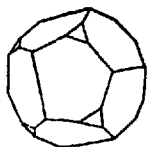


Rare earth element distribution in Plio-Quaternary volcanic rocks from southern Peru

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Rare-earth element abundances of calc-alkaline andesitic rocks from southern Peru show that these rocks cannot be produced by a single stage process. The high content of LILE, particularly LREE requires their derivation from a source already enriched in these elements and having a distinctly fractionated REE pattern. It is suggested that ascending hydrous fluids, released from the subducted oceanic lithosphere, enriched the upper mantle in LILE by zone refining. The partial melting of such an enriched upper mantle, followed by fractional crystallization, could produce andesitic rocks. REE data indicate that shoshonitic rocks from southern Peru can be derived from an unfractionated garnet-bearing peridotite by a low degree of partial melting.

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Plio-Quaternary volcanic rocks of the central Andes may be considered as a typical example of magmatism associated with an active continental margin and thus they provide an opportunity to study the relationship between volcanism and the subduction zone in the domain of the interaction of the continental and ocean lithosphere.

In the area studied, which is situated in southern Peru between latitudes 16 and 18°S, more precisely between the town of Arequipa, Lake Titicaca and the Peru-Chile border, the Plio-Quaternary volcanism is represented by calc-alkaline and shoshonitic suites of rocks (Lefevre 1973). The calc-alkaline andesite suite is composed of rocks with SiO₂ content ranging from 55 to 70%, while in the shoshonitic series SiO₂ varies between 50 and 64%. The volcanic rocks show a zonal arrangement with respect to the Peru-Chile trench, which is situated 220–320 km SW of the study area. Calc-alkaline andesitic rocks occur closer to the trench than shoshonites. In the calc-alkaline rocks, K and related trace elements (Rb, Ba) increase while Sr decreases with increase in the distance from the trench (Dupuy & Lefevre 1974). According to the distance from the

trench and the content of K, the calc-alkaline suite was further subdivided into two groups – A-1 and A-2 – the former being closer to the trench and having lower content of K, Rb and Ba (Lefevre 1973; Dupuy & Lefevre 1974). Andesitic rocks from southern Peru are characterized by a large enrichment of Rb, Ba and Sr in comparison with similar rocks from other circum-Pacific regions. The abundances of transition elements in Peruvian andesites are consistent with their derivation either by partial fusion of garnet granulites or by melting of ultramafic upper mantle (Andriambololona 1976).

Shoshonites have significantly higher K, Sr and Ba content than Peruvian calc-alkaline rocks. Dupuy & Lefevre (1974) and Andriambololona (1976) have argued that the shoshonites were not derived from the same source as the andesitic rocks. The distribution of transition elements in shoshonites is consistent with a partial melting of the ultramafic upper mantle followed by limited fractional crystallization (Andriambololona 1976). The ⁸⁷Sr/⁸⁶Sr ratios in calc-alkaline and shoshonitic rocks from southern Peru also indicate only limited interaction of the volcanics with crustal ma-

Table 1. Chemical composition of volcanic rocks from southern Peru.

Sample	49	48	47	50	59	169	168	167	114	117	245	250	255	290	95	102	103	258	
Group	A-1	A-1	A-1	A-1	A-1	A-1	A-1	A-1	A-2	A-2	A-2	A-2	A-2	A-2	A-2	Shoshonites			
SiO ₂	55.57	56.82	60.75	63.28	64.07	59.94	61.40	63.86	59.14	64.62	61.32	72.20	68.54	60.24	54.25	55.50	58.96	63.90	
TiO ₂	0.92	0.92	0.65	0.50	0.54	0.78	0.79	0.62	0.87	0.62	0.68	0.22	0.41	0.74	2.52	2.14	1.41	1.02	
Al ₂ O ₃	17.84	17.90	17.14	17.12	16.90	17.10	16.56	15.53	16.92	16.84	16.40	14.88	15.25	15.40	14.60	15.00	15.50	15.80	
Fe ₂ O ₃	3.82	5.09	4.42	3.36	3.16	3.06	4.56	3.16	3.46	3.28	3.90	1.43	2.35	3.93	4.24	5.60	4.98	3.34	
FeO	3.50	2.43	1.37	0.93	1.12	2.62	1.43	1.44	2.75	0.47	1.43	0.05	0.69	2.00	4.80	2.30	1.31	1.06	
MnO	0.12	0.10	0.12	0.11	0.09	0.09	0.10	0.09	0.09	0.07	0.09	0.03	0.05	0.12	0.13	0.13	0.07	0.04	
MgO	3.43	2.72	1.77	1.44	1.01	2.45	2.66	2.01	3.35	1.13	2.33	0.14	0.51	3.95	4.50	3.14	3.00	1.41	
CaO	7.02	6.19	5.12	4.15	4.08	5.55	4.52	4.14	5.80	3.16	4.96	1.42	2.10	6.15	6.74	5.79	4.81	2.75	
Na ₂ O	3.92	4.28	4.29	4.74	4.71	4.00	3.76	3.80	3.78	3.94	4.08	4.19	3.58	3.52	3.68	3.90	4.18	4.34	
K ₂ O	1.92	2.12	2.28	2.63	2.62	2.53	2.93	3.29	2.75	4.22	3.50	4.47	5.24	3.10	3.02	3.55	3.63	4.23	
P ₂ O ₅	0.33	0.37	0.30	0.31	0.29	0.30	0.31	0.34	0.27	0.24	0.36	0.05	0.27	0.23	1.17	1.04	0.63	0.47	
H ₂ O ⁺	0.47	0.30	0.45	0.05	0.10	0.12	0.45	0.08	0.12	0.19	0.14	-	0.25	0.16	-	0.40	0.53	0.32	
H ₂ O ⁻	1.02	0.54	0.98	0.30	0.86	0.82	0.76	0.75	0.45	0.97	0.59	1.00	0.97	0.40	0.28	1.00	0.79	0.91	
	99.88	99.78	99.64	98.92	99.55	99.36	100.23	99.11	99.76	99.75	99.78	100.08	100.21	99.94	99.93	99.49	99.80	99.59	

