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GENESIS OF SPHERICAL HALLOYSITE FROM BASALTIC ASH, AT AMBRYM (VANUATU)

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ABSTRACT

The early stages of basaltic ash weathering have been studied in the young soils of the Ambrym Island. The alteration has been observed at three levels, from the almost fresh volcanic ash in the top-soil until a loamy andic brown soil at 3m depth.

In the lower brown soil, a great enrichment in a spherical form of poorly crystalline halloysite has been observed. An attempt is made to characterize the poorly crystalline spherical halloysite. Its mineralogical and chemical composition is discussed and it is compared to the so-called "embryonic halloysite" observed by WADA.

The genesis of poorly crystalline spherical halloysite could be a metastable form of a complex halloysite-hisingerite structure. This formation seems favoured by a high supersaturation of soil in Si, Al, Mg and Fe elements.

INTRODUCTION

The early stages of basaltic ash weathering have been observed in the soils of the Ambrym Island, where an explosive volcanic activity is frequent for several millenium.

The ash weathering progresses downward, from the top-soil, according to the age of ash ejecta. In the northward, where the deposits are less abundant and the ash particles are smaller, we can see : at the top-soil, the ash particles look still fresh ; downward, they become more and more brown at their periphery and then inside, until a brown loam appears, since 3 m depth.

The age of ash layers has been estimated from the recent deposit velocity. It is probably less 100 years in the top-soil and it is around 1000-1500 years at 3 m depth. We have studied the 3 following soil samples:

- n° 2111 : 0- 10 cm ; humiferous soil, of almost unweathered ash ; < 100 y. old,
- n° 2112 : 80-120 cm ; humiferous vitric andosol, of brownish ash ; < 500 y. old,
- n° 2114 : 300 cm ; brown loam-andic paleo-soil ; 1000-1500 y. old.

We used also, in order to complete this study, the data of the two following soil samples from the near westward :

- n° 2011 : 0- 5 cm ; very fresh ash, poorly humiferous soil ; 10 y. old,
- n° 2042 : 25- 50 cm ; vitric andosol ; < 100 y. old.

The chemical composition of fresh ash (tabl. I) is near this one of an alkaline olivine basalt : $\text{SiO}_2 = 50$, $\text{Al}_2\text{O}_3 = 17$, $\text{Fe}_2\text{O}_3 = 12$, $\text{TiO}_2 = 1$, $\text{CaO} = 10$, $\text{MgO} = 5$, $\text{K}_2\text{O} = 2$, $\text{Na}_2\text{O} = 3$ %. The climate is wet tropical, with 3000 mm/y. rainfall and a very shorth dry season.

METHODS

1. Chemical analysis

- a. Element analysis, of whole soil and its < 2 μm fraction, successively on the HClO_4 extract, then on the residue (melting).
- b. Kinetics dissolution curves of Al, Fe, Si elements, from 5 g < 2 μm soil.
 - de ENDREDDY (1963) : NH_4 oxalate-oxalic acid pH 3.5, U.V. activated, 30 min ; 6 times extraction.
 - SEGALIN (1968) : alternating (8 N) HCl, 30 min and (0.5 N) NaOH, 100°C, 5 min ; 7 times extraction. Element analysis on the mixture of both acid and soda extracts for each cycle.
 - QUANTIN and LAMOUREUX (1974) SEGALIN's variant : use of (4 N) HCl instead of 8 N concentration, to get more selective dissolution of Al and Fe oxides and clays ; 10 times extraction.
 - QUANTIN (1975), in QUANTIN and BOULEAU (1983) : (2 N) HCl 30 min ; 10 times extraction.

2. Mineralogy

- X.R.D. (Co, $\text{K}\alpha$ radiation)
 - < 2 μm soil powder, untreated and after treatments by oxalate, (2 N) HCl, or Segalen's method.
 - < 2 μm orientated fraction, untreated, 100°C and 500°C heated, glycerol.
- D.T.A., on untreated < 2 μm fraction.
- I.R. Spectroscopy (KBr disc), on untreated < 2 μm fraction.
- T.E. Microscopy (JEOL, 100), on untreated < 2 μm fraction.

3. < 2 μm fraction extraction.

- H_2O pretreatment, followed by (0.05 N) HCl lixiviation.
- pH adjustment of aqueous suspension of soil, to obtain a good clay dispersion, either acid by HCl addition or alkaline by NaOH.
- Ultra-sonic wave shaking, 10 min.

