

Sr isotopic evidence on the spilitic degradation of the Deccan basalt

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Similar Sr isotopic ratios (~ 0.7055) for the tholeiite-spilite flow unit and the associated mineral phases, of Bombay (Deccan Traps) provide a direct evidence for the spilitic degradation of tholeiite. In contrast, a dramatic increase in the rare earth elements (REE) from basalt to spilite is rather puzzling as rare earths are considered to be relatively immobile. The geochemistry thus suggests that the process of spilitization is due to the reaction with a complex fluid having identical Sr-isotopic composition as that of the basaltic magma—thereby masking the details of the mixing process.

1. Introduction

An unusual occurrence of tholeiites grading into spilites in the Bhoiwada section of Bombay Island (Deccan basalt) was first described by Sukheswala (1953, 1960) who invoked a hydromagmatic model to explain such an association (Sukheswala 1974). Concurrently, Vallence (1974) proposed a secondary low-grade alteration model based on the presence of chemically similar relict clinopyroxenes in both basalt and spilite. While studying the Bhoiwada sequence, Hellman and Henderson (1977) showed for the first time that rare earth elements (REE) are mobile during spilitization, which is indeed a very significant observation. Hence the method of Sr isotopic fingerprinting of the whole rock and mineral components has been used, for the first time, for a better understanding of the process of spilite formation in the Bombay Island.

2. Bhoiwada section of Bombay

The 30 m-thick Bhoiwada section (figure 1(a)) is divided into three zones: tholeiite, transitional (spilite-tholeiite) and pillowed and non-pillowed spilite (figure 1(b)). The dark compact tholeiitic basalt (at the top) is usually aphyric with intergranular clinopy-

roxenes (Ca 36) and anhedral magnetite, occasionally with plagioclase micro-phenocrysts (An 63). The lower green albitized pillowed basalt (spilite) contains clinopyroxene (Ca 32), dusty albite (An 10), K-feldspar, prehenite and laumontite as groundmass minerals, with relatively unaltered magnetite and amygdales with chlorite and zeolite. This rock also shows distinct relict quench textures. The green rock grades upward into a transitional zone of spilite-tholeiite which is fine grained, intergranular with clouded plagioclase (An 83), clinopyroxene (Ca 30), and subordinate secondary minerals (table 1, figures 2 and 3).

3. Geochemistry

The spilite is enriched in Na, K, La, Ce, Sm and Eu relative to basalt, and the transitional type lies between the two. While the spilite is ol-hy normative, the basalt is distinctly qtz-normative. A decrease in normative diopside in spilite is observed due to lower concentrations of CaO (table 1). These changes are quite consistent and follow the geochemical principles of spilitization, i.e., as a secondary process (Vallence 1969).

As pointed out by earlier workers (Hellman and Henderson 1974; Subbarao *et al* 1979), the marked increase of RE elements in the Bhoiwada suite of

