Chapter 12: Geochemistry of the Solid Earth II: The Crust

Introduction

We now turn our attention to the crust. Though the crust forms only a small fraction of the mass of the Earth (about 0.5%), it is arguably the most varied and interesting fraction. Further, it's the fraction we can examine directly and therefore know most about. The crust has formed through igneous processes from the mantle over geologic time. There are two fundamental kinds of crust: oceanic and continental. Oceanic crust, created by magmatism at mid-ocean ridges, is basaltic in composition, thin, ephemeral, and relatively uniform. It is important in a number of respects, however. First, its composition tells us much about the composition of the mantle from which it is derived. Second, oceanic crust may be, at least some times, the raw material from which continental crust is formed. Thus we begin by briefly examining the composition of oceanic crust and the factors that control this composition. We then turn our attention to the continental crust, which is much thicker, essentially permanent, and on average andesitic in composition. The continental crust is also much more varied in composition. Although it too has formed by magmatism, its evolution is far more complex than that of oceanic crust. Though we have an excellent understanding of how oceanic crust forms, our understanding of the processes that have led to the present continental crust is far from complete. Subduction-related, or 'island arc' volcanism appears to play a particularly important role in the formation of the continental crust, so we will pay special attention to processes in islands arcs. We will then consider the problem of interaction of mantle-derived magma with the crust, then the problems of the composition and evolution and the continental crust, and finally differentiation of the crust through melting and metamorphism.
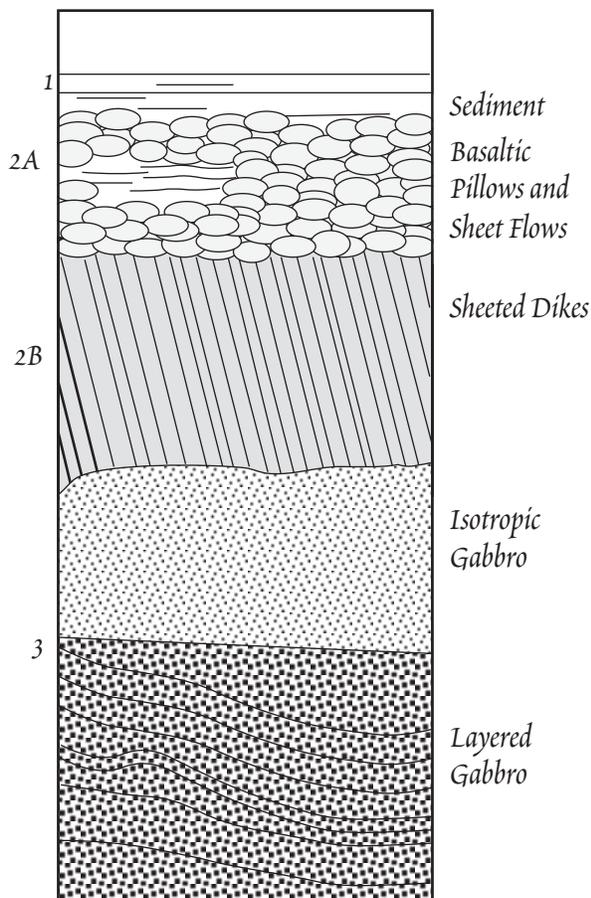

Figure 12.1. Schematic cross-section of the oceanic crust. Numbers on the left indicate the designation of seismically identifiable layers.

The Oceanic Crust

The crust beneath the oceans differs from the continental crust in a number of important respects. First, it is thinner, with a typical thickness of 6 km or, compared to an average thickness of 35 km or so for continental crust. Second, it is more mafic, i.e., richer in Mg and Fe and poorer in Si that the continental crust. Third, it is temporary, on average, the time between its creation at mid-ocean ridges and destruction at subduction zones is 100 million years or less, compared to an average age of about 2 billion years for the continental crust. Finally, it is essentially monogenetic; the vast majority of oceanic crust is created at mid-ocean ridges. As a result, it is much more uniform in composition than the continental crust. In this section, we will focus entirely on the igne-

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Table 12.1: Composition of MORB

	EPR MORB[1]		Primitive MORB[2]
	Average	Std Dev.	
SiO_2	50.39	1.89	49.10
TiO_2	1.72	0.47	0.6
Al_2O_3	14.93	1.13	16.4
ΣFeO	10.20	1.52	8.8
MnO	0.18	0.04	
MgO	7.34	1.30	10.3
CaO	11.29	1.38	12.4
Na_2O	2.86	0.46	1.9
K_2O	0.25	0.47	0.1
P_2O_5	0.35	0.48	
	99.52		99.60

[1]Average of 1266 analyses of basalts from the East Pacific Rise compiled by C. Langmuir.
[2]A primitive MORB composition from *Basaltic Volcanism on the Terrestrial Planets*

Table 12.2. Concentrations of Trace Elements in Average MORB

Element	ppm	Element	ppm
K	883.7	Nd	11.18
Sc	41.37	Sm	3.752
Co	17.07	Eu	1.335
Ni	149.5	Gd	5.077
Cu	74.4	Tb	0.885
Rb	1.262	Dy	6.304
Sr	113.2	Ho	1.342
Y	35.82	Er	4.143
Zr	104.2	Tm	0.621
Nb	3.507	Yb	3.90
Sn	1.382	Lu	0.589
Cs	0.0141	Hf	2.974
Ba	13.87	Ta	0.192
La	3.895	Pb	0.489
Ce	12.00	Th	0.1871
Pr	2.074	U	0.0711

From Hofmann (1988).

ous part of the oceanic crust. The geochemistry of ocean sediments and hydrothermal interaction between seawater and oceanic crust are discussed in a Chapter 15.

