1.4.1 X-ray fluorescence (XRF)

X-ray fluorescence spectrometry (XRF) is currently the most widely used analytical technique in the determination of the major and trace element chemistry of rock samples. It is versatile and can analyse up to 80 elements over a wide range of sensitivities, detecting concentrations from 100 % down to a few parts per million. It is a rapid method and large numbers of precise analyses can be made in a relatively short space of time. The chief limitation is that elements lighter than Na (atomic number = 11) cannot be analysed by XRF. Good reviews of the XRF method are given by Norrish and Chappell (1977), Tertian and Claisse (1982), Williams (1987) and Ahmedali (1989).

X-ray fluorescence spectrometry is based upon the excitation of a sample by X-rays. A primary X-ray beam excites secondary X-rays (X-ray fluorescence) which have wavelengths characteristic of the elements present in the sample. The intensity of the secondary X-rays is used to determine the concentrations of the elements present by reference to calibration standards, with appropriate corrections being made for instrumental errors and the effects the composition of the sample has on its X-ray emission intensities. Alternatively, the X-rays may be detected without

1.4.2 Neutron activation analysis (INAA and RNAA)

Neutron activation analysis is a sensitive and versatile method of rock analysis, chiefly applicable to trace elements and capable of determining a large number of elements simultaneously without necessarily destroying the sample. There are two approaches. Instrumental neutron activation analysis (INAA) employs a powdered rock or mineral sample; radiochemical neutron activation analysis (RNAA) involves the chemical separation of selected elements. The range of elements analysed is given in Table 1.5 and the methods are described in detail by Muecke (1980).

In instrumental neutron activation analysis (INAA), about 100 mg of powdered rock or mineral sample is placed in a neutron flux in a neutron reactor together with standards. The sample and standards are irradiated for up to about 30 hours. The neutron flux gives rise to new, short-lived radioactive isotopes of the elements present which emit gamma radiations. Particular isotopes can be identified from the gamma radiations emitted and the intensities of these radiations are proportional to the amounts of the isotopes present. The gamma-ray spectrometry (the counting) is done at set intervals (several hours, several days and several weeks) after the irradiation in order to measure isotopes with different half-lives. Corrections are made for overlapping lines in the spectrum and concentrations are determined by comparison with the standards analysed at the same time. The method is particularly sensitive for the rare earth elements, the platinum group elements and a number of high field strength elements.

When elemental concentrations are below about 2 ppm, a chemical separation may be employed following the irradiation of the sample, but prior to counting. This approach, known as radiochemical neutron activation analysis (RNAA), clearly has the advantage of increased sensitivity.

1.4.3 Inductively coupled plasma emission spectrometry (ICP)

Inductively coupled plasma (ICP) emission spectrometry is a comparatively new technique with enormous potential in geochemistry. In principle the method is capable of measuring most elements in the periodic table with low detection limits and good precision over several orders of magnitude. Elements are measured simultaneously and a complete analysis can be made in the space of about two minutes, making it an extremely rapid analytical method. A full description of the method and its application is given by Walsh and Howie (1980) and Thompson and Walsh (1983).

ICP emission spectrometry is a 'flame' technique with a flame temperature in the range 6000–10 000 K. It is also a solution technique and standard silicate dissolution methods are employed. The sample solution is passed as an aerosol from a nebulizer into an argon plasma. The inductively coupled plasma is a stream of argon atoms, heated by the inductive heating of a radio-frequency coil and ignited by a high-frequency Tesla spark. The sample dissociates in the argon plasma and a large number of atomic and ionic spectral lines are excited. The spectral lines are detected by a range of photomultipliers, they are compared with calibration lines, and their intensities are converted into concentrations.

1.4.4 Atomic absorption spectrophotometry (AAS)

Atomic absorption spectrophotometry is based upon the observation that atoms of an element can absorb electromagnetic radiation. This occurs when the element is atomized and the wavelength of light absorbed is specific to each element. Thus the atomic absorption spectrophotometer comprises an atomizing device, a light source and a detector. A lowering of response in the detector during the atomization of a sample in a beam of light, as a consequence of atomic absorption, can be calibrated and is sensitive at the ppm level. The sample is prepared in solution and aspirated via a nebulizer and atomized in an acetylene–air or acetylene–nitrous oxide flame. The method is described in detail by Price (1972). There are two limitations to the routine use of AAS in silicate analysis. Firstly, the sample must be prepared as a solution, and secondly it is element-specific, i.e. only one element can usually be analysed at a time, although this latter limitation has in part been overcome by fitting instruments with multiple-turret lamp holders.