terial (James et al. 1976). A more detailed account of the geology of the region is given by Lefevre (1973) and James (1971). The purpose of this study is to present rare-earth element (REE) data on the calc-alkaline and shoshonitic rocks from southern Peru and to discuss some of their petrogenetic implications.

Analytical methods and location of samples

The major element content of the volcanic rocks (Table 1) was determined by standard rapid methods, while REE were determined in fourteen calc-alkaline rocks (8 andesites, 4 dacites and 2 rhyolites) and four shoshonitic rocks by instrumental neutron activation (Gordon et al. 1968) using BCR-1 as a standard. The precision of the REE data is better than 10%. The locations and petrography of the analyzed samples are given by Lefevre (1973).

Results and discussion

Andesitic rocks

The REE abundances of andesitic rocks of groups A-1 and A-2 from southern Peru are given in Table 2 and are plotted, normalized to chondrites (Frey et al. 1968), in Fig. 1. The REE patterns of these rocks show distinct light REE (LREE) enrichment and only small fractionation of heavy REE (HREE). The enrichment of LREE is also reflected by the high values of the La/Yb ratio, ranging from 14 to 25. In contrast to K, Rb and Ba, the content of which distinctly increases with distance from the Peru-Chile trench (Lefevre 1973; Dupuy & Lefevre 1974), the REE abundances show only a very small increase in this northeastern direction.

In general, the REE patterns of Peruvian andesitic rocks resemble those of the continental margin andesitic rocks from some other circum-Pacific volcanic regions (Yajima et al. 1972; Condie & Swenson 1973; Lopez-Escobar et al. 1974; Thorpe et al. 1976). The main difference between the analyzed rocks and similar volcanics from Bougainville (Taylor et al. 1969), Japan (Yajima et al. 1972), and even the averages of circum-Pacific andesitic rocks (Taylor 1969) is the higher absolute REE content and greater LREE enrichment in our

Fig. 1. Chondrite-normalized REE abundances in representative southern Peruvian calc-alkaline rocks. Top - rocks of group A-1, bottom - rocks of group A-2.

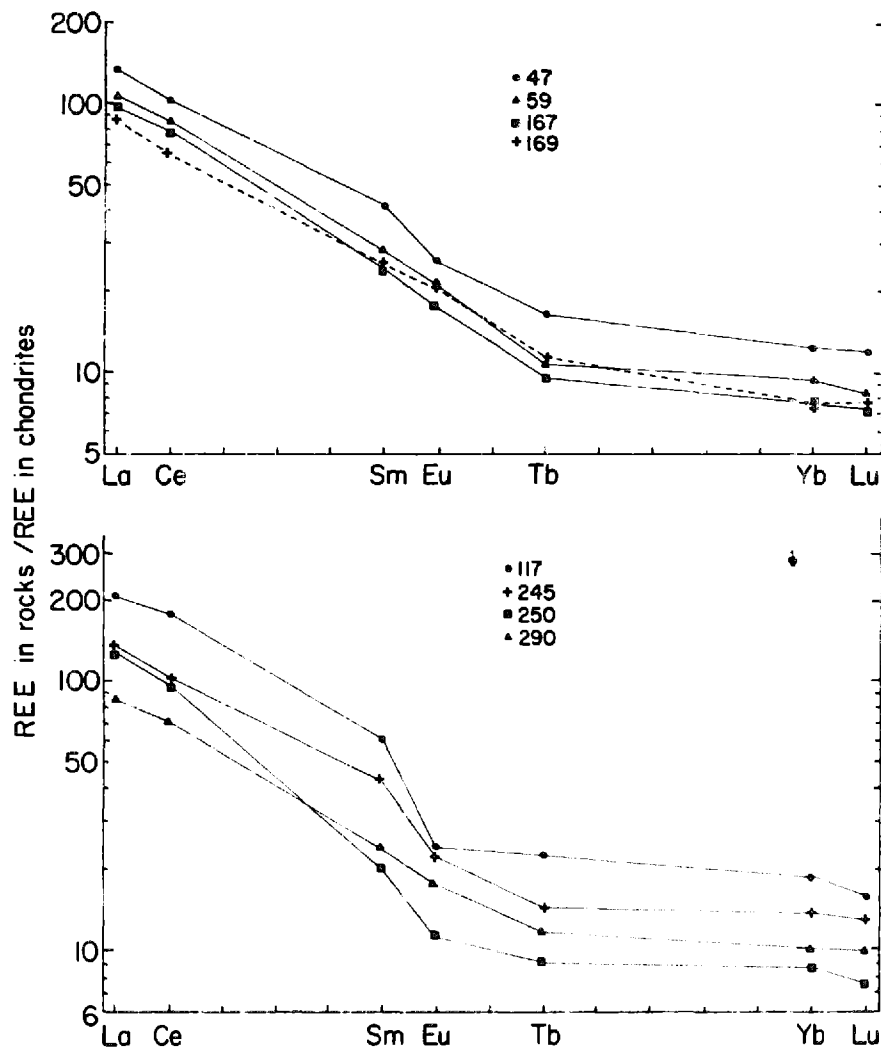


Table 2. Rare-earth element abundances (in ppm) of volcanic rocks from southern Peru.

