Magmatic Evolution of Pavin's Group of Volcanoes: Petrology, Geochemistry and Modeling of Differentiation Processes. A Preliminary Study

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Abstract

The volcanoes of the Pavin group (Montcineyre, Estivadoux, Montchal and Pavin) represent the most recent (~7 ky) volcanic activity in the Chaîne des Puys s.l.) and also occupy a particular geographical and structural position in this volcanic chain. Petrology and geochemistry of the volcanic products (lava flows, scoriae, bombs and pumice clasts) of the different edifices show that they define a magma differentiation series from primary basalts (Montcineyre lava flow) to benmoreites (Pavin pumice clasts) with close similarities with that of the Chaîne des Puys (stricto sensu). It is however characterized by some significant difference in the relative behavior of K_2O and of numerous trace elements such as Sc, Co, Y, REE, Nb, Ta. These specific behaviors, in particular the relatively high bulk partition coefficients of Nb and Ta are characteristic of the fractionation of amphibole which is the only major mineral phase able to significantly fractionate these incompatible elements in basaltic to benmoreitic magmas. A quantitative modeling of the differentiation process using major and trace element partition coefficients is proposed which evidence the very early fractionation of amphibole from the most primary basaltic melts. This result is consistent with petrological observations and confirms the earlier and more efficient fractionation of amphibole at the expense of clinopyroxene in magmas of the Pavin group compared to those of the Chaîne des Puys (stricto sensu). The results are used to discuss the influence of these specific differentiation conditions involving large H_2O contents in primary melts likely contributing to the particularly high explosivity of the Pavin eruption which produced benmoreitic to trachytic magmas.

The particular features of the Pavin group within the Chaîne des Puys volcanic system, namely, the southernmost position, the younger age, the specific magmatic evolution from the most primary basalt ever erupted in Chaîne des Puys, coupled with a short activity duration (~400 years) justify a renewal of petrological and geochemical interest for these volcanoes.

Keywords

France • Massif Central • Chaîne des Puys • Lake Pavin • Geochemistry • Trace elements • Magmatology

7.1 Introduction

On the basis of the petrology, mineralogy and major and trace element composition of the lavas of the Chaîne des Puys, Maury et al. (1980) and Villemant et al. (1980) have shown that this magma series evolves following a crystal fractionation process. Amphibole fractionation plays a critical role in its evolution, at least from the intermediate magmas (Mugearite, Benmoreite). The detailed analysis of

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trace element distribution coefficients and modeling of the differentiation process has led Villemant et al. (1981) to the conclusion that amphibole fractionation was effective from the most primary magmas. On the basis of experimental petrology Foury (1983) reached similar conclusions. The field and petrological observations of Bourdier (1980) on eruptive products of the volcanoes of the Pavin group also evidenced the especially important role of amphibole fractionation in these magmas: large abundance of amphibole phenocrysts in lava flows (resorbed; Montchal) or in basaltic tephra (unresorbed; Montcineyre, Estivadoux), and in all Pavin products (pumice, bombs, amphibole cumulates). Furthermore, a recent petrological study of trachytic magmas of the Chaîne des Puys (Martel et al. 2013) shows that from a same initial differentiation series (basalt to intermediate magma) various P and T conditions have prevailed to produce the large variety of trachytic magmas erupted during the whole volcanic history of this volcanic chain.

This preliminary geochemical study shows that the different magmas which have been emitted by the volcanoes of the Pavin group on a relatively short interval of time (~500 years) have evolved following a single differentiation process from primary basalts to benmoreite. This magmatic activity produced the most primitive basalts (Montcineyre lavas) ever erupted since 200 ky in the Massif Central. This differentiation process differs from that observed in further north volcanoes of the Chaîne des Puys (stricto sensu) by the evolution of some specific trace elements as Nb, Ta or LREE from the most primitive basalts. Modeling the differentiation process using major and trace elements distribution coefficients highlights a very early and substantial amphibole fractionation, leading to the particular features of the Pavin benmoreitic magmas and likely indicating specific differentiation conditions in relation with its specific eruptive activity.

7.2 Samples and Analytical methods

The magmas emitted by the four volcanic edifices of the Pavin group (see geological maps in chapter 6, Leyrit et al. this issue) have been sampled through their different volcanic products. Montcineyre volcano (basaltic lava flow), Estivadoux basaltic maar (scoria fall deposits), Montchal volcano (scoria fall deposit and basaltic lava flow) and Pavin benmoreitic tephra (cauliflower bombs and pumice fall deposit). Only few geochemical data have already been published for this volcanic group (see e.g. Villemant et al. 1981 for trace elements) and mainly concern the lava flows and the Pavin bombs and blocks. In this preliminary study we have completed the available sampling (mainly Estivadoux scoria falls and Pavin pumice fall) and performed new trace element measurements.

Volcanic products of the Pavin eruption are frequently contaminated by fragments of surrounding rock material (gneiss, granite and old lava fragments of Mont Dore volcano). The granite and gneiss xenoliths are more or less modified by interaction with the Pavin magma (thermal metamorphism, degassing, sometimes partial melting). As far as possible, these xenoliths have been manually separated before fine crushing. Some volcanic fragments still containing significant fractions of various types of xenoliths and bulk rocks of some basement xenoliths have also been analysed to estimate the influence of this contamination on bulk compositions of Pavin products.

Trace element analysis of around 40 samples of Pavin group magmas has been performed by ICP-MS (see below). For comparison, a suite of 35 samples representative of the whole magma series of Chaîne des Puys corresponding to the sampling of Villemant et al. (1981) have also been re-analysed, with the same method during the same runs (unpublished data). Major elements compositions of some representative samples of Pavin group magmas have also been analysed (ICP-AES, CRPG Nancy). The compositions of uncontaminated magma fragments (~30 analyses) are reported in Table 7.1. Finally some mineral separates of Pavin products (major mineral phases and glass of pumice fragments and cumulates) have been analysed by ICP-MS and by electron probe (CAMPARIS, UPMC) to calculate mineral melt distribution for quantitative modeling. Detailed analyses will be published elsewhere. Major element compositions of glass are reported in Fig. 7.1 along with bulk rock compositions.

*Analytical Method (ICP-MS) f*or trace element analyses, between 10 mg (minerals and glass separates) and 50 mg (powdered bulk rock samples) were dissolved in 5 ml of concentrated HF-HNO_3 mixture and then evaporated to dryness. The residue was dissolved in 2 ml of HNO_3-H_3BO_3 mixture and slowly evaporated to remove possible weakly soluble fluorides. The new residue was dissolved in 2 % HNO_3 (i.e., dilution factor of ~10^4) for analysis. For mineral separates, somewhat less material was used per sample (~10–20 mg), but dilution in the final solution is similar for all analysed samples. Trace element compositions of prepared samples were measured by inductively coupled plasma mass spectrometry (ICP-MS) using a X Series II instrument of Thermo Scientific at the University P& M Curie (LAGE-ISTEP). For each set of measurements, two aliquots of the geochemical reference material BHVO-2 were prepared according to the same procedure as for the samples and analysed every five samples to correct instrumental drift during analysis and to calculate unknown sample compositions. The mean reproducibility of the analytical procedure was estimated from a series of more than 20 independent measurements of BHVO-2 and reported in Table 7.1. The mean analytical error is ≤ 5 % for most trace elements, except Rb, Cs, Sc and Pb (error of ca. 10 %).

