

TRACE ELEMENT CONCENTRATION IN AMORPHOUS CLAYS OF VOLCANIC ASH SOILS IN OREGON*

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Abstract—Clay fractions in soils from a transect of the Mazama ash deposit (6600-yr-old) contained more than 80% amorphous material. Instrumental neutron activation analysis was used to compare the trace element composition of the soil clay with the unweathered volcanic glass. The clay fractions had only 10% as much Na as the volcanic glass. Conversely, the rare earth element concentrations were about three times greater and the transition metal concentrations were up to nine times greater in the clay than in the glass. The $< 2\mu$ size fraction therefore contained mostly weathering products rather than fine glass.

The abundances of Cr, Co, Sc, and Fe in the clay fraction decreased with depth. The Sc/Fe ratio was approximately 4×10^{-4} for both clay and the unweathered glass. The relationship between elemental concentration in clay and fine sand size separates from the same soil horizons indicated that the clay exists in association with the larger size particles, probably as coatings.

Dilute nitric acid removed about 80% of the rare earth elements La, Nd, Sm, Eu, Tb, Yb, and Lu from the clay. Deferration was necessary to remove Ce, a rare earth element that forms insoluble oxides upon oxidation to the Ce^{4+} state. The residue of the KOH dissolution treatment contained 2:1 layer silicates that may be derived from primary biotite.

INTRODUCTION

CLAY ($< 2\mu$ fraction) found in soils developed from Mazama pumiceous lapilli in Oregon contains about 80% amorphous material soluble in boiling NaOH (Chichester, Youngberg, and Harward, 1969). X-ray patterns of residues after treatment with boiling NaOH confirmed the presence of small amounts of a mixed suite of 2:1 layer type clay minerals in addition to amorphous clay. The clay exhibited moderate pH dependent charge, peculiar dispersive properties, a low temperature endotherm, and was largely amorphous to X-rays. However, the identification of the amorphous material as allophane could not be made due to the confounding effects of 2:1 phyllosilicates. Therefore, the nature of the amorphous component remains to be elucidated.

The possibility exists that the amorphous material is simply fine volcanic glass. This problem is amenable to solution with the techniques of instrumental neutron activation analysis (INAA). If the amorphous clay ($< 2\mu$) is fine glass produced by physical breakdown of larger particles, the trace element composition should be the same as that of the volcanic glass in larger size fractions. On the other hand, if the clay was produced by chemical weathering or alteration, a composition different from volcanic glass would be expected.

The trace element composition of the clay fraction is of interest from the standpoint of geochemistry and pedogenesis. Jenne (1968) has suggested that the hydrous oxides of iron and manganese may control the occurrence of heavy metals in natural waters, soils, and sediments. Free iron oxides can be intimately mixed with layer silicates (Roth *et al.*, 1966). The concentrations of the rare earth element, La, and the transition element, Sc, in soils (Kline *et al.*, 1969) and Fe, Mn, and Co in sediments (Moore, 1963) have been related to the clay content.

The objectives of this investigation were: (1) To determine if amorphous clays from soils in Mazama volcanic ejecta were either fine glass or a new phase; and (2) If a new phase exists, to evaluate the occurrence of trace elements in this phase.

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MATERIALS

Volcanic ash* soils were sampled at intervals along a transect extending for 450 km northeast of Crater Lake, Oregon, the source of Mazama ash (Fig. 1). The sample sites (described by Doak† and Chichester, 1967) were located on broad forested ridge tops or plateaus having less than 5% slope. The sites have been correlated with the Mazama volcanic ash deposit (Borchardt and Harward, 1971). Thickness of the Mazama ejecta was 135, 69, 85, 72, and 68 cm at the five sites, in order of increasing distance from the source. At the first two sites, the Mazama deposit consisted largely of pumiceous lapilli; at the other three sites it was fine sandy loam to silt loam pumiceous ash. At the five sites, weathering was little advanced and horizons were only weakly differentiated. The coarser soils are Orthents (too coarse for a cambic horizon) and the finer soils are Vitrandepts or Cryandepts (Soil Survey Staff, 1967).