No.	Volcano	Group	La	Ce	Sm	Eu	Tb	Yb	Lu
49	Condori	A-1 (ba)	34.2	67.0	5.85	1.43	0.731	2.40	0.323
48	Condori	A-1 (a)	42.7	83.1	6.96	1.70	0.624	2.47	0.360
47	Condori	A-1 (a)	44.0	88.9	7.46	1.74	0.765	2.46	0.397
50	Condori	A-1 (d)	42.4	79.6	5.90	1.65	0.685	2.25	0.354
59	Condori	A-1 (d)	35.1	75.1	5.02	1.42	0.505	1.83	0.282
169	Calientes	A-1 (a)	28.8	56.3	4.52	1.41	0.526	1.53	0.256
168	Calientes	A-1 (a)	31.6	71.3	4.96	1.30	0.541	1.80	0.285
167	Calientes	A-1 (d)	31.7	68.2	4.42	1.17	0.448	1.53	0.246
114	Chullunquiani	A-2 (a)	44.2	89.1	8.26	1.48	0.750	2.39	0.376
117	Chullunquiani	A-2 (d)	69.2	158.	11.0	1.65	1.06	3.79	0.515
245	Vico	A-2 (a)	44.8	90.4	7.79	1.54	0.675	2.77	0.418
250	Jajayuni	A-2 (r)	42.8	85.9	3.63	0.76	0.423	1.72	0.261
255	San Francisco	A-2 (r)	60.3	130.	6.78	1.43	0.878	3.15	0.504
290	Chiarpuio	A-2 (a)	28.5	62.9	4.24	1.21	0.556	2.03	0.311
95	Chupí	SHOSHONITES	82.5	185.	13.5	4.10	1.39	2.18	0.314
102	Chusamarca	SHOSHONITES	95.2	211.	16.1	3.99	1.28	1.94	0.300
103	Mayapata	SHOSHONITES	64.0	136.	9.90	2.64	0.738	1.17	0.200
258	Chucuito	SHOSHONITES	62.3	129.	7.98	2.27	0.539	0.968	0.156

Rock type: ba=basaltic andesite, a=andesite, d=dacite, r=rhyolite.

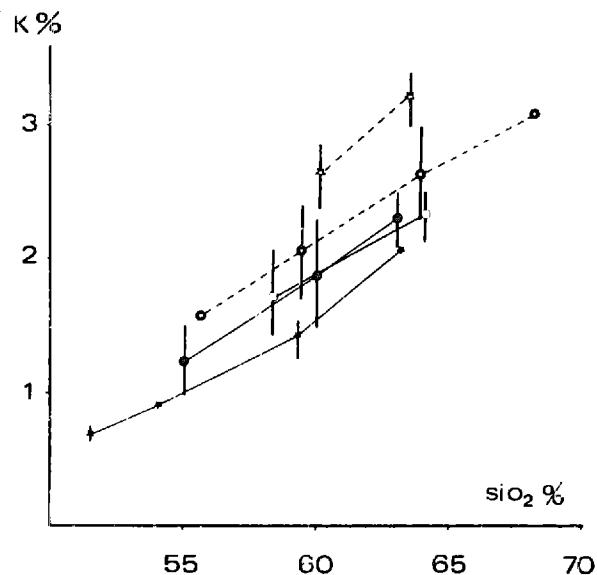


Fig. 2. Variation of K versus SiO_2 in recent calc-alkaline rocks from southern America.

- ★ - southern Chile (37–42°S) - Lopez-Escobar et al. 1974.
- - northern Chile (18–27°S) - Siegers et al. 1969.
- - northern Chile (21–22°S) - Thorpe et al. 1976.
- ⊗ - group A-1 } southern Peru (16–18°S) - Dupuy &
- ☆ - group A-2 } Lefevre 1974.

rocks. Likewise, in comparison with andesitic rocks from Chile (Lopez-Escobar et al. 1974; Thorpe et al. 1976) the Peruvian volcanics have higher La/Yb ratios and also the $[\text{La}/\text{Sm}]_{\text{E.F.}}$ ratios of Schilling (1971) and higher absolute REE concentrations.

Comparison of volcanic rocks from southern Chile (Lopez-Escobar et al. 1974), northern Chile (Thorpe et al. 1976) and southern Peru indicates a progressive increase of the total REE content and the La/Yb ratio from the south to the north (i.e. parallel to the trench). An increase in this direction is also shown by some other lithophile elements such as K (Fig. 2). For REE, the variations parallel to the trench are more pronounced than the variations noted as one moves farther from the trench. As Lopez-Escobar et al. (1974) have already pointed out for K and related elements, the north-south variations may probably be correlated with changes in the depth of the Benioff zone in a north-south direction. The dip of the Benioff zone in the south-central part of Chile (37–42°S), where volcanics have the lowest content of REE and the smallest LREE enrichment (Lopez-Escobar et al. 1974), is less than 15° (Stauder 1973). In northern

Chile (21–22°S), the zone dips about 25° beneath the continent, while in southern Peru the dip is about 30° (Megard & Philip 1976).

