# Estimation of ESR age of chibaite using organic radicals

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## Introduction

### Silica clathrates & Chibaite

Silica clathrates have a $SiO_2$ framework structure of cage-like voids occupied by guest species such as hydrocarbons and a similar framework structure to those of gas hydrates which contain molecule compounds enclosed within cage-like structures of water molecules. Chibaite is a natural analogue of gas hydrate structure II and has larger cages than melanophlogite, isostructural to gas hydrate structure I. It suggests that the cages in chibaite store 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 [1]. It occurs in quartz veins as euhedral ranging from a few mm to 1 cm thick in tuffaceous sandstone and mudstone. Although chibaite had crystallized after marine sedimentation, it is not clear when it formed.

If organic radical species in silica clathrates are thermally stable in geological time scale, electron spin resonance (ESR) dating could be applied to evaluate the formation age. To obtain a reliable ESR age, it is necessary to assess a thermal stability of the radical species in chibaite.

Our previous studies shows that methyl radical and *tert*-butyl radical are stored in the natural chibaite samples. The ESR signal intensity of *tert*-butyl radical in chibaite increased by gamma irradiation, whereas the intensity of methyl radical almost unchanged. In annealing experiments, *tert*-butyl radical is thermally as stable as the defects such as Al center and Ti center in quartz [2].

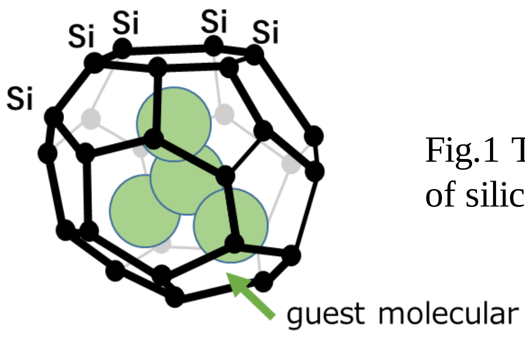



Fig.1 The structure of silica clathrate.

## The aim of this study

We have conducted to measure chibaite samples by ESR to investigate how the ESR signals of *tert*-butyl radical in chibaite respond to gamma-irradiation doses, and to estimate the ESR age of chibaite.

## Experimental

### Samples

We gently crushed chibaite samples with a mortar into several particles about 4-5 mm in diameter.


Fig.2 Chibaite samples.

### ESR measurement

X-band CW-ESR JES-FA200 (JEOL)

Microwave power : 1 mW
Modulation width : 0.1 mT, 100kHz
Temp.: room temperature

### Gamma irradiation

Chibaite: 2 samples
Source: $^{60}Co$
Dose: 80 to 390 Gy

Temp.: room temperature

ESR measurements and gamma irradiation were repeated.

## Results & Discussion

### Equivalent dose & ESR age

The ESR signal intensity of *tert*-butyl radical of these samples increased linearly with gamma-rays dose up to 390 Gy. The equivalent dose was estimated to be **30±8 Gy** by additive dose method.

Assuming the annual dose rate is 0.46 mGy/a based on sedimentary rocks in Kanto region, Japan [3], the ESR age of chibaite can be evaluated at **65±17 ka.**

