THE GREEN KAOLIN FROM TANOKAMI. IDENTITY OF THE UNIVERSAL MINOR CONSTITUENTS OF THE IGNEOUS ROCK WITH THE CHROMOSPHERIC ELEMENTS OF THE SUN.⁽¹⁾

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The Composition of the Green Kaolin. The faint yellowish green clayey matter, which occurs almost constantly associated with the radioactive manganiferous nodules and deposits from Tanokami, Oomi Province and usually forms a part of the insoluble portion of the latter,⁽²⁾ has fully been analysed. The material used for the analysis was a comparatively large lump found on the hill side, where the radioactive manganiferous deposits are disseminated. It was of an amorphous character and not perfectly homogeneous. The specific gravity was determined as 2.71 with a hardness of about 2.5∼3.5, and the streak was white. It gave the result of the second column in the following table, the third to the sixth showing the compositions of the various species of kaolin for the purpose of comparison.

Constituents	Analysis of the material. (%)	Kaolinite (monocl.)	Rectonite (amorph.)	Catlinite (amorph.)	Pyrophyllite (monocl.)
Loss on ignition $<130°$	0·23	$Al_2O_3{\cdot}2SiO_2$ $2H_2O$	$Al_2O_3{\cdot}2SiO_2$ H_2O	$Al_2O_3{\cdot}3SiO_2$ H_2O	$Al_2O_3{\cdot}4SiO_2$ H_2O
Loss on ignition $>130°$	3·56				
SiO_2	58·01	46·5	50·0	60·0	67·0
Al_2O_3	35·79	39·5	42·5	34·0	28·0
Fe_2O_3	1·32		including Halloysite, Newtonite, $Al_2O_3{\cdot}2SiO_2$ xH_2O.		including Montmorillonite, $Al_2O_3{\cdot}4SiO_2$ xH_2O.
FeO	1·10				
Mn_3O_4	0·083				
Rare earths	0·040				
MgO	0·014				
(Total)	100·15	$\left(\frac{SiO_2}{Al_2O_3}=2\right)$	(„ =2)	(„ =3)	(„ =4)

The analysis clearly shows, setting aside the iron and other minor constituents, the character of this material as a kind of kaolin which has,

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(1) Read before the Annual Meeting of the Chemical Society of Japan, April 5, 1927.

(2) This journal, 1 (1926), 43.

however, neither composition of a kaolinite nor of a pyrophyllite but of the so-called catlinite. According to the descriptions cited in Dana's Mineralogy,(1) the latter is said to be no definite mineral species and pink in colour. The material analyzed is of a greenish colour, but its composition is in quite accord with that of the catlinite, the analysis nearly satisfying the formula $Al_2O_3 \cdot 3SiO_2 \cdot H_2O$.

The noteworthy feature of this kaolin is its containing a small quantity of rare earths which chiefly consist of the yttrium group. Examining spectrographically it shows that the rare earths separated contain a small amount of the terbium group and almost no member of the cerium group. The following indicate the partial analyses of rare earths.

The material taken. (gr.)	Rare earths found		Scandia separated from the rare earths obtained	
	(mg.)	(%)	(mg.)	(%)
28.60	13.2	0.046	0.096 (a)	0.00034
27.77	8.1	0.034	(<0.19) (b)	(<0.00080)

For the determination of the terbium earths, 0.0189 gr. of oxides of the rare earths freed from scandia was used. It gave 0.00146 gr. of oxides of the terbium group with a trace of the cerium group, both having been separated as the insoluble double potassium sulphates. The results is therefore represented as follows: 0.037% yttrium earths, 0.003% terbium earths, corresponding to 7.73% of the total rare earths, and less than 0.000x% scandia.

As to the carring out of the separation of the rare earths from the material, the following procedure was mainly employed as prescribed by W. F. Hillebrand.(2) The sample was first fused with fusing mixture. Eliminating silica and then heavy metals of the hydrogen sulphide group which were contained in small amounts, the rare earths with iron were precipitated by caustic potash. The precipitates thus obtained were treated with hydrofluoric acid so as to keep the iron, manganese, titanium, etc. in solution. The insoluble residue, mainly consisting of the fluorides of the whole rare earths, was decomposed with sulphuric acid in excess. The rare earths were then repeatedly precipitated by means of oxalic acid, after the sulphates have been dissolved in dilute hydrochloric acid. The oxalates were ignited for the oxides and weighed.

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(1) E. S. Dana, "System of Mineralogy," IV Edition, p. 696.

(1) *Bull. U. S. Geolog. Survey,* 700 (1919), 176.

To separate the scandium, the oxides of rare earths obtained were dissolved in hydrochloric acid. The excess of acid was removed by evaporation, and the scandium was precipitated as basic thiosulphate by the addition of 30 per cent sodium thiosulphate solution. The figure indicated with the mark (a) in the foregoing table was obtained according to P. and G. Urbain's process,⁽¹⁾ the scandium finally having been precipitated as phosphate by ammonium phosphate after the basic thiosulphate has been dissolved in hydrochloric acid and evaporated up to dryness. Another figure marked with (b) was tentatively obtained, roughly weighing the ignition product of the basic thiosulphate as crude oxide, as the precipitate yielded on the addition of sodium thiosulphate was too small.