Table 1.5 lists the elements which can be determined by AAS with relative ease. It can be seen, for instance, that all the major elements, with the exception of P, can be measured and detection limits for Na, K, Mg and Ca are extremely low. There are methods in which all the major elements may be determined from one solution, although the cathode lamp has to be changed for each element. The trace elements Ba, Be, Co, Cr, Cu, Li, Ni, Pb, Rb, Sr, V and Zn are also readily determined.

AAS cannot compete with more rapid methods of silicate analysis such as XRF and ICP. Nevertheless, because AAS is comparatively cheap both in the capital outlay and in running costs, it most frequently finds its use in one of three specific applications.

(1) The determination of light elements such as Be and Li, with atomic numbers too low to be measured by XRF.

(2) Routine analysis of transition metals readily leached from soil or stream sediment. This application is commonly used in geochemical exploration.

(3) Non-routine trace element analysis using specialized applications of AAS in which, for example, the sample is atomized in a graphite furnace. This allows exceptionally low detection limits to be achieved for elements difficult to measure using other analytical techniques.

1.4.5 Mass spectrometry

Mass spectrometry in its various forms is the most effective method of measuring isotope ratios. It is normally preceded by the chemical separation of the element of interest. Charged ions are generated from the element to be analysed either by the bombardment of a gaseous sample with electrons (gas source) or by the volatilization of the sample on a glowing filament made of a high-melting-point metal (solid source). The ion beam is fired along a curved tube through a very powerful electromagnet which splits up the atoms according to their mass. A mass spectrum is produced in which the lighter ions are deflected with a smaller radius of curvature than heavy ions. The quantitative detection of the signal at two or more mass numbers allows an isotope ratio to be calculated. Gas source mass spectrometry is used in stable isotope studies and in argon isotope geology, whereas solid source mass spectrometry is used in other geochronological and isotope geology applications (Rb–Sr, Pb–Pb, U–Pb and Sm–Nd) and in trace element analysis by isotope dilution.

Isotope dilution mass spectrometry (IDMS)

Isotope dilution mass spectrometry is the most accurate and most sensitive of all trace element analytical techniques and is particularly suited to measuring very low concentrations. The method is described in some detail by Henderson and Pankhurst (1984) and depends upon the addition of an isotopic tracer or 'spike' to the sample. The spike contains a known concentration of a particular element whose isotopic composition is also known. If a known amount of spike and a known amount of sample are mixed, and the isotope ratio of the mixture determined, the concentration of the element in the sample can be calculated.

The method is particularly useful in determining the abundances of REE at low concentrations, although four of the REE (Pr, Tb, Ho and Tm) are mono-isotopic and cannot be analysed by this method. The main disadvantage is that even with automated mass spectrometry the method is time-consuming and expensive and so is normally reserved for measurements which can be used to calibrate other more rapid methods.

Inductively coupled plasma emission mass spectrometry (ICP–MS)

ICP–MS is a relatively new technique extending from the development of inductively coupled plasma emission spectrometry (Date and Jarvis, 1989). It is becoming increasingly accepted as a tool for trace element and isotopic analysis as a result of the very low detection limits and good accuracy and precision. It can be used for analysing a wide range of trace elements, in a single solution, using a small sample (Jenner *et al.*, 1990). Ions are extracted from the plasma through a pinhole-sized orifice into a pumped vacuum system and focused with an ion lens into a mass spectrometer.

Spark source mass spectrometry (SSMS)

This is a less widely used analytical method in geochemistry but has been used in the analysis of trace elements. The method is described by Taylor and Gorton (1977) and its usefulness was debated by Kronberg *et al.* (1988) and Jochum and Hofman (1989). It is capable of the simultaneous determination of about 40 trace elements, has high sensitivity with detection limits of 1–10 ppb, requires small amounts of sample and has high precision and accuracy when the isotope dilution technique is used (± 2–5 %). The sample is mixed with spiked graphite and briquetted into rod-shaped electrodes. A vacuum discharge is generated between the two sample electrodes. Elements are detected by mass on photoplates situated in the focal plane of the mass spectrometer. The mass spectra are analysed and ion intensities determined from line blackenings on the photoplate.

