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WEATHERING OF BASALTIC ROCKS FROM THE FRENCH MASSIF CENTRAL: ORIGIN AND FATE OF Ni, Cr, Zn AND Cu

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Abstract

We have examined the behavior of Cr, Ni, Cu and Zn during the weathering of basaltic rocks in a moderate temperate climate. Samples of unweathered basaltic rocks, moderately weathered and strongly weathered equivalents were studied at six sites from the Massif Central of France. Unweathered basaltic rocks and basanites are rich in Cr (248–455 mg/kg) and Ni (126–237 mg/kg); all four elements are present in similar amounts in all three categories of sample. The location of these trace elements was investigated by optical and electron microscopy (EMPA, SEM–EDS). In unweathered basaltic rocks, Cr bearing phases are: chromian spinel (4–42 wt%), Fe–Ti spinel (0.12–1.24 wt%) and titanian augite (200–8000 mg/kg), whereas nickel is incorporated into forsterite (830–3600 mg/kg) and the spinel-group minerals (0.11–0.14 wt%). Copper and Zn are found at lower concentrations, but regularly distributed in the phases studied. In weathered samples, authigenic phases fill fractures and also replace the primary minerals. They are composed of mixtures of clays, iron oxides and organic compounds. Authigenic phases contain lower amounts of those trace elements than primary minerals. Under conditions of moderate weathering, only 20 to 40% of the total content in Cr, Ni, Cu and Zn appears to be mobile during the weathering of the basaltic rocks. As spinel-group minerals are not affected by strong weathering under a temperate climate, only the fraction of Cr, Ni and Zn present in the silicates of the unweathered basaltic rocks is released.

Keywords: trace element, basaltic rock, weathering, forsterite, spinel, “iddingsite”, alteration sequence, Massif Central, France.

Sommaire

Le comportement des éléments traces Cr, Ni, Cu et Zn lors de l’altération de roches basaltiques en climat tempéré a été examiné à six sites situés dans le Massif Central français. Cette étude a permis d’établir un schéma général du profil d’altération dans lequel trois faciès ont été définis: les échantillons non altérés, modérément altérés et très altérés. Les roches basaltiques sont riches en Cr (248–455 mg/kg) et en Ni (126–237 mg/kg), avec des concentrations totales des quatre éléments comparables dans les trois faciès d’altération. Les phases primaires et authigéniques porteuses de ces éléments ont été identifiées et caractérisées par microscopie optique et électronique. Dans les roches basaltiques non altérées, les phases porteuses du Cr sont: le spinelle chromifère (4–42%, poids), la magnétite titanifère (0.12–1.24%) et l’augite titanifère (200–8000 mg/kg), tandis que le Ni est incorporé dans la forstérite (830–3600 mg/kg) et les deux sortes de spinelle (0.11–0.14%). L’ensemble des phases étudiées contiennent de faibles teneurs en cuivre et en zinc. Dans les échantillons altérés, les phases authigéniques remplissent les fissures et remplacent les minéraux primaires. Ces phases authigéniques sont constituées d’un assemblage d’argiles, d’oxyhydroxydes de fer et de composés organiques avec des teneurs en Cr, Ni, Cu et Zn inférieures à celles des minéraux primaires. Dans les conditions actuelles du Massif Central français, seul 20 à 40% de ces éléments sont redistribués durant l’altération supergène des roches basaltiques. Ces éléments sont libérés lors de l’hydrolyse des minéraux silicatés, tandis que les minéraux du groupe du spinelle restent peu affectés par l’altération supergène.

Mots-clés: élément trace, roche basaltique, altération supergène, forstérite, spinelle, “iddingsite”, séquence d’altération, Massif Central, France.

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INTRODUCTION

Outcrops of Tertiary basaltic rocks, abundant in many countries of western Europe, are covered by fertile soils intensively used for pasture or crops. These rocks contain high amounts of Cr, Ni, Cu, and Zn. From an environmental point of view, it is of primary importance to understand the behavior of trace elements during the weathering of basaltic rocks. Indeed, these elements, some of which are potentially toxic, could find a way into the food chain *via* underground water supplies and vegetation, thus limiting a soil's agricultural use. Mobility and effective bioavailability of such trace elements can be evaluated locally, but their long-term behavior requires an understanding of the alteration processes, and especially the identification of primary phases that are natural carriers of those trace elements, an evaluation of their stability, and their evolution during weathering.

In this context, we use mainly *in situ* petrographic, mineralogical and chemical methods to assess qualitatively and quantitatively the Cr, Ni, Cu and Zn in minerals during the weathering of basaltic rock under moderate conditions. Our aims are (i) to characterize the Cr-, Ni-, Cu- and Zn-bearing phases in the primary assemblages, ii) to locate these elements in authigenic phases, and iii) to predict the influence of micro-environmental conditions on their behavior at different stages of weathering.

BACKGROUND INFORMATION

Previous studies on the weathering of basalts have focused on the importance of climate as a variable. Chesworth *et al*. (1981), Eggleton *et al*. (1987) and Hill *et al*. (2000) studied changes in mineralogy and bulk-rock composition in terms of major elements in weathered profiles in a temperate climate. Hamidi *et al*. (1997) and Dekayir & El-Maâtaoui (2001) examined the processes of supergene alteration of basalts in a Mediterranean-type climate. Glasmann & Simonson (1985) and Prudêncio *et al*. (2002) studied influence of rainfall, average annual air temperature and topography. As the intensity of the weathering processes is enhanced by hot wet conditions, numerous studies have been carried out in tropical climates (*e.g*., Cortes & Franzmeier 1972, Motuzova & Ngo Thi Hong Van 1999).

Another way to assess the geochemical mobility of trace elements during the weathering of basaltic rock is to analyze chemically the surface runoff and groundwater. This second approach has been applied to rivers draining basaltic formations. Aiuppa *et al*. (2000) examined the concentration and flux of major, minor and trace elements during weathering and groundwater transport. Benedetti *et al*. (2003) studied the composition of waters involved in alteration processes at Mount Cameroon, in central Africa. Stefansson & Gislason (2001) sampled and analyzed river water, groundwater and peat waters from Icelandic basaltic catchments in order to define the effect of degree of crystallinity of the matrix (glassy or microcrystalline), as well as the formation of secondary phases and runoff fluxes of dissolved elements (down to the ocean).

Recent studies focus on patterns of trace-element distribution in primary phases in basaltic rocks. In Archean belts in Finland, Halkoaho *et al*. (2000) noted that nickel is preferentially incorporated into forsterite. The studies by Latrille (1998) in the Chaîne des Puys, in France, and by Nazzareni *et al*. (2003) in the Etna area, in Italy, show that in very recent basalts, chromium is mainly located in spinel-group minerals and clinopyroxene. Analytical techniques have improved the characterization of solid phases and lowered the limits of detection to a few tens of mg/kg, but the pattern of behavior of these trace elements during alteration has not been re-examined. Latrille (1998) only mentioned the minor alteration of primary silicates and oxides that are carriers of Cr, Ni, Cu and Zn in soils developed on post-Würm basalt scoria. In her opinion, the neoformation of very reactive organomineral compounds influences the mobility of Cu and Zn over the short term.

MATERIALS AND METHODS

The study areas

In the French Massif Central, Tertiary volcanic formations lie above metamorphic and granitic rocks and cover about 8000 km^2 in the central-southern part of the country. Basalts and basanites constitute around two-thirds of this volcanic area and mainly outcrop on plateaus 1000 m high known as "planèzes". During Würm and late Würm periods, owing to the presence of mountain glaciers over the entire volcanic area, earlier soils were submitted to creep and solifluxion. Soils found on the *planèzes* can be considered as the result of post-Würm pedogenesis, developed either on parent basaltic rocks, on remnants of former soils, or on translocated surficial formations.

Six weathering profiles of alkali basalts and basanites were examined from three volcanic systems, in the Cantal (Mauriac, Pierrefort and Labarrière), in the Devès (Poinsac and Saint-Christophe), and in the Monts Dore (Les Chirouzes) (Fig. 1). Although all sites are submitted to a wet, mountainous and temperate climate, microclimatic conditions vary from one site to another. Altitude ranges from 700 to 1180 m, annual rainfall, from 1900 to 760 mm from west to east in the area, and mean annual temperature ranges from 6.4 to 10.4°C (Table 1), depending on altitude and how far inland the site is located with respect to the Atlantic coast.