In a 1962 paper that he called "an essay in geopoetry," Harry Hess summarized his radical views on seafloor spreading. He speculated that mid-ocean ridges were produced by rising mantle convention currents, and that these convection currents then moved laterally away from the mid-ocean ridges, producing the phenomenon of continental drift. This concept now forms the basis of plate tectonics, the fundamental paradigm of geology. Hess did miss one detail, however. He thought the oceanic crust was hydrated mantle, consisting of "serpentinized peridotite, hydrated by release of water from the mantle over the rising limb of a [convection] current." However, when mantle decompresses as it rises, it does not merely dehydrate, it melts. This melting generates the basalts that form the oceanic crust. In some respects, though, Hess's mistake is a very minor indeed. Oceanic crust is very ephemeral, and for this reason, it is sometimes better to think of it as part of the mantle reservoir than the crustal one. Nevertheless, igneous processes at mid-ocean ridges have fascinated many geochemists and much has been learned about them in the past several decades.

Seismic studies show that the oceanic crust has a layered structure (Figure 12.1). The uppermost layer, which is not present at mid-ocean ridges, consists of sediments (Seismic Layer 1). Beneath this lies Layer 2, composed of basaltic lava flows and the dikes that fed their eruption (the "sheeted dike complex"), and finally gabbros (Layer 3). The gabbros apparently consist both of basaltic magmas that crystallized in place (isotropic gabbros) and accumulations of minerals that crystallized as the basaltic magma was held in crustal magma chambers (layered gabbros). Because of the latter, the gabbros are probably somewhat more mafic on average than are the basalts. Layer 2 is often divided into Layer 2A and Layer 2B, with the latter having slightly higher seismic velocities. For many years it was thought that boundary between the two was the boundary between the lava flows and the dikes. Based on the results the Ocean Drilling Program, however, it appears the seismic boundary reflects instead a change in porosity due to filling of voids and fractures by secondary minerals in Layer 2B. It is thus a metamorphic boundary, with the transition to the sheeted dike complex actually occurring within Layer 2B.

The average and standard deviations of the major oxides in basalts from the East Pacific Rise are listed in Table 12.1. An average of trace element concentration in mid-ocean ridge basalt (MORB) is listed in Table 12.2. The incompatible trace element abundances and isotope ratios are controlled
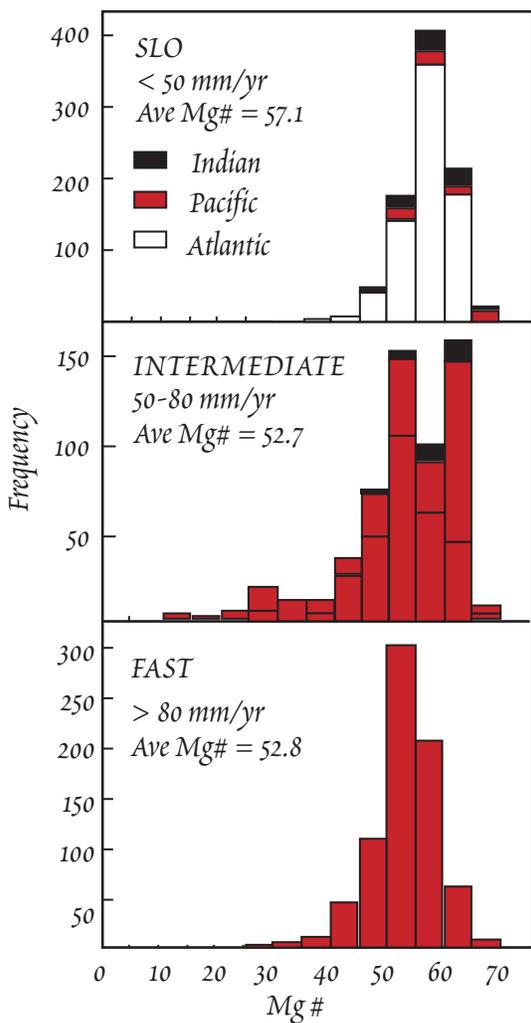
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Figure 12.2. Mg# in basalts from mid-ocean ridges of differing spreading rates. The Mg# is used as an index of the extent of fractional crystallization. Because olivine is the primary crystallizing phase, and because the Mg# of olivine is much higher than that of the liquid, Mg# will decrease during fractional crystallization. The figure shows that basalts from slow spreading ridges experience somewhat less fractional crystallization on average than basalts from fast spreading ridges. The most fractionated basalts occur on intermediate spreading rate ridges where small discontinuous melt lens can occur. After Sinton and Detrick (1992).

mainly by mantle chemistry, which we discussed in the preceding chapter. Hence here we will focus mainly on the major element composition of MORB, which is controlled mainly by igneous processes.

