INITIAL CR-ISOTOPIC AND IRIDIUM MEASURMENTS OF CONCENTRATES FROM LATE-EOCENE CPX-SPHERULE DEPOSITS. Frank. T. Kyte[1], Alex Shukolyukov[2], Alan R. Hildebrand[3], Guenter W. Lugmair[2,4], and Jana Hanova[3]. [1]Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90095-1567, kyte@igpp.ucla.edu, [2]Scripps Institution of Oceanography, University of California, San Diego, La Jolla CA 92093-0212, [3]Department of Geology and Geophysics, University of Calgary, Calgary AB Canada T2N 1N4, [4]Max-Planck-Instute for Chemistry, Cosmochemistry PO 3060, 55020 Mainz, Germany.

Introduction. In this study we attempt to constrain the provenance of the late Eocene impactor that produced global ejecta containing clinopyroxene-bearing (cpx) spherules. The late Eocene (~35 Ma) was a time of multiple impacts (see refs in [1]). At least two spherule layers are in deep sea sediments: North American (NA) microtektites and the slightly older cpx spherules. The two largest impact structures in the Cenozoic, the 100 km Popigai structure and the 45 km Chesapeake Bay structure [2,3] formed at this time. NA microtektites have a regional distribution - restricted to an area extending from the western N. Atlantic to the Caribbean Sea. They are not associated with anomalous PGEs, and their Nd and Sr isotopic compositions are consistent with derivation from Chesapeake Bay [4]. The cpx-spherule strewnfield was extended from numerous low-latitude sites to the sub Antarctic, where cpx and glassy spherules were found with an Ir anomaly in ODP Hole 689B [5,1]. This implies that the cpx-spherule layer is global in extent. Glassy spherules in 689B are isotopically similar to cpx-spherules, and not NA microtektites [5,6]. Their isotopic abundances are consistent with Popigai as the source crater [4]. Ir anomalies have been reported at 17 cpx-spherule localities [7] and the average Ir fluence at these sites is ~11 ng Ir cm^{-2}. By comparison, the average for the K/T boundary is ~55 ng Ir cm^{-2} [8].

The provenance of the late Eocene impactors has been attributed to both comets and asteroids/ordinary chondrites. Enhanced ^{3}He for ~3 m.y. in upper Eocene sediments from the Massignano quarry in Italy were explained by a comet shower [9]. ^{3}He is a tracer of fine-grained (<50 µm) interplanetary dust (IDP), which has high concentrations of solar-wind implanted ^{3}He. Because IDPs have dynamic lifetimes on the order of 10^5y, a random Oort Cloud perturbation is a suitable mechanism to maintain elevated IDPs (and ^{3}He) over 3 m.y. [10]. The oxidation state of Ni-rich spinels from spherules in Massignano sediments was interpreted to indicate ablation of dust particles in the atmosphere that were produced by cometary impact [13]. Geochemical approaches to infer the source of the impactors used PGE abundances in Popigai impact melt rocks [11] and Cr, Ni, and Co interelement ratios in cpx spherules [12] to infer likely projectiles from L and LL chondrite sources, respectively.

Samples and Methods. We report initial results on three samples taken from a larger suite of samples of late Eocene impact deposits. A sample from ODP Hole 709C (core 31, section 4, 145-150 cm) was disaggregated, sieved, and heavy liquids were used to concentrate spherules, which were hand picked by S. Liu. This sample produced >17,000 cpx spherules in the >125 µm fraction, abundant glassy spherules, shocked quartz, and coesite [14]. A 7 kg sample of marl (partly sorted by hand to select specimens enclosing worm tubes where impact spherules are concentrated) from the Massignano quarry, encompassing a ~5 cm thick bioturbated stratigraphic interval known to contain Ni-rich spinels, spherules, and an Ir anomaly [13], was acidified to dissolve carbonate, ultrasonically disaggregated, clay separated by suspension, sieved, and spherules and spinel phases concentrated magnetically. Shocked quartz grains were abundant in the residue of this sample. To date we have analyzed splits from the 125-250 µm cpx spherules from ODP 709C, and two fractions from the Massignano layer – a fine magnetic fraction primarily composed of individual spinel crystals and a coarser magnetic fraction that contains abundant spinel-coated spherules magnetically clumped with individual spinel grains. Splits of each sample were analyzed for minor and trace elements by instrumental activation analysis (INAA) including Ir, Cr, Fe, Ni, and Co. Low Ir in the ODP 709C sample required radiochemical purification [15]. Additional splits were analyzed for their Cr-isotopic composition, using thermal ionization mass spectrometry. Isotopic data are presented in epsilon (ε) units, where 1ε is 1 part in 10^4 and terrestrial ratios of $^{53}Cr/^{52}Cr$ are defined as $\varepsilon \equiv 0$. For high precision, in our method of data reduction we use a 'second order' mass fractionation correction based on the $^{54}Cr/^{52}Cr$ ratio [16]. This correction assumes no excess or deficit of ^{54}Cr, which is the case for most meteorite classes. Carbonaceous chondrites, however, have excess ^{54}Cr causing second order corrected ε53 values to be negative. This is a convenient and precise way to distinguish carbonaceous chondrites from the other meteorite classes [17]. Following the isotopic and chemical analyses, small splits of each sample were mounted in polished section and surveyed using a JEOL model 8200 electron microprobe using EDS and WDS analysis.