Sampling and analytical methods

At each site, three facies were defined, sampled and studied along the weathering profiles: 1) unweathered

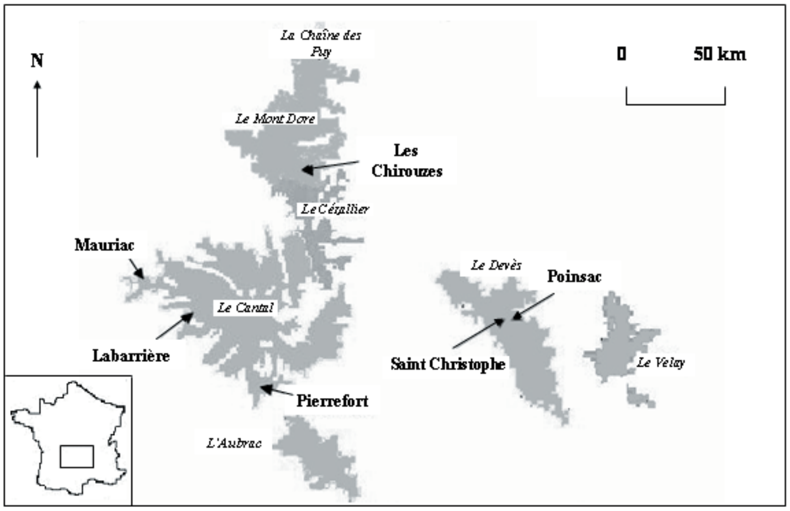

FIG. 1. Location of the six sites studied. The map shows the distribution of Tertiary volcanic formations in the French Massif Central.

TABLE 1. MAIN CHARACTERISTICS OF THE SAMPLING SITES OF BASALTIC ROCKS, MASSIF CENTRAL, FRANCE

Site	Volcanic formation	Parent rock	Altitude m	Annual precipitation mm	Mean temp. °C
Mauriac	Cantal	Basanite	700	1300	10.4
Poinsac	Devès	Basalt	820	760	9.2
Les Chirouzes	Mont Dore	Basanite	1130	1800	6.4
Labarrière	Cantal	Basalt	1180	1900	7.2
Saint Christophe	Devès	Basanite	910	860	8.2
Pierrefort	Cantal	Basanite	1030	1320	8.5

Mean temp.: mean annual temperature.

basaltic rock (parent rock), 2) moderately weathered basaltic rock (crusts of basaltic boulders or coarse fragments in soils), and 3) strongly weathered basaltic rock (soil aggregates). Bulk chemical analyses of these materials were carried out by inductively coupled plasma – atomic emission spectrometry (ICP–AES) for major elements, and by inductively coupled plasma – mass spectrometry (ICP-MS) for trace elements after crushing and fusion with an alkali flux (CRPG, Nancy). The total digestion of the material was done by melting the sample with $LiBO_2$, followed by digestion in nitric acid. Loss on ignition (LOI) was determined by heating the sample for 3 h up to 980°C.

X-ray diffraction (XRD) was used for mineralogical characterization. The <2 μm fraction was obtained by sedimentation (pipette method, AFNOR X31–107, 1983). X-ray-diffraction analyses (Siemens D–5000) were performed on <2 μm oriented preparations of untreated, Ca-saturated, ethylene-glycol-saturated and heated (105°, 450° and 550°C) samples, from 2° to 40° 2θ, with steps of 0.02°, and a counting time of 3 s per step (Daco diffractometer, Co$K\alpha$ radiation, Hydr'ASA, Poitiers). *In situ* characterization of the secondary phases was performed by micro-XRD (Philips diffractometer, Cu$K\alpha$ radiation, CIRCP, Marseille) from 5° to 45° 2θ, with steps of 0.0087°, and a counting time of 400 s per step. Fourier transform infrared (FTIR) spectra of the <2 μm fraction were recorded in the 4000–400 cm^{-1} range using a Nicolet 510 spectrometer (Hydr'ASA, Poitiers). Pellets were prepared by mixing 2 mg of samples with 300 mg of KBr.

Polished thin sections were prepared for petrographic observations and local analyses. For each sample, local analyses of primary and secondary minerals were carried out using a scanning electron microscope (SEM Philips XL–30 operated at between 15 and 30 kV, SERMIEL, Limoges) and equipped with an energy-dispersion spectrometer (EDS). An electron microprobe (Cameca SX–50) also was used for *in situ* analysis for the major and trace elements (CAMPARIS, Paris). The conditions were as follows: for major elements, voltage of 20 keV, and window aperture 4 nA; for trace elements, voltage of 35 keV, and window aperture of 500 nA using the procedure developed by Fialin *et al.* (1999) for levels of trace elements below 1000 mg/kg. Hence for trace elements, a single set of analytical data corresponds to the treatment of analytical results collected from ten spots over a short time (10-20 s counts) in order to reduce damage due to prolonged irradiation. At 35 keV and 500 nA, the area excited by the beam is about 80 μm^2, as estimated from the diameter of the catholuminescence-induced bright spot (10 μm beam). An example of a probed area is given in Figure 2d.

GENERAL CHARACTERISTICS OF THE WEATHERING PROFILES

The parent rocks

The samples studied are forsterite-bearing basalts or basanites (normative nepheline from 3 to 11%) of quite constant bulk chemical composition and loss on ignition (LOI). The composition of the parent rocks, in terms of major elements, is given in Table 2. Their trace-element contents are reported in Table 3. Like most occurrences of Tertiary basalts in France (Liotard *et al.* 1983, Downes 1985), our rocks are rich in Cr (249–455 mg/kg), Ni (126–237 mg/kg) and Zn (111–125 mg/kg). They also contain 44 to 67 mg/kg of Cu.

According to microscopic observations and XRD patterns, the parent rocks present a striking mineralogical homogeneity. They differ from one sample to another only in phenocryst size and proportion, and also in the ratio of forsterite to pyroxene. The texture is invariably microlitic and porphyritic (Fig. 2a), and the rocks are poor in glass. Rock samples show euhedral crystals of titanian augite (200 μm – 1 mm across) and forsterite ($Fo_{80–90}$) (300 μm – 2 mm across), commonly enclosing Cr-bearing titanian magnetite (10–30 μm). The mesostasis is composed of microcrystic laths of plagioclase (2–50 μm), clinopyroxene and forsterite.

Both Fe–Ti (5–10 μm) and Cr–Fe (5-50 μm) spinel-group minerals are present throughout the rocks (Fig. 2b). The relative abundance of these phases was determined by point counting of thin sections. Forsterite covers from 3 to 15% of the surface, titanian augite, from 4 to 13%, the spinel-group minerals, from 16 to 30%, and the microcrystic laths of plagioclase, from 55 to 65%.

Moderately weathered basaltic rocks

Moderately weathered basaltic rocks are heterogeneous and present evidence of spheroidal weathering, leading to centimetric pebbles (Fig. 2c). These pebbles are surrounded by an abundance of mixed phases, with colors varying from yellow to brown, where the intensity of fractures is greater. The core of the pebbles remains quite unweathered, whereas the outer parts are largely transformed. The initial texture is conserved, but numerous interconnected fractures and cracks affect both phenocrysts and matrix and cross all the samples. Some fractures and cracks are empty, whereas others are partly or completely filled with very fine yellow to brown material coating the walls of the cracks. Similarly, part of the primary minerals is replaced by very fine-grained mixture, also yellow in color.

Bulk-chemical analyses of moderately weathered basaltic rocks reveal a depletion in Mg and Ca with respect to samples of the parent rock (Fig. 3). Other major-element contents do not vary significantly. As presented in Table 3, the concentrations of Cr and Ni in the bulk samples are as high as those of the parent rock (except for the site of Labarrière): concentrations of Cr and Ni range from 236 to 507 mg/kg and from 125 to 282 mg/kg, respectively, those of Zn are quite regular (113 to 164 mg/kg), as well as Cu, but at a lower level of concentration (50 to 77 mg/kg). Regarding the pebble location at Labarrière, the very low trace-element concentrations found in the moderately weathered samples of this profile are explained by the occurrence of element translocations by solifluxion or creep. Nevertheless, weathering features at the microscopic scale are similar to those at other sites.

