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The weathering of basalt and relative mobilities of the major elements at Belbex, France

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Abstract—A basalt and its weathered profile have been analysed for major elements. Graphical examination shows Al, Fe and Ti to have been essentially immobile. Determining mobility sequences for this deposit is complicated by the long pedogenetic history of the area. Three different sequences are presented, two for different stages of weathering integrated over time, and one that reflects the weathering regime of the present day.

INTRODUCTION

NO UNIQUE mobility sequence of the elements during weathering exists, though as TARDY (1969) points out in a thorough search of the literature, there is a great similarity between many of the sequences proposed. The major factors normally stressed as determining the sequence are: (a) the nature of the parent material; (b) the nature of newly formed phases; and (c) the inherent solubility of the elements (e.g. KARPOFF, 1973, pp. 58–59). Three equally important factors, rarely stressed, are the size of the system, the stage of weathering, and the ambient conditions in the system and its surroundings.

A sequence such as POLYNOV'S (1973):

$$\mathrm{Ca} > \mathrm{Na} > \mathrm{Mg} > \mathrm{K} > \mathrm{Si} > \mathrm{Fe} > \mathrm{Al}$$

and the similar Goldschmidt-Mason scheme (MASON, 1966) are strictly applicable only on global or perhaps continental scales. On smaller scales, for example on that of the soil profile considered here, different sequences can be expected. The behaviour of Al illustrates this. Though relatively immobile in Polynov's scheme, in podzolic soils, Al moves readily from A to B horizons.

As regards the stage of weathering being important in determining the relative mobilities of elements, it should be obvious that the elements contained in the most easily weathered minerals will be released first, those in less easily weathered minerals, later. In the case of elements with a low inherent solubility, this will not affect their mobilities, other things being equal; but with more mobile elements, changes in the sequence may be quite marked (POLYNOV, 1945). Many published studies of the relative mobilities of elements hide this effect of stage, by determining a sequence from a comparison of the most weathered material with parent rock (e.g. JOHNSON *et al.*, 1968). In effect such studies result in an integration over time, of all changes that have taken place between the beginning and end points.

The effect of ambient conditions becomes most critical for the smaller scale systems. Here is where the greatest variety is found. For example, at the scale of the soil profile the geochemical environment remains ill-defined. Yet PEDRO (1968) claims four chemically distinguishable soil-forming environments on the earth, while GAUCHER (1977) recognises at least ten. Soils that have developed on landscapes stable for many thousands of years, particularly those in areas undisrupted by recent glaciations, tectonism or volcanism, are likely to have weathered under more than one pedogenic regime. Different mobility sequences are appropriate to different regimes, and again schemes worked out by comparing least weathered with most weathered materials in such areas, will result in an integration of the effects of more than one regime.

These points are illustrated below in terms of the weathering of basalt and its overlying soil at Belbex.

GEOLOGICAL BACKGROUND

Belbex, in the Cantal, at the southern end of the Massif Central (Fig. 1) is dominated by the remains of the largest European Cenozoic volcano, a stratovolcano active from 21 to 3.8 Myr ago (BELLON *et al.*, 1972). Near the city of Aurillac, on the southwest flank of the volcano, flows of alkali olivine basalt of Pontian age, are found.

Two such flows, on the eastern side of the city at Puy Courny, have been dated at 7.3 ± 0.4 Myr and 6.5 ± 0.1 Myr respectively (GILBERT, 1972). The lower flow also outcrops at Belbex, 2 km west of Aurillac. Emplacement here was in a paleovalley cut into Stampian marls. Later erosion produced an inversion of relief so that the basalt now forms a small butte.

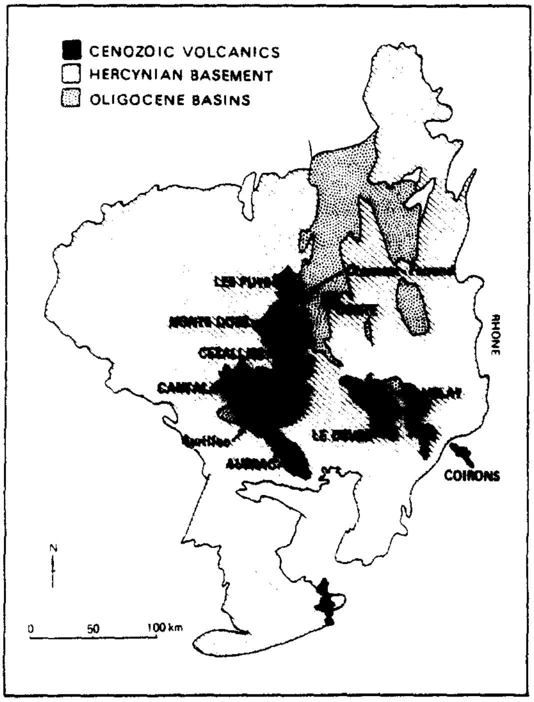


Fig. 1. Generalised geology of the Massif Central, France. The Belbex basalt outcrops 2 km west of Aurillac.