In southern Peru, the variations of total REE abundances in the rocks from a single volcano are relatively small. In fact, the variations in the REE content of different rock-types from a single volcano are usually smaller than the differences between comparable rocks from various volcanoes (Table 2). Most of the variations within each volcano can be attributed to low P fractionation, but some of them are difficult to reconcile with this process. For example, small differences of total REE between dacites and andesites of the volcano Condori (Table 2) indicate that the former rocks cannot be derived from the latter by low P fractionation. Volcanic rocks of southern Peru do not show any systematic variations of REE in relation to their major element composition. Only the La/Yb ratio shows an overall weak positive correlation with SiO_2 . As in the Cascades (Condie & Swenson 1973) and south-central Chile (Lopez-Escobar et al. 1974) it appears that each individual volcano has its own geochemical evolution and characteristics.

Some possible mechanism which may account for the genesis of andesite magma and for the observed chemical variations of the rocks from southern Peru are examined in the light of the trace element, particularly REE, data. The evaluated models (Ringwood 1974) include: (1) Fractionation of basaltic magma by the crystallization of amphibole, or partial melting of amphibolite; (2) Fractionation of basaltic magma by the crystallization of garnet and clinopyroxene, or partial melting of quartz eclogite; (3) Direct partial melting of unfractionated upper mantle under high $P_{\text{H}_2\text{O}}$; (4) Partial melting of the lower crust.

Amphibole-controlled fractionation: - Holloway & Burnham (1972) and Allen et al. (1975) have demonstrated that partial melting of subducted ocean-floor tholeiites in the amphibolite facies could produce liquids of andesitic composition. Alternatively, fractional crystallization of low-silica amphibole from basaltic magma can also yield andesitic or dacitic liquid (Green & Ringwood 1968; Holloway & Burnham 1972). However, such a partial melting process probably cannot be applied to Peruvian andesites, because the subducted ocean-floor rocks are too deep to be in the amphibolite

facies (James 1971). Regarding the REE, the model calculations of Lopez-Escobar et al. (1974) show that the relatively low content of HREE of Peruvian andesites (~10–13 times chondritic abundances) negate their derivation from either fresh or altered ocean-ridge basalts by fractionation (both fractional crystallization and fractional melting) of low-silica amphibole. Since the partition coefficients of HREE for amphibole are significantly smaller than 1 (Schnetzler & Philpotts 1970), the amphibole fractionation required to generate the major element composition of andesites from that of tholeiitic basalts (~30–40%, Holloway & Burnham 1972) should produce a larger enrichment of HREE in andesites as compared to ocean-floor basalts, which have HREE abundances 10–20 times those of chondrites. The participation of clinopyroxene, in addition to amphibole, during this process, does not change significantly the REE distribution in the melts (Lopez-Escobar et al. 1974). An amphibole controlled fractionation of a basaltic parent is also not consistent with the observed low content of transition elements, particularly of Ni, in andesitic rocks from southern Peru (Andriambololona 1976).

Eclogite-controlled fractionation: – The studies of Green & Ringwood (1968) and Green (1972) show that high pressure eclogite (garnet and clinopyroxene) fractionation of a basaltic source can produce an andesitic liquid. In particular, it has been suggested (Fitton 1971; Green 1972; Ringwood 1974) that the partial melting of subducted oceanic basalts in the eclogite facies played an important role in the generation of calc-alkaline magmas. A number of recent works (Gill 1974; Stern 1974; Lopez-Escobar et al. 1974; Noble et al. 1975), however, have demonstrated that this process is not readily consistent with the geochemical characteristics of the andesitic rocks. The major element composition of andesites requires a large degree of partial melting of quartz eclogite, while the abundances of large-ion lithophile elements (LILE) and of some transition elements in andesites can only be derived by a small degree of partial melting. In fact, the low content of Ni in the south Peruvian andesites led Andriambololona (1976) to reject this process. Assuming that eclogite has a REE content similar to the ocean-ridge basalts, then the partial melting of the eclogite

assemblages, leaving garnet as a residuum, would lead to a strong depletion of HREE in the liquid (Gill 1974). Thus the observed flat patterns of HREE in Peruvian andesites also exclude eclogites with REE abundances similar either to fresh or to altered oceanic basalts, as suitable source rocks. Similar arguments can also be invoked against the derivation of andesites from an ocean-floor basaltic magma by high-pressure fractional crystallization.

Partial melting of peridotite at high P_{H_2O} : – Kushiro et al. (1972), Mysen et al. (1974) and Mysen & Boettcher (1975) have suggested that andesitic magma can be produced directly by a small degree of partial melting of hydrous spinel or garnet peridotite, while Nicholls & Ringwood (1973) have argued that hydrous melting of upper mantle peridotite generates quartz tholeiite which, after subsequent olivine fractionation, could produce andesites. The relatively low Ni content of Peruvian andesites (~15–37 ppm) indicates that these rocks were not formed directly by the melting of peridotite. The abundances of transition elements are, however, consistent with partial fusion of the upper mantle followed by fractional crystallization of olivine ± spinel (Andriambololona 1976).

