

Mercury as a proxy for volcanogenic CO₂ buildup in Neoproterozoic snowball Earth and Volcanism in the K-T Transition

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Introduction. Mercury tends to concentrate in sediments deposited right after major glacial events [1] as a result from leaching of volcanogenic Hg from land surface and accumulation along argillaceous sediments. Wherever geological background of Hg is negligible, its concentration in sediments may be useful for investigation of climatic changes.

Volcanism is assumed to be responsible for CO₂ build up in the atmosphere during Snowball Earth event with subsequent greenhouse effect, ice melting and cap carbonate deposition [2]. Intense volcanism witnessed the Cretaceous-Paleogene transition [3] and was, perhaps, responsible for dramatic climatic change.

Results. We have used Hg as a proxy of volcanism intensity and CO₂ buildup during snowball events in Neoproterozoic cap carbonates in NE Brazil. Localities where carbonates are in sharp – but not erosional – contact with basal diamictites (earliest stages of aftermath of glacial events) and show $\delta^{13}\text{C}$ values $\sim -5\%$ were analyzed. Hg contents are usually over 10 times higher than background values ($<1 \text{ ng g}^{-1}$), occasionally reaching values $> 200 \text{ ng g}^{-1}$. Hg contents in cap carbonates of the Sergipano Belt and Ubajara Basin are similar to those in carbonates deposited coevally to volcanic activity elsewhere. This study supports mantle-origin for the CO₂ in cap carbonates, transferred to the atmosphere by volcanism.

Across the the K-T transition (KTB) in the Yacoraite Formation, Argentina, Hg contents reach $\sim 20 \text{ ng g}^{-1}$. In three drill cores in carbonate rocks across the KTB in the Paraíba Basin, northeastern Brazil, Hg increases (4 ng g^{-1}) in the early Danian right above the KTB. Hg spikes predating immediately the KTB suggest volcanism before this transition. At Stevns Klint, Denmark, Hg contents reach almost 300 ng g^{-1} within a 5 cm-clay layer (Fish Clay) that registers the KTB, and where a $^{87}\text{Sr}/^{86}\text{Sr}$ positive excursion and negative excursions of $^{206}\text{Pb}/^{204}\text{Pb}$ (T=65 Ma) and $^{187}\text{Os}/^{188}\text{Os}$ (T=65Ma) have been observed [4].

Hg content and Al₂O₃ show stratigraphically co-variation in all of the studied sections of Neoproterozoic cap carbonates or across the KTB, suggesting that Hg is probably adsorbed onto clays.

Conclusions. This study supports Hg stratigraphy as possible tracer of dramatic climatic changes as those in Neoproterozoic snowball Earth events and in the KTB.

[1] Santos et al., (2001). *Radiocarbon* **43**, 801-808. [2] Hoffman & Schrag (2002). *Terra Nova* **14**, 129–155. [3] Sheth (2005). *Gondwana Research* **8**, 109-127. [4] Frei and Frei, (2002). *Earth Planetary Science Letters* **203**, 6091-708.

Hydrothermal hydrocarbon gases: geothermometry and origins

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Upon their ascent through the crust, volcanic gases often interact with externally and internally derived fluids. For reasons of energy exploitation and surveillance of volcanic activity it is of great interest to determine hydrothermal temperatures at depth. Methane discharging from these systems has been ascribed a hydrothermal origin, with the magnitude of carbon isotope fractionation between CH₄ and CO₂ reflecting the formation temperature of CH₄ [1]. For most volcanic-hydrothermal discharges, however, apparent carbon isotopic temperatures cannot be confirmed by common gas concentration geothermometers involving redox pairs such as H₂/H₂O and CO/CO₂. In these cases, the geological significance of the carbon isotope geothermometer remains open.

We have addressed the genetic relationship between H₂, H₂O, CO, CO₂, n-alkanes and n-alkenes in volcanic-hydrothermal gases emitted from Nisyros (Greece), Vesuvio, Campi Flegrei and Pantelleria (all Italy). Our results imply that the isotopic CH₄-CO₂ geothermometer records temperatures of CO₂-water interaction at depth. In any case, apparent carbon isotopic temperatures are confirmed by measured propene/propane concentration ratios. Apparent temperatures are close to the critical conditions of pure and saline waters, i.e. $\sim 360^\circ\text{C}$ at Nisyros, $420\text{-}460^\circ\text{C}$ at Vesuvio, $\sim 450^\circ\text{C}$ at Campi Flegrei and $\sim 540^\circ\text{C}$ at Pantelleria. For temperatures $>400^\circ\text{C}$, apparent carbon isotopic temperatures are additionally confirmed by ethene/ethane ratios. At least in some systems, CH₄-CO₂ and propene-propane equilibration takes place in different water phases, implying that boiling in high-enthalpy hydrothermal systems may occur isothermally. Among the redox pairs investigated, CO/CO₂ is most prone to secondary vapor phase reequilibration reactions occurring after hydrothermal interaction at depth. Redox conditions during these reactions are homogeneously buffered by H₂/H₂O ratios of the vapor.

Methane most likely derives from an abiogenic source (Sabatier-type reduction of CO₂). In contrast to CO₂, the C₂₊-n-alkanes are not in equilibrium with CH₄. They derive either from the thermogenic decomposition of organic matter or from abiogenic methane polymerization.

[1] Fiebig et al. (2004) *Geochim. Cosmochim. Acta* **68**, 2321-2334.