The fractions obtained in the course of a duplicate analysis were examined spectroscopically using a large quartz spectrograph on Littrow mounting. The rare earth fraction showed the bulk of lines, including the whole principal lines given by Exner and Haschek, of scandium, yttrium, ytterbium, dysprosium, and also abundant lines of erbium, thullium, lutecium, terbium and gadolinium. The scandium fraction separated gave rather faintly a few of its lines, but none of other elements. The sulphide fraction of heavy metals, previously precipitated by hydrogen sulphide in acidic solution, gave the lines of copper and tin. In the precipitate obtained by ammonia from the main solution, after removal of the iron and aluminium by the succinate method, besides the lines of the above mentioned rare earths, those of nickel, cobalt, zink, titanium, zirconium, niobium, chromium, molybdenum, tungsten and ruthenium were detected, and a few lines of vanadium and lithium were also observed. Roughly having been determined, these minor constituents except the rare earths, computing as oxides, hardly amounted to 0.1~0.15 per cent of the material, hence they were omitted in the foregoing table of analysis for the convenience of manifestation.

Comparison of the Minor Constituents of the Igneous Rock with the Elements in the Solar Chromosphere. One of the well known elements existing in the highly ionized state in the high level region of the solar chromosphere is the scandium which is, as stated above, distinctly detected in the rare earth fraction of the green kaolin occurring associated with the radioactive manganiferous nodules from Tanokami. The whole chromospheric elements given by F. W. Dyson⁽²⁾ and S. A. Mitchell⁽³⁾ are conveniently tabulated as below, together with four other elements shown enclosed with the double lines.

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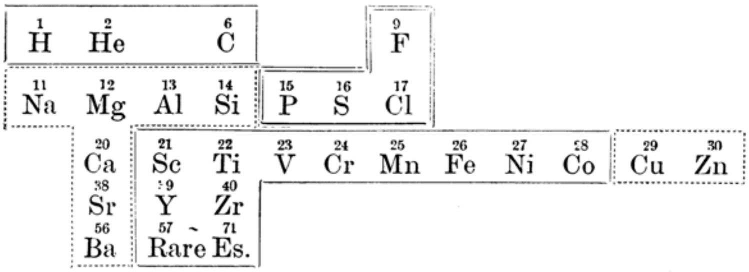
(1) *Compt. rend.*, **174** (1922), 1310.

(2) *Phil. Trans. Roy. Soc.*, A, **205** (1906), 403.

(3) *Astroph. Jour.*, **38** (1913), 407.



1 H	2 He		6 C			9 F					
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl					
	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Ni	28 Co	29 Cu	30 Zn
	38 Sr	39 Y	40 Zr								
	56 Ba	57 ~ 71 Rare Es.									

The elements inside the single line enclosure in the above table are those which give most abundant or distinct lines in the spectrum of the chromosphere, and those inside the dotted line enclosure representing the elements which are mentioned to be observed rather faintly or in deficient numbers in the spectral lines of the chromosphere.

As a matter of fact, the elements detected in small amounts in the green kaolin and the manganiferous nodules previously descrived nearly coincide with the principal members of the chromospheric elements excepting carbon and helium, and on the other hand, with what are called the universal minor constituents of the igneous rock shown by H. S. Washington,(1) W. F. Hillebrand,(2) etc. which are nothing but those elements indicated in the above table including four more elements, phosphorus, sulphur, fluorine and chlorine. Judging from the numerous results of rock analyses, hitherto put forward by several investigators, the constant minor constituents of the majority of igneous rocks are quite particular and surely to be recognized, but why they are so universally distributed among the igneous rocks is now in dispute. As will be pointed out, however, it may be seen that the universal minor constituents of the igneous rock are in close agreement with the elements constituting the solar chromosphere, and the spectroscopical lacking in some elements such as phosphorus, sulphur, fluorine and chlorine in the chromosphere will not be serious, as they give very insignificant lines, or at times no line in their spectra.

Advocating the nebular hypothesis, when the earth was formed by cooling from a gaseous mass through the same state as the sun seen at the present time, the primeval atmosphere must have been quite unlike our present envelope, and we may suppose that it was probably the same as the present chromosphere of the sun. When the liquefaction commenced over the whole surface of the our globe in the earliest state under such an atmosphere as above, no doubt there must have been contained in the liquid crust the same elements as those in the primitive atmosphere, a hetero-

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(1) H. S. Washington, " Manual of the Chemical Analysis of Rocks," (1919), p. 17.

(2) W. F. Hillebrand, " The Analysis of Silicate and Carbonate Rocks," (1919), p. 25.

geneous equilibrium between both phases having been established. As the temperature of the earth has decreased and the liquefaction proceeded, the composition of the gas phase would then gradually have changed, according as the atmospheric elements have passed into the liquid phase. Hence all the rocks afterwards solidified out from the original surface magma must have more or less been contaminated with all of these primeval atmospheric elements.

According to the view set out above, though we have no clear evidence for it yet, it should possibly be considered that the presence of helium in certain non-radioactive minerals such as beryl, fluorite, sphene, etc. and in some natural gases may be ascribed to this notable one of the constituents of the primeval atmosphere supposed. The present is not the place for any extended discussion, but the close analogy between the universal minor constituents of the igneous rock and the chromospheric elements, if it might be apparent, will not be denial.

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