

## Natural solar cells on Earth and Mars

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### Introduction

There are a range of natural settings in which semiconducting minerals can play a role in driving photochemical reactions that generally involve interfacial electron transfer. Surface, bulk, and defect states of the minerals interact. We present 3 examples of naturally-occurring semiconductor systems that may help drive chemical processes to a degree not previously appreciated.

### Example 1: Rock Varnish

There is renewed interest in rock varnishes because they may be biogenic. Some varnishes are rich in iron and manganese oxides, and can produce photovoltages. Hypothetically, sunlit varnishes can oxidize water and other materials, driving a redox cycle that supports the varnish-associated bacteria in a hybrid inorganic-biological system.

### Example 2: Perchlorate in Mars polar soil

The Wet Chemical Laboratory on the Mars Phoenix Lander found that perchlorate is remarkably concentrated in the sampled soils, rivaling chloride as the most abundant anion [1]. We have shown that chloride in solutions exposed to TiO<sub>2</sub> (anatase and rutile) surfaces and sunlight can be readily oxidized to perchlorate (20% initial current efficiency, decaying with time). The lowest perchlorate production rates we record, if operating on <0.1% of the Mars surface, are still 2000 times faster than the current atmospheric deposition rates in the Atacama [2].

### Example 3: Natural tandem cells for solar hydrogen

The products of sulfide mineral surface oxidation include soluble sulfates and, often, insoluble metal ions. Fe(III) or Mn(IV)-rich oxides and oxyhydroxides often form thin surface layers on sulfides during the incipient oxidation of the sulfides. This constitutes a natural two-semiconductor "tandem cell". Sunlight on the outer oxide layer can produce valence band holes that readily oxidize many species including water; light transmitted by the oxide layer can be absorbed by the underlying narrower bandgap sulfide. Sulfide valence band holes receive electrons from the oxide conduction band, leaving sulfide conduction band electrons available as reductants (e.g., form H<sub>2</sub> from H<sup>+</sup>). We show that Fe-based tandem cells can oxidize water and produce H<sub>2</sub> at rates ~10<sup>4</sup> times higher than needed to explain all water loss from Mars, and intriguingly, at about the same rate that iron deposition in Banded Iron Formations has been estimated to occur. We therefore suggest that mineral semiconductor photochemistry could have played a role in widespread redox processes on Earth, as well as on Mars.

[1] Hecht M.S., Kounaves S.P., Quinn R.C., et al. (2009) *Science* **325**, 64-67.

[2] Shuttlefield J.D., Sambur J.B., Gelwicks M., Eggleston C.M., Parkinson B.A. (2011) *J. Am. Chem. Soc. Comm.* **133**, 17521-17523.

## Deciphering the processes of crustal reworking during the formation of the Neoproterozoic Lufilian belt, NW Zambia

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### Introduction

Deciphering the source and *P-T-t* history of high grade metamorphic rocks exposed in the core of polycyclic orogenic belts is not an easy task. In this study, we combine structural analysis, metamorphic petrology and isotopic analyses of monazite and zircon to address these questions on the Lufilian Pan-African belt in Zambia.

### Geological setting

The Lufilian belt formed between the Congo and Kalahari cratons during the evolution of the Gondwana supercontinent [2]. The classical interpretation is that this belt is comprised by a Paleo- to Neo-Proterozoic sedimentary cover deposited on an Archean to Paleoproterozoic crystalline basement and that its formation results from tectonic inversion of a continental rift [3]. Alternatively, the identification of a nappe structure with HP mineral relics led other authors to propose that the formation of the Lufilian belt implies closure of an oceanic basin by subduction and development of an orogenic wedge in a way similar to Phanerozoic orogens [4]. It is to note that both models consider that gneisses exposed at the lowest structural level represent a continental basement.

### Results

Our field investigation across the Solwezi dome reveals that the transition from the metasedimentary cover to the gneissic basement actually corresponds to a metamorphic gradient reaching partial melting as evidenced by migmatites developed to the expense of metasedimentary protolith. U/Pb dating of zircon grains from the migmatite yields two clusters, one with a weighted mean <sup>207</sup>Pb/<sup>206</sup>Pb age of 2032±46 Ma and a second with a weighted mean <sup>207</sup>Pb/<sup>206</sup>Pb age of 1342±60 Ma. Zircon grains from paragneisses yield a weighted mean <sup>207</sup>Pb/<sup>206</sup>Pb age of 2010±15 Ma. In turn, U-Th-Pb chemical dating of monazite grains from high grade micaschist (*P*=10±4 kbar, *T*=630±40°C) give an age of 571±29 Ma.

### Discussion

Based on these data, we propose that the migmatite exposed at the lowest structural level of the Lufilian belt were developed to the expense of metasedimentary protolith containing zircon grains attesting for both Paleoproterozoic and Mesoproterozoic sources. This working hypothesis will be tested by new O and Lu-Hf isotopic analyses on zircon grains coupled with U-Pb geochronology and geothermobarometry in order to reconstruct a *P-T-t* path for the metasedimentary rocks and for the migmatites. We will discuss their significance in terms of crustal growth and orogenic evolution during the Neoproterozoic.

[1] Hawkesworth and Kemp (2006) *Chemical Geology* **226**, 144-162. [2] Unrug (1996) *Episodes* **19**, 11-20. [3] Porada and Berhorst (2000) [4] John (2001) *PhD Thesis* 75pp.