BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2475—2478 (1970)

# Titanium and Zirconium in Hydrothermally-altered Rocks from the Tateyama Jigokudani Hot Springs, Toyama, Japan

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(Received February 3, 1970)

Hydrothermally-altered rocks and muds collected from the Tateyama Jigokudani hot springs were analysed for titanium and zirconium. In order to estimate the acidity of the thermal waters which contributed to these altered rocks, the concentration factor of the elements relative to $SiO_2$ was used for convenience. The titanium and zirconium contents of the alteration products are approximately equal to those of the fresh rocks. This seems to indicate that most of these elements remain in the rocks during the alteration under acidic conditions. The muds are characterized by high values of the concentration factors and the factors proved to be dependent on the acidity of the mud-suspending waters. From the relation between the concentration factors and the pH's of the waters, we could estimate the acidities of the thermal waters which attacked the altered rocks in the earlier stages.

The alteration of silicate rocks generally involves a change in their chemical composition. Under strongly acid conditions, all the chemical constituents except $SiO_2$ and $TiO_2$ are almost entirely leached out and the altered rocks are enriched in $SiO_2$ and $H_2O$.[1] Iwasaki *et al.* reported on the chemical compositions of alteration products in the Tamagawa hot springs.[2] According to their data, the $TiO_2$ and $SiO_2$ contents of these products are larger than those of the original rocks, and the concentration factors of $TiO_2$ relative to $SiO_2$ for these alteration products have values ranging from 0.77 to 1.07. The variation in the values of the factors may depend on the nature of the thermal waters which attack the rocks. Therefore, the factor may give some useful indications for use in estimating the environmental conditions of the alteration.

Zirconium can be expected to behave like titanium because of the similarity in chemical properties. Between titanium and zirconium, however, there may be some differences in leachability and in mobility in acid solutions. The differences may depend on the acidity of the thermal waters dominating during the alteration; the changes in the pH of the waters may, that is, reflect in some way the concentrations of these elements in hydrothermally-altered rocks.

There have been no detailed studies of the distribution of titanium and zirconium in altered rocks under acid conditions. The puropse of this investigation is to determine the titanium and zirconium contents of hydrothermally-altered rocks in an acid hot spring area and to estimate the acidity of the thermal waters using the concentration factor of these elements.

## Experimental

**Samples.** The alteration products were collected from the Tateyama Jigokudani hot springs, Toyama Prefecture, where there is still volcanic actions and where there are many acid hot springs. The alteration products collected were divided into two groups according to where they occurred. The first group consisted of altered rocks; most of these are silicified and contain iron sulfide and free sulfur in small amounts. In general, the center part of the altered rocks is gray or a blackish gray, and the surface is white or a grayish white. Suffixes are used to distinguish the center part from the surface; "a" indicates a sample of the center part, "b" idicates the surface. These rocks are probably the alteration products of an earlier stage.

The second group consisted of the muds which were suspended in acid thermal waters. These samples are extremely fine-grained and contain considerable amounts of free sulfur and iron sulfide. These muds are denoted in the sample number by the prefix "s". They are presently undergoing active alteration. The fresh rocks were identified as augite hypersthene andesite by microscopic examination and by X-ray diffraction.[*1]

**Chemical Analysis.** Titanium and zirconium were determined colorimetrically using disodium 1,2-di-dihydroxy-benzene-3,5-disulfonate (Tiron) and 2,7-bis-(azo-2)-phenylarsono-1,8-dihydroxynaphthalene-3,6-disulfonic acid (Arsenazo-III) respectively. A 0.2 g—0.4 g portion of a powdered sample (under 100 mesh) was

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1) J. Ossaka, *Chinetsu*, **17**, 65 (1968).

2) I. Iwasaki, T. Katsura, T. Tarutani, T. Ozawa, M. Yoshida, B. Iwasaki, M. Hirayama and M. Kamada, "Geochemistry of the Tamagawa Hot Springs," Minami Sensei Kanreki Kinen Jigyo-kai, Tokyo (1963), p. 35.