Table I - Chemical Composition of Basalt and Soil

Sample n°	Basalt Ambrym average	< 2 mm whole soil							
		Concentr. (1)				Variations by volume (3)			
		2011	2111	2112	2114	2114	2114	2112	2114
SiO_2	49.55	30.12	49.97	49.86	48.53	- 0.52	- 5.17	- 19	- 33
Al_2O_3	17.18	16.34	16.49	18.01	21.19	+10.22	+29.68	- 15	- 15
Fe_2O_3	12.55	12.44	12.57	13.46	14.20	+ 8.20	+14.15	- 13	- 22
TiO_2	0.80	1.03	0.97	1.09	1.12	+ 5.82	+ 8.73	- 12	- 23
HfO_2	0.24	0.20	0.28	0.23	0.30	+15.00	+50.0	- 15	- 15
CaO	9.39	9.96	7.47	8.72	5.43	-12.45	-45.48	- 30	- 60
MgO	4.59	4.75	6.47	4.08	5.81	-14.11	+22.31	- 31	- 39
K_2O	1.80	1.91	2.02	1.20	0.86	-37.17	-54.97	- 49	- 69
Na_2O	3.40	2.90	3.09	2.06	1.72	-28.97	-40.69	- 50	- 66
P_2O_5	0.50	0.31	0.52	0.37	0.34	+19.35	+ 9.68	- 6	- 26
mol. $\text{SiO}_2/\text{Al}_2\text{O}_3$	4.9	5.21	5.15	4.70	3.89				
mol. $\text{SiO}_2/\text{Al}_2\text{Fe}_2\text{O}_3$	3.25	3.51	3.47	3.19	2.73				
Total	100	100	100	100	100			- 20	- 31
Sum of oxides	30.77	30.01	30.31	32.79	36.81	+ 926	+22.66	- 14	- 17
Sum of bases	19.18	19.52	19.05	16.06	13.82	-17.72	-29.20	- 34	- 51
Bulk density		1.10		0.90	0.77				

- (1) Calculated value without fire-loss.
 (2) Variations relatives to 2011 sample.
 (3) Isovolume variations.

Table II - Chemical composition of < 2 μm fraction

Sample n°	2017 (N°)			2114 (N°)		2011 Ash	
	Extract. w		Residue	Extract. w			
	1	2		1	2		
SiO_2	50.26	73.07	62.77	71.01	30.83	47.72	50.12
Al_2O_3	2.73	3.97	12.61	5.79	15.40	23.84	16.34
Fe_2O_3	10.45	15.19	9.31	13.97	16.40	23.38	12.44
TiO_2	0.62	0.90	0.76	0.88	1.20	1.86	1.03
HfO_2	0.16	0.23	0.27	0.24	0.42	0.65	0.20
CaO	1.31	1.90	7.41	3.07	0.09	0.14	9.96
MgO	1.80	2.62	3.68	2.85	0.22	0.34	4.75
K_2O	0.23	0.33	1.24	0.52	0.01	0.01	1.91
Na_2O	0.27	0.39	1.68	0.66	0.04	0.06	2.90
P_2O_5	0.95	1.38	0.27	1.14	-	-	0.31
Residue	18.44				2.27		
H_2O^+	7.47				17.25		
H_2O^-	7.22				15.31		
Total	101.93	100	100	100	99.45	100	100
mol. $\text{SiO}_2/\text{Al}_2\text{O}_3$	31.3	31.3	8.46	20.85	3.40	3.40	5.21
mol. $\text{SiO}_2/\text{Al}_2\text{Fe}_2\text{O}_3$	9.1	9.1	5.75	8.21	2.03	2.03	3.51

- w : extracted by HClO_4 1/ Analytical data
 2/ Calculated without residue and fire-loss.

Table III - Selective Dissolution Analysis of Soil

Method	Sample n°	Al_2O_3				Fe_2O_3				SiO_2				mol. $\text{SiO}_2/\text{Al}_2\text{O}_3$			
		Phase 1		2	Sum	Phase 1		2	Sum	Phase 1		2	Sum	Phase 1		2	Sum
		a	b			a	b			a	b			a	b		
OXALATE pH 3.5 - U.V. 9 extract.	2111	1.07	0.12	1.19	1.73	0.45	2.20	0.92	0.08	0.90	1.46	0.85	1.40				
	2112	1.72	0.41	2.13	3.23	0.79	4.04	1.03	0.41	1.44	1.02	1.70	1.15				
	2114	1.56	0.90	2.46	7.50	0.80	8.30	0.87	0.69	1.56	0.95	1.30	1.08				
HCl 8 N pH 0.5 - U.V. 7 extract.	2111	1.33	0.17	3.00	1.88	0.91	2.79	2.33	3.24	4.57	3.22	4.95	3.88				
	2114	8.05	2.80	10.85	9.48	1.26	10.74	18.42	6.86	25.28	3.89	4.17	3.96				
HCl 8 N pH 0.5 - U.V. 10 extract.	2111	1.24	0.09	0.20	1.53	1.07	0.00	1.20	2.27	1.37	0.93	3.30	3.70	1.74	17.6	29.8	6.3
	2114	2.83	2.36	4.94	9.13	1.83	4.80	2.62	9.27	1.90	3.48	11.88	17.26	1.76	2.51	4.09	3.21
HCl 2 N 10 extract.	2111	1.23	0.50	1.83	1.11	0.40	1.71	0.72	0.25	0.97	0.92	0.85	0.90				
	2112	2.02	1.82	3.84	1.71	1.77	3.48	0.34	1.43	1.77	0.29	1.34	0.78				
	2114	1.18	1.39	2.57	0.38	3.75	4.14	0.33	1.32	1.85	0.48	1.86	1.22				

(a) Results, 2 of < 2 μm soil, oven dry basis ; calculated from dissolution curves, in 2 or 3 phases.