Elements readily analysed by XRF, INAA, IDMS, AAS, ICP and ICP–MS

Atomic Symbol Element No.	XRF	INAA	IDMS	AAS	ICP	ICP–MS
1 H Hydrogen						
2 He Helium						
3 Li Lithium				x	x	x
4 Be Beryllium				x		
5 B Boron						x
6 C Carbon						
7 N Nitrogen						
8 O Oxygen						
9 F Fluorine						
10 Ne Neon						
11 Na Sodium	x			x	x	
12 Mg Magnesium	x			x	x	
13 Al Aluminium	x			x	x	
14 Si Silicon	x			x	x	
15 P Phosphorus	x				x	
16 S Sulphur	x					
17 Cl Chlorine	x					
18 Ar Argon						
19 K Potassium	x			x	x	
20 Ca Calcium	x			x	x	
21 Sc Scandium	x	x			x	x
22 Ti Titanium	x			x	x	
23 V Vanadium	x			x	x	
24 Cr Chromium	x	x		x	x	
25 Mn Manganese	x			x	x	
26 Fe Iron	x			x	x	
27 Co Cobalt	x	x		x	x	
28 Ni Nickel	x	x		x	x	
29 Cu Copper	x			x	x	
30 Zn Zinc	x			x	x	
31 Ga Gallium	x					
32 Ge Germanium	x					
33 As Arsenic	x					
34 Se Selenium						
35 Br Bromine						
36 Kr Krypton						
37 Rb Rubidium	x		x	x		x
38 Sr Strontium	x		x	x	x	x
39 Y Yttrium	x				x	x
40 Zr Zirconium	x				x	x
41 Nb Niobium	x				x	x
42 Mo Molybdenum						
43 Tc Technetium						
44 Ru Ruthenium		x				
45 Rh Rhodium						
46 Pd Palladium		x				
47 Ag Silver		x				
48 Cd Cadmium						
49 In Indium						
50 Sn Tin	x					
51 Sb Antimony						
52 Te Tellurium						
53 I Iodine						
54 Xe Xenon						

Table 1.5 Continued

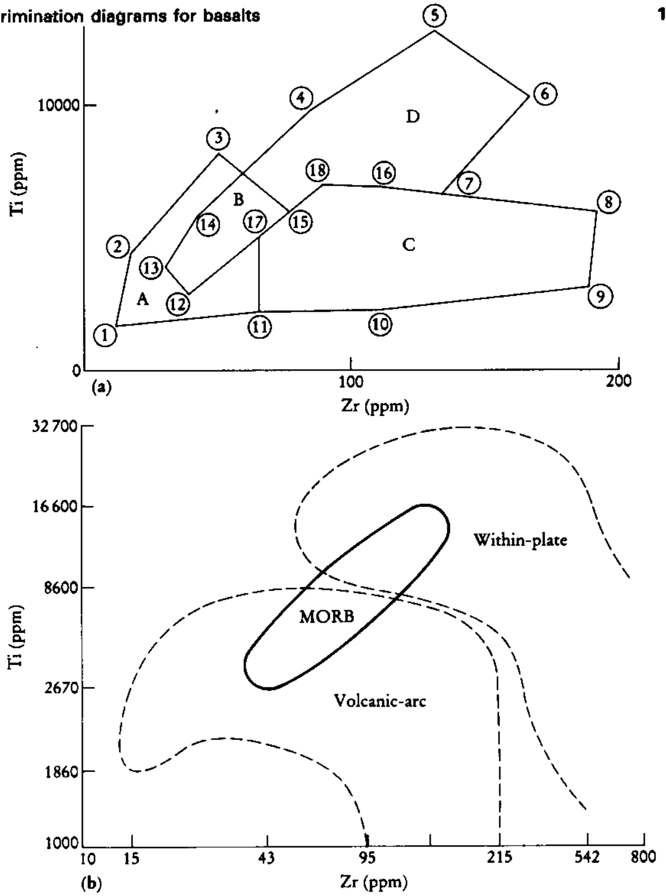
Atomic Symbol Element No.			XRF	INAA	IDMS	AAS	ICP	ICPMS
55	Cs	Caesium	x					x
56	Ba	Barium	x			x	x	x
57	La	Lanthanum	x	x	x		x	x
58	Ce	Cerium	x	x	x		x	x
59	Pr	Praseodymium					x	x
60	Nd	Neodymium	x	x	x		x	x
61	Pm	Promethium						
62	Sm	Samarium	x	x	x		x	x
63	Eu	Europium		x	x		x	x
64	Gd	Gadolinium		x	x		x	x
65	Tb	Terbium		x				x
66	Dy	Dysprosium		x	x		x	x
67	Ho	Holmium					x	x
68	Er	Erbium			x		x	x
69	Tm	Thulium		x				x
70	Yb	Ytterbium		x	x		x	x
71	Lu	Lutetium		x	x		x	x
72	Hf	Hafnium		x				x
73	Ta	Tantalum		x				x
74	W	Tungsten						
75	Re	Rhenium		x				
76	Os	Osmium		x				x
77	Ir	Iridium		x				
78	Pt	Platinum		x				
79	Au	Gold		x				
80	Hg	Mercury						
81	Tl	Thallium						
82	Pb	Lead	x		x	x		x
83	Bi	Bismuth						
84	Po	Polonium						
85	At	Astatine						
86	Rn	Radon						
87	Fr	Francium						
88	Ra	Radium						
89	Ac	Actinium						
90	Th	Thorium	x	x	x			x
91	Pa	Proactinium						
92	U	Uranium	x	x	x			x