7.3 Results

7.3.1 The Pavin Group Magmas: Comparison with Chaîne des Puys (stricto sensu)

7.3.1.1 Major Elements

The different edifices and eruptive units of the Pavin group which have been analysed correspond to a large composition domain: basalt for Montcineyre lava flows, hawaïite for Montchal lava flow ('Couze Pavin' flow) and Estivadoux scoriae, benmoreite/trachyte for Pavin products (bombs and plinian clasts).The evolution of the major element compositions is closely similar to that of the Chaîne des Puys (stricto sensu) magmas (Fig. 7.1) with however two significant differences: the Pavin group magmas are slightly more K-rich as a whole, difference which increases with magma differentiation process and Montcineyre basalts are the most primitive basaltic lavas erupted since ~200 ky. The composition of Montcineyre basalts is compared to that of primitive melt inclusions of olivines from Puy Beaunit volcano, which are also considered as the most primitive melts analysed in Chaîne des Puys products (Jannot et al. 2005). Both compositions are very close (except in Fe and Ca), but with slightly more primitive characters for Montcineyre basalts. Post-entrapment evolution and analytical difficulties inherent in melt inclusions analysis may explain the discrepancies in Ca and Fe, and they require further investigations to address these uncertainties.

The benmoreite of Pavin and the trachyte of Clierzou – emitted by a volcano north of Chaîne des Puys have a very similar mineralogy (alkali-feldspar, abundant amphibole – Hb-, minor Cpx, Fe-Ti oxides) and are very close in major element composition. The Pavin benmoreite is however sigificantly more K-rich and less Na-rich than the Clierzou trachyte. Major element evolutions from basalts to benmoreite-trachyte are thus very similar for both volcanic systems and the differentiation process is mainly driven by crystal fractionation (Maury et al. 1980; Villemant et al. 1980, 1981).

Electron-probe analyses of the interstitial glass of Pavin benmoreite in cauliflower bombs and in amphibole cumulates are also reported in Fig. 7.1 along with glass separates of Chaîne des Puys (stricto sensu) lavas (Villemant et al. 1981; Lemarchand et al. 1987). These data plot in the trachyte domain and are wholly included within the main differentiation trend of Chaîne des Puys magmas (defined by both whole rock and glass compositions of benmoreites to evolved trachytes), except for K_2O : the glass of Pavin benmoreite displays a large enrichment in K_2O from ~5 % to ~6.5 %, at almost constant SiO_2 (~65 %). The residual glass of amphibole cumulates is the most evolved glass analysed in Pavin magmas.

7.3.1.2 Trace Elements

Trace element composition evolutions in function of Th content are reported in Fig. 7.2. Th is a highly incompatible element and used as a reference because of its very low bulk solid/melt partition coefficient in these magmas. Its relative variations are almost exactly proportional to the differentiation degree of the melt (or fraction of residual melt *f*; Villemant et al. 1981). REE compositions normalized to Chondrites are reported in Fig. 7.3.

Contrary to major elements, compositions and evolution trends in most trace elements are clearly distinct between magmas of the Chaîne des Puys (stricto sensu) and of the Pavin group. Though trace element compositions of initial basaltic magmas are very close the evolution trends differ markedly from the hawaïtes to the benmoreites, indicating significant differences in the differentiation processes.

Basalts Montcineyre basalts (in fact, basanites in classification IUGS) have particularly high contents in compatible elements (3d transition series trace elements: Ni ~240 ppm, Cr ~350 ppm and Co ~ 56 ppm and major elements: TiO_2 ~ 2.8 %, FeO_t ~ 11.2 %, MgO ~ 12.8 %) which indicates their highly primitive character. Significant effects of olivine accumulation which could explain the high MgO and Ni contenst in these lavas can however be excluded because they are also enriched in Ti Sc and Co which are not compatible in olivine.As for major elements, comparison with measurements in melt inclusions of Puy Beaunit olivine (Jannot et al. 2005) often show close similarities between both magma compositions. However, it is not clear if the lowest contents in incompatible elements (Th, LREE, Nb, Ta, Hf) reported in some melt inclusions are real or related to analytical difficulties (apparent 'dilution effect' of LA-ICP-MS relative to EPMA) because they are inconsistent with their relatively low contents in Fe, Mg or Ti (compare melt inclusion data in Figs. 7.1 and 7.2). Further studies are needed to explain the apparent discrepancies between trace and major element compositions of basaltic melt inclusions and bulk rocks. The bulk composition of Montcineyre basalt thus represents the best available representative of the primary melts generated by partial melting at depth during the recent volcanic activity of Chaîne des Puys and Pavin group volcanoes. It likely represents the common initial melt from which different differentiation processes have operated to produce the large diversity of trachytic magmas produced in this area. The trace element characteristics of these primary melts have been discussed in details by Jannot et al. (2005) using melt

Table 7.1 Major and trace element composition of Pavin group magmas

Sample	Montcineyre		Estivadoux	Montchal						Pavin			
	P13-8	P7699	P13-7TE	P13-7Sa	P13-7Sb	P7698	P13-4	P13-5	P13-9	KBP2b*	KBP3b*	PAV-0	PAV1-1
	Lava Flow			Scoria fall deposit		Lava Flow (couze Pavin)				Cauliflower bombs		Plinian Fall	
				Red (Top) Black (bottom)		*Besse en Chandesse*			*Sanner*	(1981, unpub.)	in Bourdier (1980)		
SiO_2	43.80						49.20			57.71	58.45		
TiO_2	2.80						2.60			1.37	1.30		
Al_2O_3	14.10						16.30			18.01	18.05		
Fe_2O_3	5.96						5.02						
FeO	5.80						4.93			5.99	6.11		
MnO	0.17						0.17			0.15	0.15		
MgO	12.70						7.25			1.78	2.11		
CaO	10.00						9.00			4.80	4.71		
Na_2O	3.20						3.70			5.50	5.01		
K_2O	1.45						2.20			4.50	4.11		
P_2O_5										0.37			
PF	0.06												
Total	100.04						100.37			99.73	100.00		
Trace elements ppm													
Rb	39.0	33.5	60.6	62.4	71.2	56.8	62.2	61.4	55.2	134.5	141.4	132.5	132.8
Cs	0.86	0.66	1.47	1.38	1.58	0.76	0.92	1.05	0.88	0.96	2.34	2.83	2.12
Sr	685	722	627	610	640	701	422	623	649	537	731	788	729
Ba	480	466	530	545	593	559	579	589	549	881	909	901	1006
Y	21.8	21.4	23.6	22.2	23.9	23.8	24.3	24.4	22.9	21.0	24.3	27.4	25.6
La	43.0	42.0	46.3	47.5	52.3	45.8	50.3	51.1	48.3	65.6	74.5	74.3	79.6
Ce	85.6	82.3	91.9	92.7	102.0	88.6	97.9	99.9	94.6	115.0	134.7	134.3	141.5
Pr	10.1	9.6	10.8	10.7	11.7	10.0	11.2	11.5	10.9	12.1	14.0	14.5	14.7
Nd	39.2	37.1	41.3	40.4	43.8	37.8	42.2	43.0	41.3	41.8	47.8	50.1	50.0
Sm	7.70	6.84	7.91	7.72	8.32	6.92	7.93	8.16	7.89	7.09	7.95	8.45	8.19
Eu	2.47	2.36	2.50	2.44	2.60	2.36	2.54	2.55	2.48	2.39	2.44	2.77	2.81
Gd	7.56	7.79	7.85	7.58	8.13	8.11	7.96	8.06	7.83	7.05	7.85	10.13	10.10
Tb	0.98	0.95	1.02	0.99	1.05	1.00	1.04	1.05	1.02	0.87	0.96	1.14	1.12
Dy	5.01	4.54	5.39	5.16	5.51	4.88	5.41	5.42	5.29	4.59	5.03	5.39	5.08
Ho	0.92	0.83	1.01	0.97	1.03	0.91	1.01	1.02	1.01	0.89	0.97	1.04	1.00
Er	2.34	2.22	2.63	2.55	2.72	2.51	2.62	2.66	2.58	2.45	2.68	3.03	2.96
Tm	0.30	0.28	0.36	0.35	0.36	0.33	0.36	0.37	0.35	0.35	0.38	0.41	0.39
Yb	1.80	1.64	2.15	2.12	2.22	1.94	2.17	2.21	2.16	2.29	2.44	2.65	2.52
Lu	0.26	0.24	0.31	0.30	0.32	0.28	0.31	0.31	0.30	0.34	0.36	0.38	0.37
Zr	235	219	270	278	298	280	300	304	281	448	497	474	507
Hf	5.18	4.61	6.06	6.18	6.44	5.55	6.39	6.47	6.18	8.63	9.48	8.84	9.41
Nb	59.9	54.3	61.9	63.3	68.8	61.0	69.3	69.2	64.6	106.4	110.2	100.8	110.3
Ta	3.41	3.02	3.70	3.79	4.08	3.34	3.92	3.97	3.79	5.17	5.96	5.39	5.77
Pb	2.28	3.67	4.43	4	5	3	4	4	4	8	10	9	9
Th	4.74	4.73	6.87	7.13	7.74	6.94	7.29	7.35	6.92	15.98	17.12	17.51	18.04
U	1.30	1.26	1.96	2.04	2.26	1.75	1.96	2.10	1.87	4.60	4.71	4.71	4.89
Sc	27	26	23	19	18	18	22	21	21	10	10	13	12
V	280	275	223	189	202	230	232	226	216	103	103	110	96
Cr	345	377	146	108	83	148	180	145	181	10	11	16	14
Co	56.4	57.1	33.5	30.4	32.0	35.8	37.9	35.3	35.3	10.9	11.8	11.5	10.5
Ni	237	221	57	51	46	73	78	64	75	6	8	9	7
Cu	51	67	38	42	40	54	52	45	44	14	12	36	47
Zn	83	89	90	70	78	85	80	79	73	69	70	67	65

