

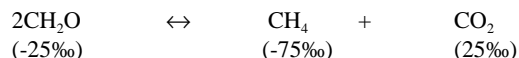
## On the possible role of gas hydrates during Neoproterozoic carbon cycle

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The carbon isotope record of both inorganic and organic phases during the Neoproterozoic indicates that the fractionation associated with biomass production and burial ( $\Delta_c = \delta^{13}C_{carb} - \delta^{13}C_{org}$ ) has varied widely (Hayes et al., 1999). This has been attributed to significant inputs from sulfide-oxidizing and other chemoautotrophic bacteria (*ibid*). Here, we present the evidences for the possibility of the role of methanogenesis during organic diagenesis in bringing about the observed variation in isotopic trends during the Neoproterozoic.

Methanogenesis can result in release of  $^{13}C$  enriched  $CO_2$  as indicated by the following reaction:



The  $CO_2$  of above reaction will lead to the enrichment of  $^{13}C$  in ocean water bicarbonate pool, provided  $CH_4$  is effectively stored in the sediments (as gas hydrates). The global  $\delta^{13}C$  record of the period between 630 and 600 Ma indicates that the  $\delta^{13}C_{org}$  remained close to the global average of -25‰, while the  $\delta^{13}C_{carb}$  rose rapidly from 2‰ to 7‰. Under such circumstances, a two component box model suggests that ~22% of  $CO_2$  produced due to methanogenesis (with  $\delta^{13}C$  of 25‰) is needed to produce the observed shift in  $\delta^{13}C_{carb}$  and  $\Delta_c$ . Significantly, a similar amount of methane should have been preserved in the form of gas hydrates during the same time interval. Preservation of such large amount of gas hydrates must have played a key role in bringing about glaciation (Marinoan/Vendian) and deglaciation as a consequence destabilization of gas hydrates, evidence for which is preserved in the form of negative  $\delta^{13}C$  excursion in "cap carbonates". It appears from the above that the gas hydrate formation and destabilization might have provided some impetus to the drastic climatic changes in geologic history at least since the Neoproterozoic.

### References

Hayes, J.M., Strauss, H. and Kaufman, A.J. (1999), *Chem. Geol.* **161**, 103-125.

## Silicate liquids: Defining and quantifying structural disorder

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The atomistic understanding of thermodynamic and transport processes in molten silicates is critical to the development of physically robust models. A key element of this understanding is the definition of the various ways in which a melt can be disordered, and the complementary problem of quantifying this disorder and the effects of pressure and temperature on it. New spectroscopic methods, particularly solid-state Nuclear Magnetic Resonance, have recently greatly increased our knowledge of these questions.

For example, models of the thermodynamics of phase equilibria of melt systems are generally (per force) based on the mixing of components which reflect, implicitly or explicitly, assumptions about which cations or "structural units" mix, and which do not. The "ideality" or randomness of some aspects of this mixing, for example that of network modifiers of varying size and charge, can now be determined in glasses by high-resolution O-17 NMR, which shows a surprising range of ordering states from nearly random to highly ordered. Such results reflect at least the structural state at the glass transition temperature, highlighting the importance of determining T effects to extrapolate to the liquidus range. Similar issues for the "speciation" of minor components of melts (e.g. trace metals, volatiles) are at the heart of models of their thermodynamic activities. Techniques such as Cl-35 and F-19 NMR are revealing for the first time the real complexity of long-proposed "melt complexes," and should allow the formulation of more accurate models of the effect of composition on activities.

The nature and extent of configurational disorder has been emphasized in recent studies of melt viscosities, and continues to motivate structural studies. Again, solid-state NMR on glasses has now begun to provide quantitative determinations of the extent of ordering of the major, thermodynamically significant structural elements, such as both non-bridging and bridging oxygens, as well as of mechanistically significant minor species such as AlO5 and SiO5 groups and Al-F and Si-F bonding.