

Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy

Volume 12

Article 14

January 2010

Sorption Of Antimony In Stream Water By Weathered And Altered Rock

Sakae Sano

Ehime University

Masayuki Sakakibara

Ehime University

Etsuko Chiba

Ehime University

Rie Hori

Ehime University

Follow this and additional works at: <https://scholarworks.umass.edu/soilsproceedings>

Recommended Citation

Sano, Sakae; Sakakibara, Masayuki; Chiba, Etsuko; and Hori, Rie (2010) "Sorption Of Antimony In Stream Water By Weathered And Altered Rock," *Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy*: Vol. 12 , Article 14.

Available at: <https://scholarworks.umass.edu/soilsproceedings/vol12/iss1/14>

This Conference Proceeding is brought to you for free and open access by ScholarWorks@UMass Amherst. It has been accepted for inclusion in Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy by an authorized editor of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.

Chapter 13

SORPTION OF ANTIMONY IN STREAM WATER BY WEATHERED AND ALTERED ROCK

Sakae Sano¹, Masayuki Sakakibara², Etsuko Chiba² and Rie Hori²

¹Earth Science Laboratory, Faculty of Education, Ehime University, Matsuyama, 790-8577 Japan; ²Graduate School of Sciences and Engineering, Ehime University, Matsuyama, 790-8577 Japan

Abstract: The ionic migration of antimony in various weathered and country rocks during chemical weathering was studied. The Ichinokawa abandoned mine of Shikoku Island, Japan is famous for the production of stibnite. The antimony deposits are mainly in Sambagawa metamorphic rocks and the brecciated rocks (Ichinokawa breccia) formed through a hydro-fracturing process associated with hydrothermal fluid related to Tertiary igneous activity around the area. Antimony content in stream water around the mine was extremely high (over 200 g/L), which indicates that antimony dissolves into the water from the country rocks by chemical weathering. We examined the antimony contents in variously weathered and altered country rocks in the streambed, to understand the transfer of the element into the stream water. Consequently, antimony content in brown-colored, strongly weathered and altered part of the rocks was higher than that in the unweathered (or weakly weathered) part. The antimony content in the strongly weathered part was several tens to hundreds ppm, although the content in unweathered part was significantly low, sometimes under the detection of XRF. This may indicate that the antimony in the stream water is adsorbed selectively in the strongly weathered and altered part of the streambed rock. The strongly weathered and altered rocks contain many iron hydroxides, which may trap antimony ion from the water. A similar phenomenon was observed in the other area. This suggests that a high distribution of antimony ion into the strongly weathered and altered rocks including iron hydroxides against the water is ubiquitous.

Key words: antimony, stibnite, Ichinokawa, Tobe, hydrothermal alteration, chemical weathering, iron hydroxide.

1. INTRODUCTION

Chemical behavior and toxicity of antimony is similar in principle to that of arsenic (Gurnani et al., 1994; WHO, 1996; Filella et al., 2002). Because of the toxicity, antimony and its compounds are considered as priority pollutants by the European Union (Council of the European Communities, 1976) and the Environmental Protection Agency of the United States (USEPA, 1979). More detailed examinations are needed to understand the chemical behavior of antimony, since the toxicity depends on the various environmental conditions. The upper limit of the concentration of antimony in drinking water is defined as 5 µg/L by WHO (1996) and CEU (1998), and 6 µg/L by USEPA (1999). Stream waters around the studied area, Ichinokawa and Tobe stibnite mine areas, Shikoku, Japan, include >200 µg/L-Sb by solvated out of antimony from the country rocks by chemical weathering (Sano et al., 2005, 2006; Ohno et al., 2006). There is a great possibility that the water originating from the stream at the downstream of the densely populated area and arable land will be contaminated. Therefore, the effect of the pollution is a major concern for the human health in the area.

Although chemical behavior at common surface water environment of arsenic belongs to the same group as antimony of metalloid elements and is therefore relatively well studied (Bowell, 1994; Smedley and Kinniburgh, 2002), the detailed behavior of antimony is still not well known (Filella et al., 2002). Based on our study, antimony contents in stream waters in a finite area vary from one locality to another (Sano et al., 2006). This is expected because of the chemical interactions between

the water and rocks or sediments of the streambed. In this paper, we reported the phenomena of selective sorption of antimony by the rocks of the streambed during chemical weathering at oxidized surface conditions. Moreover, we showed that chemical weathering is a function of natural purification of antimony in the stream water.

2. MATERIALS AND METHODS

2.1 Geologic background

Study areas of Shikoku Island in southwestern Japan are shown in Figure 1. Large amounts of Tertiary volcanic rocks are distributed along the Median Tectonic Line (MTL), which divide southwestern Japan into inner and outer zones. Hydrothermal activity related to the Tertiary volcanism developed some ore deposits at Ichinokawa and Tobe mines along the southern part of the MTL.