There was a considerable debate in the late 1960's and throughout the 1970's whether mid-ocean ridge basalts were 'primary' (or close to primary), i.e., whether they were direct mantle melts or whether they had experienced extensive fractionation crystallization before eruption. In the 1980's, this debate was resolved in favor of the view that most MORB had experienced extensive fractional crystallization. A critical observation is that all primary mantle-derived magmas must be in equilibrium with olivine of the composition found in the mantle. Mantle olivine is typically 90-92% forsterite and according to experimental studies such as that of Roedder and Emslie (1972) (see Chapter 4), a melt would have to have an atomic $Mg/(Mg+Fe^{2+})$ ratio[†] of around 0.72 to be in equilibrium with such olivine. The average compo-
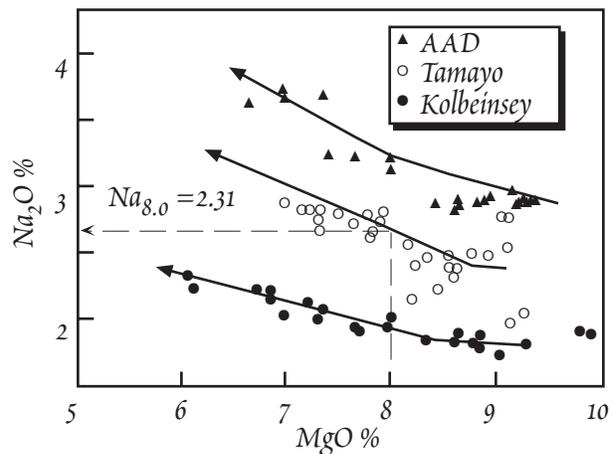

Figure 12.3. Na_2O vs. MgO in MORB from three areas of the mid-ocean ridge system: the Australian-Antarctic Discordance, the Tamayo Fracture Zone area of the East Pacific Rise, and the Kolbeinsey Ridge, just north of Iceland. Thick arrows show calculated fractional crystallization paths ('liquid line of descent') for each data set. $Na_{8.0}$ values are the intersection of the fractional crystallization path with MgO concentration of 8%. This is illustrated for the Tamayo data (dashed lines), which has $Na_{8.0}$ of 2.31. After Klein and Langmuir (1987).

[†] This ratio, multiplied by 100, is called the 'Mg number', generally written Mg#.

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sition listed in Table 12.1 has an Mg# of 59, and therefore could not be in equilibrium with mantle olivine. From this we can conclude that the oceanic crust, including the gabbroic section, is probably somewhat more mafic than the average MORB listed here. The primitive MORB composition in Table 12.1 has an Mg# of 70 and is close to a possible 'primary' composition.

One of the remarkable features of basalts erupted at mid-ocean ridges is their uniform chemistry. Nevertheless, the small variations in chemistry that do occur are significant in that they reveal the details of the magmatic processes at mid-ocean ridges. As the discussion above suggests, fractional crystallization is an important control on MORB composition. Olivine, augitic clinopyroxene, calcic plagioclase, and spinel, are, with rare exceptions, the only minerals to crystallize from MORB before eruption. Spreading rate, which is closely related to magma supply rates, seems to be an important factor in the extent of fractional crystallization: basalts erupted on fast spreading ridges are generally more fractionated than those erupted on slow spreading ridges (Figure 12.2). On fast spreading ridges, such as the East Pacific Rise, magma supplies rates are generally sufficient to maintain a small steady-state magma chamber, perhaps a few hundred meters deep and 1-2 km wide, at a depth of a few kilometers beneath the ridge axis (Sinton and Detrick, 1992). Melt trapped in this chamber will cool and crystallize. New magma rising from the mantle will mix with the fractionated magma in the chamber before eruption. In contrast, magma supply rates on slow spreading ridges, such as the Mid-Atlantic Ridge, are too low to maintain a steady-state magma chamber. As new magma injected into the crust can erupt without mixing with older, more fractionated magma.