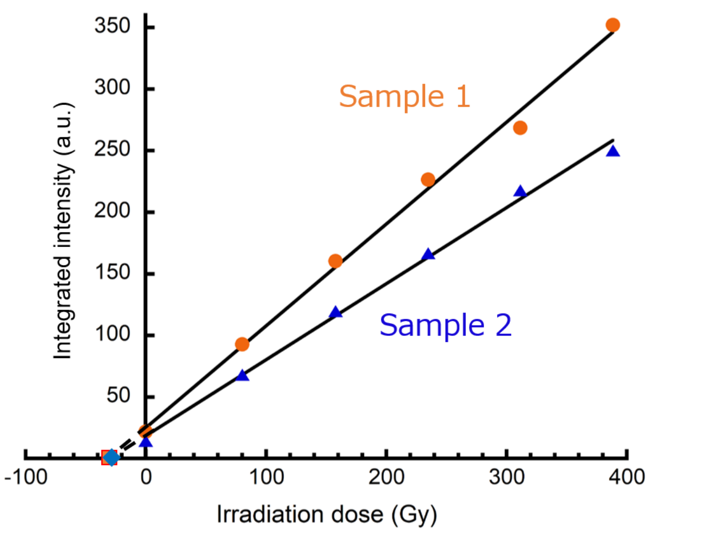
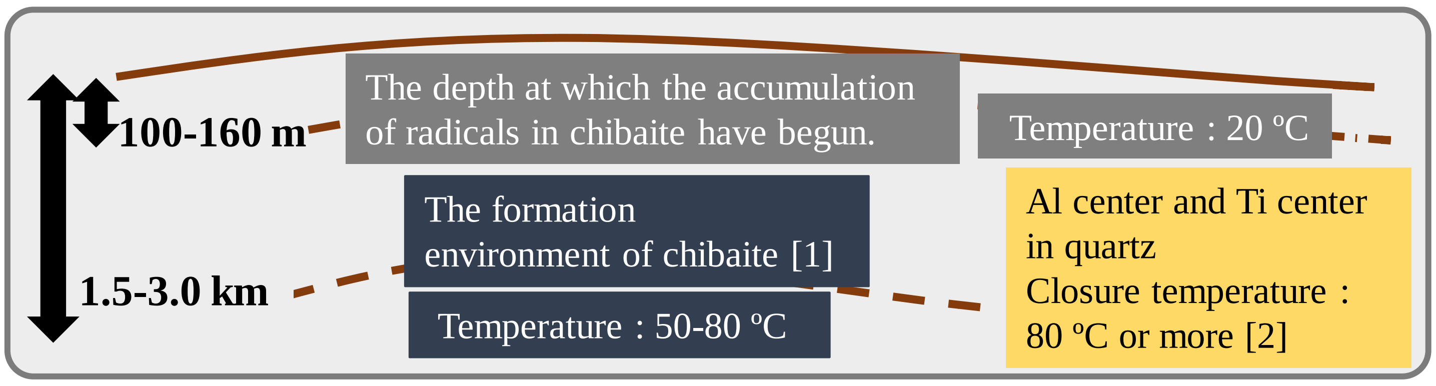



Fig.3 Dose response for *tert*-butyl radicals of chibaite samples.

### Discussion about ESR age

Based on the average uplift rate in the southern part of Boso peninsula [4, 5], our results indicate that the burial depth of chibaite formation could be around 100-160 m. It is disagreed with the formation environment (1.5-3.0 km) estimated by Momma *et al*. [1].




We would underestimate ESR age of chibaite.

#### Possible reasons for underestimation

- Artificial gamma-rays irradiation may product unstable radicals which have already disappeared with natural radiation.
- In isochronal annealing experiment (Fig.4), the intensity of *tert*-butyl radicals increases at around 210 °C. We may need pre-heat to evaluate real equivalent dose.

For the more accurate investigation of the total radiation dose, we need to consider a model including these effects.

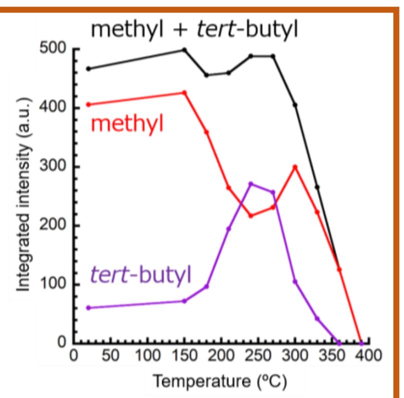



Fig.4 The signal intensity change of the radicals in isochronal annealing.

## Conclusion

- The equivalent dose of chibaite was estimated to be 30±8 Gy obtained by additive dose method and the ESR age can be evaluated at 65±17 ka.
- Considering the estimated formation environment of chibaite, we may be underestimating of ESR age.
- For the more accurate investigation of the total radiation dose, we need to consider some effects.

## Reference

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