Table 13.1. Average Chemical and Normative Composition of N-MORB and Trace Elements (ppm) for N-MORB and E-MORB

	N-MORB		N-MORB
SiO_2	49.93	*Or*	1.00
TiO_2	1.51	*Ab*	22.06
Al_2O_3	15.90	*An*	31.14
FeO	10.43	*Di*	21.04
MnO	0.17	*Hy*	15.55
MgO	7.56	*Ol*	2.47
CaO	11.62	*Mt*	3.89
Na_2O	2.61	*Il*	2.87
K_2O	0.17	*Ap*	0.19
P_2O_5	0.08		

	N-MORB	E-MORB
Cs	0.007	0.063
Rb	0.56	5.04
Ba	6.3	57
Th	0.12	0.6
U	0.47	0.18
Nb	2.33	8.3
Ta	0.132	0.47
La	2.5	6.3
Ce	7.5	15
Sr	90	155
Nd	7.3	9
Sm	2.63	2.6
Zr	74	73
Eu	1.02	0.91
Gd	3.68	2.97
Dy	4.55	3.55
Y	28	22
Yb	3.05	2.37
Lu	0.455	0.354

Top, major oxides from McKenzie and O'Nions (1991); bottom, data from Sun and McDonough (1989).



igure 5.2 Discrimination diagrams for basalts based upon Ti–Zr variations. (a) Linear scale (after Pearce and Cann, 1973); the fields are as follows: A, island-arc tholeiites; B, MORB, calc–alkali basalts and island-arc tholeiites; C, calc–alkali basalt; D, MORB. The plotting coordinates (extracted from Pearce and Cann, 1973 — Figure 2) are as follows:

Point	Zr	Ti	Point	Zr	Ti
1	12	1 700	10	113	2 400
2	18	4 600	11	65	2 400
3	52	8 500	12	39	3 100
4	84	10 400	13	31	4 100
5	131	13 000	14	42	6 000
6	167	10 900	15	78	6 400
7	135	7 100	16	113	7 400
8	192	6 600	17	65	5 400
9	190	3 400	18	89	7 400

(b) Log scale (after Pearce, 1982) showing the fields of volcanic-arc basalts, MORB and within-plate basalts. The values given on the ordinate and abscissa can be used as a guide in drawing the field boundaries (data extracted from Pearce, 1982).

