Investigation on thermal stability of radical species in chibaite

*Shusuke Isogai[1], Yuka Yokoyama[1], Kenta Kusuki[1], Hirotsugu Nishido[2], Atsushi Tani[1]

1. Graduate School of Human Development and Environment, Kobe University, 2. Faculty of Biosphere-Geosphere Science, Okayama University of Science

Silica clathrates have a framework structure with cage-like voids occupied by guest species and are very similar to gas hydrates which are crystalline inclusion compounds composed of cage-like structures with water molecules. In 2011, chibaite was discovered in Chiba prefecture (Momma et al., 2011). Chibaite is isostructural with gas hydrate structure II and has larger cages than melanophlogite which is isostructural with gas hydrate structure I. This means that it includes propane and isobutane together with methane and ethane as guest molecules. Chibaite was found in marine sediments of Early Miocene age (Hota Group) at Arakawa, Minami-boso City, Chiba Prefecture, Japan. It occurs as quartz veins ranging from a few mm to 1 cm thick in tuffaceous sandstone and mudstone. Although chibaite is formed after the formation of marine sediments, it is not clear when it formed.
If organic radical species like methyl radicals in silica clathrates are thermally stable in geological time scale, electron spin resonance (ESR) dating could be applied to obtain the formation age. In ESR dating, the total radiation dose due to natural radiation is obtained in natural minerals and fossils by the additive dose method and the formation age is estimated by considering annual natural dose. In ESR, unpaired electrons such as point defects and radical species can be detected and the amount of the ESR signal is directly related to the age of the sample. To obtain a reliable ESR age, it is necessary to know the ESR signal response to the radiation dose and the thermal stability of the defects and radical species. In chibaite, propyl radicals and butyl radicals might be formed and stored in the sample because they are enclathrated in the large cages. In this study, we measure chibaite samples by ESR to investigate whether radical species are observed at the first stage, and then if observed in natural samples, how the ESR signals of the radicals respond to artificial irradiation and how stable they are.
We gently crushed chibaite samples in a mortar into several pieces with about 1 mm in diameter and measured ESR signal of each piece before irradiation. All samples were irradiated by gamma-rays with 60-Co source with different doses from 34.5 Gy to 1 kGy and measured by ESR again. Methyl and tert-butyl radicals were observed at room temperature in the natural samples before irradiation. It suggests that chibaite formation age could be dated by ESR using these organic radicals. In dose response experiments, the amount of methyl radicals was not changed or even decreased in 12 samples, though it was increased in 4 samples. The reason might be because the amount of the methyl radicals is already saturated by natural radiation. In contrast, the ESR signal of tert-butyl radicals was increased in artificial radiation dose. In this presentation, we will show the results of annealing experiments for investigation of the thermal stability of the radical species and discuss the possibility of ESR dating especially using tert-butyl radicals.

Keywords: silica clathrate, chibaite, electron spin resonance, radical species, thermal stability

