

Distribution of U, Th, Pb and Nd between minerals in chondrules and CAIs. Y. Amelin¹, R. Stern¹, and A.N. Krot², ¹Geological Survey of Canada, 601 Booth St., Ottawa, ON, Canada, K1A 0E8, yamelin@NRCCan.gc.ca, rstern@NRCCan.gc.ca, ²Hawaii Institute of Geophysics and Planetology, SOEST, University of Hawaii at Manoa, Honolulu, HI 96822, USA, sasha@higp.hawaii.edu.

Introduction: Knowing the distribution of U, Th and radiogenic Pb in chondrules and refractory inclusions is important for accurate interpretation of U-Pb isotopic dates. For example, the distribution of U between primary and secondary minerals can indicate whether the date corresponds to formation or to alteration of a chondrule or a CAI. In the case of dating equilibrated (i.e. metamorphosed) chondrites, we need to know the host mineral of U in order to apply correct diffusion parameters for estimating closure temperatures.

Technique: Uranium contents of bulk chondrites are around 10 ppb. Measuring U, Th and Pb concentrations in materials containing these elements at low-ppb levels is not easy. Isotope dilution TIMS analysis is sensitive, precise and accurate but lacks sufficient spatial resolution. The most spatially- and compositionally-sensitive technique used for studying U distribution in meteorite phases is fission track radiography [1,2]. However, this method can be used only for determination of U and Th – a major limitation compared to the ion microprobe, which is suitable for analysis of a wide range of elements and their isotopic ratios. Most ion microprobe trace element analyses of meteorites do not include U. Previously reported ion microprobe analyses of actinides in meteorites (e.g. [3]), performed on small ion microprobes using energy filtering to minimize spectral interferences, yielded quantitative results only for U concentration ≥ 100 ppb. In order to analyze U in chondrule minerals, the sensitivity of ion microprobe measurements should be improved.

In this study made use of the optimum combination of spatial resolution and sensitivity attainable with a large, high transmission ion microprobe. The measurements were done on a SHRIMP-II at the Geological Survey of Canada. In order to minimize spectral interferences without losing sensitivity, we used high mass resolution setting ($R = 5000$) and did not apply energy filtering. The analyses, performed using a 20 μm spot and 5-7 nA primary O^- beam, included U measured as $^{238}\text{U}^{16}\text{O}^+$, and three isotopes of Pb (206, 207, and 204). Later we added Nd ($^{143}\text{Nd}^+$) and Th ($^{232}\text{Th}^{16}\text{O}^+$). Each analysis included seven scans, with a 60 seconds integration for U in each scan. The total duration of each spot analysis was between 20-30 minutes.

Two main problems to be solved for obtaining accurate concentrations were eliminating surface contamination, and matching ion yields between the sample and the standard, particularly important without energy filtering. We could not de-contaminate the surface by washing the mount in dilute acid (which is a common practice in zircon U-Pb analysis), because such treatment would dissolve phosphates and possibly some other minerals. Instead, we applied long (5 min) rastering before each analysis, and in a few cases performed repeated analyses from the same spots, sampling a deeper layer, starting 2-3 μm from the surface.

Standard minerals for U-Th-Pb-Nd analyses, matching the composition of chondrule and CAI minerals, were not available at the beginning of this project (their characterization is under way). We instead used zircon 6266 (our U-Th-Pb and trace element standard, known to be exceptionally homogeneous) and NIST glass SRM-610. Ion yields for U, Th and Nd agree within ± 20 -30% between the zircon and the glass. We assign conservative $\pm 50\%$ uncertainties to the concentrations of these elements; these uncertainties will be much reduced after analyses of compositionally matched standards. For Pb, the difference of ion yields between the zircon and the glass is much greater, and so we withhold from reporting Pb concentrations and the ratios between Pb and other elements, until the compositionally matched standards are established. We shall, however, briefly discuss Pb isotopic ratios, which are independent of standard calibration.

Results: U and Pb concentrations were measured in 36 spots from 6 chondrules from the H5 chondrite Richardton. Five out of these six chondrules were previously dated with U-Pb method [4 and Amelin et al., in prep.]. Analyses of 11 spots also included Th and Nd. All four elements were also analyzed in 16 spots from the Efremovka (CV3) CAI E-44. Count rates for U were below 0.5 counts per second for most spots, and below 2 counts per second for all analyses except one. However, with 420 s integration time per analysis for both U and the background, U signals are clearly resolved from the background (U to background count ratio > 4) in 90% of analyses. Five analyses with U/background ratio < 4 , which we consider unresolved, yielded apparent U concentration < 0.5 ppb. We therefore estimate the detection limit of our technique for U at 0.5 ppb.

Six chondrules represent different textural groups of [5]: porphyritic olivine, micro-porphyritic olivine-and olivine+pyroxene, and radial pyroxene. CAI E-44 is a Type B1 inclusion composed of melilite, Al-Ti-diopside and anorthite, all poikilitically enclosing euhedral spinel grains; secondary nepheline preferentially replacing anorthite is minor [6].