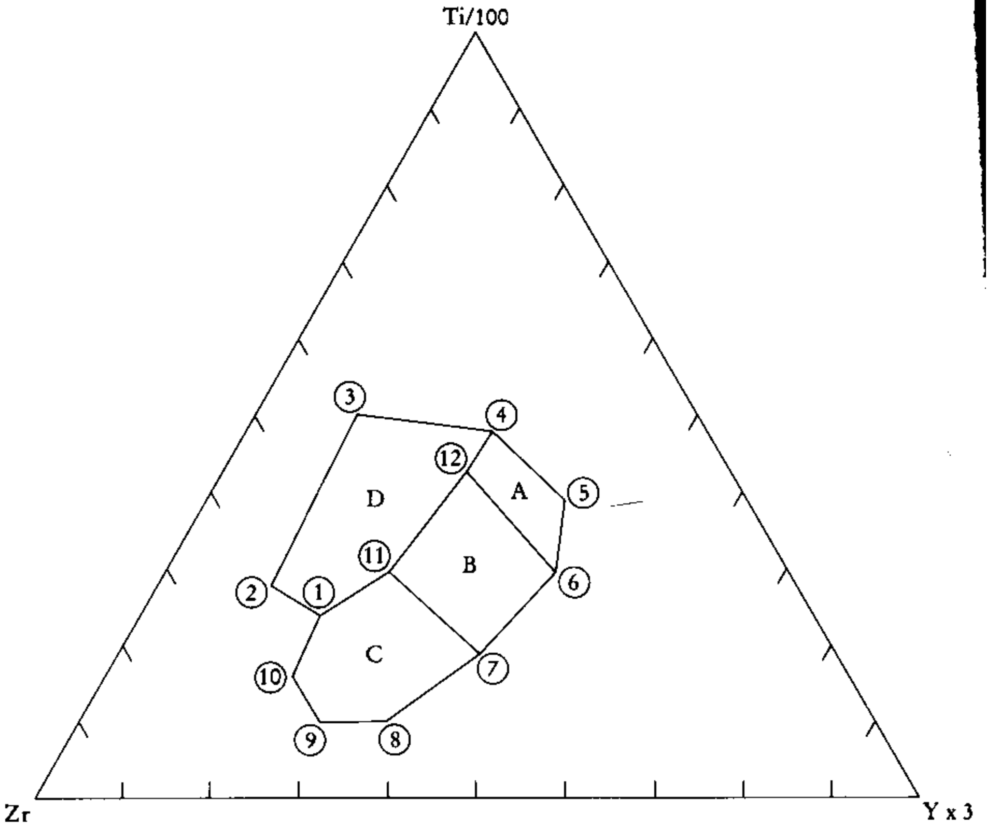
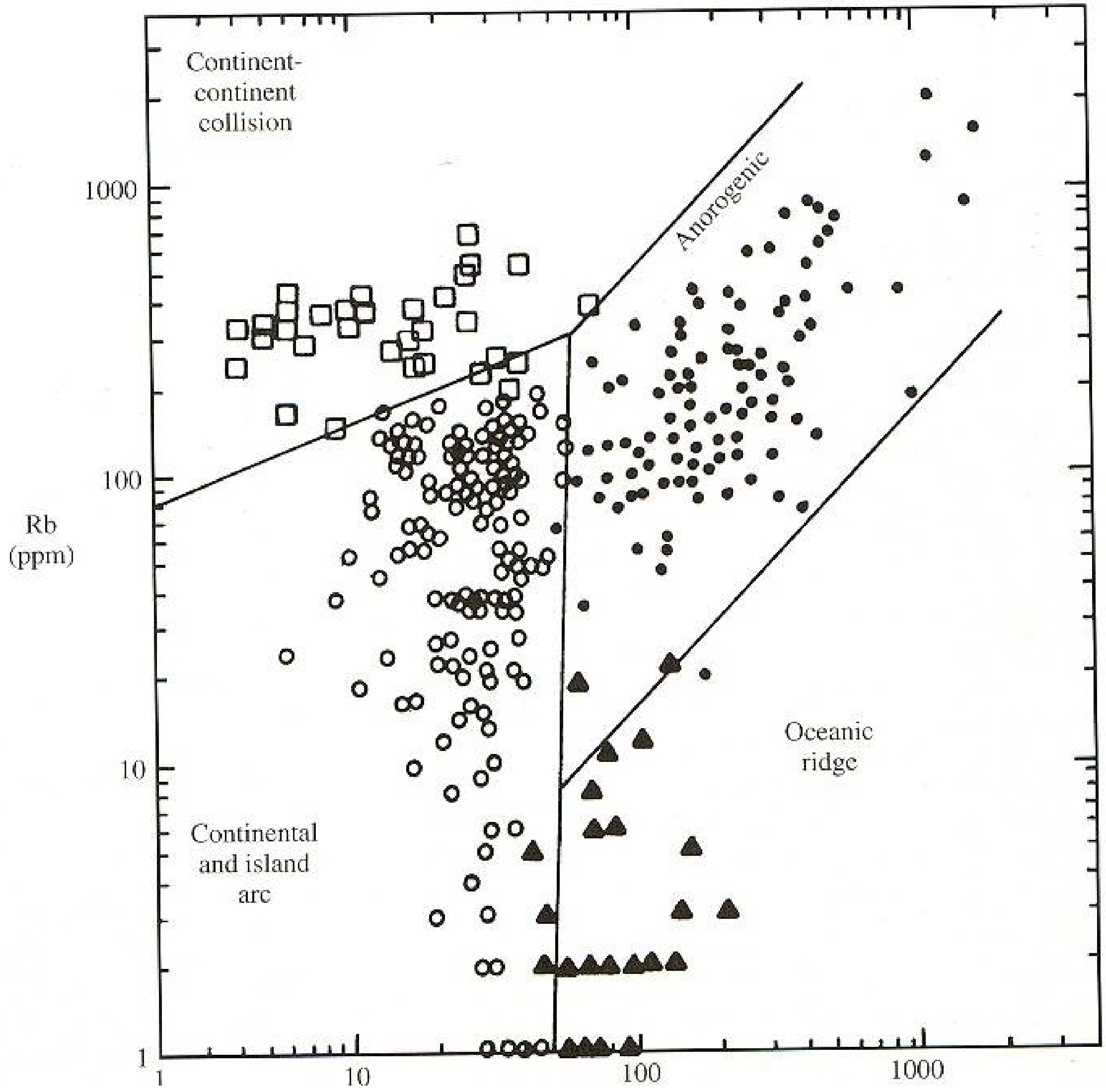


