中国山東半島北東部のエクロジャイトと単斜輝石岩のスフェーンと主要造岩鉱物間の 微量元素と希土類元素の分配関係

佐藤桂^{1,2}、David J. Ellis²、Andrew G. Christy³、平島崇男⁴ ¹ 東京工業大学 理工学研究科 地球惑星科学専攻

²Research School of Earth Sciences, The Australian National University ³Centre for Advanced Microscopy, The Australian National University ⁴京都大学 理学研究科 地質学鉱物学教室

Partitioning of trace elements and rare earth elements between titanite and major rock-forming minerals in eclogite and clinopyroxenite from the northeastern Shandong Peninsula, eastern China

Kei Sato^{1, 2}, David J. Ellis², Andrew G. Christy³ and Takao Hirajima⁴

¹Department of Earth and Planetary Sciences, Graduate School of Science and Engineering, Tokyo Institute of Technology ²Research School of Earth Sciences, The Australian National University ³Centre for Advanced Microscopy, The Australian National University ⁴Department of Geology and Mineralogy, Graduate School of Science, Kyoto University

Host minerals and/or melt for storing thorium and uranium that are important radioactive elements have the potential to be major carriers of these elements from upper mantle to crust. These elements can be incorporated into various accessory minerals [monazite, allanite, zircon, titanite (sphene), apatite etc.]. For example, zircon is a host mineral for Zr, Hf, Th, U and HREE (e.g. Sawka, 1988; Bea, 1996; O'Hara et al., 2001; Hoskin and Schaltegger, 2003), and this mineral occurs in virtually all sorts of terrestrial rocks with zirconium. On the basis of empirical knowledge, Th/U ratio of zircon has been suggested to be useful as an indicator of metamorphism or magmatism by many authors for a long time (e.g. Williams and Claesson, 1987; Maas et al., 1992; Williams et al., 1996; Hoskin and Black, 2000; Aleinikoff et al., 2002; Carson et al., 2002; Hoskin and Schaltegger, 2003; Hokada et al., 2004; Suzuki et al., 2006; Sato et al., 2010; 2011). In general, Th/U ratios in igneous zircons are > about 0.5, and metamorphosed zircons often yield lower Th/U ratios (Hoskin and Schaltegger, 2003). However, the mechanism of this element distribution has been still poorly understood. In bulk composition of continental crust, no impressive change in Th/U ratios has been caused since Archean (i.e. Th/U = about 3.8), regardless of upper crust or lower crust (Taylor and McLennan, 1985). Thus, to satisfy bulk rock constraints, there needs to be another phase which is present with a much higher Th/U ratio than bulk rock composition. Monazite and/or allanite may be typically such phases. However, titanite is a common accessory mineral that is found in various rock types of igneous, metamorphic and sedimentary rocks from different geochemical environments and petrogenetic conditions because the large number of other elements (trace elements and LREEs) can be substituted into its crystal structure (e.g. Sahama, 1946; Oberti et al., 1991; Troitzsch and Ellis, 1999). In addition, titanite appears as a stable phase even under eclogite facies metamorphic condition in felsic bulk composition (Troitzsch and Ellis, 2002) although it is often regarded as the lower pressure phase of rutile in mafic (basaltic) bulk composition (Liu et al., 1996; Ernst and Liu, 1998). Thus, here we report trace element data on titanite that can have a significant effect of the Th-U partitioning during eclogite facies metamorphism.

In the present study, three eclogite facies metamorphic rocks that were collected from Kongjiadian in the northeastern Shandong Peninsula, eastern China (the Sulu area) were examined to investigate the distribution of trace elements and REEs amongst titanite and major rock-forming minerals by using LA-ICP-MS. One of these rocks is clinopyroxenite that is mainly composed of clinopyroxene, zoisite, amphibole and titanite, and the other rocks are eclogites with garnet, clinopyroxene, amphibole, rutile and titanite. Textural characteristic in titanites from the clinopyroxenite is distinguished completely from those from the eclogites. Titanites in the clinopyroxenite occur in grain boundaries between major rock-forming minerals (clinopyroxene etc.), and its process may be related to crystallization from trapped melt amongst the major minerals. The other titanites in the eclogites are found as envelopes around rutiles, and this mineral texture suggests decompression process. The former titanites in grain boundaries acquire large amounts of Th and U as compared to the major minerals, as follows. Titanite: Th = about 60-420 ppm, U = about 100-190 ppm and Th/U = about 0.4-2.2. Clinopyroxene: Th < 0.3 ppm and U < 0.1 ppm. Zoisite: Th < 4 ppm, U = about 10 ppm and Th/U = about 0.3. Amphibole: Th < 0.1 ppm and U < 0.1 ppm. The other titanites surrounding rutiles in the eclogites contain only a few Th and U (Th < 3 ppm and U < 4 ppm). These results suggest that chemical characteristic of titanite quite depends on its formation process. It means that titanite formed from melt

can yield high Th and U concentrations. Thus, if such titanites undergo further prograde metamorphism and subsequent breakdown of this mineral, a significant amount of Th and/or U can be released into other minerals modifying the Th/U ratio of rim domains.