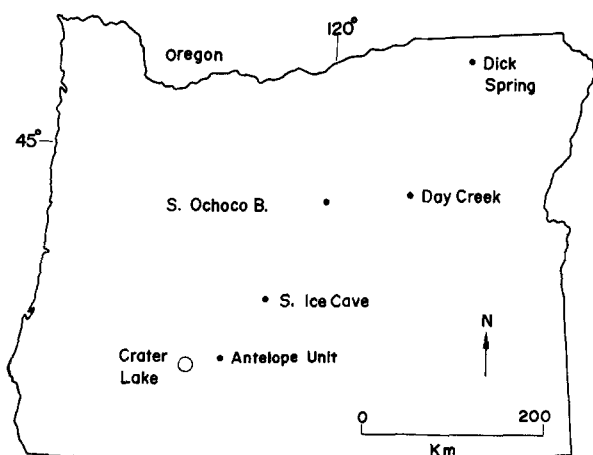


Fig. 1. Locations of the five transect soils derived from Mazama ash.

METHODS

Soil samples were treated with H_2O_2 acidified with dilute HNO_3 for removal of organic matter. Nitric acid was used to avoid the trace element contamination that might have occurred with other reagents. The soil was dispersed with 1% NH_4OH (Borchardt, 1970) and the clay (2–5% of the soil) was separated by centrifugation (Jackson, 1956). Certain clays received additional pretreatments

*The term "volcanic ash" is used loosely in reference to lapilli (> 4 mm) as well as ash (< 4 mm).

†Doak, W. H. (1969). A qualitative and quantitative characterization of porosity in volcanic ash. M.S. Thesis. Oregon State University, Corvallis.

remove exchangeable cations (1N NH_4NO_3), hydroxylated cations (0.05N HNO_3), free iron oxides (sodium dithionite–citrate–bicarbonate method given by Jackson, 1956), and amorphous material (boiling 0.5N KOH). Reagent grade NH_4OH , HNO_3 , and Specpure grade NH_4NO_3 were used to minimize trace element contamination. The treatments for removal of free iron and amorphous material were followed by 0.05N HNO_3 washing and high speed centrifugation.

Clay samples were washed free of excess salts, dried from acetone at 49°C, and weighed after oven drying at 110°C. 1 g clay samples were irradiated and analyzed for γ -ray activity (Borchardt, Harward, and Schmitt, 1971; Gordon *et al.*, 1968).

RESULTS AND DISCUSSION

Less than 2 μ glass

The hypothesis that the < 2 μ clay of the volcanic soils is fine grained volcanic glass was tested. Average trace element compositions, standard deviations, and coefficients of variation of clay from AC horizons and of unweathered glass samples separated from Mazama pumiceous lapilli (Borchardt, Harward and Schmitt, 1971) are compared in Table 1. Concentration ratios of clay to glass are shown in Table 2. The variation in the elemental concentrations within the five soil clays was less than expected in view of the large distances between sampling sites (up to 450 km). This suggests remarkably uniform weathering conditions throughout the transect.

In relation to Mazama volcanic glass, the soil clays had a much higher content of transition metals, particularly chromium and cobalt, and a much lower sodium content. The small amount of sodium remaining in the clay could be accounted for by traces of plagioclase found in clay fractions rather than by unleached volcanic glass (Chichester, 1967). The amorphous component of the Antelope AC horizon contained about 35% SiO_2 , whereas volcanic glass from Mt. Mazama has about 70% SiO_2 (Chichester, 1967). Available data, therefore, indicate the presence of phases other than volcanic glass in the clay fractions of soils from Mazama ash. The hypothesis that the clays consist of < 2 μ volcanic glass is rejected.

Trace element concentration as a function of depth

Four soil horizons were observed at the Day Creek site. Compositions of clay fractions from this soil vary significantly with depth (Fig. 2). The rare earth element (REE) content remains relatively uniform for all horizons with only a slight tendency to decrease near the soil surface. The transition metals were one and a half to three times

Table 1. Average analyses and coefficients of variation for volcanic glass and for untreated clays separated from AC horizons of the five Mazama transect soils