Figure 5.1 The Ti–Zr–Y discrimination diagram for basalts (after Pearce and Cann, 1973). A is the field of island-arc tholeiites, C the field of calc–alkali basalts, D is the field of within-plate basalts and B is the field of MORB, island-arc tholeiites and calc–alkali basalts. Rocks which plot in field B give an ambiguous result but can be separated by plotting on a Ti–Zr diagram (Figure 5.2) or if unaltered on a Ti–Zr–Sr diagram (Figure 5.3). The plotting coordinates, extracted from Pearce and Cann (1973 — Figure 3) are:

Point	Ti/100	Zr	Y × 3	Point	Ti/100	Zr	Y × 3
1	24	55.5	20.5	7	19	40	41
2	28	59	13	8	10	55	35
3	50	38.5	11.5	9	10	62.5	27.5
4	48	24	28	10	16	63	21
5	39	20.5	40.5	11	29.5	45	25.5
6	30	26	44	12	42.5	30	37.5


Continent-
continent
collision
Anorogenic
Oceanic
ridge
Continental
and island
arc
Rb
(ppm)
1000
100
10
1
1
10
100
1000

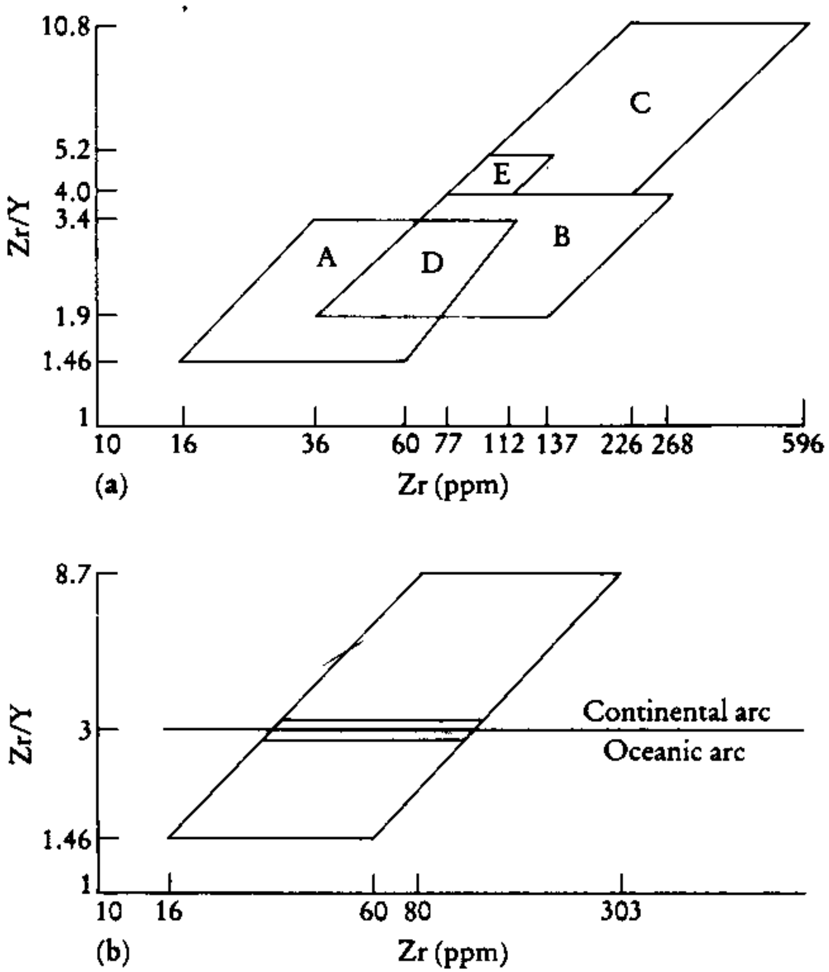


Figure 5.5 Discrimination diagrams for basalts based upon Zr/Y–Zr variations; both diagrams have a logarithmic scale. (a) The fields are A, volcanic-arc basalts; B, MORB; C, within-plate basalts; D, MORB and volcanic-arc basalts; E, MORB and within-plate basalts (after Pearce and Norry, 1979). The values along the ordinate and abscissa are on a logarithmic scale and are given to assist in constructing the field boundaries (data extracted from Pearce and Norry, 1979 — Figure 3). (b) Fields of continental and oceanic-arc basalts separated on the basis of a Zr/Y value of 3. The shaded area is the field of overlap between the two basalt types (after Pearce, 1983).