TABLE 2. COMPOSITION OF UNWEATHERED, MODERATELY WEATHERED, AND STRONGLY WEATHERED SAMPLES FROM THE SIX SITES: MAJOR ELEMENTS

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI
Mauriac											
sws	32.2	16.1	10.8	2.4	0.2	1.4	1.0	0.2	0.7	0.5	30.2
mws	37.1	20.2	13.5	3.0	0.2	1.8	0.9	0.2	0.7	0.4	22.0
uws	45.8	14.5	11.2	2.7	0.2	8.9	9.4	3.7	2.0	0.6	0.9
Poinsac											
sws	39.4	13.7	13.6	2.9	0.2	4.5	5.4	1.5	1.3	0.8	16.4
mws	41.5	19.2	12.5	2.6	0.2	3.1	4.0	1.2	1.0	0.7	14.4
uws	44.6	15.6	13.0	2.7	0.2	6.6	9.4	3.1	1.1	0.8	2.9
Les Chirouzes											
sws	33.1	13.9	10.6	2.4	0.2	5.7	5.0	0.9	0.8	0.6	25.3
mws	38.1	18.0	12.8	3.0	0.2	4.2	4.6	1.1	1.1	0.6	16.5
uws	41.7	13.6	13.2	3.2	0.2	9.4	11.5	2.7	0.5	1.0	3.0
Labarrière											
sws	25.5	13.6	10.6	2.6	0.1	1.8	2.2	0.8	0.9	0.5	35.4
mws	27.2	16.1	10.4	2.6	0.1	1.7	1.9	0.9	1.1	0.6	16.6
uws	39.8	15.0	12.1	2.8	0.2	10.6	9.5	1.4	1.2	0.7	6.8
Saint Christophe											
sws	35.3	12.4	18.4	3.3	0.4	6.5	3.8	0.8	1.0	0.6	17.6
mws	38.1	14.4	20.2	3.7	0.4	5.4	3.0	0.8	1.2	0.6	12.2
uws	44.7	13.1	12.2	2.7	0.2	10.9	10.3	2.9	1.8	0.7	0.5
Pierrefort											
sws	28.8	14.1	14.4	3.2	0.3	5.1	4.2	0.6	0.7	0.7	23.8
mws	34.6	17.4	18.4	4.1	0.3	6.1	3.0	0.6	0.8	0.7	13.9
uws	39.7	14.8	13.2	3.5	0.2	9.3	11.3	1.7	0.9	0.8	4.9

Compositions are reported in wt% oxides for unweathered (uws), moderately weathered (mws) and strongly weathered (sws) samples. The concentrations of major elements were determined by inductively coupled plasma – atomic emission spectroscopy (ICP–AES).

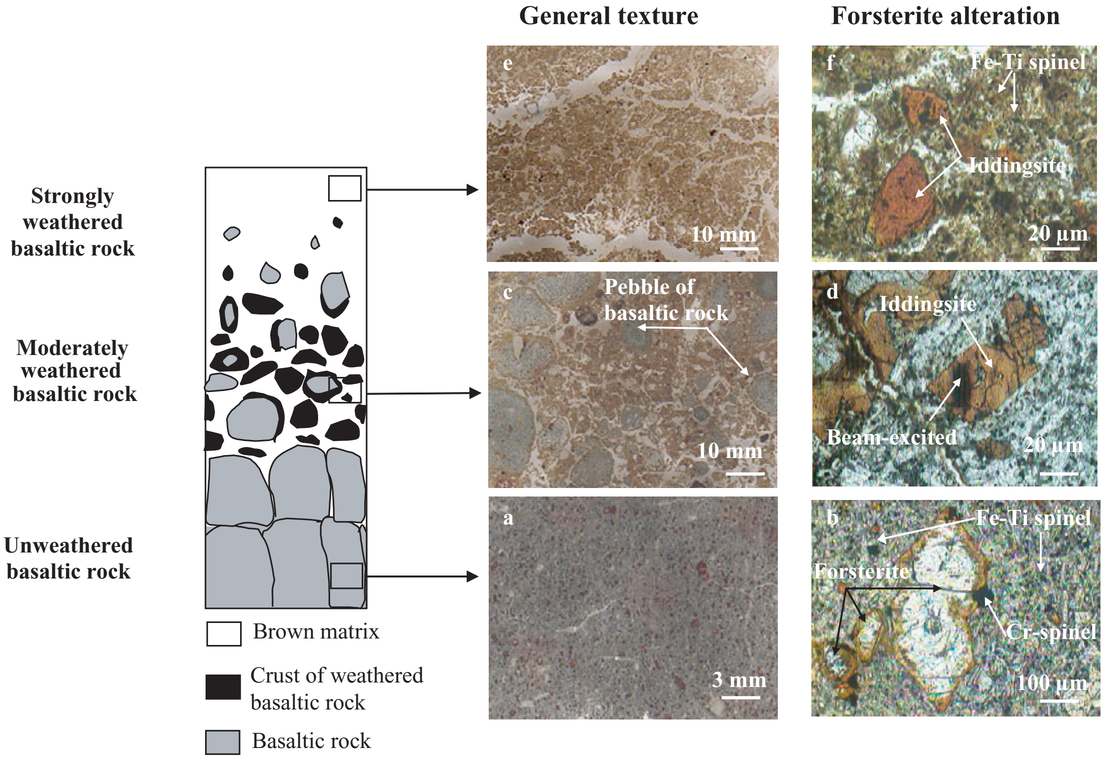

FIG. 2. Schematic profile and images in transmitted light of the general texture and forsterite alteration of unweathered (a, b), moderately weathered (c, d) and strongly weathered basaltic rocks (e, f) at Poinsac.

Strongly weathered basaltic rocks

In strongly weathered basaltic rocks, the original texture of parent rocks is invariably destroyed. Broad fractures and cracks are well developed, and hence porosity is very high (Fig. 2e). A brown matrix invades the whole samples and surrounds the remaining primary minerals (spinel-group minerals) (Fig. 2f) and other authigenic phases.

The chemical composition of the strongly weathered basaltic rocks shows a decrease in all major elements except Ti and Al. Except for the site of Labarrière, trace-element concentrations are similar and, in some cases, greater than in the parent rocks: Cr (293–686), Ni (168–291), Zn (110–168) and Cu (33–71 mg/kg).

MINERAL ASSEMBLAGES AND TRACE-ELEMENT CONTENTS OF MINERALS

Average and standard deviations of chemical compositions for primary and authigenic phases from all sites are given in Table 4.

TABLE 3. COMPOSITION OF UNWEATHERED, MODERATELY WEATHERED, AND STRONGLY WEATHERED SAMPLES FROM THE SIX SITES: TRACE ELEMENTS

	Cr	Ni	Zn	Cu	Cr	Ni	Zn	Cu
	Mauriac				**Labarrière**			
sws	293	168	143	52	75	33	163	41
mws	376	213	151	68	50	31	90	26
uws	371	214	118	49	427	219	117	52
	Poinsac				**Saint Christophe**			
sws	330	155	156	49	686	291	164	71
mws	236	147	113	50	467	259	134	68
uws	249	126	123	44	455	237	114	53
	Les Chirouzes				**Pierrefort**			
sws	300	141	110	33	554	287	168	62
mws	273	125	123	54	507	282	164	77
uws	381	218	111	45	270	142	125	67

Trace-element concentrations are reported in mg/kg for unweathered (uws), moderately weathered (mws) and strongly weathered (sws) samples. The concentrations of trace elements were established by inductively coupled plasma – mass spectrometry (ICP–MS).

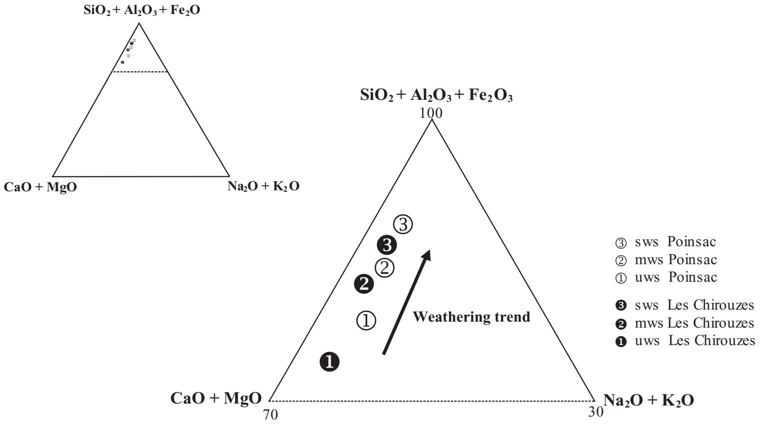

FIG. 3. Overall geochemical trend from unweathered basaltic rock to strongly weathered basaltic rock at Poinsac and Les Chirouzes.