CHEMICAL COMPOSITION

1. Evolution of the chemical composition of the whole soil (tabl. I)

The isovolume balance of major elements which are remaining in the soil, at the depths of 1 m (n° 2112) and of 3 m (n° 2114), shows the following data. Near 31% of mineral matter has been dissolved during around 1000 to 1500 years. But the leaching was neither equal nor constant for every element. The bases were the most quickly leached : 51% in average, but 66% of alkaline elements, 60% of calcium and only 40% of magnesium. The silica loss is 33%. Even the Al, Fe and Ti oxides diminish but only 17% ; their leaching seems noteworthy only during the earlier stage of weathering (< 500 y.) ; then it stops. The silica leaching velocity diminishes also downward ; this is due perhaps to a supply of silica by the weathering solutions from the top-soil.

In fact, comparing the chemical composition of the soil residue to the initial basaltic ash, we can see the following changes : a strong increase in (Al, Fe, Ti) oxides, + 20% (mostly alumina + 30%) ; a very light decrease in silica, - 3% ; a great diminution of bases, - 30%, mostly CaO, Na₂O and K₂O, but not magnesia. Consequently, the SiO₂/Al₂O₃ mol. ratio decreases from 5.2 to 3.9 and the SiO₂/R₂O₃ mol. ratio from 3.5 to 2.7.

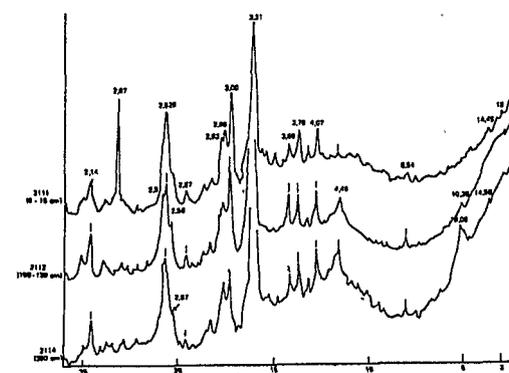
2. Chemical composition of less 2 μm fraction (Tab. II)

We analyzed only two extracts (*), one from the top-soil (n° 2042-H), another from the paleo-soil (n° 2114-Na).

a. The < 2 μm fraction of top-soil contains near 20% of insoluble substances in the perchloric acid, which correspond to microlites of feldspar, pyroxene and some silica glass. The soluble part, which derives mostly from weathering products, is very rich in silica and rather poor in alumina (SiO₂/Al₂O₃ mol. ratio = 31). This fact is common in similar soils of the Vanuatu (QUANTIN, 1972-1978). It was also observed in Japan by several authors, namely : SHOJI and MASUI (1972), TOKASHIKI and WADA (1975). In addition the soluble fraction is richer in iron oxide and phosphorus than the original ash. Some ferruginous silica products were also observed by WIELMAKER and WAKATSUKI (1984) in the young volcanic ash soils of the Kenya. Then, the soluble part contains an important amount of magnesium, calcium and potassium.

b. The < 2 μm fraction of paleo-soil, contains only 2% of insoluble minerals. It is very hydrated substance (fire loss + 32%). In comparison with the original volcanic ash, it doesn't contain more bases, except a little of magnesia ; it is greatly enriched in Al, Fe, Ti and Mn oxides. However the silica content remains high and the SiO₂/Al₂O₃ and SiO₂/R₂O₃ mol. ratios are respectively 3.4 and 2.0. These high values don't correspond neither to allophane nor to halloysite. they are similar to those which were observed by WADA and KAKUTO (1985), in a similar Ecuadorian Soil,

(*) Due to the too small quantity of other extracted < 2 μm fractions.



containing an "embryonic halloysite", and then by WADA, YAMAUCHI (et al., 1985) in a Japanese paddy-soil.

The chemical evolution of the $< 2 \mu\text{m}$ fraction, from the top-soil to the paleo-soil, shows a transformation of weathering products from silica and iron rich products to iron and alumina rich phyllosilicates.

3. Al, Fe and Si dissolution curves, from whole soil (Tabl. III)

We can compare the effects of the most selective reagents (pH 3.5 - oxalate, 2 N HCl) and of the strongest (Segalen's method). The dissolution curves show 3 mineral phases : 1st a very soluble product, composed of allophane and non crystalline (Al, Fe) hydroxides ; 2d a slowly soluble material, which could be made of opal, clay minerals, iron oxides or oxyhydroxides ; 3d an intermediate product, composed of more soluble clays or iron oxyhydroxides.