* indicates that xenoliths fragments have been removed by hand

Trace elements in ppm. BHVO-2 is used as the reference for ICP-MS measurements. Reproducibility (in %) is calculated on 25 repeated measurements

															Reproducibility	
PAV1-11	PAV1-12	PAV-1-15	PAV1-2	PAV-1-25	PAV1-3	PAV1-4	PAV2-1	PAV2-3	PAV2-5	PAV2-6	PAV2-7	PAV2-8	PAV2-9	PAV1-7	BHVO-2 Ref	%
121.6	115.1	123.6	131.9	123.9	130.0	121.1	121.1	115.2	109.1	102.8	115.0	131.9	128.3	124.3	9.60	5.0
2.26	2.10	3.05	2.65	2.70	2.37	2.24	1.98	2.05	2.05	3.04	2.02	2.65	2.38	2.29	0.03	5.0
735	746	661	725	745	719	723	696	743	779	681	723	741	700	712	381	1.2
871	840	843	884	889	908	858	910	847	872	929	844	903	886	879	133	4.7
22.8	24.7	21.7	24.5	24.8	25.4	25.2	21.2	23.1	23.2	23.9	24.3	24.1	24.4	23.6	23.1	5.0
73.0	75.0	69.5	72.4	77.4	76.3	74.0	69.3	69.5	68.4	69.4	73.2	76.6	84.1	73.9	15.2	5.5
13.03	134.2	125.6	131.9	142.1	137.3	134.4	125.6	125.9	126.2	130.2	134.5	137.0	149.7	131.7	37.9	2.3
13.7	14.1	13.1	13.7	14.9	14.3	14.2	12.9	13.4	13.6	14.0	14.2	14.3	15.3	13.8	5.38	0.1
45.8	48.2	44.5	47.1	51.3	48.8	48.1	44.2	46.0	46.4	48.3	49.0	47.9	51.6	46.5	24.4	5.1
7.77	7.81	7.36	7.64	8.45	7.94	8.03	7.14	7.59	8.04	8.37	8.31	7.69	8.45	7.57	6.06	8.0
2.52	2.65	2.25	2.62	2.56	2.60	2.63	2.57	2.59	2.67	2.76	2.69	2.61	2.64	2.55	2.05	1.7
9.20	9.66	7.34	9.41	8.33	9.78	9.75	8.94	9.14	9.44	10.07	9.98	9.63	10.37	9.29	6.22	0.1
1.05	1.10	0.90	1.05	1.02	1. 10	1.10	0.98	1.07	1.08	1.14	1.11	1.07	1.11	1.06	0.93	3.8
4.77	5.08	4.66	4.90	5.22	5.16	5.20	4.45	4.90	5.08	5.27	5.24	4.97	5.30	4.80	5.25	0.2
0.92	0.98	0.90	0.93	1.01	0.99	1.01	0.87	0.96	0.96	1.01	1.02	0.97	1.03	0.92	1.00	3.7
2.72	2.82	2.50	2.74	2.76	2.93	2.92	2.62	2.74	2.85	2.96	2.95	2.82	3.03	2.81	2.51	1.0
0.38	0.38	0.36	0.36	0.40	0.41	0.40	0.36	0.38	0.40	0.41	0.41	0.39	0.41	0.39	0.34	8.0
2.33	2.46	2.34	2.35	2.52	2.51	2.57	2.02	2.44	2.50	2.71	2.58	2.51	2.67	2.56	1.99	0.4
0.34	0.36	0.34	0.35	0.37	0.36	0.36	0.31	0.34	0.34	0.37	0.37	0.34	0.38	0.36	0.27	0.4
475	483	440	469	473	503	496	467	457	474	465	465	499	493	485	174	4.0
9.05	9.14	8.81	8.49	9.24	9.44	9.42	8.90	8.70	9.11	8.93	8.95	9.24	9.60	9.14	4.28	0.4
105.3	106.3	99.3	103.1	111.8	110.8	109.8	103.4	101.6	107.1	107.2	104.6	111.3	111.8	107.4	17.2	6.0
5.59	5.65	5.71	5.33	6.16	5.87	4.63	5.53	5.29	5.66	5.67	5.52	5.90	5.60	5.72	1.06	5.0
9	8	11	9	10	9	8	8	9	9	10	9	9	9	29	2	8
17.72	17.11	16.70	16.89	17.32	18.30	17.41	17.31	16.68	17.74	18.57	17.44	17.97	18.84	17.95	1.12	4.5
4.96	4.71	4.68	4.56	4.73	5.01	4.82	4.08	4.60	5.17	5.35	4.76	5.10	5.20	5.05	0.39	4.0
12	11	10	15	9	13	12	11	13	12	12	12	10	11	11	29	8.4
83	90	81	96	94	96	105	81	105	101	113	114	86	84	83	310	3.0
9	10	11	14	10	11	16	9	16	13	18	29	7	7	8	283	2.7
8.6	9.2	8.8	10.4	10.4	9.8	10.8	8.8	11.8	10.5	13.1	12.6	8.8	8.9	8.7	46.5	4.0
6	6	7	7	5	6	7	6	9	8	12	14	5	6	5	121	2.6
55	61	70	16	16	78	135	14	37	34	37	47	59	76	56	117	5.5
61	74	69	76	76	67	67	64	64	61	68	63	67	88	61	95	7.0

