

## Transition element abundances in Banded Iron Formations record the Great Oxidation Event

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Banded Iron Formations, ancient marine deposits originally consisting of iron- and silica-rich chemical sediments, preserve a record of the evolution of seawater by shifts in their composition over time. The Great Oxidation Event some 2.4 – 2.2 billion years ago (Ga) is recorded in the BIF rock record by dramatic excursions in the abundances of certain redox-sensitive trace elements such as molybdenum, chromium, and copper. In this work we present data from new analyses of BIF as well as from an extensive literature compilation, all of which point towards profound changes in the supply of redox-sensitive trace elements coincident with the first accumulation of free oxygen in Earth's atmosphere. Banded iron formations deposited prior to the Great Oxidation Event generally possess very low abundances of molybdenum and chromium, in accordance with the low mobility of these elements under anoxic or reducing conditions. Approximately concomitant with independent evidence for the first appearance of free oxygen circa 2.5 Ga, the abundance of these elements in BIF increases dramatically as they became increasingly mobile at Earth's surface as the result of oxidation processes. The BIF record is not entirely straightforward, however; some non-redox-sensitive trace elements also show excursions at this time. Related proxies (e.g. black shales) should provide much needed additional insight into this enigmatic period of Earth's history.

## Mineral surfaces in prebiotic polymerization

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The formation of biopolymers from preexisting small biological molecules (e.g. peptides from amino acids, or RNA from nucleotides) is likely to have been one of the key steps in the emergence of life. Polymerization reactions, being thermodynamically unfavorable in aqueous solutions, cannot have taken place in a 'primordial soup'. The most likely alternate scenarios include chemistry in hydrothermal fluids, chemistry in the adsorbed state or a combination of both.

Here we focus on amino acids (AAs) polymerization after adsorption on oxide minerals such as clays, silica, alumina or titania. Both the adsorption step and the subsequent polymerization can now be studied in detail by a combination of macroscopic and molecular-level information.

The analysis of AA adsorption isotherms, together with the application of *in situ* spectroscopic techniques, reveals that several different adsorption mechanisms must be envisaged according to the system under consideration: in addition to straightforward electrostatic adsorption, which depends on the acido-basic speciation of the surface and the AA, instances of coordinative binding to surface cations, and of specific H-bonded adducts, are well documented.

Regarding polymerization, it has long been known empirically that wetting-and-drying cycles cause the formation of oligopeptides from adsorbed AAs in many systems, but only recently has this phenomenon been studied in molecular detail by TG, vibrational spectroscopies and solid-state NMR.

Most probably, the solution to the thermodynamic problem lies simply in the possibility of working under very low water activity during the drying step, since water is a product in the peptide bond formation reaction.

However the surface also plays a more specific role in controlling the kinetics of peptide bond formation. Here an application of Sabatier's principle can be observed since the strength of the AA/surface interaction must be 'just right' for efficient surface catalysis to occur: this apparently involves the formation of well-defined H-bonding networks between the AA and surface groups such as silanols. Models of H-bonded structure have been proposed in recent DFT studies. Thus, our understanding of prebiotic polymerization processes is progressing and shows that a rich chemistry is operating in biomolecules/mineral surfaces systems.