Distribution of rare earth elements, Th and U in R chondrite. R. Maeda, N. Shirai and M. Ebihara, Department of chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan (maeda-ryoga@ed.tmu.ac.jp).

**Introduction:** Mineralogical and chemical compositions of R chondrites are similar to those of ordinary chondrites (OCs) [1]. In previous study [2], abundances of rare earth elements (REEs), Th and U in bulk R chondrites were reported to be almost equal to those of OCs. Major host phases for REEs, Th and U in OCs are known as Ca-phosphates [3, 4]. However, major host phases of these elements in R chondrite are not known. In this study, we investigated the distribution of REEs, Th and U in R chondrite by using chemical leaching technique for the goal of discussion of formation process and/or metamorphism of R chondrite.

**Experimental procedures:** Fifteen R chondrites were subjected to chemical leaching experiment. Powdered sample weighing about 100 mg for each meteorite was taken in a small vial and put into an ultra-sonic bath for 5 min with 1 mL of 0.1 M HNO₃. After the 1st leachate was separated by centrifugation, the residue was leached with 3 mL of 5 M HNO₃ for 60 min in the ultra-sonic bath. This leaching step was three times. The residual powder was decomposed with acid mixture (HF, HClO₄ and HNO₃). Because the 2nd leachate contains certain amount of silica, which may hinder the later step of the experiment, the leachate was dried and the insoluble silica was decomposed in a similar way to that used for the residual fraction. REEs, Th and U abundances for three fractions (the 1st and 2nd leachates, and the residue) for each meteorite were determined by using ICP-MS [2]. For identifying minerals recovered in the three fractions, ICP-AES was performed for the determination of most major and some trace elements (Mg, Al, Si, P, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Sr and Ba) [2, 5].

**Results and discussion:** Budgets for some elements (P, La, Sm, and Lu) of each fraction were summarized in Table 1. As shown in Table 1, 30-36% of P was recovered in the 1st leachate for R3, R4 and R (brecciated), while 70% of P was obtained for R6. These budgets of P in the 1st fraction are mirror-imaged in the 2nd leachates; for the 2nd leachates, 62-69% of P was leached for R3, R4 and R (brecciated), while only 31% was recovered for R6. Judging from ICP-AES data and the solubility property [6], it can be reasonably concluded that Ca-phosphates were selectively extracted in the 1st leaching step with weak nitric acid. It was observed that small amounts of Mg, Si, Fe and Cu were extracted in the 1st leachates, indicating that some olivine and sulfides were dissolved. Because olivine and sulfides (except oldhamite) hardly/not accommodate P and REEs [7], REEs (La, Sm and Lu) recovered in the 1st leachates must be allocated to Ca-phosphates. Such an allocation scheme for the 1st leachates is essentially the same as the case of OCs [6]. For the 2nd leachates, such a simple allocation of REEs to Ca-phosphates, however, cannot be applied. It is probable that some Ca-phosphates undissolved in the 1st leaching step were leached with more intense leaching condition with higher concentration of nitric acid for longer contact time. However, budgets of Ca-phosphates recovered in the 2nd step are comparable to (for R3 and brecciated R) or smaller than (for R4 and R6) those of the 1st dissolution step, judging from the distributions of La in the 1st and the 2nd leachates. Apparently, P recovered in the 2nd leachates is contributed from other phosphates other than Ca-phosphates (probably, Mg-phosphates and/or Fe-phosphates), which is completely different story from those for ordinary chondrites. In addition, it is to be noted that fairly large amounts of REEs, especially heavy REEs (HREEs) (Lu in the Table 1) were recovered in the 2nd leaching step. The residual fraction mainly consists of pyroxene and plagioclase according to the mineral composition of R chondrites and solubility properties of constituent minerals [6, 8]. It can be confirmed that P-containing minerals (phosphates) can be completely dissolved with nitric acid in the preceding two leaching steps. It is significant that not a small fraction of Sm and Lu are allocated to the acid-residual fraction. It may be that both pyroxene and plagioclase are partly dissolved with acid leaching (especially, in the 2nd leaching step). However, REEs budgets for the 2nd leachate seem to be too large to be explained in terms of partial dissolution of the acid-residual phases like pyroxene and plagioclase. Thus, host phase(s) for REEs (especially HREEs) selectively recovered in the 2nd leaching with nitric acid is unclear. The presence of such phase(s) is also not the same case as that for OCs.

As described above, it can be reasonably assumed that REEs as well as P recovered in the 1st fraction are...
attributable to Ca-phosphates. From this assumption, REEs, Th and U abundances in Ca-phosphates can be calculated, and their CI-normalized abundance patterns are shown in Fig. 1. The relative REEs abundances change downward from light REEs (LREEs) to HREEs with a negative Eu anomaly for all samples studied. These features of REE abundance patterns are similar to those of Ca-phosphate in OCs [10]. The CI-normalized LREEs abundances are variable from ~200 to 600 and not correlated with metamorphic grades. In OCs, REE distributions in Ca-phosphates increase from petrologic type 3 (unequilibrated OCs; UOCs) to petrologic type 6 (equilibrated OCs; EOCs) in accordance to the metamorphic degree meteorites experienced. However, even in type 6 EOCs, CI-normalized abundances of REEs are lower (less than 200 × CI) than those of any petrologic type R chondrite. These observations suggest that REEs (especially, LREEs) were preferentially partitioned in Ca-phosphates of R chondrites even with petrologic type 3. Apparently, higher abundances of REEs in Ca-phosphates for R chondrites than those for OCs result from lower contents of Ca-phosphates in R chondrites. Considering a large variation of REEs abundances in R4 chondrites (Fig. 1) and uniform contents of REEs and P in R chondrites including these R4s, it is suggested that the formation of Ca-phosphates and non-Ca-phosphates (like Mg- and Fe-phosphates) occurred locally and competitively in the R chondrite parent body. Thorium and U are fractionated in Ca-phosphates, with U being concentrated in Ca-phosphates more than Th, suggesting that apatite (probably, chlorapatite) is more abundant than merrillite in R chondrites. This implication is consistent with mineral composition of R chondrite [1, 8].

Data in Table 1 imply that considerable amounts of REEs (especially, HREEs) are distributed to the acid-residual phases in R chondrites. Figure 2 shows REEs, Th and U abundances for the acid-residues normalized to those in bulk (whole rock) meteorite samples [2]. The patterns are somewhat complementary to those shown in Fig. 1, being convex upward with a positive Eu anomaly. These features are generally the same as those observed for the acid-residues of OCs [11]. However, there appear several differences. First, abundances of REEs (especially, middle and heavy REEs) are considerably high compared with those for OCs [11]. Second, abundances of HREEs are not variable regardless of petrologic types, although abundances of LREEs seem to change in accordance with petrologic types, just like the case for OCs [11]. Apparently, REEs, Th and U in R chondrites are distributed in a different way from those in OCs. As their distributions were controlled by the thermal metamorphism on their parent bodies, R chondrites and OCs experienced the metamorphic activity in different ways.