The other factors that control the major element composition of MORB are the degree and depth of melting. The effects of these factors were investigated by Klein and Langmuir (1987). The difficulty with understanding the melting process is that all MORB have suffered some fractional crystallization, and this tends to obscure the melting effects. Klein and Langmuir found that MORB major oxide data from each locality on the mid-ocean ridge system formed a coherent and distinct array when oxide abundances or ratios of oxides were plotted against MgO (Figure 12.3). Calculated frac-
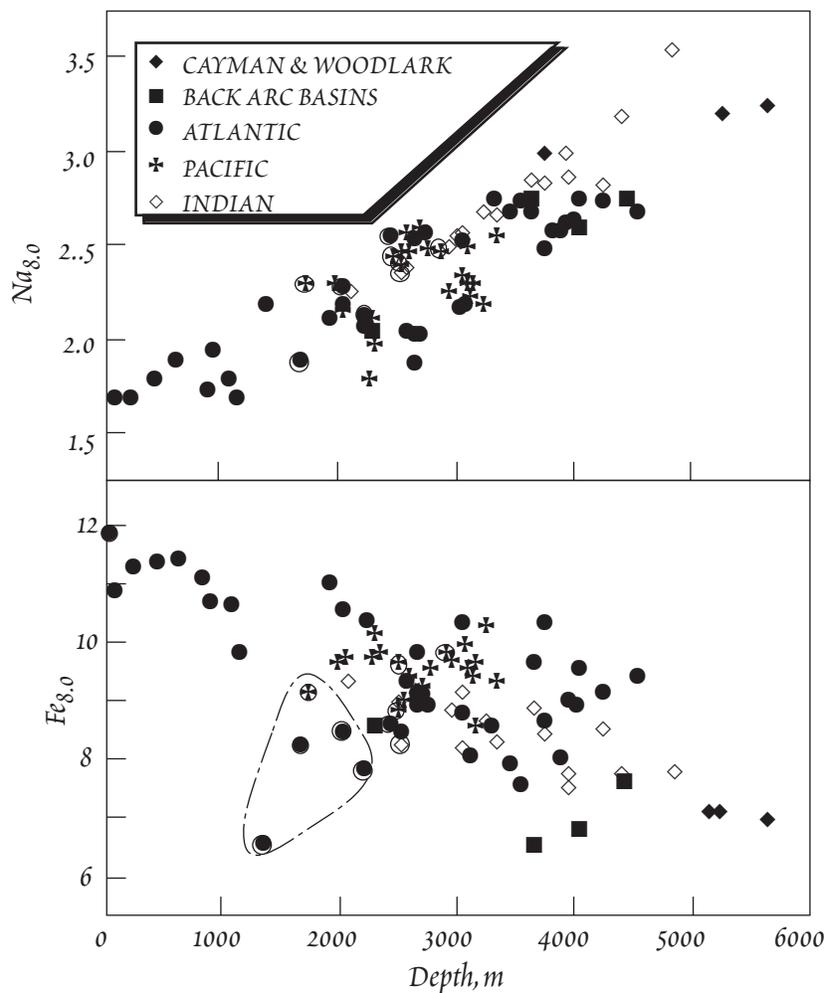

Figure 12.4. Relationship between $Na_{8.0}$ and $Fe_{8.0}$ in MORB and axial depth of mid-ocean ridges. Data from regions near hot spots are circled. Data from ridge segments near the Galápagos, Azores, and Jan Mayen hot spots, which are enclosed in the dashed field, appear to have anomalously low Fe. From Klein and Langmuir (1987).

tional crystallization paths, illustrated in Figure 12.3, passed through these arrays, so they concluded that the trends observed in these plots reflected fractional crystallization. They then argued that differences between the trends reflected differences in the melting process.

Rather than attempt to solve the difficult problem of determining the composition of parental magmas, Klein and Langmuir simply corrected regionally averaged data to a common MgO concentration of 8%. They did so simply by projecting each regional array on an oxide versus MgO plot to 8% MgO. For example, a line drawn through Na_2O data from the Tamayo Fracture Zone region of the East Pacific Rise intersects 8% MgO at 2.31% Na_2O (Figure 12.3). They called this the $Na_{8.0}$ value; thus Tamayo has an $Na_{8.0}$ of 2.31. So instead of comparing primary magma compositions, they compared compositions that had experienced similar extents for fractional crystallization.

Klein and Langmuir found that the regional corrected averages correlated strongly with the depth of the ridge axis (Figure 12.4). Comparing the variations in concentrations they observed with those in experimentally produced partial melts, they found that both variations in the mean pressure of melting and in the mean extent of melting were required to explain the data. For example, sodium concentrations in partial melts appears to be controlled only by the extent of partial melting. Iron concentrations, on the other hand, are only weakly affected
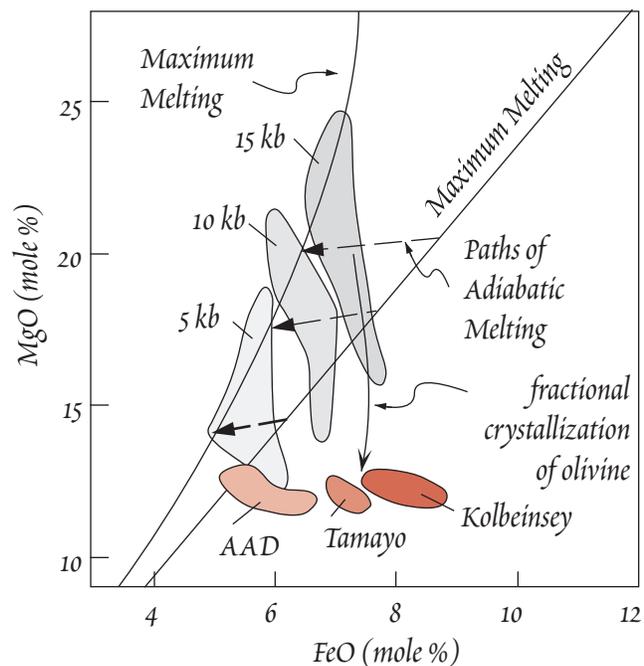

