Table 11.7 Trace element composition of the oceanic crust (all concentrations in ppm).

	Bulk crust*	Ave. MORB*	Lower crust†
Li	3.52	6.63	
Be	0.31	0.64	
B	0.80	1.80	
K	651	1237	
Sc	36.2	37	37
V	177	299	209
Cr	317	331	308
Co	31.7	44	50
Ni	134	100	138
Cu	43.7	80.8	71
Zn	48.5	86.8	38
Rb	1.74	4.05	
Sr	103	138	115
Y	18.1	32.4	13.9
Zr	44.5	103	28.4
Nb	2.77	6.44	0.93
Cs	0.02	0.05	
Ba	19.4	43.4	
La	2.13	4.87	0.86
Ce	5.81	13.1	2.75
Pr	0.94	2.08	0.52
Nd	4.90	10.4	2.78
Sm	1.70	3.37	1.1
Eu	0.62	1.20	0.58
Gd	2.25	4.42	1.6
Tb	0.43	0.81	0.31
Dy	2.84	5.28	2.09
Ho	0.63	1.14	0.46
Er	1.85	3.30	1.34
Tm	0.28	0.49	
Yb	1.85	3.17	1.27
Lu	0.28	0.48	0.19
Hf	1.21	2.62	
Ta	0.18	0.417	
Pb	0.47	0.657	
Th	0.21	0.491	
U	0.07	0.157	

*From White and Klein (2013)
†From Coogan (2012).

the oceanic crust was determined by using the MELTS program (Ghiorso and Sack, 1995; see Chapter 4) to determine which minerals would crystallize from average MORB and then adjusting the composition by adding these back. This was continued until olivine of 90% forsterite was in equilibrium with the melt composition. Trace elements are then computed for this parental composition using the fractional crystallization equations in Chapter 7.

The composition of MORB is remarkably uniform throughout the ocean basins and in this respect is unique among igneous rocks. Nevertheless, some systematic regional variations have been identified. Some of this can be related to fractional crystallization. The amount of fractional crystallization is generally greater at fast-spreading ridges. Sinton and Detrick (1992) found that the mean Mg# decreased from 57.1 for basalts erupted along ridges with full spreading rates less than 5 cm/yr, to 52.8 for basalts erupted on fast-spreading ridges (>8 cm/yr). Rubin and Sinton (2007), using a much more extensive data-set, demonstrated a more or less linear decrease in Mg# with spreading rate through the entire range. They found that lavas at the slowest-spreading ridges erupt roughly 20°C hotter than at the fastest-spreading ones. The greater extent of crystallization and lower eruption temperatures at fast-spreading ridges is likely a direct consequence of the crystallization occurring primarily at shallower depths at fast-spreading ridges.

The other factors that control the major element composition of MORB are the degree and depth of melting, which are in turn controlled by mantle temperature. The 1987 study of Klein and Langmuir elucidated how these factors affect both the thickness and composition of oceanic crust. However, to assess mantle temperature requires first correcting for the effects of fractional crystallization. Klein and Langmuir (1987) found that basalts in each region they consider formed coherent trends in plots of oxides versus MgO concentrations (Figure 11.24). Klein and Langmuir assumed these trends represented liquid line of descents produced by fractional crystallization within crustal magma chambers. To compare compositions from different regions, they defined the parameter $Na_{8.0}$ as the value of Na_2O where the trends crossed 8 wt. % MgO (Figure 11.24). $Fe_{8.0}$ was defined in a similar way.
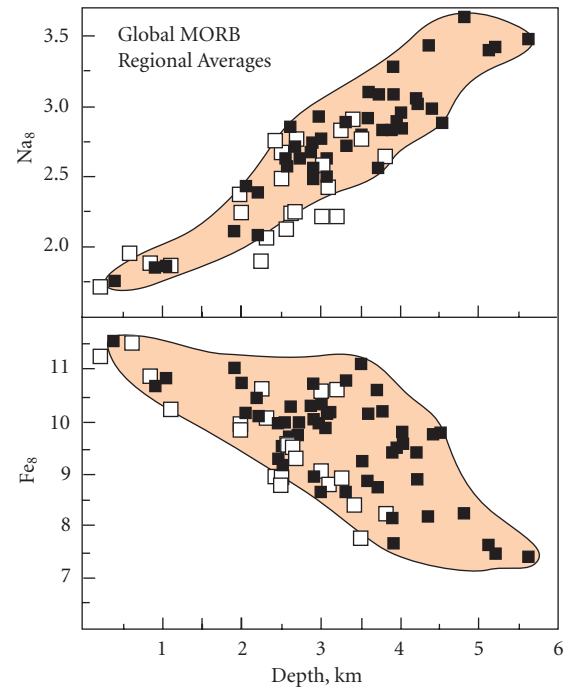
Corrected for fractional crystallization in this way, major elements correlate in revealing and predictable ways. Most significantly, regions with low mean $Na_{8.0}$ are also characterized by high mean $Fe_{8.0}$. Furthermore, these major element variations correlate with physical characteristics of the ridge axis from which
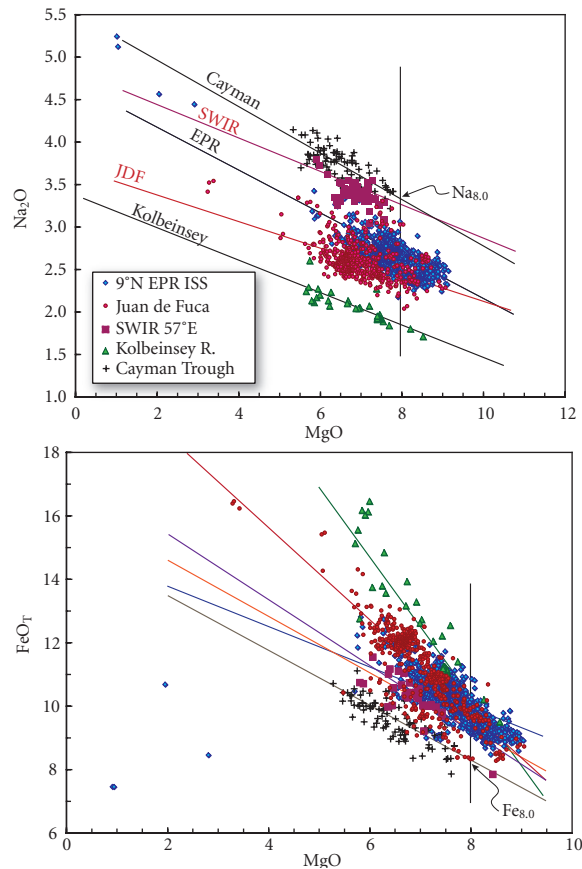
Figure 11.24 Na$_2$O and FeO vs. MgO in MORB from various regions of the mid-ocean ridge system plot along liquid lines of descent of varying slopes. Fe$_{8.0}$ and Na$_{8.0}$ are the value of Na$_2$O and FeO, respectively, of the lines at 8.0% MgO. EPR, Integrated Study Site (ISS) at 9°N on the East Pacific Rise; JDF, Juan de Fuca Ridge; SWIR, Southwest Indian Ridge; Kolbeinsey Ridge is north of Iceland, and the Cayman Trough is a small spreading center in the Caribbean. White and Klein (2013). With permission from Elsevier.

Figure 11.25 Regional average Fe$_{8.0}$ and Na$_{8.0}$ versus axial depth in the mid-ocean ridge system. Solid squares are MORB from "normal" ridge segments; open squares are from ridges influenced by the Galapagos, Azores, Jan Mayen, Tristan, Iceland, and Bouvet hotspots. The shaded field encompasses normal ridge basalts. After Klein and Langmuir (1987) and White and Klein (2013).

they were recovered. Regional averages of Na$_{8.0}$ and Fe$_{8.0}$, for example, showed a positive and an inverse correlation, respectively, with the average ridge depth from which the lavas were recovered (Figure 11.25). Na$_{8.0}$ correlated inversely with seismically and geologically determined estimates of the crust thickness in each region.
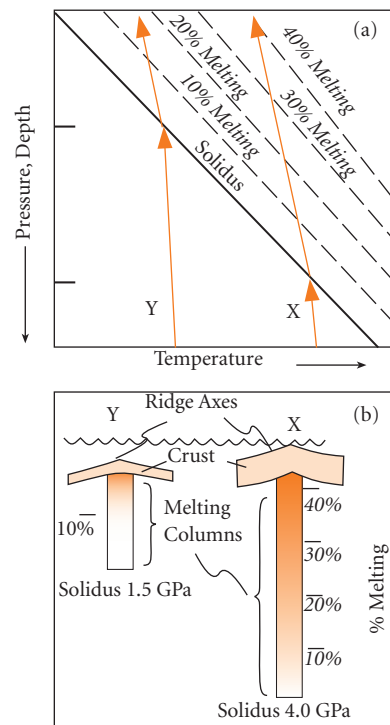
These relationships can be understood as the interplay between the extent of melting and the pressure of melting. Sodium is mod-

erately incompatible during melting of mantle minerals (D~0.02–0.03), and therefore will be concentrated in the melt at small extents of melting. Iron, on the other hand, varies in the melt as a function of the pressure of melting (Figure 11.26). Thus, the inverse correlation between mean Na$_{8.0}$ and mean Fe$_{8.0}$ suggests that there is a positive correlation between the mean extent of melting and the mean pressure of melting.

