Eoarchaean crust in the Dniestr-Bug region, Ukrainian Shield – Pb-Hf-O isotope constraints

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In the Ukrainian shield, enderbites of the Dniester-Bug Series contain zircons as old as c. 3.75 Ga with initial Hf isotope ratios indicating their derivation from mildly depleted sources. Most Dniester-Bug rocks are strongly tectonized and metamorphosed. We present here new U-Pb, Hf and O isotope results for zircon separated from enderbite, a supracrustal garnet-mica schist, and an assumedly clastic quartz-rich rock enclosed in enderbite.

Zircon from all these rocks yields variably discordant U-Pb ages up to c. 3.75 Ga. Hf isotope compositions for the oldest zircons indicate these crystallized from magmas with chondritic to slightly depleted isotope signatures at c. 3.75 Ga. The majority of zircons with younger U-Pb ages also appear to be ultimately derived from similar crustal sources. This supports that there was an important period of formation of continental crust at c. 3.75 Ga

δ^{18}O(Zrc) for two enderbites range from mantle values to slightly more evolved compositions. δ^{18}O(Zrc) up to 7.2‰ for the garnet-mica schist indicates this includes materials which in parts are derived from more evolved sources. δ^{18}O(Zrc) for the quartz-rich rock stands out, with a few analyses as low as 7‰ or less, but the majority in the range 8-10‰. Few Archaean zircon crystals with such high δ^{18}O(Zrc) values have been reported previously.

If the quartz-rich rock originally is a clastic sediment and the zircon has preserved its magmatic δ^{18}O signature, most of the source rocks had evolved O isotopic compositions. Secondary alteration of O in clastic zircon may also be a possibility. Alternatively, the quartz-rich rock may be heavily metasomatized enderbite and the O isotope composition of the zircons altered in a process which at the same time not has erased the original Hf isotope signature.

Clues to atmospheric evolution in Earth's ancient sediments

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Sulfur isotopes are fractionated in a mass-anomalous fashion when SO_2 gas is subjected to ultraviolet light. Amazingly, the subtle fractionations (MIF-S) resulting from this process are preserved in sedimentary rocks of Archean age, but are absent in younger rocks. The MIF-S data provides direct constraints on the composition of the ancient atmosphere, and have been described as the "smoking gun" for an anoxic Archean atmosphere. In the thirteen years since their initial discovery (Farquhar *et al*. 2000), the database of Archean MIF-S has grown to include detailed temporal (and stratigraphic-level) changes in both sign and magnitude of Δ^{33}S and Δ^{36}S, although our theoretical understanding hasn't advanced much beyond the notion of a 1ppm threshold concentration of atmospheric oxygen (Pavlov and Kasting, 2002). I will summarize my recent numerical modeling efforts made in conjunction with new geochemical data (Zerkle *et al*., 2012 ; Kurzweil *et al*., 2013 ; Claire *et al*., 2013), which reveal how MIF-S might constrain atmospheric methane levels, the presence of an organic haze, the widespread radiation of oxygenic photosynthesis, and changes in the redox-state of the atmosphere/hydrosphere/ geosphere prior to the Great Oxidation Event.

Farquhar *et al*. 2000 *Science* ; Pavlov and Kasting, 2002 *Astrobiology* ; Zerkle *et al*. 2012 *Nature Geoscience* ; Kurzweil *et al*. 2013 *EPSL ;* Claire *et al*. 2013 (in prep)

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