Element	Glass*			Clay			Clay/Glass
	Conc.†	± s	CV	Conc.	± s	CV	
Na%	3.44	0.17	5	0.31	0.08	25	0.1
Rb	50	9	18	40	11	28	0.8
Cs	3.9	0.8	20	5	1	29	1.3
Ba	660	80	12	690	260	38	1.0
La	21.5	2.2	10	60	23	37	2.9
Ce	44	3	6	140	32	23	3.3
Nd	29	5	18	99	50	51	3.4
Sm	5.0	0.4	9	15	3	21	3.0
Eu	0.89	0.09	10	2.5	0.6	26	2.8
Tb	0.83	0.15	18	2.5	0.7	28	3.0
Yb	3.5	0.7	21	9.3	1.5	17	2.6
Lu	0.56	0.08	14	1.3	0.4	28	2.3
Th	6.5	0.4	6	13.8	1.5	11	2.1
Hf	6.4	0.4	6	10.8	0.6	6	1.7
Ta	0.23	0.09	37	0.51	0.09	18	2.2
Co	2.6	0.4	14	18	2	10	6.7
Fe%	1.48	0.09	6	5.4	0.6	11	3.6
Sc	6.4	0.4	7	21.5	0.6	3	3.3
Cr	1.6	0.6	38	15	3	22	9.4

†Conc. = concentration, in ppm except for Na and Fe which are in %; ± s = standard deviation; CV = coefficient of variation, in %; Clay/Glass = concentration in clay divided by concentration in glass.

*Average composition of eight unweathered Mazama volcanic glass samples from Borchardt, Harward and Schmitt (1971).

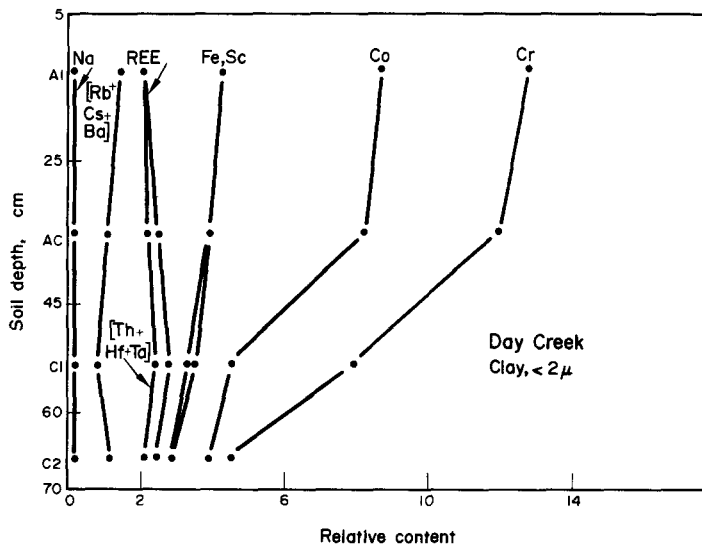


Fig. 2. Relationship between soil depth and elemental composition of soil clays separated from Mazama ash. Data normalized to reference Mazama samples. The factor for unweathered Mazama glass equals 1.0.

Table 2. Ratios to Mazama volcanic glass composition ($\times 100$) for clay fractions from AC horizons of the transect soils

Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr	
12	70	180	60	474	455	640	410	400	300	330	340	222	156	220	591	312	302	730	
Antelope Unit (5-28 cm)																			
South Ice Cave (5-31 cm)																			
10	70	80	100	262	308	250	294	270	270	260	210	204	177	270	686	339	342	1030	
South Ochocho Butte (18-45 cm)																			
7	80	130	110	219	262	260	268	240	230	230	190	185	164	170	648	361	342	960	
Day Creek (25-45 cm)																			
7	100	120	90	208	299	230	243	210	260	220	180	247	175	210	777	378	369	1210	
Dick Spring (22-50 cm)																			
7	120	140	170	303	324	330	316	290	450	270	230	207	169	230	665	425	316	780	
± 1	35	25	25	6	5	40	2	20	60	20	20	7	5	40	17	5	5	160	

* \pm = one average standard deviation for counting statistics of clay only (without considering the standard deviations of the glass analysis).

Table 3. Ratios to Mazama volcanic glass composition ($\times 100$) for Day Creek AC horizon clay receiving various pretreatments

Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr	
7	100	120	90	208	299	230	243	210	260	220	180	247	175	210	780	378	369	1210	
Control, dispersed with 1% NH ₄ OH																			
1N NH ₄ NO ₃ extracted																			
8	100	150	60	228	315	150	280	250	270	180	160	262	177	310	880	416	409	1120	
0.05N HNO ₃ extracted to remove hydroxylated cations																			
11	160	190	70	68	244	60	85	70	0	10	50	281	202	400	920	470	297	1340	
Dithionite-citrate-bicarbonate iron removal (DCB)																			
14	200	180	80	48	70	53	110	80	0	100	140	159	390	990	272	232	1340		
0.5N KOH + DCB for amorphous material removal																			
28	160	380	70	100	102	0	93	80	210	40	110	265	89	1010	1000	275	425	2410	
± 1	45	35	25	5	6	40	2	30	60	15	30	11	6	50	30	6	5	140	

* \pm = average standard deviation for counting statistics of clay only (without considering the standard deviations of the glass analysis).

more abundant in clay from upper horizons than in clay from the C horizons. Chromium enrichment in upper horizons was greater than that of cobalt.