Primary minerals in the parent rocks

All the mineralogical assemblages identified in the rocks by XRD and optical microscopy can be considered to be primary. All basaltic rocks show a similar mineralogy, and the primary minerals from different locations present few compositional variations.

The *Fe–Ti spinel* is euhedral low-Mg titanian magnetite ($Fe_{3-x}\,Ti_x\,O_4$), which contain up to 1.2% Cr_2O_3, with an average of 0.5%. The proportion of FeO varies from 59 to 72%, and that of TiO_2, from 12 to 25%. The *Cr-rich spinel* (up to 41% Cr_2O_3) is invariably associated with forsterite crystals (Fig. 4), and contains Al (up to 22% Al_2O_3), Mg and Fe. Depending on its abundance in the rocks, such a spinel incorporates from 80 to 90% of the total chromium. The Ni content of this spinel varies between 0.11 and 0.14% NiO. Its Zn content is low but significant (mean value: 540 mg/kg). *Forsterite* ($Fo_{80–90}$) is Ni-rich (up to 0.5% NiO), whereas it is poor in Cr (mean value 284 mg/kg). On the contrary, *titanian augite* is, on average, richer in Cr (0.02 to 0.81% Cr_2O_3) and poorer in Ni (0.02 to 0.3% NiO) than the forsterite. Copper is present in all the minerals, but at a low level (28–35 mg/kg). The *plagioclase* (mainly labradorite) does not contain significant quantities of these trace elements (measurements below the detection limit in all cases).

Moderately weathered basaltic rocks

In comparison to the parent rock, XRD patterns of moderately weathered bulk samples (Fig. 5: Poinsac example) display a decrease in the peak intensities for labradorite and forsterite, and evidence of the appearance of authigenic minerals. XRD analyses performed on <2 μm oriented preparations emphasize the presence of 7 Å phases (halloysite), 10 Å phases (illite) and a small peak at a *d* value of 15 Å (air-dried samples), indicating a swelling smectite, on the basis of solvation with ethylene glycol (17 Å). Heating to 450° and 550°C caused the collapse of this peak to 10 Å. Fourier transform infrared spectra in the 3600–3100 cm^{-1} region show two characteristic bands of halloysite at 3620 and 3680 cm^{-1}.

Primary mineralsin the moderately weathered rocks

In moderately weathered basaltic rocks, both the Fe–Ti spinel and chromian spinel are present in the same proportions as in unweathered basaltic rocks. Electron-microprobe analyses of individual grains for both major elements and trace elements give similar results as those found in unweathered basaltic rocks. In all samples, *forsterite* commonly is affected by cracks, is surrounded by an orange to brown rim of "*iddingsite"* and, at the Poinsac site, it is completely replaced by this product (Fig. 2d). The *titanian augite* is invariably preserved, but is deeply fractured and cracked. It does not contain products of alteration that could be detected at the scale of optical microscopy. Compared to the parent rocks, the laths of *labradorite* do not present any modification in their morphology or chemical composition, except where they are cross-cut by fractures and filled by a yellow product.

Authigenic phases in the moderately weathered rocks

An estimate of the proportion of authigenic products (30 to 50%) in weathered basaltic rocks is given by calculating the proportions of these phases in three samples. According to their color, size, location and shape, three main materials were distinguished:

"*iddingsite*" replaces forsterite (3 to 12% of the rock), *euhedral yellow products*, regular in shape, replace the primary silicates (2 to 8%), and *irregular yellow products* (3 to 5%) are located in fractures and cracks affecting the whole sample.

Chemically, *"iddingsite"* (Fig. 5) is characterized by an increase in the Fe : Mg ratio (from 0.15 to 1) in comparison with fresh forsterite. The Ni content (560–2460 mg/kg) remains high, but is invariably lower than in the forsterite. Other elements do not vary significantly.

In view of their euhedral pseudohexagonal shape and their size (200–500 μm), the *euhedral yellow product* seems to replace forsterite (Fig. 6). From one zone to another, it presents quite homogeneous SiO_2, Al_2O_3 and FeO contents (respectively 44 to 52, 18 to 26 and 12 to 15%). The Ni content remains high (630 to 725 mg/kg) in the euhedral yellow product, but is lower than in forsterite and in "iddingsite". The *euhedral yellow product* has a low and homogeneous chromium content. The amounts of zinc and copper do not vary significantly.

The *irregular yellow product*, so-called because the domains are irregular in shape, is located at the periphery of basaltic pebbles and along cracks (Fig. 7). Although it also is mainly composed of SiO_2 (mean content 46%) and Al_2O_3 (mean content 30%), it is not as homogeneous as the previously described euhedral

TABLE 4. AVERAGE COMPOSITION OF PRIMARY AND AUTHIGENIC PHASES AT ALL SITES

	Unweathered basaltic rock					Moderately weathered basaltic rock			Strongly weathered basaltic rock			
	Forsterite	Augite	Fe-Ti oxide	Fe-Cr oxide	plagioclase	"Iddingsite"	Euhedral yellow product	Irregular yellow product	Brown matrix	Euhedral black product	Orange product	Irregular black product
n	69	53	20	22	6	36	10	20	18	6	23	10
SiO_2 wt%	39.13	46.88	0.34	0.30	51.58	35.94	48.01	45.73	25.56	7.09	36.21	25.31
	[0.89]	[2..38]	[0.25]	[0.51]	[0.23]	[2.45]	[2.27]	[3.74]	[7.42]	[1.25]	[9.64]	[6.56]
Al_2O_3	0.07	5.88	3.7	12.48	27.93	0.74	21.89	29.33	15.91	5.92	22.78	12.01
	[0.18]	[1.82]	[1.35]	[5.25]	[2.04]	[0.39]	[2.43]	[5.24]	[6.28]	[4.15]	[8.33]	[7.08]
MgO	43.2	13.34	3.74	6.60	0.05	28.72	1.92	0.66	1.34	0.26	0.62	1.28
	[2.85]	[1..30]	[0.82]	[2.21]	[0.03]	[4.98]	[0.27]	[0.4]	[1.75]	[0.19]	[0.22]	[1.72]
FeO	15.57	7.57	65.08	46.54	0.79	28.01	13.66	7.68	9.57	61.34	17.23	15.06
	[3.19]	[1.31]	[2.67]	[10.47]	[0.12]	[3.77]	[1.27]	[4.62]	[7.83]	[7.33]	[13.43]	[11.12]
TiO_2	0.07	2.35	20.38	7.82	0.15	0.10	0.07	0.76	1.46	0.04	1.07	1.30
	[0.06]	[1.12]	[3.08]	[4.76]	[0.03]	[0.11]	[0.03]	[0.28]	[0.70]	[0.03]	[0.45]	[1.19]
CaO	0.25	21.6	0.25	0.11	9.99	0.49	0.58	0.52	1.68	0.14	0.49	1.91
	[0.09]	[0.93]	[0.19]	[0.09]	[2.02]	[0.12]	[0.12]	[0.32]	[2.26]	[0.14]	[0.23]	[2.80]
MnO	0.28	0.21	0.73	0.57	0.07	0.49	0.02	0.05	0.08	0.67	0.74	12.36
	[0.14]	[0.12]	[0.24]	[0.24]	[0.05]	[0.14]	[0.02]	[0.04]	[0.10]	[0.27]	[1.29]	[10.34]
Na_2O	0.04	0.67	0.05	0.10	4.99	0.05	0.01	0.10	0.50	0.08	0.11	0.44
	[0.04]	[0.27]	[0.03]	[0.09]	[0.58]	[0.04]	[0.02]	[0.06]	[0.44]	[0.03]	[0.06]	[0.66]
K_2O	0.03	0.19	0.05	0.05	0.48	0.03	0.36	0.32	0.57	0.03	0.3	0.42
	[0.03]	[0.16]	[0.11]	[0.03]	[0.28]	[0.02]	[0.08]	[0.16]	[0.45]	[0.02]	[0.15]	[0.34]
Cr_2O_3	*	0.24	0.51	20.83	<d.l.	*	*	*	*	*	*	*
		[0.23]	[0.33]	[8.69]	<d.l.							
NiO	0.25	0.11	0.11	0.14	<d.l.	*	*	*	*	*	*	*
	[0.11]	[0.07]	[0.07]	[0.10]	<d.l.							
Cr mg/kg	284	**	**	**	<d.l.	200	75	89	160	407	115	172
	[73]				<d.l.	[79]	[16]	[56]	[55]	[38]	[31]	[112]
Ni	1448	334	**	**	<d.l.	1017	678	164	147	241	143	174
	[716]	[210]			<d.l.	[520]	[67]	[76]	[44]	[37]	[14]	[107]
Cu	30	34	35	28	<d.l.	87	104	93	257	64	133	154
	[31]	[10]	[20]	[20]	<d.l.	[53]	[65]	[80]	[153]	[63]	[10]	[150]
Zn	147	74	545	540	<d.l.	236	208	43	89	66	89	59
	[87]	[15]	[150]	[430]	<d.l.	[53]	[44]	[25]	[34]	[33]	[26]	[27]

n: number of analyses, [x]: standard deviation; * : concentration not measured with "the major-element procedure"; ** : concentration not measured with "the trace-element procedure".

