# CHEMICAL WEATHERING RATES FROM WATERSHEDS IN THE TATEYAMA CALDERA, CENTRAL JAPAN

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## ABSTRACT

The Tateyama Caldera located in the northern part of central Japan is a well-known area of extremely high sediment yield. Unstable sediments yielded by chemical weathering play an important role of sediment disaster occurrences. Chemical weathering rates for watersheds in the caldera were estimated to be ranging from 0.39 to 5.29 mm/yr by the mass balance equation between solute fluxes of stream waters and solute losses comparing fresh and weathered rocks. Two watersheds showing much higher rates corresponded to the area where debris flows have continually occurred. Solute fluxes of each stream are useful for the susceptibility mapping of sediment disasters. The cause of the high chemical weathering rate is the leaching of soluble components from fresh bedrocks by sulfuric acid produced by the oxidation of pyrite and native sulfur in hydrothermally altered rocks, because the waters from the alteration zones are characterized by high  $SO_4^{2-}$  concentration. Such a simple hydrochemical signature is also useful for the detection of alteration zones covered with vegetation and thick soil layers.

Keywords: chemical weathering, hydrochemistry, the Tateyama Caldera, landslide, debris flow

### INTRODUCTION

The combination of weathered materials on slopes and heavy rainfall can lead to high landslide frequencies and also to the removal of soils and sediments by landslides, debris flows and fluvial erosion. The removal of soils and sediments that covered the bedrocks allows for the production of new weathered materials from exposed bedrock during physical and chemical weathering processes. Several investigators have recently reported that the chemical weathering rates are directly related to the rates of mechanical erosion in watersheds (e.g. Louvat and Allègre, 1997; Gaillardet et al., 1999; Millot et al., 2002; Lyons et al., 2005; Watanabe et al., 2005). Under the similar climatic and geologic condition, high landslide frequencies or erosional potentials are generally connected with high weathering rates and sediment yields.

Landslides and debris flows have frequently occurred in the Tateyama Caldera, central Japan. The caldera is a well-known area of the highest erosion yields in Japan. Although the caldera is situated under the similar climatic, geomorphologic and geologic condition, the landslide frequencies or erosional potential are considerably different in each watershed in the caldera.

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Here we focus on chemical fluxes in stream waters from watersheds and attempt to estimate the chemical weathering rates for eight watersheds in the caldera. The estimated data from each watershed provide us with a key factor in assessing the susceptibility of landslide or debris flow occurrences in each individual watershed.

### OUTLINE OF STUDY AREA

The Tateyama Caldera, an erosion caldera at the Tateyama Volcano, is located in the northern part of the Japan Alps, central Japan and approximately 210 km north-west away from Tokyo, and is the source of the Zyouganzi River (Fig.1). Quaternary andesitic rocks and pre-Tertiary granitic rocks are distributed in the caldera and both rocks include a large number of plagioclase as a phenocryst. There are several weak alteration zones in the caldera during previous hydrothermal activities. The altered rocks include secondary minerals such as pyrite, native sulfur, quartz and smectites. Such low temperature hydrothermal activities as hot spring are found in the caldera even now.



Fig.1 Location of study area

On April 9 in 1858, a large-scale landslide with an estimated failure volume of  $1.27 \times 10^8 \text{ m}^3$  triggered by the Hietsu Earthquake with M7.1 occurred and formed a landslide dam. After 14 days and 59 days from the earthquake, two debris flows caused by the collapse of the dam subsequently brought serious damage to the downstream area of the Zyouganzi River. These destructive debris flows destroyed 163 villages and 1,600 houses and killed 1,800 people. Until now several sizes of landslides and debris flows triggered by intensive rainfalls have frequently occurred in the caldera. Due to landslides and debris flows in the caldera, many people living in the downstream area of the Zyouganzi River suffered from 21 sediment-related disasters in the period between 1891 and 1969. (e.g. Harayama et al., 2000; Tabata et al., 2002)

### SAMPLES AND ANALYTICAL METHOD

Water samples were collected from six streams around the caldera (Fig.2) and eight streams in the caldera (Fig.3) once a month during base flow conditions for the period between July and

October from 2004 to 2006. These samples were preserved in 250ml polyethylene bottles for chemical analyses in laboratory. Eight rock samples of fresh and altered andesites and fresh and altered granites were collected from breccias in debris flow deposits.