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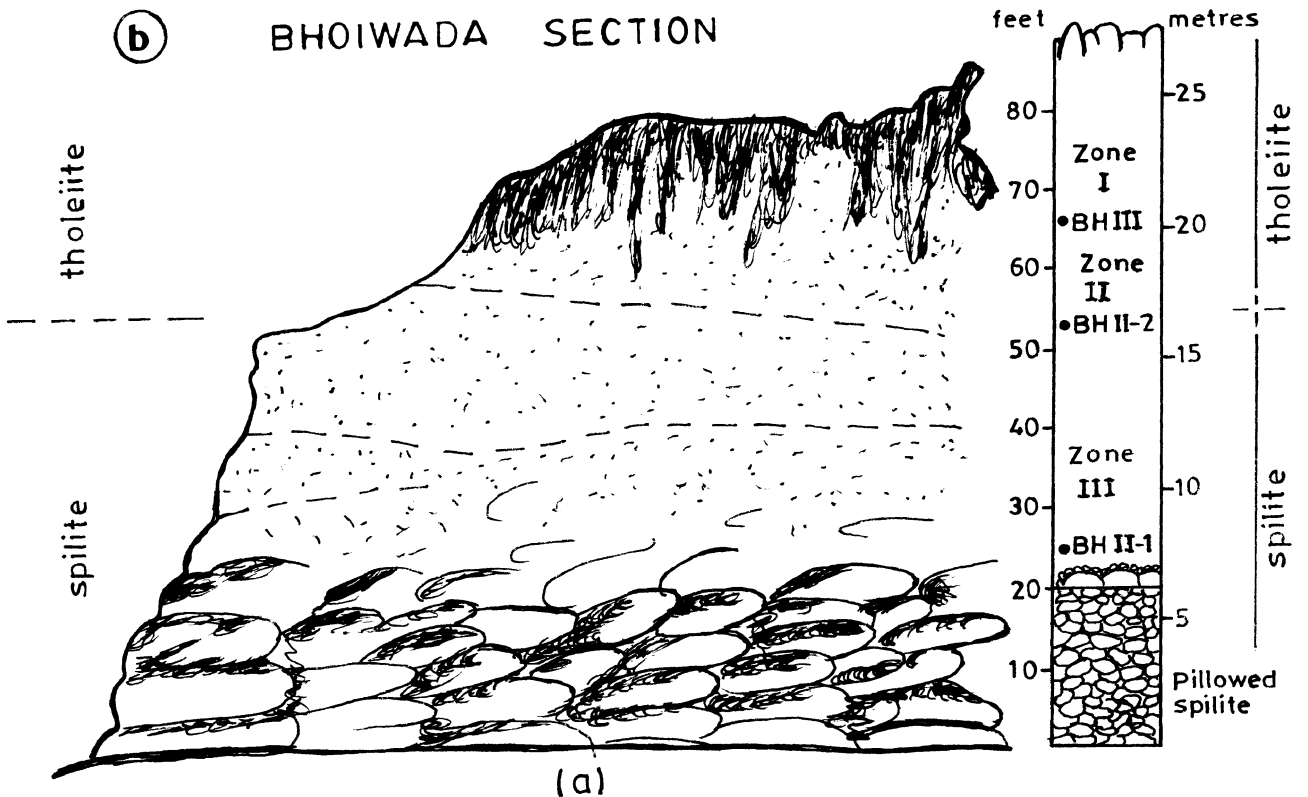
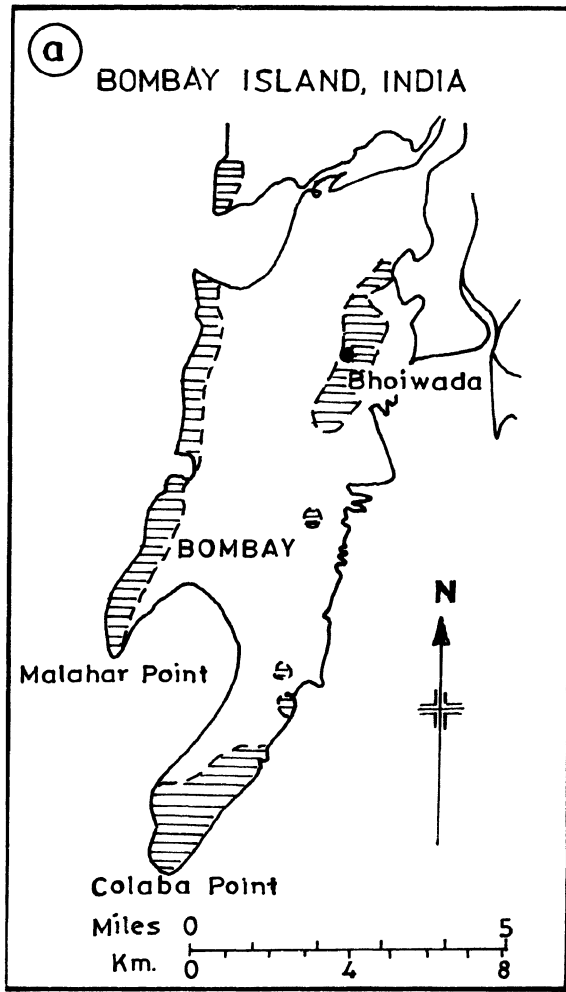


Figure 1(a). Location of Bhoiwada spilite-basalt section, Bombay island (Deccan Traps). Shaded areas represent basalt exposures; (b). Schematic section at Bhoiwada showing different zones and location of samples included in this study (zone I: sample BH III basalt; Zone II: sample BH II-2 spilite-basalt transitional rock; Zone III: sample BH II-1 spilite).

