

**On Calcio-gadolinite, a New Variety of Gadolinite
Found in Tadati Village, Nagano Prefecture.**

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In May 1936, when the author with O. Nagashima was searching for minerals of the rare elements in Nagano Prefecture, a mineral which seemed to be gadolinite was found by us in the pegmatite region of Tukano, Tadati Village.⁽¹⁾ It occurs associated with several other rare minerals such as allanite, zircon, fergusonite, etc.

No good crystal for goniometric measurement has yet been found; however, by chemical and physical examinations mentioned below, the mineral was proved to be a variety of gadolinite containing a considerable

(1) This village is situated about 12 kilometers north-northeast of Naegi, one of the most famous places in Japan for its production of rare minerals.

quantity of calcium which seemed to replace a part of the rare earth elements. To this new variety of gadolinite, the author wishes to give the name "calcio-gadolinite."

The mineral occurs usually in a small massive state and rarely in imperfect prismatic crystals. Its colour is black and its streak greenish dark grey. It shows weak radioactivity. Its specific gravity determined by pycnometer method is 4.5 at 22°C.

The refractive indices of the mineral were determined by T. Sueno by means of the dispersion method using methylene iodide as dispersion medium and glass powder as standard. The result obtained is as follows:⁽²⁾

$$\alpha_D = 1.765; \beta_D = 1.774; \gamma_D = 1.787; \beta_F - \beta_C = 0.018.$$

The pleochroism is very strong. Z (Dark brown) > Y (Light yellow) \rightleftharpoons X (Light brown).

About 0.7 g. of the selected sample was taken for chemical analysis. The analysis was carried out by the method which was previously used by K. Kimura and M. Miyamoto⁽³⁾ for the analysis of gadolinite from Yamaguti Village. The analytical result obtained is shown in Table 1.

Table 1. Analysis of calcio-gadolinite from Tadati.

CaO	11.91%	Ce ₂ O ₃ *	4.69%
MgO	0.14	(La, Y) ₂ O ₃ etc.*	24.47
MnO	0.84	ThO ₂	0.80
FeO	11.24	SiO ₂	23.89
BeO	10.73	U ₃ O ₈	0.10
Al ₂ O ₃	1.68	H ₂ O (-)	0.14
Fe ₂ O ₃	7.65	H ₂ O (+)	2.05
		Total	100.34%

* The mean atomic weight of the rare earth elements (including cerium) was found to be about 130 from the ratio, oxide/anhydrous sulphate.

With the sample of rare earths extracted from the mineral, L-series spectral lines of lanthanide elements were photographed using a vacuum spectrograph and a metal X-ray tube of Siegbahn's type. The relative intensities of the spectral lines are given briefly in Table 2.

From the result given in Table 2, this mineral is supposed to be rich in basic lanthanide elements such as lanthanum, cerium, praseodymium

(2) α , β , and γ were determined by S. Tsuboi's statistical method, *J. Geol. Soc. Tôkyô*, **25** (1918), 40.

(3) K. Kimura and M. Miyamoto, *J. Chem. Soc. Japan*, **57** (1936), 1200.

Table 2.

Elements	Relative intensities of lines
La, Ce, Pr, Nd	+ + +
Sm, Gd	+ +
Dy, Er	+
Eu, Tb, Ho, Tu, Yb, Lu	—

and neodymium and poor in terbide elements. It is very interesting to see that the type of the distribution of rare earth elements in this mineral is quite different from that in common gadolinite.⁽⁴⁾

By comparing the analytical result of this mineral with those of gadolinite, some resemblance between them may be recognised, especially in the amounts of beryllium oxide and silica, but the high content of calcium oxide and the low percentage of rare earths in the former mineral are remarkable enough to distinguish it from common gadolinite.

Now, the analytical result of the mineral of Tadati is expressed by the empirical formula,



if the minor constituents are neglected. This formula may be derived from that of typical gadolinite, $\text{Be}_2\text{Fe}^{\text{II}}(\Sigma\text{Y})_2\text{Si}_2\text{O}_{10}$, if we assume that about a half of the rare earth elements in the latter formula is replaced by calcium, a part of ferrous iron by ferric iron, and a part of oxygen by hydroxyl group. As mentioned already, the mineral of Tadati is unusually poor in lanthanide elements of higher atomic numbers, and it is quite possibly expected that calcium replaces chiefly the elements of yttrium group, ion radii of which bear closer resemblance to that of calcium.⁽⁵⁾

The powder diagram of the mineral was photographed by Debye-Scherrer's method using a metal X-ray tube of iron anticathode. The diagram obtained was proved to be almost identical with that of common gadolinite.

Thus, it can be evidently concluded that the mineral found in Tukano, Tadati Village, Nagano Prefecture, should be a variety of gadolinite which

(4) Cf. V. M. Goldschmidt and L. Thomassen, "Geochemische Verteilungsgesetze der Elemente," III, Kristiania (1924).

(5) Cf. V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente," VII, Oslo (1926).

contains a considerable quantity of calcium in the place of the rare earth elements. As far as the author knows, there is no variety of gadolinite on record which contains such a remarkable amount of calcium, and he believes he is justified in giving the name "calcio-gadolinite" to this mineral.

The radium content of the mineral was determined by the following method: A quantity of pulverized mineral was decomposed and brought into solution and the resulted solution was kept closed in a Curie bottle until the equilibrium was established between the radium contained and the radon generated from it. The generated radon was transferred into an ionization chamber and its radioactivity was measured by an electrometer which was previously calibrated with a standard solution of radium. The radium content of the mineral thus determined was $3.15 \times 10^{-8}\%$, i.e. 1 g. of the mineral contained 3.15×10^{-10} g. of radium.

As shown in Table 1, the mineral contains 0.10% of U_3O_8 . Hence 1 g. of the mineral contains 0.00085 g. of uranium, and the ratio of radium to uranium in this mineral is

$$[Ra]/[U] = 3.71 \times 10^{-7}.$$

Therefore it can be presumed that in the mineral the equilibrium is established between radium and uranium.

In conclusion, the author wishes to express his hearty thanks to Professor K. Kimura for his kind advices and suggestions rendered during the course of this work. Thanks are also due to Professor T. Sueno of the Tokyo University of Engineering, who kindly measured the refractive indices of this mineral, and to Mr. O. Nagashima for his enthusiastic assistance in collecting the mineral used in this investigation. A part of the cost of this investigation was defrayed from the grant of the Nippon Gakujutsu Shinko-kwai (the Japan Society for the Promotion of Scientific Research) for which also the present author wishes to record his thanks.

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