- a. From the top-soil (n° 2111), 2 main phases were extracted :
 - 5% of very soluble products : 3% of allophane and 2% of iron hydroxide ;
 - 5% of + slowly soluble materials : 3% of opale, 1% of clays and 1% of iron oxide.
- b. From the paleo-soil (n° 2114), 3 main phases were dissolved :
 - 6-7% of very soluble products : 4-5% of allophane and 2% of iron hydroxides ;
 - 12% of intermediate products : 7% of very soluble clay, with a halloysite composition, and 5% of iron oxyhydroxide ;
 - 19-25% of slowly soluble materials : 15-22% of clay, with a montmorillonite composition, 2-3% of iron oxide and probably $< 1\%$ of opal.
- c. From the intermediate andosol (n° 2112) were extracted :
 - 5-6% of very soluble products : 3-4% of allophane and 2% of iron hydroxide ;
 - 5-6% of intermediate products : 3-4% of very soluble clays, with halloysite composition and 2% of iron oxyhydroxide ;
 - the slowly soluble phase has not been analysed.

These results show the following evolution results : the top-soil, which derives of very recent ash, doesn't present more than 9-10% of weathering products, of which 3% of "free" silica, 3-4% of para-crystalline clays and 2% of iron hydroxide. The paleo-soil (1000-1500 y. old) contains near 45% of soluble weathering products. But the very soluble fraction didn't increase, or very little, and the "free" silica disappeared. Whereas more than 30% of less soluble products were forming. These products seem a mixture of 1:1 and 2:1 clay minerals and of iron oxyhydroxides.

MINERALOGY

1. X-ray diffraction

a. Whole soil powder (fig. 1 and 2)

The diffractogram of top-soil (n° 2111) shows only the rays of the basaltic ash minerals, for instance : plagioclases, augite and magnetite.

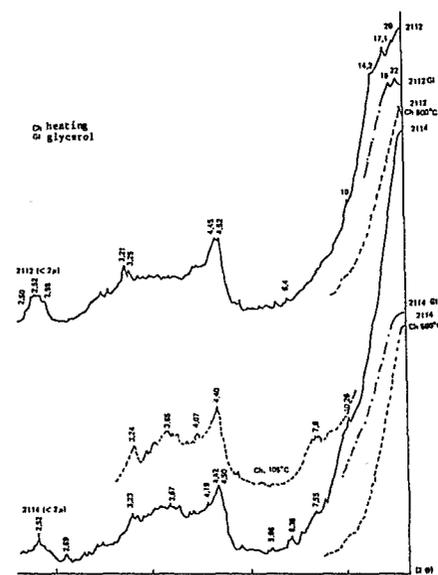


Figure 3 - X.R. Diffraction on $< 2 \mu\text{m}$ fraction

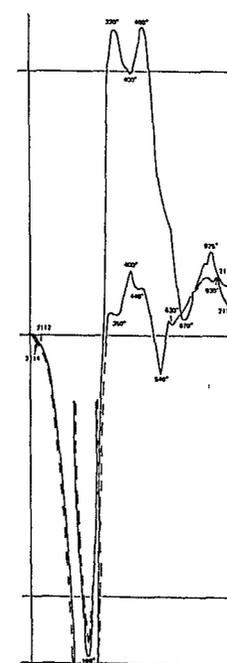


Figure 4 - D.T.A on $< 2 \mu\text{m}$ fraction

On the intermediate soil diagram (n° 2112) begins to appear a ray near 4.5-4.45 Å, which could mark a trace of clay minerals.

On the paleo-soil (n° 2114), the rays of pyroxene appear smaller whereas the rays of clay minerals become more evident around 10, 4.45 and 2.57-2.50 Å. After an oxalate treatment of soil (dissolving allophane and iron hydroxide), these 3 rays remain, although the rays of plagioclase and pyroxene become a little stronger. We don't see, neither any clear ray of 14 Å clay mineral, nor of goethite or hematite.

b. Orientated < 2 μm fraction (fig. 3).

On the top-soil extract (n° 2111), the diffractogram shows only the rays of primary minerals, for instance a plagioclase.

On the intermediate soil (n° 2112) diagram, two rays at 4.50-4.45 Å and a band near 2.50 Å show the presence of ill-crystallized clay minerals.

On the paleo-soil (n° 2114) diagram, the presence of a 10 Å clay mineral is confirmed. This ray moves to 7.6 Å after dehydration at 105°C; but disappears after heating at 500°C. We don't observe any clear evidence of rays between 10-14 Å, before and after heating, neither the swelling effect of glycerol treatment. This < 2 μm fraction contains probably an ill-crystallized 10 Å halloysite and some allophane, and perhaps a trace of goethite.

2. Differential thermal analysis (fig. 4)

a. The diagram of < 2 μm fraction of the intermediate andosol (n° 2112) characterizes very hydrated amorphous products. Two strong exothermic reactions at 320 and 460°C, could mask some other endothermic reactions of dehydroxylation.

b. The diagram of the paleo-soil (n° 2114) shows a mixture of predominant allophane and of halloysite (endothermic peaks at 180 and 540°C, exothermic peak at 925°C). But, a little endothermic inflexion near 630°C suggests also a few smectite. The slight inflexion near 350°C, shows some traces of goethite.