Table 1. Representative rock and mineral analyses from the Bhoiwada basalt-spilite sequence.

Oxides	Zone I: Basalt			Zone II: Basalt-Spilite Transition			Zone III: Spilite		
	BH III-2	BH III-1F	BH III-1Px	BH II-2	BH II-2F	BH II-2Px	BH II-1	BH II-1F	BH II-1Px
SiO ₂	50.73	53.33	51.62	50.14	47.39	50.09	50.53	67.68	49.64
Al ₂ O ₃	13.85	29.33	1.94	13.18	32.79	1.69	13.18	21.20	2.34
TiO ₂	1.11		0.42	1.11		0.60	1.04		0.65
FeO	8.21	1.22 ⁺	11.32 ⁺	7.54	0.64 ⁺	18.45 ⁺	7.98	0.35 ⁺	17.2 ⁺
Fe ₂ O ₃	3.64			4.38			3.31		
MgO	6.99	0.10	15.93	6.60	0.17	13.50	7.19		13.85
CaO	11.36	12.87	17.54	11.36	17.12	14.81	8.66	1.71	15.25
Na ₂ O	2.73	3.99	0.19	2.64	1.90	0.24	3.58	10.44	0.22
K ₂ O	0.64	0.16		0.64	0.06		1.50	0.05	
MnO	0.19		0.32	0.15		0.42	0.19		0.38
P ₂ O ₅	0.14			0.16			0.14		
Moisture	0.81			0.99			0.86		
L.O.I	0.39			1.21			2.60		
Mg*	57.89		76.63	56.34		63.03	59.74		65.23
Rb(ppm)	12.70			12.70			44		
Sr	192			195			634		
Ba	140			183			676		
Zr	69			69			58		
Y	25			25			21		
La	10.30			13.53			31.50		
Ce	18			26.17			74.70		
Sm	3.04			2.81			7.06		
Eu	0.93			1.02			2.38		
Yb	3.81			2.77			3.06		
CIPW Norm									
Q	4.88			5.73					
Or	3.79			3.79			9.11		
Ab	23.1			22.34			31.13		
An	23.65			22.23			15.9		
Di	22.38			23.26			22.23		
Hy	7.04			5.65			3.43		
Ol							10.91		
Mt							4.93		
Hm	12.76			12.76					
Il	0.4			0.32			2.03		
Tn	2.2			2.31					
Ap	0.33			0.38			0.34		
Cc									
Plagioclase									
Ca		63.50			83			8.30	
Na		35.60			16.70			91.50	
K		0.90			0.30			0.30	
Pyroxene									
Ca			36.10			30.80			31.80
Mg			45.70			39.10			40.20
Fe			18.20			30			28

- **BH III-2** = Basalt; **BH II-2** = Spilite-basalt transitional type; **BH II-1** = Spilite; **F** = Felspar; **Px** = Pyroxene (this study).
 - **Major elements Ba, Zr and Y**: Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES) at the Royal Holloway, University of London (Thompson & Walsh 1981).
 - **REE**: INAA at BARC Mumbai.
 - **Rb & Sr**: Isotope dilution at the University of British Columbia, Vancouver.
 - **Mineral Analyses**: Electron microprobe (Macquaria University, North Ryde, Australia).
 - **Mg***: $100 * \text{MgO} / (\text{MgO} + (0.85 * \text{FeO}))$. The Mg-number is calculated assuming 15% of the Fe is Fe₂O₃ following Cox (1980).
- ⁺ All the Fe is expressed as FeO.

basalt-spilite undermines the utility as a petrogenetic indicator (figure 4; this study). On the contrary, however, the basalts and zeolite facies metabasalts from the Troodos massif and Carlsberg Ridge (basalt-

spilite) display similar REE patterns (Smewing and Potts 1976; Subbarao *et al* 1979), unlike the basalt-spilite suite of the Deccan province. The reasons for this diverse chemical behaviour of REEs are not clear.