THE BASALT AND ITS WEATHERED PROFILE

The Belbex basalt is alkaline in nature and contains phenocrysts of olivine in a groundmass of clinopyroxene (salite), labradorite, titaniferous magnetite and glass. Within the glass, small needles of apatite occur. Except for the absence of modal feldspathoid, the rock displays the characteristics of a basanite.

The profile of alteration from bedrock to soil can be divided into six horizons on the basis of macroscopic features visible in the field. (Fig. 2). The pedochemical environment of the present day is one of brunification (GAUCHER, 1977; DUCHAFOUR, 1977, Chap. 9). An earlier pedochemical regime is indicated by horizon 5 (Fig. 2). Rubefaction, characteristic of a hotter climate than the current humid, temperate one is displayed there. That a hotter climate prevailed in this part of Europe, in Tertiary times is attested to by several studies (e.g. COINCON *et al.*, 1975).

EXPERIMENTAL RESULTS

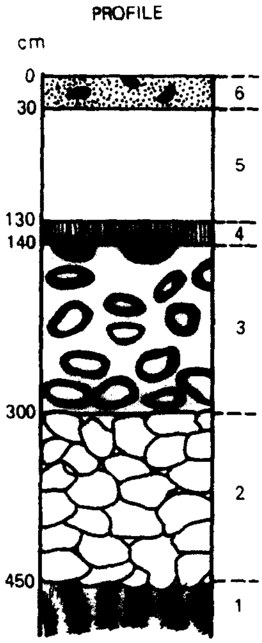
A description of the samples is given in the Appendix. Bulk chemical analyses were performed by XRF, individual phases were analysed by microprobe and clay mineralogy was determined by diffraction techniques.

Chemistry

Bulk analyses are given in Table 1. In terms of the triangular projection used by CHESWORTH (1973b): the trend of alteration, as expected, is clearly towards residua relatively enriched in SiO_2, Al_2O_3, and Fe_2O_3 and relatively impoverished in CaO, MgO, K_2O and Na_2O (Fig. 3). The behaviour of the accumulating components is more clearly seen in Fig. 4. On weathering, the material moves towards the base of the tetrahedron. Once the spheroids are completely disintegrated, beginning at level 4, there is a marked enrichment of SiO_2 in the residuum relative to Al_2O_3 and Fe_2O_3.

Mineralogy

Compositions of unaltered phases in the bedrock are shown, in Table 2. The sequence of breakdown of these phases, determined from observations on thin sections is: (1) glass; (2) olivine; (3) clinopyroxene; (4) plagioclase. In horizons 4, 5 and 6, allochthonous phases of quartz and



HORIZON DESCRIPTIONS

6	Recent soil (Brun Andique), polyhedric, silty sand texture. Allochthonous phase (Chert)
5	Reddish zone of alteration, saprolitic, lacks spheroids, polyhedric, clay-silt texture. Abrupt boundary at top.
4	Mn stained horizon
3	Intensely altered basalt. Alteration is spheroidal, with a weathered rim on each spheroid increasing in thickness from bottom to top of horizon. At upper boundary spheroids are altered completely to the core. Spheroids separated by a disintegrated matrix.
2	Compact, hard, basalt, unweathered irregular spheroidal structure (rapid chilling) no matrix between spheroids. Irregular deposits and veins of calcite.
1	Unaltered, hard, basalt.

Fig. 2. The weathered profile at Belbex.