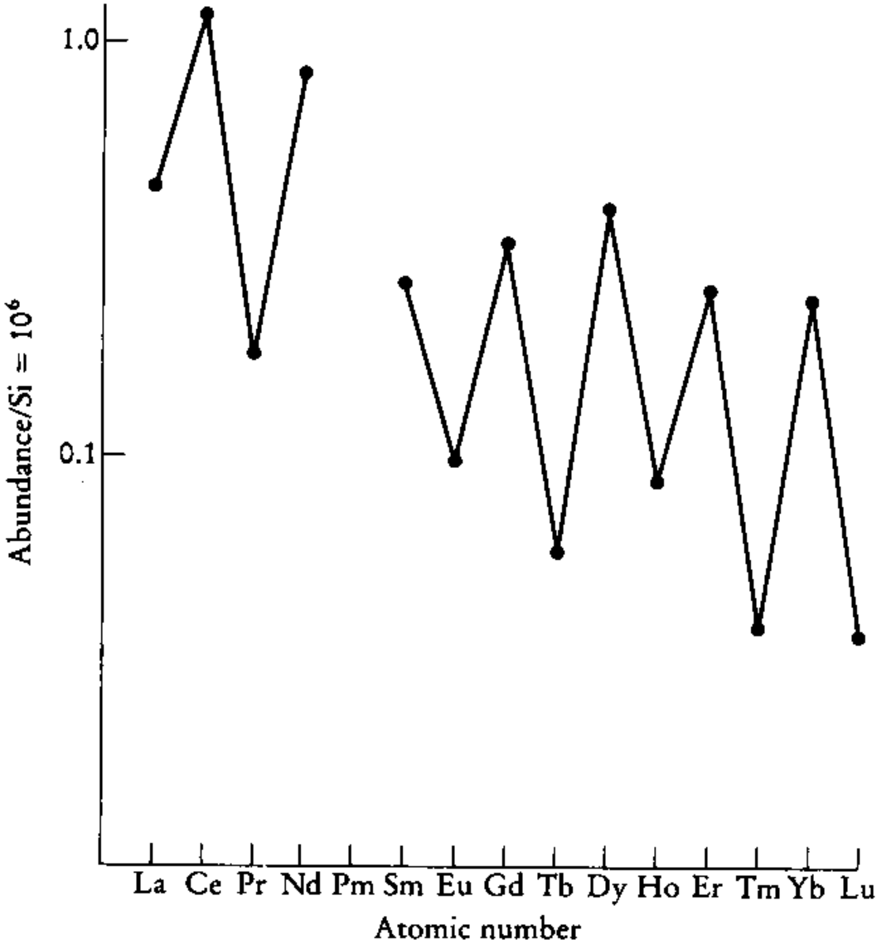


Figure 4.19 Rare earth element abundances (log scale) in the solar system plotted against atomic number. Data from Anders and Ebihara (1982), normalized to Si = 10^6 atoms. Elements with even atomic numbers have higher abundances than those with odd atomic numbers.

