

Mobility of base metal elements and rare earth elements during the chemical weathering of volcanic ash soil profile in Kanto area, central Japan

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1. Introduction

Several researchers investigated the rare earth elements (REEs) and base metal elements mobility during the chemical weathering of granitic rocks (Nesbitt, 1979), sedimentary rocks (Kimura et al., 1999), and laterite soil (Dequindy et al., 2002). In contrast to the studies on these rocks, no systematic analytical data on the REEs and base metals in weathered volcanic ash soils have been obtained. Therefore, we report analytical data of REEs and base metal elements in the basaltic ash soil in Japan and consider the causes for the REEs mobility of these elements during the weathering.

The volcanic ash soils are in the properties of surface A horizons and usually have melanolic A horizons and are characterized by A-type humic acid with a high degree of humification and are of thickness more than 30cm (Sase and Hosono, 1996). Such soils are called Andosols.

The Andosols are mainly composed of basaltic ash soil and dark gray in appearance. It was formed during the last ten thousands years and covers wide area in the Japanese Islands (about 16% of total area). The Andosols are underlain by Loam which is defined as weathered clay-rich volcanic ash material in red-yellow in color. The Loam is widely distributed in Japanese islands, particularly in the Kanto area, central Japan. The Kanto-loam is mainly composed of fine-grained weathered volcanic ash, lithic fragments and aerosol derived from Asian continent. Volcanic materials came from volcanoes in the Kanto area (Fuji, Hakone etc.).

The objectives of this study are (1) to obtain the variations of mobilities of major elements, REEs and base metal elements in the Andosols and Kanto-loam, (2) to interpret the causes for these variations and their difference between the Andosols and Kanto-loam, considering the mechanism of elemental mobility and mineralogical

changes in the weathering profile, and (3) to interpret the different mobility of each REEs and base metal in the Andosols and the Kanto-loam.

2. Sampling site

The sampling site is located about 40km east of Mt. Fuji, central Japan. The Andosols have been formed since ca.10000 years ago to present, related to volcanic activity of Mt. Fuji. The Andosols are underlain by the Kanto-loam. The Kanto-loam has been formed since a hundred thousands years ago. Forty samples of the Andosols and Kanto-loam were collected at natural exposures. The thickness of the Andosols and Loam studied is 1.7 – 1.5m.

3. Mineralogy

The primary materials in the Andosols include volcanic glass, olivine, pyroxene, feldspar, quartz and magnetite. The change in abundances of these primary materials and secondary minerals indicate that volcanic glass which is the dominant primary material decreases in abundance with depth, relative abundances of olivine, pyroxene, feldspar and magnetite are small, and the abundance of halloysite increases with depth. The Kanto-loam is predominantly composed of olivine, pyroxene, feldspar, halloysite and small amounts of quartz and magnetite. Dominant clay mineral is halloysite.

4. Chemical compositions of bulk rocks and elemental mobility

The chemical compositions of bulk rocks for major elements (Si, Al, Fe, Ti, Mn, Na, K, Ca, Mg, P), base metal elements (Zn, Pb, Cu, Co, Ni), and the REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were determined by X-ray fluorescence analysis and by ICP-MS method, respectively.

$(MO/Al_2O_3)_{\text{sample}} / (MO/Al_2O_3)_{\text{parent-rock}}$ ratio (Al-normalized value; Al.n.v.) was calculated in order to estimate elemental mobility because it is generally thought that Al is most immobile element under normal weathering conditions. Parental composition was taken from that of the most surface sample which is thought to be the least weathered material.

It was found that Al.n.v. for Fe, Ti, and Mn increase with depth, while those for Na, K, Ca, Mg and Si decrease with depth in Andosols. The order of relative elemental mobility during the weathering of Andosols is Na, Mg>P>Si>Ti = Fe>Al>Mn.

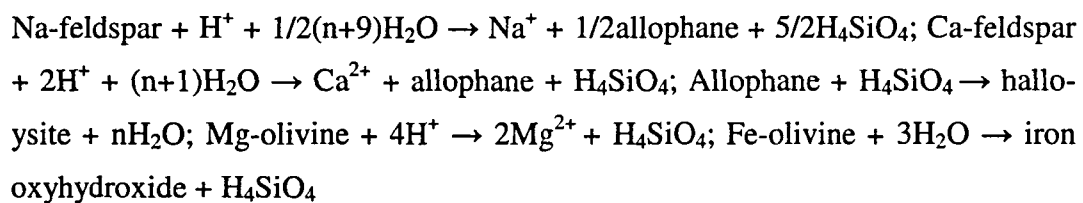
The Al.n.v. for Na, K, Si, Fe, Mn and Ti do not change with depth in the Kanto-loam, while those for Ca and Mg increase with depth.

