8–7 Dating Calcium Carbonate Using a Micro-Scale Analytical Method
—A Method for Tracing Prior Underground Water Environments—

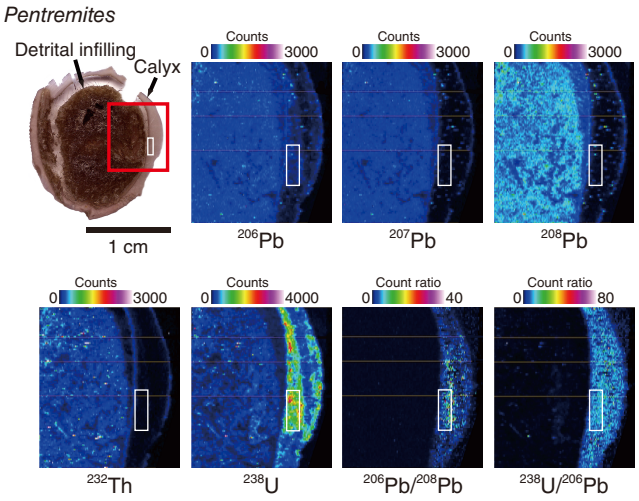

Fig.8-19 Elemental imaging map of the *Pentremites* sample
Here, the red square indicates the area of elemental imaging, and the white box indicates the area suitable for the dating method because of the higher ^{238}U concentration and higher radiogenic ^{206}Pb concentration (^{206}Pb/^{208}Pb ratio).

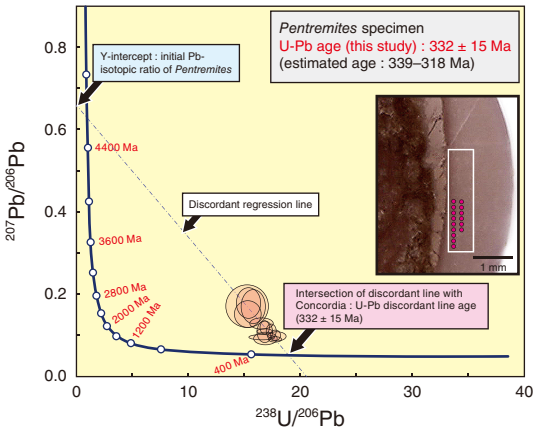

Fig.8-20 The dating result of *Pentremites* sample (Concordia plot)
As a result of the U–Pb isotopic analysis of the *Pentremites* sample, the sample was dated 332 Ma, corresponding to almost the middle of the age range of this specimen (~339 to ~318 Ma). The 15 pink solid circles in the right photograph show the laser-irradiated points selected using the prior elemental imaging map (Fig.8-19).

Because calcium carbonate (hereinafter, carbonate) is as common filling mineral in rocks, the internal zoning of precipitation age, the chemical composition, and the carbonate's crystallographic structure offers a wide-use indicator to reconstruct past environmental variations. Chronological studies of fracture-filling carbonate in rocks can provide precious geological information about groundwater flow and fault movement in geological history.

As carbonate minerals often form a microscopic chemical zoning structure during growth, high spatial resolution is necessary to analyze and date these solid samples. Therefore, a uranium (U)–lead (Pb) carbonate dating method was developed using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Difficulties applying LA-ICP-MS U–Pb dating to carbonate samples have been shown to include a lack of an international standard for *in-situ* dating and of a methodology for selecting suitable areas for dating because of the low U (parent nuclide of U–Pb systematics) concentrations.

Quantitative two-dimensional imaging maps of U, thorium (Th), and Pb isotope abundances of the carbonate samples were obtained using a LA-ICP-MS imaging technique to select suitable areas for dating (Fig.8-19). A carbonate reference material, named WC-1 and collected from marine calcite cement from the western side of the Delaware Basin in New Mexico, USA, was used for LA-ICP-MS U–Pb dating based on previous research (*). To check the validity of the proposed dating technique, a well-preserved calcareous Carboniferous fossil specimen, *Pentremites*, (collected from the strata of the Chesterian age, from mid-Mississippian to earliest Pennsylvanian, in northeastern Oklahoma, USA, corresponding to an estimated age of ~339 to ~318 Ma), was dated.

The U–Pb age of the *Pentremites* sample was dated 332 ± 15 Ma (1σ), corresponding well to the age range of this specimen (~339 to ~318 Ma) (Fig.8-20). Thus, the proposed LA-ICP-MS dating method was successfully used to date the carbonate sample. Additionally, an examination of robust ICP condition was performed. It may be suggested that we do not need to prepare a carbonate reference material such as WC-1 under the condition to introduce nitrogen (N_2) gas into ICP.

Future work will aim to improve the analytical precision and validate the applicable age range to apply the proposed dating technique to research the long-term stability of the geological environment.

This study was part of the result conducted "R&D program supporting the development of technology for geological disposal of high-level radioactive waste", and supported by the Agency of Natural Resources and Energy (ANRE), the Ministry of Economy, Trade and Industry (METI), Japan.

* Roberts, N. M. W. et al., A Calcite Reference Material for LA-ICP-MS U-Pb Geochronology, Geochemistry, Geophysics, Geosystems, vol.18, issue 7, 2017, p.2807–2814.

Reference

Yokoyama, T. et al., U-Pb Dating of Calcite Using LA-ICP-MS: Instrumental Setup for Non-Matrix-Matched Age Dating and Determination of Analytical Areas Using Elemental Imaging, Geochemical Journal, vol.52, issue 6, 2018, p.531–540.