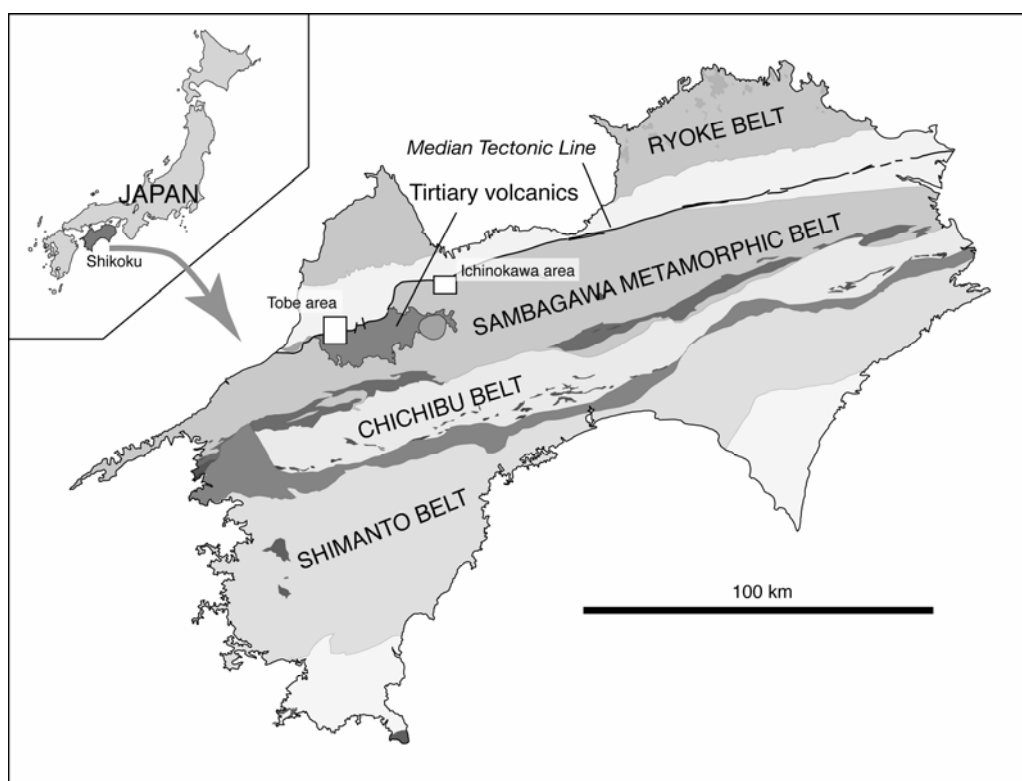


Figure 1. Geologic outline of Shikoku Island, Japan. Studied areas are shown as open squares with “Ichinokawa area” and “Tobe area”. Both areas locate to just southern border of Median Tectonic Line. Tertiary volcanics are widely distributed around the studied areas.

2.1.1 Ichinokawa area (Figure 1)

Ichinokawa mine is a famous stibnite yielding mine in Japan. The host rocks of the ore deposit are Mesozoic Sambagawa metamorphic rock and Ichinokawa conglomerate. Rocks around the ore deposit suffer severe hydrothermal alteration. The conglomerate, country rock of the stibnite deposit, can be divided mainly into fracture-filling breccia in the Sambagawa pelitic schist and carbonaceous sandstone with andesite pebbles. The brecciated rocks are formed by a hydraulic fracturing process of

the Tertiary hydrothermal influx into the fault zone related to MTL movement in the Sambagawa metamorphic rocks (Sakakibara et al., 2005a). Stibnite precipitates from the hydrothermal fluid.

2.1.2 Tobe area (Figure 1)

Many small mines of sulfide minerals such as pyrite, chalcopyrite, arsenopyrite and stibnite were developed in the Tobe area located in the southern part of the MTL. The ore deposits of the Tobe area were developed in the Tertiary andesite body and surrounding Mesozoic Sambagawa metamorphic rocks. The country rocks of the deposits also suffer severe Tertiary hydrothermal alteration (Chiba et al., 2005; Sakakibara et al., 2005b), which is also the case in the Ichinokawa area.

