

Deep ocean circulation and its link to carbon storage through glacial cycles

D.J. WILSON^{1,2*}, A.M. PIOTROWSKI², A. GALY² AND V.K. BANAKAR³

¹Department of Earth Science and Engineering, Imperial College London, London, SW7 2AZ

(*correspondence: david.wilson1@imperial.ac.uk)

²Department of Earth Sciences, University of Cambridge, Cambridge, CB2 3EQ

³National Institute of Oceanography, Dona Paula, Goa, 403 004, India

Storage of carbon in the deep ocean during glaciation and its release during deglaciation is widely called upon in order to explain glacial-interglacial changes in atmospheric CO₂ [1,2], but the mechanisms involved remain uncertain and the locations of carbon storage are poorly quantified through time. Changes in water mass volumes in the global ocean exert one first order control on carbon storage [3], suggesting a sensitivity of atmospheric CO₂ to reorganisations of ocean circulation. However, modelling studies tend to disagree over the nature and timing of paleoceanographic changes influencing atmospheric CO₂ [4,5].

Better paleoceanographic constraints are therefore required, particularly from the deep Indo-Pacific, which has significant potential for carbon storage during glacial periods. Here we characterise its chemical evolution over the last 250 thousand years using Nd isotopes (ϵ_{Nd}) and benthic carbon isotopes ($\delta^{13}C$) in deep Indian Ocean core SK129-CR2 [6]. The ϵ_{Nd} record indicates a significant glacial reduction in the North Atlantic Deep Water component in Circumpolar Deep Water, consistent with increased oceanic carbon storage [3]. However, the ϵ_{Nd} - $\delta^{13}C$ relationship evolves over the course of each glacial cycle, indicating a changing global distribution of water masses and carbon. During glaciation and early glacial periods, ϵ_{Nd} and $\delta^{13}C$ are decoupled, revealing carbon cycling changes that are independent of Atlantic circulation changes. This decoupling may reflect the processes involved in carbon sequestration in Antarctic Bottom Water at these times. In contrast, coupled ϵ_{Nd} - $\delta^{13}C$ changes during late glacials and deglaciation suggest a close link between deep ocean circulation and carbon release to the atmosphere.

[1] Toggweiler, Russell & Carson (2006), *Paleoceanography* **21**. [2] Sigman, Hain & Haug (2010), *Nature* **466**, 47-55. [3] Skinner (2009), *Clim. Past* **5**, 537-550. [4] Brovkin *et al.* (2007) *Paleoceanography* **22** [5] Hain, Sigman & Haug (2010) *Glob. Biogeochem. Cycle* **24**. [6] Piotrowski *et al.* (2009) *Earth Planet. Sci. Lett.* **285**, 179-189

Co-precipitation of arsenate with calcite – an example from Greece

LENNY H.E. WINKEL^{1,2}, BARBARA CASENTINI³, FABRIZIO BARDELLI⁴, ANDREAS VOEGELIN¹, NIKOLAOS P. NIKOLAIDIS⁵ AND LAURENT CHARLET⁴

¹Eawag: Swiss Federal Institute of Aquatic Science and Technology, Ueberlandstrasse 133, P.O. Box 611, 8600 Duebendorf, Switzerland, lenny.winkel@eawag.ch, andreas.voegelin@eawag.ch

²Swiss Federal Institute of Technology (ETH) Zurich, 8092 Zurich, Switzerland, lwinkel@ethz.ch

³Water Research Institute-National Research Council, Via Salaria, 00015 Monterotondo (RM), Italy, casentini@irsa.cnr.it

⁴Université Joseph Fourier, Grenoble, 1381 rue de la Piscine, 38400 Saint-Martin d'Hères, France, fabrizio.bardelli@gmail.com, charlet38@gmail.com

⁵Technical University of Crete, Polytechniupolis, 73100 Chania, Greece, nikolaos.nikolaidis@enveng.tuc.gr

The uptake of arsenic (As) in calcite may represent an important immobilization process for As in calcareous rocks. Nevertheless, knowledge on this retention mechanism in the natural environment is limited since As incorporation in calcite has mostly been studied on synthetic samples.

We identified very high levels of As (up to 913 mg/kg) in travertine deposits derived from geothermal As-enriched groundwaters on the Greek peninsula Chalkidiki. We analyzed two different types of travertine from this region using both bulk and micro-focused X-ray absorption spectroscopy (XAS and μ -XAS) and micro-focused X-ray fluorescence spectroscopy (μ -XRF) to determine the mechanism of arsenic uptake in the travertines¹. Bulk XAS showed that in all of the studied samples As is present as arsenate (As[V]), and μ -XRF analyses revealed that As is closely associated with the calcite matrix. Iron on the other hand was found to be mainly present as a constituent of clay minerals, of presumably detrital origin, suggesting that Fe-(hydr)oxides were not sufficiently abundant to act as major scavengers for As in the Chalkidiki travertines.

From our results we estimate that the natural travertines could sequester at least 25% of groundwater As(V) via co-precipitation with calcite. The formation of As-enriched calcite is thus an efficient mechanism to immobilize As in the geothermal groundwaters of Chalkidiki and could possibly also occur in other environments characterized by high As and CO₂ contents.

[1] L.H.E. Winkel; B. Casentini; F. Bardelli; A. Voegelin; N.P. Nikolaidis; L. Charlet. *Geochim. Cosmochim. Acta* 2013, 106 99–110.