

Characteristics of the Eemian from the Greenland Ice Sheet at GISP2

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The Eemian (115-128ka) is arguably the warmest the Earth's Arctic has been for the past 800ka. Recent data from NEEM (northwestern Greenland) show peak surface temperatures at ~126ka of $8 \pm 4^\circ\text{C}$ above the mean of the past thousand years, and a decrease in elevation of $400 \pm 250\text{m}$ between 128-122ka. Here, we focus on Summit Greenland at GISP2. The depth interval of GISP2 between 2750 and 3040m contains clean, disturbed ice, which is largely warm ice of Eemian age. We have constrained the age of this ice by measuring CH_4 and $\delta^{18}\text{O}_{\text{atm}}$ of O_2 , and analyzing the results in the context of the well-known histories of these gases from the Greenland NGRIP record to 121ka, and the Antarctic EDML and Vostok records beyond 121ka. Dating is not yet definitive but the most parsimonious interpretations align climate at GISP2 with change at NEEM. Dating of 44 sections of the warm, disturbed ice fall predominately into three distinct time periods: 104-107ka, 118-121ka, and 126-128ka. We do not find any evidence for ice between 121.5-125ka. The net change from ~127ka to ~118ka indicates an increase in total air content from 86-98ml/kg (~12%), similar to the change in observed total air content and inferred elevation at NEEM. Over the same interval, we see an increase in $\delta^{18}\text{O}$ of the ice from 128-126ka, and a decrease from 121-118ka, yielding a net increase of ~2‰ (~4°C). CH_4 concentrations in excess of 870ppb were observed at depths greater than 3030m, precluding the ability to date these samples. Our inferred elevation and temperature histories are generally consistent with recent results from NEEM, however we do not observe prevalent melt layers at the summit location.

Xenoliths, XANES and redox-related processes in the cratonic lithosphere

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The oxygen fugacity ($f\text{O}_2$) of peridotite upper mantle is predicted to decrease with increasing pressure because of molar volume changes of redox buffering reactions in peridotitic assemblages [1].

Fe K-edge XANES spectroscopy can now be routinely used to measure $\text{Fe}^{3+}/\Sigma\text{Fe}$ (where $\Sigma\text{Fe}=\text{Fe}^{2+}+\text{Fe}^{3+}$) in garnet from peridotite xenoliths [2]. Combined with conventional thermobarometry and experimentally calibrated oxybarometers [1] this enables rapid (30 min. acquisition), precise ($\pm 0.1 \log_{10}$ units) $f\text{O}_2$ determinations at micron-scale spatial resolution, as well as quantitative mapping of the distribution of Fe^{3+} in garnet crystals [3].

We have used the XANES technique [2] at the X-ray Fluorescence Microscopy beamline of the Australian Synchrotron to investigate $f\text{O}_2$ -depth variation in the Siberian Craton (Udachnaya East and Obnazhennaya kimberlites), the Slave Craton (Panda kimberlites) and the Kaapvaal Craton (Kimberley and Wesselton kimberlites).

In the Siberian and Slave cratonic lithosphere the $f\text{O}_2$ of peridotite xenoliths decreases with depth to $\Delta \log_{10} f\text{O}_2^{\text{FMQ}}$ of ≈ -4 to -5 at ≈ 200 - 220 km [1,4]. Such values approach the limiting Fe-Ni precipitation curve. Metasomatic events however, have locally perturbed this trend, and lead to oxidation by 1-2 \log_{10} units [3,4]. In the case of Wesselton, we mapped the Fe^{3+} distribution in compositionally zoned garnets, demonstrating that metasomatic overgrowth rims grew at $f\text{O}_2 > 2 \log_{10}$ units higher than the cores [3] only a very short time before eruption.

Redox conditions in the deep lithosphere are in general too reduced for carbonate melt stability [1,5], unless carbonate activity is substantially reduced by other components (silicates, halides etc).

[1] Stagno *et al.* (2013) Nature doi:10.1038/nature11679; [2] Berry *et al.* (2010) Chem Geol 278, 31-37; [3] Berry *et al.* (2013) Geology, *in press*; [4] Yaxley *et al.* (2013) Lithos 140-141 (142-151); [5] Woodland & Koch (2003) EPSL 214, 295-310.