

Age determination of spherical carbonate concretions by Sr isotope stratigraphy

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Isolated spherical carbonate (CaCO_3) concretions are frequently observed in marine clayey sediments but do not always contain index fossils. Although carbonate concretions with fossil inside can be used to estimate sedimentation ages, concretions without fossils inside have never previously been used for age determination. In this study, we used $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to determine the ages of these spherical concretions.

The studied concretions formed in the Yatsuo Group of Miocene age in central Japan. Some formed post-mortem around tusk-shells (*Fissidentalium* spp.), while other concretions have no shell fossils inside. The concretions formed under highly constrained conditions by reactions between the decay products of organic matter and Ca^{2+} from the marine water (Yoshida et al., 2015; 2018). And the sedimentary structure around the concretions and geochemical analyses reveal that Sr was incorporated into the CaCO_3 concretions during their rapid formation.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of calcite in the tusk-shell concretions lie within 0.70865~0.70867 and vary little. The values are similar to those of tusk-shell aragonite, 0.70865~0.70868. In addition, the isolated carbonate concretions without shell fossils have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70865~0.70868, which are also well consistent with the tusk-shell aragonite values. Based on the Sr isotope stratigraphy (McArthur et al., 2001) and the measured $^{87}\text{Sr}/^{86}\text{Sr}$ values, the age of the tusk-shell concretions lies within a narrow range of 17.08 (+0.27, -0.28) Ma. The age determined from the $^{87}\text{Sr}/^{86}\text{Sr}$ of the tusk-shells themselves (16.86 +/- 0.34 Ma) is almost the same. The age determined from the $^{87}\text{Sr}/^{86}\text{Sr}$ of concretions without fossils, 16.95 (+0.36, -0.37) Ma, is almost the same as that of the tusk-shell concretions. Strontium isotopic stratigraphy using $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of all concretions with tusk-shell and without fossils indicates an age of 17.02 +/- 0.27 Ma, with higher accuracy than the ages estimated using microfossils from the Yatsuo Group. The results imply that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of isolated spherical carbonate concretions can be applied generally to estimate the ages of all kinds of spherical concretions in marine sediments (Yoshida et al., 2019).

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