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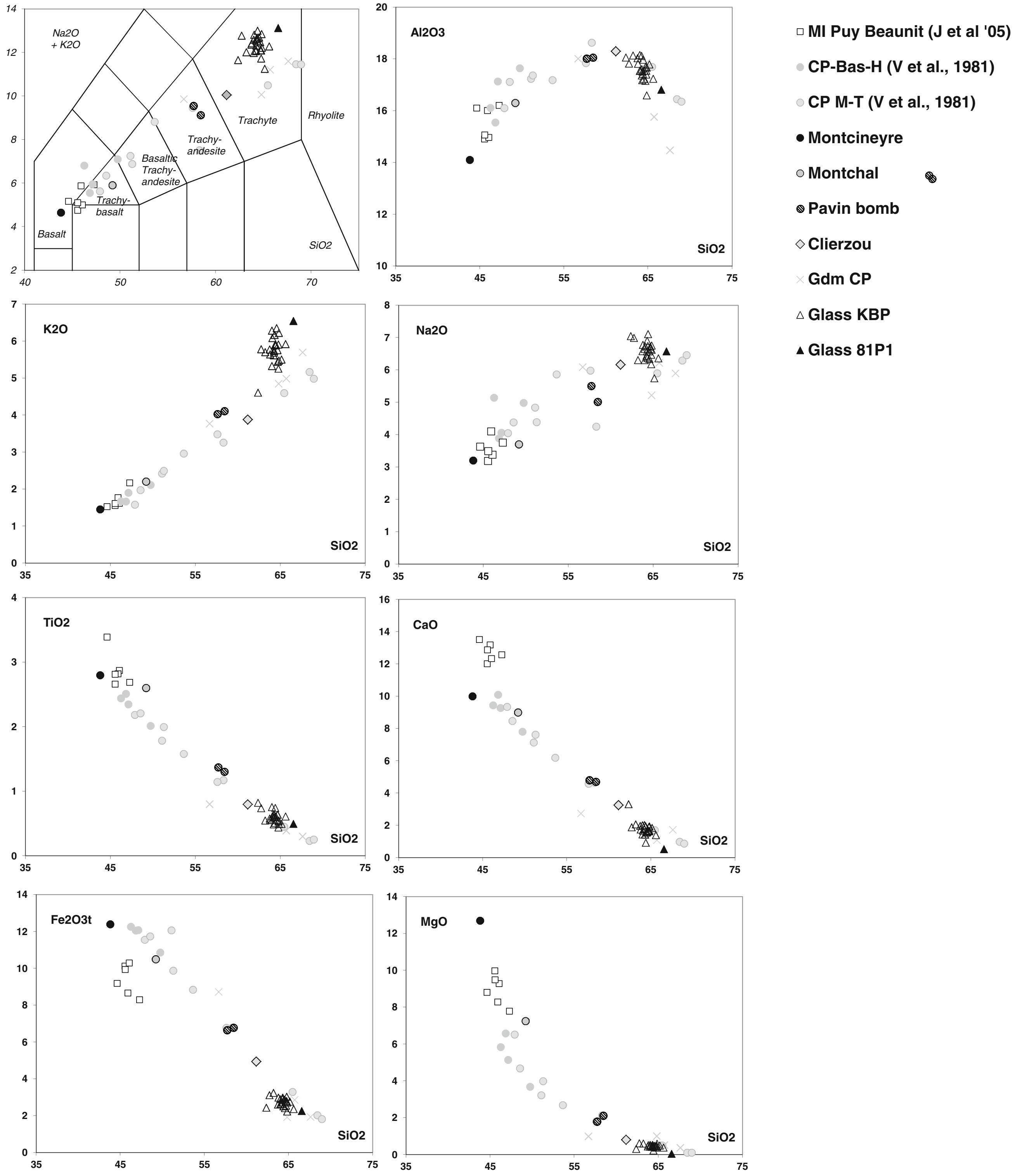

Fig. 7.1 Evolution of major element compositions (wt%) of Pavin group magmas. *Black dot*: Montcineyre basalt (lava flow); *circled grey dot*: Montchal hawaïite (lava flow); *dashed circles*: Pavin benmoreites (bombs). *Triangles*: glass compositions of Pavin benmoreite (*open triangles bombs* (KBP), *solid triangle*: residual glass of amphibole cumulates(81P1)). *Light grey dots*: compositions of Chaîne des Puys (stricto sensu) magmas (Bas-H: basalts- hawaïites, M-T: mugearites-trachytes; Villemant et al. 1981 and unpublished data). *Light grey crosses*: glass compositions of Chaîne des Puys (stricto sensu) samples (data from Villemant et al. 1981; Lemarchand et al. 1987). *Grey diamond*: amphibole-bearing trachyte of Clierzou volcano (north Chaîne des Puys). *Open squares*: compositions of melt inclusion in olivine of Puy Beaunit (north Chaîne des Puys; data from Jannot et al. 2005)

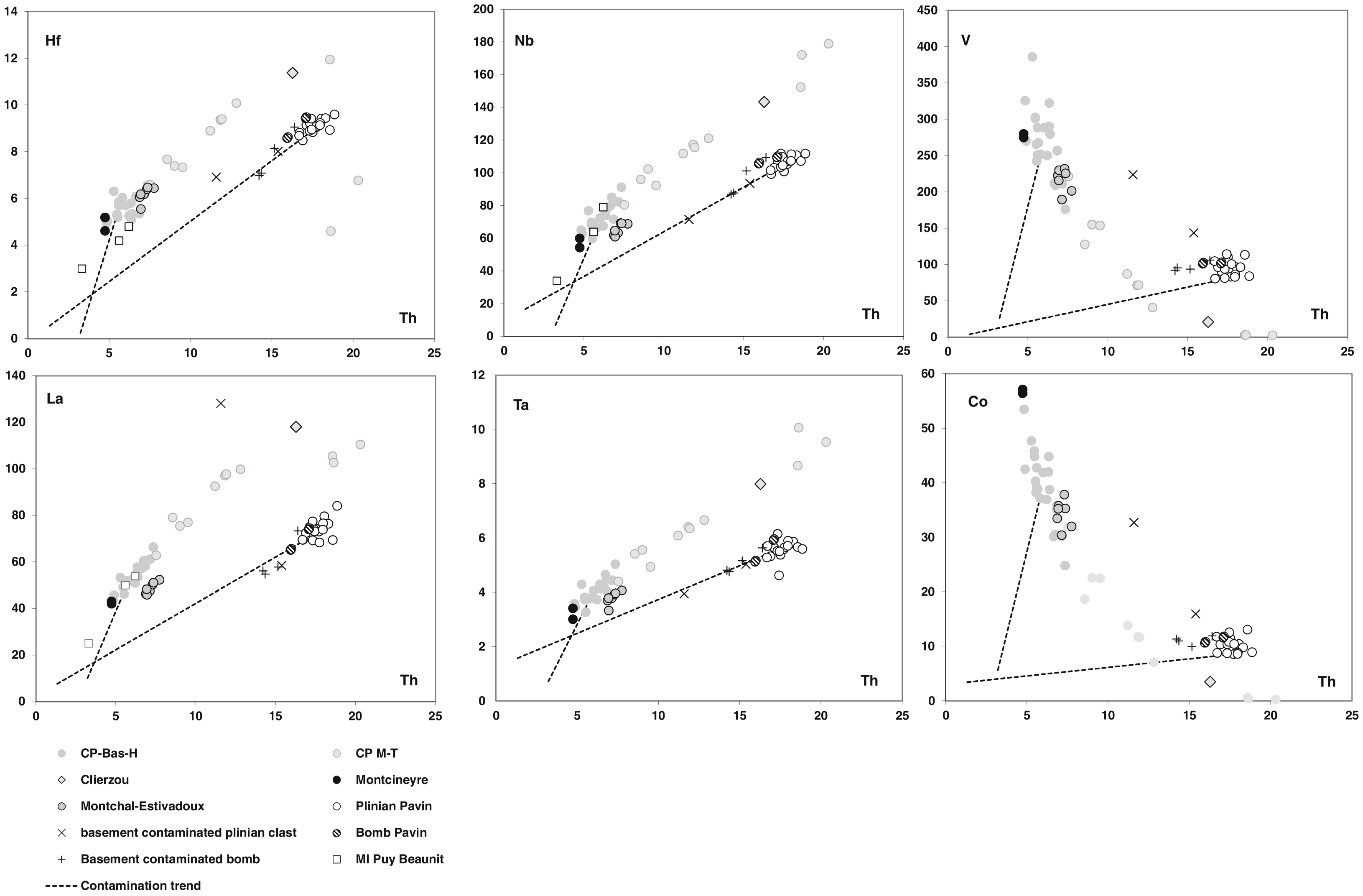

Fig. 7.2 Evolution of trace element compositions (ppm) of Pavin group magmas. *Black dots*: Montcineyre basalts (lava flows); *circled grey dots*: hawaïtes of Montchal (lava flows and scoria fall) and Estivadoux maar (scoria fall); Pavin benmoreites: *dashed circles* (cauliflower bombs), *open circles* (plinian clasts). *Crosses* : basement contaminated magmas (+ bombs, × plinian clast). Chaîne des Puys magma compositions (unpublished data): symbols as in Fig. 7.1. *Dotted line*: possible contamination trends of Pavin clasts by xenoliths (basement xenoliths or older basaltic fragments –unpublished data; not represented-) and emitted during the phreato-magmatic activity

inclusion compositions. Though some analytical limitations (see above) may slightly blur the geochemical signature of the primary magmas, the Montcineyre basalt and Puy Beaunit olivine melt inclusions are close enough to assume that the same mantle source produced the primary basalts of Chaîne des Puys (stricto sensu) and of Montcineyre at the origin of distinct differentiation suites.

