

## Can modern methane events and $\delta^{13}\text{CH}_4$ measurements say anything about glacial/interglacial transitions?

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Over the past decade several major excursions, in the southern tropics, mid-latitudes and Arctic, have occurred in the atmospheric methane record. These recent growth rates, though short-lived, are comparable to those seen in the glacial-interglacial transitions. In the tropics recently, transient growth rates in excess of 10 ppb/yr have been observed, with sustained though lower growth rates through 2007-late 2012. This southern tropical event was apparently driven by increased rainfall, not directly by anthropogenic emissions as in the high  $\text{CH}_4$ -growth events in the 1980s. A brief strong growth event occurred in the Arctic in 2007/8, while high growth in the northern mid-latitudes occurred in 2003 and again in 2009. These latter events may have been partly driven by anthropogenic inputs.

$\delta^{13}\text{CH}_4$  studies of sources and polar flights suggest that Arctic and boreal wetlands, not hydrates, have been the dominant regional summer  $\text{CH}_4$  source in recent years. Hydrate-fed submarine plumes occur but their main near-future impact may be local ocean acidification and deoxygenation. In winter, Arctic anthropogenic emissions likely dominate. These modern changes, and their rapid fluctuations, suggest boreal and tropical wetland emissions, responding very quickly to warming or cooling, could have dominated the increase in  $\text{CH}_4$  at glacial terminations. Modern Atlantic transects and observations also show the importance of distinct air masses in shaping the annual average record.

## Temperature effects on cathodoluminescence of calcite

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Cathodoluminescence (CL) of calcite has been extensively investigated by many researchers, and used for a wide range of geoscientific applications. The CL features are affected by many factors such as activator, sensitizer and quencher of transition metal elements. However, the temperature effects on calcite CL have not been precisely clarified so far. In this study we have quantitatively evaluate temperature quenching effects on calcite CL with various activator concentrations.

Six calcite samples with Mn concentrations of 13, 129, 1259, 3520, 9170, 66500 ppm were selected for CL spectral measurements at various temperatures from  $-190\sim 25\text{ }^\circ\text{C}$ .

CL intensity of low-Mn calcite increases with an increase in sample temperature, but the intensity of medium-Mn calcite shows almost unchangeable at a wide range of temperature. In contrast CL intensity of high-Mn calcite decreases with increasing temperature. These facts imply that temperature effects on calcite CL depend on activator concentrations in calcite, whereas luminescence efficiency generally decreases with rising temperature due to an increase in non-radiative transitions, which has been known as temperature quenching.

A least-square fitting of the Arrhenius plot by assuming a Mott-Seitz model provides an activation energy of 0.04~ 0.07 eV for high-Mn calcite in a temperature quenching process. These values correspond to lattice vibration energy, suggesting that the energy of non-radiative transition might be transferred to lattice as phonon. The result leads that activator (Mn ion) concentration considerably affects temperature quenching effect on CL of calcite.