A PINK KAOLIN, AND RUTHENIUM AS A MINOR CONSTITUENT OF THE TANOKAMI KAOLINS.

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A pink kaolin-like mineral has been found as one of the ingredients of somewhat weathered granite lying on the south side of the Tanokami Hill, Oomi Province (Shiga Prefecture), where the green kaolin and radioactive manganiferous deposits happen to occur.(1) It usually associates with small grains of quartz, orthoclase and biotite, each measuring about one or two millimeters across, and the kaolin as irregularly shaped masses also measures one millimeter or so in diameter. It is essentially of an amorphous nature, but on being examined microscopically, sometimes reveals microcrystalline structure in part. Most of the kaolin granules are usually faintly pink in colour, but frequently of light brown or flesh colour. The hardness is 2.5 and streak white. It does not adhere to the tongue. The index of refraction at 12°C. was determined to be 1.515 ± 0.001 by Mr. T. Tomita of the Mineralogical Laboratory, Tokyo Imperial University. For analysis, pink coloured pieces were selected with care. The result obtained is given in the following table:

SiO_2	53.91%	MgO	0.09
Al_2O_3	26.28	Rare earth oxides	0.67
Fe_2O_3	1.69	K_2O	0.62
FeO	0.26	Na_2O	1.03
MnO	0.39	F(less O-equiv.)	0.03
TiO_2	0.03	Loss on ignition	15.60
CaO	0.12		
		Total	100.72

The mineral contains, as given in the analysis shown above, a fairly marked quantity of rare earths. The spectrographical examination

(1) This Bulletin, **1** (1926), 43.; **2** (1927), 274.

showed that the latter consist chiefly of yttrium and contain insignificant quantities of La, Dy, Nd, Sc, Ce, Yb and Tm. Hence the mineral differs somewhat from the green kaolin[1] found in the same district, in its containing certain members of cerium group, such as lanthanum, neodymium and cerium and by far an inferior amount of scandium. Disregarding these minor constituents, the analysis is nearly in agreement with the formula $2\ Al_2O_3.7\ SiO_2.7\ H_2O$ with alumina to silica as 1 to 3.5; it lies, therefore, just between the two well known pink clays, catlinite and montmorillonite in the ratio of alumina to silica, the former being $Al_2O_3.3\ SiO_2.\ H_2O$[2] and the latter $Al_2O_3.\ 4\ SiO_2.\ n\ H_2O$[3]. The present mineral, therefore, seems to be considered as neither of these two, but as a new species of pink clay, and will be named *Takizolite* after the name of a villager, the late Takizo Ueno, of Tanokami who had first taken notice of this mineral and long been a collector of minerals occurring in this district. The pink colour of this mineral is, however, hardly explicable from the result of analysis, since the presence of the elements such as erbium, europium and terbium which gives rise usually to rose-coloured compounds could not be proved even spectroscopically, and it must be ascribed to some other causes which are at present unaccountable.

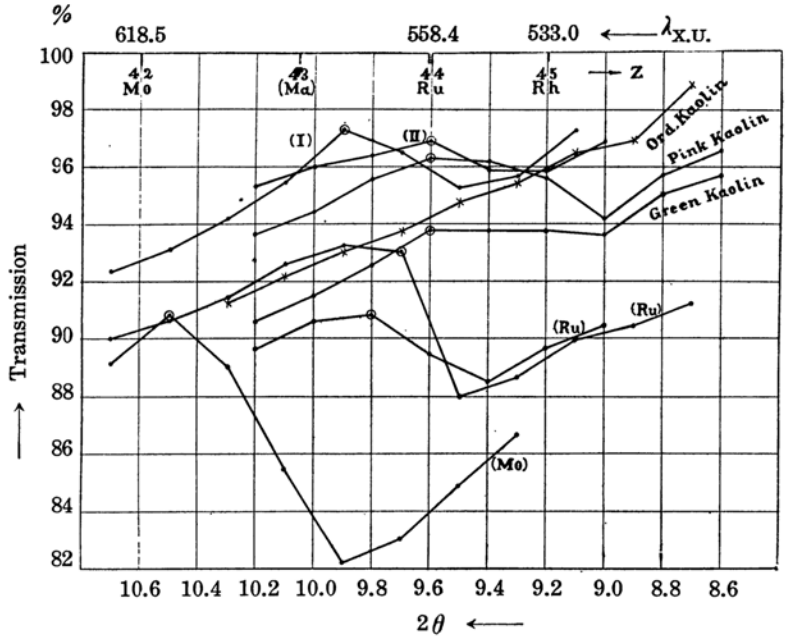
By the way, it seems rather striking, that this pink kaolin as well as the green kaolin from Tanokami give a distinct X-ray absorption corresponding to the element of atomic number 44 or 43, the minerals being directly subjected to examination, previously without letting them touch any platinum articles. The zinc-manganese fraction extracted from the green kaolin, being separated from iron and aluminium by the succinate method and subsequently precipitated by ammonium sulphide, displays pink-red colour after being ignited for the oxide, and gives more distinctly the same absorption limit. Dr. M. Nakaizumi of the Nishikawa Research Laboratory in the Institute was kind enough to carry out for us the absorption measurement in the X-ray spectra, the result being shown in the following figure. The measurement was made by the ionization method using Bragg's spectrometer. In the figure, θ denotes the glancing angle, the pyramidal face of quartz being used as the reflector, and the point marked with circlet in each curve the absorption edge respectively.

