Nanoscale probing of the reactivity of biologically *versus* chemically formed green rusts

A. ZEGEYE[1,2]*. M. ETIQUE[1,2]. P. SCHAAF[3]. C. RUBY[1,2]. AND G. FRANCIUS[1,2].

[1] Université de Lorraine, Laboratoire de Chimie Physique et Microbiologie pour l'Environnement, UMR 7564, Villers-lès-Nancy, F-54601, France(*correspondance: asfaw.zegeye@univ-lorraine.fr)[2] CNRS, Laboratoire de Chimie Physique et Microbiologie pour l'Environnement, UMR 7564, Villers-lès-Nancy, F-54601, France[3] Institut Charles Sadron, CNRS UPR 22, BP 84749, Strasbourg Cedex 2, F-67034, France

Iron containing nanoparticles such as green rusts (GR) display very high reactivity against organic and inorganic contaminants and present a great potential for the remediation of polluted surfaces and subsurfaces. Since GR can either be formed by chemical or biological pathways, an understanding of their reactivity at the nanoscale level is fundamentally necessary for establishing an efficient remediation process. For the first time, we demonstrated that the combination of atomic force microscopy and chemical force microscopy is a powerful platform for probing the reactivity of GR at the nanoscale. In the presence of nitrate, we probed the nano minerals surface of both the chemically and biologically formed GRs, which enabled us to show a significant deprotonation of the H^+ present on the basal surface of the chemically formed GR, in contrast the biologically formed GR displayed virtually no reaction. Furthermore, by using the free chain model to model the force curves obtained from our spectroscopy data, we showed that the absence of reactivity of the biological GRs was due to the presence of biopolymers on its surface.

Undoubtedly, the experiments and results presented in this study open new avenues for understanding the potential difference in reactivity between biologically and chemically formed GR.

The oldest zircons of Africa - Their implications for Hadean to Archean crust-mantle evolution

A. ZEH[1,*], A. GERDES[1] AND R. STERN[2]

[1]Goethe University Frankfurt, Altenhöferallee 1, D-60438 Frankfurt am Main, Germany (correspondence: a.zeh@em.uni-frankfurt.de)[2]Canadian Centre for Isotopic Microanalysis (*CCIM*), University of Alberta *Edmonton*, AB T6G 2E3, Canada

More than 450 detrital zircon grains from Limpopo Belt quartzites were carefully investigated by CL/BSE imaging, U-Pb dating, $\delta^{18}O$, and Lu-Hf isotope analyses in order to get faithful information about the early Earth's crust - mantle evolution. The zircon grains have crystallisation ages between 3.95 Ga and 3.40 Ga, show near chondritic to subchondritic εHf_t between +1 to -15 (±1 ε-unit), and $\delta^{18}O$ mostly between +5.5 and +8.1 ‰ (±0.2‰)VSMOW. Trace elements point to zircon formation in (mostly) granitoid rocks.

The new U-Pb-Hf-datasets provide evidence for three distinct crust evolution (εHf_t-age) trends. All three trends start from nearly chondritic mantle sources at about 4.5 Ga (trend 1), 4.05 Ga (trend 2), and 3.75 Ga (trend 3), and require $^{176}Lu/^{177}Hf$ between 0.018 and 0.020, typical for mafic crust. $\delta^{18}O$ values mostly above 6.0 ‰ (VSMOW) indicate that the mafic crust has been altered, perhaps by interaction with cold oceanic water.

The new datasets from the Limpopo Belt and compilation of data from worldwide sources indicate a significant εHf_t-gap of about 5 epsilon units between trend 1 and 2. Furthermore, they reveal that many zircon analyses plot well below trend 1 (mostly at ages <4.3 Ga), or have (super)chondritic composition between 4.4 and 4.0 Ga. These findings together support an interpretation that the early Earth was covered by a long-lived, but volumetrically insignificant Hadean mafic protocrust, perhaps an unstable "stagnant lid" [1], which was affected by internal reworking [2], and injected and overlain by melts from chondritic and (highly) depleted mantle sources. This mafic protocrust was locally transformed into a TTG crust starting at <4.3 Ga [3], perhaps due to successive resurfacing [4], accompanied by crust cooling and enhanced foundering. Eventually, the complex Hadean protocrust became re-worked completely during new crust formation at <4.05 Ga.

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DOI:10.1180/minmag.2013.077.5.26