

# Characterization of individual particles in water samples from the Fuji and Sagami Rivers, central Japan by SEM-EDX

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**ABSTRACT:** The selective enrichment behaviors of labile substances such as hydroxides to the surface of specific mineral particles in river water were clarified by scanning electron microscopy/energy dispersive X-ray microanalysis (SEM-EDX). Individual particles with particle size between 0.45 and 10 $\mu$ m other than diatom in water samples from the Fuji and Sagami rivers, central Japan were analyzed by SEM-EDX and classified into seventeen groups according to the chemical composition and the shape. Phosphorus, sulfur, chlorine, manganese and copper detected in each particle could be used successfully in order to elucidate the insoluble components secondary formed in river water, because the detection frequencies of such elements are usually quite low or negligible in fresh mineral particles derived from igneous rocks. Almost all parts of manganese detected in individual particles are ones adsorbed afresh as the hydroxides together with iron and aluminum. Anions such as phosphorus, sulfur and chlorine form the complexes with the hydroxides and/or are incorporated in them. The detection frequencies of such labile species were predominantly high in Mg and/or Ca rich aluminosilicates.

**Key Words:** individual particle, river water, Mg and/or Ca rich aluminosilicates, scavenger of hydroxides, SEM-EDX

## Introduction

One of the process determining dissolved elemental concentration in river water is the interaction between liquid and solid phases (Salbu and Steinnes, 1995). However, the chemistry of river water has been ever discussed concentrating on the dissolved species only (Salbu and Steinnes, 1995; Koshimizu and Kyotani, 2002). Consequently, the information on the chemical composition of suspended particle in river water is not so much and the role in the elemental fractionation between dissolved species and suspended particle has not yet been clarified satisfactory. The main removal processes of dissolved elements in natural waters are coprecipitation with hydroxides and the formation of metal-fumic complexes (Appelblad et al., 1999; Haraguchi et al., 2000; Kawakubo et al., 2002; Kyotani and Koshimizu, 2000). Recently, the

latter has been intensively discussed from the speciation studies of trace elements by many researchers (Appelblad et al., 1999; Haraguchi et al., 2000; Kawakubo et al., 2002). While, although the former has been sometimes discussed using labile iron existing in colloidal fraction from 0.45 $\mu\text{m}$  filtrates (Kawakubo et al., 2002), the particles with size above 0.45 $\mu\text{m}$  have been usually neglected.

The aim of this study is to clarify the factors affecting the dissolved elemental concentrations in river water in terms of the chemical compositions of insoluble individual particles. In this study, the chemical compositions of individual particles with size above 0.45 $\mu\text{m}$  in river water were determined by scanning electron microscopy/energy dispersive X-ray microanalysis (SEM-EDX). Phosphorus, sulfur, chlorine, manganese and copper detected in individual particles were used in order to estimate the labile substances secondary formed in river water. Consequently, the selective enrichment behaviors of the labile substances to specific mineral particles were clarified.

## Materials and Methods

Study area is the Fuji river whose geology is mainly andesitic and granitic, and the Sagami river characterized by mainly basaltic, central Japan. Sampling sites are shown in Fig.1. River water samples were collected in polypropylene container (1 L) at each four point in the Fuji (F1-F4) and Sagami (S1-S4) rivers on 1 March, 2000. The samples were shaken thoroughly prior to use. The 500 ml portion was immediately filtered through a 0.45 $\mu\text{m}$  PTFE membrane filter. The insoluble particles on the filter were detached by both sides-adhesive carbon tape and were fixed on the aluminum sample stand for SEM-EDX. Thereafter, the particles were carbon coated ( $\sim 200\text{\AA}$ ) and the specimens were subjected to SEM-EDX analysis. About 200 particles with particle size between 0.45 and 10 $\mu\text{m}$  other than diatom in each specimen were analyzed under the condition of accelerating voltage of 20kV, probe current of 0.3 nA and counting time of 100 s. The characteristic intensities of the elements detected were normalized to the total sum of characteristic X-ray intensities of elements with atomic number over 11 to avoid the particle size effect (Jambers and Van Grieken, 1997). Obvious single particles were classified into sixteen groups according to the relative X-ray intensity. Aggregates or biomineral-like substances were firstly discriminated from other particles by the peculiar shape, and then were re-classified using the relative X-ray intensity.