3. Infrared spectrometry (fig. 5).

All diagrams of I.R. absorption are similar of those of andosols, which are rich in very hydrated paracrystalline substances (H-OH bands near 3200, 2920 and 1630 cm⁻¹). However we can distinguish a clear evolution between the diagrams from the top-soil and from the paleo-soil.

a. On the < 2 μm fractions of top-soil (n° 2011, 2042), the spectra show the characteristic bands of Si-O-Si of opal near 795 and 1060-1090 cm⁻¹, as also two shoulders near 930 and 1220 cm⁻¹ (TOKASHIKI and WADA, 1975).

b. On the < 2 μm fractions of the intermediate andosol (n° 2112) and the paleo-soil (n° 2114), the spectra show clearly the disappearance of the characteristic band of opal near 790 cm⁻¹. Whereas are growing the bands of Si-O-Al near 1015-1030 cm⁻¹, or Al (Fe)-OH near 915 cm⁻¹. These bands could mark the presence of 1:1 clay mineral, for instance halloysite. But, due to the great hydration of these products, the other bands, which could

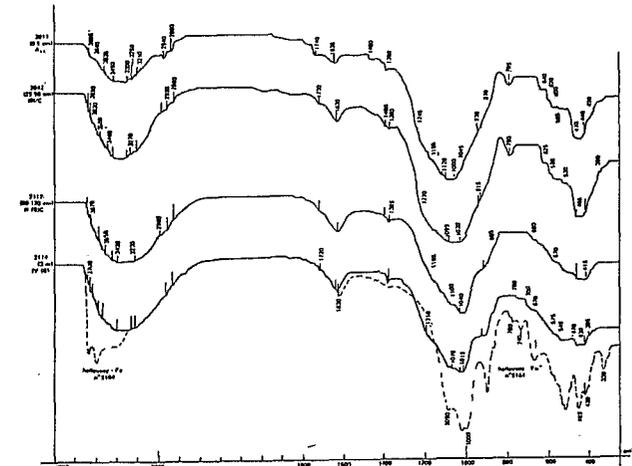


Figure 5 - I.R. Spectroscopy on < 2 μm fraction

- a)- 2011-2042 samples = Topsoil: opal, Fe-allophane
 b)- 2112-2114 samples = Andosol and Paleosol: allophane, spherical halloysite
 c)- 5154 sample = Paleosol: well tubular halloysite

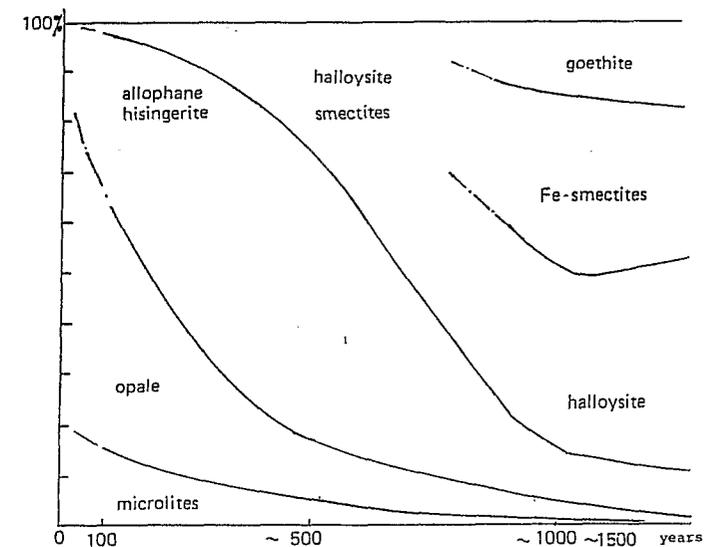


Figure 6 - Schematic Evolution of < 2 μm Mineral Composition

characterize the 1:1 clay minerals, at 3620, 3650 and 3690 cm^{-1} , don't appear. The enlargement of these bands to 3550 and 3420 cm^{-1} could show the presence of interlayer water (3550 cm^{-1} band in the case of halloysite) and a mixture or an interstratification with some swelling 2:1 clay mineral.

4. Transmission electron microscopy.

The T.E. microscopy, on the $< 2 \mu\text{m}$ fraction of the three soil horizons, shows a clear evolution of mineral forms from the top-soil downward the paleo-soil.

a) In the top-soil (n° 2011, 2042), the residual forms of weathered microlites and glass, as well several new forms of silica, chiefly diatom-skeletons and discs of opal, are predominant (photo 1). But we can also observe a little of allophane and some siliceous products of the diatom-skeleton alteration, in a shape of flakes, or very thin plates, discs or rings. We remark some very scarce early forms of micro-clays, in the shape of thin plates, crumpled lamella, spherical or tubular sheets (photo 2); these later forms are probably a first sketch of smectite and halloysite.

b) In the intermediate soil (n° 2112), the presence of microlites, glass and diatom-skeleton becomes rare. Their forms are very altered. On the side of diatom-skeletons, or in the little holes, we can see the formation of minute clay particles (photo 3). The most frequent products are flakes of allophane, micro-discs of opal, and thin crumpled lamella; these later could be some smectite or halloysite forms. We can observe also, but less frequently, some rolled minute clay particles, in the shape of ring, sphere or tube. These forms are probably the early sketch of halloysite (photo 4).

c) In the paleo-soil (n° 2114), the very thin clay particles are predominant. Only few pieces of scarce and very altered microlites and diatom-skeletons remain (photo 5). We can still see some scarce micro-discs of opal. The allophane flakes are rare.

