22. *Chemical and Mineralogical Study of Japanese Volcanogenous Ash-Loams.*

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The volcanogenous ash-loams are widely distributed in Japan as the upper layers of diluvial formations, forming hilly lands of less altitude in almost every district. The ash-loams are of mealy to fine arenaceous textures, and when wet they exhibit plasticity only slightly. They are commonly of light brownish yellow colour, though not unfrequently dark coloured owing to the presence of organic matters.

The ash-loams of those regions can be classified into three main groups: (1) the *oxyphilous*; (2) the *basophilous*; and (3) the *strongly basophilous*. The methylene blue and acid fuchsine were used in my experiments as dye materials and the typical colour tones of stained samples of the above mentioned three groups are as follows:

(1) Oxyphilous	{ M.B.: light olive to yellowish green.
	{ A.F.: orange red to deep carmine.
(2) Basophilous	{ M.B.: green to greenish blue.
	{ A.F.: orange yellow to orange.
(3) Strongly	{ M.B.: blue to indigo.
Basophilous	{ A.F.: without visible reddish tint.

(A) *Oxyphilous Ash-Loams.*

The majority of oxyphilous ash-loams is the weathering product of volcanic ash of hyperthene augite andesite and many of them are highly pumiceous. The typical pumiceous ash-loams are called "*Onji*" in the western part of Shikoku. The name took its origin from the fact that they give a peculiar sound when suddenly and strongly trodden on.

The molecular ratios of silica and alkaline bases to alumina in the parts decomposed by hot 20 per cent hydrochloric acid show very small values, the former fluctuating between 0.77 and 1.40 and the latter between 0.07 and 0.25. The averages of those molecular ratios are shown in the following table:

District	Molecular Ratios		
	Silica	Alumina	Alk. Bases.
Kiūshū (8)	1.17	1.00	0.11
Shikoku (7)	1.03	1.00	0.11
Chūgoku (7)	1.02	1.00	0.14
Average	1.07	1.00	0.12

The figures in brackets show the numbers of data.

The area of occurrence of oxyphilous ash-loams occupies relatively low situation with an annual temperature higher than 14°C. and an annual rainfall of over 1500 mm. The chemical compositions of the ash-loams on the higher mountain lands in this area resemble those of northern Japan, both being strongly basophilous. The fact shows the remarkable influence of climatic condition on weathering.

VAN BEMMELEN regarded the *laterites* as the weathering products characterized by small contents of silica and alkaline bases and pointed out that the molecular ratios of silica to alumina in the parts of laterites decomposed by dilute hydrochloric acid and alkali fluctuate between 0 and 1 (Zeitschr. f. Anorg. Chem., 1904). The more recent scientific investigations have shown that the laterites are composed of amorphous clays with large amounts of aluminium hydrate *crystalline or colloidal* and ferric hydrate *turgitic or limonitic*. The oxyphilous ash-loams exhibit some resemblance to laterites in their chemical relations.

The vividly oxyphilous characters of ash-loams struck my attention and induced me to enquire whether they contain free aluminium hydrate, because the latter is the only possible soil ingredient which is distinctly oxyphilous. Ferric hydrate is also oxyphilous, but not so intense as to change its original colour and limonite even in fine powder is almost or completely indifferent to acid aniline dyes.

SCHLÖSING used the method of extracting free alumina by boiling the samples with large quantities of very dilute aqueous solution of sodium hydrate in his study of the soils of Madagascar (Comptes Rendus, 132 (1901), Nr. 20. I found that method inconvenient for our ash-loams on account of the dissolving action of his solution on colloidal clays. The better results were obtained by boiling samples shortly with the 10 per cent solution of sodium carbonate, the dissolved silica being negligible in most cases. The alumina dissolved reaches at times to 4 per cent and the quantities hold commonly almost constant ratios to those of acid fuchsine absorbed. The strongly basophilous ash-loams give very small

quantities or only traces of alumina dissolved by treatment with my carbonate solution.

The chemical composition of *collyrite*, white earthy mineral, show considerable variation fluctuating between those of *allophane* and *bauxite*, even in the samples of same locality. DANA considered this mineral as the mixture of *allophane* and *aluminium hydrate* (System of Mineralogy, 1906). I have tried the staining with a specimen of *collyrite* and found it to be distinctly oxyphilous and moderately basophilous. The microscopical examination of the double-stained sample have shown that it is the mixture of oxyphilous and basophilous particles. In double-stained samples of ash-loams many sorely oxyphilous aggregates were detected among numerous basophilous ones.

From the preceding data I came to the conclusion that the argillaceous substances in oxyphilous ash-loams are constituted mainly of more or less basophilous colloidal clays resembling to *allophane* with smaller smounts of vividly oxyphilous *aluminium hydrate* and weakly oxyphilous *ferric hydrate*, the both being in colloidal state. In the majority of cases the greater part of ferric hydrate will probably be in the form of *limonite* derived from *magnetite* in original volcanic shes.

The wet colloidal clays deficient in alkaline bases give commonly *acid reaction* on litmus paper. The oxyphilous ash-loams react nearly neutral notwithstanding they contain very small quantities of alkaline bases. The experiments have shown that the fresh colloidal aluminium and ferric hydrates eliminate the acid reaction of colloidal clays when the latter are mixed intimately with the former. In oxyphilous ash-loams the neutrality is undoubtedly caused by aluminium hydrate, because ferric hydrate is commonly in smaller proportion and mainly in the form of *limonite*.

The extremely high absorptive power of the ash-loams for ammonia and phosphoric acid can be explained by the presence of two groups of colloidal substances acting oppositely. The observation of practical agriculturists coincide in the view that the soils act unbenefecial to farm crops especially in wet years. This fact can also be explained by the presence of active colloidal substances imbibing and retaining large quantities of water.