Klein and Langmuir concluded mantle temperature was the key factor in accounting for both depth of the ridge axis and the composition of melts erupted, because mantle temperature affects both degree of melting and the mean depth of melting. Shallow segments of the mid-ocean ridge system overlie relatively hot mantle. The hot mantle intersects the solidus at greater depth and ultimately
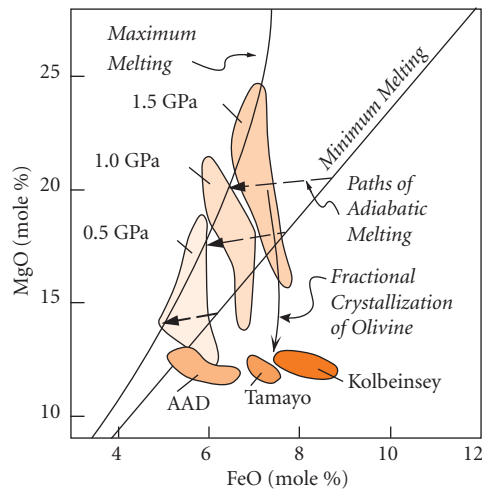
Figure 11.26 Variation of MgO and FeO in partial melts of mantle peridotite. Grayed fields show the compositions of experimentally produced partial melts of peridotite at three different pressures. Colored fields show compositions of high MgO basalts from the Australian–Antarctic Discordance (AAD), the Tamayo Fracture Zone of the East Pacific Rise, and Kolbeinsey regions. Dashed arrows show the path of melt composition produced by melting of adiabatically rising mantle. The curved arrow shows how the composition of a 1.5 GPa melt will evolve due to fractional crystallization of olivine. Klein and Langmuir (1987). Reproduced with permission of the American Geophysical Union.

Figure 11.27 (a) Pressure–temperature relationship of adiabatically rising mantle undergoing melting. Hotter mantle (X) intersects the solidus at higher pressure and ultimately melts to a higher degree than cooler mantle (Y). The break in slope occurs because energy is consumed by melting (enthalpy of fusion). (b) Relationship between axial depth, crustal thickness, melting, and mantle temperature. Hotter mantle (X) maintains the ridge at higher elevation because of its buoyancy. It also has a deeper melt column and melts to a greater degree, producing thicker crust than cooler mantle (Klein and Langmuir, 1987). Reproduced with permission of the American Geophysical Union.

melts to a greater degree (Figure 11.27). Hotter mantle is less dense and therefore more buoyant, so that ridges overlying hotter mantle will be more elevated. Cooler mantle will not begin to melt until it reaches shallower depths, and the total extent of melting will be more limited. Klein and Langmuir concluded that a range in degree of melting of 8–20% and in mean pressure of melting of 0.5 to 1.6 GPa were required to produce the range in compositions observed. The hottest regions of the mantle occur near mantle plumes such as Iceland. Some of the coolest mantle is found at the Australian-Antarctic Discordance, a region where the ridge is particularly deep and isotope studies have suggested is a boundary between mantle convection cells. Overall, the data suggest a range in mantle temperature of some 250°C.

11.6.2 The continental crust

The continental crust is the part of the Earth that is most readily sampled and the part with which we are most familiar. It is, however, very likely the most variable part of the Earth in every respect, including compositionally. It is the part of the Earth where geology reveals the planet's history. In this respect, the continents are arguably the most interesting part of the planet. We'll first consider the composition of the continental crust, then we'll see

what geochemistry can reveal about its creation and evolution.

The continental crust is extremely heterogeneous, thus the task of estimating its overall composition is a difficult one. Furthermore, only the upper part of the continental crust is exposed to direct sampling: the deepest scientific borehole, drilled by the Russians in the Kola Peninsula, reached only 12 km. The average thickness of the continental crust is about 35 km so we have been able to directly sample only the upper third. Fortunately, however, tectonic and volcanic processes sometimes bring bits of the deep crust to the surface where it can be studied. Nevertheless, geochemists must rely heavily on inferences made from indirect observations to estimate the composition of the continental crust. Beginning with Clarke* (1924) and Goldschmidt (1933), a number of such estimates of the composition of the continental crust have been made. These have become increasingly sophisticated with time. Among the most widely cited works are those of Taylor and McLennan (1985, 1995), Weaver and Tarney (1984), Wedepohl (1995) and Rudnick and Fountain (1995). These estimates are not entirely independent. For example, Weaver and Tarney (1984) and Rudnick and Fountain (1995) both rely in part on versions of Taylor and McLennan's studies. Taylor and McLennan in turn rely on the work of Shaw (1967) for many elements, as does Wedepohl (1995). In the following, we will focus particularly on the estimates of Taylor and McLennan (1985, 1995), and Wedepohl (1995), and the recent work of Rudnick and Gao (2003).

We can divide the problem of estimating crustal composition into two parts. The first is to estimate the composition of the upper, accessible parts of the crust. This is referred to as the "upper crust". Direct observations provide the most important constraints on the composition of this part of the crust. The second problem is the composition of the deeper, less accessible part of the crust. For this part of the crust, indirect observations, particularly geophysical ones such as seismic velocity and heat flow, provide key constraints on composition. As we shall see, these observations indicate that the continental crust is compositionally stratified, with the lower part being distinctly more mafic – richer in Mg and Fe and poorer in SiO_2 and incompatible elements. Some workers divide the deep crust into a middle and lower crust, while others consider only a single entity that they refer to as the lower crust. The chemical contrasts between the upper and deep crust are much stronger in continents than in the ocean. We should emphasize, however, that any division of the continental crust into layers is done for convenience and is somewhat arbitrary. The continental crust does not appear to have a systematic layered structure that directly results from its creation in the way that the oceanic crust does. Instead, chemical zonation in the continents has evolved over time through a variety of processes.

11.6.2.1 Composition of the upper continental crust

Historically, two approaches to estimating the composition of the upper continental crust have been used. The first approach, pioneered by F.W. Clarke in 1889, is to average analyses of samples taken over a large area. An alternative is to mix sample powders to form *composites* of various rock types and thus reduce the number of analyses to be made (e.g., Shaw *et al.*, 1986; Wedepohl, 1995; Borodin, 1998; Gao *et al.*, 1988). Studies of these kinds consistently produce an average upper crustal composition similar to that of granodiorite, with the concentrations of major oxides agreeing within 20% and most within 10% (Figure 11.28). This is encouraging since

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* Frank Wigglesworth Clarke (1847–1931) shares the title of "father of geochemistry" with Victor Goldschmidt. After receiving his Bachelor of Science degree from Harvard, Clarke taught at Cornell University, Howard University, and the University of Cincinnati before joining the US Geological Survey in 1883 as Chief Chemist. His work *The Data of Geochemistry*, the first edition of which was published as USGS Bulletin 330 in 1908, was the first attempt to determine the composition of the continental crust. In addition to his work in geochemistry, Clarke had strong interests in mineralogy (he was honorary curator of minerals at the Smithsonian Institution), education, and the value of physical standards. He was a founder of the American Chemical Society and served as its president in 1901. The Geochemical Society awards the F.W. Clarke medal to an early-career scientist for an outstanding single contribution.
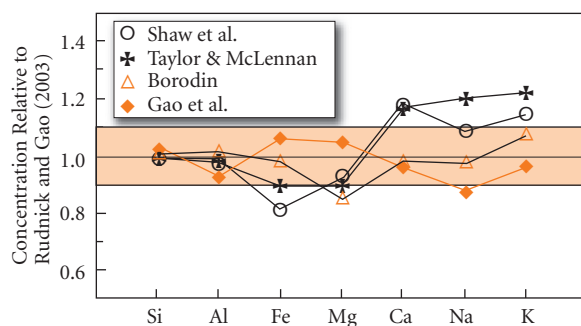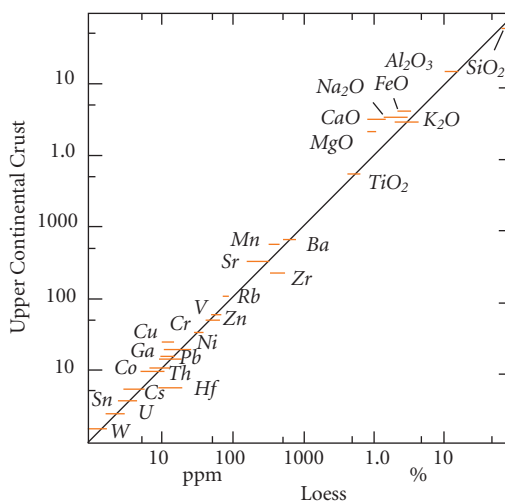
Figure 11.28   Estimates of major element concentrations in the upper continental crust by studies mentioned in the text, derived from analysis of crustal composites, compared with the estimated upper crustal composition of Rudnick and Gao (2003). Rudnick and Gao (2003), Figure 2. With permission from Elsevier.

Figure 11.29   Comparison of elemental concentrations in loess with estimated upper crust. Taylor and McLennan (1985). With permission from John Wiley & Sons.

granodiorite is the most common igneous rock in the crust. Such estimates also tend to produce relatively similar average concentrations for minor and trace elements. Most modern estimates of upper crustal major element and soluble trace element concentrations are based on this approach.

The second method is to let the Earth make the composites for us. A couple of kinds of such materials are available. Goldschmidt (1933) suggested the use of glacial clays in meltwater lakes adjacent to the Pleistocene ice front. An alternative but similar approach is to use *loess*, which is fine-grained aeolian material of Pleistocene age. The most readily available of this kind of natural composite, however, is simply sediments. One advantage of sediments over glacial material is that whereas most glacial deposits are of Pleistocene age (but there are various glacial deposits of ages ranging up to 2.3 Ga), sediments of all ages are available so that secular variations in crustal composition can be determined.

