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Raman spectroscopic study of apatite in the concretion: new insights into the formation process of concretion

MOTOHIRO TSUBOI, RYOSUKE KITANAKA AND YUKIHIRO OZAKI

Kwansei Gakuin University

Presenting Author: tsuboimot@kwansei.ac.jp

The formation mechanism of concretions has attracted attention because of not only the presence of well preserved fossils in it but also the application for civil engineering. Previous studies on concretions have been conducted by analyzing major elements and isotopes. Those studies have revealed that concretions form extremely faster than previously thought and that they originate from organic materials such as the remains of organisms. However, there have been few studies on the origin of phosphorus which is abundantly contained in concretions. In this study, we analyzed Raman spectra of apatite in concretions, which enables in-situ analysis of samples, to investigate the origin of concretions. The concretions used in this study were with diameters of several centimeters from the Cretaceous Kitaama Formation of the Izumi Group in the southern part of Awaji Island, Hyogo Prefecture, southwestern Japan. The ν_1-PO_4^{3-} and FWHM of apatite in the fossil-bearing and non-fossil-bearing concretions were analyzed. The Raman spectra revealed that there are two types of apatite in the concretion; group W and N. In group W, the ν_1 band appears at low wavenumbers and has a wide FWHM. On the other hand, in Group N, the ν_1 band appears at high wavenumbers and the FWHM is narrow. The apatite belonging to Group W is rich in Sr and shows FWHM similar to that of biogenic apatite such as bone and teeth of living organisms[1]. Therefore, it is suggested that the apatite belonging to Group W is a biogenic apatite derived from the soft parts of living organisms. On the other hand, apatite belonging to Group N was plotted between geologic apatite and fossil teeth. Group N is F-rich, has a high band position, narrow FWHM, and similar characteristics to geologic apatite. Two types of apatite were observed in the concretion, suggesting that the apatite at the time of concretion formation was biogenic apatite, but the biogenic apatite changed to geologic apatite as the concretion underwent diagenetic processes.

[1] Thomas et al. (2011), Palaeogeography, Palaeoclimatology, Palaeoecology 310, 62-70.