Among the thin clays, the rolled forms of sphere or ring are predominant. These forms are probably related to halloysite. We obtained some very weak electron diffractions around 3.6, 2.5 and 1.5 \AA on a spherical particle. The sphere size is 200-800 \AA (photo 6). The concentric ribbons, of 50-100 \AA width, comport probably 5 to 10 layers. The center is often hollow, of around 50 \AA size. It contains sometime a minute corn of opal (photo 7). Perhaps, this corn has been used as nucleus for the rolling of clay layers.

The other forms of clay, as tubular halloysite or crumpled lamellar smectite, are less frequent than the spheric ones. But they are some transitions between these diverse forms. In addition, we remark these diverse clay phyllites are very thin, irregular and they show some gaps or voids between the layers or the ribbons.

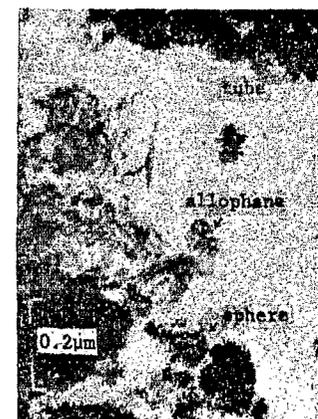
INTERPRETATION

A general interpretation of the results puts forward several problems, concerning the position of iron and of silica in the mineral constituents, the characteristics and the composition of clay minerals, especially the spherical halloysite.

T.E. Microscopy



Ph.1 - fresh diatom skeleton in top soil



Ph.2 - early minute clays in top soil



Ph.3 - early diatom skeleton dissolution in medium soil



Ph.4 - spherical and lamellar clays in medium soil

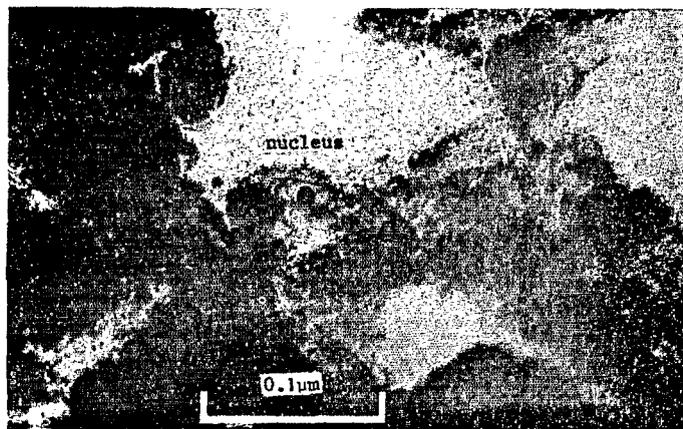
T.E. Microscopy



Ph.5 - late diatom skeleton dissolution in lower soil



Ph.6 - spherical and tubular halloysite in lower soil



Ph.7 - opal nucleus in spherical halloysite

1. Synthesis of results

a) In the top-soil (< 100 y. old), the < 2 μm fraction represents at most 5% of soil. It is rich in silica, iron and bases, but poor in alumina. Its composition is approximately :

- 20% of poorly altered glass and microlite,
- the most part of silica is under a form of opal (diatom-skeleton, micro-discs), soluble in (0.5 N) NaOH, identified by I.R. spectrometry,
- a noticeable part of allophane, soluble in oxalate or 2N HCl,
- a noticeable part of non crystalline iron hydroxide, very soluble, but perhaps related to allophane or silica-rich para-crystalline minerals ?
- traces of minute clay particles, in crumpled lamella, tube and sphere, only perceptible on T.E. microscopy.

These data show the early products of weathering are rich in opal and non crystalline silica. They contain also some allophane, which is probably more siliceous and ferriferous than usually. The first shapes of minute clay particles appear, but very scarcely.

b. In the intermediate andosol (< 500 y. old), the weathering products represent 10-15% of soil. They show a great decrease in the opal content and the development of allophane and of micro-clay particles, as well a little of paracrystalline iron oxyhydroxide.

