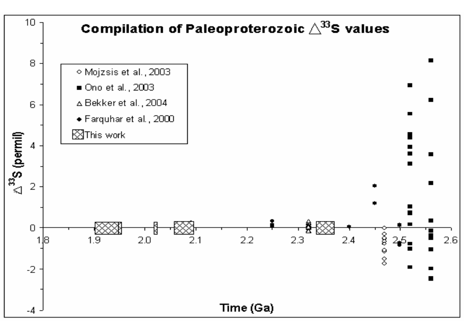
6.5.32

Multiple sulfur isotopic analyses of sulfides from Paleoproterozoic sediments by ion microprobe

D. PAPINEAU[1], S.J. MOJZSIS[1], K.D. MCKEEGAN[2] AND J.A. KARHU[3]

[1] Dept. of Geological Sciences, Center for Astrobiology, University of Colorado, Boulder, CO 80309-0399, USA (dominic.papineau@colorado.edu)
[2] Dept. of Earth and Space Sciences, University of California, Los Angeles, CA 90095-1567, USA.
[3] Dept. of Geology, University of Helsinki, FIN-00014 Helsinki, Finland.

Paleoproterozoic sediments hold manifold geochemical evidence for the transition from the Archean anoxic atmosphere to the oxygenated atmosphere. This transition resulted in important changes *e.g.* in the geochemistry of multiple sulfur isotopes in sedimentary sulfides and sulfates [1]. The actual timing of oxygenation can now be explored using mass independently fractionated (MIF) sulfur isotope systematics expressed as $\Delta^{33}S$. Recently reported sulfide data from the 2.32 Ga Timeball Hill Fm. (South Africa) show no MIF [2], while sulfide from the 2.47 Ga Brockman Iron Fm. (Western Australia) has resolvable $\Delta^{33}S$ [3]. This indicates that the oxygen level in the terrestrial atmosphere increased above ~10^{-5} PAL [4] in that ~150 Ma span and that significant atmosphere oxygenation began to occur before the onset of the Paleoproterozoic $\delta^{13}C_{carb}$ excursion(s) [5]. With the goal of establishing possible relationships between multiple sulfur isotopes and this $\delta^{13}C_{carb}$ excursion, we report more than 70 sulfur isotopic analyses of sulfides from 26 separate samples of well-characterized carbonates and shales from Finland spanning ~500 Ma (see figure) using a new ion microprobe multicollector technique [3]. Results indicate the presence of microbial sulfate reduction, hydrothermally-derived sulfur and no obvious MIF sulfur in the samples so far investigated for this time interval.



References
[1] Farquhar *et al.* (2000) *Science* **289**, 756-758.
[2] Bekker *et al.* (2004) *Nature* **427**, 117-120.
[3] Mojzsis *et al.* (2003) *GCA* **67**, 1635-1658.
[4] Pavlov, A.A. and Kasting, J.F. (2002) *Astrobio.* **2**, 27-41.
[5] Karhu, J.A. (1993) *Geol Surv. Fin. Bull.* **371**, 87p.

6.5.33

Fe, Mn mobility in Precanmbrian paleosols: Implications on atmospheric oxygen evolution

B. SREENIVAS[1,2] S. DAS SHARMA[1] AND T. MURAKAMI[2]

[1] National Geophysical Research Institute, Hyderabad 500007, India
[2] Dept. EPS, The University of Tokyo, 7-3-1 Hongo, Tokyo 113-0033, Japan (bulusu@eps.s.u-tokyo.ac.jp)

Retention values of Fe and Mn oxides in paleosols of Late Archean to Paleoproterozoic age have been calaculated to understand the effect of Great Oxidation Event. These results are integrated with other indicators such as $\delta^{13}C$ and $\Delta^{33}S$ records to comprehend the atmospheric oxygen evolution during the Precambrian. The values of retention for iron ($Fe_2O_3T_R$) and manganese (MnO_R) of five definite paleosols are presented in Fig. 1.

The $Fe_2O_3T_R$ value of ~1 has been observed in paleosols of ≤2250 Ma, while the MnO_R close to 1 only in 1800-1900 Ma old Flin Flon paleosols. These are also characterized by Ce anomalies [1]. The $\Delta^{33}S$ record indicates that the atmopsheric P_{O_2} increased from <10^{-5} to >10^{-5} PAL by 2322 Ma [2], and it might have been high enough to retain entire iron in the paleosol by ~2245 Ma. The oxygn level is suffeciently high to cross the oxidation barriers of both Ce and Mn by ~1900 Ma. It appears that the P_{O_2} has increased between 2470 and 2245 Ma due to change in redox states of volcanic gases. A sgnificant rise in P_{O_2} by ~1900 Ma was caused by the disturbance in carbon biogeochemical cycle reflected in the form of global Paleoproterozoic $\delta^{13}C$ excursion recorded in sedimentary carbonate successions spanning from 2200 to 2060 Ma.

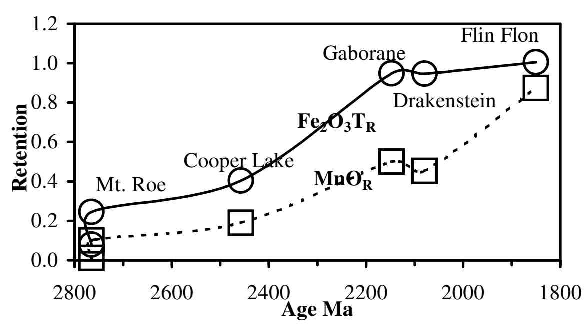


Fig.1 Retention of Fe and Mn in Late Archean to Paleoproterozoic paleosols.

References
[1] Pan Y., and Staufffer, M.R. (2000) *Am. Mineral.* **85,** 898-911.
[2] Bekker A., Holland, H.D., Wang, P.-L., Rumble III, D., Stein, H.J., Hannah, J.L., Coetzee, L.L. and Beukes, N.J. (2004) *Nature* **427,** 117-120.