

## The first hydrogen economy: A sulfur isotopic record of S<sup>0</sup> metabolisms for early life

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Many hyperthermophilic, deep-branching organisms in the domains Bacteria (*Thermotogales*, *Proteobacter*) and in various Archaea (sub-Domain Crenarcheota and *Pyrococcus*, *Thermoplasma* in sub-Domain Euryarcheota) reduce S<sup>0</sup> to H<sub>2</sub>S in elemental sulfur reduction (ESR) with either H<sub>2</sub> (derived for example from serpentinization reactions in the hydration of ultramafic rocks) or hydrogenated organic compounds, as an electron donor. Perhaps this pathway emerged from the first proto-metabolic metal-S cycles? Now it involves a short electron transport chain controlled by S reductase, polysulfide reductase and hydrogenase. Anaerobic respiration with S<sup>0</sup> is performed by both deep-branching bacterial and archaeal lineages that eat hydrogen to reduce sulfur, so ESR could be an inherited trait from an early high-temperature biosphere. These organisms can readily obtain their sulfur from rapid cooling of fumarole gases and then catalyze the reaction:  $4S^0 + 4H_2O \rightarrow 3H_2S + SO_4^{2-} + 2H^+$ . With Fe hydroxides present and abundant in the early oceans, the reaction:  $H_2S + 4H^+ + 2Fe(OH)_3 \rightarrow 2Fe^{2+} + S^0 + 6H_2O$  can proceed. This chemistry potentially feeds back into anaerobic photoautotrophic Fe(II) cycling. Transition metal-sulphur chemistry figures prominently in the biochemistry of many deeply-branching microbes beyond Fe-S. Many metals such as Zn, Mo, Co and Ni are abundant in mafic and ultramafic rocks and readily react with S. Yet, most of the various catalytic roles of metal-S clusters other than Fe await experimental verification from analysis of controlled (culture) experiments. Such experiments represent an important new avenue for research into the question of a biological origin for the most ancient multiple (<sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S and <sup>36</sup>S) S-isotope fractionations found in the geologic record (up to ca. 3.85 Ga) and the nature of the biomes that constituted this first “hydrogen economy” on Earth.

## Geochemistry and isotope tracing of the subduction related volcanism in the Timok magmatik complex, East Serbia

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The Timok volcanic complex (TMC) is part of the mineralized ABTS (Apuseni-Banat-Timok-Srednogie) belt in SE Europe. During the upper Cretaceous this belt was formed in an arc setting due to the northward subduction of the Vardar Ocean under the European platform. In the TMC the calc-alkaline volcanism can be approximately divided into three stages; (1) the initial stage in the eastern part mainly composed of subaerial andesitic volcanism; (2) middle subaqueous basaltic to andesitic volcanism in the central and western part; (3) last stage intrusive granites in the western part. The magmatic products are represented in extrusive as well as intrusive facies, whereas only the initial stage shows porphyry Cu mineralization.

Literature data show that the magmatic activity and related ore formation in the initial stage occurred during 92-60 Ma (Late Cretaceous-Paleocene). Nevertheless these K/Ar 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. εHf<sub>i</sub> data for zircons are ranging between +8 and +13 showing a mantle derived origin. The second phase volcanism (82.7-82 Ma) together with the last intrusive phase (70.5 Ma) show lower εHf<sub>i</sub> zircon data (+4 to +8) indicating a rising influence of crustal material. <sup>87</sup>Sr/<sup>86</sup>Sr<sub>i</sub> isotope data also indicate this increasing crustal influence. <sup>87</sup>Sr/<sup>86</sup>Sr<sub>i</sub> values are changing from 0.7039 in the initial stage to 0.7055 in the last stage intrusive volcanism.

Fluid-mobile elements such as Cs, Rb, U and K show enrichment due to their transport from the slab into the source region. The High Field Strength Elements (HFSE) like Nb, Ta and Hf in contrast are depleted. The relatively flat middle (MREE) to heavy (HREE) rare earth element patterns probably reflect pyroxene and plagioclase fractionation. Most of the samples show an additional slight negative Eu anomaly confirming the plagioclase fractionation. High Sr/Y (>20) show an adakite-like signature that may be the product of melting of eclogitic portions of the subducted slab. However this scenario may be unlikely because of the subduction of Jurassic “cool” oceanic crust in the late Cretaceous.