Canadian Mineralogist
Vol. 17, pp. 561-567 (1979)

DISTRIBUTION OF LEAD, SILVER AND CADMIUM IN SOME IGNEOUS ROCKS AND THEIR CONSTITUENT MINERALS

J. DOSTAL[1] AND C. ELSON[2]
Departments of Geology[1] and Chemistry[2], Saint Mary's University, Halifax, Nova Scotia B3H 3C3

C. DUPUY
Centre Géologique et Géophysique, Université des Sciences et Techniques du Languedoc, 34060 Montpellier, France

ABSTRACT

The abundances of Pb, Ag and Cd, and for comparison also Cu, Zn, K, Rb and Ba, in the minerals and rocks of alkali-basalt series from two Central Pacific islands (Nuku-Hiva and Rapa) and ignimbrites from Tuscany have been determined by atomic absorption. Pb increases with differentiation and is closely related to K and Rb. K–feldspar and titanomagnetite have D^{Pb} (concentration in solid/concentration in matrix) > 1. The behavior of Cd in the alkali-basalt series is similar to that of Zn, although differences between their *D*s for titanomagnetite ($D^{Zn} \sim 4$, $D^{Cd} \ll 1$) lead to the different variation trends of these elements when an opaque mineral crystallizes. In acid rocks, Ag and Cd do not show any obvious affinities with either Zn or Cu. Biotite and plagioclase have high contents of Ag whereas Cd is enriched in both feldspars.

SOMMAIRE

Nous avons déterminé par absorption atomique la teneur en Pb, Ag et Cd (ainsi qu'en Cu, Zn, K, Rb et Ba, à titre de comparaison) des minéraux et des roches des séries différenciées de basaltes alcalins de Nuku-Hiva et Rapa (îles du Pacifique central) et des ignimbrites de Toscane. Pb augmente avec la différenciation, tout comme K et Rb. Pour le feldspath potassique et la titanomagnétite, le rapport D^{Pb} des concentrations du Pb (dans le solide et dans la pâte) est supérieur à 1. Dans les séries de basaltes alcalins, Cd se comporte comme Zn, quoique la différence entre les *D* de la titanomagnétite ($D^{Zn} \sim 4$, $D^{Cd} \ll 1$) soit la cause de variations différentes pour Cd et Zn dans la cristallisation d'un mineral opaque. Dans les roches acides, Ag et Cd ne montrent d'affinité ni pour Zn, ni pour Cu. Biotite et plagioclase accusent de hautes teneurs en Ag, mais c'est en Cd que s'enrichissent les deux feldspaths.

(Traduit par la Rédaction)

INTRODUCTION

The partition coefficients of trace elements have greatly contributed to an understanding of the behavior of these elements during magmatic processes and have put constraints on the various petrogenetic models (Gast 1968). Although the partition coefficients for a number of elements, *e.g.*, the rare earths, Sr, Ba and Rb, are reasonably well-established (*cf.*, Schnetzler & Philpotts 1968, 1970), for some other elements (*e.g.*, Ag and Cd), they are practically unknown; furthermore, there are only a few data on the behavior of these elements during magmatic processes. The purpose of this paper is to present some data on the distribution of Ag, Cd, Pb and the geochemically similar elements Cu, Zn, K, Rb and Ba in several rock-forming minerals and rocks, and to discuss briefly some implications of the results.

Two sets of samples have been analyzed. The first set includes two Plio-Pleistocene alkali basalt series from French Polynesia (Rapa and Nuku-Hiva islands), whereas the second set is composed of ignimbrites from Tuscany (Italy) and a granodiorite from the island of Elba (Italy). The geology and geochemistry of the rocks from the two Pacific islands have been described by Maury *et al.* (1979). The alkali basalt series of Rapa comprises alkali basalts, hawaiites, mugearites, phonolites and cumulates, whereas the Nuku-Hiva series is composed of alkali basalts, hawaiites, mugearites, trachytes and cumulates. In each series, more evolved rocks were probably derived from alkali basalts by fractional crystallization. The two series differ in the degree of Fe-enrichment shown by ferromagnesian minerals and in the fractionation trends of Ti and V. These differences have been attributed by Maury *et al.* (1979) to the crystallization of magnetite, which took place in the Nuku-Hiva series in the early stages of fractionation; in Rapa, magnetite crystallized at a later stage. They probably reflect differences in $P(O)_2$ during the evolution of the two series.

