

Glacial ocean temperatures from 'clumped isotope' thermometry in foraminifera and coccoliths

A. TRIPATI^{1,2*}, R. EAGLE², J. EILER² AND L. BEAUFORT³

¹UCLA, Los Angeles, CA 91125, USA

(*correspondence: ripple@zephyr.ess.ucla.edu)

²California Inst. of Technology, Pasadena, CA 91101, USA

³CEREGE, Aix en Provence, CEDEX 4, 1345 France

A primary goal of paleoclimate research over several decades has been to establish the magnitude and spatial patterns of temperature change in the oceans since the Last Glacial Maximum (LGM; ~21 ka). We are using 'clumped isotope' thermometry to develop a global map of sea surface temperatures (SSTs) for the LGM. This thermometer is based on the principle that ordering, or 'clumping', of heavy isotopes into bonds with each other in molecules is temperature-dependent due to an internal isotope exchange reaction which requires no knowledge of seawater isotope composition. We have previously calibrated the clumped isotope thermometer in foraminifera and coccoliths and shown that the proportions of ¹³C-¹⁸O bonds in these biogenic carbonates are not subject to non-equilibrium biological fractionations, and are independent of the composition of the water in which the mineral precipitated (Triпати *et al.*, in revision). Here we present the first record of Pleistocene and Holocene temperatures that is purely thermodynamically based, based on clumped isotope measurements of samples from the West Pacific warm pool. The warm pool is the warmest oceanic region and a benchmark for climate models. Reconstructions of the glacial-interglacial change in SSTs in the region vary from 1 to 6°C, differing systematically between methods. At the LGM average SSTs in the region were 25.5°C (~3.9°C cooler than today), and the δ¹⁸O_{S_{MOW}} of surface waters was 0.9‰. Assuming these results are representative for the region, then SSTs derived from alkenones, transfer functions, multi-proxy syntheses (i.e. MARGO) are systematically underestimating glacial cooling in this region. Mg/Ca SSTs appear to be the most accurate empirical proxy of SST in the region. Salinity-corrected Mg/Ca SSTs, and some terrestrial reconstructions, are indistinguishable from clumped-isotope derived temperatures. The predicted LGM temperature difference, defined as the difference in annual mean SSTs between LGM and pre-industrial simulations, generated by PMIP2 models for the region ranges from 1.0 to 2.4°C. All models predict less warming in the warm pool than our reconstruction. This mismatch could arise if there are problems in modelling tropical processes (e.g. if the models were not simulating changes in ENSO correctly), if the LGM simulations were incomplete (e.g. not including dust changes), and/or if these models systematically underestimate climate sensitivity.

The solubility behavior of CePO₄ and YPO₄ in H₂O-NaCl at 800°C and 1 GPa: Implications for the role of brines for REE transport during high-grade metamorphism

P. TROPPEL^{1,2*}, C.E. MANNING² AND D.E. HARLOV³

¹Institute of Mineralogy and Petrography, University of Innsbruck, Innrain 52, A-6020 Innsbruck, Austria

(*correspondence: Peter.Tropper@uibk.ac.at)

²Dept. of Earth and Space Sciences, University of California, Los Angeles, CA 90095, USA

³Helmholtz Zentrum Potsdam, Deutsches GeoForschungs-Zentrum, Telegrafenberg, D-14473 Potsdam, Germany

Monazite (CePO₄) and xenotime (YPO₄) are important accessory minerals because they host REE and Y and are useful for geochronology. It is therefore essential to understand their behavior during high-grade metasomatic processes. To constrain solubilities at high *P* and *T*, we carried out weight-loss experiments on synthetic single crystals of each phosphate at 800°C, 1 GPa, with H₂O and H₂O-NaCl (methods of [1, 2]). The results indicate that the molality (*m*, mol/kg H₂O) of CePO₄ and YPO₄ in pure H₂O is very low (CePO₄: 0.00004 *m*; YPO₄: 0.0003 *m*) but CePO₄ solubility increases strongly with increasing NaCl to 0.0079 *m* (*X*_{NaCl} = 0.5), similar to fluorite and calcite [2, 3]. In addition, solubility of a natural monazite at *X*_{NaCl} = 0.3, is very similar to pure CePO₄. In contrast, solubility of YPO₄ increases only moderately to 0.0044 *m* (*X*_{NaCl}=0.5); CePO₄ thus shows a stronger solubility enhancement by NaCl than YPO₄. CePO₄ solubility shows a linear correlation with *X*_{NaCl}² and a possible dissolution reaction thus could be: CePO₄ + 2NaCl = CeCl₂⁺ + Na₂PO₄⁻. The enhancement of YPO₄ with NaCl relative that in H₂O displays a maximum at *X*_{NaCl} ≈ 0.33, indicating 2 H₂O per NaCl. A possible dissolution reaction could be: YPO₄ + NaCl + 2H₂O = YCl(OH)₂ + H₂NaPO₄. CePO₄ and YPO₄ solubility increase less strongly with *X*_{NaCl} than apatite, implying lower solubility of Ce and Y relative to Ca. The data indicate that REE and Y mobility can be promoted by complexing with Cl in the aqueous phase during high-grade metamorphism [4].

[1] Tropper & Manning (2005) *American Mineralogist* **90**, 502–505. [2] Tropper & Manning (2007) *Chemical Geology* **242**, 299–306. [3] Newton & Manning (2002) *American Mineralogist* **87**, 1401–1409. [4] Newton & Manning (2010) *Geofluids* **10**, in press.