- The opal is only perceptible on the T.E. microscopy, under the forms of microdiscs and scarce altered diatom-skeletons.
- The allophane, identified by D.T.A., I.R. spectroscopy and oxalate or (2N) HCl dissolution curves, is predominant (~ 35-50%). It is more aluminous than in the top-soil, but remains probably ferriferous.
- The micro-clays become important (~ 30%). Their chemical composition is close of halloysite. But the T.E. microscopy shows mostly crumpled lamellar forms and some spherical clays, but very scarce tubes. These clays are ill-defined, poorly crystalline (X.R.D. at 4.50-4.45 Å and 2.52-2.50 Å ; I.R. spectrometry, shoulder 915 cm⁻¹ and band 1015-1035 cm⁻¹), and very hydrated.
- The iron location is indefinite ; one half could be a non crystalline hydroxide, or partially related to allophane ; other half is apparently a para-crystalline oxyhydroxide, or could be partially related to clay minerals.

c) In the andic brown paleo-soil (1000-1500 y. old), the weathering products represent 40-45% of soil. The clay fraction is predominant in the < 2 μm fraction, although the clay minerals remain poorly crystalline. In proportion, the allophane is less and the opal has almost disappeared. The iron oxyhydroxides remain still non crystalline or poorly crystalline.

- The chemical dissolution curves show : 1st very soluble products, composed of 5% allophane, 7% clay of halloysite composition, 2% non crystalline iron hydroxide and 5% para crystalline iron oxyhydroxide; 2nd less soluble material, composed at least of 15% clay of montmorillonite composition and 2-3% iron oxide.
- The opal amount, only perceptible on T.E.M., is probably < 1% ; it is under the forms of micro-discs (< 0.01 μm) and very scarce altered diatom skeletons. We remark some opal corns at the centre of hollow spheres of halloysite.

- The allophane is typically aluminous ($\text{Si}/\text{Al} \sim 0.5$).
 - The T.E.Microscopy shows micro-clay particles predominate over allophane. they are mostly spherical shapes and scarcely tubes, which characterize usually halloysite. X.R. diffractions and D.T.A. confirm it. But these diagrams, as also the I.R. spectroscopy, show poorly crystalline and very hydrated minerals, close of allophane. In addition, D.T.A., I.R. spectroscopy as well the crumpled lamella seen in T.E.M., suggest the presence of a few 2:1 clay minerals.
 - The iron position is indeterminate. The less soluble fraction of iron oxyhydroxide is clearly increasing. However, only traces of goethite are perceptible on X.R.D. and D.T.A. diagrams. Perhaps these oxyhydroxides are paracrystalline or related to some clay minerals ?
- A schematic diagram (fig. 6) summarizes the evolution of $< 2 \mu\text{m}$ fraction from top-soil downward to the paleo-soil.

2. Characteristics of spherical halloysite.

The determination of spherical micro-clays is difficult, because the mineralogical properties are imperfect and the chemical composition of $< 2 \mu\text{m}$ fractions is a mixture of allophane, clays and oxyhydroxides.

- a) Halloysite is strongly suggested by the following data ($n^\circ 2114$) :
- X.R.D. : broad ray at 10 \AA ; stable after oxalate dissolution ; moving to 7.6 \AA after 100°C heating ; but disappearing after 500°C heating ; no swelling effect of glycerol.
 - T.E.M. : spherical (and scarcely tubular) phyllites ; average width of one layer 10 \AA .
 - D.T.A. : clear endothermic peak near 540°C (in addition of 180°C endothermic and 925°C exothermic peaks).
 - I.R. spectroscopy : clear bands of 1:1 clay near 915 cm^{-1} , $1015\text{--}1030 \text{ cm}^{-1}$ and 1095 cm^{-1} ; but the strong hydration, of this mineral could mask the typical bands of 1:1 clay, between 3620 and 3690 cm^{-1} .

All diagrams show a poorly crystalline and very hydrated halloysite.

- b) The presence of 2:1 clay mineral, separately or interstratified with halloysite, is not evident on the X ray diffractograms, because it doesn't remain any ray between 10 and 14 \AA after heating at 500°C . However, this presence is suggested by the following data :
- T.E.M. : crumpled lamellar clays, similar to beidellite ;
 - D.T.A. : slight endothermic inflexion near 630°C ;
 - I.R. spectroscopy : wide bands between 3420 and 3550 cm^{-1} .
- But, no diagram shows clearly any 2:1 clay mineral.

- c) The chemical composition of $< 2 \mu\text{m}$ fraction, with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mol. ratio = 3.4, could not correspond to a mixture of allophane and halloysite only. It is confirmed by the analysis of curves of chemical dissolution, which reveals 3 successive phases, of allophane, halloysite and finally 2:1 clay composition. But this doesn't exclude the possibility of an incongruent dissolution of some complex clay edifice.

The presence of non crystalline silica or of opal, can partially explain the high silica content of $< 2 \mu\text{m}$ fraction. But the amount of "free" silica seems low, because I.R. spectroscopy doesn't show any characteristic band.