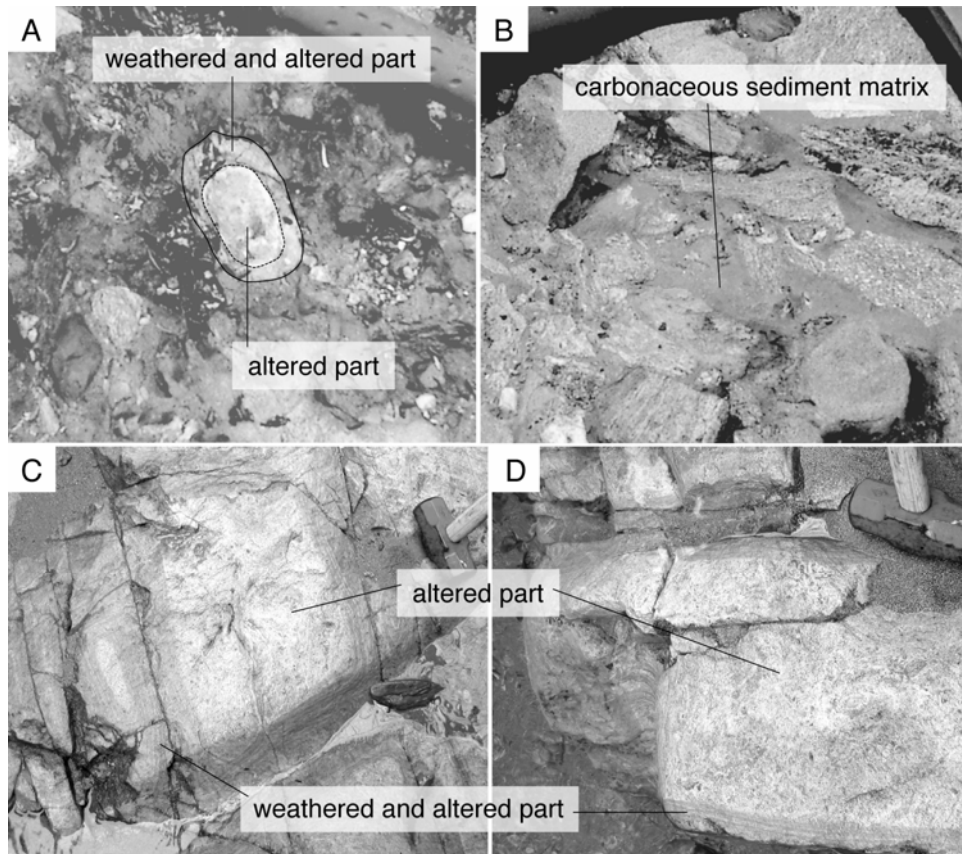


Figure 2. Photos of rock surface condition in fields. A & B: Ichinokawa area, and C & D: Tobe area. A: hydrothermally-altered andesite pebble in carbonaceous sediment matrix. Thick weathered crust surrounds unweathered part. B: carbonaceous sediment matrix. C & D: streambed of altered andesite. The hydrothermally-altered rocks are rimmed by brown colored weathered parts.

Hydrothermally altered rocks, including sulfide minerals, undergo chemical weathering due to the oxidation conditions at the surface. Consequently, it has been shown that stream waters around the Ichinokawa and Tobe areas contain high concentrations of arsenic and antimony liquated from the rocks of the streambeds (Sano et al., 2005, 2006; Ohno et al., 2006). High contents of antimony ($>200 \mu\text{g/L-Sb}$) were detected from the waters downstream of the adit portals of the both mines. At the Tobe area, stream water contained locally $>700 \mu\text{g/L-Sb}$. The pH values of the stream water from both areas were about 7 and did not show extreme features of acid mine drainage (AMD).

2.2 Rock Description

The color of hydrothermally altered andesites without significant weathering is whitish. They include sulfides as secondary minerals. The primary minerals of the altered andesites are completely replaced by secondary products. Based on the pseudomorphs of primary minerals at weakly altered parts and the secondary mineral assemblages, we estimate primary minerals to include the following: plagioclase, orthopyroxene, opaque mineral, and apatite. Identified secondary minerals are quartz, opal, carbonates (calcite/dolomite), chlorite, titanite, anatase, illite, kaolinite, pyrite, marcasite, arsenopyrite, stibnite, chalcopyrite, and/or iron hydroxide. Although sulfides can be visible by eye at the unweathered (or weakly weathered) part, it is difficult to recognize the sulfides at the weathered part because they are replaced by iron hydroxides. The weathered part displays brownish color due to the formation of abundant iron hydroxides. Quartz, kaolinite, chlorite, anatase, and illite are also formed in the weathered part.

Carbonaceous sandy sediments including the andesite pebbles are mainly composed of quartz and white mica fragments originating from pelitic schists, and interstitial carbonates such as rhodochrosite, siderite, and calcite/dolomite.

2.3 Samples and analytical methods

We collected rock samples of pairs of weathered and unweathered parts of andesite pebbles and the carbonaceous matrix of streambeds from the Ichinokawa area (Figure 2A and B). As shown in Figure 2A, hydrothermally altered andesite pebble has an unweathered and whitish core with a weathered and brownish crust. Unweathered and surrounding weathered parts of the altered andesites of the streambed, which intrudes into Sambagawa pelitic schist, were collected from the Tobe area (Figure 2C and D). We also acquired drilled core samples from the hydrothermally altered andesite body. The depth was 15–23 m from ground level. We distinguished each level rock as weathered and unweathered. We determined major and trace element abundances for rocks of streambeds from the lower reaches of the Ichinokawa and Tobe mining areas, utilizing the XRF of Ehime University. Detailed analytical procedures and accuracy results are described in Yoshizaki et al. (1996) and Hori and Higuchi (1996).