The petrography and geochemistry of the rocks of the second set have been reported by Dupuy (1970) and Dupuy & Allègre (1972), Plio-Pleistocene ignimbrites of Tuscany form a discontinuous chain of small volcanic massifs (San Vincenzo, Roccastrada, Monte Amiata and Monte Cimino) over a distance of about 170 km. The ignimbrites are of rhyolitic to latitic composition and contain phenocrysts of sanidine, plagioclase and biotite. Accessory hypersthene and cordierite are also present in the rocks of some volcanic massifs. Granodiorite from a small stock about 10 km long and 7 km wide on the island of Elba is genetically related to ignimbrites; it represents the early stage of the magmatic event that produced the ignimbrites.

The problem of equilibrium between phenocrysts and glassy matrix in the ignimbrites from Tuscany was treated in some detail by Dupuy (1970), who concluded that at least quasi-equilibrium was attained for a number of major and trace elements in sanidine, plagioclase and biotite. Although there are fewer data on the alkali-basalt series, the study of Maury *et al.* (1979) indicates that the analyzed minerals were probably also in equilibrium with the liquid.

TABLE 1. ANALYSES OF SOME STANDARD REFERENCE ROCKS

	W-1	AGV-1	G-2	GSP-1	PCC-1
Rb (ppm)	21 (1)	66 (1)	160 (3)	236 (5)	– –
Ba	177 (11)	1187 (18)	–	1317 (26)	
Cu	115 (2)	56 (2)	–	–	–
Zn	85 (3)	91 (4)	–	–	–
Pb	6.4 (1.1)	38.8 (3.4)	34.7 (1.7)	47.6 (2.6)	13.3 (1.1)
Ag (ppb)	77 (5)	106 (4)	47 (8)	100 (7)	< 20
Cd	–	95 (6)	33 (6)	69 (6)	–

The values in brackets correspond to 1 standard deviation; – = not determined.

ANALYTICAL NOTES

Pb, Ag and Cd were determined by an atomic absorption technique after chemical separation as described by Elson *et al.* (1978). Briefly, 0.5 g of the samples were dissolved in HF–$HClO_4$ and the elements were extracted with methyl–isobutyl–ketone. The organic layer was then introduced into a graphite furnace (Model HGA–2100, Perkin–Elmer) of the atomic absorption spectrophotometer (Model 403, Perkin–Elmer). K, Rb, Ba, Zn and Cu

TABLE 2. ELEMENT ABUNDANCES IN ROCKS OF ALKALI BASALT SERIES

NUKU-HIVA

	BASALT	HAWAIITE			MUGEARITE		BENMOREITE		TRACHYTE				CUMULATE	
	77B	63D	70S	76K	76M	63D	61G	62J	76Z	70Z	70X	76X	76P	76R
SiO_2 (wt%)	45.79	47.03	44.25	48.40	50.19	51.83	55.92	54.75	58.65	59.82	62.16	61.58	43.06	40.53
K_2O	1.71	1.78	1.95	2.59	2.07	3.20	5.25	5.78	4.47	5.94	5.27	5.96	1.00	0.62
Rb (ppm)	43	87	54	85			131	147	130	167	143	201	17	15
Ba	435	650	595	660	745		1020	970	1200	575	895	375	336	240
Cu	64	45	40	50	37	36	20	26	19	17	18	7	54	46
Zn	122	126	158	136	134	104	76	82	122	114	74	116	120	150
Pb	< 0.3	1.35	1.11	1.26			4.24	4.28	10.8	2.45	4.19		< 0.3	< 0.3
Ag (ppb)	20	53	< 20	< 20	20		< 20	< 20	26	< 20	< 20	< 20	227	64
Cd	18	27	32	6	20	23	20	16	28	13	36	25	24	20
D.I.	33	39	38	44	51	60	75	74	81	85	89	90	25	23

