Trace element analysis of zircon and garnet in Nijyo-san rhyolite, SW Japan by LA-ICP-MS

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Sample

Trace element composition of zircon and garnet have been measured in situ by LA-ICP-MS in Miocene rhyolite from Nijyo-san SW Japan. The rhyolite have peraluminous bulk rock composition with plagioclase and minor amount of biotite and garnet phenocrysts. Bulk rock REE composition of the rhyolite is characterized by steep fractionated pattern (La/Yb_N=177) and absence of conspicuous negative Eu anomaly. Zircons are euhedral prismatic crystal 50-100μm in length. Garnets are euhedral-subhedral crystal ca. 0.5mm in diameter.

Results and discussions

Both zircon and garnet shows negative Eu anomaly, suggesting crystallization along with plagioclase. Both garnet and zircon shows strong LREE depletion and HREE enrichment. Negative slope in HREE pattern of garnet (Yb/Gd_N=0.28-0.56) corresponds to the HREE depletion of bulk rhyolite. Slope of HREE of zircons is highly variable (Yb/Gd_N=1.2-7.1). U-Pb age were also determined for zircon simultaneously, and most of grains have age close to magmatic age of rhyolite, so the variation of zircon chemistry is not due to the presence of inherited grains. HREE variation of zircons could be explained by HREE fractionation of the effective melt composition equilibrated with zircon during the continuous crystallization of garnet. Assuming rim of garnet and zircon of the lowest HREE content is in equilibrium, partition coefficients of REE for zircon/garnet is gradually increase from MREE to HREE, which is conformable to the result obtained for metamorphic zircon and garnet (Rubatto, 2002).

Reference

Rubatto, D. (2002) Chem. Geol., 184, 123-138.

Stable carbon isotope ratio of steroids in Pliocene to Pleistocene fossil whale bones

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Introduction

Dietary preferences and habits of archaeological and paleontological animals have been investigated based on stable carbon isotope ratios ($\delta^{13}C$) of collagen and non-collagenous proteins in fossil bones. The $\delta^{13}C$ of individual compound in lipids from fossil bones were recently applied to the reconstruction of paleodietary of animals (Stott *et. al.*, 1996, 1999). In the present study, the $\delta^{13}C$ of steroid in fossil whale bone was preliminarily investigated to evaluate its potential as indicators of paleodietary and paleohabits.

Samples and Methods

Three fossil whale bones collected in Kitahiroshima area, Hokkaido, Japan (one sample of the Middle Pleistocene) and in Kakegawa area, Shizuoka Pref., Japan (two samples of the Upper Pliocene; 2 and 2.5Ma, respectively) were used for the study. Lipids were extracted with organic solvent and separated into acidic and neutral fractions. Neutral fraction was further fractionated with silicagel column into three fractions; aliphatic and aromatic hydrocarbons, and polar compounds. Steroids were identified by GC-MS, and their compound-specific $\delta^{13}C$ were determined by GC-C-IRMS.

Result and Discussion

Cholesterol and cholestanol were detected in the youngest Kitahiroshima and the younger Kakegawa samples. However, these steroidal alcohols are very poor in the older Kakegawa sample, of which major steroids are hydrocarbons as cholestanes. A large amount of cholestene characterizes the younger Kakegawa sample. These analytical results are consistent well with diagenetic processes for the formation of steroidal hydrocarbons from sterols, showing that all the steroidal compounds in fossil whale bones are indigenous.

The $\delta^{13}C$ values of cholestanes in the older Kakegawa sample are -22.3‰ and -21.9‰. Whereas, the $\delta^{13}C$ value of cholestene in the younger Kakegawa sample is -26.4‰. These $\delta^{13}C$ values are concordant with those of cholesterols in living and fossil whale bones reported by Stott *et.al.* (1997). The $\delta^{13}C$ of steroids in fossil bones can be a useful tool for paleontological and archaeological studies, and can be applied to the fossils bones without any collagen and proteins.

References

Stott *et al.*, 1996 *Anal. Chem.* **68**, 4402-4408, Stott *et al.*, 1997, *Org. Geochem.* **26**, 99-103, Stott *et al.*, 1999, *J. Archaeol. Sci.* **26**, 705-716