Iron and scandium increased in conjunction with one another, reflecting their similar chemistry in this system. The Sc/Fe ratio for the clay and glassy fine sand (Borchardt and Harward, 1971) from each horizon was 4×10^{-4} . The depth relationships for the glassy fine sand fractions (Borchardt and Harward, 1971) were very similar to those for the clay fractions in Day Creek soil (Fig. 2). The untreated sand fractions in the upper soil horizons apparently were coated with clay containing relatively high amounts of Cr and Co and moderate amounts of Sc and Fe.

The significance of enrichment of transition metals in upper horizons can be explained by a theory proposed by Jenne (1968). He suggested that the transition metals are associated with and controlled by iron and manganese hydrous oxides in natural waters, soils and sediments. In these soils the $< 2\mu$ material may exist as coatings, probably as hydroxy compounds, on larger particles. The tendency for an element to accumulate in upper horizons of soils may be partly related to the solubility product of the hydroxide. For example, the mobility of chromium is so low that its migration is dependent upon the high oxidation states observed only in desert soils (Vinogradov, 1959).

Effects of chemical pretreatments

A sequence of chemical treatments was used to investigate the relative strengths of retention of trace elements within the clay fraction. The four classifications: hydroxylated cations, free iron oxides, amorphous material, and crystalline minerals are used largely as a matter of convenience. Saturation and exchange with 1N NH_4NO_3 showed that the elements analyzed either were not exchangeable or had already been removed during the prior dispersion and clay separation with 1% NH_4OH (Table 3). Analyses of the control sample and the NH_4NO_3 treated sample were thus considered as duplicates for comparison with other treatments.

With the exception of Ce, washing the Mazama soil clay samples with 0.05 N HNO_3 greatly reduced the amounts of the rare earth elements, La through Lu (Table 3). Significant amounts of HNO_3 insoluble Ce were removed by the reducing agent (dithionite) in the free iron oxide removal treatment (DCB) confirming the results of Robinson *et al.* (1958). Ce^{3+} is one of the few rare earth elements (REE) capable of attaining a higher oxidation state and forming very insoluble com-

pounds (Robinson *et al.*, 1958; Haskin *et al.*, 1966).

Boiling 0.5N KOH followed by deferation dissolved 82% of the clay from the Day Creek AC horizon. The abundances of Na, Cs, Ta, Sc, and Cr were highest in crystalline minerals surviving the treatment (Table 3). The amount of sodium in the residue indicated the treatment was probably concentrating plagioclase.

The changes in chemical composition were partitioned to reflect the weight loss undergone by the clay sample during dissolution treatments (Table 4). For example, the Day Creek KOH treated sample residue had 100 units of La (Table 3) but the residue weight was only 18% of the original clay weight. Thus, only 18 units of La occurred in crystalline minerals, while 218 units (average of NH_4OH and NH_4NO_3 treated samples) were present in the original sample. The crystalline minerals had 8% of the total La, the remainder being removed by HNO_3 , DCB, or KOH. Negative values obtained as a result of large analytical error due to counting statistics were set equal to zero.

The alkali elements tended to remain with the more resistant fractions, while the rare earth elements were removed more easily (Table 4). The table clearly shows the insolubility of cerium compared to the other REE which were easily removed with dilute nitric acid. The REE are probably not included in the structures of the amorphous or crystalline silicates of Day Creek soil clay.

