American Mineralogist, Volume 89, pages 1254–1259, 2004

Influence of water thermal history and overpressure on CO_2-hydrate nucleation and morphology

O.Y. ZATSEPINA,[1] D. RIESTENBERG,[1] S.D. MCCALLUM,[1] M. GBORIGI,[1] C. BRANDT,[1] B.A. BUFFETT,[2] AND T.J. PHELPS[1,*]

[1]Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6036, U.S.A.
[2]The University of Chicago, Chicago, Illinois 60637, U.S.A.

ABSTRACT

The onset of gas hydrate nucleation is greatly affected by the thermal history of the water that forms its lattice structure. Hydrate formation experiments were performed in a 72 L pressure vessel by injecting bubbles of carbon dioxide through a 1 L tube at hydrate formation pressures (1.4 to 3.7 MPa) and temperatures (2 to 5 °C). The results revealed that when even a small fraction (e.g., 5–35%) of the water in which the hydrate formed was recently thawed the overpressure for nucleation was reduced by an average of 50% as compared to untreated distilled water. This observation was confirmed by an analysis of variance (ANOVA) test that indicated that recently thawed water required a significantly lower overpressure compared to the untreated distilled water. In experiments where hydrate nucleated at low overpressure (e.g., 0.75 MPa), hydrate formed at the vapor-liquid interface, encrusting the bubbles with less than 1 g of hydrate accumulation in the first minute. When a higher overpressure was required for nucleation (e.g., 1.3 MPa), hydrate was observed to form abruptly not only on bubbles but also from the bulk liquid phase, typically accumulating a mass of more than 100 g in the first few seconds. Our results show that initiation of hydrate formation is strongly influenced by temperature-dependent pre-structuring of water molecules prior to their contact with gas. Although as little as a 5% volume fraction of pre-structured water may decrease the required overpressure, once hydrate formation commences the mass of hydrate accumulation is dependent on the overpressure.