

The Paleozoic minimum in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the Capitanian (Middle Permian): Records from the mid-Panthalassa paleo-atoll limestones

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We report a detailed secular change of the Middle-Late Permian seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with the unique 'Permian minimum' interval detected in mid-Panthalassa (superocean) paleo-atoll carbonates. The analyzed limestones at Kamura and Akasaka sections in Japan occur as exotic blocks within the Jurassic accretionary complex. On the basis of fusuline biostratigraphy, both sections span across the Middle-Upper Permian or the Guadalupian-Lopingian (G-L) boundary characterized by a major biotic crisis. Two sections are separated from each other for 500 km at present, thus were likely derived from different paleo-seamounts existed in mid-Panthalassa.

A 30 m-thick interval with low $^{87}\text{Sr}/^{86}\text{Sr}$ value (< 0.7070) was detected in the Capitanian (Upper Guadalupian) interval, i.e. the *Yabeina* (fusuline) Zone, *Lepidolina* Zone, and the barren interval in the Kamura section. Data from Akasaka section confirm that extremely low $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.70688) similarly characterize the *Yabeina* Zone and the barren interval. A remarkable rise in $^{87}\text{Sr}/^{86}\text{Sr}$ values for 0.00073 up to 0.70761 occurred in the barren interval after the 'Permian minimum' in both sections, suggesting a general isotopic trend in the superocean. This increase in Sr isotope after the 'Permian minimum' likely suggests that a huge amount of highly radiogenic terrigenous clastics have been shed into Panthalassa by connecting intra-Pangean drainage systems directly to the superocean. The development of the new drainage systems might be related to large-scale continental rifting, thus the initial breakup of Pangea. It is noteworthy that carbonate stable carbon isotope ratio ($\delta^{13}\text{C}_{\text{carb}}$) also shifted dramatically in the latest Capitanian barren interval immediately before the G-LB.

Fe(II) oxidation under very low O_2 conditions: New rate law and its implication

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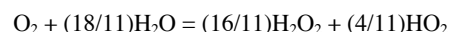
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Many geological proxies point the great rise of atmospheric oxygen in the Paleoproterozoic (Great Oxidation Event). The proxies including mass independent fractionation in sulfur isotopes reveal that atmospheric oxygen increased from very low concentration ($< \sim 10^{-6}$ atm of pO_2) to low concentration ($> \sim 10^{-3}$ atm of pO_2) between 2.5 and 2.0 Ga. However, many of the proxies are useful for deciphering the timing of the transition in pO_2 levels rather than its quantitative pattern. On the other hand, paleosols formed during the Paleoproterozoic have recorded the ratios of Fe (III)/Fe (II) at the time of their formation and these kinetical data can give more quantitative estimates of pO_2 . To quantitatively estimate pO_2 through the ratios of Fe (III)/Fe (II), the rate law of Fe (II) oxidation should be understood.

Experimental data of Fe (II) oxidation have been obtained under the conditions of $\text{pO}_2 = 10^{-3} - 10^{-5}$ atm and $\text{pH} = 7.57 - 8.12$. Combined with previous oxidation data at $\text{pO}_2 > 10^{-3}$ atm, newly discovered is that the rate law changes its form from $d[\text{Fe (II)}]/dt = -k[\text{Fe (II)}][\text{OH}^-]^2[\text{O}_2]$ at $\text{pO}_2 > \sim 5 \times 10^{-3}$ atm to $d[\text{Fe (II)}]/dt = -k'[\text{Fe (II)}][\text{OH}^-]^2[\text{O}_2]^{0.55}$ under the conditions of $\text{pO}_2 = 5 \times 10^{-3} - 10^{-5}$ atm.

In interpretation of this new rate law, especially the change in the power of $[\text{O}_2]$ from 1 to 0.55, we suggest that under the very low O_2 conditions intermediate oxygen species (superoxide, hydrogen peroxide and hydroxyl radical) attack Fe (II) more effectively, which results in faster Fe (II) oxidation rate than previously considered. Out of possible reactions that produce oxygen species from oxygen, the reaction,



gives the power of $[\text{O}_2]$ of 0.55. Combination of this reaction and those proposed by Haber and Weiss reproduces the experimental results well under the conditions of $10^{-5} - 0.2$ atm of pO_2 .

The new rate law was applied to the ratios of Fe (III)/Fe (II) of paleosols formed during the Paleoproterozoic, revealing that atmospheric oxygen increased gradually, linearly on the logarithmic scale, from $< \sim 10^{-6}$ to $> \sim 10^{-3}$ atm of pO_2 between 2.5 and 2.0 Ga.