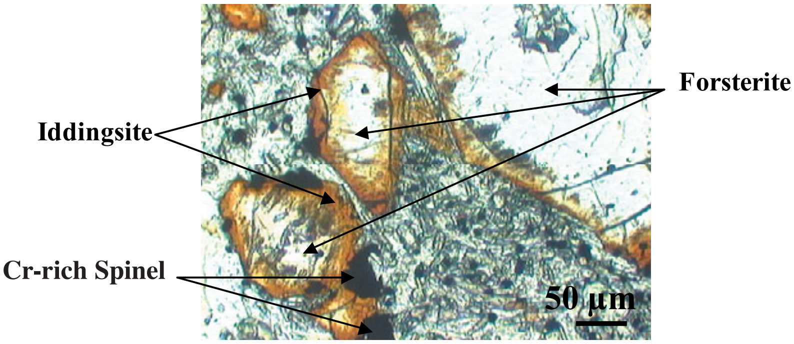

FIG. 4. Image of forsterite grain with a rim of "iddingsite" from moderately basaltic rock at Poinsac.

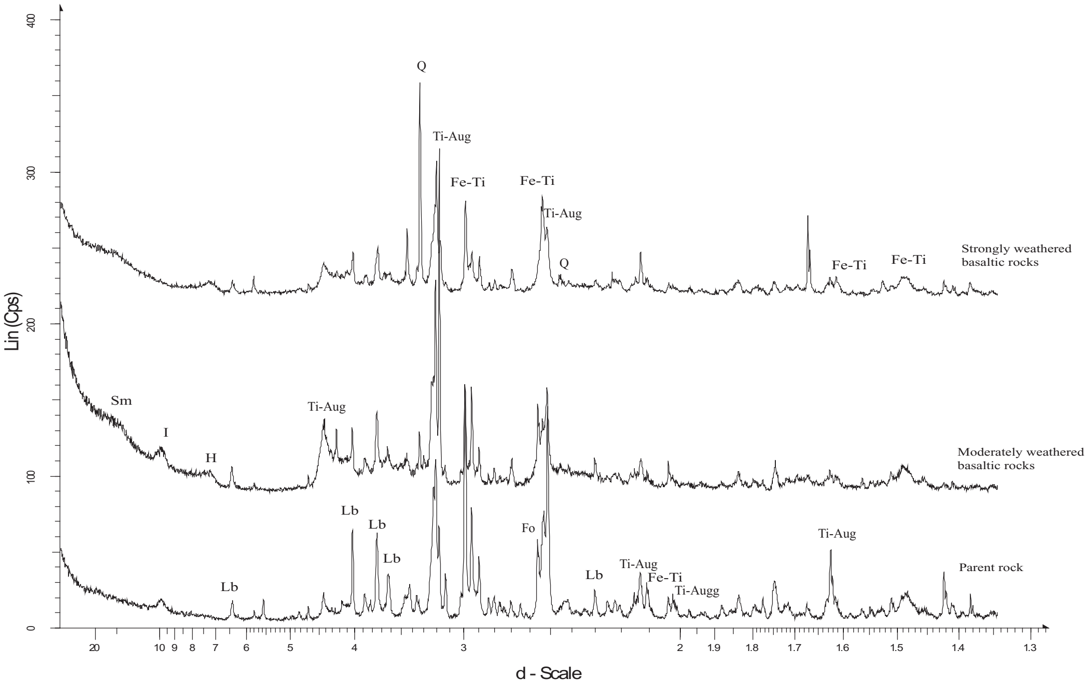

FIG. 5. Bulk XRD spectra (Cu$K\alpha$ radiation) of the three samples at Poinsac: parental rock (uws), moderately weathered sample (mws) and strongly weathered sample (sws), Lb: labradorite, Ti-Aug: titanian augite, Fo: forsterite, Fe–Ti: Fe–Ti spinel, I: illite, H: halloysite, Sm: swelling smectite.

yellow product. It presents a low Mg content, but differs in its highly variable Fe content (2 to 18% FeO). Nickel ranges from 61 to 309 mg/kg, Cr from 26 to 203 mg/kg, Zn from 0 to 81 mg/kg, and Cu between 35 to 276 mg/kg.

The irregular yellow product was analyzed by microdiffraction XRD in weathered basaltic rock from Poinsac. Results (Fig. 8) emphasize the presence of peaks around 7.54 Å, 4.48 Å and a double peak at 3.71–3.66 Å relative to 7 Å phase (like halloysite).

Strongly weathered basaltic rocks

XRD patterns (Fig. 4) of strongly weathered bulk samples reveal the disappearance of forsterite peaks and a decrease in the intensity of peaks of the other primary

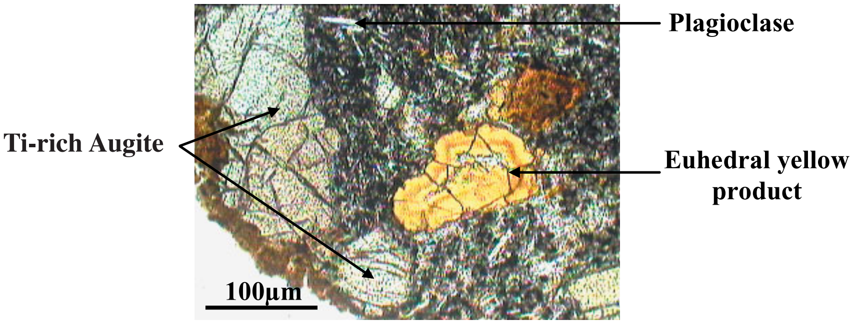

FIG. 6. General image of weathered basaltic rock at Les Chirouzes: *euhedral yellow products* (Fe-rich smectite).

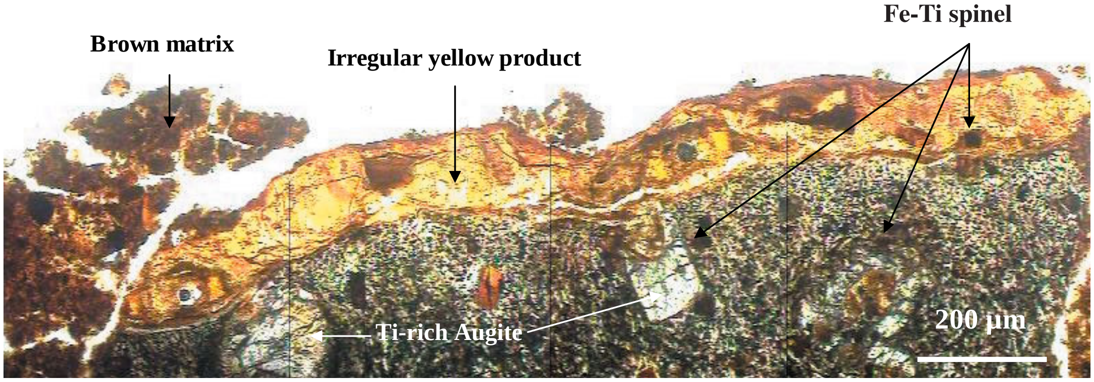

FIG. 7. General image of *irregular yellow products* (halloysite and iron oxyhydroxide) in weathered basaltic rock at Mauriac.

silicates. Peaks of the Fe–Ti spinel remain visible. X-ray diffractograms of the <2 µm oriented preparations indicate the presence of the same secondary phases as in the moderately weathered samples: 7 Å phases (halloysite), 10 Å phases (illite) and a swelling smectite.