References

- Aleinikoff, J.N., R.P. Wintsch, C.M. Fanning, M.J. Dorais, U-Pb geochronology of zircon and polygenetic titanite from the Glastonbury Complex, Connecticut, USA: an integrated SEM, EPMA, TIMS, and SHRIMP study, Chemical Geology, 188, 125-147, 2002.
- Bea, F., Residence of REE, Y, Th and U in granites and crustal protoliths; implications for the chemistry of crustal melts, Journal of Petrology, 37, 521-552, 1996.
- Carson, C.J., J.J. Ague, C.D. Coath, U-Pb geochronology from Tonagh Island, East Antarctica: implications for the timing of ultra-high temperature metamorphism of the Napier Complex, Precambrian Research, 116, 237-263, 2002.
- Ernst, W.G. and J. Liu, Experimental phase-equilibrium study of Al- and Ticontents of calcic amphibole in MORB—A semiquantitative thermobarometer, American Mineralogist, 83, 952-969, 1998.
- Hokada, T., K. Misawa, K. Yokoyama, K. Shiraishi, A. Yamaguchi, SHRIMP and electron microprobe chronology of UHT metamorphism in the Napier Complex, East Antarctica: implications for zircon growth at >1,000°C, Contributions to Mineralogy and Petrology, 147, 1-20, 2004.
- Hoskin, P.W.O. and U. Schaltegger, The composition of zircon and igneous and metamorphic petrogenesis, Reviews in Mineralogy and Geochemistry, 53, 27-62, 2003.
- Hoskin, P.W.O. and L.P. Black, Metamorphic zircon formation by solid-state recrystallization of protolith igneous zircon, Journal of Metamorphic Geology, 18, 423-439, 2000.
- Liu, J., S.R. Bohlen, W.G. Ernst, Stability of hydrous phases in subducting oceanic crust, Earth and Planetary Science Letters, 143, 161-171, 1996.
- Maas, R., P.D. Kinny, I.S. Williams, D.O. Froude, W. Compston, The earth's oldest known crust: a geochronological and geochemical study of 3900-4200 Ma old detrital zircons from Mt. Narryer and Jack Hills, Western Australia, Geochimica et Cosmochimica Acta, 56, 1281-1300, 1992.
- Oberti, R., D.C. Smith, G. Rossi, F. Caucia, The crystal-chemistry of high-aluminum titanites, European Journal of Mineralogy, 3, 777-792, 1991.
- O'Hara, M.J., N. Fry, H.M. Prichard, Minor phases as carriers of trace elements in non-modal crystal-liquid separation processes II: illustrations and bearing on behaviour of REE, U, Th and the PGE in igneous processes, Journal of Petrology, 42, 1887-1910, 2001.
- Sahama, T.G., On the chemistry of the mineral titanite, C. R. Soc. Géol. Finlande, 19, 88-120, 1946.
- Sato, K., M. Santosh, T. Tsunogae, Y. Kon, S. Yamamoto, T. Hirata, Laser ablation ICP mass spectrometry for zircon U-Pb geochronology of ultrahigh-temperature gneisses and A-type granites from the Achankovil Suture Zone, southern India, Journal of Geodynamics, 50, 286-299, 2010.
- Sato, K., M. Santosh, T. Tsunogae, T.R.K. Chetty, T. Hirata, Laser ablation ICP mass spectrometry for zircon U-Pb geochronology of metamorphosed granite from the Salem Block: Implication for Neoarchean crustal evolution in southern India, Journal of Mineralogical and Petrological Sciences, 106, 1-12, 2011.
- Sawka, W.N., REE and trace element variation in accessory minerals and hornblende from the strongly zoned McMurry Meadows Pluton, California. Transactions of the Royal Socety of Edinburgh, 79, 157-168, 1988.
- Suzuki, S., M. Arima, I.S. Williams, K. Shiraishi, H. Kagami, Thermal history of UHT metamorphism in the Napier Complex, East Antarctica: Insights from zircon, monazite, and garnet ages, The Journal of Geology, 114, 65-84, 2006.
- Taylor, S.R. and S.M. McLennan, The continental crust: its composition and evolution. Blackwell Scientific Publications, 328 p, 1985.
- Troitzsch, U. and D.J. Ellis, The synthesis and crystal structure of CaAlFSiO₄, the Al-F bearing analog of titanite, American Mineralogist, 84, 1162-1169, 1999.
- Troitzsch, U. and D.J. Ellis, Thermodynamic properties and stability of AlF-bearing titanite CaTiOSiO₄–CaAlFSiO₄, Contributions to Mineralogy and Petrology, 142, 543-563, 2002.
- Williams, I. S. and S. Claesson, Isotopic evidence for the Precambrian provenance and Caledonian metamorphism of high grade paragneisses from the Seve Nappes, Scandinavian Caledonides, Contributions to Mineralogy and Petrology, 97, 205-217, 1987.
- Williams, I.S., I.S. Buick, I. Cartwright, An extended episode of early Mesoproterozoic metamorphic fluid flow in the Reynolds Range, central Australia, Journal of Metamorphic Geology, 14, 29-47, 1996.