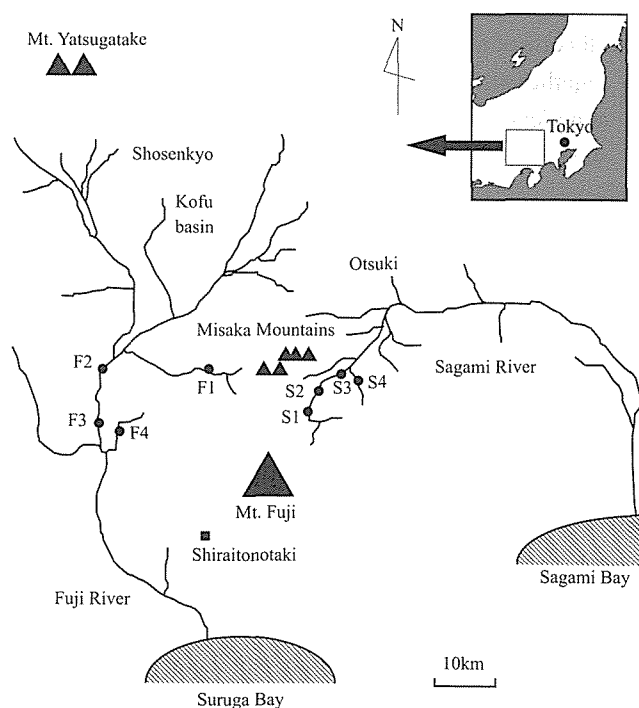


Fig. 1. Sampling locations.

## Results and Discussion

### Particles adsorbing labile substances

Fig.2 shows the abundances of phosphorus, sulfur, chlorine, manganese and copper detected in individual particles from river waters and several source materials. Fig.2(a) expresses all particles other than diatom. As shown in Fig.2(b), the detection frequencies of these elements are usually quite low or negligible in fresh mineral particles from igneous rocks, because the detection limits of SEM-EDX are not enough to detect these elements being the contents below approximately 0.01-0.1%. Thus, individual mineral particles in rocks or atmospheric aerosol (Kyotani and Koshimizu, 2001) being the major source materials of suspended particles in river water do not contain significantly above 5 elements. Therefore, most of them detected in individual particles from river water can be considered to be not the constituents of aluminosilicates but labile substances adsorbed afresh or secondary formed in water. In the conventional SEM-EDX studies (Jambers and Van Grieken, 1997), the contribution of labile species to individual particle surfaces has not ever been considered sufficiently.

Also, the distribution in river water of the insoluble manganese detected in individual particles well corresponds to it of dilute-acid (0.02M nitric acid) soluble manganese measured in our previous work (Kyotani and Koshimizu, 2000). These results suggest that most of manganese exists as easily soluble forms. It was also already shown that manganese is one of the predominant elements together with iron and aluminum

in the dilute-acid soluble fraction from suspended particles in river water and manganese which can be released easily from particles are mainly hydroxides (Kyotani and Iwatsuki, 1998; Kyotani and Koshimizu, 2000). Thus, the labile manganese forms mainly the hydroxides together with labile iron and aluminum, and adsorbs on the surfaces of mineral particles. At the same time, it is suggested

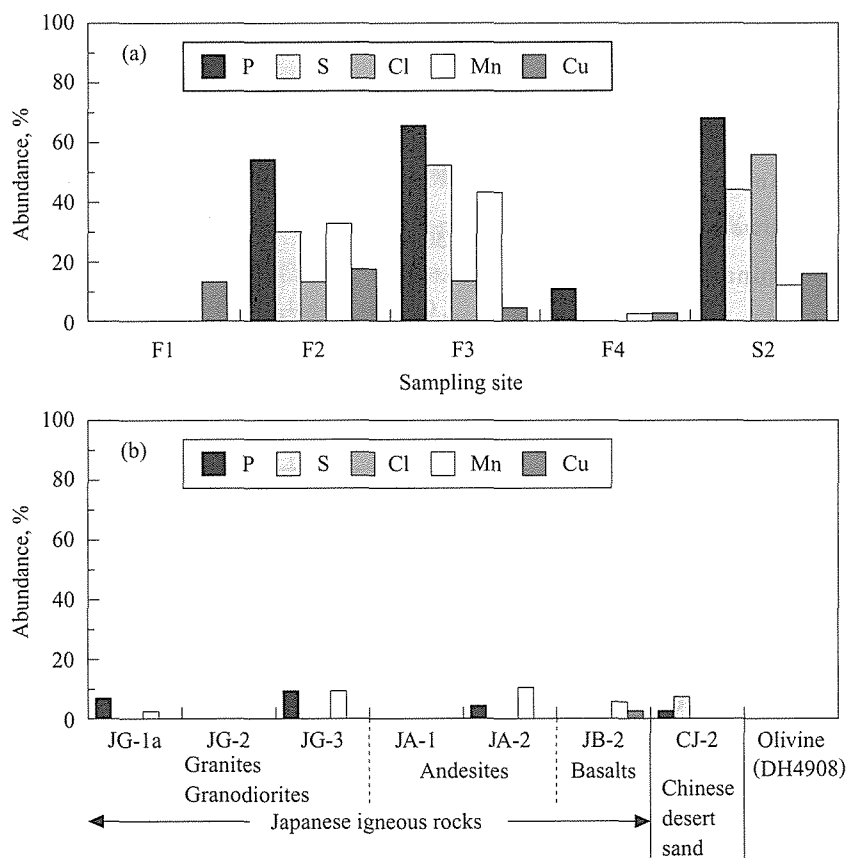


Fig. 2. Abundances of phosphorus, sulfur, chlorine, manganese and copper detected in individual particles from river waters (a) and several source materials (b).