(1) Loc. cit.

(2) E. S. Dana, "The System of Mineralogy," (1914), p. 696; G. Catlin, *Am. J. Sci.*, **38** (1840), 138.

(3) E. S. Dana, "The System of Mineralogy," (1914), p. 690; C. Doelter, "Handbuch Min. Chem." Vol. II, (1917), p. 138.

The K-Absorption Edges for Kaolins.



As will be seen in the figure, whilst the ordinary white kaolin never shows the absorption in this region of wave-lengths, both of the kaolins from Tanokami and the zinc fraction (shown by the curve (II) in the figure) separated by the basic acetate method from the green kaolin exhibit the distinct K-absorption edge just corresponding to the ruthenium. The zinc fraction (shown by the curve (I) in the figure) obtained from the same green kaolin, being separated by the succinate method from the iron and aluminium, shows the edge more closely approaching to the element 43. The curves (Mo) and (Ru) are the results shown by the pure molybdic acid and metallic ruthenium (Kahlbaum's preparations) respectively and are depicted for comparison. In this case the K-absorption limit of the second order of praseodymium does not come to consideration, since the experimental condition of the arrangement was not suited to show this absorption, and the L-absorption limit of uranium which is also to appear in this region of wave length was also out of question, because the uranium as well as praseodymium were not detected chemically nor spectroscopically in the kaolins examined. The material of the pink kaolin was too scanty to allow the zinc-manganese fraction to be extracted for examination, so the measurement could not be made about the latter fraction of this kaolin.

The arc-spectrum of the zinc-manganese fraction, giving the X-ray absorption expressed by the curve (I) in the foregoing figure, gave a few lines which are to be ascribed to ruthenium and rhodium but to none of other elements. The lines were examined by a large Hilger spectrograph on Littrow mounting, the wave-lengths having been determined referring to the Exner and Haschek's scale[1] of the iron lines (the Rowland system) for the region of 2700 to 3700 Å which are given in the following table:

Lines observed, Å	A part of the lines of ruthenium, given by	
	H. Kayser[2]	F. Exner & E. Haschek
3696.81	3696.58	3696.74
3316.55	3316.38	3316.52
3297.14	—	3297.39
3296.15	3296.11	3296.25
3268.01	3268.20	3268.34
3238.90	3238.53	3238.65
3213.06	—	3213.10
3192.56	—	3192.20
3190.13	3189.96	3190.10
3177.16	3177.04	3177.16
3160.17	3159.91	3160.03
3045.72	3045.71	3045.83
3038.21	—	3038.29
2980.05	2979.94	2980.05
2976.62	2976.58	2976.70
2955.26	—	2955.48
2902.38	—	2902.20
2806.87	—	2806.86
2765.60	—	2765.54
2752.37	2752.76	2752.37
2745.22	—	2745.20
2743.90	—	2744.00

Lines observed, Å	A part of the lines of rhodium, given by	
	H. Kayser	F. Exner & E. Haschek
3268.93	—	3268.62
3155.90	3155.76	3155.90
2977.42	2977.69	2977.81
2819.49	2819.24	2819.35
2681.82	2680.62	2681.69

Lines observed, but not identified.

λ (Å)	Intensity
3383.06	6
2819.05	1
2804.47	2
2804.20	3

Further, on examining the fraction of heavy metals of the pink kaolin, precipitated by hydrogen sulphide from the acid solution, some of the chemical reactions, e.g. the rhodanate colour reaction, of ruthenium were perceived. The occurrence of ruthenium in such rock minerals has not been recorded hitherto, but from the foregoing evidence, it would seem that ruthenium or rhodium exists in the Tanokami kaolins

(1) F. Exner u. E. Haschek, "Die Spektren der Elemente bei Normal Druck," (1911).
(2) H. Kayser, "Tabelle der Hauptlinien der Linienspektra aller Elemente," (1926).

as their minor constituent, though no hint was obtained as to its state of existence.

According to W. Noddack, I. Tacke and O. Berg.[1] the zinc fraction extracted from tantalite, columbite, fergusonite, etc. is said to give always the distinct K-lines of *masurium*, as they called the element of the atomic number 43; hence the presence of the latter element in these kaolins may also be highly probable, and thus the unidentified lines of the optical spectrum pointed out in the above table might be attributed to this element.

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(1) *Naturwissenschaften*, **13** (1925), 567; *Z. angew. Chem.*, **38** (1925), 1157.