Figure 12.5. Variation of MgO and FeO in partial melts of mantle peridotite. Grayed fields show the compositions of experimental produced partial melts of peridotite at 3 different pressures. Hashed fields show compositions of high MgO basalts from the AAD, Tamayo, and Kolbeinsey regions. Curves for the calculated compositions at maximum and minimum melting are also shown. Dashed arrows show the path of melt composition produced by melting of adiabatically rising mantle. Curved arrow shows how the compositional a 15 kbar melt will evolve due to fractional crystallization of olivine. After Klein and Langmuir (1987).

by degree of partial melting, but are strong functions of the pressure at which melting occurs (Figure 12.5).

Klein and Langmuir concluded mantle temperature was probably 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 melts to a greater degree (Figure 12.6). 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 depth, and 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 produced the range in compositions observed. The hottest regions of the mantle occur near mantle plumes such Iceland. The coolest region occurs 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 suggested a range in mantle temperature of some 250° C.
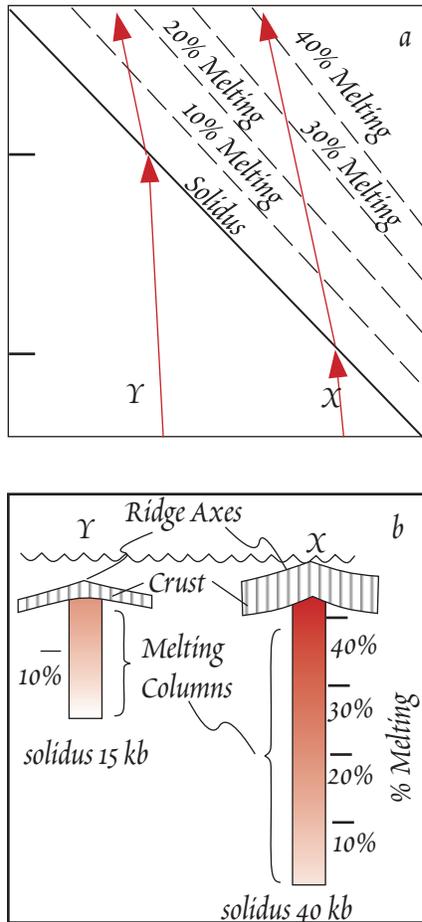
Figure 12.6. a.) Cartoon of the pressure-temperature relationship of adiabatically rising mantle undergoing melting. Hotter mantle (X) intersects the solidus at higher pressure and ultimately melts to a higher degree than cooler mantle (Y). The break in slope occurs because energy is consumed by melting (enthalpy of fusion). b.) Cartoon illustrating the 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 (Y). After Klein and Langmuir (1989).

PROCESSES IN SUBDUCTION ZONES AND ISLAND ARC GEOCHEMISTRY

Though the evolution of the continental crust has undoubtedly been complex and involved a number of processes, there is virtual unanimous agreement among scientists that magmatism is primary way in which the continental crust has formed. Today, and throughout the Phanerozoic, additions to the continental crust occur primarily by magmatism associated with subduction. As we shall see, there are also good chemical arguments that subduction zone volcanism has been the most important, though not necessarily exclusive, mechanism by which the continents have formed. Volcanos of the Andes Mountains of South America, which overlie the subducting Nazca Plate, are perhaps the best example of this process. Not all subduction zones are located along continental margins; indeed, most are not. The Marianas are a good example of an intra-oceanic subduction zone. Some old island arcs, however, such as Japan, parts of Indonesia, and the Aleutians have crustal seismic structures that are intermediate between those of continental and oceanic crust. This suggests that island arcs may eventually transform to continental crust. Plate motion may eventually result in these arcs accreting to continents. Thus intra-oceanic arcs may also contribute to continental growth. Thus in attempting to understand how the continental crust has formed, it is well worth while to consider subduction zone processes.