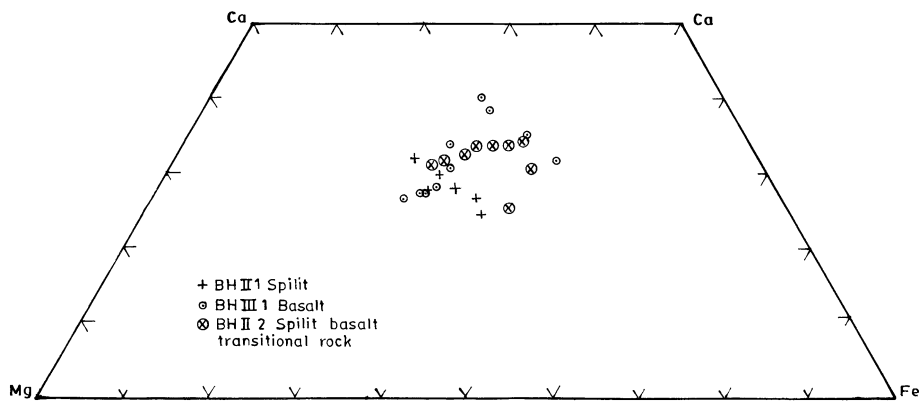


Figure 2. Pyroxene compositional plots (Ca-Mg-Fe diagram) for spilite-basalt sequence.

4. Sr isotopic composition

In this paper Sr isotopic composition and concentrations of Sr and Rb for the basalt, transitional rock and spilite, and the associated minerals (Pl, Cpx) are reported to trace the ancestry of the spilite (table 2).

The age corrected ($^{87}\text{Sr}/^{86}\text{Sr}$)_i and Rb/Sr ratios of the basalt, transitional rock and spilite are nearly identical (0.7055, 0.7056, 0.7056; 0.066, 0.065, 0.069; table 2). Interestingly, the minerals (Pl and Cpx) from all the three rock types have similar 87/86 ratios as their respective host rocks (see table 2 for details). These results suggest that

- (a) both minerals and the respective host rocks are in equilibrium despite low-degrees of alteration metamorphism, and
- (b) the isotopically similar basalt-spilite association represents a single isochronous flow unit.

5. Discussion

The observed variations in the mineralogy (albite in spilite and An rich plagioclase in basalt; chlorite, zeolites, prehenite) and major element geochemistry in the Bombay basalt-spilite association are largely due

