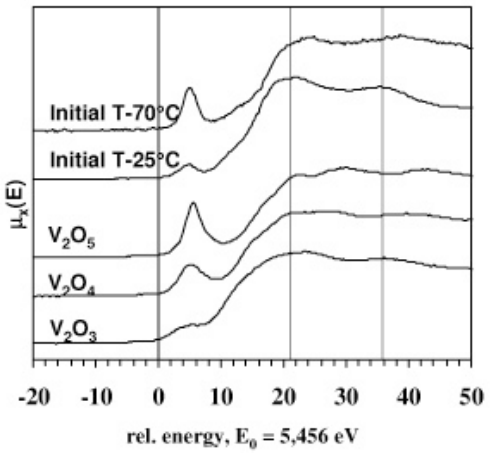
Temperature dependent $V^{3+/4+/5+}$ substitution(s) in goethite (α-FeOOH)

N. KAUR[1], B. SINGH[1]*, B. KENNEDY[2] AND M. GRÄFE[1]

[1]Faculty of Agriculture, Food and Natural Resources, The University of Sydney, NSW 2006, Australia (*correspondence: b.singh@usyd.edu.au)
[2]School of Chemistry, The University of Sydney, NSW 2006, Australia

Temperature is likely to affect V-substitution in goethite due to the redox-sensitive nature of V. To assess the effect of temperature on V substitution in goethite, a series of V-substituted goethite were prepared under varying temperature regimes, and analysed using wet chemical and multi-spectroscopic techniques. Increasing temperature enhanced the proportions of $V^{4+/5+}/V^{3+}$ incorporated in goethite as indicated by X-ray absorption near edge spectroscopy (XANES, see figure).



The oxidation state of V dictates the symmetry of the V polyhedron, with octahedral syummetry being preserved better for $V^{3+} > V^{4+} > V^{5+}$. The total vanadium substitution (V^{5+} + V^{4+} + V^{3+}) dropped by 94% with increase in initial aging temperature from 25 to 70°C suggesting that higher temperatures favour the oxidation of V^{3+} to V^{4+} and V^{5+}. The results show that low nucleation temperatures preserved the oxidation state of V^{3+}, which has a similar ionic radius, hydrolytic properties and octahedral symmetry as Fe^{3+} leading to 13.3 mol per cent substitution. This work provides information about the interaction between temperature, V oxidation and incorporation into the goethite structure. These aspects are important for sequestration strategies of V.

Accurate chronology of Antarctic climate and greenhouse gas changes over the past 470 ky

K. KAWAMURA[1,2]*, S. AOKI[2], T. NAKAZAWA[2], H. MATSUSHIMA[2], S. ISHIDOYA[2], S. SUGAWARA[3], L. LISIECKI[4], M. E. RAYMO[4] AND J.P. SEVERINGHAUS[5]

[1]National Inst. of Polar Res., Tokyo 173-8515, Japan (*correspondence: kawamura@nipr.ac.jp)
[2]Center for Atmospheric and Oceanic Studies, Tohoku U., Sendai 980-8578, Japan
[3]Miyagi U. of Education, Sendai 980-0845, Japan
[4] Dept. of Earth Sciences, Boston U., MA 02215 USA
[5]Scripps Inst. of Oceanography, U. of California San Diego, CA 92093-0244 USA

In order to evaluate the roles of orbital and greenhouse-gas forcings on global climate (glacial cycles in particular), one needs a paleoclimate chronology with accuracy better than 2 ky (~1/10 of precession cycle). Kawamura *et al.* (2007, *Nature*) established such an Antarctic ice-core chronology for the past 360 ky through orbital tuning of O_2/N_2 ratio of trapped air in the Dome Fuji and Vostok ice cores, which records the local summer solstice insolation without lag.

Here we extend the Dome Fuji O_2/N_2 chronology back to 470 ky ago, which covers MIS 11 and Termination V. The onset of Antarctic warming for the last five Terminations is found to occur within the rising phase of summer insolation at high northern latitudes. Furthermore, null hypotheses that the last five Terminations are not linked with precession can be rejected at 5 % significance level, while the null hypothesis for obliquity cannot be rejected with high statistical power. Antarctic cooling at the last four glacial inceptions appears to be in phase with the decline of northern summer insolation and obliquity, but earlier than atmospheric CO_2 decrease by a few millennia. These results are consistent with the classic Milankovitch theory that high northern latitude summer insolation is the primary pacemaker of the late Pleistocene glacial cycles.