RAPA

	BASALT				HAWAIITE		MUGEARITE	PHONOLITE	CUMULATE	
	RA7	R27	R25	R19	R24	R54	R43	R50	R57	R23
SiO_2 (wt%)	45.20	45.00	43.84	44.68	44.23	46.38	49.50	57.39	41.71	43.20
K_2O	1.10	1.29	1.64	0.88	1.97	1.40	2.27	4.58	1.97	2.54
Rb (ppm)	25	22	26	20	38	25	45	99	41	59
Ba	315	385	410	331	500	365	610	865	582	707
Cu	44	84	74	43	50	32	26	10	106	117
Zn	134	134	142	115	162	116	144	159	135	120
Pb	< 0.3	< 0.3	0.56	3.44	1.24	1.93	2.13	6.30	0.86	1.42
Ag (ppb)	20	140	96	42	51	52	< 20	< 20	< 20	< 20
Cd	8	13	31	52	7	51	48	49	< 4	< 4
D.I.	26	33	33	33	38	37	57	81	26	47

D.I. Differentiation index of Thornton and Tuttle (1960).

TABLE 3. ELEMENT ABUNDANCES IN MINERALS OF ALKALI BASALT SERIES

	Hb	Opq	Cpx		Ol	Plg
Host rock	76R	76R	76R	R19	RA7	77B
Cu (ppm)	12	44	7	12	12	25
Zn	125	705	82	60	160	34
Pb	1.72	4.81	1.82	1.79	<0.3	
Ag (ppb)	41	58	<20	<20	60	<20
Cd	45	17	68	11		8

Hb - hornblende, Opq - opaque (titanomagnetite), Cpx - clinopyroxene, Ol - olivine, Plg - plagioclase

were analyzed by atomic absorption directly after the $HF–HClO_4$ dissolution. The precision and accuracy of both these methods can be judged from the replicate analyses of several standard rocks given in Table 1. The major-element compositions of the analyzed samples from the Pacific islands and Italy were reported by Maury *et al.* (1979) and Dupuy (1970), respectively.

The minerals were separated by standard magnetic and heavy-liquid techniques until the estimated purity of the concentrates was better than 98–99%. The purity was estimated optically; the concentrates of titanomagnetite were also examined in the reflected light.

RESULTS AND DISCUSSION

Alkali-basalt series

The abundances of Pb, Ag and Cd, and for comparison also Cu, Zn, K, Rb and Ba, in the minerals and rocks of the two Pacific islands are given in Tables 2 and 3. The Pb content of the mineral phases is comparable to the values reported by Doe (1974). Among the analyzed minerals, titanomagnetite has the highest concentrations, followed by clinopyroxene and hornblende. The partition coefficients (D = mineral to matrix concentration ratio) for hornblende and clinopyroxene are less than one, whereas D^{Pb} for the opaque phase is slightly greater than one (Table 4).

The abundances for the whole rocks are well within the range of data compiled by Doe (1974) for similar rocks, although alkali basalts and phonolite are poorer in Pb than his general average for alkali olivine basalts and phonolites (4.3 and 14.3 ppm, respectively). In both alkali-basalt series, Pb, like K and Rb, gradually increases with the increase of differentiation (Fig. 1). The decrease of Ba in the last stages of differentiation in Nuku-Hiva (Fig. 1) can be attributed to the crystallization of K-feldspar (Maury *et al.* 1979) and indicates that K-feldspar has $D^{Ba} > D^{Pb}$.

The concentrations of Ag in the major rock-forming minerals are rather low, with the opaque mineral and olivine having the highest content. The values are comparable to the data compiled by Boyle (1968) and Vincent (1974) for equivalent mineral phases. The low Ag abundances in the analyzed minerals and rocks do not allow a reliable determination of partition coefficients. From the data in Tables 2 and 3, however, it seems that olivine has $D^{Ag} > 1$, whereas clinopyroxene has $D^{Ag} < 1$. Regarding the relatively high D^{Ag} of olivine, Taylor (1965) suggested that Ag^{2+} replaces Fe^{2+} in silicates.

