COMMENTS

Comment to the Moudrakovski et al. Letter, "Hydrate Layers on Ice Particles and Superheated Ice: A ^{1}H NMR Microimaging Study"

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In a Letter by Moudrakovski et al.,[1] the authors dispute some of our published interpretations of results concerning the conversion of granular H_2O ice to methane (CH_4) hydrate by warming the reactants (ice + CH_4 gas) above the H_2O melting point.[2−4] Moudrakovski et al. report on experiments conducted to test the hypothesis as stated in the opening of their abstract: "Recent observations on the interaction of methane gas with ice surfaces have lead to the suggestion that the resulting hydrate layer prevents the encapsulated ice from melting as its usual temperature. This would require the ice to exist in a 'superheated' state".[1] The authors attribute this working hypothesis to our previously published work,[2,3] with which we take exception, as it seriously misrepresents our interpretations. The authors then present results that disprove this stated hypothesis; their NMR microimages show conclusively that at their experimental conditions, unreacted ice cores melt in bulk at the expected ice melting temperature and that the hydrate-encased liquid can maintain grain shape integrity with little or no collapse of the outer hydrate shell. This remarkable demonstration of very thin hydrate rinds masking the pressure signature associated with the ice → water phase change clearly refutes our published skepticism concerning such pressure sealing abilities (as discussed below). These results, however, do not necessarily disprove our hypotheses regarding suppressed rates of melting during conversion of ice to hydrate by our published standard procedures. We note that Moudrakovski et al. neither described nor duplicated the test conditions at which we previously reported the absence of a measurable bulk-melting signature, nor do they discuss the possible importance of their different test conditions. Furthermore, they do not note that all of the tests reported in their Letter were conducted at the same, relatively low pressure conditions at which we *also* observed and reported bulk melting of ice grains.[3,4] Here, we discuss the relationship of the Moudrakovski et al. work to our own results and interpretations regarding hydrate formation from warming ice + gas mixtures, in an attempt to clarify some physical chemistry considerations of hydrate synthesis and the possible "superheating" of ice.

We discussed and demonstrated in our papers[2−4] that the conditions required for full and efficient conversion of granular ice to methane hydrate under static conditions, without measurable segregation of a bulk melt phase, requires a very high overstep of methane gas pressure (P_{CH_4}) above the methane hydrate equilibrium curve (we work at 27−33 MPa), thermal ramping and subsequent holding of temperature (T) at warm conditions (∼290 K for 8−12 h), and a small initial grain size of the granular "seed" ice (<250 μm). The conditions may also be specific to the method we use to prepare the ice grains to minimize defects, impurities, or grain boundaries that can act as sites for melt nuclei.[2−4] We postulated, on the basis of our measurements and observations, that in situ conversion of ice grains to hydrate initiates along grain surfaces and then migrates inward by what we speculated to be an essentially solid-state transport or diffusion-controlled reaction.[2,3,4]

In regard to this hydrate-forming reaction process, it was not our intent to suggest that "the presence of a hydrate layer prevents liquid under the hydrate layer from nucleating";[1] nor to "postulate the existence of superheated ice"[1] from that previous statement. We acknowledge that this interpretation of our work by Moudrakovski et al. could have been formed from certain phrasing in our first article published in *Science*,[2] which was written to announce a breakthrough and that therefore contained some ideas that were not fully developed. Ambiguities in the *Science* paper regarding our hypothesized mechanism for hydrate formation from ice + methane, however, as well as further testing of these hypotheses, were addressed in detail in our subsequent work[3] that was also cited by Moudrakovski et al.

A key factor discussed in our papers is that the success of our method for full conversion of ice to hydrate appears to be dependent on those aspects of our standard procedure that influence the availability, transport, and concentration of the hydrate-forming species at the growth front, i.e., those factors that influence diffusion rates, such as high pressure overstep, high temperature, high surface-to-volume ratio of the reacting grains, and small grain size that minimizes the thickness of the developing hydrate barrier to the unreacted core. We hypothesized that such conditions may enable transport of methane through the outer hydrate rind and inward to the hydrate/ice interface at a rate sufficiently fast such that incipient melt nuclei react to form methane hydrate faster than they can grow to the critical size necessary for bulk melting.[2,3,4] In *J. Phys. Chem. B*,[3] we suggested that "surface melting may be a necessary condition for appreciable hydrate nucleation, and the very limited growth of hydrate under ice subsolidus conditions suggests that such growth requires continued nucleation of melt at the hydrate (mantle) and ice (core) interface. At supersolidus conditions, by corollary, a high driving potential for hydrate formation may be required to maintain a stable site for both continuous melt nucleation and hydrate formation at the hydrate/ice interface, to suppress macroscopic melting."[3]

Our ongoing observations are consistent with this hypothesis. We suggested that the bulk melting observed in tests on coarse-grained (1−2 mm) ice might have been due to the eventual development of a thick hydrate barrier to the hydrate growth front that greatly slowed methane diffusion.[3,4] In a different set of tests, we varied the P_{CH_4} overstep of the methane hydrate

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equilibrium curve and successfully induced and observed rapid bulk melting at 275 K in previously intact grains by reducing P_{CH_4} from our standard working pressure of ~30 to 4 MPa.[3,4] In another test (unpublished, 1997), we observed the same melting behavior during synthesis at 11 MPa. This is the pressure range at which Moudrakovski et al. imaged melting ice cores (they report tests at $P_{CH_4} = 5.7-11.9$ MPa). We noted even in our earliest work that while all of our samples routinely synthesized at 27−32 MPa do in fact show evidence for some melting of the ice cores (discussed in Figure 3A in (2), for example), we observed no evidence for complete melting, even though full conversion of ice to hydrate takes about 8 h by our methods.[2,4] We offered the explanation of possible short-term superheating of ice, based on these ideas of promoting conditions where the rate of CH_4 transport and hydrate formation at the hydrate/ice interface essentially "balances" the growth rate of melt nuclei to critical size, because we were unable to find a satisfactory alternative explanation for our observations.[2]

One alternative explanation that we believed was highly improbable was the supposition that thin rinds of hydrate could act as pressure seals around melting cores, masking the pressure−temperature signature of rapid bulk melting and the accompanying volume reduction.[2] On this matter, the Moudrakovski et al. work clearly disproves our skepticism, at least in regard to masking of the pressure signature. Their NMR microimages elegantly show that the interiors of ice grains pressurized with CH_4 gas at $P_{CH_4} = 5.7-11.9$ MPa can in fact melt to liquid water with little or no collapse of the outer hydrate shell. This is quite astonishing to us, as we had speculated that hydrate rinds forming at $T < 273$ K are vanishingly thin and therefore unlikely to remain rigid enough to prevent collapse around a rapidly melting ice core as the reactants are warmed through the H_2O melting point.[2] (We estimated that at our rate of heating, less than 2% of the ice converts to hydrate in the H_2O subsolidus region,[2] and Moudrakovski et al. report ≤1% conversion; such low amounts correspond to a rind thickness that is initially only a fraction of a micron.) We find this result of their work to be exceptionally noteworthy.

The key unanswered question, however, is whether it is possible to create test conditions that induce transport of methane through the outer hydrate rind and inward to the hydrate/ice interface, at a rate sufficiently fast such that incipient melt nuclei react to form methane hydrate faster than they can grow to the critical size necessary for bulk melting. As the NMR microimaging technique is ideally suited for addressing this question, we hope that this Comment will help prompt further investigations to test this hypothesis.

References and Notes

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(4) Stern, L. A.; Kirby, S. H.; Durham, W. B. *Energy Fuels* **1998**, *12*, 201.