

Geosphere stability project (6) Chronological and chemical analyses of carbonate minerals

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Chronological and geochemical studies of fracture filling calcite in rocks provide the information for changes in geochemical condition, such as redox potential and pH in deep geological environments ^{1,2)}. Because the calcite can be found as common filling minerals in the natural samples, age zoning and spatial distribution of chemical composition in the calcite could be a wide-use indicator to estimate the past environmental changes ^{3,4)}. Radiometric ages of bulk calcite samples have been reported ⁵⁾. On the other hand, U-Pb dating in a micro scale area (less than 10 micrometer) on the filling mineral surface by laser ablation-inductively coupled plasma mass spectrometry system (LA-ICPMS) has been applied to geological samples (zircon, apatite and other minerals) ¹⁾. Additionally, Fe, U, rare earth elements, and other chemical composition in the calcite have proven to be a useful means for the estimation of past geochemical changes. Past redox potential has been estimated by Fe contents in the carbonates, which is based on the distribution coefficient of Fe between calcite deposit and groundwater ^{3,4)}. In this study, we evaluated the possibility of in-situ radiometric dating for the filling minerals by LA-ICPMS and past redox potential by the theoretical calculation using the distribution coefficient. Our new results are shown as follows.

(1) Radiometric dating by LA-ICPMS

In order to develop high spatial resolution dating of the filling minerals, we should make clear the trace element fractionation (U and Pb) on a sample surface during LA-ICPMS measurements and establish the high precision measurements of Pb isotope ratios based on the authentic carbonate standard materials. Therefore, we made efforts to find natural carbonates as possible standard materials with homogeneous U and Pb contents as well as Pb isotope ratios. Imaging analyses (two-dimensional mapping) of the trace element contents and the isotope ratios were adopted to decide the suitable sample analysis points by laser ablation for the radiometric dating of carbonates ¹⁾. Besides, we performed high precise and sensitive measurements in Pb isotope ratios by the LA-ICPMS using the multiple ion counters and the multiple Faraday collectors with high gain amplifiers ¹⁾.

(2) Redox potential by the theoretical calculation

For the inorganic geochemical analyses, drilling core samples (DH5, 6, 7, 8, 12) from southeastern Gifu in the middle Japan, and modern carbonate deposits from Shimane and Yamanashi in Japan were analyzed by ICP-MS. For the DH6, 7, 8, calculated redox potential values by the Fe contents were coincident with the observed values of ground water. However, those of other samples showed disagreement with the observed values, which could be caused by secondary mixing with oxic surface water. Therefore, applicable methods and condition (e.g. range of the redox potential values, ground water source and/or their matrices) should be cleared for the theoretical calculation of redox potential by Fe contents in carbonates.

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References

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