U, Th and Pb distribution between minerals in achondrites. Y. Amelin, K. Yi, Korea Basic Science Institute (KBSI), Ochang, Cheongju, Chungbuk 28119, Korea, (email yuri.amelin@anu.edu.au).

Introduction: Achondrites are igneous rocks modified by various degrees of metamorphism and metasomatism. To accurately interpret the time of primary and secondary events of their geological history recorded in Pb-isotopic ages, we need to identify the mineral hosts of uranium and radiogenic lead in these rocks.

Here we present a study of distribution of U, Th and all isotopes of Pb in rapidly cooled angrites Northwest Africa (NWA) 13363 and Oued Namous 001, and in unbrecciated eucrite NWA 15417, as a part of an ongoing effort to establish reliable Pb-isotopic chronology of achondrite formation.

Methods: The U, Th, Pb concentrations were measured on KBSI SHRIMP Ile in July-August 2023. The procedure described below differs in some details from the procedure for U, Th, Pb concentration measurement in CAIs [1] in October 2022. The achondrite samples were analyzed using primary O$_2$-ion beam with intensity of 7.5 ± 0.5 (SD) nA, focused to an elliptical spot of 48 x 22 µm (dubbed “large spot”), or smaller 2.0 ± 0.1 nA beam focused to a spot of 25 x 17 µm (dubbed “small spot”). Smaller spot was used for analyses of small crystals of minerals rich in U and Th, mainly Ca-phosphates apatite and merrillite (Fig. 1), whereas the larger spots were used for analysis of all major minerals. The peak sequence included positive ions 172Yb$^{16}$O, background at mass 204.1, all isotopes of Pb, 232Th$^{16}$O, and 230U$^{16}$O. Each analysis included 10 scans, with duration of ion acquisition of 10 seconds on Yb, major Pb isotopes, and Th, 20-50 seconds on 206Pb and background, and 50 seconds on 238U$^{16}$O in each scan. Each measurement was set up with 10 repeated cycles. Each spot is pre-cleaned before analysis by beam rastering for 120 seconds.

All measurements were carried out using an ETP secondary electron multiplier (SEM). The SEM that was used during the first session was approaching the end of its usage and was operated at the voltage of 2733 V. Running the SEM at these conditions yielded the relatively high but stable dark noise of 0.115 ± 0.020 counts per second (cps). The SEM was replaced shortly after the end of the first session, and the measurements of the second session were run with a new multiplier that was operated at 1966-2135 V, yielding the average dark noise of 0.015 ± 0.011 cps [1]. The large difference in the dark noise allows to evaluate the influence of the background noise on the analytical performance. The detection limits are estimated at 0.36 ppb for U, 0.96 ppb for 206Pb, and 1.8 ppb for Th using “large” spots, and 1.3 ppb for U, 3.6 ppb for 206Pb, and 6.8 ppb for Th using “small” spots. The reference materials and data processing are the same as in [1].

Fig. 1 Backscattered electron (BSE) image of a “small” (~25 µm long) spot after SHRIMP analyses of U, Th and Pb distribution in the angrite Oued Namous 001. Orange outline shows the crystal of Ca-phosphate surrounded by silicate minerals. The SHRIMP pit is ~80% within the phosphate grain, and ~20% within silicate.

Results: The distribution of U, Th and Pb between minerals in two studied angrites is similar, and is discussed together. The median concentrations of U are 4.5 ppb in pyroxene (n=13), 2.3 ppb in olivine (n=27), 2.0 ppb in plagioclase (n=7), and 1.69 ppm in phosphates (n=32). Two analyses of Fe,Ti oxide yielded U concentrations of 10 and 69 ppb. Most olivine analyses yielded U concentrations below 2 ppb, but some showed unusually high concentrations up to 47 ppb. These values can be related to the presence of micro-inclusions of phosphate minerals in the olivine crystals.

The igneous minerals in NWA 15417 analyzed in the parts of the section without visible secondary effects yielded the following median concentrations of U: pyroxene (n=15) – 18.7 ppb, plagioclase (n=7) – 1.4 ppb. The minerals in the large secondary vein are generally more U-rich: ilmenite (n=6) – 57 ppb, phosphate (n=4) – 10.3 ppm, mixed fine-grained mineral assembly in the alteration vein (n=7) – 242 ppb, silica (n=6) – 17 ppb.

The U concentrations and Th/U ratios in phosphate minerals in all studied meteorites are summarized in Fig. 2. Phosphate population in the angrites can be divided into two groups: grains with Th/U between 2.5-5 and U concentrations up to 6 ppm, and grains with Th/U between 8-28, and U concentrations below...
3.5 ppm. Comparison with published U-Th-Pb of angrite phosphates suggest that these groups represent apatite and merrillite, respectively. Four phosphate analyses from the eucrite comprise a group of three U-rich (10-14 ppm) grains with unusually low Th/U ~0.3, and one grain with U concentration of ~ 2 ppm and Th/U ~40.

Fig. 2. Uranium concentrations and Th/U ratios in phosphate minerals in angrites NWA 13363 and Oued Namous 001, and eucrite NWA 15417.

Discussion: In all studied meteorites, phosphate minerals constitute a significant part of the mineral inventory of uranium. Among the igneous silicate minerals, pyroxene appears to be the main host of U, although the concentration of U in angritic pyroxene is surprisingly low. The contributions of olivine and plagioclase to U budget are low.

Although age determination is not the main purpose of this study, high abundance of uranium and radiogenic isotope composition of Pb in angrite phosphates allowed construction of a Pb-Pb isochron (Fig. 3). The isochron age of 4561 ± 12 Ma, although imprecise, is consistent with the published high-precision ages of rapidly cooled angrites [2, and references therein].

High U concentrations in the minerals from secondary vein in the eucrite NWA 15417 also allows construction of a Pb-Pb isochron (Fig. 4):

Fig. 3. Pb-Pb isochron diagram for phosphate minerals from the angrite NWA 13363.

Fig. 4. Pb-Pb isochron diagram for phosphate, ilmenite, silica, and mixed fine-grained mineral assembly from the secondary vein from the eucrite NWA 15417.

We interpret the Pb-Pb isochron date of 4518 ± 9 Ma as the time of formation of the secondary vein, which can represent an episode of metasomatic activity on the eucrite parent body. If the host rock of the eucrite NWA 15417 formed, like most known achondrites, within the first 10 Ma after the Solar System formation, then the metasomatic event recorded in this meteorite post-dated magmatism by ~40-50 Ma. The extent of this event can be determined through U-Pb dating of secondary mineral assemblages in various types of HED meteorites.