Marine carbonate burial rates at the Phanerozoic mass extinctions

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Several mass extinctions have disturbed the evolution of life during the Phanerozoic Eon. Information about the past environmental conditions and triggers for the extinctions can be inferred from the geological record and in particular from the analysis of different isotope systems (i.e. carbon, sulfur, and calcium) as well as the extinction selectivity [1].

To extend earlier published mass extinction scenarios we measured radiogenic (87 Sr/ 86 Sr) and stable strontium (Sr) isotope ratios ($\delta^{88/86}$ Sr, [1]) simultaneously on globally distributed brachiopod and belemnite samples to constrain changes in Phanerozoic seawater chemistry. This includes quantitative information about the marine Sr output flux, primarily controlled by the burial of marine carbonates, as the precipitation of calcite and aragonite preferentially incorporates the light Sr isotope [2,3], leaving seawater isotopically heavier.

Our Phanerozoic $\delta^{88/86}$ Sr seawater record shows considerable variability from 0.25% to 0.60% suggesting major changes of the marine carbonate burial fluxes. To quantify our results we developed a numerical box model to reconstruct changes in the inventory and fluxes of seawater Sr, calcium (Ca), and total alkalinity (TA).

The model results reveal severe disturbances in the marine budgets of Sr (0-300 µmol/l), Ca (0-40 mmol/l), and TA (0-30 mmol/l) at the Phanerozoic extinction events, especially at the Permian/Triassic boundary. These changes in the marine carbonate system are explained by processes including carbonate production rates, (shelf) carbonate dissolution, ocean anoxia associated with bicarbonate production by bacterial sulfate reducers (BSR), and shifts in the dominant carbonate mineralogy (calcite/aragonite). The first time geochemical quantification of these processes is a novelty in the field of Paleocanography and will help to identify the causal processes leading to global mass extinctions in the marine realm.

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Do mountains withdraw CO₂?

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Common gospel holds that the rise of mountains in the late Cenozoic has increased global rates of silicate weathering, and, as a consequence, increased withdrawal of atmospheric CO₂. Seawater isotope ratio curves of radiogenic Sr, radiogenic Os, and most recently, stable Li [1] supposedly testify to this change. We challenge this hypothesis on three grounds.

- 1) A compilation of weathering and denudation rates at both the soil scale and the river catchment scale show that "speed limits" restrict both soil formation (270 t km² yr⁻¹, or 0.1mm yr⁻¹) and silicate weathering (135 t km² yr⁻¹). Even in high, active mountains, these limits are obeyed. We use a global topographic model to show that due to the combination of weathering speed limit and the small spatial extent of active mountain belts, areas in which erosion exceeds the soil formation speed limit contribute <10% to global weathering fluxes today. In the geologic past, due to the limited range of weathering rates imposed by speed limit, large global changes in uplift and erosion would have resulted in only small changes in global weathering.
- 2) A reassessment of global and regional erosion rates inferred from global sedimentation rates has shown that a supposed increase in global mountain erosion rates in the late Cenozoic is only an apparent one, and that the underlying increase in sedimentation rates is due to incomplete preservation of sedimentary strata [2].
- 3) An increasing body of evidence shows that the seawater curves of radiogenic Sr and Os isotope ratios record provenance of these elements [3], or the increasingly glacial contribution to erosion [4] rather than weathering rates. The new stable Li isotope data [1] is intriguing, but we still lack detailed insight into these metal stable isotope systems to attribute their variability with certainty to an increase in terrigenous weathering. In contrast, the ocean ¹⁰Be(meteoric)/⁹Be ratio, a weathering proxy that combines an isotope of constant flux with a stable one of weathering-dependent flux, is steady over the last 10My [2]. It is therefore unlikely that changes in CO₂ withdrawal over this period were engineered by silicate weathering.

We conclude that the optimal conditions for CO_2 withdrawal are those where a large fraction of the terrestrial Earth surface is soil covered, and is eroding near soil production speed limit. At lower global denudation rate, global soils will be transport-limited. The consequence of such a low global denudation regime is that the potential for feedbacks between climate, weathering, and CO_2 withdrawal to operate is low. In such a period the Earth system could fail all climate weathering feedbacks.

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