Hawaïites they are represented by both the Puy Montchal lava flows (in particular the 'Couze Pavin' flow) and strombolian scoriae and by the tephra generated by the Estivadoux maar. The trace element compositions of Pavin group hawaïites are relatively close to those of Chaîne des Puys (stricto sensu) but are slightly more rich in Th, U, and significantly depleted in REE, Nb, Ta, Y and Ba. They have similar contents in compatible elements (3d transition series elements) except enrichment in Ni (80–180 ppm) against 20–100 ppm in hawaïites of Chaîne des Puys (stricto sensu). Clear evolution trends are defined by the Montcineyre basalts and the Montchal-Estivadoux hawaïites. They are clearly distinct from that of Chaîne des Puys (stricto sensu), except for some highly incompatible elements: U, Th, Rb, Zr and Hf. For all other incompatible (such as Nb, Ta or REE) and compatible elements (as 3d transition series elements) the trends defined in binary diagrams using Th as a reference (Fig. 7.2) are significantly distinct from those of the Chaîne des Puys (stricto sensu)

Pavin Benmoreites differentiated magmas are only represented in the phreato- magmatic and plinian products of Pavin eruption. Cauliflower bombs are magma fragments more or less rapidly quenched by interaction with rock and water of the surrounding basement. Due to this explosive interaction they are very frequently contaminated by solid fragments of basement rock material (mainly granite and gneiss) which is also sometimes (mainly for small < cm fragments) thermally metamorphosed and sometimes partially melted and/or degassed. Plinian clasts collected in the pumice fall deposit are less frequently contaminated. Though careful magma fragment selection was performed before crushing, accidental contamination by solid rock fragments or contamination by fluids and partial melts of interacting rocks may not be a priori discarded. In order to estimate the possible effects of these interactions, different xenoliths fragments and magmatic clasts with evidence of contamination have been analysed together with 'fresh' material. A detailed study of the interaction of surrounding material with Pavin magma is beyond the scope of this study. To test however the possible role of such contamination processes we have also reported in Fig. 7.2 the compositions of 'basement-bearing' magma fragments and two 'tie-lines' between xenolith fragments and their host magma (a Pavin cauliflower bomb and a basalt of Tartaret volcano, north the Pavin group). The compositions of contaminated benmoreites display linear trends which are close to the benmoreite-xenolith tie line. These common trends are clearly distinct from the basalt – hawaïite – benmoreite trends (Pavin group or Chaîne des Puys). In addition the basalt-xenolith tie line does not correspond to any magmatic trend. Finally, some contaminated clasts from plinian deposit display a distinct trend to the main contamination trend for compatible elements (see e.g. Cr, Co, Ni, Sc, V; Fig. 7.2) suggesting an additional contamination by basaltic clasts. These observations indicate that the late interactions of differentiated magmas and the surrounding rock material during their explosive eruption, do not significantly affect the melts compositions and that their effect are restricted to a pure mechanical contamination of erupted products. In addition, most plinian clasts of Pavin are uncontaminated and define a narrow composition range for all trace elements. Finally the basaltic and hawaïitic magmas are clearly unaffected by these processes.

Though close in major element composition (except K_2O) to the Clierzou trachyte, the Pavin benmoreite has very different trace element contents and specifically much lower contents in numerous incompatible elements such as REE, Nb, Ta, Zr, Hf and Ba. Pavin benmoreites are also significantly richer in 3d transition series elements compared to their benmoreitic and trachytic equivalents (i.e. at similar Th or SiO_2 contents) of Chaîne des Puys (stricto sensu). They are particularly rich in Co and V and in Ti and Fe.

The compositions in REE of Pavin group magmas, normalized to Chondrites are reported in Fig. 7.3 and compared to Chaîne des Puys (stricto sensu) compositions. It displays a typical REE pattern of alkaline series with a large enrichment in LREE relative to HREE ($(La/Yb)_N$ ~20) and a bulk enrichment of REE with differentiation degree. It is in the same range as other Chaîne des Puys magmas, with a particular feature for Clierzou trachyte which is significantly more enriched than all other magmas. A specific feature of Pavin group magma is that differentiation leads to enrichment in LREE and HREE, but more limited enrichment in MREE. This particular evolution is typically due to the fractionation of accessory minerals as apatite or titanite which is usually only observed in most differentiated alkaline magmas (Villemant et al. 1979). This is consistent with petrological observations which point out the significant fraction of apatite inclusions in clinopyroxenes of Pavin group magmas (Bourdier 1980).

The trends defined by the three main magma types (basalts, hawaïites, benmoreites) of the Pavin group represent an actual magma differentiation process which is significantly distinct from that of the main Chaîne des Puys series.

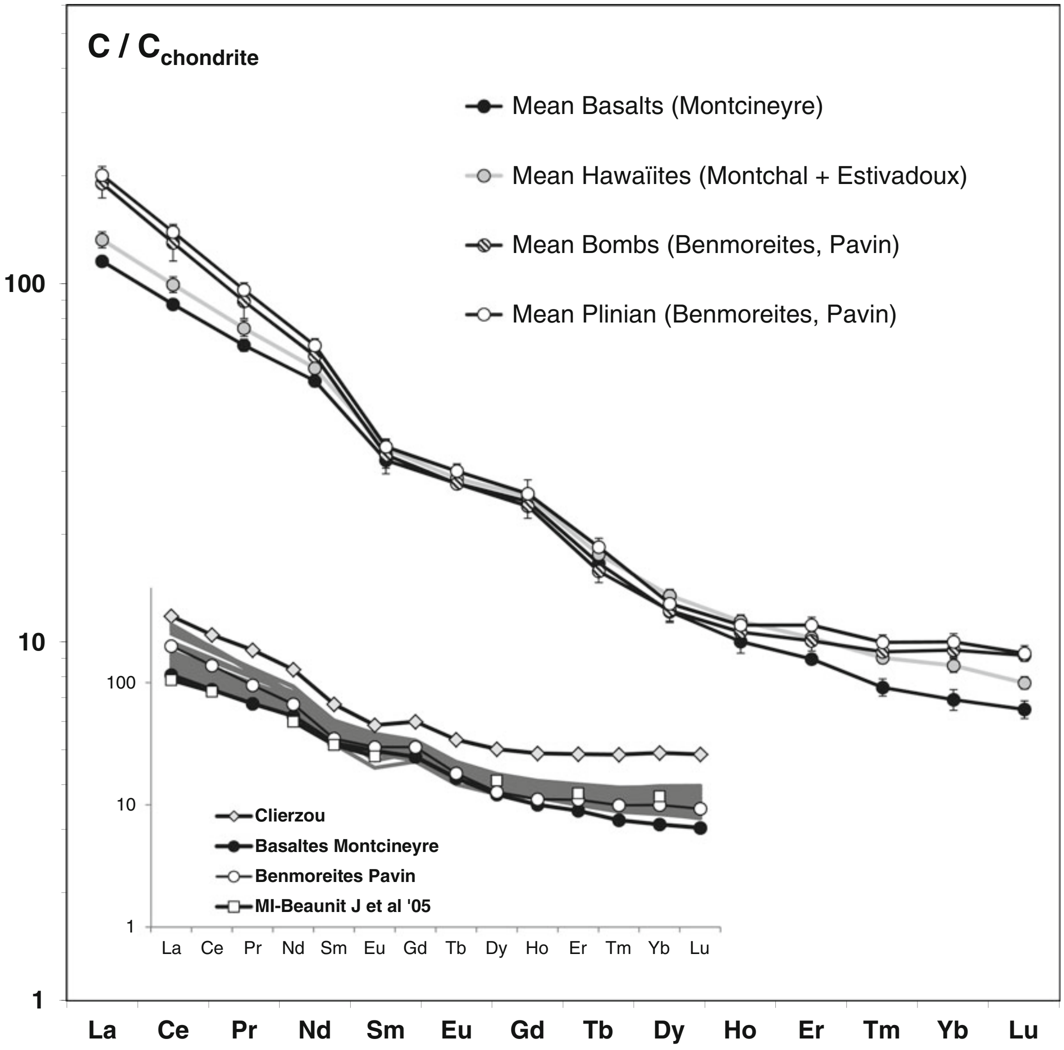

Fig. 7.3 Chondrite normalised REE diagrams of Pavin group magmas. Symbols as in Fig. 7.2. *Inset*: comparison with Chaîne des Puys magmas (*grey lines*)