The relationship between Sc and Fe was of theoretical interest because these elements have similar chemical properties and Sc/Fe ratios seem to be constant throughout the volcanic ash profile (Borchardt and Harward, 1971). HNO_3 removed Sc but not Fe (Table 4). Half of the Fe and Sc was removed from clay after the iron removal treatment. The amorphous material (KOH + DCB soluble fraction) had a Sc/Fe ratio of 2.8×10^{-4} . On the other hand, the crystalline minerals in the residue had a Sc/Fe ratio of 6.7×10^{-4} . Sc^{3+} (radius = 0.81 Å) should enter Fe^{2+} (radius = 0.74 Å) rather than Fe^{3+} (radius = 0.64 Å) positions. Since Sc-O bonds are more ionic than Fe-O bonds, this may also aid in capture of Sc in Fe^{2+} positions (Taylor, 1965). Fe associated with the amorphous fraction is probably in the 3+ oxidation state, since these are all well drained soils. Thus, the low Sc/Fe ratios for the fraction associated with amorphous Si and Al would be consistent with pedogenic formation of this amorphous component.

Origin of 2:1 layer silicates

The synthesis of 2:1 layer silicates from soil

Table 4. Trace element allocation to the chemical phases present in Day Creek clay fractions

Phase*	% of untreated sample	Percentage of untreated concentration																		
		Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
Hyd	5.2	0	0	0	11	71	25	70	70	67	86	95	63	0	0	0	0	0	27	0
FeOx	16.9	0	0	0	5	12	57	1	15	0	0	1	0	57	30	0	7	46	26	10
Amor	59.7	32	71	49	67	9	12	29	9	27	0	0	25	24	61	29	71	41	27	52
Crys	18.2	68	29	51	17	8	6	0	6	6	14	4	12	9	9	71	22	13	20	38
Day Creek AC																				

*Hyd = hydroxylated or organic matter complexed cations (0.05N HNO₃ soluble fraction); FeOx = free iron oxides (dithionite-citrate-bicarbonate soluble fraction (DCB)); Amor = amorphous material soluble in 0.5N KOH + DCB following the first iron removal; Crys = crystalline material resistant to the treatments above.

solution has been proposed for soils developed from coarse Mazama pumice (Chichester *et al.*, 1969). Perhaps an origin from primary mica should also be considered. Minute amounts of biotite in silt fractions of Mazama pumice were observed with the aid of a light microscope. This biotite must be considered part of the soil parent material. Other sources of primary biotite must not be overlooked. The relatively high Sc/Fe ratios in the crystalline residue would be predicted for biotite containing considerable Fe²⁺. Biotite may be the precursor of the 14 Å 2:1 layer silicate found in the residue of the KOH boiling treatment.

Only 2% clay was found in the Day Creek AC horizon (Borchardt, 1970, p. 115) and since only 20% of this survived the KOH boiling treatment, the content of 2:1 layer silicates was less than 0.5% of the Day Creek soil sample. This was representative of the quantity of layer silicates found for other soils derived from Mazama ash. Certainly, the synthesis of 2:1 layer silicates from solution has not been a major reaction in Mazama volcanic ash during the past 6600 yr of soil formation. The transformation of primary biotite to vermiculite and chlorite intergrades remains a possibility for the origin of 2:1 layer silicate clays developed in Mazama ash.

CONCLUSIONS

(1) Clay fractions of soils developed from Mazama ash were not < 2 μ volcanic glass. The amorphous clays were weathering products containing large amounts of hydrous silica, aluminum, and iron oxides occurring as colloidal coatings on larger particles of volcanic glass.

(2) Rare earth element (REE) abundances in the clay fractions were about three times the amounts in unweathered volcanic glass. Sodium in clays was only 10% of the value for glass while the transition metals were as much as nine times higher in clay than in glass. These elemental accumulations were remarkably similar for clays from five soils along a 450 km transect of the Mazama fallout area.

(3) Abundances of Cr and Co, as well as Fe and Sc in the clay fractions decreased with depth in a typical soil developed in Mazama ash.

(4) The amorphous material removed by boiling KOH was low in many trace elements, particularly the REE.

Résumé— Les fractions argileuses des sols provenant d'un transect du dépôt de cendres de Mazama (âge: 6600 ans) contiennent plus de 80% de matériau amorphe. L'analyse par activation neutronique a été utilisée pour comparer les compositions en éléments traces de l'argile de sol et du verre volcanique non altéré. La teneur en Na des fractions argileuses n'atteint seulement que 10% de celle du verre

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volcanique. Par contre, dans l'argile, les concentrations en éléments de la série des terres rares sont environ trois fois plus grandes que dans le verre, et les concentrations en métaux de transition, jusqu'à neuf fois plus grandes que dans le verre. Ainsi, la fraction inférieure à 2μ contient essentiellement des produits d'altération plutôt que du verre finement divisé.