With the exception of the mafic rocks, the abundances of Ag in both alkali-basalt series are below the detection limit of the analytical technique used (< 20 ppb). This may indicate that Ag concentrations decreased with differentiation (Fig. 2) as suggested by Nesterenko *et al.* (1969), who have also correlated the distribution of Ag in some Siberian traps with the occurrence of accessory copper-sulfide minerals. This may also apply to these basaltic suites, in which Cu decreases with increasing degree of differentiation (Fig. 2), owing to the crystallization of sulfides (Maury *et al.* 1979). Alternatively, however, the lower Ag content in the more differentiated rocks and the relatively high Ag concentration in the olivine-rich cumulate (76P) are also consistent with

TABLE 4. PARTITION COEFFICIENTS[1] OF SOME ROCK-FORMING MINERALS

	ALKALI BASALT SERIES					IGNIMBRITES		
	Cpx	Ol	Plg	Hb^2	Opq^2	Plg	Kf	Bio
Cu	0.3	0.3	0.4	0.5	1.9	0.1-0.7	0.1-0.8	1.8-3.6
Zn	0.5	1.2	0.3	0.8	4.3	0.4-0.6	0.06-0.3	5.3-11
Pb	0.5	-	-	0.5	1.3	0.7-1.0	2.0-6.7	0.08-0.21
Ag	<0.5	3.0	-	<1.0	<1.5	2.6-4.4	< 1.0	7.4-21
Cd	0.2	-	0.7	0.1	0.05	5.3-5.7	1.8-4.1	0.3-1.5

1 = solid/liquid, 2 = calculated from Cpx/liq., Hb/Cpx and Opq/Cpx values.
Cpx - clinopyronene, Ol - olivine, Plg - plagioclase, Hb - hornblende, Opq - opaque (titanomagnetite), Kf - sanidine, Bio - biotite.

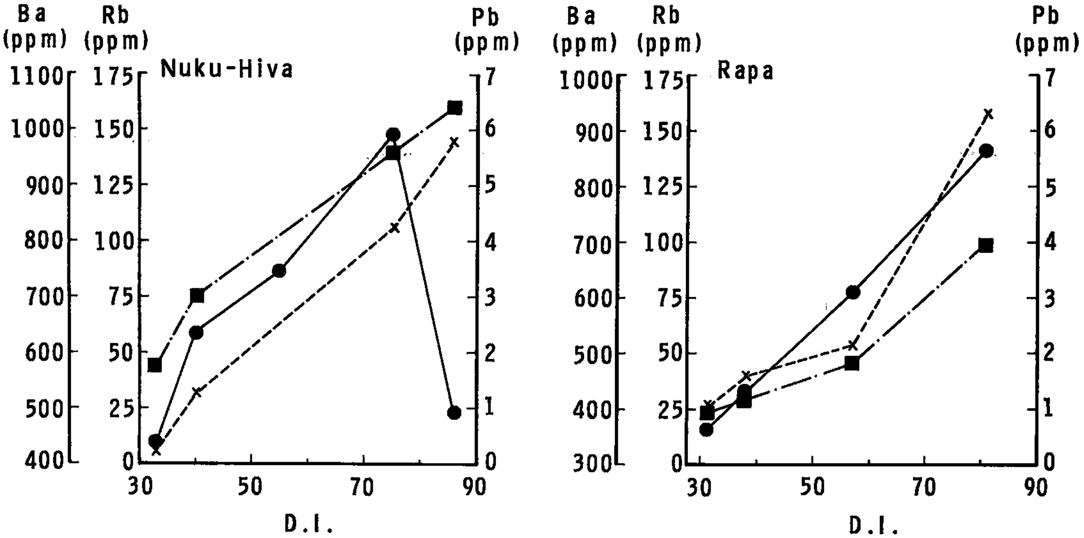

FIG. 1. The average Ba (filled circles), Rb (filled squares) and Pb (crosses) concentrations of the individual rock-types of two alkali-basalt series from the Pacific plotted against the differentiation index (D.I.) of Thornton & Tuttle (1960). The Pb content of the basalt from Nuku-Hiva series (< 0.3 ppm) was arbitrarily plotted as 0.2 ppm.