The Al.n.v. for the REEs decrease with depth in the Andosols, while they are rela-

tively constant in the Kanto-loam. The mobility of the REEs in the Andosols is less than alkali and alkali earth elements and Fe, Mn, Ti and Al are relatively immobile but Fe and Mn contents slightly increase with depth in deeper part of Andosols, reflected by the increased abundance of Fe-oxyhydroxides with depth, but decrease in the Kanto-loam. In the Kanto-loam the Al.n.v. for the REEs are constant with depth, that means the slight enrichment of the REEs in the Kanto-loam. The REEs with larger ionic radius (light REEs; LREE) are more depleted in the Andosols than those with smaller ionic radius (heavy REEs; HREE) and slightly increase with depth in the Kanto-loam.

5. Discussion-interpretation of elemental mobility and enrichment

The characteristics of elemental mobility are interpreted in terms of the dominant mechanism governing the mobility. Volcanic glass and silicates decrease in abundance with depth in Andosols. Allophane, clay minerals and iron oxyhydroxides increase in abundance, indicating that the following dissolution precipitation reactions occurred during the chemical weathering of the Andosols.



It is considered from these dissolution-precipitation reactions that alkali and alkali earth elements remove significantly, Si removes but the mobility of Si is smaller than that of alkali and alkali earth elements due to the precipitation of allophane, and Al and Fe do not remove because dissolved Al and Fe are almost totally fixed as allophane and halloysite. The mobility of the REEs and base metals in the Andosols could be explained by the dissolution of silicates and fixation of these elements by adsorption of these elements on to the surfaces of secondary minerals (allophane, iron oxyhydroxides, halloysite).

Alkali elements (Na, K) do not change with depth in Kanto-loam and alkali earth elements (Ca, Mg) increase with depth. This could be explained by the fixation of these elements migrating downward from upper part (Andosols) that were dissolved from silicates and volcanic glass.

Considering surface areas and maximum surface-site densities (chiefly negative), the sorptive abilities of iron oxyhydroxide (ferrihydrite), and montmorillonite are high compared with other minerals (silicates, oxides).

It is worthy to point out that pH of soilwater in the Andosols and Kanto-loam is 6.5 ± 0.5 which is close to PZNPC (point of zero net proton charge) (pH=7) for iron oxyhydroxide. In addition to above-argument, a slight increase or constant variation of Fe content in the Kanto-loam supports that the REEs are adsorbed on to the surface of iron oxyhydroxides. PZNPC is about 2 and 7 for clay minerals (kaolinite, halloysite) and allophane, respectively. Thus, it seems likely that the REEs are adsorbed also on to clay minerals.

At pH = 6.5 ± 0.5 , predominant states of the REEs are cation and probably neutral species such as carbonate complex and those of the base metals are cation. Therefore, it is likely that the cations of the REEs and base metals are adsorbed by iron oxyhydroxides and clay minerals (halloysite, montmorillonite).

Relatively constant contents of Si, Fe, Al, Mn and Ti in the Kanto-loam suggest that dissolution, precipitation and adsorption-desorption did not considerably influence the migration behavior of these elements in the Kanto-loam.

Increased trend of Mg and Ca contents with depth in Kanto-loam suggests that the formation of minerals containing these elements (e.g., montmorillonite) took place in the Kanto-loam.

It is notable that the REEs with larger ionic radius (LREE) more efficiently remove from the Andosols than those with smaller ionic radius (HREE). This different migration behavior of the REEs could be explained by the adsorption of the REEs on to the surface of secondary minerals which is controlled by the formation of surface hydroxide complex on the surface. The more adsorption tendency of the HREE than LREE is considered to be due to smaller hydrolysis constants for HREE. The order of adsorption tendency for base metal elements is Pb, Cu > Zn > Ni, Cr, Mo > Ca. This can be also explained by the intrinsic surface complex constant for the adsorption by hydrous ferric oxide.

6. Comparison with other soils in Japan

Geochemical characters of the Andosols and Kanto-loam studied are compared with those of other soils in Japan (Masa and Red soil).

Highly weathered and clay rich Masa (weathered granite) and red soil from sedimentary rocks (limestone) are characterized by LREE enrichment compared with HREE. This could be explained by high tendency of adsorption by 2 : 1 – type clay minerals (illite, vermiculite, smectite) which are dominant secondary minerals in these soils.