(B) *Basophilous and Strongly Basophilous Ash-Loams.*

The comparative studies on the ash-loams of those groups in central Japan are now in the way to accomplishment. So the merely preliminary sketches will be given here.

The area of occurrence of *strongly basophilous ash-loams* extends in the norther part of central Japan with annual temperature 12°–14° and annual rain-fall over or about 2000 mm. The majority of ash-loams found in this area is distinctly to strongly acid, indicating serious influence of climatic conditions. The two examples of acid ash-loams will be given in the following table :

Locality (Prov.)	Molecular Ratios		
	Silica	Alumina	Alk. Bases
Inokuchi (Echizen)	1.37	1.00	0.09
Kamitaki (Etchū)	1.31	1.00	0.22

The strong basophilous ash-loams are also met with in the higher part of the somma of Aso-Volcanoe in Kiūshū. On the foot of the mountain the oxyphilous loams are occurring. Two examples of ash-loams of Aso will be given in the following table :

Locality (Prov.)	Molecular Ratios		
	Silica	Alumina	Alk. Bases
Ogata (Bungo)	2.37	1.00	0.29
Takeda (Bungo)	2.55	1.00	0.19

Those ash-loams are almost neutral and resemble in many respects to the ash-loam of Morioka in the north Japan.

The *basophilous ash-loams* are scattered in many places in central Japan in the south of the area of strongly basophilous ash-loams. The ash-loams covering the higher part of Kanto-Plain in great extension furnishes the good example. Twelve years ago I have studied the loam occurring near Tokyo and reported the results on "Die Landwirtschaftlichen Versuchs-Stationen." 79 u. 80 (1913).

The loam is weathered volcanic ash of olivine bearing hypersthene-augite andesite with smaller quantity of glassy particles. The parts decomposed by hot 20 per cent and cold 10 per cent hydrochloric acid amount to 63 and 51 per cent of dry materials respectively. The molecular ratios of silica and alkaline bases to alumina of those two parts are as follows :

The part Decomposed by	Molecular Ratios		
	Silica	Alumina	Alk. Bases
20 per cent HCl	1.63	1.00	0.36
10 per cent HCl	1.36	1.00	0.17

As the cold dilute hydrochloric acid attacks olivine and basic plagioclase the molecular ratios of silica and alkaline bases must be less than those above given. From this reason and its basophilous character I have assumed the main part of argillaceous substances to be constituted of those resembling *allophane*. It was afterwards found that a small quantity of free alumina is extracted by the solution of sodium carbonate. The weak oxyphilous nature of the loam can be explained by the latter fact. The loam contains comparatively large quantity of *limonitic ferric hydrate* derived mainly of magnetite which amounts 2-3 per cent.

The strong absorptive power of the loam for ammonia and phosphoric acid can be explained by the presence of colloidal hydrates together with large quantity of *allophanoidal* clay. It was recently been proved that about two third of the alkaline bases decomposed by 20 per cent hot hydrochloric acid are replaced by ammonia when the loam is treated with the solution of ammonium chloride. The wet loam gives very faint acid reaction to sensible blue litmus paper. The fact that the wet loam does not give rise to remarkable plasticity can also be explained by the presence of large quantity of *allophanoidal* clay instead of *kaolinitic* one.

An example of the basophilous ash-loams resembling to those of Kantō-Plain in the chemical composition of parts decomposed by hot 20 per cent hydrochloric acid is shown in the following table :

Locality (Prov.)	Molecular Ratios		
	Silica	Alumina	Alk. Bases
Komuro (Shinano)	1.95	1.00	0.38

Summary and Conclusion.

GANS published the opinion that the molecular ratios of silica and alkaline base to alumina in the parts of normal soils decomposed by hydrochloric acid amount to > 3 and 1 respectively (Intern. Mitt. f. Bodenkunde, 1913). In Japanese soils such cases are exceedingly rare owing to the climatic conditions, namely, higher temperature and abundant rainfall. The wide distribution of the soils derived from more basic volcanic ashes may also be an important factor.

The oxyphilous ash-loams can be regarded as the soils proceeding a step into lateritic weathering as already stated.

MOHR (1909) and HARRISON (1911) suggested that the lateritization occurs principally in the region of more basic plagioclase rocks as quoted by Clarke (The Data of Geochemistry, 1920). The pyroxene andesite is a good representative of such groups of rocks.

GLINKA pointed out the possibility of occurrence of lateritic weathering in the hot raing districts beyond tropical zone (Typen der Bodenbildung, 1914). RAMANN assumed the presence of small quantities of free alumina in soils of temperate zone (Boden und Bodenbildung, 1198). The opinion of the present auther came to coincidence with the views of those famous agrogeologists from the results of investigations of ash-loams of our native land.

It is my assumption that the colloidal clays are the initial decomposition products of volcanic ashes from which aluminium hydrate is subsequently set free. It is highly probable that the hydrate is derived from colloidal clays as decomposition product by long continued action of water assisted by higher temperature and carbonic acid, the silica and alkaline bases being leached off by abundant water.

From the statements given above the following conclusion can be accepted as highly probable. The colloidal clays in initial stage contain large quantities of alkaline bases being weak alkaline or almost neutral in reaction, but by continual leaching of silica and alkaline bases the clays become acid. The acid clays give rise to aluminium hydrate and become almost neutral by the process already mentioned. The acid ash-loams canbe regarded as the intermediate stage between the „*absorptively saturated*“ neatral and the „*unsaturated*“ neutral ones (oxyphilous ash-loams). There may also be many loams whose acidity is diminished more or less by active colloidal ferric hydrate.

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