

Microbial community structure and atmospheric oxygen *ca.* 2.4 Ga

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Major changes in the structure and composition of microbial and eukaryotic populations have induced profound effects on biogeochemical cycles over Earth history. Atmospheric oxygen was no exception, but why it rose when it did is a matter of debate. Molecular biomarkers in Archean shales were used to infer the existence of oxygenic photosynthesizers (cyanobacteria), and eukaryotes at ~2.7 Ga. But, this is now in doubt, as the biomarkers post-date peak metamorphism of the rocks at 2.2 Ga [1]. Stromatolites extend back to the Paleoarchean, and were long taken as fossil cyanobacterial mats, but even modern stromatolites can form from anoxygenic photoautotrophs. Banded iron-formations (BIFs) did not require direct $(\text{Fe}^{2+})_{\text{aq}} \rightarrow \text{Fe}^{3+}$ via O_2 from cyanobacteria, but were modulated by Fe(II)-oxidizers [2]. These results seem to do away with an uncomfortably long (~300 Myr) delay between the apparent advent of cyanobacteria and inexorable O_2 rise by ~2.4 Ga. Before cyanobacteria, we suggest the microbial biosphere was dominated by photoferotrophs [3]. Archean oceans had high $[\text{Fe}^{2+}]_{\text{aq}}$, but low $[\text{PO}_4^{3-}]_{\text{aq}}$ [4, cf. 5] and very low $[\text{SO}_4^{2-}]_{\text{aq}}$. Evidence suggests O_2 began to affect geochemical cycles of redox-sensitive metals, S and N in the oceans by 2.5 Ga [6]. After, the atmosphere underwent a step-wise irreversible O_2 accumulation at ~2.4 Ga [7]. Population doubling-time and diffusion models show that cyanobacteria should colonize the planet on timescales of months to years after origin. We propose that competition with photoferotrophs and nutrient limitations [8] stymied cyanobacterial takeover before ~2.45 Ga. Sedimentology, geochronology, multiple S-isotopes, and trace elements [9] from Paleoproterozoic interglacial shales from W. Australia and Canada were used to test this model.

- [1] Rasmussen *et al.* (2008) *Nature* **455**, 1101-1104.
[2] Konhauser *et al.* *EPSL* **258**, 87-100. [3] Crowe *et al.* (2008) *PNAS* **105**, 15938-15943. [4] Bjerrum & Canfield (2002) *Nature* **417**, 159-162. [5] Konhauser *et al.* (2007) *Science* **315**, 1234. [6] Anbar *et al.* (2007) *Science* **317**, 1903-1906 [7] Papineau *et al.* *EPSL* **255**, 188-212. [8] Van Mooy *et al.* (2006) *PNAS* **103**, 8607-8612. [9] Ji and Sherrell (2008) *Limnol. Oceanogr.* **53**, 1790-1804.

A missing link in the formation of the porphyry-Cu belt in Eastern Europe: New U/Pb zircon ages in the Timok magmatic complex (E-Serbia)

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The Timok magmatic complex (TMC) is a 20 x 80 km large segment of the mineralized Apuseni-Banat-Timok-Srednogie belt in SE-Europe. This belt is a calc-alkaline magmatic arc of Late Cretaceous age. The metallogeny can be linked to the northward subduction of the Vardar ocean beneath Europe, followed by major continental collision between Africa and Europe. The belt hosts a variety of magmatic-hydrothermal Cu, Au, Mo, Zn, Pb and Fe deposits.

Based on field evidence, the TMC magmatism can be approximately divided into three stages; (1) the initial stage in the eastern part, mainly composed of subaerial andesitic volcanism; (2) slightly later subaqueous basaltic to andesitic volcanism in the central and western part; (3) a last stage intrusive granites in the western part.

K/Ar data in the literature imply that the magmatic activity extended over the period of 94-60 Ma (Late Cretaceous to Paleocene). However, these ages are not very precise. First high-precision U/Pb single zircon analyses indicate an age of 86.2-84.6 Ma for the initial volcanism in the eastern part of the TMC. For the Veliki Krevelj porphyry-Cu deposit, the ore bearing magmatism is restricted to 0.6 m.y. For the northern part of the TMC the magmatic rocks of the porphyry-Cu deposit of Majdanpek and polymetallic-Au deposit of Tenka show ages of 82.7 Ma and 89.9 Ma, respectively. The youngest ages can be found in the intrusions of the eastern part of the TMC around Valja Strz. These area shows significantly younger ages around 78 Ma.

The magmatism and its relationship to the mineralization is still poorly studied. First results show a total duration of 11 m.y. and a younging from east to west for the TMC, analogous to the north to south age trend observed in the Bulgarian continuation of the former arc [1]. Ongoing investigations aim to refine the duration and geodynamical evolution of the Cretaceous volcanism, and the life time of mineralizing porphyry systems within the TMC.

- [1] von Quadt, Moritz, Peytcheva, Heinrich (2005), *Ore Geol. Rev.* **27**, 95-126.