The advantages of using geologic composites should be obvious, but there are disadvantages as well. The primary problem is that chemical fractionations are involved in producing sediments from their parents. Weathering of rock typically produces three fractions: sands consisting of resistant minerals, clays, and a solution. These products are transported with varying degrees of efficiency away from the site of production. Since elements tend to be concentrated in one of these three fractions, none of the fractions will have a composition representative of the parent rock. Because it is produced primarily by physical, rather than chemical, action, glacial loess is less susceptible to this kind of chemical fractionation, though some fractionation nevertheless occurs. For example, loess is enriched in SiO_2, Hf, and Zr (Figure 11.29) as a consequence of its enrichment in mechanically and chemically stable minerals, such as quartz and zircon. That in turn results from clays being carried further from their site of origin by wind and water. Loess is also depleted in Na, Mg, and Ca, reflecting loss by leaching.

Numerous studies have shown that when rock weathers to produce a sediment, the rare earth pattern of the parent is usually preserved in the sediment. This is because the rare earths are concentrated in the clay fraction, which ultimately forms shales. Other Group 3 elements (Sc and Y), as well as Th, behave similarly to the rare earths during weathering. Furthermore, rare earth patterns are remarkably similar in different shales, suggesting shales are indeed good averages of crustal composition. This is illustrated in Figure 11.30, which compares three shale composites from three continents. Because of these properties of the rare earths, S.R. Taylor
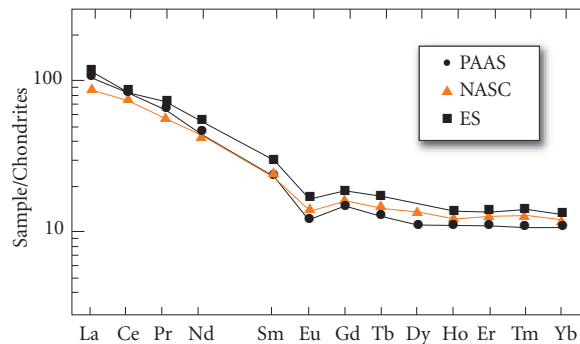
Figure 11.30 Rare earth patterns of Post-Archean Australian Shale (PAAS) composite, the North American Shale Composite (NASC) and the European Shale (EC) composite. Taylor and McLennan (1985). With permission from John Wiley & Sons.

and colleagues at the Australian National University used them as a point of departure for estimating the composition of the upper continental crust.

Most recent estimates of crustal composition are based on a combination of both approaches, together with assumptions about the ratios between elements. The most recent comprehensive study of crustal composition is that of Rudnick and Gao (2003). Their estimate of upper crustal composition is compared with earlier ones in Table 11.8. The estimates are broadly similar, and indicate an upper crust of "granodioritic" or "tonalitic" composition (although there are a few elements, such as Cu, where there is considerable disagreement). One should note, however, that Rudnick and Gao (2003) relied heavily on the work of Taylor and McLennan, and both Taylor and McLennan's and Wedepohl's estimates derive in part from the earlier work of Shaw *et al*. (1986).

11.6.2.2 Composition of the middle and lower continental crust

Rocks from the middle and lower crust, typically in *amphibolite* and *granulite* metamorphic facies, are sometimes exposed at the surface by tectonic processes and hence can provide insights into the nature of this part of crust. Amphibolites are, as their name implies, metamorphic rocks that are relatively rich in amphibole, a mineral that contains water in its structure, but less water than mica-bearing

rocks, such as granites and rocks metamorphosed at lower temperature. Granulites, on the other hand, are anhydrous, with pyroxene replacing amphibole and biotite. Middle crustal cross-sections of amphibolite- to granulite-facies rocks contain a wide variety of lithologies, including metasedimentary rocks, but they are dominated by igneous and metamorphic rocks of dioritic, granodioritic, and granitic composition.

However, these *granulite terranes* have often been subjected to retrograde metamorphism (metamorphism occurring while temperatures and pressure decrease), which compromises their value. Furthermore, questions have been raised as to how typical they are of lower continental crust. These questions arise because granulite terranes are generally significantly less mafic than xenoliths from the lower crust. Xenoliths perhaps provide a better direct sample of the lower crust, but they are rare. The point is, any estimate of the composition of the middle and lower crust will have to depend on indirect inference and geophysical constraints as well as analysis of middle and lower crustal samples. There are two principal geophysical constraints:

- Heat flow in the continental crust. A portion of the heat flowing out of the crust is produced by radioactive decay of K, U, and Th within the crust (other radioactive elements do not contribute significantly to heat generation because of their long half-lives and low abundances). The concentrations of these elements can be related to rock type, as indicated in Table 11.9.
- Seismic velocities in the continental crust. Seismic velocities depend upon density, compressibility and the shear modulus (eqns. 11.1 and 11.2), which can in turn be related to composition.

Both tell us something of first-order importance about the nature of the continental crust: it is vertically zoned, becoming more mafic (i.e., richer in Fe and Mg and poorer in Si and incompatible elements, including K, U, and Th) with depth. Let's consider them in greater detail.

The average heat flow of the continents is about $60\,mW/m^2$. This heat has two components: heat conducted out of the mantle, and

Table 11.8 Composition of the upper continental crust.

Oxide (wt %)	T & M	Wedepohl	R & G	Normative mineralogy (T & M)	
SiO_2	66.0	64.9	66.6	Quartz	15.7
TiO_2	0.5	0.52	0.64	Orthoclase	20.1
Al_2O_3	15.2	14.6	15.4	Albite	13.6
FeO	4.5	3.97	5.04	Diopside	6.1
MnO	0.07	0.07	0.10	Hypersthene	9.9
MgO	2.2	2.24	2.48	Ilmenite	0.95
CaO	4.2	4.12	3.59		
Na_2O	3.9	3.46	3.27		
K_2O	3.4	4.04	2.80		
P_2O_5	0.20	0.15	0.15		

	T & M	Wedepohl	R & G		T & M	Wedepohl	R & G
Li	20	22	21	Sb	0.2	0.31	0.4
Be	3	3.1	2.1	Te			
B	15	17	17	I		1.4	1.4
C		3240		Cs	3.7	5.8	4.1
N		83	83	Ba	550	668	624
F		611	557	La	30	32.3	31
S		953	621	Ce	64	65.7	63
Cl		640	370	Pr	7.1	6.3	7.1
Sc	11	7	14	Nd	26	25.9	27
Ti	3000	3117		Sm	4.5	4.7	4.7
V	60	53	97	Eu	0.88	0.95	1.0
Cr	35	35	92	Gd	3.8	2.8	4.0
Co	10	11.6	17	Tb	0.64	0.5	0.7
Ni	20	18.6	47	Dy	3.5	2.9	3.9
Cu	25	14.3	28	Ho	0.8	0.62	0.83
Zn	71	52	67	Er	2.3		2.3
Ga	17	14	17.5	Tm	0.33		0.30
Ge	1.6	1.4	1.4	Yb	2.2	1.5	2.0
As	1.5	2	4.8	Lu	0.32	0.27	0.31
Se	0.05	0.083	0.09	Hf	5.8	5.8	5.3
Br		1.6	1.6	Ta	2.2	1.5	0.9
Rb	112	110	82	W	2	1.4	2
Sr	350	316	320	Re ppb	0.4		0.20
Y	22	20.7	21	Os ppb	0.05		0.031
Zr	190	237	193	Ir ppb	0.02		0.022
Nb	25	26	12	Pt ppb			0.5
Mo	1.5	1.4	1.1	Au ppb	1.8		1.5
Ru ppb			0.34	Hg ppb		56	50
Pd ppb	0.5		0.52	Tl	0.75	0.75	0.9
Ag ppb	50	55	53	Pb	20	17	17
Cd ppb	98	102	90	Bi	127	123	0.16
In ppb	50	61	56	Th	10.7	10.3	10
Sn	5.5	2.5	2.1	U	2.8	2.5	2.6

Concentrations in ppm except where noted. T & M, Taylor and McLennan (1985, 1995); Wedepohl, Wedepohl (1995); R & G, Rudnick and Gao (2003).

Table 11.9   U, Th, and K concentrations and heat production in various rock types. From Pollack (1982). Reproduced with permission.

Igneous rock type	U (ppm)	Th (ppm)	K (%)	Th/U	K/U	Density g/cm^3	Heat production 10^{-6} W/m^{-3}
Granite/rhyolite	3.9	16.0	3.6	4.1	0.9×10^4	2.67	2.5
Granodiorite/dacite	2.3	9.0	2.6	3.9	1.1×10^4	2.72	1.5
Diorite/andesite	1.7	7.0	1.1	4.1	0.7×10^4	2.82	1.1
Gabbro/basalt	0.5	1.6	0.4	3.2	0.8×10^4	2.98	0.3
Peridotite	0.02	0.06	0.006	3.0	0.3×10^4	3.28	0.01
Continental crust	1.25	4.8	1.25	3.8	1.0×10^4	–	0.8

heat generated by radioactive decay within the continents. The concentrations of K, U, and Th observed at the surface of the crust would produce more heat than is observed to be leaving the continental crust, if these concentrations were uniform through the crust. Thus, the concentrations of these elements must decrease at depth. The problem is complicated, however, by variations in the "mantle" heat flow, which averages about 20 mW/m^2. Heat flow varies significantly with tectonic age. If, as we believe, the continental crust is created by magmatism, it will be initially hot and then cool over time. Subsequent episodes of magmatism may also heat the crust. In addition, variation in mantle heat flow can result from different thicknesses of the lithosphere (Vitorello and Pollack, 1980; Nyblade and Pollack, 1993). The lithosphere is a conductive boundary layer, so that the thicker the lithosphere, the lower the mantle heat flow out the top of it. Nyblade and Pollack (1993) have argued that regions of old Archean crust are underlain by particularly thick mantle lithosphere, an argument supported by geochronological and thermobarometric studies of mantle xenoliths from these regions. Despite these complexities, heat flow in the crust suggests the middle and lower crust contains significantly less K, U, and Th than the upper crust. This in turn suggests the deep continental crust is more mafic than the upper crust.

