Gradual rise of atmospheric oxygen between 2.5 and 2.0 Ga revealed by Fe oxidation kinetics

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The evolution of atmospheric oxygen during the Precambrianis a key to understand the co-evolution of life and environment. A change in the redox state of the atmosphere during the Paleoproterozoic has been recognized from geologic records being termed as the Great Oxidation Event. The disappearance of mass independent fractionation in sulfur isotopes confirms that oxygen increase from $\leq \sim 10^{-6}$ atm to $\geq \sim 10^{-3}$ atm took place between 2.45 and 2.0 Ga indicating the timing of P_{O_2} transition rather than its quantitative pattern. Despite this advancement, the precise nature of quantitative evolution of atmospheric oxygen during the Paleoproterozoic has remained elusive.

The fractions of redox sensitive elements such as Fe and Mn retained in weathering profiles should reflect the concentrations of atmospheric oxygen at the time of weathering. We calculated retention fractions of Fe and Mn (ratios of the concentrations in a paleosol relative to the parent rock on isovolumetric basis), Fe_R and Mn_R, corrected for compaction factors using available literature data. The Fe_R and Mn_R increased gradually with age during the Paleoproterozoic (Mn_R showing less steep slope than Fe_R) suggesting an almost continuous increase in the oxidation of Fe^{2+} and Mn^{2+} in paleosols between 2.5 and 2.0 Ga.

We, then, applied Fe oxidation kinetics $(-d[Fe^{2+}]/dt = k[Fe^{2+}] [OH^-]^2 (P_{O_2})^x$; x is the variable) to the data set of Fe^{2+} and Fe^{3+} concentrations in paleosols to quantitatively model the atmospheric oxygen increase. The above equation was finally converted to:

$$\psi/\psi_A = (P_{O_2})_A^{x'}/(P_{O_2})^x$$

where ψ is the ratio of [flowing-out Fe^{2+}]/[dissolved Fe^{2+}] and the parameters with subscript A are values for reference paleosol A. We also considered formation time of weathering and variation of P_{CO_2} with time in our calculations. Our results suggest that the atmospheric oxygen increased linearly in the logarithmic scale from $\sim 10^{-6}$ atm at 2.5 Ga to $\sim 10^{-3}$ atm at 2.0 Ga, which is in contrast to the drastic rise at $\sim$ 2.3 Ga. The gradual rise of oxygen is consistent with isotopic records of carbon and sulphur.

Influence of microbial activities on the behavior of iodine in soil

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Studies of iodine in soil are important because of the following two reasons. From the nutritional viewpoint, iodine is an essential element for human because of its role in thyroid gland. Therefore, it is necessary to know the levels and behavior of this element in the soil-vegetation system. From the radiological viewpoint, ^{129}I (half-life: 16 million years) is released from nuclear industries into the environment. Because of its long half-life, it is important to understand the fate of iodine in the soil environment. In this study we have carried out laboratory experiments on the sorption, desorption and volatilization phenomena of iodine in soil with a special reference to the role of microorganisms. We also analyzed iodine concentrations in various soils collected in Japan.

Very high iodine concentrations (on average: ca. 40 ppm) were found in Andosols, the most common soil type in Japanese upland fields, although its parent materials such as volcanic ash contain very low iodine (ca. 0.04 ppm). This indicates that iodine evaporated from the ocean into the atmosphere was deposited on the soil surface and accumulated there. Using radiotracer experiments, we found that fresh soils had a very high sorption capacity for both iodide (I^-) and iodate (IO_3^-), whereas that of autoclaved soils was markedly small, specifically for iodide. This suggests the possibility that microorganisms or their products (e.g. enzyme) play an important role in the iodine adsorption. Desorption of iodine from soil under flooded conditions was observed, i.e. iodine associated with soil was dissolved into water due to the reducing conditions (low Eh) created by the effects of microbial activities. Low iodine concentrations observed in rice paddy soils can be explained by this effect.

From the soil-plant system, iodine evaporated as organic iodine. In order to investigate this mechanism, we have performed experiments by using bacteria. It was found that a wide variety of bacteria had capacities for producing methyl iodide (CH_3I) and they contributed to the volatilization of iodine from soils and also from seawater. Some kinds of fungi also showed a high ability in methylating iodine. We have also carried out studies on the oxidation and reduction of iodine by bacteria. Iodide-oxidizing bacteria, which oxidize iodide to molecular iodine (I_2), were isolated from underground brines containing very high iodide. Oxidation of iodide was found to be mediated by an oxygen-requiring enzyme. Iodate-reducing bacteria, which reduce iodate to iodide, were also found. Our results showed that microbial activities influence the chemical form of iodine, which is important to understand the fate of stable and radioactive iodine in the environment.