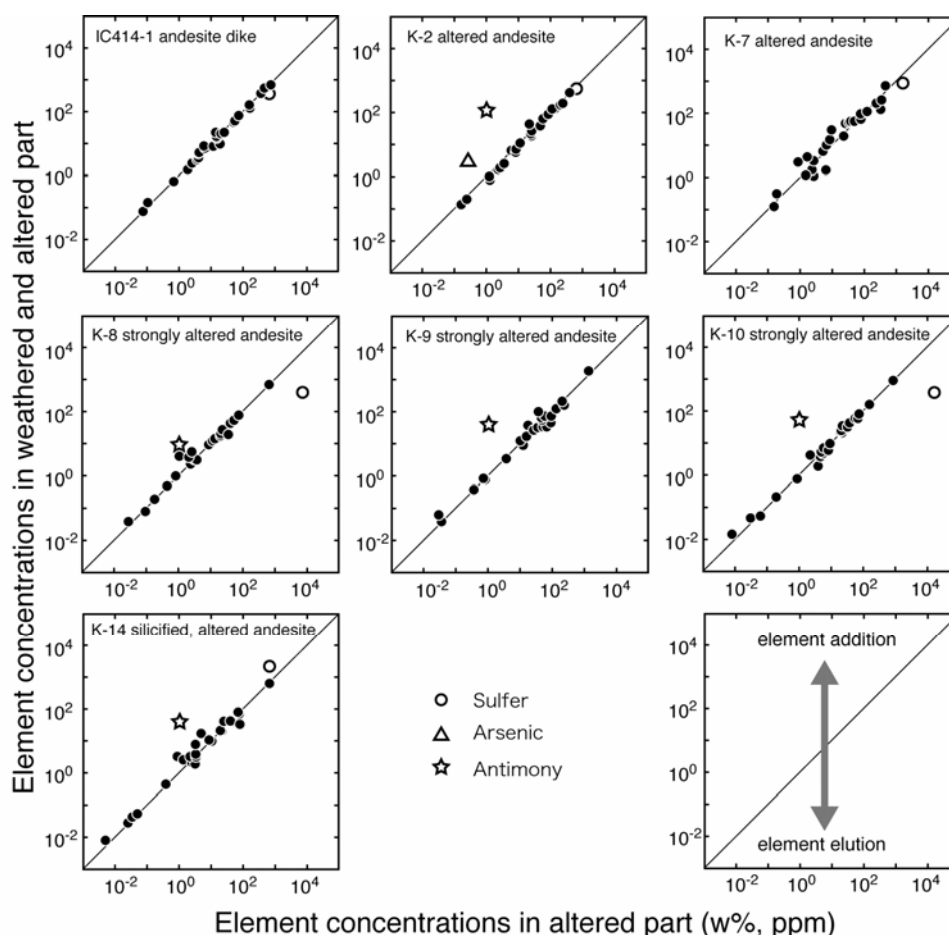


Figure 3. Plot of major and trace elements abundance of pairs of weathered/alternated and unweathered/alternated andesite pebbles from the Ichinokawa streambed.

3. RESULTS

Relatively high antimony content was detected on weathered rocks as compared with unweathered parts. On the Ichinokawa altered andesite pebble, although antimony contents of most unweathered core parts were under the lower limit of detection (LLD: ca. 1 ppm Sb), the contents of weathered crust part were 9.2–119 ppm. Weathered parts of carbonaceous sandy sediment matrix of the altered andesite pebble contained antimony of 32–54 ppm, while the antimony of the weakly weathered part was under the detection. Furthermore, on the Tobe altered andesite, although antimony contents of unweathered parts were from LLD to 13 ppm, the contents of weathered parts were 3–27 ppm. The antimony contents of weathered parts of drilled samples from the altered andesite body were 13–190 ppm, while the unweathered parts contained antimony of 3–33 ppm. It has been reported that the average antimony content in the upper continental crust was 0.2 ppm (Taylor and McLennan, 1995). If we compare the antimony content of the upper continental crust to that of a common andesite, antimony of the weathered and altered andesites in this study enriches to ca. 1000 times of common andesite.