Fig.2 Location of stream water samples in and outside the Tateyama Caldera



Fig.3 Location of stream water samples in the Tateyama Caldera. Numbers as 1 to 8 represent watersheds as follows; 1: Shintani watershed, 2: Nishitani watershed, 3: Dashiwadani watershed, 4: Dorodani watershed, 5: Kanayamadani watershed, 6: Usagidani watershed, 7: upper stream of Yukawa River, 8: Yukawa River The pH, the electric conductivity (E.C.) and the temperature of the water samples were measured at the sampling locations. The alkalinity as  $HCO_3^-$  concentration was measured by titration with 0.02N-HCl. Other major ions (Na<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>-</sup>) in water samples were analyzed by ion chromatography using a Dionex DX-120 instrument. The mineral assemblage and chemical composition (SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>) of rock samples were determined by XRD using a Rigaku RAD-B SYSTEM instrument and by XRF using a Rigaku RIX3000 instrument, respectively.

#### HYDROCHEMISTRY

The mean E.C. values of six stream waters from the outside of the caldera range from 1.8 mS/m to 5.0 mS/m, whereas the value of the Yukawa River at the outlet of the caldera shows 16.3 mS/m and is three to nine times higher than the values of streams around the caldera (Fig.4). It suggests that the solute flux from the caldera is also much higher than watersheds around the caldera.



Fig.4 The mean electric conductivities of stream waters from the outside of the Tateyama Caldera

Water samples from each watershed are chemically classified mainly into two types of Ca-HCO<sub>3</sub> and Ca-SO<sub>4</sub>. Ca-HCO<sub>3</sub> type waters showing low total ion concentration (TIC) in meq/L are extensively distributed in the outside of the caldera and limitedly found in the caldera, and are formed by water-rock interaction consuming atmospheric or subsurface CO<sub>2</sub> gas during the chemical weathering process. Ca-SO<sub>4</sub> type waters are characteristically found in the other watersheds in the caldera and show high E.C. and TIC (Fig.5, Fig.6). For example, the stream water from the Dashiwaradani watershed shows the highest TIC of 13.4 meq/L and E.C. of 69.4 mS/m of all watersheds, and is dominated by concentrated Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. In addition, the pH value of the stream water showing much less than 5.0 is the lowest value in all watersheds. The water from the Dorodani watershed also shows much higher TIC of 12.2 meq/L and E.C. of 58.5 mS/m than the other watersheds, and is also dominated by  $Ca^{2+}$  and  $SO_4^{2-}$  (Fig.6). This reflects a characteristic process of chemical weathering under the oxidative environment in the caldera. Sulfuric acid  $(H_2SO_4)$  is easily produced by the oxidation of pyrite or native sulfur included in the hydrothermally altered rocks. Soluble minerals, especially Carich plagioclase, included in fresh andesitic and granitic rocks are rapidly leached with H<sub>2</sub>SO<sub>4</sub>, and Ca<sup>2+</sup> is released to stream water. Ca-SO<sub>4</sub> type waters of high concentration are formed through the unique chemical weathering resulting from the oxidation of pyrite or native sulfur.

The hydrothermally altered rocks including pyrite or native sulfur as a source material for  $H_2SO_4$  are thought to be a key factor in relation to the acceleration of the chemical weathering in the caldera.



Fig.5 The mean electric conductivities and pH values of stream waters in the Tateyama Caldera



Fig.6 Chemical characteristics of stream waters in the Tateyama Caldera

## ESTIMATION OF CHEMICAL WEATHERING RATE

The rate of chemical weathering is represented as an integral function that consists of many parameters (e.g. climate, vegetation, topography, lithology, hydrology, etc.). However, several parameters can be excluded because of the following reasons.

- (1) Andesitic and granitic rocks predominate in the caldera. Such a monotonous lithology is useful for estimating the chemical weathering rate.
- (2) The caldera is a small basin having approximately 26km<sup>2</sup> in area. Therefore, the average atmospheric temperature, the annual precipitation and evapotranspiration, and the vegetation in the caldera are assumed to be similar.

 $Ca^{2+}$  is the predominant cation in most of the stream waters and is mainly derived from Carich plagioclase in andesitic and granitic rocks.