Table 1. Bulk chemical analyses of Belbex basalt and its weathered products

	Coherent samples												Non-coherent samples		
	Fresh basalt (level 1)			Spheroid (level 2)		Spheroid cores (level 3)			Spheroid envelopes (level 3)				(level 4)*	(level 5)†	(level 6)‡
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO_2	45.07	45.26	45.32	44.79	45.09	42.31	41.71	41.23	43.31	40.63	39.17	35.69	50.25	54.91	53.40
Al_2O_3	12.92	12.91	13.06	14.09	14.94	14.78	14.95	15.20	17.32	19.05	21.51	22.61	21.45	21.06	19.06
Fe_2O_3	12.66	11.85	11.41	13.38	13.47	13.68	13.92	14.42	15.84	20.08	21.85	20.62	19.94	16.22	17.20
MgO	9.70	9.61	8.90	8.93	7.55	8.87	8.21	7.71	5.76	4.26	3.94	3.18	0.91	0.64	2.55
CaO	12.12	12.14	12.72	13.16	12.96	12.48	12.32	12.68	12.35	8.59	7.09	7.36	0.87	0.72	1.92
Na_2O	2.03	2.26	2.57	1.18	1.41	1.50	1.29	1.17	0.76	0.24	0.19	0.18	0.03	0.00	0.33
K_2O	1.73	1.89	2.09	0.86	0.91	0.56	0.73	0.44	0.31	0.26	0.16	0.16	0.46	0.73	1.06
TiO_2	2.96	2.84	2.75	3.18	3.42	3.40	3.49	3.68	4.02	5.15	5.52	5.90	4.89	5.11	3.91
MnO	0.21	0.24	0.19	0.22	0.17	0.11	0.10	0.14	0.32	0.19	0.15	0.11	0.58	0.24	0.37
P_2O_5	0.65	1.00	0.98	0.11	0.16	2.31	3.28	3.34	0.31	1.58	0.23	4.19	0.26	0.16	0.37
L.O.I.	2.94	3.84	3.62	2.72	5.70	6.83	7.31	8.12	18.52	12.55	13.90	n.d.	12.47	11.23	14.01

* Mn-stained layer.
† Zone of rubefaction.
‡ Present day soil, (solum).

chert appear. The clay minerals produced during weathering are smectite, halloysite, hematite/goethite and an amorphous phase (DEJOU and CHESWORTH, 1979).

INTERPRETATION

In a thermodynamic sense, weathering systems are invariably open. Two general models may be considered, the distinction being whether or not there are any components that can be classed as immobile:

Model 1:

1 or more components immobile ⟶ ⟵ 1 or more components added and/or subtracted

Model 2:

No components immobile ⟶ ⟵ All components added or subtracted

The principal agent of mobilisation is water, which, reacting with minerals in the weathering zone to produce an aqueous solution, moves downwards in the gravitational field and modifies the composition of a given system by leaching. Since all components in the soil are soluble to some degree, *model 2* is the only one that is rigorously tenable. However, weathered profiles generally have only short existences in terms of the geological time scale so that during the lifetime of a deposit, components with extremely low aqueous solubilities will not be significantly mobilised. In such cases *model 1* is appropriate.

Several methods are used to determine the relative mobilities of elements in systems of this kind. For example HARRIS and ADAMS (1966) contrast soil with parent rock; an internal standard of comparison may be used (Al in GOLDICH, 1938, quartz in LELONG and SOUCHIER, 1979); or parent material may be compared with soil water (e.g. TARDY, 1969). Each has its usefulness though as the following account shows, a complex pedogenetic history presents problems, especially for the first.