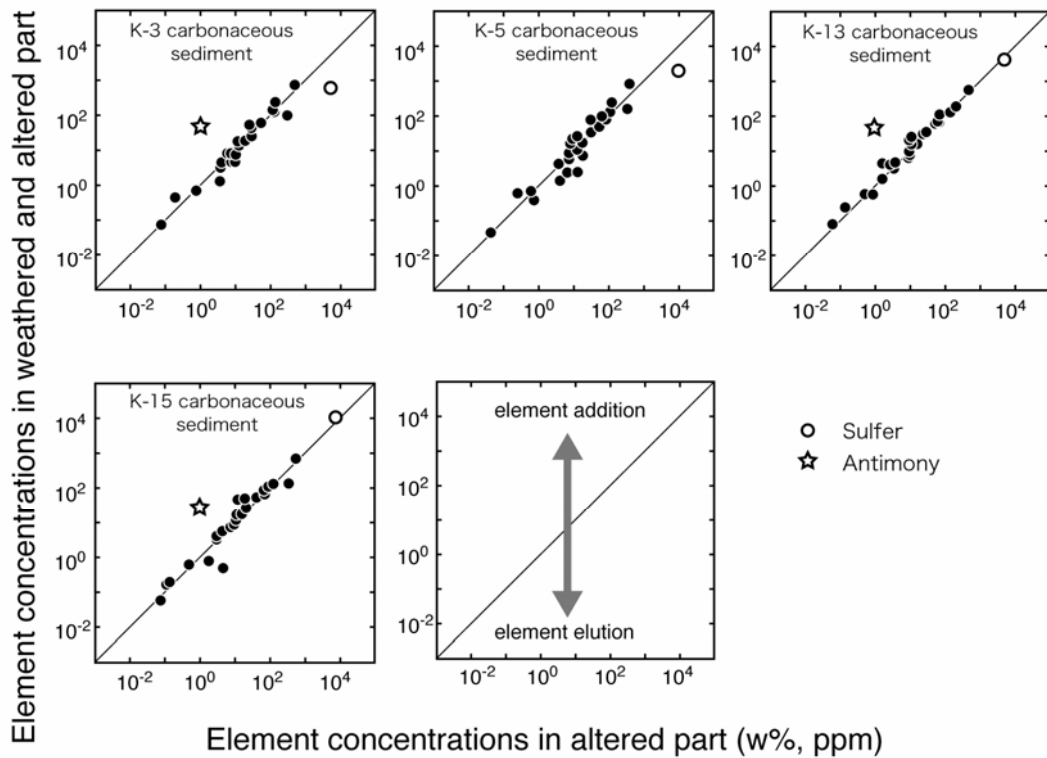


Figure 4. Plot of major and trace elements abundance of pairs of weathered/alternated and unweathered/alternated parts of carbonaceous sediment from Ichinokawa streambed. These rocks form matrix of the andesite pebbles (Figures 2A & B).

To examine the element behavior during chemical weathering, analytical results of paired data sets of weathered and unweathered parts are plotted in Figures 3–5. The horizontal axis represents contents of major (wt%) and trace elements (ppm) for unweathered but altered rock, and the vertical axis represents those for weathered and altered rock. That is, the plot on the 1:1 line means that the element does not show significant removal during chemical weathering. On the contrary, plot above the 1:1 line indicates an increase of the content, and the plot below the line indicates a decrease of the content during weathering. Plots in Figure 3 display the results of samples from the streambed of Ichinokawa altered andesite pebbles in the carbonaceous sediment matrix. On the five pairs, increase of antimony and decrease of sulfur are apparent. Figure 4 shows the results of carbonaceous sandy sediments. Three of four samples indicate the increase of antimony. On the other hand, relative increases of antimony are also observed in the altered andesite from the Tobe area (Figure 5), although result of the Tobe area was not as clear compared with that of the Ichinokawa area. In the same figure, results of altered andesite from the drilled core are consistent with other results. Altered andesite samples of 15–23 m from the ground display increase of antimony and decrease of sulfur during chemical weathering. Consequently, it is clear that the increase of antimony and decrease of sulfur are ubiquitous phenomena during chemical weathering.

