

古土壌中の鉄保持率を用いた大気酸素レベルの見積もり Fe retention fraction of paleosol as a barometer of atmospheric oxygen level

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Although various geological records indicate that there was a great rise of oxygen in the Paleoproterozoic (2.5 - 1.6 Ga) (the Great Oxidation Event, Holland, 2006), the quantitative knowledge about how oxygen increased is still unclear. The paleosols formed during the Neoproterozoic (2.8 - 1.6 Ga) can be used to strongly constrain the atmospheric oxygen levels, because they are formed by direct interactions with the contemporary atmosphere and water. Quantification of oxygen levels has been tried using Fe records, because iron is redox-sensitive element (Holland, 1984; Murakami et al., 2011). Recently, Murakami et al. (2011) demonstrated that the amount ratio of precipitated Fe(III) to dissolved Fe(II) in weathering process (the phi ratio) can be used to quantify the atmospheric levels, because the phi ratio can be converted to Fe(II) oxidation rate, which is a definite function of oxygen concentration. Although the phi ratios are useful, all the literatures of the Neoproterozoic paleosols have not always reported both Fe(II) and Fe(III) contents required to calculate the phi ratios; some literatures report only total iron contents (Fe(II) + Fe(III)), from which only the Fe retention fraction can be calculated. Although the time-transition of Fe retention fraction levels throughout the Neoproterozoic paleosols indicates qualitatively the gradual rise of oxygen (Murakami et al., 2011), quantitative use of Fe retention fraction is more desirable but not yet attempted.

Using Fe retention fraction along with those of the other major cations (Mg, Ca, Na and K) and Si, we attempted to estimate Fe(II) oxidation rate at the time of weathering. The estimation is based on (1) the mass balance of elements (Fe, Mg, Na, K and Si) between the solid and water phases and (2) the volume balance during chemical weathering, with an assumption that Fe(III) oxyhydroxides are the dominant secondary minerals of iron. The validity of the method is confirmed by reasonable agreement of the estimated Fe(II) oxidation rates based on the method with those calculated from measured phi ratios in olivine dissolution experiment under various oxygen levels conducted by Sugimori et al. (2012), although, when oxygen level is decreased, the method tends to calculate the oxidation rate higher than that calculated from the phi ratio. By application to the paleosols with known phi ratios (Cooper Lake, Pronto/NAN, Gaborone, Drakenstein and Flin Flon paleosols), we further assessed the validity. For the ~2.2 Ga Gaborone, ~2.1-Ga Drakenstein and ~1.8-Ga Flin Flon paleosols, oxidation rates estimated by phi ratios and Fe retention fractions are consistent, while for the ~2.5-Ga Cooper Lake and Pronto/NAN paleosols, again the Fe retention fraction method calculated Fe(II) oxidation rates higher than those calculated from the phi ratios. The deviation of Fe(II) oxidation rates derived from Fe retention fractions are attributed to the violation of the assumption that Fe(III) oxyhydroxides are the major secondary minerals of Fe. Under low O₂ conditions, some Fe(II)-bearing clay minerals can be also secondary minerals of Fe (MacFarlane et al., 1994). Therefore, although Fe retention fraction method cannot calculate Fe(II) oxidation rates as precisely as phi ratios when oxygen level is low, it still can give strong upper constraints on Fe(II) oxidation rates and therefore oxygen levels at the time of weathering, even for the paleosols with phi ratios unavailable.

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