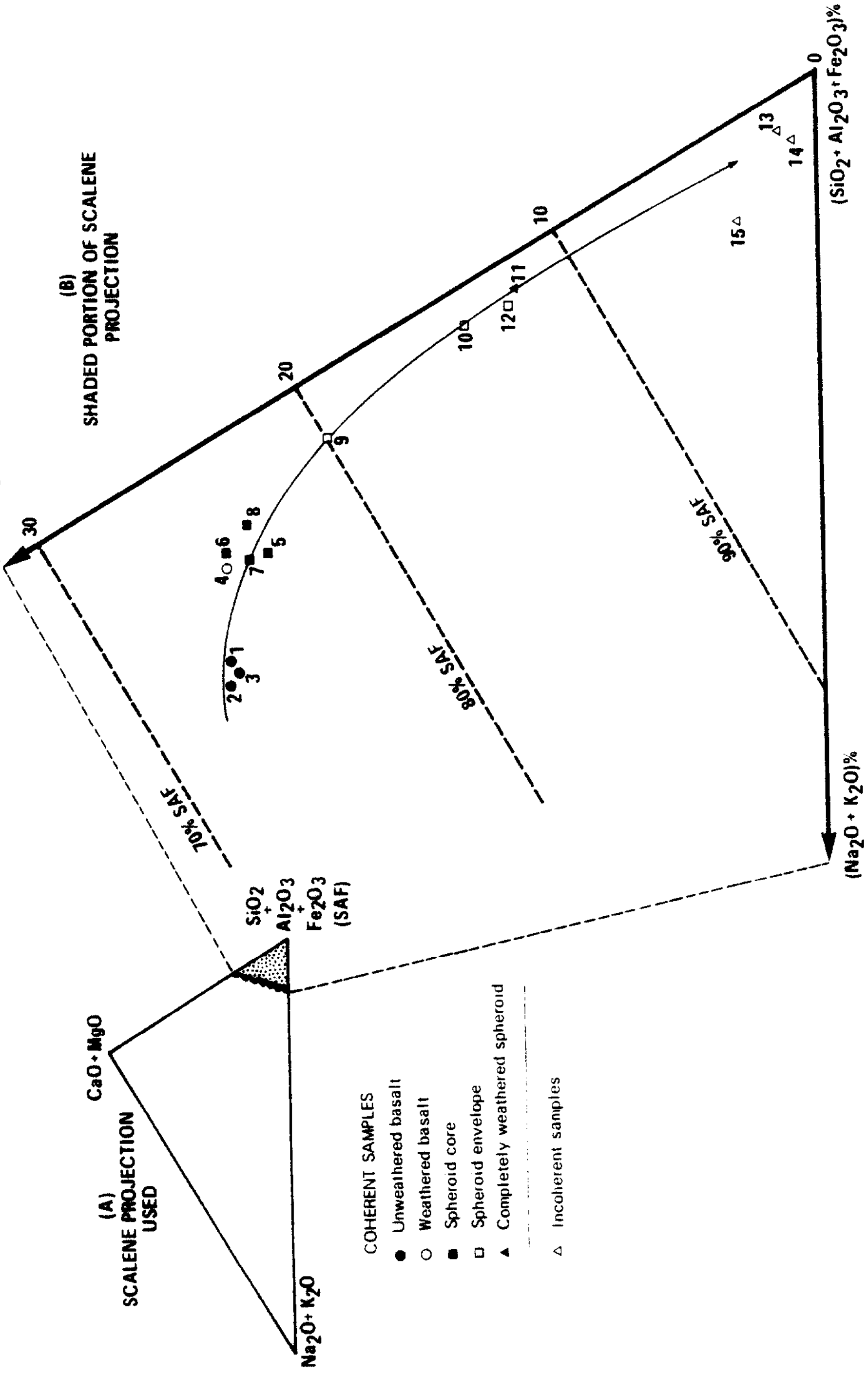


Fig. 3. The overall geochemical trend from unaltered basalt to soil at Belbex.

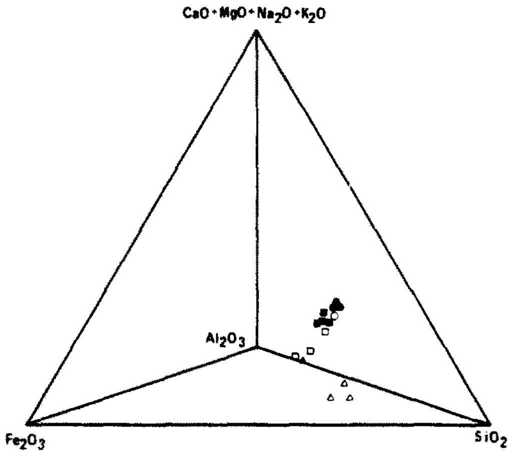


Fig. 4. Tetrahedral plot to show the trend of Fig. 3 in more detail.

A CHECK FOR IMMOBILE COMPONENTS

The easiest way to check for immobility amongst components is to determine intercomponental ratios. In the present case these show that the ratio Al:Fe:Ti is sensibly constant (Fig. 5). One, two or all therefore may be used as internal standards against which to measure the comings and goings of other components.

Table 2. Composition of unaltered phases in the bedrock

1. Olivine (av. of 4)	Si	5.94
	Fe	2.43
	Mg	9.62
	O	24
2. Clinopyroxene (av. of 5)	Si	6.88
	Al	1.30
	Ti	0.21
	Fe	0.92
	Mg	2.71
	Ca	3.14
	O	24
3. Plagioclase (av. of 5)	Si	7.09
	Al	4.96
	Fe	0.08
	Ca	1.78
	Na	0.85
	K	0.07
	O	24
4. Opaques (av. of 2)	Al	1.29
	Ti	3.50
	Fe	13.15
	Mg	1.53
	O	24
5. Glass (av. of 3)	SiO_2	57.06
	Al_2O_3	23.22
	ZrO_2	0.01
	TiO_2	1.01
	FeO	4.42
	MnO	0.12
	CaO	1.39
	Na_2O	4.80
	K_2O	7.78
	P_2O_5	0.01
	Cl	0.17
		100

Analyses 1–4 are expressed in atomic proportions with respect to 24 oxygens. Analysis 5 is in weight percent.