7.3.2 The Pavin Differentiation Series: A Crystal Fractionation Trend Dominated by Amphibole Fractionation

The compositions of Pavin group magmas define variation trends that have the same main characteristics as those observed for the Chaîne des Puys (stricto sensu) series: from basalts to benmoreites and trachytes, early depletion in 3d transition series elements (Sc, Ti, V, Cr, Fe, Co, Ni) correlated to a large enrichment in highly incompatible elements (Th, U, Rb, LREE among others) that is characteristic of a dominant evolution by crystal fractionation (Villemant et al. 1980, 1981). In addition, for all the northern edifices of Chaîne des Puys (stricto sensu), there is a single mode of differentiation from basalts to benmoreites, and it diverges in several distinct paths only at the stage of trachytes differentiation (Villemant et al. 1981; Martel et al. 2013). For the Pavin group the differentiation process differs significantly from that of Chaîne des Puys (stricto sensu) as early as at the stage of evolved basalts indicating significant differences in deep differentiation conditions between both volcanic systems.

The differentiation steps from basanite to hawaïite and from hawaïite to benmoreites in Pavin group series are not represented by erupted magmas contrary to what is observed for the whole Chaîne des Puys series. These apparent discontinuities are however not surprising because the Pavin group represents only a very short activity period (~400 years). If Pavin benmoreitic magmas is actually related by a continuous crystal fractionation process to Montcineyre basalts through Montchal and Estivadoux hawaïites, it is therefore possible to quantify this process using the method developed by Villemant et al. (1981).

The basic ideas of this classical modeling method are summarised thereafter. The Rayleigh law describing the crystal fractionation process writes $C_i = C_i^\circ f^{(Di-1)}$, where C_i and C_i° represent the concentration of element *i* in the melt and in the initial melt respectively. *f* is the residual melt fraction ($f = M_L/M_L^\circ$, where M_L and M_L° are the mass of residual melt and of initial melt respectively). *Di* is the bulk solid/melt partition coefficient of element *i* ($D_i = C^s_i/C_i$, where C^s_i is the concentration of element *i* in the solid in equilibrium with the melt). If a highly incompatible element as Th is used as a reference, it can be shown that in $\log(C_i) - \log(Th)$ diagrams, for composition domains where D_i is constant to first order the crystal fractionation trend is represented by a straight line with a slope $\Delta_i \sim 1 - D_i$. It has been shown that the Chaîne des Puys series evolved by steps over which the D_i values are approximately constant (Villemant et al. 1980, 1981; see Fig. 7.4a). During each differentiation step the modal composition of the fractionating minerals is in first approximation constant, and the abrupt changes in D_i values are clearly related to the changes in the mineralogy of the fractionating solid. The bulk solid/melt partition coefficients D_i are directly related to the mineral (j)/melt partition coefficients d^j_i by the relation: $D_i = \Sigma\, \alpha^j d^j_i$, where the α^j are the weight fraction of minerals j in the fractionating solid. If the d^j_i are known or measured independently (see for example Lemarchand et al. 1987, for determination in alkali basalt series or Blundy and Wood 2003, for theoretical calculation of mineral/melt partition coefficients) it is thus possible to calculate the modal composition of the fractionating solid (see Villemant et al. 1981 for resolution methods and a detailed application to the Chaîne des Puys model) and to compare it to petrological observations (determination of modal composition using point counting) or mass balance calculations on major elements (see e.g. Wright and Doherty (1970) and derived methods).

We have reproduced this model for the Pavin group magmas assuming a single continuous differentiation process and calculated the composition of the fractionating solid consistent with this interpretation. The data are compared to the modeling already performed for the Chaîne des Puys (Villemant et al. 1981) and to the mass balance calculations performed on major elements by Bourdier (1980). In Table 7.2 and Fig. 7.4 are reported the bulk solid/melt partition coefficients of trace elements calculated for the Pavin group and the Chaîne des Puys (stricto sensu) for the first two differentiation steps: Basalts-Hawaïites and Hawaïites-Benmoreites.

The bulk partition coefficients calculated in log diagrams are very different for Pavin group and for Chaîne des Puys (stricto sensu) for both differentiation steps, especially for elements usually considered incompatible. The D values of REE, Nb, Ta are unusually large (Fig. 7.4b) in both series which has been attributed to the fractionation of amphibole at the expense of clinopyroxene in crystallising solid (Villemant et al. 1981), in agreement with petrological observations (see e.g. Foury 1983). This effect is even more pronounced for Pavin group magmas and consistent with the ubiquitous presence of amphibole from basalts to benmoreites (Bourdier 1980). The mineral/melt partition coefficients of highly incompatible elements for amphibole and clinopyroxene are different enough to induce a significant effect on corresponding bulk D values (Fig. 7.4b). Indeed, for most elements mineral/melt partition coefficients of these two minerals are very close (Lemarchand et al. 1987) except in Nb and Ta and LREE. For these elements, other major mineral phases that may crystallise in basic and intermediate magmas (olivine, feldspars, Fe-Ti oxides) have all very low mineral/melt partition coefficients. Thus, the bulk D value patterns directly reflect the fraction of amphibole and/or clinopyroxene that are involved in crystallising solid. Fig. 7.4b provides a clear evidence for the predominance of amphibole as early as in basaltic melts in Pavin group differentiation series. However, this comparison also shows that REE behavior cannot only be explained by amphibole fractionation and requires also the fractionation of mineral phases having higher partition coefficients for MREE than HREE and LREE. This qualitative result also suggests that an accessory mineral phase (such as apatite) may also play a significant role in REE fractionation.

Mass balance calculations using the method described above and mineral/melt partition coefficients measured in alkaline series (Lemarchand et al. 1987) allow estimation of the modal compositions of the crystallizing solids during the two differentiation steps (Table 7.3). They are consistent with modal compositions calculated using other mass balance methods (major elements) and with petrological data (point counting). In agreement with the above discussion the weight fraction of amphibole and the total fraction of clinopyroxene + amphibole that crystallise in basaltic melts are larger in Pavin series than in Chaîne de Puys series. The mean calculated amphibole/clinopyroxene ratio is ~1:2 in Chaîne des Puys basalts and ~2:1 in Pavin group basalts. Amphibole is generally absent in Chaîne des Puys basalts and hawaïite lava flows but it sometimes occurs in basaltic tephra of Chaîne des Puys as resorbed phases, and its presence is ubiquitous in Montcineyre basaltic scoriae (Bourdier 1980). Notice that only modeling using trace elements is able to quantify the amphibole fractionation in Chaîne des Puys basic magmas. Conversely, during the second differentiation step (hawaïite-benmoreite) amphibole fraction is larger in Chaîne des Puys series. More generally, the crystallisation of ~75 % of basaltic melt are necessary to produce benmoreite magmas of which approximately one half consists in amphibole in Pavin series against only one third in Chaîne des Puys series.