Spot locations were chosen on the basis of BSE images for the Richardton chondrules, and X-ray elemental maps for the CAI E-44. Mineral identification in the analyzed spots was confirmed using EDS spectra and BSE imaging. The spots were divided into three groups: analyses of pure minerals (A), pure minerals with minor fractures (B), and spots overlapping grain boundaries or larger fractures (C). The analyses are distributed relatively evenly between the groups.

The distribution of U between minerals in the Richardton chondrules is shown in Fig. 1. The “impure pyroxene” group consists of analyses of low-Ca pyroxene closely intergrown with olivine (e.g. fine-scale barred zones) and fractured pyroxene grains (purity group C). All other minerals are essentially pure (purity groups A and B). All pyroxene analyses except one were performed on low-Ca pyroxene. One analysis of high-Ca pyroxene intergrown with lesser amount of low-Ca pyroxene yielded 20 ppb U, within the range of low-Ca pyroxene. Concentration of U in pyroxene is variable, mostly between 5-50 ppb, but lower and higher values are also observed. The concentration ranges for pure and impure pyroxene are similar, suggesting that amount of U contained at grain boundaries and in fractures is relatively small. Olivine and troilite have consistently low U, mostly below 2 ppb. Two analyses of mesostasis gave the values of 2-3 ppb.

Uranium concentrations in minerals in the CAI E-44 are within the same range as in the chondrules, but the overall variations are smaller – between 2-20 ppb. Higher concentrations are found in the mixed phases (intergrown fine-grained spinel and melilite), suggesting that a part of uranium may reside in volumetrically minor, grain boundary phases.

Limited database of Th and Nd analyses shows correlation between Th and U concentrations both in the chondrules ($R^2=0.92$) and in the CAI minerals ($R^2=0.75$). No correlation is observed between Nd and either U or Th. Th concentration ranges mostly between 1-100 ppb, are similar for the chondrules and the CAI, but the Nd concentrations in the CAI minerals (4-200 ppm) are higher than in the chondrule minerals (0.03-15 ppm).

Precision of Pb isotopic analyses is limited by very low count rates for ^{204}Pb , however the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios suggest ubiquity of common Pb at low level in all studied chondrule and CAI minerals.

Eight pyroxene and one olivine analyses from the chondrules yielded $^{206}\text{Pb}/^{204}\text{Pb}$ ratios between 50-150, demonstrating measurable contribution of radiogenic Pb. None of the analyses, however, yielded very radiogenic Pb ($^{206}\text{Pb}/^{204}\text{Pb}$ between 318-792), as measured by isotope dilution TIMS in acid-washed splits of the same chondrules. More complete assessment of Pb distribution can possibly be achieved by SHRIMP analyses of chondrules with and without acid washing.

Conclusion: Low-Ca pyroxene is the main host of U in the Richardton chondrules. In the CAI, U is more evenly distributed between minerals.

References: [1] Jones J.A. and Burnett D.S. (1979) *GCA*, 43, 1895-1905. [2] Crozaz G. et al. (1989) *EPSL*, 93, 157-169. [3] MacPherson G.J. and Davis A.M. (1994) *GCA*, 58, 5599-5625. [4] Amelin Y. (2001) *LPS*, XXXII, Abstract #1389. [5] Gooding J.L. and Keil K. (1981) *Meteoritics*, 16, 17-43. [6] Goswami J.N. et al., *GCA*, 58, 431-449.

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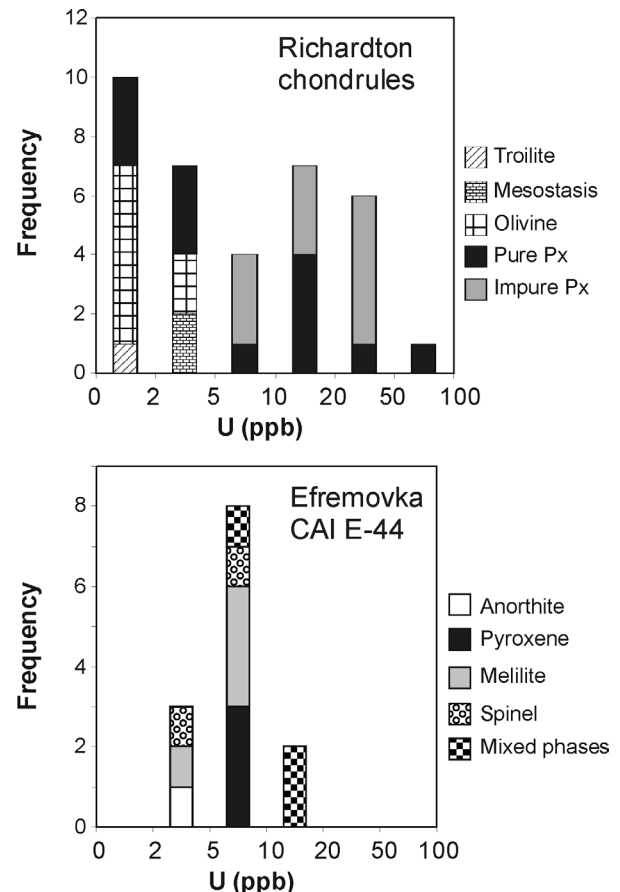


Fig. 1. Distribution of uranium between minerals in six chondrules from Richardton, and in the Efremovka CAI E-44.