Regarding REE, relatively flat patterns for HREE in analyzed andesites exclude the melting of garnet peridotite (Fig. 3). The partial melting of spinel peridotite can produce a liquid with unfractionated HREE, but only with relatively small LREE enrichment (Fig. 3). Even subsequent fractional crystallization of such a magma cannot account for the observed REE abundances in andesites. Fractionation of olivine and also of plagioclase, pyroxenes and magnetite, all minerals with low partition coefficients (Schnetzler & Philpotts 1970), leads essentially to an increase of the total REE in the residual liquids without any distinct change of the fractionation patterns (Fig. 4). Thus subsequent fractional crystallization will not explain the strong LREE enrichment of andesites. The same argument applies to any low-pressure fractionation of basaltic magma (Fig. 4). The derivation of andesites by this process would require a parental basaltic magma already strongly enriched in LREE and with a flat HREE pattern, i.e. with a REE pattern similar to that of andesites. However, such a distribution of REE is not

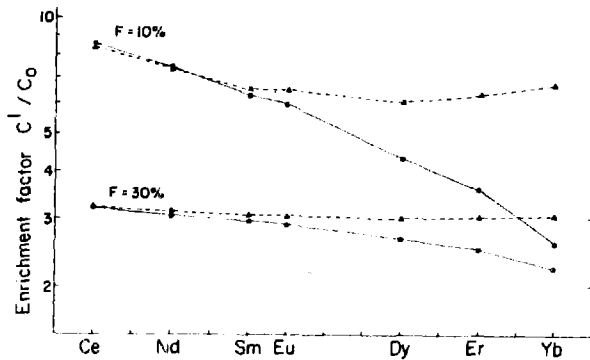


Fig. 3. Enrichment factor C^1/C_0 (concentration in melt/concentration in source rock) for REE in melts produced by partial melting (the degree of partial melting - $F=10$ and 30%) of garnet peridotite (solid lines) and spinel peridotite (broken lines) using equation 15 of Shaw (1970) and the partition coefficients (D) of Shimizu (1975) for garnet and those of Kay & Gast (1973) for the other mineral phases. Mineral percentages after Shaw (1972). Garnet peridotite: parent - 55 ol., 20 cpx., 15 opx., 10 gt.; melt with $F=10$ and 30% - 40 ol., 25 cpx., 15 opx., 20 gt. Spinel peridotite: parent - 55 ol., 25 cpx., 15 opx., 5 sp.; melt with $F=10$ and 30% - 35 ol., 50 cpx., 15 opx.

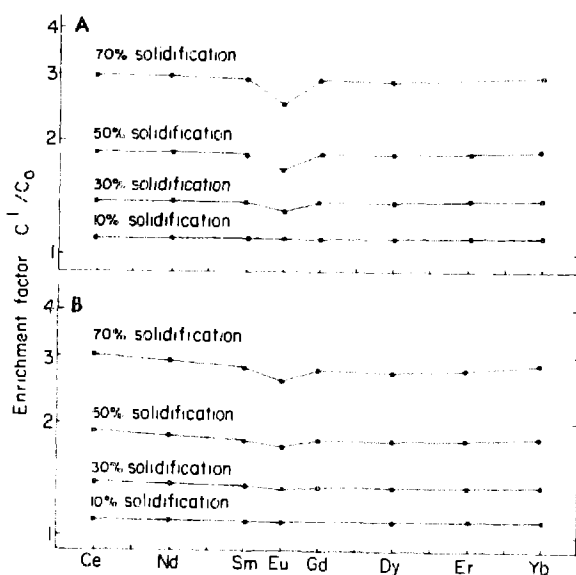


Fig. 4. Enrichment factor C^1/C_0 for REE in residual liquids produced by low pressure fractional crystallization. Separated solid phases: A - 50 plg., 30 cpx., 10 opx., 10 opq. (cf. Ewart et al. 1973). B - 50 cpx., 25 ol., 25 plg. (cf. Arth & Hanson 1975). The equation of Greenland (1970) for the crystallization of phases in constant proportions with constant partition coefficients was used together with D of Arth & Hanson (1975) for plagioclase and those of Kay & Gast (1973) for the other phases.

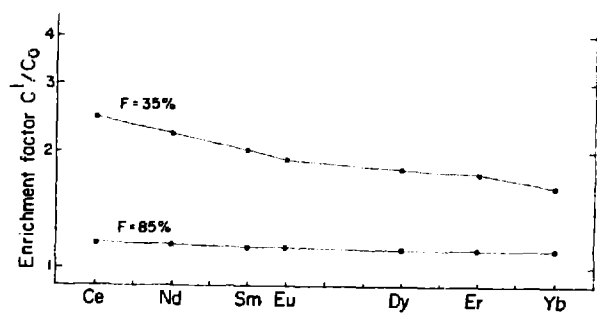


Fig. 5. Enrichment factor C^1/C_0 for REE in melts produced by partial melting of garnet granulites using equation 15 of Shaw (1970) and D of Kay & Gast (1973) for clinopyroxene, D of Shimizu (1975) for garnet and D of Arth & Hanson (1975) for plagioclase. Mineral percentages after Green & Ringwood (1968). Mineral percentages are: Parent - 55 cpx., 20 gt., 15 plg., 10 qtz.; melt with $F=35\%$ - 14 cpx., 43 gt., 14 plg., 29 qtz.; melt with $F=85\%$ - 47 cpx., 23 gt., 18 plg., 12 qtz.