Subduction zones are, of course, the place where oceanic crust and lithosphere (often referred to as "the slab") are returned to the mantle. However, oceanic crust is not chemically identical to the basalt produced at mid-ocean ridges. Two important things have happened to the crust between its creation and subduction. First, it has reacted with seawater at a variety of temperatures. This process, which we discuss in detail in Chapter 15, hydrates the oceanic crust, adds some elements to it from seawater (e.g., Mg, U), and extracts others. Isotopic exchange with seawater affects the isotopic composition of Li, B, and Sr. The second thing that happens is that the oceanic crust acquires a sedimentary veneer. Elements gained through hydrothermal alteration and the elements in sediments are derived almost entirely from the continental crust. Thus the subducting oceanic crust carries with it a certain amount of continental crustal material (particularly when sediment is subducted) and subduction zones are therefore the principle sites of crust—to—mantle mass transfer.

MAJOR ELEMENT COMPOSITION

Magmas found in island arcs (we'll 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 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 intraoceanic arcs.

In major element composition, island-arc volcanics (IAV) are not much different from other volcanic rocks. Compared to MORB, the principal difference is perhaps simply that siliceous compositions are much more common among the island-arc volcanics. Most IAV 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*. The principle difference is that the tholeiites differentiate initially toward higher Fe and higher Fe/Mg than the calc-alkaline lavas. This is illustrated in Figure 12.7. In addition, the tholeiites tend to be poorer in K and some other incompatible elements than the calc-alkaline rocks. Kay et al. (1983) argued that the difference, at least for the Aleutians, relates to tectonic environment and depth of magma stagnation and crystallization. Tholeiites occur in extensional environments in the arc where magma can ascend relatively rapidly and cool less. Fractional crystallization occurs at shallow levels. Calc-alkaline lavas ascend more slowly and undergo crystallization at greater depth.

A third series is sometimes defined, the high-alumina series. IAV in general tend to have slightly higher Al contents on average than MORB or OIB, but there is very considerable overlap with the OIB and MORB fields.

IAV also tend to be somewhat poorer in Ti than MORB and OIB, though this is not necessarily a primary feature. Perfit et al. (1980) argued that the difference in Ti content is due to early crystallization of Fe-Ti oxides (e.g., magnetite and ilmenite) in IAV, which buffers the Ti concentration. Thus the higher Ti concentrations in MORB may reflect the way the magmas differentiate rather than higher Ti concentrations of MORB primary melts or MORB sources. The same is true for iron enrichment. Fe-Ti oxide precipitation may in turn depend
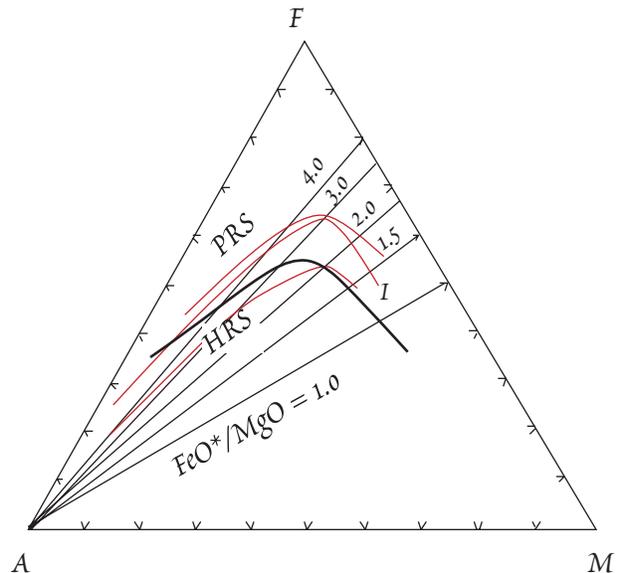

Figure 12.7 AFM ($A=K_2O+Na_2O$, $F=FeO+MnO$, $M=MgO$) diagram illustrating the difference between tholeiitic and calc-alkaline lava series of island arcs. Calc-alkaline rocks plot below the heavy line, tholeiites above. PRS is Kuno's pigeonite rock series; HRS is Kuno's hypersthene rock series. I is the Thingmuli series of Iceland. After Carmichael, et al. (1973).

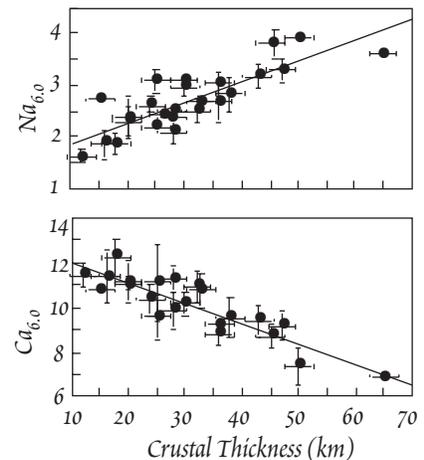Figure 12.8 Correlation of $Ca_{6.0}$ and $Na_{6.0}$ with crustal thickness in island arc basalts. $Ca_{6.0}$ and $Na_{6.0}$ are the CaO and Na_2O concentrations after correction for fractional crystallization to 6.0 MgO. From Plank and Langmuir (1988).

on oxygen fugacity. Oxygen fugacity is higher in IAV because of the higher water contents. IAV are enriched in water as well as other volatiles compared to MORB and at least some OIB (e.g., Hawaii). Island arc volcanics may also have higher CO_2/H_2O ratios than MORB (Perfit et al., 1980).