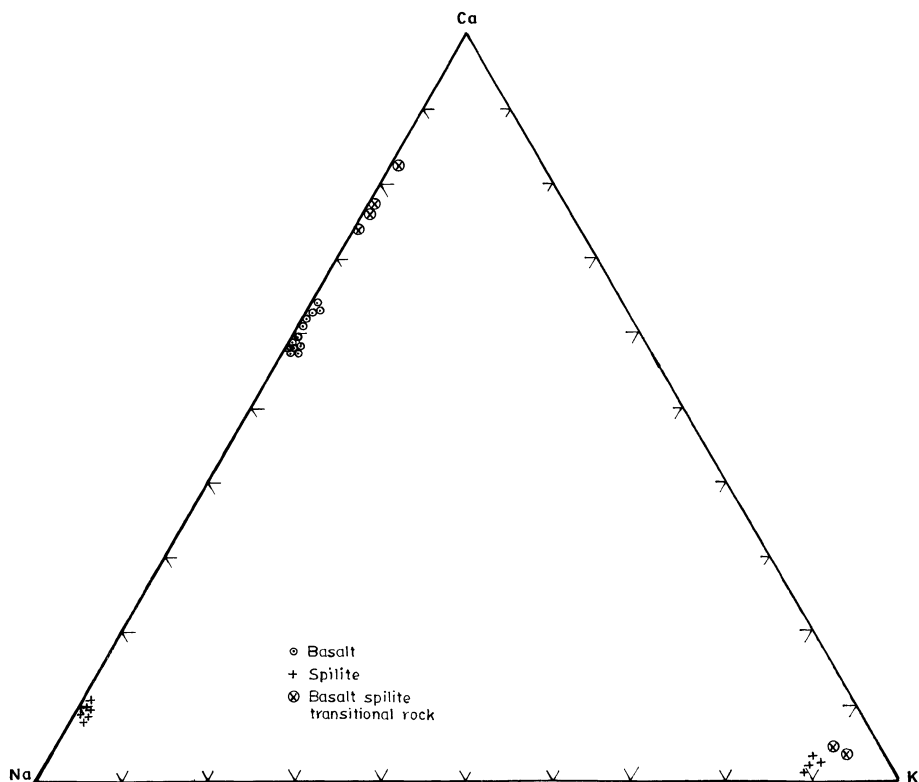


Figure 3. Variation in feldspar compositional data (Ca-Na-K diagram) from spilite-basalt sequence. Note the presence of K-feldspars in the spilite and transitional rocks.

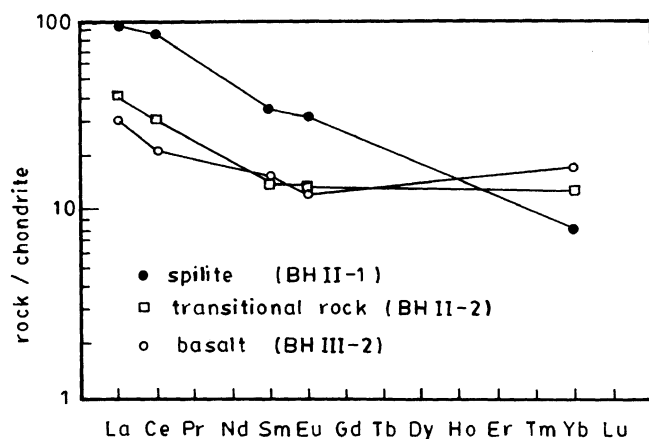


Figure 4. Chondrite normalized REE patterns (see table 1 for data).

to secondary reaction process. Interestingly the pyroxene display limited variation and rather remained unchanged in the basalt-spilite sequence (figure 2). This indeed is a very valuable signature to trace the ancestry of spilites (Vallence 1974).

5.1 Alteration

It is clearly evident from the petrography (sericitization) and mineralogy (chlorite, prehenite, calcite) that the spilite and spilite-basalt transitional rock suffered different degrees of alteration, while the basalt remained nearly fresh or least altered. In terms of the "Alteration-Index (A.I)" of Sloman (1987; see figure 5), the Bhoiwada rocks fall approximately into three groups, i.e., A.I.: 1–2 (basalts), 3–4 (basalt-spilite transitional rocks, spilites), 5–6 (spilites) (1 = least altered, 6 = highly altered associated with high degree of sericitization). Figure 5 shows that SiO_2 and CaO decrease from basalt (A.I.=1–2) to spilite (A.I.=5–6) indicating an increase in secondary minerals; where as increase of Na_2O , K_2O , Ba and Rb reflects the change from the An-rich to Ab-rich plagioclase and also the

presence of K-feldspars. Marked increase in Sr with rising A.I., is perhaps reflected in the presence of laumontite (Sr can proxy for Ca). As expected, the immobile elements (Ti, Zr, Y) remained unaffected by the alteration process. However, the presence of similar Sr isotopic composition for the basalt and spilite is rather unusual and uncommon, and strongly contrasts with Sloman's observations on the Triassic spilites of Italy (basalt: ~ 0.7040 , spilite: 0.7060).

