

## OCEAN AND ATMOSPHERE CHEMISTRY DRIVE CYCLES OF BASIN-HOSTED ORE DEPOSITS THROUGH TIME

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Trace element concentrations in marine pyrite, measured by laser ablation ICP-MS, have opened a new window into deep time ocean chemistry, atmosphere oxygenation and genesis of basin-hosted ore deposits<sup>1-3</sup>. A database of over 5000 marine pyrite trace element analyses has enabled the development of deep time proxies for nutrient supply, productivity, ocean pH and atmosphere oxygenation. These proxies suggest that the Archean ocean was enriched in Fe, Ni, Co, As, Au and Hg compared with modern oceans, probably related to composition of erosive flux from the continents and active seafloor hydrothermal activity. This was also a time for major iron, gold and nickel ore formation in sedimentary and greenstone settings. In the Palaeoproterozoic there was a decrease in Ni, Co, As and Au replaced by increasing Cu, Zn and SO<sub>4</sub><sup>2-</sup> in the oceans and O<sub>2</sub> in the atmosphere. The first appearance of red beds and evaporates is a response to the rise in O<sub>2</sub> and SO<sub>4</sub>, and provided the conditions necessary for sediment-hosted Cu and Pb-Zn-Ag deposits. Through 1700 to 1500 Ma, phosphorous, gold and most other nutrient TE dropped to a minimum in the ocean, possibly related to tectonic stasis and changes in atmosphere O<sub>2</sub> and/or ocean pH. Sediment-hosted Au, orogenic Au and VHMS deposits are virtually absent from this period, whereas mineral systems that required relatively oxidized ore fluids, such as SEDEX Zn-Pb and IOCG became more abundant, due to these changed conditions. All redox sensitive and nutrient TE rose dramatically in concentration at the Proterozoic-Phanerozoic boundary and peaked in the mid to late Cambrian, accompanied by black shale deposition enriched in Mo, Se, Ni, Ag +/- Au and PGE. Cyclic variation in nutrient TE increased in frequency through the Phanerozoic on a wavelength of 50 to 100 Ma, compared with 500 to 1000 Ma in the Proterozoic. The more frequent Phanerozoic cycles relate to repeated episodes of continent collision, mountain building and increased erosive flux of TE into the oceans. Ore deposit cycles in the Phanerozoic of SEDEX Zn-Pb, orogenic sediment hosted Au and VHMS have a similar time frame to the tectonic and seawater chemistry cycles.

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	<b>Archean 3500-2600 Ma</b>	<b>A/P</b>	<b>2400 – 1800 Ma</b>	<b>Boring Billion 1800-800 Ma</b>	<b>800-540 Ma</b>
<b>Upper Continental Crust*</b>	Mafic- ultramafic	F	Mafic	Felsic K-U-Th-REE granites	Mixed
<b>Ocean TE enriched</b>	Mg, Fe, Ti Ni, Co, Cr, As, Au		Fe, Mg Co, Cu, Zn	K, U, Th, P, Ca HREE, As, Cu, Ti, Zn, Mo	Na, K, Mg, P, Ca, Ti Co, Cu, Mn, Mo,
<b>Atmosphere</b>	CH <sub>4</sub> , CO <sub>2</sub> , CO H <sub>2</sub> , O <sub>2</sub>		GOE 1: Rise in O <sub>2</sub> and fall back	Rise in CO <sub>2</sub> Decrease in O <sub>2</sub>	Rising O <sub>2</sub> , variable CO <sub>2</sub>
Basin Hosted Ore Deposits	Fe BIF, Au, VMS		Fe BIF, Au, VMS	Sed-Cu, Sed-Zn-Pb, IOCG, U	mixed
* Dominant crustal composition					

2600-2400 Ma  
Felsic-mafic mix  
Mg, Fe, K, Ca, Mn  
Ni, Co, As, Cu, Zn, Mn  
Rise in O<sub>2</sub> and CO<sub>2</sub>  
Drop in CH<sub>4</sub>, CO