

## Preface to the *Clathrate Hydrates* special issue

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Clathrate hydrates are of an immediate and practical concern, because of the hazards they pose to oil and gas drilling and production operations in both deep marine and onshore Arctic environments. Drilling operations have encountered numerous problems (gas kicks, blowouts, and fires) when gas hydrates are penetrated, due to the large and often uncontrolled gas release from their dissociation. In addition, the conditions in the deep marine oil and gas production facilities and many kinds of pipelines can promote the growth of clathrate hydrates. In these situations, they can form costly and hazardous blockages in pipelines and sub-sea wellheads. Flow assurance in pipelines is a major concern of all deepwater oil and gas companies. In pipeline systems, clathrate hydrates are thermodynamically suppressed by adding antifreeze materials such as salts or glycols. Nucleation and growth of hydrates can also be kinetically inhibited by the addition of certain polymers.

The interests in clathrate hydrates are broad and diverse. Natural marine and permafrost deposits offer a vast untapped reserve of methane, which is conservatively estimated to exceed by a factor of two all other fossil fuels combined. Natural gas from clathrate hydrates might be essential to provide a transition to a hydrogen-based economy that will be independent of carbon-based fuels.

Despite the widespread natural occurrence of at least three structure types of clathrate hydrates, none are designated as minerals. Indeed, no mineralogy texts mention clathrate hydrates, even though they qualify as rock-forming minerals in terms of their abundance. The lack of mineral distinction does not detract from their importance as natural materials. Clathrate hydrates of methane and other small alkanes occur terrestrially in marine sediments of the continental margins and in permafrost sediments of the arctic (Max 2000; Paull and Dillon 2001). Air clathrate hydrates have also been recovered from ice cores in Antarctica and Greenland (Pauer et al. 1996). Clathrate hydrates of various compositions, including carbon dioxide, have been inferred to exist on other planets and their moons, Mars (Durham et al. 2003) and Titan (Loveday et al. 2001) in particular. Powder diffraction studies at extremely high pressures have shown the clathrate hydrates to exhibit a variety of new polymorphs (Loveday et al. 2003), and have also proven the formation of hydrogen clathrate hydrate (Mao et al. 2002). Clathrate hydrates are familiar to mineralogists who study fluid inclusions (Samson et al. 2003), because they are commonly encountered in freezing point studies as daughter crystals (Bakker and Thiery 1994). Quantitative study of natural clathrate hydrates is hampered by the difficulty in obtaining pristine samples. Bringing samples of clathrate hydrate from the seafloor at depths greater than 500

m without compromising their integrity is not trivial (Paull et al. 2000). Most physical property measurements are based on studies of laboratory-synthesized samples.

Methane is powerful greenhouse gas, and discharge of large amounts of methane into the atmosphere would contribute to global warming. Since the proposal of the clathrate gun hypothesis (Kennett et al. 2002), the role of marine methane hydrates in global climate change (over the past 1.5 million years) has been hotly debated by climatologists and geophysicists. This idea proposes that the marine methane hydrate reservoir has repeatedly reloaded and discharged in response to changes in sea level and sea-floor temperatures. The American Association of Petroleum Geologists' Distinguished Lecturer for 2004, Richard J. Behl, was one of the coauthors of the paper and his lecture on the subject, "Methane Hydrates and Climate Change: The Clathrate Gun Hypothesis," seeks to explain the dramatic variations observed in ice-core atmospheric methane records during the Pleistocene and to establish the role methane hydrate will play in future climatic changes.

The causes of continental-slope failures have also implicated methane hydrate (Maslin et al. 2004). Glacial-period slope failures are mainly associated with lowering of the sea level, suggesting that reduced hydrostatic pressure and the associated destabilization of methane hydrate may be the primary cause. Moreover, continental slope failures would be accompanied by large tsunamis. Several examples of possible gas hydrate related slumps have been described on the Norwegian continental margin (Bugge et al. 1987), where debris from the giant, three-part Storegga slide, over 450 m thick, is spread over a distance of 800 km. One of the Storegga slides caused a tsunami that deposited sediment up to 4 m above the high water line in Scotland (Nisbet and Piper 1998).

Because fossil fuels will continue to be our primary source of energy for at least several more decades, the production of greenhouse gases is a major concern due to their role in global atmospheric warming. Carbon dioxide sequestration is among the schemes to mitigate the affects of greenhouse gases. Of the competing technologies for CO<sub>2</sub> sequestration, CO<sub>2</sub> clathrate hydrates retard any dissolution of deep ocean injection of liquid CO<sub>2</sub>. The effects of deep ocean injection of CO<sub>2</sub> are being studied from various aspects (Brewer 2003).

Natural Gas Hydrates (NGH) are drawing renewed attention as a cost effective gas transportation media for stranded gas fields, defined as being too small to justify a liquefaction facility and more than 400 km from a pipeline. The amount of natural gas contained in NGH, at ambient conditions, is equivalent to 170 times the volume of NGH. Feasibility studies show that hydrate

technology for large-scale and long-distance transport of natural gas will cost about one-quarter of that established for liquefied natural gas technology (Børrehaug and Gudmundsson 1996).

As crystalline materials, clathrate hydrates have anomalously low thermal conductivity, approaching glass-like behavior at low temperatures. In this regard, the study of the dynamical properties of the guest molecules and the guest-host interactions are a fertile ground from which we can develop an understanding of the mechanisms of low thermal conductivity in crystalline materials.

Clay methane hydrate intercalates have been theoretically proposed (Titiloye and Skipper 2000) and recent experimental evidence for their existence has been reported from attempts to synthesize clay clathrate intercalates in the laboratory (Guggenheim et al. 2003). If clay clathrate hydrate intercalates occur in nature, the mineralogy and petrology of clathrate hydrate bearing sediments might be significantly richer than previously known.

This special issue provides a selection of clathrate hydrate papers from some of the major research groups worldwide. In this issue, the coverage of all of the interests in clathrate hydrates is not complete, but it should serve to remind mineralogists that these materials will be an important topic for some time, and that the mineralogical community is ideally experienced to contribute significantly to understanding clathrate hydrates.

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