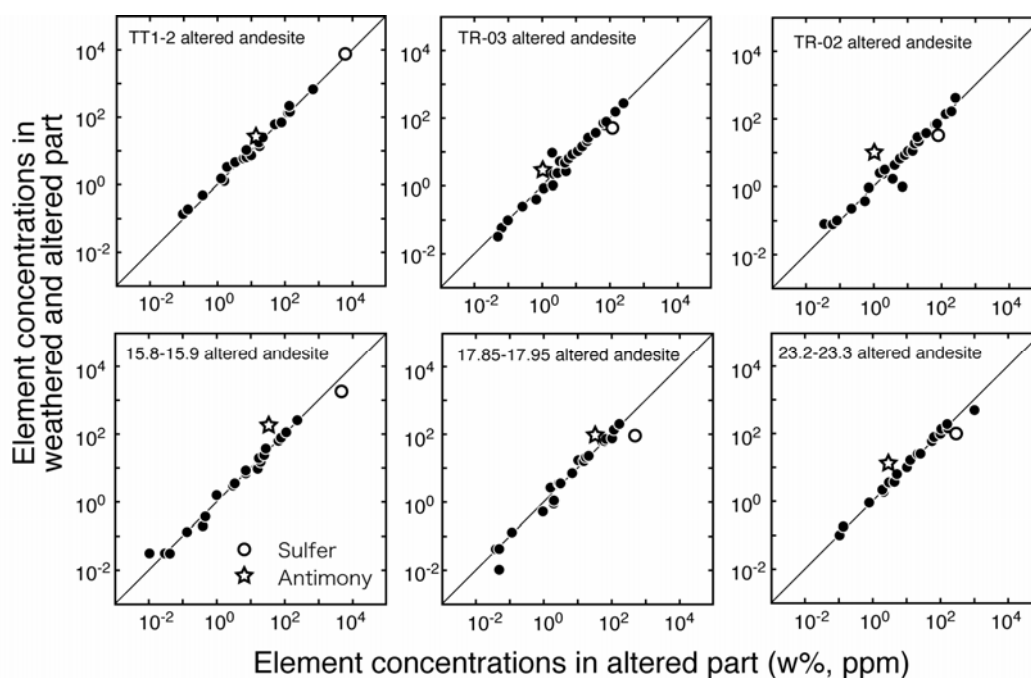


Figure 5. Plot of major and trace elements abundance of pairs of weathered/alternated and unweathered/alternated andesites of streambed from the Tobe area.

4. DISCUSSION

4.1 Mobilization of antimony during weathering

Sorption of metals dissolved in water by iron oxyhydroxides is well documented. Metalloids such as arsenic and antimony especially are adsorbed effectively by iron oxyhydroxides (Thanabalasingam and Pickering, 1990; Bowell, 1994). The weathered crust of the altered andesites and the pebbles from the Ichinokawa and Tobe areas exhibit brownish color by formation of a large amount of iron hydroxides. It is expected the selective sorption of metalloids dissolved in water to weathered part of the rocks. The relationship of elemental distribution between the brownish weathered part and the whitish unweathered part, do not show apparent migration during the weathering, except for sulfur, arsenic, and antimony (Figure 3–5). Migration of arsenic is not very obvious. Because antimony contents of unweathered and altered andesites often could not be detected by the XRF, we plotted the contents as 1 ppm instead of the LLD (ca. 1 ppm) on these figures (Figure 3–5). Andesites, in this study, suffered severe hydrothermal alteration. Rock color changed to a whitish color and many sulfide minerals were formed. Therefore, sulfur contents of the rocks as a whole are higher than that of usual andesite. Though arsenic and antimony contents of sulfide concentrated parts were high, the contents of other normal parts were almost the same level with common andesites. Many rock samples from the unweathered part had low antimony contents under the LLD. However, antimony contents of weathered and altered parts were significantly higher than the LLD level. To consider the mobilization of elements during the chemical weathering, we estimated the mobilization factors (MF). The factor is defined as follows:

$$\text{MF for element } i = (C_{i,w} - C_{i,uw}) / (C_{i,uw}) * 100$$

where, $C_{i,w}$ and $C_{i,uw}$ represent concentrations of element i in the weathered part and unweathered part, respectively. Results of element mobilization during chemical weathering are shown in Figure 6. Each diagram represents averaged value on every rock types, Ichinokawa altered andesite pebbles (conglomerate), Ichinokawa carbonaceous sediments (matrix of the conglomerate), and Tobe altered

andesites (body). Based on the diagram, it is clear that the increasing elements are iron, manganese, arsenic, and antimony, and the decreasing elements are magnesium, calcium, and sulfur. Especially, the mobilization factor of antimony was exceptionally large at approximately 260–5300 times of unweathered rocks compared with that of other elements. Arsenic and antimony belong to a same metalloid group. However, the chemical behavior during weathering of antimony must be different from that of arsenic.

Tighe et al. (2005) reported sorption of Sb(V) effectively by amorphous iron (III) hydroxide and humic acid in organic matter rich soils. Mueller et al. (2006) considered the major and trace element abundances in stream waters and the sediments on the streambeds around gold mine areas of Alaska and Yukon districts. They showed the possibility that the chemical behavior between arsenic and antimony is different under certain conditions, because the oxidation state of antimony adsorbed on sediment is Sb(V), while that of arsenic exists as mixture of As(III) and As(V), at the surface environmental condition. Under the condition of existence of amorphous iron oxyhydroxide, Sb(III) is oxidized to Sb(V), and adsorbed on the oxyhydroxide (Belzile et al., 2001). Furthermore, it has been reported that antimony in stream water is adsorbed selectively on the co-existing amorphous iron hydroxides under the pH of around 7 (Sano et al., 2006).