It is possible, of course, for components to maintain a constant ratio with each other if they leave or enter a system at rates proportional to their concentrations in the parent material. Physical processes might accomplish this rather easily, (e.g. by erosion), but the chances of it happening chemically, with elements as distinct as Al, Fe and Ti, must be accorded a very low probability.

It is interesting to note that GOLDICH (1938) studying the Morton gneiss, used Al as an internal standard. However, his analyses (Fig. 5) come closer to showing a relatively constant Fe_2O_3/TiO_2 ratio implying virtual immobility for these two components, and implying equally a loss of Al during weathering. Thus Al in this case was a poor standard of comparison.

WEATHERING TRENDS

Since Al_2O_3, Fe_2O_3 and TiO_2 can be assumed immobile, their sum can be taken as a measure of degree of alteration and the behaviour of other components can be contrasted with them.

In looking for trends it is convenient to divide the samples into two groups, coherent and non-coherent. By coherent, we mean those materials such as bedrock, spheroid cores, and envelopes of spheroids, that have notable coherency and retain some part at least, of the original rock structure. Thus on visual evidence alone, a genetic relation between samples can be assumed. The non-coherent samples are those that are loose and particulate and which on structural evidence alone cannot be unequivocally shown to have developed solely from the underlying basalt.

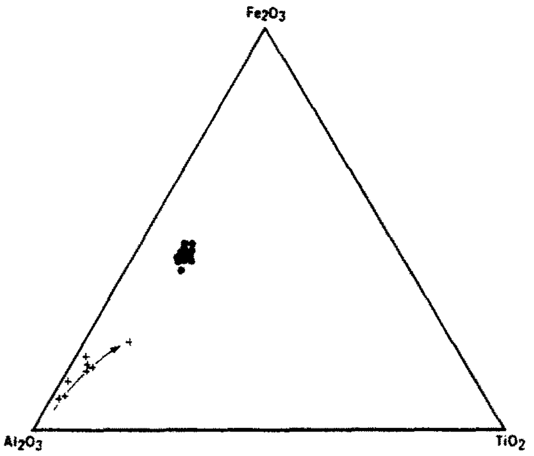


Fig. 5. All samples (dots) plotted in triangular coordinates to show the constancy of mutual ratios between Al_2O_3, Fe_2O_3 and TiO_2. The crosses represent analyses of the Morton gneiss and its weathered products. The arrow indicates the weathering trend which can be interpreted to show a loss of Al relative to Fe and Ti. GOLDICH'S (1938) choice of Al as an internal standard is hard to justify.