A part of iron, which is abundant in the $2 \mu\text{m}$ fraction, could come from the clay mineral themselves. The $\text{SiO}_2/\text{Fe}_2\text{O}_3$ mol. ratio is 2. A little part, which is very soluble, is probably non crystalline. But for the less soluble part, X.R.D. and D.T.A. diagrams show only traces of goethite. Therefore, an important part of iron could be related to the clay structure, as that has been observed elsewhere for some halloysites (WADA and MIZOTA, 1982 ; QUANTIN, HERBILLON et al., 1984). We proposed the hypothesis of an irregular 1:1 and ferriferous 2:1 clay interstratification, to explain the properties of these unusual clay minerals.

These data could be also compared with the observations of WADA and KAKUTO (1985) and WADA, YAMAUCHI et al. (1985), on a spherical and poorly crystalline halloysite, from Ecuadorian and Japanese soils. They called it "embryonic halloysite", for its intermediate properties between allophane and halloysite. But in this case, the clay contains also too much silica (and eventually iron) to have the normal formula of halloysite. To take into account this abnormal composition, WADA and KAKUTO proposed a structural formula of incomplete 2:1 clay mineral, intermediate between the 1:1 and the 2:1 clay structures.

In the present case, we propose the hypothesis of an irregular interstratification of halloysite and hisingerite, to take into account the probability of an important part of iron and a little of magnesium in the clay network. This imperfect mineral could be a transition between the spherical hisingerite (SHAYAN, 1983 ; QUANTIN, 1985) and the "classic" halloysite, which is observed in older soils.

3. Genesis of poorly crystalline spherical halloysite.

The previous observations have shown the spherical halloysite was growing straight and progressively from soil solutions, in some peculiar conditions, for instance : from the weathering products of basaltic glass, rich in silica, iron and magnesium ; to a pH near 7 ; through the progressive desilication of the former products and their enrichment in alumina.

In the top-soil, from fresh ash, the weathering of basaltic glass, releases quickly a great quantity of bases and of silica. The excess of silica in solution, contributes to form opal and ferruginous silica gels ; because of a lack of available alumina for the clay formation. However, a little of allophane, perhaps ferriferous, appears, as well the earlier and still very rare forms of minute clay particles ; some of which, spherical or tubular, look like halloysite.

Then progressively downward, to older and more weathered ash layers, opal is dissolving and contributes to form micro-clays. Indeed, we see the minute clays around or inside the voids of altered diatom-skeletons ; even, we can see some opal micro-discs in the center of

spherical clay particles. These opal corns could serve as nucleus for the rolling of clay layers. In addition, the clays are growing downward, as well the spherical forms, which are increasing simultaneously in proportion. This process is parallel with the progression of weathering and of the desilication-aluminisation process of the earlier weathering products.

The abundant formation of spherical clay, could be, after TOMURA, SHIBASAKI et al. (1985 a, 1985 b), the consequence of a slow crystallisation, in a high supersaturated solution in silica, alumina and other cations, and at a low temperature. This form is metastable.

The conditions of clay genesis, in the case of silica, and magnesium rich solutions, are not favourable to the formation of 1:1 clay minerals, but rather to 2:1 clays. However, the formation of spherical 10 Å clays, similar to halloysite, is predominant. But these clays are imperfect and poorly crystalline. Indeed, their chemical composition, as well their chemical and physical properties are intermediate between those ones of beidellite and halloysite. This fact suggests the formation of some composite and irregular edifices, made of 1:1 and 2:1 clay minerals, the former being predominant. This unusual formation could be due to the abnormal richness of soil solution and weathering products in silica, iron and magnesium.

This intermediate clay structure could be a transitional phase to halloysite. It is an "embryonic halloysite" (WADA and KAKUTO, 1985). With a longer time and a more advanced weathering process, we can expect the genesis of a well crystalline halloysite, as it has been observed many times in the several thousands years old soils.

CONCLUSION

The sequence of basaltic ash weathering in a soil of Ambrym, in correlation with the soil depth as well with the age of deposits, shows the following facts.

The early weathering products, at the top-soil level, are very rich in silica, iron and magnesium. There, are forming opal and a ferri-ferrous allophane, as soon as early minute clays appear.

The frequent top-soil rejuvenation by ash allows to maintain an intense weathering and to produce silica and bases rich solutions which are percolating downward. In addition, the slow dissolution of opal maintains the high supersaturation of soil solution and favours the clay genesis, especially a clay of a spherical form, which seems to be rolled around some opal micro-corns.

The spherical clays become predominant in the lower part of soil. Some of their properties are related to a 10 Å halloysite. But, their mineralogical properties are imperfect. No doubt, that is due to the soil solution environment, which is more favourable to the formation of beidellite than kaolinite minerals. The chemical composition of these spherical halloysites, which is more silica and iron-rich than a normal halloysite, as well their unusual physical and chemical properties,

suggest that they are some irregular, interstratified or composite, edifices of halloysite and iron-rich 2:1 layers.

The formation of spherical clay minerals is very quick : as soon as some hundred to one thousand years. These spherical clays could be a transitional and metastable phase, perhaps intermediate between hisingerite and halloysite.

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