[*1] The identification was performed by Dr. J. Ossaka, to whom the author wishes to express his thanks.

decomposed with 10 m$l$ of concentrated hydrofluoric acid on a hot plate. One milliliter of concentrated perchloric acid was then added, and the mixture was evaporated to dryness. The evaporated residue was fused sodium bisulfate, and the cooled melt was dissolved in dilute hydrochloric acid. The volume of the solution was made up to 50 m$l$ with water.

An 1—2 m$l$ aliquot of this solution was taken out and titanium was determined according to the method described by Rygg and Wagenbauer,[3] To determine the zirconium, a 5—10 m$l$ aliquot of this solution was taken out and evaporated to white fumes with 1 m$l$ of concentrated perchloric acid. The solution was then transferred to a 25 m$l$ volumetric flask; 13 m$l$ of concentrated nitric acid, 2 m$l$ of a 10% urea solution, and 2 m$l$ of a 0.1% Arsenazo-III solution were added, and the mixture was diluted with water to 25 m$l$. The zirconium content was determined from the absorbance at 660 m$\mu$.[4] Elements commonly in rocks scarcely interfered with the determination at all. The experimental errors (relative) for the titanium and zirconium determinations were within ±3% and ±5% respectively.

## Results and Discussion

**Contents of Titanium and Zirconium.** The titanium and zirconium contents of the alteration products and of fresh rocks are shown in Table 1, along with the percentage of $SiO_2$ and the ignition loss. Although the $SiO_2$ content of the altered rocks is larger than that of the fresh rocks, the titanium and zirconium contents are not necessary so; these, rather, have a tendency to scatter. This indicates that considerable portions of all the major constituents except $SiO_2$ were removed, while titanium and zirconium partly remained in the rocks or were leached out according to the environmental conditions. There is, at any rate, no considerable difference in the contents between the altered and the fresh rocks, so it may be considered that these elements in the rocks are generally resistant to alteration.

In the case of the muds, the $SiO_2$ content is apparently smaller than that of the altered rocks because considerable portions of these samples are ignition losses largely of free sulfur and water. On the other hand, the titanium and zirconium contents of the muds are approximately equal to those of the altered rocks; this leads to the conclusion that the concentration factors of the these elements in the muds are above unity, as will be discussed below.

**Concentration Factors.** In order to normalize the concentrations of these elements, relative to

TABLE 1. TITANIUM AND ZIRCONIUM CONTENTS OF ALTERATION PRODUCTS

| No. | $SiO_2$ (%) | Ign. loss (%) | Ti (%) | Zr (%) | $r$(Ti)* | $r$(Zr)* | $r$(Ti)/$r$(Zr) |
|---|---|---|---|---|---|---|---|
| 1 | 56.82 | 1.42 | 0.42 | 0.017 | — | — | — |
| 2a | 65.11 | 11.71 | 0.32 | 0.0088 | 0.68 | 0.45 | 1.5 |
| 2b | 87.72 | 9.03 | 0.28 | 0.0094 | 0.44 | 0.36 | 1.3 |
| 4 | 65.78 | 20.09 | 0.35 | 0.0080 | 0.74 | 0.41 | 1.8 |
| 5 | 77.62 | 10.46 | 0.58 | 0.019 | 1.04 | 0.82 | 1.3 |
| 6 | 81.27 | 9.95 | 0.54 | 0.018 | 0.92 | 0.75 | 1.2 |
| 7a | 78.84 | 11.52 | 0.44 | 0.022 | 0.78 | 0.94 | 0.83 |
| 7b | 89.72 | 7.35 | 0.61 | 0.026 | 0.95 | 0.97 | 0.98 |
| 8 | 64.05 | 0.80 | 0.47 | 0.019 | — | — | — |
| 13a | 85.34 | 7.93 | 0.38 | 0.016 | 0.62 | 0.63 | 0.98 |
| 13b | 91.63 | 6.57 | 0.42 | 0.013 | 0.64 | 0.48 | 1.3 |
| 14a | 65.16 | 15.11 | 0.50 | 0.019 | 1.07 | 0.98 | 1.1 |
| 14b | 73.73 | 13.35 | 0.93 | 0.030 | 1.74 | 1.37 | 1.3 |
| 24a | 66.00 | 14.86 | 0.46 | 0.011 | 0.97 | 0.56 | 1.7 |
| 24b | 73.19 | 12.70 | 0.57 | 0.014 | 1.08 | 0.65 | 1.7 |
| s-1 | 42.44 | 33.82 | 0.64 | 0.018 | 2.10 | 1.43 | 1.5 |
| s-2 | 21.91 | 71.13 | 0.49 | 0.016 | 3.12 | 2.46 | 1.3 |
| s-3 | 49.07 | 25.94 | 0.62 | 0.016 | 1.75 | 1.09 | 1.6 |
| s-4 | 42.11 | 42.83 | 0.63 | 0.016 | 2.09 | 1.28 | 1.6 |
| s-5 | 50.17 | 20.31 | 0.49 | 0.010 | 1.36 | 0.67 | 2.0 |
| s-8 | 53.33 | 30.04 | 0.60 | 0.015 | 1.56 | 0.95 | 1.6 |
| s-9 | 39.00 | 50.74 | 0.38 | 0.0093 | 1.33 | 0.80 | 1.7 |
| s-11 | 39.38 | 50.22 | 0.60 | 0.019 | 1.67 | 1.62 | 1.0 |
| s-12 | 49.72 | 36.50 | 0.82 | 0.023 | 2.30 | 1.55 | 1.5 |