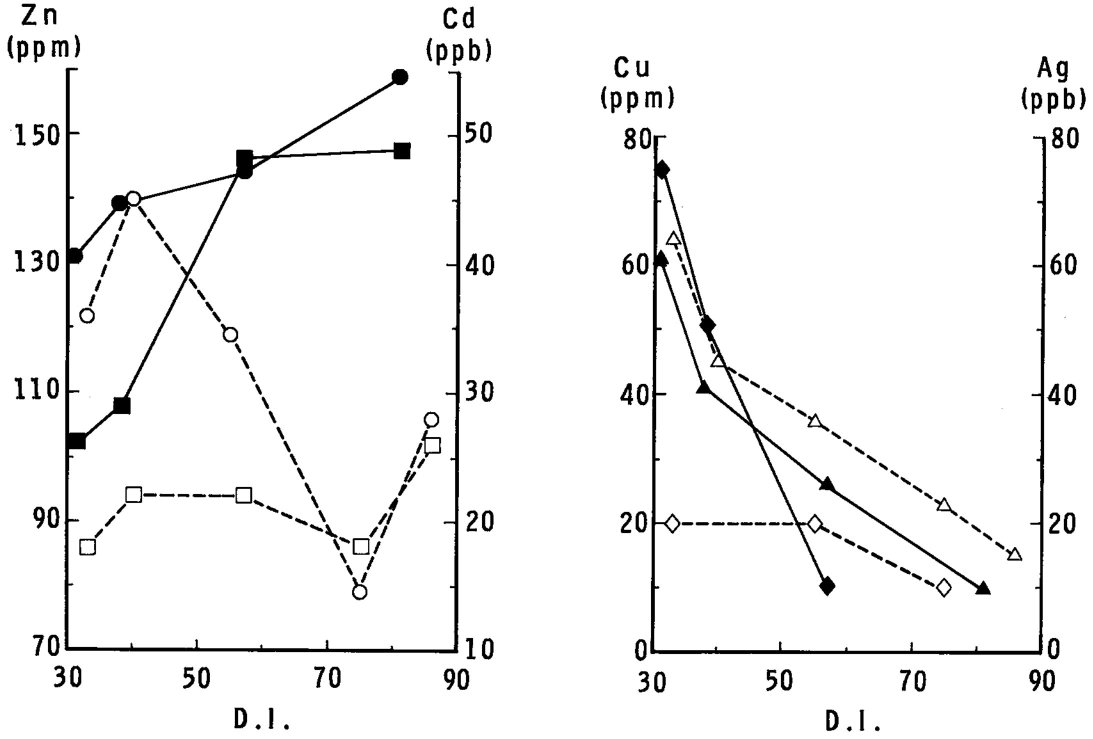

FIG. 2. The average Zn and Cd (left) and Cu and Ag (right) concentrations of the individual rock-types of the alkali-basalt series from Nuku-Hiva (open symbols) and Rapa (solid symbols) islands plotted against the differentiation index (D.I.) of Thornton & Tuttle (1960). The Ag contents below the detection limit (20 ppb) were arbitrarily taken as 10 ppb. Zn: circles, Cd: squares, Cu: triangles, Ag: diamonds.

the early fractionation of olivine and an opaque phase. The fractionation of these two minerals may also explain the contrasting behavior of Cu and Ag during the differentiation of the Great Lake dolerite sheet, Tasmania, as reported by Greenland & Fones (1971). Silicic differentiates of this dolerite sheet are distinctly enriched in Cu owing to the late crystallization of sulfide minerals.

The concentrations of Cd in the rock-forming minerals of the alkali-basalt series fall below 70 ppb. D^{Cd} for all analyzed minerals, including titanomagnetite, are < 1, smaller than values for Zn (Table 4), the element geochemically similar to Cd (Vlasov 1966). The largest difference in the partitioning of these two elements is shown by titanomagnetite, which has $D^{Zn} \sim 4$. The whole-rock abundances of Cd are well within the range reported by Wakita & Schmitt (1970) for mafic and intermediate rocks. Unlike Pb and Ag, Cd has different variation trends in the two series. In the Rapa suite, Cd, like Zn, increases slightly with differentiation (Fig. 2) but, as indicated by the partition coefficients given in Table 4, Cd is more enriched in the differentiated rocks than Zn. In the Nuku-Hiva alkali-basalt series, which underwent the early crystallization of magnetite, Zn shows an overall negative correlation with the differentiation index of Thornton & Tuttle (1960), whereas Cd remains nearly constant. The decrease in Zn is consistent with the fractionation of an opaque phase with high D^{Zn}. However, as D^{Cd} values for the analyzed rock-forming minerals are < 1, such a process cannot explain the variation trend of Cd, which requires separation of a Cd-rich phase. As in the case of Cu (Maury *et al.* 1979), the abundances of Cd in this series seem to have been affected by crystallization of sulfides, known to be enriched in Cd (Vlasov 1966, Wakita & Schmitt 1970).