5.2 Sr isotopes

Sr isotopic similarity between spilite and basalt and associated mineral phases-pl and cpx confirms the ancestry of the spilites (i.e., tholeiite) through secondary degradation scheme. If this were to be due to hydromagmatic process, the isotopic ratios ought to have been different. Despite compositional adjustments in spilitization, the Bombay suite permits a still unique opportunity to examine such adjustments (in particular, the mobility of REE) and also establishes the usefulness of isotopic finger printing to get an insight into the magmatic systems as well as the pathways of secondary processes.

5.3 Nature of the fluids

Field and fossil evidences indicate shallow marine or brackish water environment for the Bombay eruptions (Sukheswala 1974). Thus the process of low-temperature spilitization involves ionic exchange between solid rock and alkaline rich marine fluids with adjustments in chemistry in both phases. It is likely that the alkaline saline conditions could have been achieved in the early part of the secondary adjustments due to an increase in pH with base leaching. The hydrolysis of basalt results in residues impoverished in Ca, alkalis and Si as seen in the interstitial chloritic material of the Bhoiwada spilites. In places, chlorite is also associated with other secondary hydrous minerals

Table 2. Sr isotopic and Sr and Rb isotope dilution data.

	Sample no.	Name	Sr (ppm)	Rb (ppm)	Rb/Sr	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
Zone I	BH III-1	Basalt	192	12.7	0.066	0.192	0.7055
	BH III-1F	Feldspar	337	3.1	0.009	0.026	0.7053
	BH III-1Px	Pyroxene	36.8	11.1	0.302	0.873	0.7058
Zone II	BH II-2	Spilite-Basalt Transition	195	12.7	0.065	0.189	0.7056
	BH II-2F	Feldspar	192	1.3	0.007	0.021	0.7055
	BH II-2Px	Pyroxene	33.7	6.6	0.195	0.565	0.7057
Zone III	BH II-1	Spilite	634	43.7	0.069	0.199	0.7056
	BH II-1F	Feldspar	935	50.3	0.054	0.156	0.7054
	BH I- 2Px	Pyroxene	100	8	0.08	0.23	0.7056

• Isotopic data are reported relative to standard values measured at the University of British Columbia: ($^{87}\text{Sr}/^{86}\text{Sr}$) = 0.70800 for E & A Sr and 0.71022 for NBS 987 Sr.

• Isotopic fractionation correction $^{87}\text{Sr}/^{86}\text{Sr} = 0.1194$.

• Total procedural blanks are < 100 picograms for Sr and < 20 picograms for Rb.

• Uncertainties on Sr and Rb abundances: < 0.5% and < 1%.