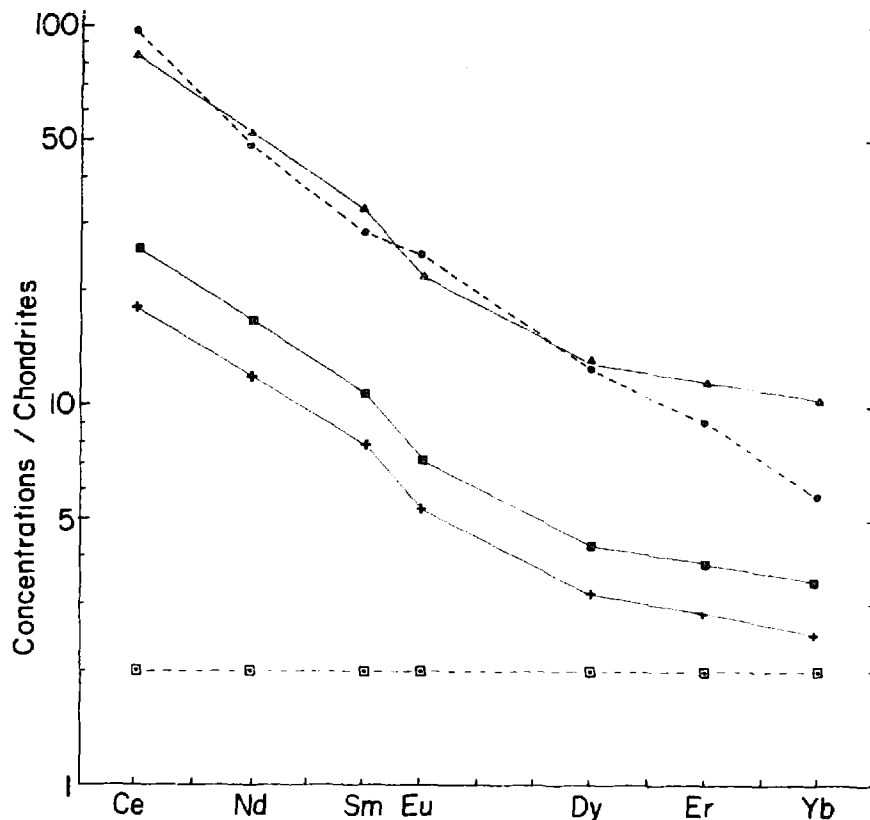
characteristic for any common type of basalts (Herrmann 1970).

Anatexis of the lower crust: - Pichler & Zeil (1972a, b) and Fernandez et al. (1973) have proposed the hypothesis that Andean andesites were generated by partial fusion of the lower crust. This process is consistent with the abundances of transition elements in andesites of southern Peru, assuming that the lower crustal source corresponds to garnet granulites (Andriambololona 1976). The model calculation of partial melting of garnet granulites for REE is shown in Fig. 5. It indicates that, in order to generate the observed REE abundances in Peruvian andesites, the granulites would have to have REE patterns similar to those of andesites. Although it is possible that some granulitic rocks may have REE patterns comparable to those of Peruvian andesites, typical granulites (e.g. Green et al. 1972) do not have such REE patterns. A process of partial melting of the lower crust also does not explain the spatial variations of LILE and the presence of similar andesites in some island arc environments where sialic crust is lacking. Furthermore, James et al. (1976) have negated such a process on the basis of geophysical and geological arguments.

Petrogenesis of andesitic rocks: - The trace element distribution in andesites from southern Peru is not compatible with a single stage process of origin. Geochemical requirements

Fig. 6. The plot of zone refining model for REE

- - minimum upper mantle composition (2 times chondritic abundances).
- - maximum upper mantle composition produced by zone refining of garnet peridotite (Harris 1957, 1974) when $\frac{C^1}{C_0} \rightarrow \frac{1}{D}$
- ▲ - average REE content of andesites of group A-1 taken as representative of the melt produced by partial melting of spinel peridotite with $F=20$ and 30%.
- + - REE content of spinel peridotite, which produces average andesite of A-1 by 20% of partial melting.
- - REE content of spinel peridotite which produces average andesite of A-1 by 30% partial melting. D and mineral percentages used are the same as in Fig. 3.



indicate that they evolved in a multistage process. This fact probably applies to andesites of the continental margin in general. Any model for the genesis of these continental margin rocks should explain the fact that in the rocks of a given SiO_2 content there is a relatively uniform major and transition element composition, while their content of incompatible elements shows spatial variations indicating their close relation to the Benioff zone. However, as noted above, parental magmas of andesites were not directly derived from the subducted ocean ridge basalts either in amphibolite or eclogite mineralogy. Neither is 'normal' unfractionated upper mantle a suitable source. If the upper mantle peridotite has chondritic proportions of REE, but two to five times higher total REE abundances than chondrites, as is usually assumed (Kay & Gast 1973; Allegre et al. 1973; Frey & Green 1974), then the direct partial melting of this rock cannot produce the observed REE distribution of andesites, even if the magma subsequently underwent fractional crystallization. The available data, however, indicate that the upper mantle peridotite is probably still a source for andesitic rocks.

