Elevated concentrations of trace greenhouse gases during ancient ‘greenhouse’ climates

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Trace greenhouse gases (GHGs) are a fundamental, fast-responding component of Earth’s global climate system that is sensitive to global change. However, their concentration in the pre-Quaternary atmosphere is highly uncertain due to the lack of biological or geochemical proxies. Here, we report new 3-D Earth system modeling simulations showing that the ‘greenhouse’ worlds of the late Cretaceous (90 Ma) and early Eocene (55 Ma) with 4× pre-industrial CO_2 are compatible with high concentrations of methane, surface ozone, and nitrous oxide. Higher concentrations of these nonCO_2 GHGs exerted marked planetary heating, amplified in high latitudes by lower surface albedo feedbacks. An Eocene sensitivity analysis indicates inclusion of the positive forcing by elevated trace GHGs increases the Earth system sensitivity to a doubling of atmospheric CO_2 by 1K. These results point to the requirement for including fast-feedback processes in climate models in order to draw more appropriate comparisons with emprical estimates from palaeoclimate data.

All in motion – The dynamic exchange of CO_2 and CH_4 in gas hydrates

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Methane recovery from gas hydrates (GH) coupled to subsequent sequestration of CO_2 into the same formation is often seen as an ideal solution to the demand for fossil fuel on the one hand and the reduction of antropogenic CO_2 on the other hand.

Several promising experimental results on that exchange of CO_2 for CH_4 in GH have been published in recent literature [e.g. 1, 2, 3] but the follow-up scenario – the possible CO_2 hydrate dissolution and renewed CH_4 hydrate formation from the original source, has not been investigated yet.

Here we present results of a simple set of experiments using a small scale cryo-cell mounted to a Raman spectroscope that impressively demonstrate the CO_2-CH_4 exchange in both directions.

Although the thermodynamic stability of CO_2 hydrate exceeds that of CH_4 hydrate, the CH_4 production from GH is incomplete and abates, despite continuous CO_2 gas inflow, at approximately 50%. This is due to interference of the more ideal guest-to-cavity ratio of CH_4 in small cages of sI hydrate with the unfavourable larger dimensioned CO_2 molecule. A mixed CO_2-CH_4 hydrate forms.

If the transformed CO_2-CH_4 hydrate is then exposed to CH_4 to convert back into the former CH_4 hydrate, an incomplete CO_2 release is observed. This is expected from a thermodynamic point of view, because of the higher stability of mixed CO_2-CH_4 hydrate compared to that of pure CH_4 hydrate. The restricted exhange occurs due to the chemical dis-equilibrium caused by the high CH_4 concentration in the surrounding environment.

To converge on a real production scenario by means of CO_2 sequestration, mixed CH_4-C_3H_8 hydrates (2% C_3H_8) as well as impure CO_2 (containing 1%SO_2) have been tested for the exchange process and proved to behave similarly.

The competing factors of aiming for chemical equilibrium and best guest-to-cavity ratio strongly influence the CO_2-CH_4 exchange in gas hydrates and need to be considered when exploring for an effective CH_4 production from hydrate deposits coupled to long term CO_2 storage.

[1] Ersland *et al.* (2009) *Chem. Eng. J.*, in press. [2] Ota *et al.* (2007) *AIChE* **53**(10), 2715–2721. [3] Ohgaki *et al.* (1996) *J. Chem. Eng. Jap.* **29**(3), 478–483.