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Behaviors of trace elements in Paleoproterozoic paleosols: Implication for atmospheric oxygen level and ocean chemistry

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Atmospheric oxygen increased during the Paleoproterozoic (2.5 - 2.0 Ga). The atmospheric oxygen rise, climate, ocean chemistry and life evolution have been considered to be mutually affected. Fe and Mn, redox-sensitive elements, in paleosols have been used to estimate atmospheric oxygen levels (e.g., Rye and Holland, 1998). On the other hand, the concentration variations of trace elements such as Mo, Cr and Ni in the ocean with age can be related to atmospheric oxygen levels, and therefore, such trace elements can be proxies for oxygen evolution (e.g., Scott et al., 2008; Frei et al., 2009; Konhauser et al., 2009). The concentration variations of trace elements are also considered to result from continental weathering (Scott et al., 2008; Frei et al., 2009). In addition, such trace elements are usually critical components of enzymes, and therefore, the concentration variations of trace elements in the ocean can bring important information on life evolution. Here we report the behaviors of trace elements in paleosols to give a deeper understanding of atmospheric oxygen evolution during the Paleoproterozoic and to correlate the behaviors with change in ocean chemistry with age.

The samples used were paleosols formed between 2.76 and 1.85 Ga. The trace elements measured were V, Cr, Co, Ni, Cu, Zn, Mo and W. Their concentrations were measured at different depths of each sample, an elemental depth profile for each trace element of each paleosol was made normalizing by Ti, immobile element, a variation of elemental retention fraction (a mole fraction of a profile to parent rock on isovolumetric basis) with age was estimated, and finally, the behaviors of the trace elements in paleosols were examined considering thermodynamic properties indicated in Eh-pH diagrams.

The behaviors of the trace elements can be described as follows: (1) V was retained in a weathering profile before about 2.3 Ga and flowed from the system since then. The V concentration in the ocean increased since about 2.3 Ga; (2) Cr was retained in a weathering profile by the late Archean and flowed from the system in the Paleoproterozoic. The Cr concentration in the ocean increased in the Paleoproterozoic; (3) Co showed an inverse behavior to those of V and Cr and a similar behavior to that of Fe. Co flowed from a weathering profile before about 2.3 Ga and was retained since about 2.3 Ga. The Co concentration in the ocean decreased since about 2.3 Ga; (4) Ni tended to flow from a weathering profile before about 2.4 Ga and to be retained since about 2.4 Ga. The Ni concentration in the ocean decreased since about 2.4 Ga; (5) Cu flowed from a weathering profile during the entire Paleoproterozoic, and the Cu concentration in the ocean increased; (6) Zn flowed from a weathering profile before about 2.3 Ga and was retained since about 2.3 Ga. The Zn concentration in the ocean decreased since about 2.3 Ga; (7) Mo flowed from a weathering profile during the entire Paleoproterozoic, and the Mo concentration in the ocean increased; and (8) W flowed from a weathering profile during the Paleoproterozoic, and the W concentration in the ocean did not decrease. These behaviors suggest that the atmospheric oxygen concentration increased at about 2.45 Ga and a further increase took place at about 2.3 Ga, which favors a model of gradual increase of atmospheric oxygen rather than that of drastic increase during the Paleoproterozoic. The resulting behaviors of the trace elements in paleosols predict the changes in concentrations of trace elements in the ocean, which is consistent

with the results of previous studies except for Cu. This consistency supports that continental weathering controlled the changes in ocean trace elements.

Keywords: atmospheric evolution, weathering, paleosol, trace element, ocean chemistry