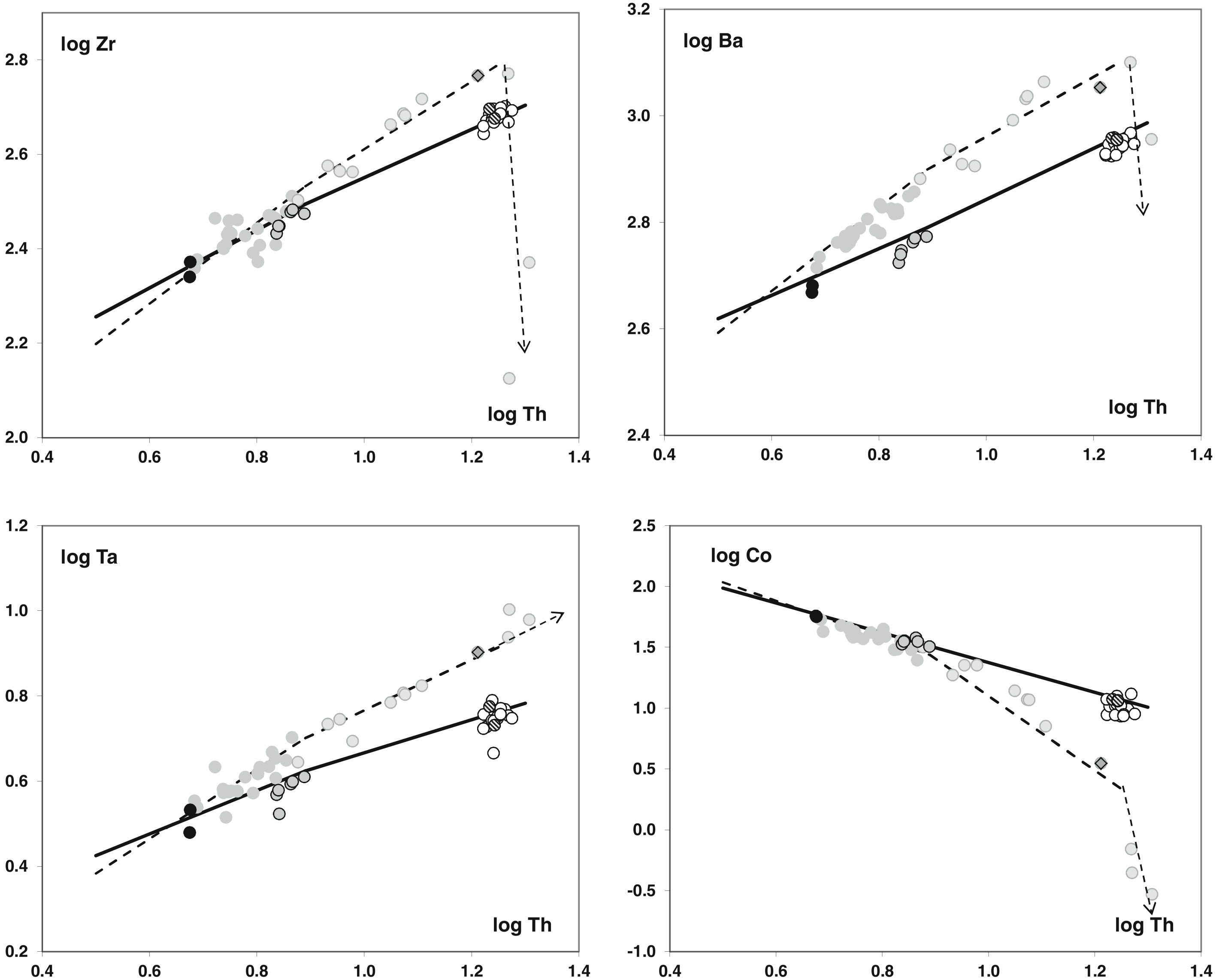

Fig. 7.4 Calculation of bulk D values in logarithmic diagrams. (**a**) Example of logarithmic diagrams. Symbols as in Figs. 7.1 and 7.2. Lines are regression lines of slopes Δ_i with Δ_i ~1–Di. Comparison between Chaîne des Puys (stricto sensu) and Pavin group magmas evidence a stepwise differentiation process, each step being characterized by approximately constant D_i values. (**b**) Bulk D values of some incompatible elements, comparison with amphibole and clinopyroxene/melt partition coefficients. Zr, Hf, Nb, Ta and REE partition coefficients calculated for Basalt-Hawaïte and Hawaïte-Benmoreite differentiation steps in Pavin group (Dg Pav) and Chaîne des Puys (stricto sensu; Dg CP) differentiation series. Mineral/melt partition coefficients for clinopyroxene (d CPx) and amphibole (d Amph) in alkaline series are from Lemarchand et al. (1987). For Basalt-Hawaïte differentiation step, mineral/melt partition coefficients vary in a relatively large range: extreme values are represented). Notice the large differences in bulk D values of LREE in basalt-hawaïte differentiation steps in Pavin and Chaîne des Puys series. The mineral/melt partition coefficients of amphibole and clinopyroxene are generally close for all elements ('parallel D values patterns'), except Nb and Ta which are much more efficiently partitioned into amphibole

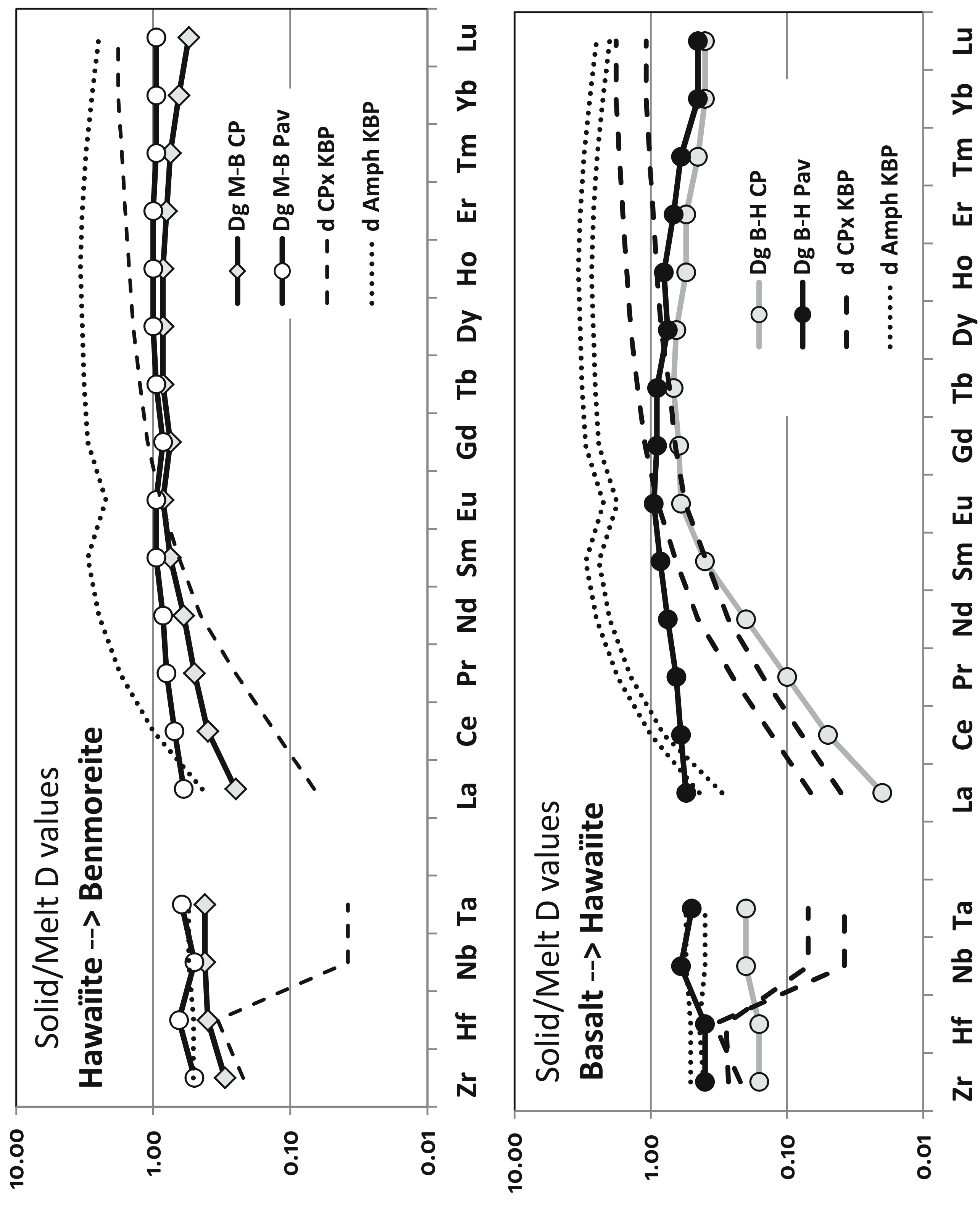

Fig. 7.4 (continued)