Seismic velocity profiles vary widely from place to place, as does crustal thickness, but in general p-wave velocities increase with depth in the crust from about 6 km/sec in the upper crust to about 7 km/sec in the lower crust. Rudnick and Fountain (1995) exam-

ined a global database of seismic cross-sections and found that they can be divided into nine classes, which are illustrated in Figure 11.31. One must next relate seismic velocity to composition by making measurements of seismic velocity in the laboratory on samples of known composition. For example, Figure 11.32 shows the relationship between SiO_2 and seismic velocity in a variety of rock types. Recalling that seismic wave speed is inversely related to density (eqns. 11.1 and 11.2), we might have expected mafic rocks, which are poorer in SiO_2 and richer in Mg and Fe and are denser (Table 11.9), to have slower seismic velocities. However, the lower compressibility of mafic rocks results in seismic waves traveling faster through them. Seismic velocities are thus consistent with the heat flow evidence that the middle and lower crust is more mafic than the upper crust.

To produce an estimate of crustal composition, Rudnick and Fountain assigned an average lithology to the seismic sections shown in Figure 11.31. They then assigned a composition to each lithology using a database of the composition of lower crustal xenoliths. Then by estimating the areal extent of each type of crustal section, and averaging analyses of middle and lower crustal rocks and xenoliths, they produced the compositional estimates. These estimates were subsequently updated by Rudnick and Gao (2003) and are listed Table 11.10. This table shows that the composition of the lower crust corresponds to that of tholeiitic basalt; in metamorphic terminology it would be a mafic granulite. The composition of the middle crust corresponds to that of an andesite. At the prevailing pressures and temperatures this
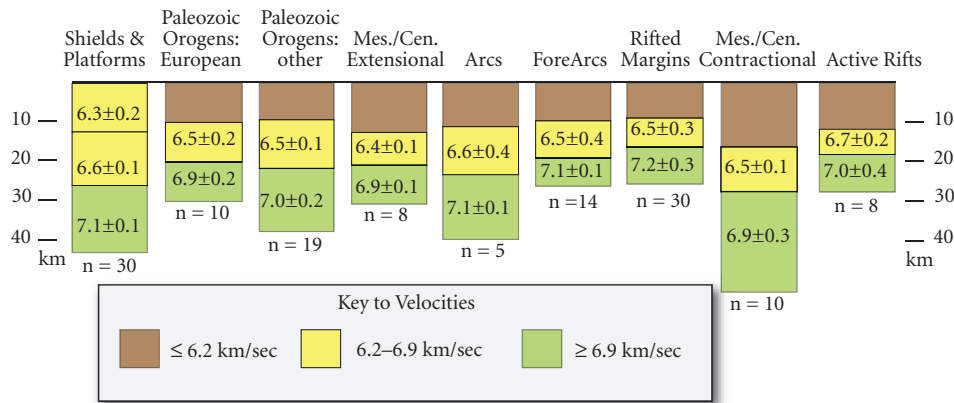
Figure 11.31   Seismic velocity structure of the continental crust, illustrating its three-layered nature. Velocity structure falls into nine types. The number of profiles used to construct each type is shown below each type. From Rudnick and Fountain (1995). Reproduced with permission of the American Geophysical Union.
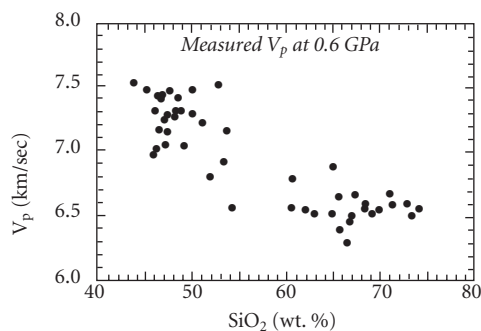
Figure 11.32   Correlation between measured seismic velocity (v_P) and SiO_2 concentration. From Rudnick and Fountain (1995). Reproduced with permission of the American Geophysical Union.

rock would be an amphibolite, consisting mainly of amphibole and plagioclase.

Wedepohl (1995) used the European Geotraverse as a model of the seismic structure of the crust. This seismic cross-section runs from northern Scandinavia to Tunisia and crosses a great variety of tectonic provinces, ranging from the Archean Fennoscandian Shield to the young fold belts to the young Alpine orogen. He assigned three lithologies to three ranges of seismic velocities: sediments, granites, and gneisses ($V_P < 6.5$ km/s) corresponding to the upper crust, felsic granulites ($6.5 < V_P < 6.9$ km/s), and mafic granulites ($6.9 < V_P < 7.5$ km/s). He

used a database of compositions of felsic and mafic granulites from both xenoliths and exposed terranes to calculate an average composition for each of the latter two. He then computed a lower crustal composition by weighting felsic and mafic granulites in the proportions that their characteristic seismic velocities were observed in the European Geotraverse. His estimate of the composition of the lower crust is also listed in Table 11.10.

Rare earth patterns of upper, middle and lower crust as estimated by Rudnick and Gao (2003) are compared in Figure 11.33. The negative Eu anomaly in the upper crust and slight positive anomalies in the middle and lower crust (such positive anomalies are typical of many granulites) are an interesting feature of these patterns. Eu is strongly held in plagioclase (Chapter 7). The presence of plagioclase in the melting residue would result in melts having a negative Eu anomaly and the residue having a positive one. Thus these anomalies suggest that the crust has at least partially differentiated to form distinct layers through partial melting, with granitic melts forming the upper crust and granulitic residues of gabbroic composition forming the lower crust. The actual evolution of the deep crust is undoubtedly more complex, however. Intrusion and ponding of mantle-derived magmas of basaltic composition is likely to be another important reason for the mafic composition of the lower crust.

Table 11.10 Composition of the middle and lower continental crust.

Major oxides, %

	R & G Middle	Wedepohl Lower	R & G Lower
SiO$_2$	63.5	59.0	53.4
TiO$_2$	069	0.85	0.82
Al$_2$O$_3$	15.0	15.8	16.9
FeO	6.0	7.47	8.57
MnO	0.10	0.12	0.10
MgO	3.59	5.32	7.24
CaO	5.25	6.92	9.59
Na$_2$O	3.39	2.91	2.65
K$_2$O	2.30	1.61	0.61
P$_2$O$_5$	0.15	0.20	0.10

Trace elements in ppm except as noted

	R & G Middle	Wedepohl Lower	R & G Lower		R& G Middle	Wedepohl Lower	R & G Lower
Li	12	13	13	Sb	0.28	0.3	0.1
Be	2.29	1.7	1.4	I		0.14	0.1
B	17	5	2	Cs	2.2	0.8	0.3
C		588		Ba	532	568	259
N		34	34	La	24	26.8	8
F	524	429	570	Ce	53	53.1	20
S	20	408	345	Pr	5.8	7.4	2.4
Cl	182	278	250	Nd	25	28.1	11
Sc	19	25.3	31	Sm	4.6	6.0	2.8
V	107	149	196	Eu	1.4	1.6	1.1
Cr	76	228	215	Gd	4.0	5.4	3.1
Co	22	38	38	Tb	0.7	0.81	0.5
Ni	33.5	99	88	Dy	3.8	4.7	3.1
Cu	26	37.4	26	Ho	0.82	0.99	0.7
Zn	79.5	79	78	Er	2.3		1.9
Ga	17.5	17	13	Tm	0.32	0.81	0.24
Ge	1.13	1.4	1.3	Yb	2.2	2.5	1.5
As	3.1	1.3	0.2	Lu	0.4	0.43	0.25
Se	0.064	0.17	0.2	Hf	4.4	4.0	1.9
Br							
Br		0.28	0.3	Ta	0.6	0.84	0.6
Rb	65	41	11	W	0.60	0.6	0.6
Sr	282	352	348	Re			0.18
Y	20	27.2	16	Os			0.05
Zr	149	165	68	Ir			0.05
Nb	10	11.3	5	Pt	0.85		2.7
Mo	0.60	0.6	0.6	Au	0.66		1.6
Ru			0.75	Hg	0.0079	0.021	0.014
Pd ppb	0.76		2.8	Tl	0.27	0.26	0.32
Ag ppb	48	80	65	Pb	15.2	12.5	4
Cd	0.061	0.101	0.1	Bi	0.17	0.037	0.2
In		0.052	0.05	Th	6.5	6.6	1.2
Sn	1.3	2.1	1.7	U	1.3	0.93	0.2