The *Fe–Ti spinel* and *chromian spinel* do not decrease in proportion compared to the unweathered basaltic rocks. The shape and chemical composition of the grains do not change, within analytical errors. A typical grain of *chromian spinel* from a strongly weathered sample from Mauriac does not present visible signs of alteration, as monitored by optical and electron microscopy, and SEM–EDS analyses reveal a homogeneity in Cr, Fe and Al contents (Fig. 9).

In the strongly weathered basaltic rocks, the proportion of authigenic phases reaches 50 to 70% of the area of a polished thin section. Five main materials are distinguished: "*iddingsite*", *black products regular in shape* appearing as a replacement of euhedral primary minerals, *irregular black products*, *orange products* and *brown granular matrix*.

Grains of *"iddingsite"* remain in the strongly weathered samples (Fig. 2f). EMP analyses show that these "iddingsite" grains are not significantly different from those in the moderately weathered basaltic rocks except for the Mg content, which drops from 30–35% MgO in "iddingsite" in moderately weathered basaltic rock to 21–25% in the strongly weathered sample from Poinsac.

Black products are observed in two different forms. *Euhedral black products* (Fig. 10) are mainly composed of Fe (50 to 68% FeO), in some cases in association with nuclei rich in silica (90 to 95% SiO_2); this material may be a pseudomorph of augite or forsterite. Nickel ranges from 161 to 350 mg/kg, Cr, from 384 to 451 mg/kg, and levels of Cu and Zn are low (average values: 64 and 66 mg/kg). These euhedral black products correspond to the most Cr-rich secondary phases. Domains of the second type of black product have a more diffuse border. Electron-microprobe analyses of these *irregular black products* show a strong heterogeneity in Fe (6 to 41% FeO) and Mn (0 to 29% MnO) and a highly

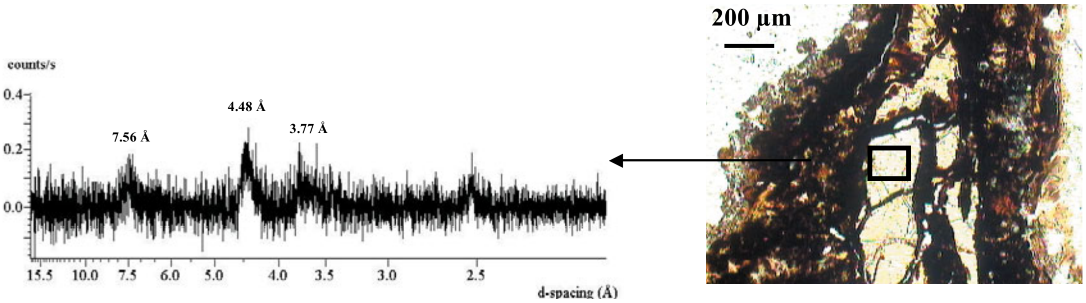

FIG. 8. X-ray microdiffractogram (Cu$K\alpha$ radiation) of a thin section from a selected area of *irregular yellow products* (halloysite and iron oxyhydroxide) in the weathered basalt at Poinsac.

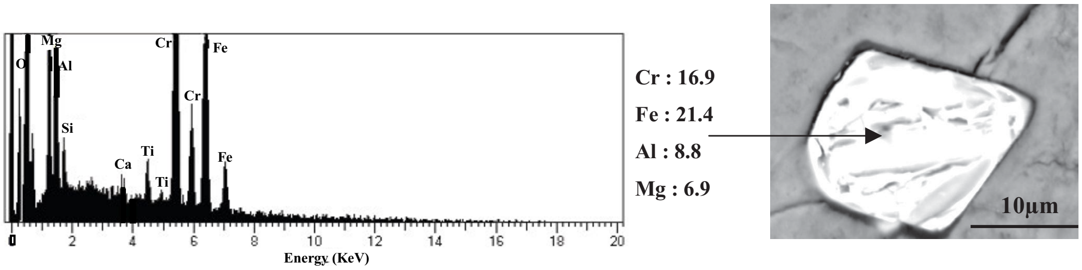

FIG. 9. Chemical composition (in wt.%) and EDS spectrum and back-scattered electron (BSE) image of chromian spinel (strongly weathered sample of Poinsac).

variable content of Ni (from 45 to 306 mg/kg), Cr (from 56 to 314 mg/kg), Zn (remains at 24 to 85 mg/kg), and Cu (highly variable, ranging from 17 to 404 mg/kg).

The *orange products* (domain size between 10 and 50 µm) either have well-defined borders or form a ring around the euhedral black products. These orange products are irregular in shape and in chemical composition. They are mainly composed of Si and Al (17 to 47% SiO_2, and 11 to 37% Al_2O_3, respectively) and have a highly variable Fe content (3 to 44% FeO). Magnesium and Ca are virtually absent. The trace-element contents are highly variable: Ni ranges from 68 to 358 mg/kg, Cr, from 57 to 170 mg/kg, Zn, from 32 to 217 mg/kg and Cu, from 52 to 495 mg/kg.

The most important characteristic of the strongly weathered samples is the presence of an abundant *brown granular matrix* of variable optical density, coating both primary and secondary minerals and constituting more than 50% of the sample. According to our electron-microprobe data, this matrix seems to be a highly hydrated mixture of clay minerals (total percentages for the determination by EMPA are never above 50%), oxides or hydroxides (Fe and perhaps Al phases) associated with organic matter. The brown granular matrix is relatively rich in Cu, with an average of 257 mg/kg.

DISCUSSION

The sequence of alteration

In the classic sequence of alteration, for example that of Goldich (1938), one expects, in order of increasing stability, forsterite, plagioclase in the mesostasis, pyroxenes and, finally, spinel-group minerals. Figure 11 summarizes the sequence of authigenic minerals present in our samples.

Forsterite is the first mineral to be weathered. In parent basaltic rocks, forsterite is cracked and incipiently replaced by a composite assemblage of phases referred to as "iddingsite". It appears very early as a 10–50 µm rim around phenocrysts. In moderately weathered and strongly weathered samples, this material is more strongly developed, and does not contain any relics of forsterite at the micrometer scale. It does not significantly change in chemical composition except to decrease in Mg content. Eggleton (1984) demonstrated that "iddingsite" resulting from the alteration of olivine phenocrysts in a Tertiary basalt from Germany is composed of an intimate assemblage of saponite and iron oxyhydroxides (goethite). Welch & Banfield (2002) showed that "iddingsite" results from deuteric alteration and is composed of a mixture of unaltered olivine, a defect-bearing iron-dominant olivine-group mineral (laihunite) and goethite. The very low Al content in our samples is more compatible with the presence of iron oxyhydroxides (not detected by microdiffraction) mixed with unaltered forsterite, rather than the occurrence of significant quantities of phyllosilicates.

In other weathered samples, especially at Les Chirouzes and Labarrière, another sequence of forsterite alteration exists, involving the presence of Fe-rich smectite (euhedral yellow product), replacing, more or less completely, the crystals of forsterite. However, such Fe-rich smectite is never encountered in the

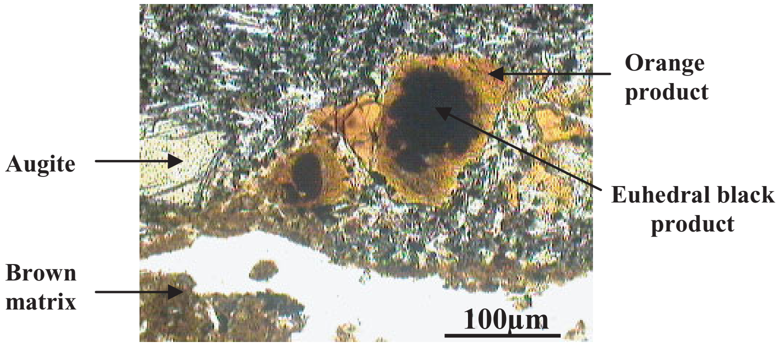

FIG. 10. Image of *euhedral black product* (iron oxyhydroxides) and *orange product*.

