REPLY

Martin J. Kennedy
Department of Earth Science, University of California, Riverside, California 92521, USA
Nicholas Christie-Blick
Linda E. Sohl
Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York 10964, USA

Hoffman et al. (2001) acknowledge that methane may have played an important role in unusual events associated with Neoproterozoic glaciation, but they question our permafrost gas hydrate hypothesis for ^{13}C-depleted cap carbonate formation. They focus on three issues: (1) an interpretation for tube structures in cap carbonates unrelated to gas migration; (2) the absence of a suitable source for methane gas; and (3) the degree of ^{13}C depletion in sheet-crack cements.

Origin of tube structures. Hoffman et al. suggest that the tube structures represent the locus of 1- to 3-cm-wide dimples within a lattice of stromatolitic ridges on the synoptic surface of larger microbial bioherms and that the lack of tubes in the basal cap carbonate and in underlying diamictite rules out a buried source of gas.

Comprehensive studies of the best examples of tubes in Neoproterozoic microbial dolomites in California and Namibia (Cloud et al., 1974; Hegenberger, 1987) favor an origin related to gas or fluid flow. (1) The tubes are oriented close to paleovertical, up to several meters long, and are approximately circular in transverse section. (2) Microbial laminae are commonly planar adjacent to tubes, and do not form stromatolitic columns. (3) Some tubes are filled with sediment derived from overlying deposits, as much as 10 m above. (4) Others originate or terminate upwards at spar-filled sheet cracks and ‘‘gas blisters.’’ Together, these features are inconsistent with the interpretation of Hoffman et al. (2001). They confirm the existence of open spaces, and that gas or fluid movement was not restricted to tubes.

The tube characteristics are consistent with observations at modern cold seeps, where microbial mats acting as a seal permit the pressurization of buoyant gas. This gas is able to penetrate the mats at regular intervals determined by the permeability and cohesiveness of the sediment. If the sediment is sufficiently cohesive, the gas is forced sideways, splitting layers into gas blisters (Bohrmann et al., 1998). In relatively permeable sediment, such as the laminated dolomitic silt of the basal cap carbonate and underlying diamict, gas passage would have been more diffuse. Thus the observed inhomogeneous distribution of tubes is expected in heterolithic sediment.

Source of methane. Hoffman et al. (2001) assert that insufficient organic matter is present in either the cap carbonate or preglacial strata ($<$0.01% and $<$0.08% total organic carbon [TOC], respectively) to generate the methane needed for the development of gas hydrates. The distribution of gas hydrate is sensitive to the mass of buried organic matter (via migration), as well as its local concentration reflected in the TOC value. Even so, organic-rich intervals (TOC $\sim$11%) are common within preglacial strata in Namibia, locally constituting hydrocarbon-producing source rocks (Ypma, 1979). Within parts of the Damara fold belt, some of these ancient rocks have undoubtedly passed through the oil window, with a concomitant loss of organic material reflected in the low present-day TOC values quoted by Hoffman et al. (2001). Low TOC values are characteristic even of laterally continuous, black, sulfide-rich intervals indicative of a high organic content at the time of deposition.

Sheet cracks. The sheet cracks relevant to our hypothesis involve localized regions of extreme bedding disruption, multiple generations of fringing cements and internal sediment accumulation at sites at which evidence exists for subaerial exposure prior to cap carbonate deposition. The existence of sheet cracks in deep water facies of the Keilberg cap carbonate merely suggests a role for the degradation of marine gas hydrates or an origin unrelated to gas hydrates for those particular features. Hoffman et al. (2001) suggest that the absence of strongly negative δ^{13}C values in cement-rich zones is evidence against our hypothesis. However, both Hoffman et al. (1998) and Kennedy et al. (1998) analyzed bulk rock samples, not early diagenetic fringing cements. Most cements in the sheet-crack facies are later-stage, burial-diagenetic, void-filling spar, and precipitated from fluids in equilibrium with the bulk composition of the strongly positive (+5‰–10‰) preglacial carbonates. Early isopachous marine cements are rarely more than 5 mm thick, and they recrystallized to stoichiometric dolomite in the presence of isotopically heavier fluids.

Hoffman et al. (2001) fail to address other pertinent evidence for the role of gas hydrate destabilization in the development of ^{13}C-depleted cap carbonates. That evidence includes a time evolution for δ^{13}C excursions indicative of a pulse addition of isotopically depleted carbon to the ocean-atmosphere system at the end of each ice age, and mass balance considerations. The latter should be regarded as reasonable if independent estimates concur within an order of magnitude. Widespread development of gas hydrate is an inevitable consequence of globally frigid conditions. Destabilization of permafrost gas hydrate during the global deglaciation that followed ought to have left some record.

REFERENCES CITED

Bohrmann, G., Greinert, J., Suess, E., and Torres, M., 1998, Authigenic carbonates from the Cascadia subduction zone and their relation to gas hydrate stability: Geology, v. 26, p. 647–650.

Cloud, P., Wright, L.A., Williams, E.G., Diehl, P., and Walter, M.R., 1974, Giant stromatolites and associated vertical tubes from the upper Proterozoic Noonday Dolomite, Death Valley region, eastern California: Geological Society of America Bulletin, v. 85, p. 1869–1882.

Hegenberger, W., 1987, Gas escape structures in Precambrian peritidal carbonate rocks: Communications of Geological Survey of South West Africa/Namibia, v. 3, p. 49–55.

Hoffman, P.F., Halverson, G.P., and Grotzinger, J.P., 2001, Are Proterozoic cap carbonates and isotopic excursions a record of gas hydrate destabilization following Earth's coldest intervals?: Comment: Geology, v. 29, p. 286.

Hoffman, P.F., Kaufman, A.J., Halverson, G.P., and Schrag, D.P., 1998, A Neoproterozoic snowball Earth: Science, v. 281, p. 1342–1346.

Kennedy, M.J., Runnegar, B., Prave, A.R., Hoffmann, K.-H., and Arthur, M.A., 1998, Two or four Neoproterozoic glaciations?: Geology, v. 26, p. 1059–1063.

Ypma, P.J.M., 1979, Mineralogical and geological indications for the petroleum potential of the Etosha Basin, Namibia (S.W. Africa), Parts I and II: Proceedings of the Koninklijke Nederlandse Akademie van Wetenschappen, Series B: Palaeontology, Geology, Physics, Chemistry, v. 82, p. 91–112.