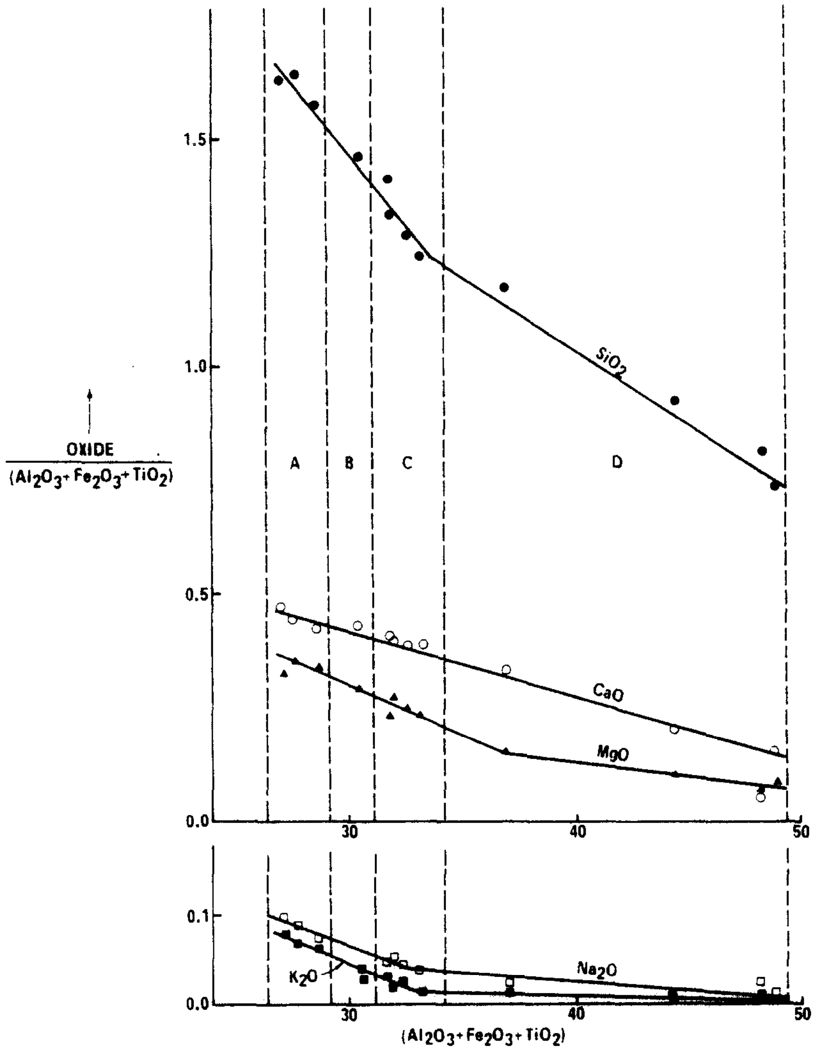


Fig. 6. Rates of loss of major oxides with respect to $Al_2O_3 + Fe_2O_3 + TiO_2$ used here as an index of weathering. (A) unweathered basalt; (B) weathered basalt; (C) spheriod core; (D) spheroid envelope and completely weathered spheroid.

Coherent samples

Major oxide components, normalised with respect to $Al_2O_3 + Fe_2O_3 + TiO_2$ are plotted against $Al_2O_3 + Fe_2O_3 + TiO_2$ (Fig. 6). The linear relationship, of course, is built in (CHAYES, 1960). However, the rate of decrease of the normalised values on the graphs is proportional to the rate of loss of a component, given the sum $Al_2O_3 + Fe_2O_3 + TiO_2$ as a measure of the degree of alteration. Noteworthy breaks in slope occur for SiO_2, MgO, Na_2O and K_2O, implying a slowdown in the rates of loss of these components when the envelope stage of alteration is reached.

Non-coherent samples

Bulk samples of the manganese stained layer, the reddish zone of alteration and soil, again show a virtual constancy in Al_2O_3–Fe_2O_3–TiO_2 ratios, so that

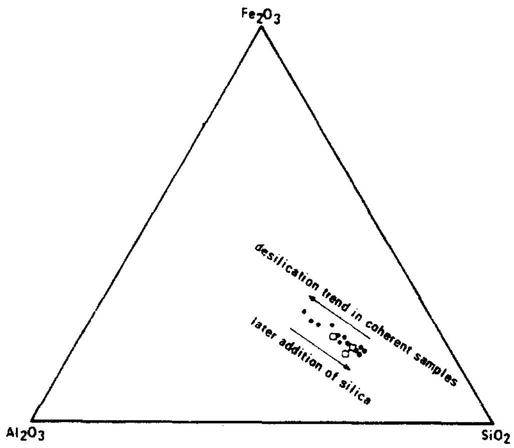


Fig. 7. Desilication of coherent samples (dots), and resilication of incoherent samples (squares).

Belbex basalt can still be claimed as a parent material, (Fig. 3). However, a marked increase in SiO_2 to the system is obvious (Fig. 7) indicating an addition of SiO_2 to the system in the upper levels of the profile. Later, this will be related to the geomorphological history of the area.

DISCUSSION

The behaviour of the weathering system at Belbex is in accordance with model 1. Specifically it involved two steps:

Al_2O_3, Fe_2O_3 → Step 1: SiO_2, MgO, CaO, Na_2O, K_2O subtracted from

TiO_2 coherent samples

immobile ← Step 2: SiO_2 added to noncoherent samples

Data from the coherent materials allows us to deduce an order of mobility for major components. Before the weathered material has altered to the stage of a separable envelope on the spheroids, the slopes of the curves in Fig. 6 indicated the following order of decreasing mobility:

$$Si > K, Na, Mg > Ca > Fe, Al, Ti.$$

At the envelope stage the rates of loss of Si, Mg, Na and K decrease, and the mobility sequence changes slightly:

$$Si > Ca > K, Na, Mg > Fe, Al, Ti.$$

The mobility sequences can be explained in terms of the factors emphasized by KARPOFF (1973). First the nature of the parent material: fresh basalt at Belbex contains two easily weathered phases (glass and olivine) and two that are weathered less easily (pyroxene and plagioclase). While glass and olivine are still present, they release their components relatively rapidly giving rise to the initial high mobilities of Si, Mg, Na and K indicated by the steeper parts of the curves in Fig. 6. When these phases are exhausted the rate of release of Si, Mg, Na and K is governed by the slower breakdown of the other phases. Ca, the bulk of which is to be found in pyroxene and plagioclase is released and mobilised at a steady rate throughout. Secondly the effect of the secondary phases becomes clear at the envelope stage. Smectite and halloysite form to fix and 'slow down' some of the Si, Mg, Na, K and Ca. Thirdly, the effect of an inherently low solubility for a component is most obvious in the cases of Al, Fe and Ti which precipitate virtually on release from primary phases, partly in amorphous, but also in crystalline forms, such as hematite, goethite and the clay minerals.

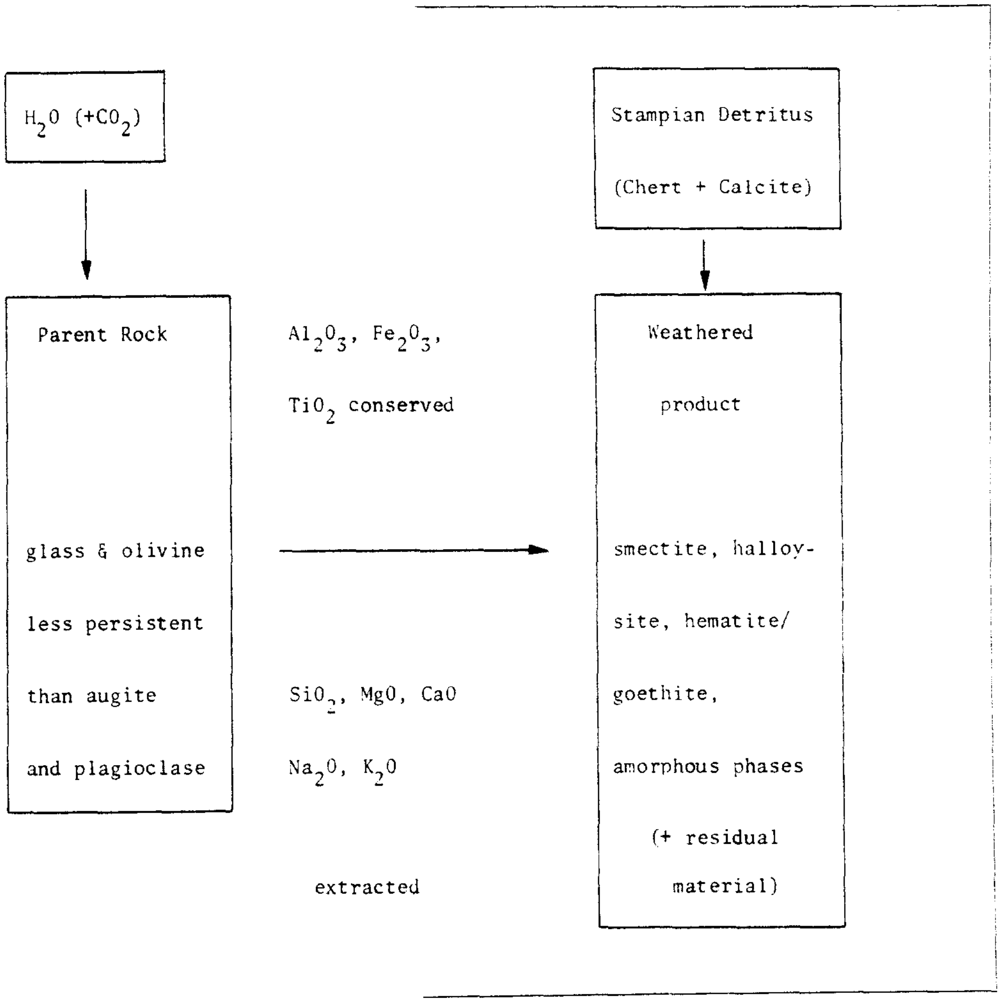
An important feature of mobility sequences of the kind given above, is that they represent an integration of weathering changes over time. They may not therefore be representative of the present day pedogenic regime. This must be true of most studies of geochemical mobilities in soil, certainly of soils found on landscapes such as that at Belbex which predate the late Cenozoic glaciations.