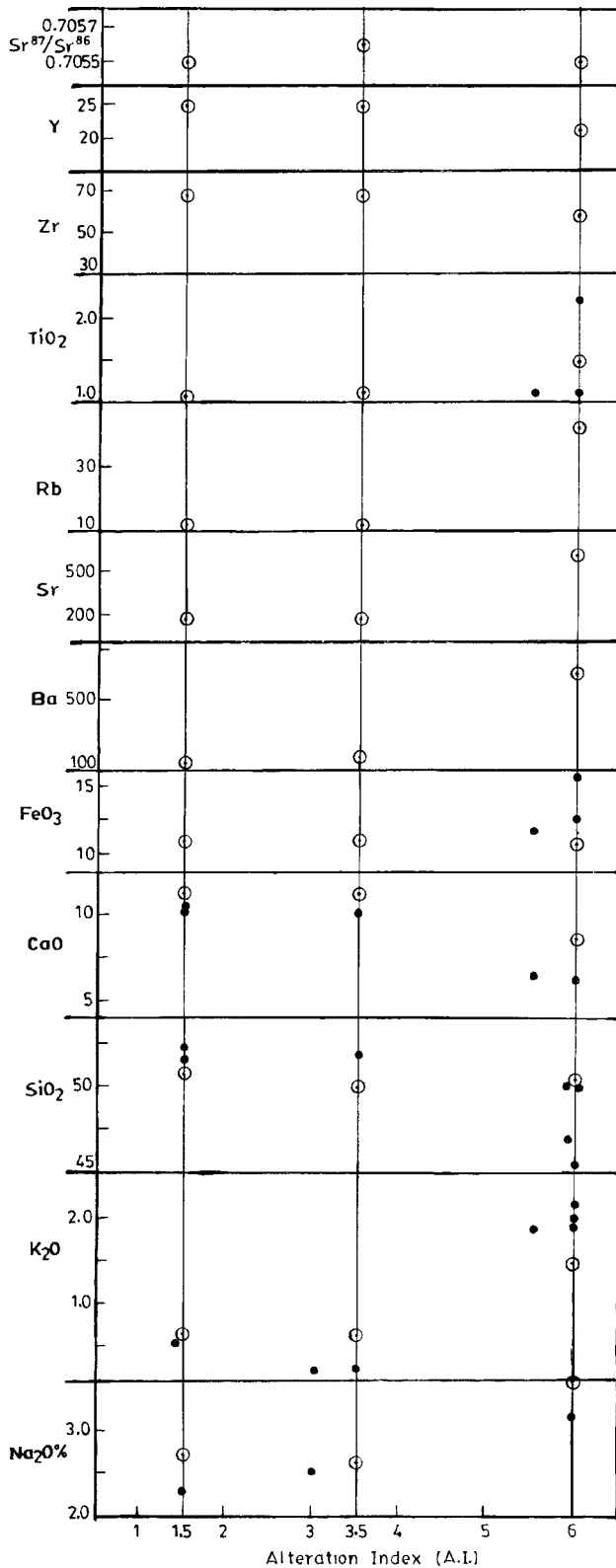


Figure 5. Variation of selected elements with "Alteration Index (I.D)". Open circle with dot represents analyses from this study (see table 1 for data). Solid dot represents analyses from the literature (Sukheswala 1974; Vallence 1974).

such as laumontite, prehnite, calcite and quartz, which perhaps represent the products of subsequent reaction between chlorite and fluid (Vallence 1974).

The important point to be considered at this stage is the absence of any change in Sr-isotopic composition between the basalt and spilite as well as their mineral phases—Pl and Cpx. Based on the field and chemical evidences, we are justified in assuming sea water as the principal fluid that is responsible for spilitization. If so, the Sr-isotopic composition of Tertiary sea water (~ 0.708 , Burke *et al* 1982) should have been reflected in the spilitized basalt. From the available data, it thus appears that the fluid and magma have nearly identical Sr-isotopic composition and therefore not picking up a mixing or equivalent process. This might suggest that the fluid is of a more complex or unexpected origin unlike originally assumed.

The second puzzling problem relates to the dramatic increase of REE in the spilite, while the Sr isotopic composition in the entire basalt-spilite sequence remained nearly constant. Earlier, Menzies *et al* (1993) demonstrated that "extremely high water/rock ratios ($> 10^4$) are required to promote the exchange of REE between basaltic rocks and sea water...". However, the mineralogical data and Sr isotopic composition negate the role of high-temperatures in the case of the Bhoiwada spilite association. It is also unlikely that the secondary hydrothermal fluids (zeolitization) would have had any effect, as the zeolites are formed around 200°C (Jeffrey *et al* 1988) with extremely poor REE concentrations (James and Walsh, in press; and personal discussions).

6. Summary

New Sr isotopic and elemental data for the unique sequence of basalt grading into albite-chlorite spilite from the Bombay island (Deccan Traps) provide new clues to the problems of spilitization.

- Nearly identical $^{87}\text{Sr}/^{86}\text{Sr}$ (~ 0.7055) for the basalt-spilite and associated pyroxene and plagioclase indicates perfect equilibrium condition; and points out either the inert nature of the minerals (in particular pyroxene) or the presence of a complex fluid.
- REE are preferentially mobilized during spilitization. This is rather unexpected in such a low temperature hydrothermal system.
- Reaction between interstitial residues (i.e. chlorite) and fluid could easily result in the formation of secondary minerals such as laumontite, prehnite, calcite and quartz.

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