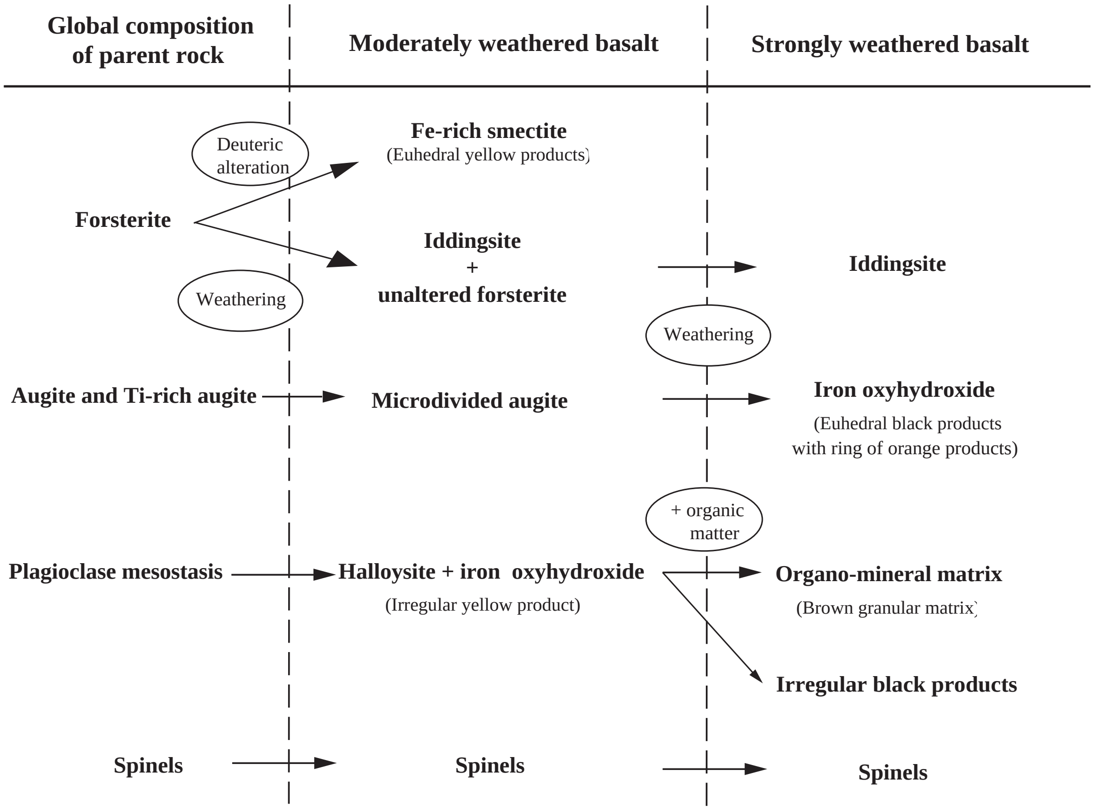

FIG. 11. Alteration sequence of basaltic rocks under temperate climatic conditions.

parent unaltered rocks, and is unstable in strongly weathered samples. It lies in the composition field of Fe-rich smectite (Table 4). Moreover, "iddingsite" and the Fe-rich smectite (euhedral yellow product) never coexist in our samples. This observation allows us to highlight another aspect of forsterite alteration: the deuteric conversion to "iddingsite" seems to preclude all subsequent forms of alteration of forsterite under the temperate microclimatic conditions of the Massif Central. This finding complements the observations of Ildefonse (1987) made on material in a tropical climate characterized by an annual rainfall of 2000 mm and a mean annual air temperature of 21°C. Ildefonse did not observe "iddingsite", but found that the forsterite grains are replaced during deuteric alteration by a mixture of tri- and dioctahedral phyllosilicates. He suggested that the lack of formation of "iddingsite" could be due to deuteric alteration under more reducing conditions. On the contrary, Dekayir & El-Maâtaoui (2001) showed, using infrared spectrometry and microstructural observations, that forsterite tends to convert to "iddingsite" in a Mediterranean climatic context; it is then destabilized, forming a mixture of goethite and halloysite with the remaining unaltered forsterite. In our samples, "iddingsite" is a product of deuteric alteration and in a context of strong weathering, it releases Mg without further transformation.

In the grains of pyroxene, cracking becomes more and more prominent from unweathered to weathered rocks. In the strongly altered samples, only small subhedral crystals remain. This cracking greatly increases the possibility of interactions with meteoric water. Altered zones in titanian augite from the first stages of alteration were not large enough to be analyzed. During later stages, the titanian augite in moderately and strongly weathered samples progressively "merge" into the organomineral matrix (brown matrix). These observations do not greatly differ from those of Dekayir & El-Maâtaoui (2001), who indicated that in the Mediterranean climate of the Middle Atlas in Morocco, titanian augite is the last mineral to be altered before the spinel-group minerals; there, it is transformed into a mixture of halloysite and goethite associated with illite.

The plagioclase-rich mesostasis, initially composed of labradorite, is converted to clay as a heterogeneous assemblage of submicroscopic phases, *i.e.*, the irregular yellow product, then the organomineral matrix (brown matrix). The irregular yellow product appears in moderately weathered samples and persists in local zones in the strongly weathered samples. According to micro-diffraction XRD, EMPA and FTIR (<2 μm fractions), the irregular yellow product consists of a mixture of halloysite and iron oxyhydroxides. Ildefonse (1987) observed that plagioclase from basalt is converted to a mixture of halloysite and gibbsite associated with iron oxyhydroxides in a tropical climate. The ultimate stage of alteration differs from the previous one by the disappearance of halloysite. In our samples, the organomineral matrix (brown matrix) is characterized by a strongly heterogeneous chemical composition. The microprobe data indicate that Si, Al, Fe and Mg vary by a factor of 4 to 8 from one spot to another, and the sum of the elements is invariably less than 60%. This deficit includes a large LOI (3–25%) and carbon, up to 12% (bulk analyses), which illustrates the presence of organic matter in the phases sampled in the upper horizons. It was not possible, under these conditions, to separate the phases and to use the results of *in situ* analyses to determine the nature of the individual mineralogical phases that constitute the organomineral matrix (brown matrix).

Spinel-group minerals represent 20 to 30% of all samples. They are barely affected by supergene alteration of basaltic rocks under climatic conditions at the Massif Central, which demonstrates their stability under temperate climatic conditions. On the contrary, in tropical or subtropical contexts, spinel-group minerals are destabilized into an intermediate phase, titanian maghemite, then into an assemblage of hematite and anatase (Ildefonse 1987, de Oliveira *et al.* 2002). In a Mediterranean climate, Karrat *et al.* (1998) and Hamidi *et al.* (1997) indicated, without providing details, that Fe–Ti oxides (titanian magnetite and ilmenite) remain almost unaltered under supergene conditions in near-surface horizons.

Influence of microclimatic conditions

Despite a similar sequence of alteration for the six sites, each profile shows certain specific changes: development of Fe-rich smectite-group phases (yellow euhedral product) or "iddingsite" for the olivine, relics of various size and quantity for the pyroxene, and a variable proportion of brown matrix in the most altered samples. In seeking to understand the reason for local differences, clues are provided by comparing micro-climatic (temperature, rainfall), microenvironmental (drainage, slope) and petrographic variables (grain size, texture, cracks), *i.e.*, all affecting the extent of water : rock interaction. According to Prudêncio *et al.* (2002), there is a general tendency common to all basaltic rocks weathered in temperate climates for secondary minerals to form with a predominance of smectite or 1:1 minerals, according to drainage intensity, which depends on the climate and geomorphic location. In a well-drained profile with a high water : rock ratio, 1:1 clay minerals form instead of a smectite-group mineral. Where the water : rock ratio is low, a smectite-group phase is dominant. In this study, all the sampled profiles have a similar geomorphic location and are well drained; they are located at the top of slopes or on the edges of the *planèzes*. The clay minerals formed at the various sites are mainly halloysite, illite and a swelling smectite. However, yellow and black euhedral products were observed only in Labarrière and Les Chirouzes profiles. Rainfall at Les Chirouzes and Labarrière; it is

>1800 mm/yr, *i.e.*, twice as much as at the other sites. Furthermore, the texture of the basaltic rocks differs somewhat: they are all poor in glass, but differ in proportions of forsterite and augite phenocrysts.

