

## Syn depositional formation of calcareous nodules on muddy sea floor: elucidating depositional history by C, O, S isotope characterization

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Calcareous nodules are commonly observed in mudstone sequences, however, paleodepositional condition including paleothermometry have never been discussed based on its chemistry without exceptional case such as methane seepage. It partly owes to their complicated depositional history. We characterized dark grey muddy carbonate nodules collected from Cretaceous strata in Hokkaido, Japan with carbon, oxygen, sulfide sulfur and sulfate sulfur isotopes, and demonstrated the syn depositional formation of some nodules. It is notable that initial formation of carbonate "precursor" for all muddy nodules studied here were syn depositional near oxic/anoxic boundary at shallower depth of muddy sea floor.

Some outcrop observations demonstrate calcareous nodules can be formed just below the sea bottom (JBSB). Structure suggesting consolidation JBSB includes burrows that eject calcareous precursor material from nodule. JBSB origin of the nodules consolidated associated with anaerobic oxidation of methane (identified by carbon isotope ( $d^{13}C$ ) values) with sulfate reduction are also demonstrated with oxygen isotope ( $d^{18}O$ ) and sulfur isotope ( $d^{34}S$ ) values. Such nodules show the exactly same  $d^{18}O$  values with that of benthic foraminifers. A bivalve fossil found on one of the methane seep nodules preserved aragonite of the shell and yielded close  $d^{18}O$  paleotemperature with that of host nodule.

The cross-plot of the  $d^{13}C$  and  $d^{18}O$  data can emerge "upper limit line" of  $d^{18}O$  values showing syn depositional formation. On the other hand, nodules from the Oyubari area characterized with  $d^{34}S$  (sulfate) lower than -18 permil indicating JBSB formation had conflicting  $d^{18}O$  values. It can be ascribed to the difference of burial depth between sediments of the Haboro and Oyubari areas. Even if precursor of the nodules initially crystallized JBSB, strong compaction during burial would have caused permeation of pore water into the incomplete nodules. Carbon dioxide or bicarbonate ions derived from decomposed organic matter would have caused recrystallization of calcite with  $d^{18}O$  as low as -10 permil in the nodule.

Keywords: calcareous nodule, oxygen isotope, sulfur isotope, carbon isotope