Plank and Langmuir (1988) investigated the factors that control the 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 12.8). They argued that crustal thickness determines the height of the mantle column available for 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 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 $Ca_{6.0}$ in the parental magmas.

TRACE ELEMENT COMPOSITION

The differences in trace elements between island arc volcanics and those from other tectonic environments are probably 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 LRE depleted to LRE enriched (Figure 12.9). IAV are virtually never as LRE depleted as MORB, but absolute REE concentrations are, however, 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. The significance of the Ce anomalies remains uncertain.
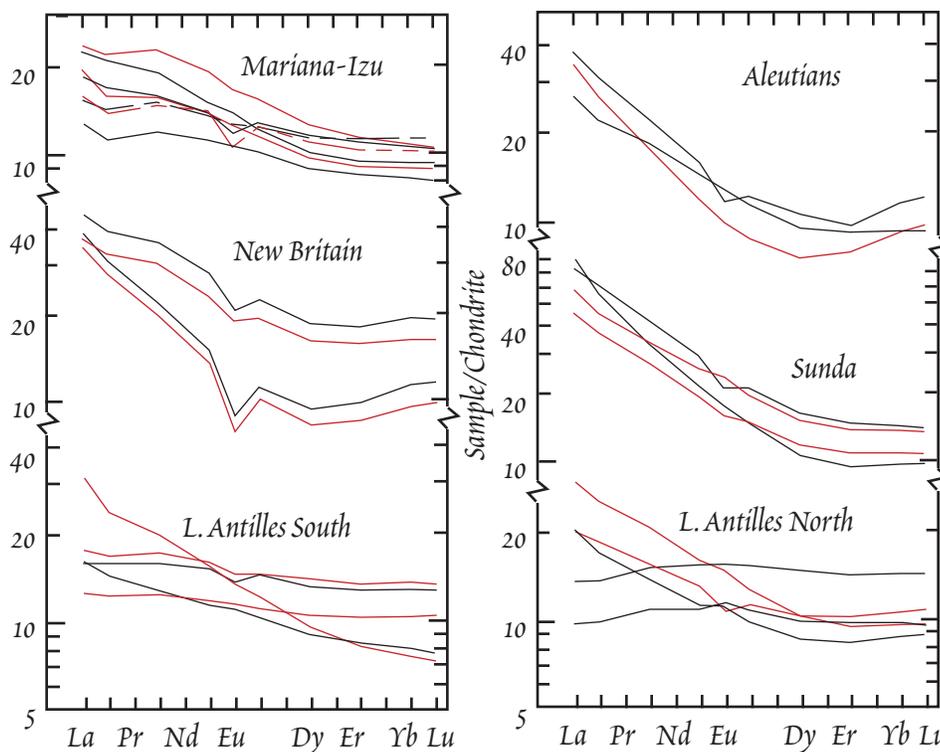

Figure 12.9. Rare earth patterns of some typical island arc volcanics. From White and Patchett (1984).
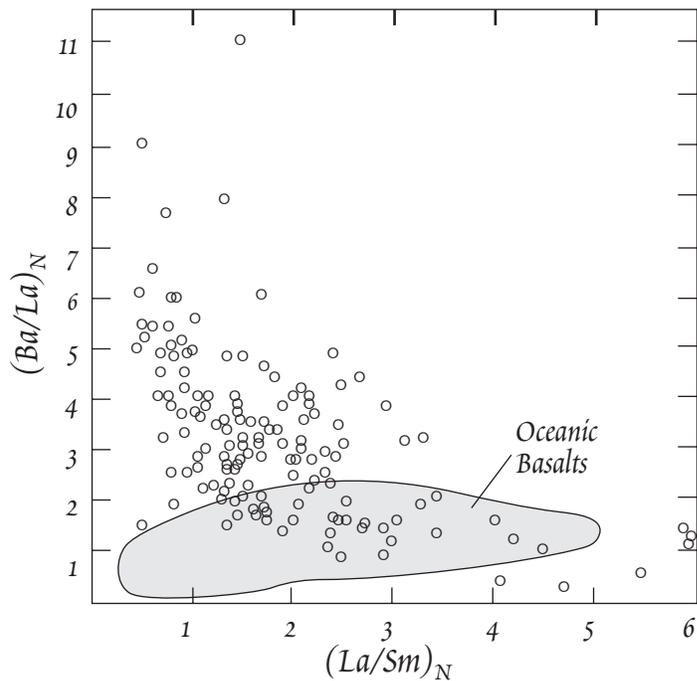
Figure 12.10. Relative alkali-alkaline earth enrichment of IAV illustrated by plotting the $(Ba/La)_N$ ratio vs. the $(La/Sm)_N$ ratio. The subscript N denotes normalization to chondritic values. From Perfit et al. (1980).

Ce anomalies occur in sediment, so there is the immediate suspicion that the anomalies in IAV could be inherited from subducted sediment.