Acid rocks

The concentrations of Pb, Ag, Cd, Cu, Zn, K, Rb and Ba in the rhyolitic rocks from Italy and component mineral phases and glasses are given in Table 5; the values of the partition coefficients are reported in Table 4. Among the analyzed minerals, K–feldspars have the highest content of Pb. Coexisting plagioclases are lower in Pb, with the ratio Pb in K–feldspar/Pb in plagioclase ranging from 6.7 to 1.7. A similar distribution of Pb between coexisting feldspars of plutonic, volcanic and metamorphic rocks has been reported by Doe & Tilling (1967). Biotite, cordierite and hypersthene have significantly lower Pb concentrations than feldspars. K–feldspars are the only analyzed minerals having $D^{Pb} > 1$, although the values are smaller than D^{Ba}. Comparison with the geochemically similar elements K, Rb and Ba indicates that Pb has closer affinities with K and Rb than with Ba. Anomalously high abundances of K,

TABLE 5. ELEMENT ABUNDANCES IN THE ACID ROCKS, GLASSES AND MINERALS FROM ITALY

	Ignimbrites					Glass				Plagioclase			
	R-2	R-3	R-4	R-5	R-6	R	V	A	C	V	A	C	E
K_2O (%)	4.7	5.0	5.1	4.9	4.9	5.3	5.2	6.2	6.2	0.8	0.6	0.6	0.6
Rb (ppm)	433	445	447	477	478	615	397	540	412				
Ba	130	175	150	80	80	21	225	133	407	136	60	95	92
Cu	5	11	8	6	6	5		6	20	4	4	3	2
Zn	50	54	49	50	37	56		26	50		15	22	6
Pb	57	35	68	74	103	20		43	55	61	30	54	79
Ag (ppb)	69	81	137	148	69	39	34	27	24	108	120	63	
Cd	37	16	34	48	22	8	15	9		80	51		64

	K-feldspar					Biotite					Opx	Crd
	R	V	A	C	E	R	V	A	C	E	C	R
K_2O (%)	11.1	11.9	13.4	12.8	13.0	7.9	8.3	8.8	8.9	8.3		
Rb (ppm)	404	313	408	321	509	847	542	684	672	848		
Ba	2150	3100	2900	6500	1100	280	280	1980	1975	500		
Cu	4	4	5	3	4	18	15	12	36	44	9	14
Zn	5	8	8	3	8	512	575	273	265	335	470	194
Pb	133	309	200	113	131	1.6	< 0.3	1.9	11.2	< 0.3	< 0.3	< 0.3
Ag (ppb)	< 20	< 20	< 20	< 20	< 20	290	450	259	496	770		100
Cd	16	27	37	27	46	12	5	8	10	48	70	37

R- Roccastrada, V = San Vincenzo, A = Monte Amiata, C = Monte Cimino,
Opx - orthopyroxene, Crd - cordierite

Rb (Dupuy 1970) and also of Pb in ignimbrites of Tuscany are consistent with the close association of these three elements.

The distribution of Ag among the coexisting minerals of felsic rocks shows relatively large variations. Biotite and plagioclase have a high content of Ag, with $D^{Ag} > 1$, whereas K–feldspar is depleted, having $D^{Ag} < 1$. In agreement with the modal composition of ignimbrites (Dupuy 1970) and the partition coefficients, glasses are depleted in Ag relative to the whole rocks. On average, the whole-rock Ag abundances of ignimbrites are higher than those of granites (Vincent 1974).

The distribution of Cd in the analyzed acid rocks differs from that of Zn. Feldspars have the highest content of Cd; Zn is mainly concentrated in biotite. There are also differences between glasses and whole rocks in the relative abundances of these elements. Glasses and whole rocks have similar Zn contents, but the glasses are depleted in Cd with respect to the whole rocks. It should be noted that the high contents of Cd and Ag in plagioclase are not due to sulfide impurities, as the concentrations of Cu and Zn in plagioclase are low, with both D^{Cu} and $D^{Zn} < 1$. A similar argument can also be applied to K–feldspars.