The behavior of the trace elements during weathering

In the analyzed parent basaltic rocks from areas of Tertiary volcanism in France, there are two potentially toxic elements, Cr and Ni, with concentrations of each ranging from 120 to 700 mg/kg. Copper and Zn are less abundant (40 to 170 mg/kg) and distributed more regularly among the different phases. Figure 12 shows the mean Cr and Ni contents in primary silicates and in authigenic phases. From the parent basaltic rocks to the strongly altered samples, the trace elements, Ni and Cr being the most abundant (>75%), vary only by small amounts in the six series of samples studied. Nevertheless, the carrier phases of these elements differ, depending on the degree of alteration, with the exception of spinel-group minerals, which retain the same Cr and Ni contents in moderately altered and strongly altered contexts. The primary phases containing Cr can be divided in two groups: oxides (70 to 80% of the total Cr) and Mg–Fe silicates, mainly titanian augite (10 to 20% of the total Cr). According to their abundance in parent rocks, oxides bear the greatest part (80–90%) of the total Cr. Owing to their small size (<30 μm) and their greater resistance to physical processes of weathering compared to the mesostasis or to silicate phenocrysts, spinel-group minerals are not cross-cut by the cracks developed in moderately weathered and strongly weathered basaltic rocks. Thus they are less affected by circulation of water than silicates, and they retain their original Cr content. Chromium released by the breakdown of titanian augite is captured by the iron oxyhydroxides (euhedral black product) and by the organomineral matrix (brown matrix), dominant phase in the strongly weathered basaltic rocks. The latter captures up to 270 mg/kg Cr; its heterogeneity

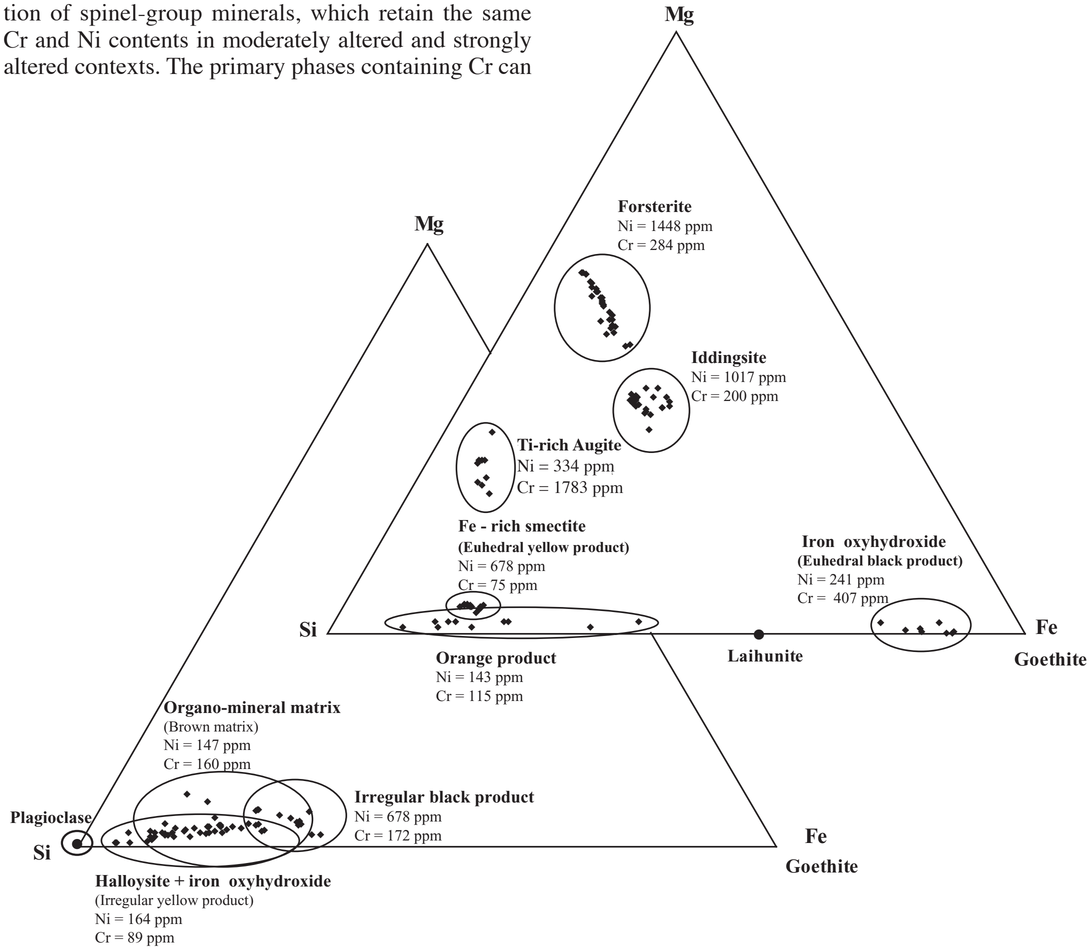

FIG. 12. Evolution of silicates and authigenic phases with Ni and Cr contents in terms of Si, Mg and Fe.

and irregular shape suggest a potential mobility for this part of the chromium.

Nickel-bearing primary phases are also divided in two groups: forsterite and spinel-group minerals. The phases replacing forsterite present a much lower Ni content than the precursor (one-third less, on average). Eggleton (1984) noticed a decrease in Ni and Cr contents in "iddingsite" compared to unaltered forsterite (a two-thirds decrease, on average). In the strongly weathered samples, Ni remains in primary oxides, and a part of it is removed from forsterite in favor of the organomineral matrix (brown matrix) and the Fe-rich smectite (euhedral yellow product). But the Fe-rich smectite (euhedral yellow product), which contains 678 mg/kg Ni, on average, represents only 2 to 8% of the total sample, whereas the organomineral matrix (brown matrix) (mean value 147 mg/kg) represents 40%.

There is little Zn present in the samples (90 to 168 mg/kg). In the parent rocks, the main part of the Zn is found in the spinel-group minerals (80 to 90% of the total), and smaller quantities in silicates (augite and forsterite). Zinc appears in a very irregular way in all of the authigenic phases analyzed except for the irregular yellow products, formed by the alteration of the plagioclase-rich mesostasis, in which it is absent. In the first stages of the alteration of forsterite ("iddingsite" or euhedral yellow products), Zn is systematically present at a higher level of concentration than in the precursor (by a factor of 1.5). On the other hand, in the final stages of alteration (irregular black and orange products), the concentration of Zn in authigenic phases is lower or equal to that in the primary silicates.

Copper is present in small quantities in bulk samples (33 to 71 mg/kg). Its distribution is diffuse over all primary phases. As with Zn, the Cu content of all the authigenic phases formed from the alteration of primary silicate minerals is two to five times greater than that of the primary silicate minerals themselves, on average. The organomineral matrix, representing more than 40% of the strongly weathered samples, is the authigenic phase richest in Cu. Copper released during the breakdown of both forsterite and titanian augite is thus distributed in a diffuse manner in the newly formed phases and in the organomineral matrix. Denaix *et al.* (1999) and Latrille *et al.* (2003) showed that Cu and Zn are present in allophane, organic matter and organomineral complexes. Our results, which are more quantitative, confirm the affinity of Cu and Zn for the organomineral matrix. They also show that forsterite and augite exert an important control over the distribution of these two elements in soils covering basaltic rock.

CONCLUSIONS

With progression of weathering of basaltic rock, we studied the behavior of Cr, Ni, Zn and Cu in a wet temperate climate. We have documented a series of stages from unaltered low-porosity basalt to a strongly weathered final stage. The early stages of weathering are defined by the breakdown of the main primary minerals: first a pseudomorph of forsterite, then of the pyroxene, involving fine-grained mixture of clays and iron oxides, and a progressive replacement of the plagioclase-rich mesostasis by authigenic clays and organomineral matrix. The spinel-group minerals show very little alteration and remain unaltered even in strongly weathered basaltic rocks.

Factors controlling weathering are deuteric events, resistance of some minerals to fracturing, water-to-rock ratio, and abundance of organic matter. The amounts of chromium and nickel do not vary significantly with progress of alteration: their total concentrations invariably remain at high levels. However, the carrier phases of the trace elements considered are quite different in altered samples. Whereas the total Cr content of the spinels does not differ in strongly weathered basaltic rocks, the breakdown of silicates induces the release of Ni and Cr and their trapping by the organomineral matrix, which shows a lower local concentration but a more regular distribution. About 80% of Cr and 60% of Ni are carried by oxides. Consequently, the redistribution induced by weathering concerns only 20% of the total Cr content and 40% of the total Ni content.

Under conditions of moderate weathering, the trace elements Cr, Ni, Zn and Cu in basaltic rocks are not very mobile during the development of soils: only 20 to 40% of their total content is involved in a mineralogical change of the carriers. Nevertheless, owing to their diffuse presence in the organomineral matrix of the samples, procedures of chemical extraction are required to further investigate their potential mobility from the authigenic phases.

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