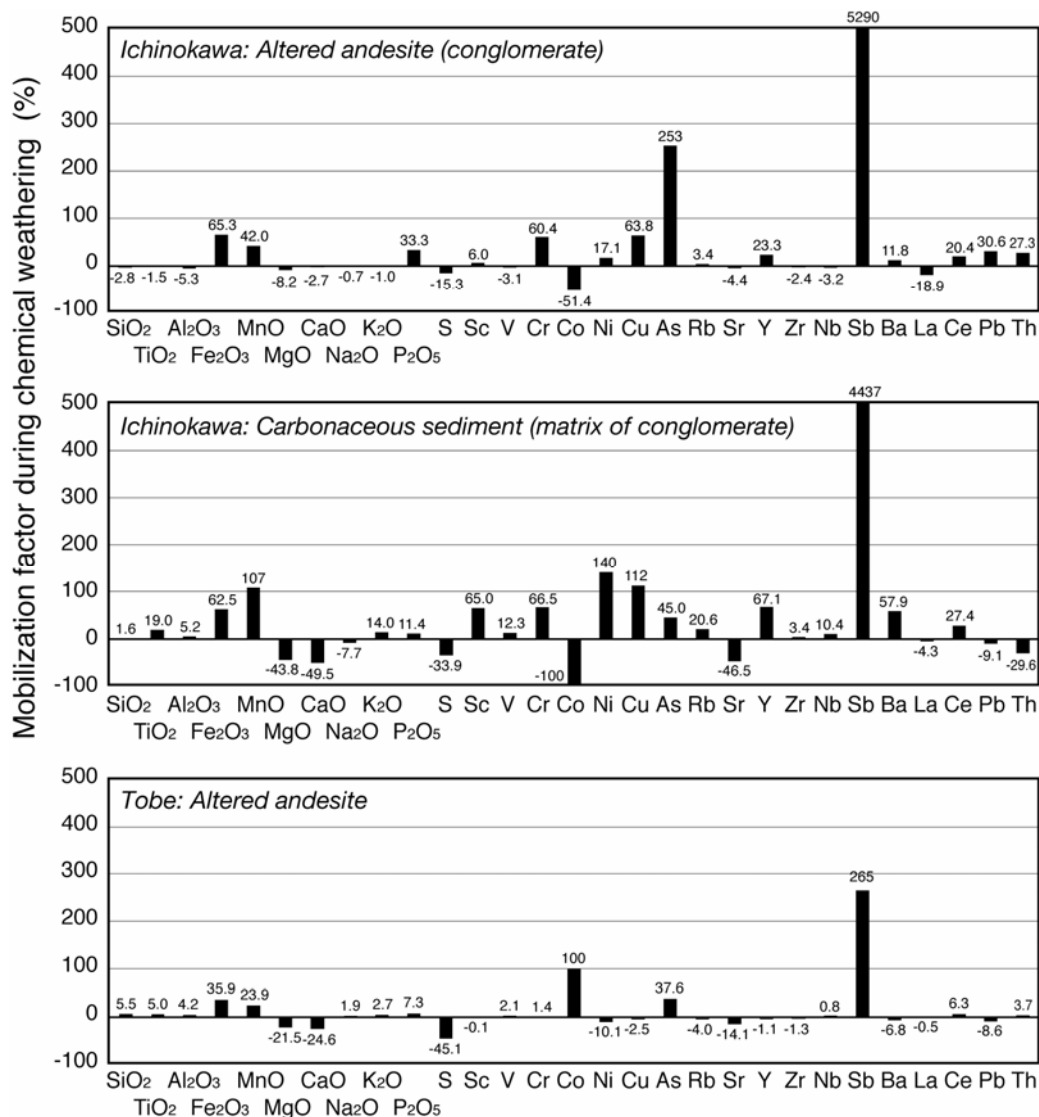


Figure 6. Mobilization factors for major and trace elements in streambed rocks. The factor means the mobilization of elements during the chemical weathering. That is, bars showing positive side mean high mobility into weathered parts as compared with relatively unweathered parts of the rocks. Each bar graphs represent averaged value on rock type, Ichinokawa

altered andesite pebbles (conglomerate), Ichinokawa carbonaceous sediments (matrix of the conglomerate), and Tobe altered andesites, respectively. Note the special positive mobilization of antimony to weathered part.

Sano et al. (2006) observed some precipitation of amorphous iron hydroxides at the stream downward of the Ichinokawa stibnite mine area. At the lower reaches of appearance of the hydroxides, the antimony contents in the water decreased drastically from $>200 \mu\text{g/L}$ at the upper reaches to $3.6 \mu\text{g/L}$ with the appearance of the amorphous iron hydroxides. They showed that the amorphous iron hydroxides have high distribution for antimony. Iron hydroxides are common in oxidized, natural earth's surface environment. The weathered rock surface consisting of abundant iron hydroxides of streambeds might be a natural and efficient purification system for antimony dissolved in stream water.

5. CONCLUSION

In this study, we mainly reported sorption of antimony in stream water by weathered and altered rocks composing the streambed. Element mobilization during chemical weathering was considered by results of the major and trace element abundances in hydrothermally altered/weathered or unweathered andesites and carbonaceous sediments. Iron, manganese, arsenic, and antimony distribute to the weathered part of the rocks, but magnesium, calcium, and sulfur are removed to the stream water. The mobilization factor of antimony is exceptionally high as compared with other element such as arsenic. Antimony distributes strongly into amorphous iron hydroxides under the common stream water environment. Because the abundant iron hydroxides are often formed in weathered rocks, the chemical weathering process contributes naturally to purification of antimony from the stream water.

ACKNOWLEDGEMENTS

We thank the Grant for Research and Development Assistance of Ehime University for their support.