R & G, Rudnick and Gao (2003); Wedepohl, Wedepohl (1995).
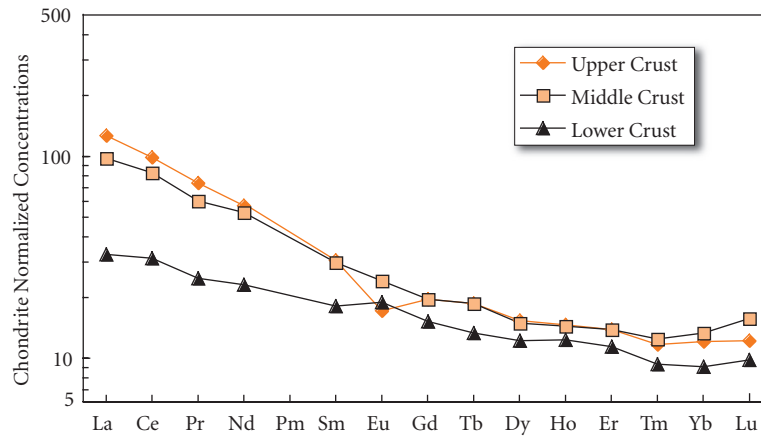
Figure 11.33 Comparison of chondrite-normalized rare earth patterns in upper, middle and lower crust. Data of Rudnick and Gao (2003).
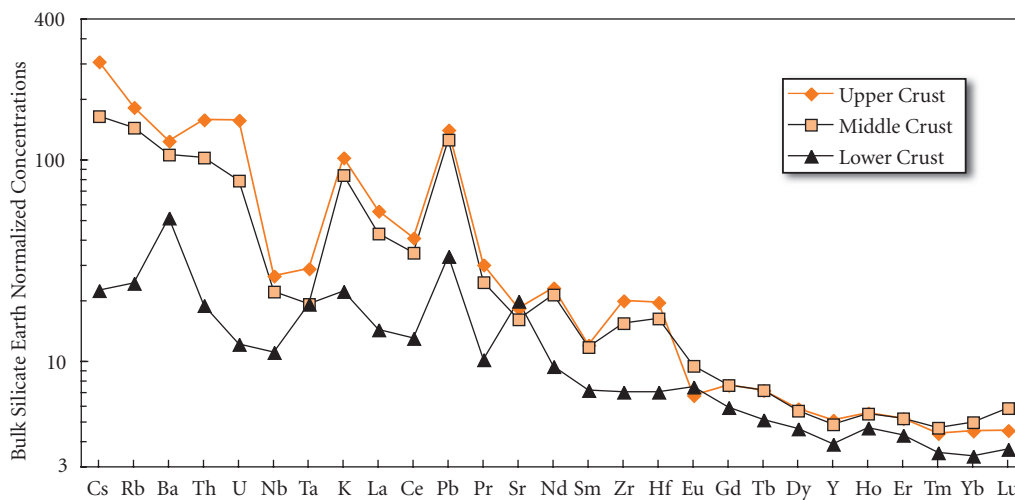
Figure 11.34 Enrichment of incompatible elements relative to bulk silicate Earth (Table 11.3) in the upper, middle, and lower crust. Data from Rudnick and Gao (2003).

Figure 11.34 is a "spider diagram" comparing incompatible element abundances in the upper, middle, and lower continental crust. The lower and middle crusts are less enriched in incompatible elements than the upper crust. This is also consistent with the idea that magmatic processes have been important in creating the compositional layering observed in the crust.

11.6.2.3 Composition of the total continental crust

The approach used by most workers to estimate the composition of the total continental crust is simply to calculate a weighted average of crustal layers considered earlier. This was done, for example, by Rudnick and Fountain (1995) and Weaver and Tarney (1984), both

of whom divided the crust into an upper, lower, and middle section, and relied on Taylor and McLennan's upper crustal estimate. Weaver and Tarney (1984) used average Lewisian* amphibolite as their middle crust composition and average Lewisian granulite as their lower crust composition. Shaw *et al*. (1986) and Wedepohl (1995) used a similar approach, but divided the crust only into upper and lower parts. An important step in this approach is estimating the thickness of the various sections. Here, seismological constraints again come into play.

Taylor and McLennan (1985, 1995) used an entirely different approach to estimating total crustal composition, one based on the "andesite model" of Taylor (1967). Taylor (1967) noted the role played by subduction-related volcanism in creation of the continental crust and assumed that, on average, the crust consisted of island arc andesite. Thus average island arc andesite was used as the estimated composition of the continental crust. This approach was modified in subsequent work, as Taylor concluded that while post-Archean crust was created at subduction zones, Archean crust was not and is compositionally different. Taylor and McLennan (1985) essentially modified the Taylor (1967) andesite model for their estimate of Archean crustal composition.

Estimates of the major element composition of the continental crust by Weaver and Tarney (1984), Shaw *et al*. (1986), Taylor and McLennan (1995), Wedepohl (1995), and Rudnick and Gao (2003) are given in Table 11.11. Also listed are estimates of trace element concentrations by Taylor and McLennan (1995), Rudnick and Gao (2003), and Wedepohl (1995). The ranges of estimates for SiO_2 and Al_2O_3 in Table 11.11 are about 10% and 8% respectively; the range in Mg# (52 to 57) is similarly only about 10%. Interestingly, earlier estimates of crustal SiO_2 and Al_2O_3, going back to Goldschmidt (1933), also fall within this range. Thus we can conclude with some confidence that the continental crust on the whole is similar to that of diorite (or andesite).

The details of the composition of the crust are less certain, however. Ranges for the other oxides are substantially larger: 75% for FeO, 68% for MgO, and 100% for MnO. Of these estimates, the composition of Taylor and McLennan is the most mafic, and that of Weaver and Tarney the least mafic (ranges for FeO and MnO decrease to 30% and 21% respectively if the estimates of Taylor and McLennan are excluded). Wedepohl's (1995) estimated crustal composition is significantly more enriched in incompatible elements than that of Taylor and McLennan (1985, 1995); Rudnick and Gao's (2003) estimated concentrations of incompatible elements generally fall between the two.

Figure 11.35 compares the rare earth element patterns in the total continental and oceanic crusts. Both are enriched in all rare earths relative to bulk silicate Earth as well as chondrites, but whereas the continental crust is enriched in the light rare earths relative to the heavy rare earths, the opposite is true of the oceanic crust. The light rare earth enrichment of the continental crust is clear evidence that it, like the oceanic crust, originated as a partial melt of the mantle. The oceanic crust is produced through comparatively large extents of melting of mantle that has already been depleted in incompatible elements through previous episodes of melting. The evolution of the continental crust has been more complex. The strong light rare earth enrichment, however, suggests that relatively small degree melts have been important in its evolution. Figure 11.36 compares the incompatible enrichment of the oceanic and continental crusts. Although the continental crust is enriched in incompatible elements overall, it is significantly less enriched in Nb and Ta and elements of similar incompatibility such as U and K; the oceanic crust exhibits a slight excess enrichment in these elements. It is also much more strongly enriched in Pb than either Ce or Sr, which are similarly incompatible. This negative Nb-Ta "anomaly" and positive Pb anomaly are characteristics of continental crust. They provide important hints as to the mechanism(s) by which continental crust has been created, a topic we consider in the next section.

* The Lewisian, which crops out in northwest Scotland, is perhaps the classic exposure of lower crust.

Table 11.11   Composition of the continental crust.

Major oxides, wt. %				
	R & G	**T & M**	**W & T**	**We**	**Shaw**
SiO_2	60.6	57.3	63.2	61.5	63.2
TiO_2	0.7	0.9	0.6	0.68	0.7
Al_2O_3	15.9	15.9	16.1	15.1	14.8
FeO	6.7	9.1	4.9	5.67	5.60
MnO	0.1	0.18	0.08	0.10	0.09
MgO	4.7	5.3	2.8	3.7	3.15
CaO	6.4	7.4	4.7	5.5	4.66
Na_2O	3.1	3.1	4.2	3.2	3.29
K_2O	1.8	1.1	2.1	2.4	2.34
P_2O_5	0.1		0.19	0.18	0.14

Trace elements (in ppm unless otherwise noted)

	R & G	T & M	We		R & G	T & M	We
Li	15	13	18	Sb	0.2	0.2	0.3
Be	1.9	1.5	2.4	Te, ppb			5
B	11	10	11	I, ppb	700		800
C			1990	Cs	2	1	3.4
N	56		60	Ba	456	250	584
F	553		525	La	20	16	30
S	404		697	Ce	43	33	60
Cl	244		472	Pr	4.9	3.9	6.7
Sc	21.9	30	16	Nd	20	16	27
V	138	230	98	Sm	3.9	3.5	5.3
Cr	135	185	126	Eu	1.1	1.1	1.3
Co	26.6	29	24	Gd	3.7	3.3	4.0
Ni	59	105	56	Tb	0.6	0.6	.65
Cu	27	75	25	Dy	3.6	3.7	3.8
Zn	72	80	65	Ho	0.77	0.78	0.8
Ga	16	18	15	Er	2.1	2.2	2.1
Ge	1.3	1.6	1.4	Tm	0.28	0.32	0.3
As	2.5	1	1.7	Yb	1.9	2.2	2.0
Se	0.13	0.05	0.12	Lu	0.30	0.3	0.35
Br	0.88		1.0	Hf	3.7	3	4.9
Rb	49	32	78	Ta	0.7	1	1.1
Sr	320	260	333	W	1	1	1.0
Y	19	20	24	Re, ppb	0.188	0.4	0.4
Zr	132	100	203	Os, ppb	0.041	0.005	0.05
Nb	8	11	19	Ir, ppb	0.037	0.1	0.05
Mo	0.8	1	1.1	Pt, ppb	1.5		0.4
Ru, ppb	0.6		0.1	Au, ppb	1.3	3	2.5
Rh, ppb			0.06	Hg, ppb	30		40
Pd, ppb	1.5	1	0.4	Tl, ppb	500	360	520
Ag, ppb	56	80	70	Pb	11	8	14.8
Cd, ppb	80	98	100	Bi, ppb	180	60	85
In, ppb	52	50	50	Th	5.6	3.5	8.5
Sn	1.7	2.5	2.3	U	1.3	0.91	1.7

