, 7] suggests that the effects in ^{53}Cr for non-FUN CAIs may reasonably be expected to reflect effects due to ^{53}Mn decay rather than preserved nucleosynthetic heterogeneity. We are currently analyzing less altered CAIs from Efremovka and from Leoville, in an effort to identify evidence for less disturbed Mn-Cr systems. These measurements will take advantage of the analytical developments described here. They same techniques are also applicable to high precision Ca isotope measurements.

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Fig. 1

Fig. 2

Fig. 3
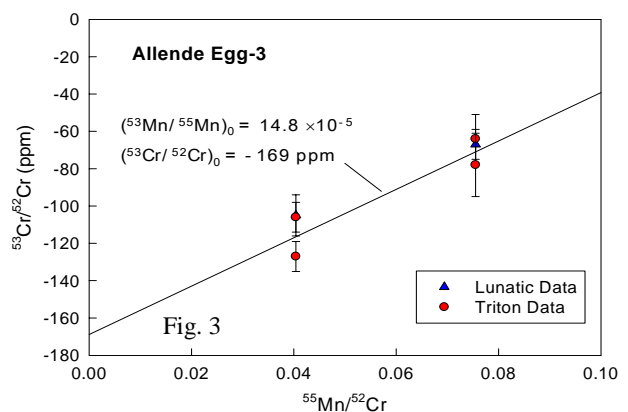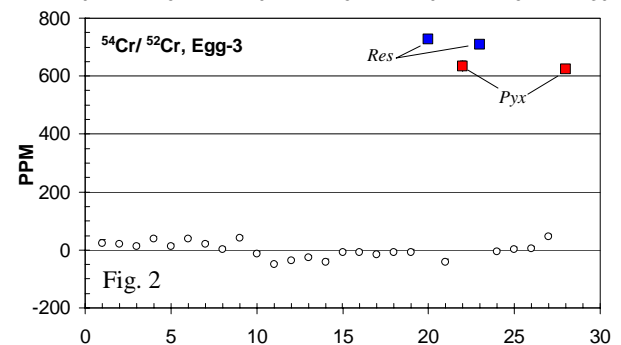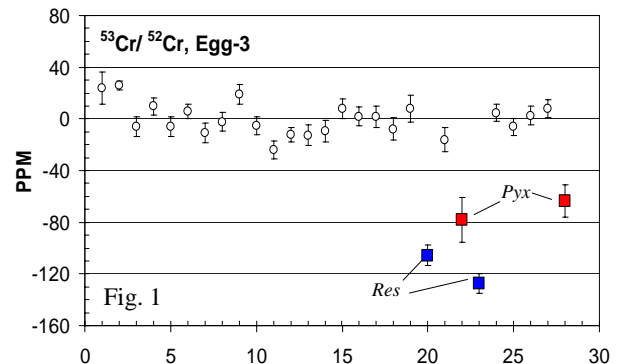
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