

## High-resolution geochemical changes and astronomical forcing through the early Toarcian OAE

DAVID B. KEMP<sup>1\*</sup>, ANGELA L. COE<sup>2</sup>  
AND ANTHONY S. COHEN<sup>2</sup>

<sup>1</sup>Department of Earth Sciences, University of Cambridge,  
Downing Street, Cambridge, CB2 3EQ, UK  
(\*correspondence: dkem08@esc.cam.ac.uk)

<sup>2</sup>Department of Earth Sciences, The Open University, Walton  
Hall, Milton Keynes, MK9 7AA

The early Toarcian Oceanic Anoxic Event (OAE) represents one of the most severe environmental perturbations of the Phanerozoic. A key feature of the event is a -4 to -8‰  $\delta^{13}\text{C}$  excursion in marine organic matter, marine carbonate and terrestrial plant material, which has been attributed by a number of authors to a greenhouse gas release event. Work on an early Toarcian section in Yorkshire, UK, has demonstrated that the precise structure of this negative  $\delta^{13}\text{C}$  excursion comprises 4 abrupt shifts to more negative values, and that these shifts were paced by astronomical forcing [1]. Recent work from the same section [2] has also revealed changes in molybdenum isotopes through the OAE that reflect the ephemeral development of global marine anoxia in phase with the astronomically paced  $\delta^{13}\text{C}$  changes.

To further investigate the key role astronomical forcing played in pacing environmental changes during the early Toarcian OAE, we have measured  $\text{CaCO}_3$ , S, TOC and sulphate reduction index (*sensu* Bertrand and Lallier-Vergès, 1993 [3]) at high resolution across the Yorkshire succession.

The high-resolution sampling of these measurements (>3000 datapoints) permits the precise appraisal of key trends in sulphate reduction and palaeoproductivity through the OAE in Yorkshire. Time series analysis of the geochemical data reveals the pervasive presence of astronomical forcing, thus allowing for the rates and durations of geochemical changes to be constrained. A fundamental change in the expression of astronomical forcing across the OAE interval is also discerned. This manifests itself as a change in phase relationships between the measured geochemical parameters, and a weakening of cyclicity in the post-OAE interval. Evidence for a shift in astronomical forcing mode across the event (i.e. a shift from precession dominated forcing to obliquity forcing), which has been recently recognised from other sections [4], cannot be unequivocally demonstrated.

[1] Kemp *et al.* (2005) *Nature* **437** 396-399. [2] Pearce *et al.* (2008) *Geology* **36(3)** 231-234. [3] Bertrand and Lallier-Vergès (1993) *Nature* **364** 786-788 [4] Suan *et al.* (2008) *EPSL* **267** 666-679.

## Photoemission study of the reaction of $\text{Fe}_3\text{O}_4(100)$ with water at near ambient conditions

T. KENDELEWICZ<sup>1\*</sup>, S. KAYA<sup>2</sup>, J. NEWBERG<sup>3</sup>,  
H. BLUHM<sup>3</sup>, A. NILSSON<sup>2</sup>, G.E. BROWN, JR.<sup>1,2</sup>,  
R. PENTCHEVA<sup>4</sup> AND W. MORITZ<sup>4</sup>

<sup>1</sup>Dept. Geol. Environ. Sci., Stanford University, Stanford, CA  
94305, USA

(\*correspondence: kendelewicz@stanford.edu)

<sup>2</sup>SLAC Nat. Accelerator Lab, Menlo Park, CA 94309, USA

<sup>3</sup>Lawrence Berkeley National Lab, Berkeley CA 94720 USA

<sup>4</sup>Dept. Earth Env.Sci., University of Munich, Germany

Polar surfaces of magnetite are difficult to study at the atomic level due to major reconstructions, involving vacancy formation, charge redistribution and localization, and/or adsorption of ions. Understanding surface structure and stoichiometry is prerequisite for studies of adsorbate reactions including  $\text{H}_2\text{O}$ . A great deal of attention has been paid to the  $(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$  surface, which exists on magnetite(100) under a range of preparation conditions. Only two terminations exist along [100]; one, referred to as A, contains a monolayer of tetrahedral Fe,  $\text{Fe}_\text{T}^{3+}$ , and the other, referred to as B, contains octahedral Fe,  $\text{Fe}_\text{O}^{2+}$  and  $\text{Fe}_\text{O}^{3+}$ , and all  $\text{O}^{2-}$  ions. Although initial studies related the  $(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$  surface to the A termination, with half of the  $\text{Fe}_\text{T}^{3+}$  removed, newer data and theory support the B-like termination. We studied water reactions with the  $(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$  surface using high-pressure core-level photoemission. Adsorption isotherms at 273 and 300 K using  $\text{P}(\text{H}_2\text{O})$  from  $10^{-8}$  to 2 Torr and back to UHV showed a continuous increase in OH coverage with the largest change at  $10^{-4}$  to  $10^{-2}$  Torr. Above  $10^{-2}$  Torr, additional physisorbed molecular  $\text{H}_2\text{O}$  was observed. Upon evacuation, molecular  $\text{H}_2\text{O}$  is reversibly removed from the surface, with only a marginal decrease of OH. Based on a uniform layer model, we estimate maximum OH and  $\text{H}_2\text{O}$  coverages of 1 ML, in agreement with DFT calculations, which indicates formation of a full layer of OH on an unreconstructed B-like termination.