REFERENCES

- Belzile, N., Chen, Y.-W. and Wang, Z. 2001. Oxidation of antimony (III) by amorphous iron and manganese oxyhydroxides. *Chem. Geol.* 174, 379-387.
- Bowell, R.J. 1994. Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Appl. Geochem.* 9, 279-286.
- CEC (Council of the European Communities). 1976. Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. *Official Journal L* 129, 18/05/1976, 23-29.
- CEU (Council of the European Union). 1998. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. *Official Journal L* 330, 05/12/1998, 32-54.
- Chiba, E., Sakakibara, M., Sano, S., Hori, R., and Nakai, Y. 2005. Behavior of major and trace elements of the Mannen altered andesite during chemical weathering in the Tobe Town, Ehime Prefecture, Japan. *Mem. Fac. Sci. Ehime Univ.* 11, 39-46. (in Japanese with English abstract)
- Filella, M., Belzile, N., and Chen, Y.-W. 2002. Antimony in the environment: a review focused on natural waters I. Occurrence. *Earth Sci. Rev.* 57, 125-176.
- Gurnani, N., Sharma, A., and Tulukder, G. 1994. Effects of antimony on cellular systems in animals: a review. *Nucleus* 37, 71-96.
- Hori, R.S., and Higuchi, Y. 1996. Quantitative analysis of trace elements in rock samples by X-ray fluorescence spectrometry, using Rh anode tube. *Mem. Fac. Sci., Ehime Univ.* 2, 27-36. (in Japanese with English abstract)
- Mueller, S., Trainor, T., Ritchie, V., and Newville, M. 2006. Antimony mobility and speciation associated with the oxidation of stibnite-bearing waste rock from the eastern Tintina gold province, Alaska and Yukon. 102nd Annual Meeting of the Cordilleran Section, GSA, 81st Annual Meeting of the Pacific Section, AAPG, and the Western Regional Meeting of the Alaska Section, SPE, Paper No. 18-9.

- Ohno, H., Sano, S., and Sakakibara, M. 2006. Trace element abundance in river water of the Tobe River system, Tobe Town, Ehime Prefecture, Japan. *Mem. Fac. Sci. Ehime Univ.* 12, 11-18. (in Japanese with English abstract)
- Sakakibara, M., Hiraoka, Y., Hori, R., Kimura, K., and Nakajima, K. 2005a. Behavior of arsenic and antimony in Ichinokawa breccia formed by Miocene hydrothermal activities, Saijo City, Ehime Prefecture, Japan. *Mem. Fac. Sci. Ehime Univ.* 11, 65-80. (in Japanese with English abstract)
- Sakakibara, M., Chiba, E., Chikaishi, S., and Nakai, Y. 2005b. Geology and hydrothermal alteration of Mannen altered andesite in the Tobe Town, Ehime Prefecture, Japan. *Mem. Fac. Sci. Ehime Univ.* 11, 19-26. (in Japanese with English abstract)
- Sano, S., Okada, T., Sakakibara, M., and Chiba, E. 2005. Trace element abundance in river water around the Mannen altered andesite body, Tobe-town, Ehime Prefecture, Japan. *Mem. Fac. Sci. Ehime Univ.* 11, 47-57. (in Japanese with English abstract)
- Sano, S., Sakakibara, M., and Chiba, E. 2006. Arsenic and antimony abundances in river water and the environmental mobility by iron hydroxide: Case study of Ichinokawa mine area. *Jour. Geo-pollution Sci., Medical Geol, Urban Geol.* (submitted) (in Japanese with English abstract)
- Smedley, P.L. and Kinniburgh, D.G. 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochem.* 17, 517-568.
- Taylor, S.R. and McLennan, S.M. 1995. The geochemical evolution of the continental crust. *Reviews in Geophysics* 33, 241-265.
- Thanabalasingam, P., and Pickering, W.F. 1990. Specific sorption of antimony (III) by the hydrous oxides of Mn, Fe, and Al. *Water, Air, Soil Pollut.* 49, 175-185.
- Tighe M, Lockwood P, Wilson S. 2005. Adsorption of antimony(V) by floodplain soils, amorphous iron(III) hydroxide and humic acid. *J Environ Monit.* 1177-1185.
- USEPA (United States Environmental Protection Agency). 1979. *Water Related Fate of the 129 Priority Pollutants*, vol. 1. USEPA, Washington, DC, USA, EP-440/4-79-029A.
- USEPA (United States Environmental Protection Agency). 1999. *National Primary Drinking Water Standards*. USEPA Office of Water, Washington, DC, USA, Doc. 810-F-94-001.
- WHO (World Health Organization). 1996. *Guidelines for Drinking-Water Quality: Volume 2. Health Criteria and Other Supporting Information* (2nd ed.). World Health Organisation, Geneva. 973.
- Yoshizaki, T., Tamura, Y., Sano, S., Hori, R., and Komatsu, M. 1996. X-ray fluorescence analysis of major elements for silicate rocks. *Mem. Fac. Sci., Ehime Univ.* 2, 15-25. (in Japanese with English abstract)