Thus a process of partial melting of an 'enriched' upper mantle appears to be plausible (Ringwood 1974; Best 1975). The large enrichment of LREE requires the upper mantle source to be enriched in LILE, perhaps by the process suggested by Best (1975), who has argued that ascending hydrous fluids, released from the subducted oceanic lithosphere along the Benioff zone, extract K and other incompatible elements by scavenging and zone melting from the overlying wedge of the upper mantle. The amount of these elements liberated from the upper mantle is then directly proportional to the thickness of the overlying peridotite (Best 1975). Such fluid phases, which would probably not affect the major and minor transition element composition of andesites to any large degree, may be expected to be strongly enriched in LREE (Frey & Green 1974) and thus their presence could explain the LREE enrichment in these rocks.

In order to evaluate this process quantitatively, the model of zone refining was calculated according to Harris (1957, 1974) and the results are given in Fig. 6. Since the upper mantle just above the subduction zone in southern Peru is probably in the garnet stability

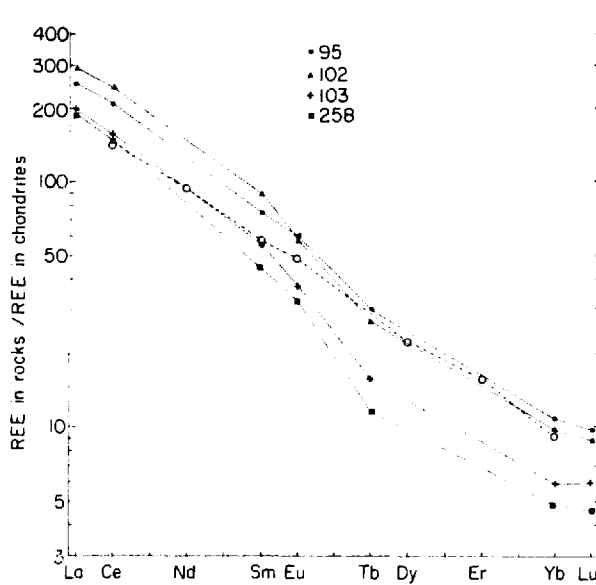


Fig. 7. Chondrite-normalized REE abundances in shoshonitic rocks. Also shown is the REE content in melt produced by partial melting ($F=1\%$) of garnet peridotite having 3 times chondritic abundances of REE (broken line). The REE distribution in the melt does not practically change with the increase of F accompanied by the increase of REE content of the source rock. Mineral percentages after Kay & Gast (1973); D are the same as in Fig. 3. Parent - 55 ol., 10 cpx., 25 opx., 10 gt.; melt - 50 cpx., 50 gt.

field (James 1971), it was assumed that the zone refining took place in garnet peridotite. Fig. 6 shows the field of the REE compositions of the upper mantle peridotite which underwent zone refining. The lower limit of this field is given by unfractionated peridotite having REE abundances twice those of chondrites and the upper limit is represented by the 'maximum' composition of the upper mantle, i.e. the highest possible content of REE produced by zone refining (Harris 1974). If the process played a role in the genesis of andesites, then their source material should lie in this field. For the calculation of the REE composition of the source material for andesites, the average content of andesites of group A-1 was taken as representative of the liquid produced by partial melting of the upper mantle. The degree of partial melting was considered to be 20% and 30% (Green & Ringwood 1968). The flat HREE patterns of andesites, however, exclude the presence of garnet during the melting, so it was assumed that the partial fusion which produced andesitic liquids took place in the higher part of

the upper mantle, in spinel peridotite. The calculated composition of source material for andesites lies well within the field of the enriched upper mantle peridotite (Fig. 6). This suggests that the zone refining process can produce a suitable source for andesites from unfractionated upper mantle peridotite.

This process is also consistent with the spatial variations of K, Rb and total REE. The increase of the incompatible elements with distance from the trench and their increase with increase in the dip of the Benioff zone from south to north thus correlate with an increase in the thickness of the peridotite wedge. Magma produced by partial melting of the LILE enriched upper mantle, fractionates as it rises. The relatively low Ni content of andesites implies crystal fractionation of olivine \pm spinel. Further extensive low P fractional crystallization is indicated by the ubiquitous presence of numerous phenocrysts, mainly of pyroxenes and plagioclase, in these rocks. However, such a crystal fractionation does not significantly change the relative fractionation of REE and leads mainly to an increase in their absolute contents (Fig. 4).

Shoshonites

The REE content of shoshonites is given in Table 2 and plotted, normalized to chondrites, in Fig. 7. The REE patterns of shoshonites are strongly fractionated with a distinct enrichment of LREE and progressive depletion of HREE and without any Eu anomaly. Their relative and absolute REE concentrations are comparable to those of shoshonite (AYA-1A) from central Peru given by Noble et al. (1975). The REE distribution of shoshonites differs, however, from that of andesites. Although shoshonites have lower contents of SiO_2 than andesites, they have higher REE contents and more fractionated REE patterns. In addition, shoshonites also have higher abundances of some other LILE such as K, Ba and Sr (Dupuy & Lefevre 1974). These differences indicate that andesitic and shoshonitic rocks are not directly genetically related, nor are they derived from the same parental source.