CONCLUSIONS

In consanguineous alkali-basalt series, Ag, Cd and Pb display variation trends that are generally in agreement with the values of the partition coefficients determined for rock-forming minerals. Pb, whose content increases with differentiation in both alkali-basalt series, is closely related to K and Rb. This geochemical coherence is maintained even in acid rocks. Although Pb shows some similarities in behavior to Ba, these two elements differ in the later stages of differentiation when K–feldspar starts to crystallize. So far as the limited amount of data allows, it seems that in the alkali-basalt series, Ag may show a coherence with Cu, as suggested by Nesterenko *et al.* (1969). The behavior of Cd is, overall, similar to that of Zn, although the differences in partition coefficients for opaque minerals lead to diverse variation-trends of these two elements when the opaque phase crystallizes. In acid rocks, however, Ag and Cd do not show any obvious affinities with either Zn or Cu. It is also of interest that in comparison with tholeiitic rocks (Vincent 1974) Ag, like Cu (Andriambololona & Dupuy 1979), is generally lower in alkali basalts.

ACKNOWLEDGEMENTS

This study has been supported by the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

ANDRIAMBOLOLONA, R. & DUPUY, C. (1979): Répartition et comportement des éléments de transition dans les roches volcaniques. *Bur. Rech. Geol. Minières Bull.* **2**, 121-138.

BOYLE, R.W. (1968): The geochemistry of silver and its deposits. *Geol. Surv. Can. Bull.* **160**.

DOE, B.R. (1974): Lead. *In* Handbook of Geochemistry II-4 (K. H. Wedepohl, ed.), Springer-Verlag, Berlin.

——— & TILLING, R.I. (1967): The distribution of lead between coexisting K-feldspar and plagioclase. *Amer. Mineral.* **52**, 805-816.

DUPUY, C. (1970): *Contribution à l'étude du fractionnement des éléments en trace alcalins et alcalino-terreux, au cours des processus magmatiques. Application aux roches volcaniques plio-quaternaires de Toscane.* Thèse Doct. Etat., Univ. Montpellier, France.

——— & ALLÈGRE, C.J. (1972): Fractionnement K/Rb dans les suites ignimbritiques de Toscane. Un exemple de rejuvénation crustale. *Geochim. Cosmochim. Acta* **36**, 437-458.

ELSON, C.M., DOSTAL, J., HYNES, D.L. & DE ALBUQUERQUE, C.A.R. (1978): The silver, cadmium and lead contents of some rock reference samples. *Geostandards Newsletter* **2**, 121-123.

GAST, P.W. (1968): Trace element fractionation and the origin of tholeiitic and alkaline magma types. *Geochim. Cosmochim. Acta* **32**, 1057-1086.

GREENLAND, L.P. & FONES, R. (1971): Geochemical behavior of silver in a differentiated tholeiitic dolerite sheet. *Neues Jahrb. Mineral. Monatsh.*, 393-398.

MAURY, R.C., ANDRIAMBOLOLONA, R. & DUPUY, C. (1979): Evolution comparée de deux séries alcalines du Pacifique central: rôle de la fugacité d'oxygène et de la pression d'eau. *Bull. Volc.* 41-2, 1-22.

NESTERENKO, G.V., BELYAYEV, YU. I. & PHI, P.H. (1969): Silver in the evolution of mafic rocks. *Geochem. Int.* **6**, 119-126.

SCHNETZLER, C.C. & PHILPOTTS, J.A. (1968): Partition coefficients of rare-earth elements and barium between igneous matrix material and rock-forming mineral phenocrysts. *In* Origin and

Distribution of the Elements (L. H. Ahrens, ed.), Pergamon, London.

——— & ——— (1970): Partition coefficients of rare-earth elements between igneous matrix material and rock-forming mineral phenocrysts. II. *Geochim. Cosmochim. Acta* **34**, 331-340.

TAYLOR, S.R. (1965): The application of trace element data to problems in petrology. *Phys. Chem. Earth* **6**, 133-214.

THORNTON, C.P. & TUTTLE, O.F. (1960): Chemistry of igneous rocks. I. Differentiation index. *Amer. J. Sci.* **258**, 664-684.

VINCENT, E.A. (1974): Silver. *In* Handbook of Geochemistry II-3 (K. H. Wedepohl, ed.), Springer-Verlag, Berlin.

VLASOV, K.A. (1966): *Geochemistry of Rare Elements.* Israel Program for Scientific Translation, Jerusalem.

WAKITA, H. & SCHMITT, R.A. (1970): Cadmium. *In* Handbook of Geochemistry II-3 (K. H. Wedepohl, ed.), Springer-Verlag, Berlin.

Received October 1978; revised manuscript accepted February 1979.