* Average values of fresh rock samples, Nos. 1 and 8, were used for the calculations

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3) T. Rygg and H. A. Wagenbauer, *Anal. Chem.*, **33**, 1347 (1961).

4) O. Kammori, I. Taguchi and R. Komiya, *Bunseki Kagaku*, **14**, 106 (1965).

$SiO_2$, for the alteration products, the concentration factor, denoted by $r$, is used. It is expressed by the following relation; $r(M)=(M/SiO_2)_a/(M/SiO_2)_f$, where M is the element to be considered and where the subscripts "$f$" and "$a$" stand for the fresh and the altered rocks respectively. In the case of discussion of the concentration factors, it must be assumed that the titanium and zirconium contents of the original rocks are essentially constant.

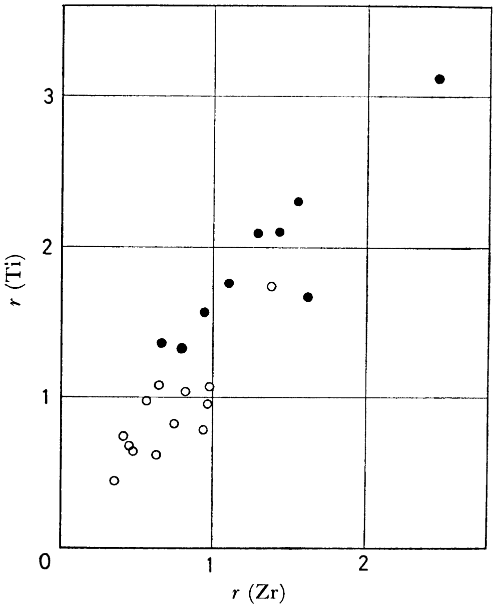

Fig. 1. Relationship between $r$(Ti) and $r$(Zr).
○: altered rock, ●: mud

The $r$ values for titanium and zirconium and the ratio of $r$(Ti) to $r$(Zr) are shown in Table 1. Figure 1 represents the relationship between these values. These values fluctuate rather widely. However, it is certain that the values of the muds are above unity and that those of the altered rocks are below unity, with a few exceptions. As Fig. 1 shows, there is a linear relationship between these values, but the values of the muds are apparently different from those of the altered rocks. This suggests that there is no considerable difference in the rate of leaching between titanium and zirconium, but that the rates of these elements are different from those of silica. That is, the leaching rates of titanium and zirconium for the altered rocks were higher than those of silica, in contrast with the case of the muds. This may also suggest that the altered rocks were attacked by thermal waters with slightly lower pH values.

The large $r$ values of the muds can be explained in terms of the difference in the leachabilities between these elements and silica and the occurrence of these elements in a resistant fraction in such an environment. Thus, the $r$ values may be effectively used in estimating the conditions of the alteration.