Shoshonites show an over-all weak increase of the La/Yb ratio with increase of K and with decrease in the total REE content. However, there is no positive correlation of the La/Yb ratio or total REE content with SiO_2 .

In fact, the shoshonites with the higher REE abundances have generally lower contents of SiO_2 . This suggests that shoshonitic rocks cannot be derived by a simple low-pressure fractionation from a common magma.

The high REE content and well-fractionated REE patterns of shoshonites, with La/Yb ratios ranging from 38 to 64, resemble those of alkali basalts. The content of some other LILE (K, Rb, Ba, Sr) is also comparable to that of alkali basalts. The similarity of shoshonites to alkali basalts suggests a similar mode of origin (Dupuy & Lefevre 1974). Such rocks are thought to be generated by a small degree (<5%) of partial melting of the upper mantle source, at pressures of about 30 kb (Green 1970, 1971). The strong fractionation of HREE both in alkali basalts (Kay & Gast 1973) and in shoshonites indicates that these rocks underwent garnet fractionation, as garnet is the only major rock-forming mineral which preferentially incorporates HREE. The model calculations for REE (Fig. 7) show that shoshonites could have been derived by a small degree of partial melting of garnet peridotite with a chondritic REE pattern but with 2–5 times higher absolute REE contents than that of chondrites. The same process and the same upper mantle source can also account for the observed abundances of other LILE (K, Rb, Sr and Ba) in shoshonites. The calculations of the partial melting model for these elements, using D of Sun & Hanson (1975) and estimates of the upper mantle abundances of Griffin & Murthy (1969) (in ppm – K=160; Rb=0.64; Ba=16; Sr=15), give the following concentrations in the melt: for F=1%; K=1.52% (2.13), Rb=61 ppm (59); Sr=885 ppm (1003) and Ba=1504 ppm (1543). The values in parentheses are the abundances in southern Peruvian shoshonites reported by Dupuy & Lefevre (1974). These calculations suggest that, contrary to andesites, the large enrichment of LILE in shoshonites can be due to a small degree of partial melting of the upper mantle. The problem of high content of K, Rb, Ba and Sr in alkali basalts and related rocks has been discussed recently by Kay & Gast (1973) and Sun & Hanson (1975) who have also argued that these abundances are produced directly by a low degree of partial melting without any secondary enrichment process such as wall-rock reaction.

It appears that shoshonites could have been derived from the garnet-bearing upper mantle

material, which is not enriched by water or fluids released from the subducted oceanic crust. However, the relation of shoshonites to a subducted zone is not very clear. Jakes & White (1969) have shown that shoshonitic rocks need not be related to seismic activity on a Benioff zone. Regarding southern Peru, the data of Stauder (1973) indicate that shoshonites occur in an area under which a subduction zone is already disappearing. Thus, it seems probable that even if the subducted zone might have triggered partial melting in the upper mantle, it did not affect the chemical composition of the upper mantle.

Conclusion

The late Cenozoic volcanics of southern Peru are composed of two suites of rocks: calc-alkaline and shoshonitic, which show a zonal arrangement with respect to the Peru–Chile trench. The presented REE data confirm the suggestion of Dupuy & Lefevre (1974) and Andriambololona (1976) that these two rock series were derived from different sources. It appears that andesites and related rocks of the calc-alkaline suite cannot be generated by a single stage process. Their derivation from subducted ocean-floor basalts or from 'normal' upper mantle peridotite cannot explain the geochemical characteristics of these rocks. The geochemical and geophysical data also indicate that andesites are not formed by anatexis of old crustal material (James et al. 1976) and that their upper crustal contamination was only of a limited nature (James et al. 1976; Noble et al. 1975).

The high content of LILE of andesitic rocks, particularly the strong enrichment of LREE requires their derivation from a source already enriched in these elements and having a distinctly fractionated REE pattern. There are two possible sources to be considered: enriched subducted oceanic lithosphere and enriched upper mantle peridotite. The oceanic crust can, however, be eliminated as it would not produce the observed distribution of transition elements in andesites (Andriambololona 1976). Thus, the source of andesitic rocks from southern Peru appears to be an enriched upper mantle peridotite. In fact, James et al. (1976) have suggested that the South American continental lithosphere may be locally enriched in

LILE by their addition from the asthenosphere. On the other hand, Best (1975) has argued that hydrous fluids, released from the descending oceanic crust, could enrich the upper mantle peridotite by scavenging and zone refining. The calculation of the zone refining model supports such a process.

Although both mechanisms could have participated in the generation of andesitic rocks, the model of Best (1975) seems to be more consistent with the available data. It can explain the systematic spatial variations of LILE both perpendicular to the trench and parallel with the trench. This mechanism is also consistent with the presence further from the trench of 'normal' upper mantle peridotite from which the shoshonites were probably derived. It seems that this model is applicable to calc-alkaline andesitic rocks associated with subduction zones in general, as none of the single stage processes proposed for their origin can explain their geochemical characteristics (Gill 1974; Lopez-Escobar et al. 1974). The magma generated by partial melting of the upper mantle then underwent a varying degree of fractional crystallization and crustal contamination as it rose.

The presented data show that shoshonites can be derived from a 'normal' garnet-bearing upper mantle source by a low degree of partial melting. The major and transition element composition of shoshonites implies that they subsequently underwent low-pressure fractionation (Andriambololona 1976).

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