First-principles simulation of arsenate adsorption on the $(1\bar{1}2)$ surface of hematite

M. BLANCHARD*, G. MORIN, M. LAZZERI, E. BALAN AND F. MAURI

MPMC, Univ. Paris VI, CNRS, IRD, Univ. Paris VII, IPGP, 4 Place Jussieu, 75252 Paris Cedex 05, France (*correspondence: marc.blanchard@impmc.upmc.fr, guillaume.morin@impmc.upmc.fr, michele.lazzeri@impmc.upmc.fr, etienne.balan@impmc.upmc.fr, francesco.mauri@impmc.upmc.fr)

Recent experimental studies [1, 2] revealed an unprecedented bimodal distribution of arsenate at the hematite $(1\bar{1}2)$ surface, with a simultaneous adsorption of inner-sphere and outer-sphere complexes. In the present study, first-principles calculations based on density functional theory were performed to make a detailed analysis of the structural and electronic properties of these inner-sphere and outer-sphere adsorption complexes on two hydroxylated terminations of the hematite $(1\bar{1}2)$ surface. For bidentate corner-sharing complexes, the most-stable adsorption configurations display interatomic distances in excellent agreement with EXAFS-derived data (i.e. As-Fe distances of ~3.3 Å). Our calculations also suggest that edge-sharing bidentate complexes can also form on clean $(1\bar{1}2)$ hematite surfaces and do not necessarily need step edges. These edge-sharing complexes would display two As-Fe distances at about 2.85 and 3.45 Å, instead of the unique short As-Fe contribution that is usually considered. For outer-sphere complexes, the most favorable adsorption configurations indicate the stabilization of the arsenate molecule by strong hydrogen bonds as well as the involvement of electrostatic forces. It is therefore essential to include these outer-sphere complexes in the thermodynamic models used to understand the arsenic fate in the environment.

[1] Catalano *et al*. (2007) *GCA* **71**, 1883-1897. [2] Catalano *et al*. (2008) *GCA* **72**, 1986-2004.

Response of vegetation and erosion dynamics to changes in precipitation in the Nile River drainage basin during the African Humid Period

CECILE L. BLANCHET[1,2], JANNE LORENZEN[3], RIK TJALLINGII[2], STEFAN SCHOUTEN[2] AND MARTIN FRANK[1]

[1]IFM-GEOMAR at the University of Kiel, Whischhofstrasse 1-3, 24148 Kiel, Germany
[2]NIOZ Royal Netherlands Institute for Sea Research, Landsdiep 4, 1797 SZ 't Horntje, The Netherlands
[3]University of Kiel, Ludewig-Meyn-Strasse 14, 24118 Kiel

During the mid-Holocene, the gradual decrease in summer insolation induced a decrease in monsoon strength and subsequent aridification of northern Africa. However, the timing of environmental and climatic responses to this slow orbital forcing is still being debated, with studies reporting either a gradual or an abrupt termination of the African Humid Period (AHP).

Here we use 6 m-long sediment core P362/2-33 that was retrieved at 700 m water-depth on the Nile deep-sea fan. Detailed ^{14}C dating shows that the core covers the last 9,500 years, with laminated sediments being deposited at very high rates (up to 600 cm/ka) during the AHP. These sediments allow to investigate the linkages and feedbacks between climate, vegetation and erosion dynamics at millennial to seasonal resolution. The variations in sediment and fresh-water input, as well as sediment provenance and vegetation changes are monitored using a combination of inorganic and organic geochemical proxies (major and trace elements ratios, $\delta^{18}O$ and $\delta^{13}C$ of planktonic foraminifera, radiogenic isotope compositions of sediments, foraminifera and seawater-derived ferromanganese coatings, and abundance and isotope composition of specific biomarker lipids). Massive amounts of fresh water and sediments were delivered by the Nile River to the deep-sea fan between 9.5 and 8 ka, as indicated by high sedimentation rates, high titanium/calcium ratios and sea-water εNd values similar to the Nile River. This time interval was also characterised by the dominance of C4 grasses and soil development, as indicated by heavier $\delta^{13}C$ values for higher plants n-alkanes and elevated concentrations in soil biomarker. A first rapid decrease in fresh-water and sediment delivery was recorded around 8.5 ka in sea-water εNd and sedimentation rate followed by a gradual decrease between 8 and 4 ka identified in all proxies. The transition from C4- to C3-dominated environment occurred between 8 and 6 ka, and might reflect the aridification of the Sahara, with n-alkanes mainly originating from southern sources after 6 ka. Sediment source tracing by mean of their radiogenic isotope composition is being processed.