For example, the chemical weathering rate at the Dashiwaradani watershed is estimated by considering a mass balance of Ca as follows.

The Rate of Chemical Weathering:

Chemical weathering Rate = 
$$\frac{(P-E) \times C}{X \times La \times Da + Y \times Lg \times Dg} = 5.29 \text{ mm/yr}.$$

The Rate of sediment yield (weight):

Sediment Yield Rate = 
$$\frac{S \times (P - E) \times C}{X \times La + Y \times Lg} = 13,607 \text{ ton / yr}.$$

The meaning of parameters represented as S, P, E, C, La, Lg, Da and Dg are given in Table 1. The losses of Ca in weathered andesitic and granitic rocks are calculated by using data after Hizuka (2007MS). X and Y regulated as X + Y = 1 represent the ratio of distribution areas for andesitic and granitic rocks in each watershed. The Ca contents in fresh and weathered rocks are normalized with insoluble elements (e.g. Ti and Al).

Tab 1 Parameters for the estimation of chemical weathering

Example of the Dashiwaradani watershed				
Area of watershed; S	1.15 (km <sup>2</sup> )			
Annual preciptation; P	2277.4 (mm/yr)			
Evapotranspiration; E	766.0 (mm/yr)			
Ca concentration in water; C	100.1 (mg/L)			
Loss of Ca in andesite; La	16.1 (g/kg)			
Loss of Ca in granite; Lg	11.9 (g/kg)			
Density of andesite; Da	$2.4 (ton/m^3)$			
Density of granite; Dg	2.2 (t/m <sup>3</sup> )			
Ratio of distribution area for andesite; X	0.26			
Ratio of distribution area for granite; Y	0.74			

Based on the above mass balance equation between Ca fluxes of stream waters from each watershed and Ca loss comparing fresh and weathered rocks, we estimated the chemical weathering and sediment yield rates per unit area from all watersheds as shown in Table 2. Fig.7 illustrates the degrees of chemical weathering rates in each watershed in the caldera on the basis of the estimation results in Table 2.

<b>1 ab.</b> 2 Estimation result of chemical weathering rate in each watershed				
Name of	Catchment	Ca flux	Sediment yield	C.W.R.
watershed	area (km <sup>2</sup> )	(ton/km <sup>2</sup> /yr)	(ton/km <sup>2</sup> /yr)	(mm/yr)
Shintani	0.62	10.57	871.88	0.39
Nishitani	0.85	16.39	1279.49	0.57
Dashiwaradani	1.15	151.24	11832.35	5.29
Dorodani	0.77	115.74	8431.65	3.70
Kanayamadani	0.54	49.54	3136.79	1.32
Usagidani	2.85	50.52	3314.12	1.41
Upper Yukawa	14.54	30.41	2179.97	0.95
Yukawa	26.23	31.98	2311.69	1.01
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C.W.R.: Chemical Weathering Rate



Fig.7 Degree of chemical weathering rate in each watershed in the Tateyama Caldera

There is a good correlation between the estimated chemical weathering rates and E.C. in each watershed as shown in Fig.8 even if the ratios of distribution areas for andesitic rocks (X) and granitic rocks (Y) varies from X=0.06 and Y=0.94 (the Shintani watershed) to X=0.94 and Y=0.06 (the Kanayamadani watershed) in each watershed in the caldera. In this study area, the essential is that E.C. is not only very useful for field surveys but also could serve as proxy for the above estimation of chemical weathering rates.

## CONNECTION BETWEEN CHEMICAL WEATHERING AND LANDSLIDE

Due to intensive rainfall unstable soils on the slopes erode down and unstable sediments in the stream valley are removed by the fluvial erosion or debris flow. The continual removal of weathered and unconsolidated materials forms new slope surfaces or exposes fresh bedrocks that are easily affected by chemical weathering. The removal of soils and sediments from watersheds is a preparation for the production of new material from bedrock weathering.