Les teneurs de la fraction argileuse en Cr, Co, Sc et Fe diminuent avec la profondeur. Le rapport Sc/Fe est environ 4×10^{-4} , à la fois pour l'argile et le verre non altéré. La comparaison entre les concentrations en éléments chimiques dans les fractions argile et dans les fractions sable fin provenant des mêmes horizons de sol montre que l'argile existe en association avec des particules de plus grande taille, probablement sous forme de revêtement.

L'acide nitrique dilué fait disparaître de l'argile environ 80% des éléments de la série des terres rares, La, Nd, Sm, Eu, Tb, Yb et Lu. La déferrification est nécessaire pour enlever Ce, un lanthanide qui forme des oxydes insolubles par oxydation à l'état Ce^{4+} . Le résidu du traitement de dissolution par KOH contient des phyllosilicates 2:1 qui peuvent éventuellement provenir de la biotite primaire.

Kurzreferat—Tonfraktionen in Böden aus einer Durchschneidung des Mazama-Aschelager (6600 Jahre alt) enthielten mehr als 80% amorphes Material. Es wurde Neutronenaktivierungsanalyse verwendet zum Vergleich der Spurenelementzusammensetzung des Bodentones mit unverwittertem, vulkanischem Glas. Die Tonfraktionen wiesen nur 10% des Na-Gehaltes des vulkanischen Glases auf. Umgekehrt waren die Konzentrationen an seltenen Erden etwa dreimal so hoch und die Konzentrationen an Übergangsmetallen waren bis zu neunmal grösser im Ton als im Glas. Die Fraktion $< 2\mu$ Grösse enthielt daher in erster Linie Verwitterungsprodukte eher als feines Glas.

Die grossen Mengen von Cr, Co, Sc und Fe in den Tonfraktion nahmen mit der Tiefe ab. Des Sc/Fe Verhältnis war ungefähr 4×10^{-4} sowohl für Ton als auch für unverwittertes Glas. Das Verhältnis zwischen Elementkonzentrationen in Ton- und Feinsandabscheidungen aus den gleichen Bodenniveaus zeigt an, dass der Ton in Verbindung mit Teilchen höherer Grössenordnung vorhanden ist, vermutlich als Belag.

Verdünnte Salpetersäure entfernte etwa 80% der seltenen Erden La, Nd, Sm, Eu, Tb, Yb und Lu aus dem Ton. Enteisung war erforderlich zur Entfernung des Ce, eines Elements aus den seltenen Erden, das bei der Oxydation unlösliche Oxyde zur Ce^{4+} Stufe bildet. Der Überrest nach der Lösungsbehandlung mit KOH enthielt 2:1 Schichtsilikate, die aus primärem Biotit entstanden sein könnten.

Резюме — Глинистые фракции почв из разреза пепловой залежи Мазама (возраст 6600 лет) содержат более 80% аморфного вещества. Для сравнения содержания рассеянных элементов в глинистых почвах и в невыветрелом вулканическом стекле использовался инструментальный нейтронно-активационный анализ. Глинистые фракции содержали лишь 10% Na от его количества в вулканическом стекле. Напротив, концентрация редкоземельных элементов в глинистых фракциях примерно в 3 раза, а концентрация переходных металлов до 9 раз больше, чем в вулканическом стекле. Фракция $< 2\mu$ мк содержала больше продуктов выветривания, чем тонкодисперсное стекло.

Содержание Cr, Co, Sc и Fe в глинистой фракции уменьшается с глубиной; Sc/Fe составляет примерно 4×10^{-4} как в глине, так и в невыветрелом стекле. Соотношение между концентрацией элементов в глине и размерами частиц тонкого песка, выделенного из тех же почвенных горизонтов, указывает на то, что глина ассоциируется с частицами большего размера, вероятно, в виде пленок.

При обработке разбавленной азотной кислотой из глины удалялось около 80% редкоземельных элементов (La, Nd, Sm, Eu, Tb, Yb, и Lu). Для удаления Ce, образующего нерастворимые окислы при окислении до Ce^{4+} , необходимо освобождение от железа. Остаток после обработки KOH содержал слоистые силикаты типа 2:1, которые могут быть производными первичного биотита.