Results. Concentrations of Ir and other chemical tracers of meteoritic material vary widely between samples. Significant concentrations of Ir were found in all samples, with the highest levels in the Massignano coarse sample and the lowest in the 709C sample. In all cases, element/Ir ratios are much higher than in chondritic meteorites (e.g., Cr/Ir ratios are 50 to 100 times CI in all three samples). Possible explanations for this include 1) the projectile was not chondritic, 2) significant amounts of Cr, Fe, Ni, and Co are terrestrial, or 3) elemental fractionation due to impact (e.g., concentration of Cr in spinel in the fireball) and/or sedimentary processes have fractionated Ir from other elements. The Cr-isotopic compositions of the 709C and Massignano coarse samples are both non-terrestrial with a positive ε53, indicating a $^{53}Cr/^{52}Cr$ ratio higher than in terrestrial materials. Less precise, "raw" (not second order corrected) data showed no indication of anomalous ^{54}Cr in any samples. The Massignano fine sample has ε53 indistinguishable from terrestrial values. Microprobe surveys showed that the Massignano samples had significant terrestrial material that was probably not from the impact. The coarse sample had numerous clay spherules with Ni- and Cr-rich oxides concentrated near their rims. However, abundant amounts of smaller oxide grains occurred that were not Ni- or Cr-rich, including Ti-rich spinels. These are all likely terrestrial contaminants. A few small (≤100 µm) grains of Fe,Ni,Cr metal were also observed, which are probably flakes from the hammer and chisels used to extract these samples. The Massignano fine sample did not contain spherules and larger grains were dominated by Ti-rich terrestrial spinels. In contrast, the ODP 709C sample is a pure extract of generally well-preserved cpx spherules composed of clinopyroxene in a glass matrix indicating a substantially more benign post depositional history. Sub-micron spinels are a trace component in the 709C spherules.

Discussion. The Massignano fine sample is dominated by terrestrial components. Both the Massignano coarse and the 709C cpx samples have sufficiently high ε53 values that it is clear that a large proportion of their Cr is from meteoritic sources. Since the Massignano coarse has terrestrial components mixed in with the spherules, we believe the ε53 for this sample will be higher when we analyze a purified spherule concentrate. It is likely that these two samples are derived from similar materials produced by the same impact event, but due to the large differences in chemical compositions, this is far from certain. At first glance it is paradoxical that although the 709C sample has the highest, and thus most non-terrestrial ε53, this sample has the lowest concentrations of Ir, Cr, and Ni, but this is at least partly due to the 709C sample being free of impurities not formed by the impact.

The positive ε53 values for these samples exclude carbonaceous chondrites as a reasonable source for the meteoritic component. All measured C-chondrites [18] have excess ^{54}Cr, resulting in a negative corrected ε53. Since comets are carbonaceous, it is logical to suggest comets might also have excess ^{54}Cr, and would be ruled out as a source of the Cr in these samples. But since the Cr-isotopic composition of comets has never been measured, such a conclusion is tentative at best. An enstatite chondrite source is excluded because the ε53 for enstatite chondrites is ~0.17ε [17], significantly lower than in our samples. Our results are generally consistent with an ordinary chondrite source for the Cr; the 709C data overlap with the lower end of the known range for these meteorites. Thus our results are consistent with arguments for L or LL chondrites based on elemental ratios [11,12]. But the highly non-chondritic ratios (e.g., Cr/Ir) we measured suggest that conclusions based solely on elemental data are probably skewed by fractionation processes during the impact.

The indication of a possible ordinary chondrite source for the largest of the Late Eocene impacts is also consistent with an H chondrite projectile. We note that the ~35 Ma spike in cosmic ray exposure ages for the H chondrites [19] could derive from a major collision event in the asteroid belt. An asteroid shower initiated by disruption of a large asteroid near a Main Belt resonance can have durations as short as 5 m.y. [20], but repeated collisions of disrupted fragments would be necessary to keep dust levels sufficiently high for ~3 m.y. to explain the ^{3}He peak at Massignano. If the Late Eocene impact flux peak in multi-kilometer to dust-sized projectiles is due to an ordinary (H) chondrite asteroid disruption event, several implications for Solar System history follow: 1) observational constraints are available on asteroid shower duration, dynamics, and resultant projectiles; 2) in contrast to the cometary shower scenario, the Late Eocene shower impacts will have occurred only in the inner Solar System; 3) evidence for the existence of hypothesized periodic cometary showers related to mass extinctions [10] becomes even more tenuous as the late Eocene event has often been cited as one such example; 4) understanding the dynamical structure of the current Earth-crossing asteroid population requires knowledge of recent disruption events in the Main Belt.

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Table 1. Elemental and Cr-isotopic compositions of three late Eocene samples. Data for CI and H chondrites provided for reference [17,21]

Sample	Ir ng/g	Cr µg/g	Fe mg/g	Ni mg/g	Co µg/g	53Cr/52Cr ε53
709C 125-250µm spherules	1.6	493	37	0.85	46	0.39 ±0.03
Mass. magnetic coarse	31	8480	495	11.5	640	0.27 ±0.03
Mass. magnetic fine	3	1720	592	0.3	180	– 0.04 ±0.05
CI chondrite	465	2650	18.2	1.1	505	~ – 0.43
H chondrite	770	3500	27.2	1.71	830	~ 0.48
Terrestrial standards						0.00 ±0.03*

*- the average value for the standards measured at the same time period as the late Eocene samples.
The ε53 values are the average values obtained in repeat measurements: several dozens of runs (300 ratios each). The presented uncertainties for ε53 are 2σ mean.