Fig.8 Relationship between chemical weathering rate and electric conductivity in each watershed in the Tateyama Caldera.  $R^2 = 0.975$  means a correlation coefficient

The estimated rates of chemical weathering in the Dashiwaradani and the Dorodani watersheds were respectively 5.29 mm/yr and 3.70 mm/yr, and were considerably high values in Japan. The estimated sediment yields during chemical weathering in these watersheds were approximately 11,800 ton/km<sup>2</sup>/yr, and 8,400 ton/km<sup>2</sup>/yr, respectively. These watersheds show actually the highest frequencies of landslides and debris flows of all watersheds in the caldera. According to literatures, the large-scale landslide in 1858 occurred at the uppermost part of the Dashiwaradani and Dorodani watersheds. High  $SO_4^{2-}$  waters also suggest the existence of not only the hydrothermally altered rocks near surface but also the alteration zones inner slopes or beneath thick soils in both watersheds. In general, such alteration zones are extremely weakened in comparison with the distribution area of hard bedrocks and increase the potential for catastrophic landslides that can lead to destructive debris flow (e.g. Lopez and Williams, 1993). However, evaluating the hazards associated with such alteration zones is difficult because the distribution of subsurface alteration zones is largely unknown. It is most likely that there were several alteration zones at the uppermost part of the Dashiwaradani and the Dorodani watersheds before the large-scale landslide triggered by the Hietsu earthquake in 1858 occurred. Because there are a large amount of gravels, boulders and blocks derived from altered zones in the Dashiwaradani and the Dorodani watersheds. Such altered rocks scattered by the landslide in 1858 have produced H<sub>2</sub>SO<sub>4</sub> under the oxidative environment and have consequently accelerated the chemical weathering and sediment yields in both watersheds.

The chemical weathering in the caldera is thought to be one of the most important factors for landslide and debris flow occurrences. Solute fluxes and E.C. from each watershed could be useful for susceptibility mappings of landslide and debris flow occurrences at each watershed in the caldera. Furthermore, such a simple investigation method using hydrochemical signatures of stream waters and spring waters could be a useful substitute for the expensive

and time consuming geophysical explorations to detect the alteration zones covered with vegetation and thick soil layers.

### CONCLUSION

This study provides a hydrochemical approach to the hazard assessment in the Tateyama Caldera where the erosional potential is extremely high in Japan. Several major conclusions can be drawn:

- (1) Water samples from each watershed are chemically classified mainly into two types of Ca-HCO<sub>3</sub> and Ca-SO<sub>4</sub>. Ca<sup>2+</sup> is a predominant cation in water samples.
- (2) Stream waters from the Dashiwaradani and Dorodani watersheds are characterized by Ca-SO<sub>4</sub> type with the TIC of 13.4 and 12.2 meq/L and the E.C. of 69.4 and 58.5 mS/m, respectively. These high TIC and E.C show that the chemical weathering rates of the Dashiwaradani and Dorodani watersheds are much higher than the other watersheds in the study area.
- (3) In particular, the high concentration of  $SO_4^{2-}$  and  $Ca^{2+}$  indicates the following two processes during the chemical weathering.
  - i) The oxidation of pyrite or native sulfur, secondary minerals in hydrothermally altered rocks, produces  $H_2SO_4$  of pH < 4.
  - ii)  $H_2SO_4$  rapidly leaches out solutes, especially  $Ca^{2+}$  from Ca-rich plagioclase, from fresh bedrocks composed of andesite and granite.
- (4) The annual rates of chemical weathering and sediment yield is estimated by the mean of the annual precipitation and evapotranspiration, the catchment area, the Ca<sup>2+</sup> concentration in mg/L in stream water, the density of soil and fresh bedrocks, and the Ca content in wt.% of fresh and weathered bedrocks. As a result, the estimated rates of chemical weathering and sediment yield in the Dashiwaradani and the Dorodani watersheds were 5.29 mm/yr and 3.70 mm/yr respectively, and were approximately 11,800 ton/km<sup>2</sup>/yr and 8400 ton/km<sup>2</sup>/yr respectively.
- (5) The large-scale landslide that occurred in 1858 was situated at the uppermost part of the Dashiwaradani and the Dorodani watersheds. Until now these watersheds show much higher frequencies of landslides and debris flows than the other watersheds in the caldera.
- (6) There is a good correlation between the chemical weathering rate and the E.C. values of water samples. This correlation enables to use the E.C. as a proxy for the rate of sediment yield related to chemical weathering.
- (7) The high SO<sub>4</sub><sup>2-</sup> in stream waters might indicate the buried hydrothermally alteration zones. Therefore, such a hydrochemical approach could be useful for the detection of the alteration zones covered with vegetation and thick soil layers.

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