R & G, Rudnick and Gao (2003); T & M, Taylor and McLennan (1985, 1995); We, Wedepohl (1995); Shaw, Shaw *et al.* (1986); W & T, Weaver and Tarney (1984).
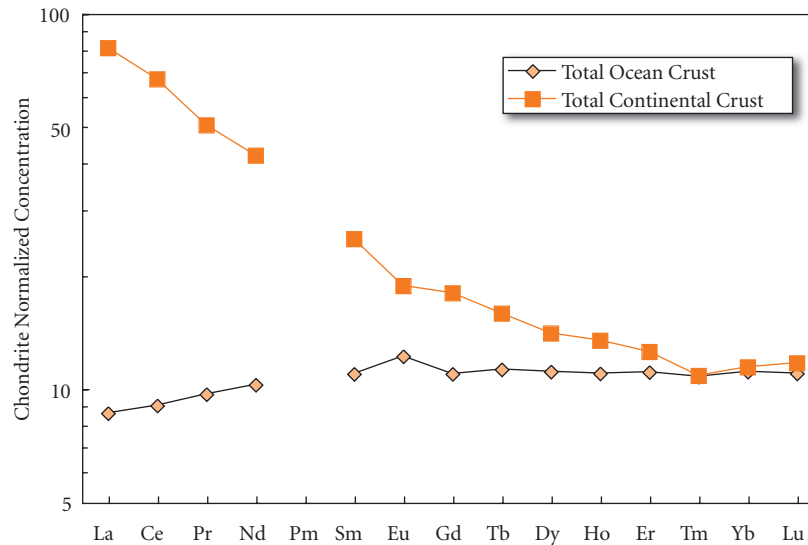
Figure 11.35 Comparison of rare earth patterns of the total oceanic (estimate of White and Klein (2013) listed in Table 11.7) and continental crust (estimate of Rudnick and Gao (2003) listed in Table 11.11).
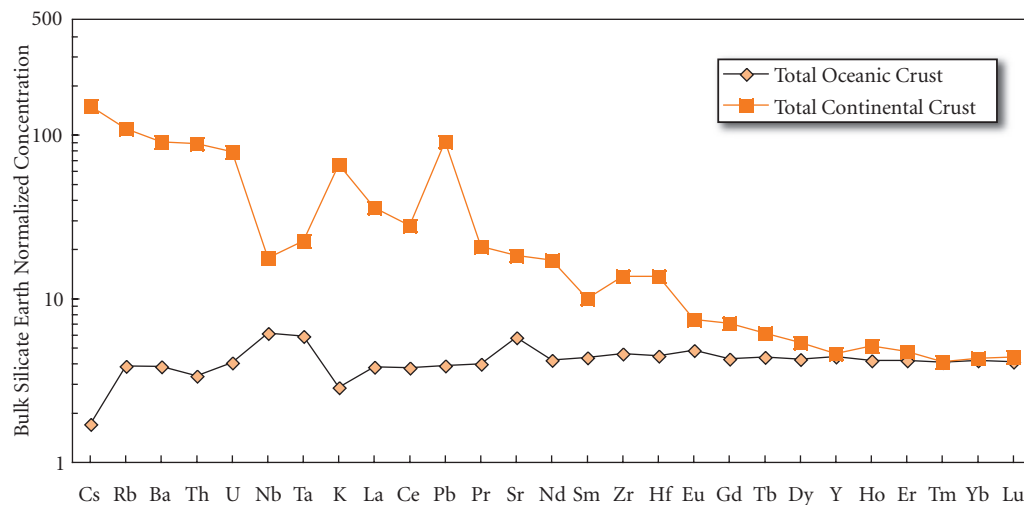
Figure 11.36 Comparison of the incompatible element enrichments of the continental (estimate of Rudnick and Gao listed in Table 11.11) and oceanic crusts (estimate of White and Klein listed in Table 11.7). Negative Nb-Ta and positive Pb anomalies, as well as the overall incompatible element enrichment, are significant characteristics of continental crust.

11.6.3 Growth of the continental crust

The oceanic crust is ephemeral; its mean age is 60 Ma and, with the exception of possible Permian age crust preserved in the Eastern Mediterranean, it is nowhere older than about 167 Ma. In contrast, the continental crust is much older. The oldest crustal rocks, Acasta gneisses in Canada's Northwest Territory, give Sm-Nd ages of 3.98 Ga. Individual zircons separated from a sandstone metamorphosed about ~3 Ga ago into quartzite in the Jack Hills of western Australia have U-Pb ages of 4.0 to 4.4 Ga. The chemical and O isotopic

compositions of these grains clearly show they were once part of "continental"-type rocks such as granites or granodiorites. There are also hints, based on $^{142}Nd/^{144}Nd*$–Sm/Nd correlations, that rocks from the Nuvvagittuq Belt of northwestern Labrador are remnants of continental crust formed at 4.28 Ga (O'Neil *et al.*, 2008). Conventional Sm-Nd dating of these rocks, however, gives an age of 3.84 Ga, which records a subsequent metamorphism. Clearly, then, some continental crust was present very early in Earth's history. More may have been present but has not survived. Most surviving continental crust is, however, much younger.

The question of the age of the continents (very definitely a geochemical question because radiometric dating is a geochemical technique) is a complex one. Because metamorphism, remelting, and so on, can reset radiometric ages, the radiometric age of a rock does not necessarily correspond to the time the material that makes up that rock first became part of the continental crust. Indeed, early efforts to systematically determine the ages of continents and rates of continental growth, such as that of Hurley and Rand (1969), substantially underestimated continental ages because they relied heavily on Rb-Sr ages, which are readily reset during metamorphism. This problem is now widely recognized and modern efforts to determine "crystallization ages" rely primarily on U-Pb dating of zircons.

Zircons are, in a sense, the ultimate natural clock/time capsule. There are several reasons for this. First, U substitutes readily for Zr in the zircon ($ZrSiO_4$) structure, but Pb is excluded (just as we might expect from our consideration of trace element behavior in Chapter 7, since Zr and U have the same charge, +4, and similar size (Zr = 72 pm; U = 89 pm), whereas Pb has a +2 charge and 119 pm radius). Second, the two U isotopes have short half-lives compared with most other radioactive nuclides used in geochronology. The short half-lives and high U concentrations result in rapid build-up of radiogenic Pb in zircon, allowing for more precise age

determinations than other methods can provide. Third, zircon is a chemically robust mineral that resists weathering and chemical breakdown. Fourth, it is a mechanically robust mineral (Moh's hardness of 7.5) and readily survives transport in rivers and streams. Finally, because U has two isotopes that decay to isotopes of Pb at different rates (see Chapter 8), it is possible to determine whether or not the system has been disturbed by subsequent events such as metamorphism. When ^{236}U-^{207}Pb and ^{238}U-^{206}Pb ages agree, the age is said to be *concordant*. The systematics of U-Pb often allow the original crystallization age to be determined even when ages are discordant. Finally, it is also possible, using approaches that include mechanical and chemical abrasion and *in situ* analysis, to analyze only the least disturbed parts of zircon crystals.[†] Thus zircon dating has become the "gold standard" for determining rates of continental growth. The most recent compilation of ages, that of Condie and Aster (2010), is shown in Figure 11.37.

We can draw several important inferences from Figure 11.37. First, continent production has been episodic. Pulses occurred at approximately 750, 850, 1760, 1870, 2100,
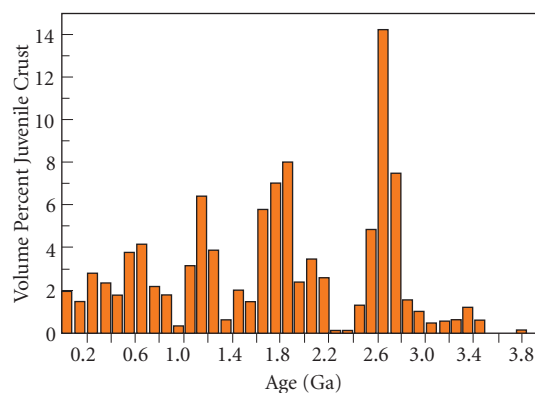
Figure 11.37 Estimated volume of juvenile (i.e., new) crustal additions as a function of geologic age, estimated from a database of 40,000 U-Pb ages of granitoid and detrital zircons. Condie and Aster (2010). With permission from Elsevier.

* Recall that ^{142}Nd is the daughter of the extinct radionuclide ^{146}Sm, whose half-life is 103 Ma.
† Radiation damage is a major cause of discordance in zircon ages. U concentrations that are too high are a curse, since this leads to severe radiation damage and discordant ages. Damaged zircon crystals or parts of the crystals are said to be *metamict*. These can be seen under the microscope and avoided in *in situ* analysis.

2650, 2700, and 2930 Ma. Other studies have found similar episodicity, which is widely thought to be related to supercontinent cycles. Second, only a small fraction of the surviving continental crust is older than 2.8 Ga (about 6%, according to Condie and Aster). Third, after the large pulse in crust production at 2.8 to 2.6 Ga, each succeeding pulse has been smaller. Condie and Aster (2010) conclude that only 14% of the continental crust is younger than 600 Ma.

Zircons, however, are an imperfect recorder of crustal growth. One of the problems is that zircons do not crystallize from mafic melts. As we noted earlier, $^{142}Nd/^{144}Nd$–Sm/Nd correlations suggest that rocks from the Nuvvagittuq Belt of Labrador may have first formed 4.28 Ga ago, but their ^{147}Sm-^{143}Nd ages are much younger (O'Neil *et al.*, 2008). The ^{147}Sm-^{143}Nd age was probably reset during a metamorphic event. The rocks themselves, which might have originally been basaltic dikes, are mafic amphibolites and contain no zircons. Since mantle melts are almost always mafic in nature, their lack of zircons greatly complicates identifying new additions to the continents from the mantle. Furthermore, remelting of crustal rocks, undoubtedly an important process, may destroy any original zircons with younger ones crystallizing in their place.

