## A half million years of suborbital variability from the Cariaco Basin: A proxy for Greenland "ice core" records?

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It is becoming increasingly apparent that rapid climate change on suborbital timescales is a persistent feature of Pleistocene climate. The best-studied archives of rapid climate change are Greenland ice cores, the longest of which presently available extends back to Marine Isotope Stage (MIS) 5e. The Cariaco Basin, located in the southern Caribbean, is a location that holds the potential to extend our understanding of suborbital scale climate variability. The basin is in a region sensitive to changes in the migration of the Intertropical Convergence Zone (ITCZ), has high sedimentation rates (≥30 cm/kyr) and excellent preservation due to periodic deep-water anoxia. The tight linkage between proxies for productivity in Cariaco and  $\delta^{18}\!O$  records in Greenland has been well established [1,2], suggesting the basin could serve as a proxy for conditions in Greenland prior to MIS 5e.

We present a half-million year long scanning X-Ray Fluorescence (XRF) record of sedimentary Molybdenum (Mo) from Ocean Drilling Program (ODP) Hole 1002C in the Cariaco Basin. The Mo record appears to serve as a reasonable proxy for high latitude conditions over the last ~500 kyr. Greenland ice core  $\delta^{18}$ O and Cariaco Mo records can be mechanistically linked by changes in the position of the ITCZ during the last glacial period. In earlier glacial periods, Mo enrichments covary with peaks in CH<sub>4</sub> from Epica Dome C and depletions in planktonic  $\delta^{18}$ O from Hole 1002C, giving confidence that they record interstadial-like conditions over the full ~500 kyr studied here. The distribution of millennialscale variability during the last six glacial periods is not consistent, and coupled with evidence for millennial-scale variability during interglacial periods, suggests that ice volume is not the only control on its occurrence. Alternative mechanisms for triggering periods of millennial-scale variability include the influence of precession on high-latitude insolation and the distribution of sea ice, or the influence of precession (and semi-precessional cycles) on the insolation and hydrologic cycle of the tropics.

[1] Hughen et al., (1996) Nature, **380**, 51-54. [2] Peterson et al., (2000) Science, **290**, 1947-1950

## Experimental investigations on halogen-rich agpaitic phase equilibria

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High concentrations of Cl and F are known to affect phase relations in magmatic rocks. In this study, we present phase equilibrium experiments investigating an iron-rich peralkaline phonolitic composition with variable Cl and F content. The starting material resembles a potential parental melt composition of the peralkaline Ilímaussaq plutonic complex/South Greenland [1].

Nominally dry experiments were performed at 100 MPa, 1000 - 650 °C and low oxygen fugacity adjusted with graphite-lined gold capsules in an internally heated argon pressure vessel and in hydrothermal rapid-quench cold seal pressure vessels. To cover the large T interval of crystallization we applied a two-step fractional crystallization strategy. The synthesized mineral phases are titano magnetite, fayalitic olivine, clinopyroxene, alkali feldspar, nepheline and aenigmatite (± native iron). Increased Cl and F concentrations additionally stabilize fluorite  $(CaF_2)$ , hiortdahlite  $((Ca,Na)_6(Zr,Ti)_2Si_4O_{14}F_4),$ Cl-bearing sodalite (Na<sub>8</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>Cl<sub>2</sub>) and, characteristic for agpaitic rocks, eudialyte (Na<sub>4</sub>Ca<sub>2</sub>(Fe,Mn)ZrSi<sub>8</sub>O<sub>22</sub>(Cl,OH)<sub>2</sub>). ZrO<sub>2</sub> melt concentrations necessary to stabilize hiortdahlite and eudialyte are different (0.9 and ~1.2 wt%, respectively). Thus early hiortdahlite saturation shifts euclidyte saturation to lower T.

In the Ilímaussaq rocks, magmatic clinopyroxene shows a gap between Ca-rich and Na-rich compositions, common in evolved peralkaline rocks [2]. This gap may be induced by Carich hiortdahlite and fluorite at the expense of Ca-rich clinopyroxene by reason of increasing F content in the residual melt. Na-rich clinopyroxene, not influenced by Ca-F phases, may then be stabilized coexisting with a more evolved melt at lower T. Both the Cl/OH ratio in eudialyte and Fe/Mn partition coefficients between clinopyroxene and eudialyte/aenigmatite decrease systematically with T. The comparison with existing data indicates that these ratios may have the potential for geothermometers, rarely available for agpaitic phase assemblages.

[1] Marks & Markl (2003) *MinMag* **67**, 893-919. [2] Njonfang & Nono (2003) *Eur J Min* **15**, 527-542.

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