The study by HARRIS and ADAMS (1966) is a case in point. Their Georgia profiles were collected in an area covered by acrisols, relatively ancient soils, that were probably preceded by podzols. To what extent the mobility sequence they propose relates to the present environment is impossible to say from the evidence published. Furthermore, their technique of comparing soil with bedrock is only valid if it can be shown that physical processes have not intervened to modify the composition of the weathering system. At Belbex this was patently not the case, and although dramatic geomorphological changes may not have occurred on the Georgia landscapes studied, aeolian additions or subtractions to a soil are common.

At Belbex the basalt has weathered under at least two pedogenic regimes, the present one of brunification and an earlier one of rubefaction. The latter produced the reddish zone (level 5) which then became the parent material of the present day soil. A present day (or 'instantaneous' as opposed to integrated) mobility sequence can be estimated by comparing the composition of the reddish zone with the composition of waters draining soils formed on basic rocks in the Massif Central (TARDY, 1969, Table 38). Omitting Ti (not determined by Tardy) the sequence is $Na > Ca > Mg > K > Si > Fe > Al$ which is almost identical to POLYNOV'S (1937) global sequence. The notable change between this and the two earlier sequences is in the position of Si, and is a reflection of the addition of forms of SiO_2 of low solubility to the weathered basalt. This contamination of the profile by SiO_2 was revealed geochemically in Fig. 7. It is explainable on the basis of the complex geomorphological history of the region. The basalt was originally emplaced in a valley cut into Stampian marls. In this situation, the upper surface of the flow would be in a position to receive detritus derived from the valley sides. That this happened is indicated by the presence of brownish fragments of chert in the upper, non-coherent part of the Belbex profile, identical to chert found in the Stampian marls. The carbonate component of the added marls would tend to be removed by CO_2-charged leaching waters and would only reprecipitate when the pH had increased to about 7.8 (KRUMBEIN and GARRELS, 1952). This appears to have happened in the lower part of the profile where calcite is found on rock surfaces and in cracks in spheroids.

CONCLUSIONS

The final version of model 1 that can be advanced for the Belbex deposit is shown diagrammatically.



The basalt weathered over a period of time which encompassed at least two different pedogenic regimes, an early one of rubefaction and a later of brunification.

At the present day the order of mobility of major components is:

Na > Ca > Mg > K > Si > Fe > Al.

This, which can be looked upon as an instantaneous order, compares with two sequences integrated over time:

Si > K, Na, Mg > Ca > Fe, Al, Ti.

(earlier stage of basaltic weathering)

Si > Ca > K, Na, Mg > Fe, Al, Ti.

(later stage of basaltic weathering)

Many such sequences must exist, especially on the scale of a soil profile. At this scale, not only such commonly recognised factors as: (a) nature of parent material; (b) nature of secondary phases; and (c) inherent solubility of components, are important in determining the order, but the nature of the pedogenic environment becomes important, several distinct environments having been identified (GAUCHER, 1977).

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APPENDIX

Location and description of samples

1. Fresh basalt, samples 1, 2, 3, horizon 1. Hard, fresh, black, prismatic alkali basalt. Olivine phenocrysts in groundmass of clinopyroxene, plagioclase, Fe–Ti oxide, glass and minor olivine. Olivine has iddingsite rim.

2. Slightly altered basalt, sample 4, horizon 2. Just above top of intact prisms of horizon 1. Fresh-looking in bulk. Glass and olivine beginning to alter in thin section.

3. Spheroid cores, samples 5, 6, 7, 8, horizon 3. Hard, compact, fresh-looking when broken open. Glass and olivine altered in thin section.

4. Spheroid envelopes, samples 9, 10, 12, horizon 3. Friable yellow to grey-green, easily detached from core stones. Glass and olivine completely altered with olivine retaining its form in individual cases. Clinopyroxene beginning to alter. Plagioclase fresh-looking.

5. Completely altered spheroid, sample 11, horizon 3. No separable core. Yellow, friable with characteristics of spheroid envelopes above.

6. Incoherent material, sample 13, horizon 4. No spheroids, yellow-brown with black Mn oxide stains on surfaces of cracks. Significant clay fraction. No visible glass or olivine. Few altered clinopyroxenes. Altered plagioclase common. Minor quartz and chert fragments.

7. Incoherent material, sample 14, horizon 5. Red stained silty-clay. Quartz and chert fragments. Minor altered plagioclase.

8. Solum of present day soil, sample 15, horizon 6. Brownish-grey. Quartz and chert fragments in silty clay. No evidence of primary phases of basalt.