Sm-Nd model ages, or crustal residence times, introduced in Chapter 8, provide one

way of discriminating between mere reprocessing of pre-existing crust and production of new crust from the mantle. The study of the western US by Bennett and DePaolo (1987) provided an example of the insights Sm-Nd model ages can provide into crustal evolution. Figure 11.38 is a map of the western US showing contours of Nd crustal residence times (τ_{DM}). The data define three distinct provinces and suggest the existence of several others. Ages deduced in this manner are significantly older than those determined by Hurley and Rand (1969) using Rb-Sr dating. Figure 11.39 shows the initial ε_{Nd} values of granites from the three numbered provinces of Figure 11.38 plotted as a function of their crystallization age. Although the crystallization ages are often much younger, crustal residence times indicate Provinces 1–3 all formed between 1.65 and 1.8 Ga. Only in Province 3 do we find rocks, tholeiitic and calc-alkaline greenstones, whose Sm-Nd crustal residence age is equal to their crystallization ages. From this we can conclude that only Province 3 was a completely new addition to the crustal mass at that time. In the other regions, the oldest rocks have initial ε_{Nd} values that plot below the depleted mantle evolution curve. This sug-
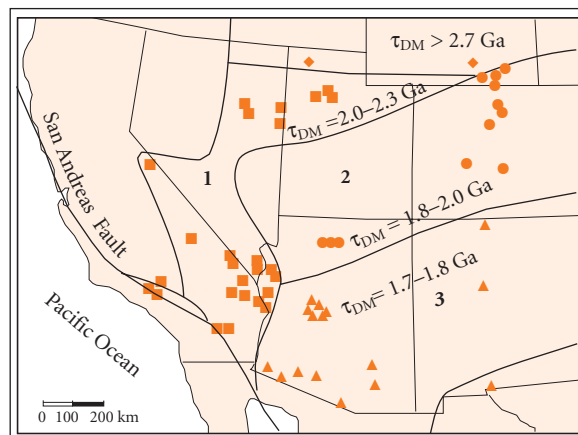
Figure 11.38 Isotopic provinces, based on crustal residence times (τ_{DM}) of the western US. From Bennett and DePaolo (1987). Reproduced with permission of the Geological Society of America.
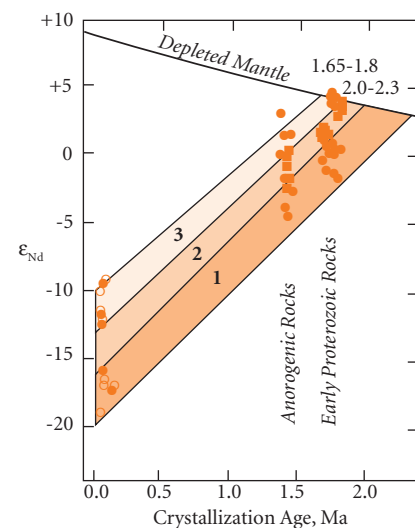
Figure 11.39 Initial ε_{Nd} as a function of crystallization age for igneous rocks of the western US. Groupings 1, 2, and 3 refer to provinces shown in Figure 11.38. From Bennett and DePaolo (1987). Reproduced with permission of the Geological Society of America.

gests that mantle melts mixed with pre-existing crust, perhaps by assimilating crust (which would have a lower melting temperature) as they ascended through it. Alternatively, pre-existing continental crust might have been carried into the mantle by sediment subduction or subduction erosion (topics we consider later) and mixed with mantle before melting.

Throughout the region there were subsequent episodes of magmatism, including one in the Tertiary. However, the initial ε_{Nd} lies along the same growth trajectory as the older rocks. This suggests that these subsequent igneous events involved remelting of existing crust with little or no new material from the mantle. Lu-Hf model ages can also discriminate between reprocessing existing crust and new additions to crust in an analogous manner. This system has the advantage that Hf is strongly concentrated in zircons (not surprisingly, given the similar chemical behavior of Hf and Zr) while Lu is not. Consequently, initial Hf isotopic compositions of zircons are readily determined. These can be compared with models of Hf isotopic evolution in the mantle and, hence, whether or not a zircon, and the rock containing it, was a crustal- or mantle-derived melt. Combined with U-Pb age determinations in the same zircons, this provides a powerful tool that will likely see more common use in the future. A drawback of the Lu-Hf system is that Lu and Hf are readily fractionated within the crust, particularly by weathering and sedimentary processes, whereas Sm and Nd are not.

Figure 11.37 and Sm-Nd and Lu-Hf model ages inform us only about continental crust that has survived to the present day. As we will discuss later, continental crust can be destroyed. This could bias the inferences we draw from Figure 11.37. However, this should produce a bias for younger crust; thus declining crustal production is unlikely to be an artifact. Declining rates of magmatism and tectonism should, in any case, come as no surprise since radioactive decay and original heat provide the energy for those processes. It is also difficult to see how the apparent episodicity in Figure 11.37 could be an artifact of crustal destruction, unless the destruction were also pulsed in tandem with crustal production, which is exactly what Hawkesworth *et al.* (2010) have proposed.

Nevertheless, one of the most enduring debates in geology is the question of how crustal mass has changed over time and what the *net* rate of crustal growth has been. Armstrong (1968, 1981) argued that despite evidence of new additions to crust throughout geologic time, the mass or volume of continents has remained essentially unchanged since 4.0 Ga because the rate of destruction of continental crust has matched the rate of production. Others, for example, Hurley and Rand (1969) and Vezier and Jansen (1979), argued that there was little crust present before 2.0 Ga. There are at least three mechanisms by which continental crust can be destroyed: (1) erosion and transport of sediment to the ocean where it is subsequently subducted into the mantle; (2) subduction erosion, the process by which a subducting plate abrades and removes material from the overriding plate and carries it into the mantle; and (3) lower crustal floundering or delamination, whereby during plate convergence, crust becomes over-thickened, resulting in the lower crust being converted to dense eclogite and sinking into the mantle. There is good evidence that all three mechanisms operate, and some have argued that the rates of the first two processes are sufficient to balance rates of new crustal addition and, therefore, produce a steady-state crustal volume, just as Armstrong proposed. However, no consensus has formed around these views and the question of the net change in crust mass is still debated.

In summary, we can say that continental crust has been produced over much, if not all of the history of the Earth, but crustal production has been very much episodic. The rate of new crust production has been declining over the last 2.5 Ga. Rates of crustal destruction and *net* continental growth remain controversial.

11.6.4 Subduction zone processes and the origin of continents

As we have often stated, the crust has grown through magmatism. In the modern Earth and throughout the Phanerozoic, nearly all magmatism occurs and has occurred in one of three tectonic environments: (1) along divergent plate boundaries, such as the Mid-Atlantic Ridge, or intraplate rifts, such as the Great African Rift or the Rio Grande Rift; (2)
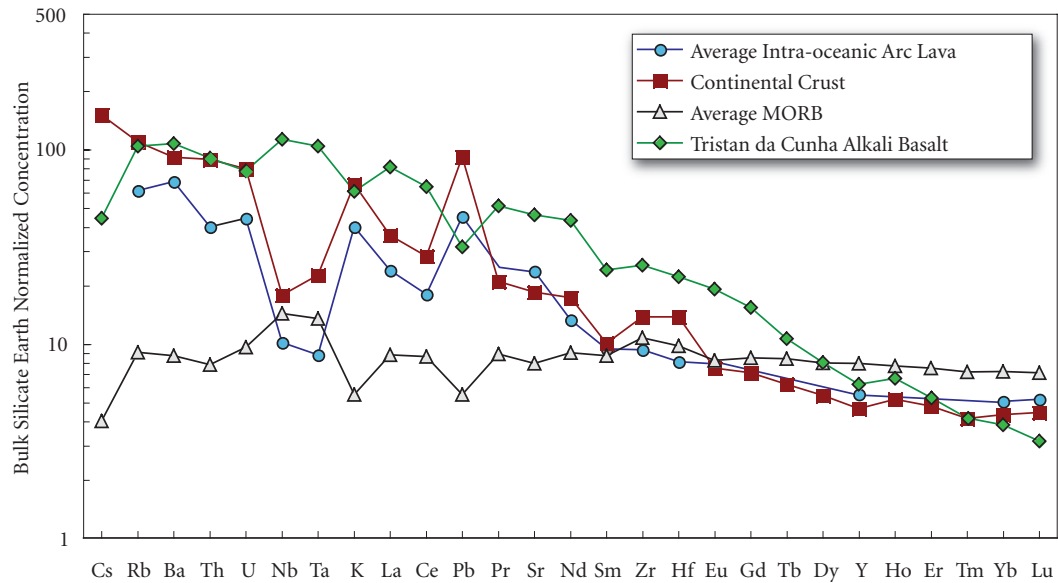
Figure 11.40 Normalized incompatible enrichments of average MORB (Table 11.7), average composition of lavas from eight intra-oceanic island arcs studied by Porter and White (2009), and an alkali basalt from Tristan da Cunha, compared with incompatible element enrichment of the total continental crust (Table 11.11). Only the pattern of island arc lavas matches that of the continental crust.

above mantle plumes, Hawaii for example; and (3) above subduction zones at convergent plate boundaries such as the Andes. While magmatism in all three environments has undoubtedly contributed to continental growth, geochemical evidence suggests that the latter has been the dominant process by which the continents have grown. Figure 11.40 compares incompatible element abundances in the continental crust with examples of magmas produced in these three environments: average MORB for convergent boundary settings, an alkali basalt from the South Atlantic volcanic island of Tristan da Cunha, and average intra-oceanic island arc lava. There are clear similarities between the continental crust and the island arc lava: both exhibit incompatible element enrichment, negative Nb-Ta anomalies, and positive Pb anomalies. MORB and the Tristan da Cunha example exhibit slightly positive Nb-Ta anomalies and negative Pb anomalies. It is also true that at present, most new additions to crust occur in subduction zones, for example, the volcanoes of the Andes and Alaskan Peninsula. Let's consider

the geochemistry of subduction zone volcanism in a bit more detail.

