

Spatial pollution gradients in Central Europe after 25 years of decreasing industrial emissions

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Industrial pollution in the Czech Republic (Central Europe) peaked in the mid-1980s. Soft coal combustion in the north of the country was one of the largest sources of many trace elements for the atmosphere and ecosystems. Introduction of more advanced technology in the 1990s led to a steep decrease in nationwide industrial emission rates of pollutants. In the mid-1980s, the Northern Czech Republic was 4 to 10 times more polluted than the Southern Czech Republic, which is less industrialized. In 2009, we established a new network of 10 monitoring stations near the borders between the Czech Republic, Germany, Austria and Poland. Samples of vertical and horizontal atmospheric deposition (snow and ice accretions, respectively) are collected each winter (Oct. 15- April 15). Monitoring sites are situated on mountaintops at an elevation of 1000 m. All samples are treated in a clean laboratory (class 7). Concentration of 19 elements (Al, As, Bi, Be, Cu, Co, Cr, Cd, Fe, Mn, Ni, Pb, Sb, Sc, Ti, Th, U, V, and Zn) is determined using SF ICP MS. Preliminary data from 2009 suggest that, for most of the environmentally relevant elements, spatial pollution gradients differ from previous decades. For example, for arsenic (As) and lead (Pb), the eastern part of the country (Jeseniky and Beskydy Mts.) exhibits the highest pollution loads. At the same time, the northern and southern part of the country show lower pollution loads. The northern part of the country, situated near a cluster of coal-burning power plants, experienced a faster decrease in pollution rates over the past 25 years than the south; its current atmospheric deposition is not significantly higher than in the south. For antimony (Sb), all 10 sites have similar atmospheric inputs. For zinc (Zn), the highest concentrations in atmospheric input were found in the northwest. Novohradské Mts. (south) have similar Zn inputs as Jizerské Mts. (north). Overall, pollution levels are up to 20 times lower compared to the late 1980s. They are more site-specific, and reflect temporal changes in operation of distant vs. local point sources of pollution.

The Paleozoic $\delta^{88/86}\text{Sr}_{\text{seawater}}$ record – Quantifying carbonate production rates at mass extinction events

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Within the Phanerozoic Eon strata boundaries are often associated with the extinction of marine organisms. The reasons for these events are still discussed and a quantification of observed changes in the marine carbonate system is missing.

Strontium (Sr) is one of the most important divalent cations in calcium carbonate minerals and a carrier of important proxy information. In terms of the Sr output flux of the ocean ($\delta^{88/86}\text{Sr}_{\text{seawater}}$: $\sim 0.39\%$), isotopically light carbonates ($\delta^{88/86}\text{Sr}_{\text{carbonates}}$: $\sim 0.15 - 0.25\%$) represent the major Sr sink. Consequently, variations in Sr/Ca and paired $^{87}\text{Sr}/^{86}\text{Sr}$ - $\delta^{88/86}\text{Sr}$ values are a suitable tool to investigate the global carbonate budget throughout Earth's history including the biotic turnover of calcifying organisms at stratigraphic boundaries. Latter processes are expected to have a large influence on Sr geochemistry and isotope composition of seawater.

We measured paired $^{87}\text{Sr}/^{86}\text{Sr}$ - $\delta^{88/86}\text{Sr}$ ratios of ~ 120 modern and Paleozoic marine brachiopod samples which were screened for diagenetic alteration prior to the measurement. Reproducibility of double spike-derived $\delta^{88/86}\text{Sr}$ based on an international coral carbonate standard (JCP-1) is 0.019% (2SD, n=26).

We observe major drops in $\delta^{88/86}\text{Sr}_{\text{seawater}}$ of $0.05 - 0.15\%$ at mass extinction events which coincide with a decrease of 10-50% in the number of marine genera [1]. This emphasizes the strong coupling of the carbonate system to $\delta^{88/86}\text{Sr}$ of seawater. In contrast, $\delta^{44/40}\text{Ca}_{\text{seawater}}$ changes are much less pronounced at these biotic turnovers. Furthermore, excursions in $\delta^{13}\text{C}_{\text{carbonate}}$ at strata boundaries are related to changes in the organic carbon production rather than to the carbonate production.

By taking changes in $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{88/86}\text{Sr}$ and Sr/Ca into account we are able to make quantitative statements on the Sr input and output fluxes of the ocean at the major Paleozoic mass extinction events, including the Permian/Triassic boundary.

[1] Sepkoski (1997) *J. of Paleontology* **71**, 533–539.