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## Large Igneous Province Volcanism, Ocean Anoxia and Marine Mass Extinction

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Past global marine mass extinction events are often linked to terrestrial Large Igneous Province (LIP) volcanism, but exact mechanisms driving extinction are often not well constrained.

We studied two of Earth's largest mass extinction events, at the Triassic-Jurassic (~201.4 Ma) and Permian-Triassic (~252 Ma) boundaries, which coincide with Central Atlantic Magmatic Province (CAMP) and Siberian Trap volcanism, respectively. The Triassic-Jurassic mass extinction is often contributed to carbon release driven ocean acidification while the Permian-Triassic mass extinction is suggested to be related to widespread ocean anoxia.

We compare Permian-Triassic and Triassic-Jurassic ocean redox change along continental margins in different geographic regions (Permian-Triassic: Greenland, Svalbard, Iran; Triassic-Jurassic: UK, Austria) and discuss its role in marine mass extinction.

Speciation of iron  $[(Fe_{HR}/Fe_T)$  and  $(Fe_{PY}/Fe_{HR})]$  and redox-sensitive trace element concentrations (e.g. Mo, V etc.) show that the Triassic-Jurassic marine mass extinction directly coincides with a rapid shift to anoxic and euxinic conditions at the onset of CAMP volcanism and increased atmospheric  $pCO_2$ . Biotic recovery after the extinction event only commences when redox-conditions return from a euxinic to a ferruginous state and stabilization of marine ecosystems only commences after decreasing atmospheric  $pCO_2$  and a return to more oxic marine conditions.

Iron-speciation at both the Triassic-Jurassic and Permian-Triassic mass extinctions however shows 2 phases of euxinia along continental margins, with an initial short peak at the onset of volcanism followed by a shift to ferruginous conditions, possibly due to a strongly diminished ocean sulphate reservoir because of massive initial pyrite burial.  $D^{34}S_{pyrite}$  suggests that following prolonged (several 100kyr) euxinic conditions only commence when the ocean sulphate reservoir is replenished by the release of sulphur from volcanism.

## Geochemistry of cassiterite and wolframite from quartz veins in Central Iberian Zone (Spain)

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Sn- and Sn-W-bearing quartz veins in the Central Iberian Zone mainly cut across the granites. Some of these veins were mined during the last century. The paragenetic sequence corresponds to two oxide-silicate stages and a sulfide stage in that order. Massive crystalline quartz is the main mineral of the three stages. Stage 1 consists of muscovite, cassiterite and arsenopyrite, stage 2 of wolframite and arsenopyrite, pyrite, pirrotite, sphalerite and chalcopyrite.

Cassiterite from Sn- and Sn-W-bearing quartz veins shows Ti> Fe> Mn content, and Ti replaces Sn. The chemical variation of cassiterite crystals is controlled by the direct substitution of Sn<sup>4+</sup> by Ti<sup>4+.</sup> Cassiterite generally shows lighter and darker zones, and Nb content is higher in darker than in the lighter zones. Wolframite consists almost entirely of FeO, MnO, and WO<sub>3</sub>, with less than 1% Ta<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, and TiO<sub>2</sub>. It shows Mn and Fe substitution. Wolframite individual crystal shows a decrease in the hübnerite component from core to rim. Likewise, Nb increases toward the rim of the wolframite crystal. Ta content of cassiterite and wolframite is generally higher than Nb content. Cassiterite has a higher Nb and Ta content than wolframite [1].

Tungsten is carried as  $H_2WO_4$ ,  $WO_4^{2-}$  [2] and wolframite can be precipitated by the cooling of an Fe-W-bearing fluid, without wall rock reaction [3]. Mineralizing fluid deposites cassiterite, associated with muscovite selvages in the paragenetic stage 1. This fluid evolves and precipitates wolframite, mainly within quartz veins in stage 2.Tungsten shows different behavior from that of tin and consequently, cassiterite is generally not associated with wolframite.

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