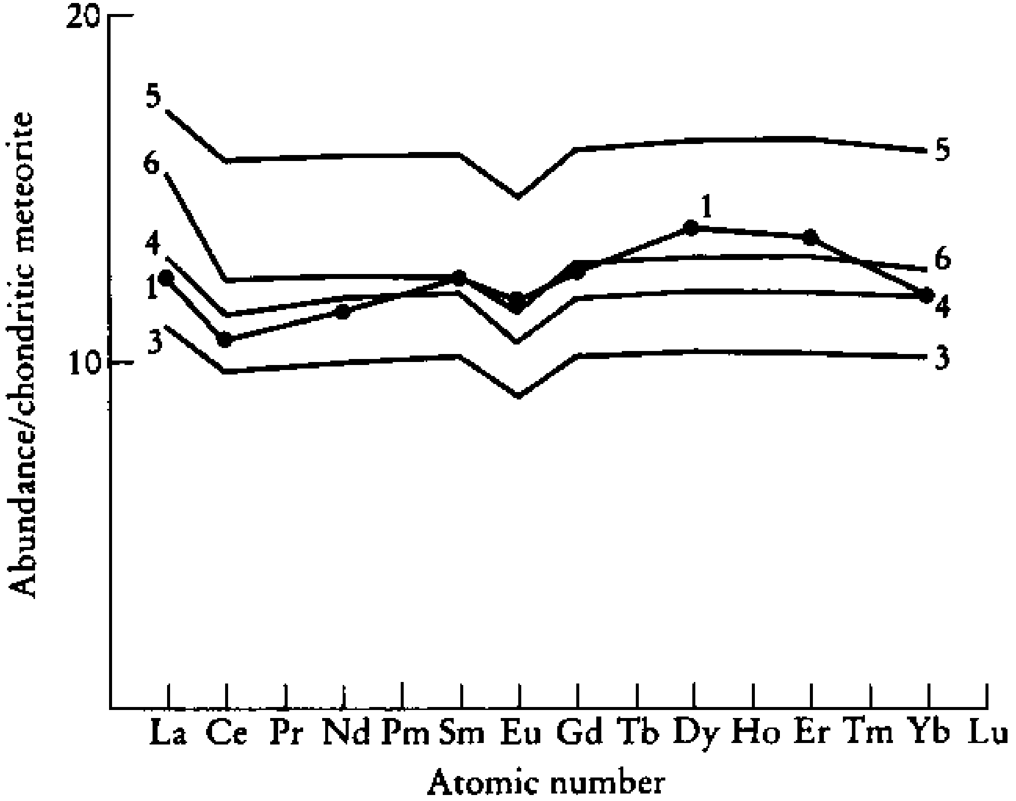


Figure 4.20 Rare earth element abundances normalized to chondritic meteorite values plotted agai atomic number for an Archaean tholeiitic basalt (sample 11 — Rollinson, 1983). The sam sample has been normalized using five different sets of values; the numbers refer to th columns of normalizing values listed in Table 4.5.

Table 4.5 Chondrite values used in normalizing REE (concentrations in ppm)

	Wakita	Haskin	Masuda	Nakamura	Evensen	Boynton	T & M	Primitive mantle value
Analytical method	NAA	NAA	IDMS	IDMS	IDMS	IDMS	IDMS	
Chondrite(s) analysed: (Ref.)	Composite (1)	Composite (2)	Leedey (3)	Composite (4)	Avg.CI (5)	Avg.CI (6)	Avg. CI (7)	(8)
La	0.340	0.330	0.3780	0.3290	0.244 60	0.3100	0.3670	0.7080
Ce	0.910	0.880	0.9760	0.8650	0.637 90	0.8080	0.9570	1.8330
Pr	0.121	0.112			0.096 37	0.1220	0.1370	0.2780
Nd	0.640	0.600	0.7160	0.6300	0.473 80	0.6000	0.7110	1.3660
Sm	0.195	0.181	0.2300	0.2030	0.154 00	0.1950	0.2310	0.4440
Eu	0.073	0.069	0.0866	0.0770	0.058 02	0.0735	0.0870	0.1680
Gd	0.260	0.249	0.3110	0.2760	0.204 30	0.2590	0.3060	0.5950
Tb	0.047	0.047			0.037 45	0.0474	0.0580	0.1080
Dy	0.300		0.3900	0.3430	0.254 10	0.3220	0.3810	0.7370
Ho	0.078	0.070			0.056 70	0.0718	0.0851	0.1630
Er	0.200	0.200	0.2550	0.2250	0.166 00	0.2100	0.2490	0.4790
Tm	0.032	0.030			0.025 61	0.0324	0.0356	0.0740
Yb	0.220	0.200	0.2490	0.2200	0.165 10	0.2090	0.2480	0.4800
Lu	0.034	0.034	0.0387	0.0339	0.025 39	0.0322	0.0381	0.0737
Y							2.1000	

(1) Wakita *et al.* (1971): composite of 12 chondrites.
(2) Haskin *et al.* (1968): composite of nine chondrites.
(3) Masuda *et al.* (1973): Leedey chondrite.
(4) Nakamura (1974).
(5) Evensen *et al.* (1978): average of C1 chondrites.
(6) Boynton (1984).
(7) Taylor and McLennan (1985): 1.5 x values of Evensen [column (5)].
(8) McDonough *et al.* (1991).