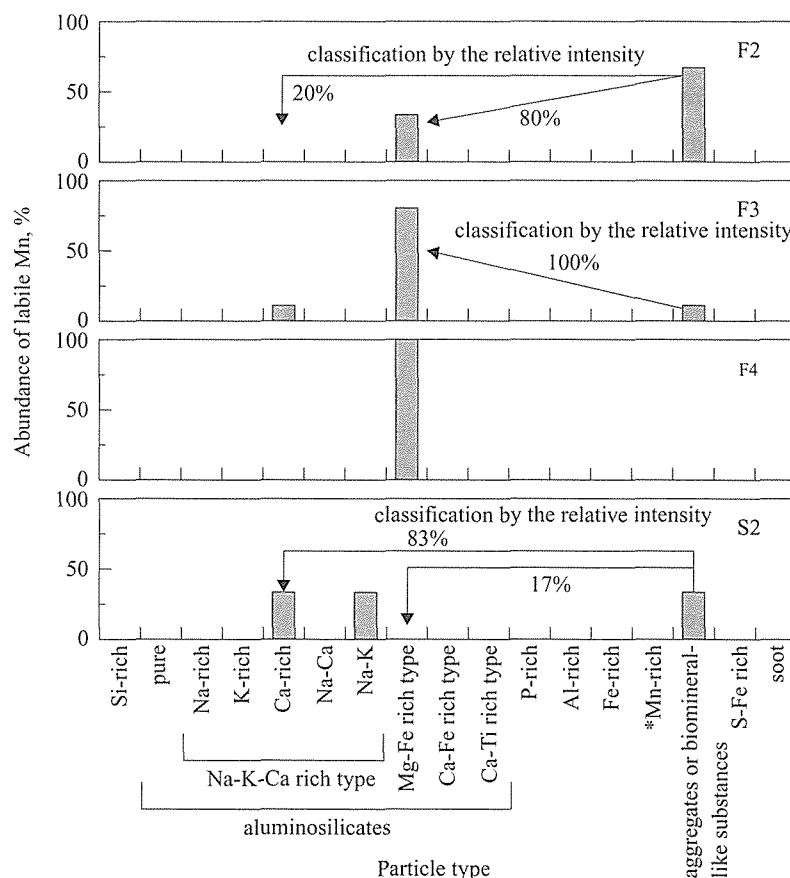
that not only heavy metals but also anions such as phosphorus, sulfur and chlorine form the complexes with the hydroxides and/or are incorporated in them. Judging from these points, the Fuji river has the high removal efficiency of dissolved species.

### Selective enrichment of hydroxides to the surface of specific minerals

As an example, Fig.3 shows the abundance of the labile manganese by the particle type. The detection frequency of the labile manganese was predominantly high in Mg-Fe rich aluminosilicates and aggregates or biomineral-like substances, especially in the Fuji river. This result suggests that the latter is aggregates of hydroxides or humic substances. The former is a predominant component in solutions containing the large amounts of soluble components. However, the former is an expedient existence, because almost all parts of the manganese and most of the iron can be regarded as secondary formed hydroxides, judging from their relative X-ray intensity ratio. Namely, Mg-Fe rich aluminosilicates classified expediently in Fig.3 should be considered to be essentially Mg and/or Ca rich aluminosilicates being the low iron contents.

Manganese was not detected significantly even in olivine being the typical Mg-Fe rich aluminosilicates as shown in Fig.2(b). This result well corresponds to the feature of original Mg-Fe rich aluminosilicates from the Sagami river which characterized by basaltic rocks. Namely, original Mg-Fe rich aluminosilicates do not adsorb significantly labile species. Furthermore, aggregates or biomineral-like substances were re-

classified using the relative X-ray intensity as shown in Fig.3. As the results, the abundance of labile manganese is changed as follows. That is, it is predominantly high not in Fe-rich particles but in Ca-rich, and Mg and/or Ca rich aluminosilicates. While, although Na-, K- and Na-Ca rich aluminosilicates such as alkali feldspars or plagioclase are main minerals in the Fuji river, they do not significantly adsorb the labile manganese. Thus, the adsorption behaviors of hydroxides to mineral particles show the remarkable



**Fig. 3.** Abundance of labile manganese by the particle type.  
\*Mn-rich particle was excluded from the calculation.

selectivity. These results indicate that Mg and/or Ca rich aluminosilicates in river water play important roles as the scavengers of Mn-, Fe- and Al- hydroxides adsorbing dissolved trace elements and affect the elemental fractionation between liquid and solid phases.

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