Calcite ($CaCO_3$) growth as a function of calcium-to-carbonate ratio in the presence of strontium

J.N. BRACCO, M.C. GRANTHAM AND A.G. STACK

School of Earth and Atmospheric Sciences, Georgia Institute of Technology (andrew.stack@eas.gatech.edu)

Incorporation of impurities such as strontium into calcite ($CaCO_3$) has a number of implications for the geosciences, such as a proposed as a method of remediation of ^{90}Sr for groundwater contamination. While some studies of impurity incorporation into calcite exist, the mechanism (s) of incorporation during crystal growth is still unclear [1]. For example, microscopic examination of calcite growth rate in the presence of aqueous strontium has previously been shown to have complex behaviour [2]. That is, lower concentrations of strontium increase calcite growth rate while higher concentrations inhibit growth through a postulated step pinning mechanism. Furthermore, this study found that strontium preferentially incorporates into obtuse step orientations over the acute by a factor of two.

Studies of calcite growth as a function of calcium-to-carbonate ratio in the absence of strontium have shown that total growth rate is maximized at high calcium-to-carbonate ratio for obtuse steps and moderate or low calcium-to-carbonate ratio for acute steps [3]. This implies that the preferential incorporation of strontium into obtuse steps is due to the enhanced growth rate of this step orientation under high calcium-to-carbonate ratios. Here, calcite growth is examined in the presence of strontium as a function of varying ratio of aqueous calcium to carbonate ions. This data is fit to a model where attachment and detachment of aqueous calcium and carbonate ions is treated individually. The step velocity at fixed strontium concentration and saturation state but variable calcium to carbonate ratio is measured.

[1] Rickaby *et al.* (2002) Growth Rate dependence of Sr incorporation during calcification of *Emiliania huxleyi*. *Global Biogeochem. Cycles*. **16**, 61–68. [2] Wasylenki, Dove, Wilson & De Yoreo (2005) *Geochim. Cosmochim. Acta* **9**, 5135–5144. [3] Stack & Grantham (in press) *Cryst. Growth Des.*

Methane hydrates: A principal source of atmospheric methane?

JAMIE L. BRAINARD* AND HIROSHI OHMOTO

NASA Astrobiology Insttitute and Department of Gesociences, The Pennsylvania State Univ., Univ. Park, PA 16802 (*correspondence: jlb5156@psu.edu)

Methane hydrates occur in deep terrestrial permafrost (up to 400Gtons) and in sediments on marine continental shelves at depths > ~500m. Many researchers have discussed the possible effects of the methane released from the methane hydrate zone (MHZ) on climate, but few have given a numerical estimate and the discussions were based on old (inaccurate) estimates on global hydrate reserves. Based on the temperature-depth profiles for water and sediment columns in major marine basins and on the P-T-salinity phase diagrams of methane hydrates, we have derived the equations linking the thickness of MHZ to the seawater depths, bottom water temperatures, and geothermal gradients. Our calculation gives a value of 4550 Gt of CH_4 for the global reserve, compared to a widely used value of 750 to 6400 Gt.

Thickness of MHZ decreases with decreasing pressure (i.e. decreasing sea level) and/or increasing bottom-water temperature. For example, a 10 m drop in sea level or a 1°C increase in the bottom water temperature may result in a release of 19 Gt and 330 Gt, respectively, of CH_4 from the seafloor to the overlying seawater (and to the atmosphere). If all the released CH_4 accumulated in the atmosphere without being converted to CO_2, the atmospheric CH_4 concentration may increase by 6.7 ppm and 115.9 ppm, respectively. For comparison, the atmospheric CH_4 concentration during the inter glaciation periods was approximately 450 ppb.

Results of our study suggest that large variations in atmospheric CH_4 are largely derived from the MHZ, rather than biological activity, and that the increased CH_4 release during the interglaciation periods were due to the increased destabilization of the MHZ.