11.6.4.1 Major element composition

Magmas found in island arcs (we will use the term *island arc* for all subduction zone magmatism, including continental margin type) appear to be predominantly andesitic. It seems unlikely that andesite is the principle magma produced in arcs, however. Generally, we don't see the lower parts of arc volcanic edifices, which may be basaltic. There is also considerable doubt as to whether an andesite can be produced by partial melting of the mantle, particularly at depth. Most arcs sit about 100 km above the Benioff zone, and magmas may be generated close to this depth. A safer bet is that the primary magma is actually basaltic, of which andesites are fractional crystallization products. In any case, basalt is not uncommon in intra-oceanic arcs.

In major element composition, island arc volcanics (IAV) are not much different from other volcanic rocks. Compared with MORB,

the major difference is perhaps simply that siliceous compositions are much more common among the island arc volcanics. Most IAV are silica-saturated or oversaturated; silica undersaturated magmas (alkali basalts) are rare. In that sense, we might call them *tholeiitic*. However, in the context of island arc magmas, the term *tholeiite* has a more restrictive meaning. Two principal magma series are recognized, one called *tholeiitic*, the other called *calc-alkaline*. There are two principal differences between these rock series.

First, tholeiites differentiate initially toward higher Fe and tend to maintain higher Fe/Mg than the calc-alkaline lavas (Figure 11.41). The lower Fe content of the calc-alkaline series reflects the suppression of plagioclase crystallization as a result of (1) higher pressure and (2) higher water content of the magma (Grove and Baker, 1984). In the tholeiitic series, the crystallization sequence is typically olivine, plagioclase, followed by clinopyroxene. At higher pressure or higher water content, clinopyroxene supplants plagioclase as the second crystallizing phase, which buffers the iron concentration. As we shall see, another characteristic of subduction zone magmas is that they can have much higher water content than magmas found in other tectonic settings. Kay *et al.* (1983) found that, at least for the Aleutians, occurrence of these two phases could be related to tectonic environment. Tholeiites occur in extensional environments within the arc where magmas can ascend relatively rapidly into the upper crust where they undergo fractional crystallization at low pressure. Calc-alkaline lavas tend to occur in compressional environments within the arc where they cannot so readily ascend to shallow depths, and hence undergo crystallization at greater depth.

The second difference is that calc-alkaline magmas are richer in alkalis (K_2O and Na_2O) than tholeiites. Indeed, the calc-alkaline magmas are defined as those that have $Na_2O + K_2O \approx CaO$, whereas tholeiites have $Na_2O + K_2O < CaO$, and alkaline rocks have $Na_2O + K_2O > CaO$.

IAV also tend to be somewhat poorer in Ti than MORB and OIB. Perfit *et al.* (1980) argued that the difference in Ti content is due to early crystallization of oxides, ilmenite ($FeTiO_3$) in IAV, which buffers the Ti concentration. That in turn, they argued, reflected higher oxygen fugacities. Kelley and Cottrell (2009) have confirmed higher fugacities in IAV by measuring the Fe^{2+}/Fe^{3+} ratio in glass inclusions in phenocrysts using synchrotron-based near-edge structure spectroscopy (μ-XANES). The technique makes use of small differences in the X-ray adsorption spectra of Fe^{2+} and Fe^{3+}. A synchrotron produces a sufficiently high intensity X-ray beam for this analysis to be performed on the micron scale. They found that while MORB had $Fe^{3+}/\Sigma Fe$ of 0.13 to 0.17, IAV had $Fe^{3+}/\Sigma Fe$ of 0.18 to 0.32. They also found that $Fe^{3+}/\Sigma Fe$ correlated directly with water content.

Plank and Langmuir (1988) investigated the factors that control the variation in major element composition of island arc basalts. They treated the data in a manner analogous to Klein and Langmuir (1987), correcting regional data-sets to a common MgO content, but they used 6% MgO rather than the 8% used by Klein and Langmuir. They found that $Na_{6.0}$ and $Ca_{6.0}$ (i.e., Na_2O and CaO concentrations corrected to 6% MgO) correlated well with crustal thickness (Figure 11.42). They argued that crustal thickness determines the height of the mantle column available for
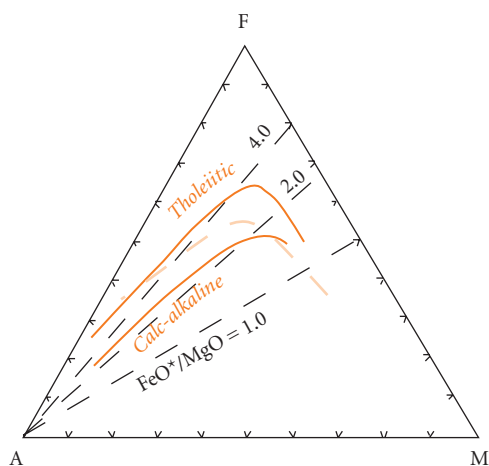
Figure 11.41   AFM (A, $K_2O + Na_2O$; F, FeO + MnO; M, MgO) diagram illustrating the difference between the tholeiitic and calc-alkaline lava series of island arcs. Calc-alkaline rocks plot below the heavy gray line, tholeiites above.
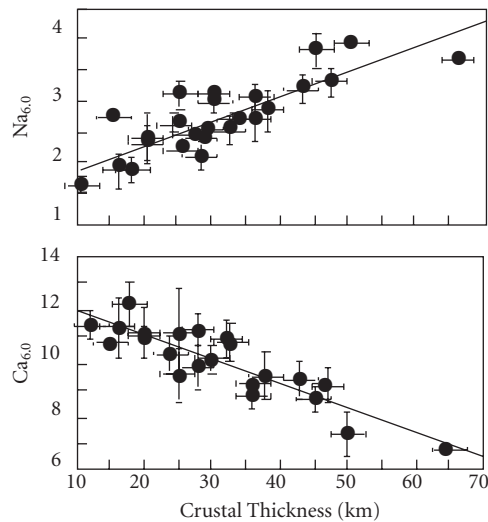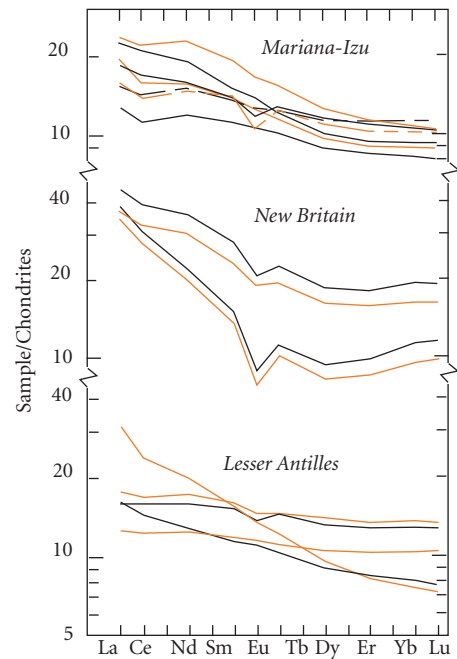
Figure 11.42 Correlation of $Ca_{6.0}$ and $Na_{6.0}$ with crustal thickness in island arc basalts. $Ca_{6.0}$ and $Na_{6.0}$ are the CaO and Na_2O concentrations after correction for fractional crystallization to 6.0% MgO. Plank and Langmuir (1988). With permission from Elsevier.

Figure 11.43 Rare earth element patterns of some typical island arc volcanics. White and Patchett (1984). With permission from Elsevier.

melting. Most island arc volcanoes are located above the point where the subducting lithosphere reaches a depth of 100–120 km. This suggests that melting begins at a relatively constant depth in all island arcs. If this is so, then the distance over which mantle can rise and undergo decompressional melting will be less if the arc crust is thick, leading to smaller extents of melting beneath arcs with thick crust, and higher $Na_{6.0}$ and lower $Ca_{6.0}$ in the parental magmas.

11.6.4.2 Trace element composition

The differences in trace elements between island arc volcanics and those from other tectonic environments are more significant than the differences in major elements. Rare earths, however, are not particularly distinctive. There is a very considerable range in rare earth patterns: from light rare earth (LRE) depleted to LRE enriched (Figure 11.43). IAV are virtually never as LRE depleted as MORB, but absolute REE concentrations are often low, and it is not unusual for the middle and heavy rare earths to be present at lower concentrations than in MORB. One other aspect

is of interest. Ce anomalies occur in some IAV, whereas they are never seen in MORB or OIB, though they have been observed in continental carbonatites and kimberlites. Ce anomalies occur in sediment, so there is a suspicion that the anomalies in IAV are inherited from subducted sediment.

An important and ubiquitous feature of island-arc volcanics is a relative depletion in Nb and Ta, which can be seen in Figure 11.40. Island-arc volcanics are also richer in the incompatible alkalis and alkaline earths (K, Rb, Cs, Sr, and Ba) relative to other incompatible elements, when compared with MORB or OIB. This is illustrated in Figure 11.44, using the Ba/La ratio. Though both IAV and oceanic basalts can have a large range in rare earth patterns, as illustrated by the range in La/Sm ratios, the Ba/La ratios of IAV are generally higher.

11.6.4.3 Isotopic composition and sediment subduction

Island arcs overlie subduction zones, which raises the obvious question of the degree to