Table 7.2 Bulk solid/melt partition coefficients of Pavin and Chaîne des Puys series

	Pavin group		CP	
	β–H	M–B	β–H	M–B
SiO_2	0.72	0.82	0.75	0.70
TiO_2	1.20	1.80	1.20	2.50
Al_2O_3	0.70	0.90	0.70	1.10
Fe_2O_3 t	1.30	1.60	1.10	2.50
MgO	2.50	2.50	2.00	3.50
CaO	1.28	1.80	1.30	2.20
Na_2O	0.35	0.60	0.35	0.60
K_2O	0.10	0.25	0.10	0.25
Th (reference)	0.02	0.02	0.02	0.02
Zr	0.40	0.50	0.16	0.30
Hf	0.40	0.65	0.16	0.40
Ta	0.50	0.62	0.20	0.42
Ba	0.57	0.53	0.23	0.45
Sr	1.21	0.85	1.21	1.06
Rb	0.02	0.20	0.02	0.02
Cr	3.35	3.80	5.50	4.50
Co	2.20	2.20	2.50	4.00
Ni	4.50	3.00	3.60	6.00
Sc	1.69	1.50	2.50	2.30
La	0.55	0.60	0.02	0.25
Eu	0.95	0.95	0.60	0.85
Tb	0.90	0.95	0.68	0.85

The D values are calculated from logarithmic diagrams (see Fig. 7.4) for the first two differentiation steps (Basalts-Hawaïites and Mugearites-Benmoreites)

Table 7.3 Modal composition of fractionating solids (mass balance calculations)

Differentiation	Minerals weight fractions (wt %)								
Step		Δϕ[a]	OI	Cpx	Hb	Mt	Fp	Total	MSRRT
CP $\beta - H$	1	50 %	10 %	50 %		10 %	30 %	100 %	
	2	50 %	12 %	57 %		10 %	21 %	100 %	
	3		10 %	40 %	20 %	5 %	25 %	100 %	
Pavin β – H	***This work***	**39 %**	**13 %**	**25 %**	**45 %**	**7 %**	**11 %**	**100 %**	**4.7**
	Bourdier (1980)	**52 %**	**18 %**	**26 %**	**48 %**	**8 %**	**-**	**100 %**	
CP M – B	*1*	20 %		30 %	25 %	10 %	35 %	100 %	
	2	33 %		10 %	43 %	10 %	36 %	100 %	
	3			10 %	60 %	5 %	25 %	100 %	
Pavin M - B	***This work***	**63 %**		**10 %**	**31 %**	**0.2 %**	**59 %**	**100 %**	**6.0**
	Bourdier (1980)	**40 %**	**6 %**	**18 %**	**37 %**	**6.4 %**	**33 %**	**100 %**	

Modal compositions for each differentiation step (Basalt-Hawaïite and differentiated Hawaïite-Benmoreite) have been calculated using the method of Villemant et al. (1981) and this work. Δϕ is the weight fraction of crystallised melt and is calculated from Th contents: Δϕ (1−>2) is the fraction of melt crystallised between steps 1 and 2: $\Delta\phi \sim 1 - [Th]_1/[Th]_2$. MSRR values (mean square reduced residuals) give estimates of the quality of fit; they should be close to 1. The relatively high MSRR values indicate a moderate fit quality (see text for further explanations). Results are compared to petrological estimations (Foury 1983 for Chaîne des Puys) and mass balance calculations based on major elements (Wright and Doherty 1970) performed by Bourdier (1980) for Pavin group and Maury et al. (1980) for Chaîne des Puys. Agreement between the different methods is relatively good

1 Maury et al. 1980; point counting (lavas)
2 Foury 1983, point counting (scoriae)
3 Villemant et al. 1981; mass balance calculations (major and trace elements)
4 Bourdier 1980; mass balance calculations on major elements

[a] $\Delta\phi$ measured from Th contents

7.4 Conclusions

This preliminary study of the geochemistry of the eruptive products of Pavin group magmas shows that they define a single differentiation series from basalts to benmoreïtes. Though having very close major element compositions both magma series (Pavin and Chaîne des Puys (stricto sensu)) have specific trace element characteristics that distinguish them from the earliest differentiation steps. The basalts erupted at Montcineyre volcano are the most primary melts ever erupted in Chaîne des Puys and likely represent the primary melt at the origin of the two magma series. The Pavin series is characterized by the very large fractionation of amphibole from the most primitive basalts, whereas amphibole becomes the dominant mineral phase in Chaîne des Puys (stricto sensu) only at the step of benmoreite differentiation. This indicates the differentiation conditions of the Pavin group basalts are significantly different from that of the northern volcanoes with likely much higher initial H_2O content to favor amphibole crystallization at the expense of clinopyroxene. Comparison of the trace element composition and mineralogy of Clierzou and Pavin magmas (both close to the benmoreite-trachyte limit) suggests that they have been likely produced in significantly distinct P (or P_{H2O}) and T conditions. Martel et al. (2013) have shown that Clierzou trachyte was produced at a well constrained T of around 800°c, but the presence of amphibole as the only Fe-Mg silicate did not allow to constrain precisely the P_{H2O} (= P total). The Pavin benmoreite is on the contrary characterised by the coexistence of both amphibole and clinopyroxene at liquidus (and likely low Fo olivine, as described in some amphibole cumulates). The petrological grid of Martel et al. (2013) suggests that the mineral paragenesis of Pavin benmoreite could have equilibrated at 750–800 °C and possibly P_{H2O} ~250–300 MPa, but new experiments and comparison with the Pavin phenocrysts compositions are needed to refine these conditions.

In addition this study shows that there is no evidence that the interaction of the benmoreitic magma with the basement material during the phreato-magmatic and plinian activity of Pavin have significantly modified the melt compositions of the erupted products (cauliflower bombs and pumice clasts). However, since some highly incompatible elements as REE, Nb and Ta display unusual behaviors (unusually high bulk solid/melt partition coefficients) and since Bourdier (1980) reported increasing $^{87}Sr/^{86}Sr$ from Montcineyre basalts to Pavin benmoreite (0.7033–0.7040) the possible role of an assimilation-crystal fractionation process (ACF) involving surrounding rock assimilation cannot be discarded.

The volcanoes of Montcineyre, Montchal, Estivadoux and Pavin, form the most southern and the most recent volcanic area of the Chaîne des Puys (s.l.) and that evolve following a very specific magma differentiation path, although initiated from a primary basaltic melt identical to those of the northern edifices. The short duration of this volcanic activity (~400 years) is also an opportunity to estimate the duration of differentiation processes. The highly original features of Pavin group magmas justify the development of more complete mineralogical, petrological and geochemical studies to establish the particular emplacement and differentiation conditions of this magma series and their possible role in controlling, at least *pro-parte*, the explosive activity of Pavin volcano.

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