**Estimation of the Acidity of Thermal Waters.** The variation in $r$ values found for the muds and the altered rocks may be due to the environmental characteristics of the sample locality. The mobility and the leachability of a chemical element during alteration are known to be greatly affected by the acidity of the environment. Therefore, it can be assumed that the acidity is a factor governing the differences in leachability between titanium and zirconium. In Table 2, the acidity and the temperature of the mud-suspending waters are given. Because the disparity of temperature of the mud-suspending waters is not very large, as is shown in Table 2, and as the chemical compositions of the waters are nearly equal to each other, it may be possible to disregard the influences of other factors. In Fig. 2, the $r$(Ti)/$r$(Zr) ratio is plotted against the pH of the water in which the mud was suspended. The figure shows that the ratios tend to increase with an increase in the pH of the waters. Thus, these ratios prove to be affected by the pH of the mud-suspending waters; the ratios may provide some indications for use in estimating the acidity of the thermal waters dominating during the alterations.

As is shown in Table 1, the ratios of the altered rocks have values ranging from 0.83 to 1.8. From these values and from Fig. 2, it can be estimated

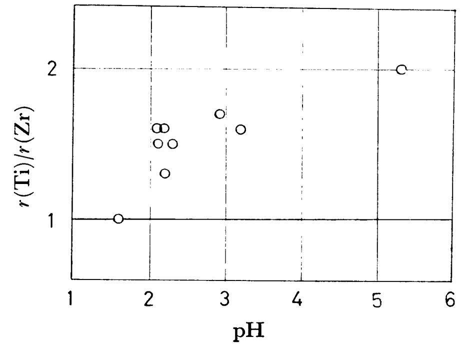

Fig. 2. Relationship between $r$(Ti)/$r$(Zr) ratio of muds and pH of the mud-suspending waters.

Table 2. Acidity and temperature of mud-suspending waters

| No. | pH | T (°C) | $SO_4^{2-}$ (g/$l$) | $Cl^-$ (g/$l$) |
|---|---|---|---|---|
| s-1 | 2.3 | 51 | 1.22 | 0.00 |
| s-2 | 2.2 | 75 | 1.09 | 0.09 |
| s-3 | 2.1 | 71 | 1.49 | 0.00 |
| s-4 | 3.2 | 62 | 0.12 | 0.03 |
| s-5 | 5.3 | 29 | 0.16 | 0.23 |
| s-8 | 2.2 | 88 | 0.91 | 0.03 |
| s-9 | 2.9 | 77 | 0.15 | 0.26 |
| s-11 | 1.6 | 80 | 1.61 | 0.02 |
| s-12 | 2.1 | 83 | 0.92 | 0.02 |

that the pH values of the thermal waters which attack the altered rocks range from about 1 to 4, provided that none of the conditions except the acidity in the earlier stage change up to the final stage. It may be concluded that the pH values of the thermal waters are slightly lower than, or approximately equal to, those of the mud-suspending waters. This is consistent with the pH's of hot spring waters in the Tateyama Jigokudani area.[5]

In igneous rocks, most of titanium and zirconium may be incorporated in resistant minerals, such as ilmenite and zircon.[6] In a certain stage of the alteration, however, these elements gradually enter into solutions, but the titanium in an acid solution is slightly less mobile than is zirconium; the pH values of solutions which give rise to the precipitates of titanium and zirconium hydroxides are 1.4 and 2.0 respectively.[7] Moreover, titanium secondary minerals, such as rutile and anatase, are generally resistant to acid.[8] Consequently, during the alteration the Ti/Zr ratio in an alteration product may be changed and it may gradually increase in the later stage of the alteration. The higher the pH values of thermal waters, the larger will be the ratios.

It is necessary to make further leaching experiments on titanium and zirconium obtained from rocks with acid solutions and to study the occurrences of these elements in hydrothermally-altered rocks. These results will be reported in a future paper.

The author wishes to express his thanks to Prof. Masami Ichikuni for his valuable advice and for his critical reading of the manuscript.

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[5] K. Noguchi and T. Nishiido, *Nippon Kagaku Zasshi,* **90**, 781 (1969).

[6] K. Rankama and Th. G. Sahama, "Geochemistry," The University of Chicago Press, Chicago (1950), p. 557.

[7] B. A. Gavrusevich, "Fundamentals of General Geochemistry," Nedra, Moskow (1968), p. 291.

[8] W. A. Deer, R. A. Howie and J. Zussman, "Rock-forming Minerals," Vol. 5, Longmans, London (1962), p. 34.