Island-arc volcanics are 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 12.10, 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.

Island-arc volcanics tend to be poor in the so-called high-field-strength elements (HFS), i.e., those elements with charge of +4 or +5 (Chapter 7). While Nb and Ta are almost invariably depleted in arcs, Zr, Hf, and Th are not. It would be better to speak of Nb and Ta depletion. This is illustrated in Figure 12.11.

Figure 12.12 is a spider diagram summarizing the trace element differences between island arc volcanics and

MORB. To summarize, IAV may be either light-rare-earth enriched or light-rare-earth depleted. They generally are enriched relative to MORB in the alkalis and alkaline earths. Significantly, these are the elements most enriched in sediments, and the most soluble elements. Relative to MORB, IAV tend to be depleted in Nb, and Ta, and sometimes in Ti, Hf, and Zr. These are the elements least enriched in sediments, and are generally highly insoluble in aqueous solutions because of their high ratios of ionic charge to radius (Z/r).
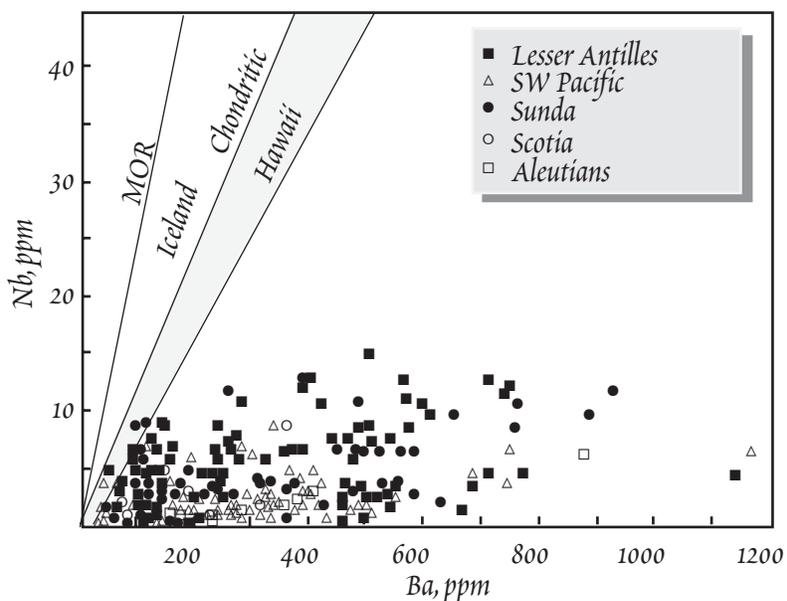

Figure 12.11. Low Nb concentrations of IAV compared to MORB and OIB illustrated by plotting Nb vs. Ba. From Perfit et al. (1980).
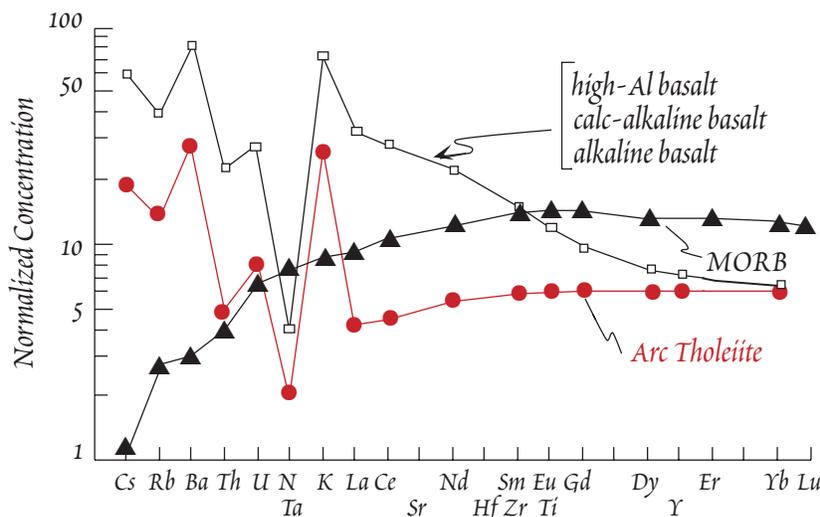
Figure 12.12. Spider diagram comparing typical incompatible element contents of island arc volcanics and MORB. Note the relative enrichment in alkalis and alkaline earths and the depletion in Ta in the island arc volcanics. After Sun (1980).

Isotopic Composition and Sediment Subduction

Island arcs overlie subduction zones, which raises the obvious question of the degree to which subducting oceanic crust and sediment might contribute to island arc magmas. These questions have been most successfully addressed through isotope geochemistry.

Sr isotope ratios are generally higher, and Nd isotope ratios generally lower than in MORB, with $^{87}Sr/^{86}Sr$ ratios around 0.7033 and ε_{Nd} of +8 being fairly typical of intraoceanic IAV (Hawkesworth et al., 1991). Though there is considerable overlap with oceanic basalts (MORB and
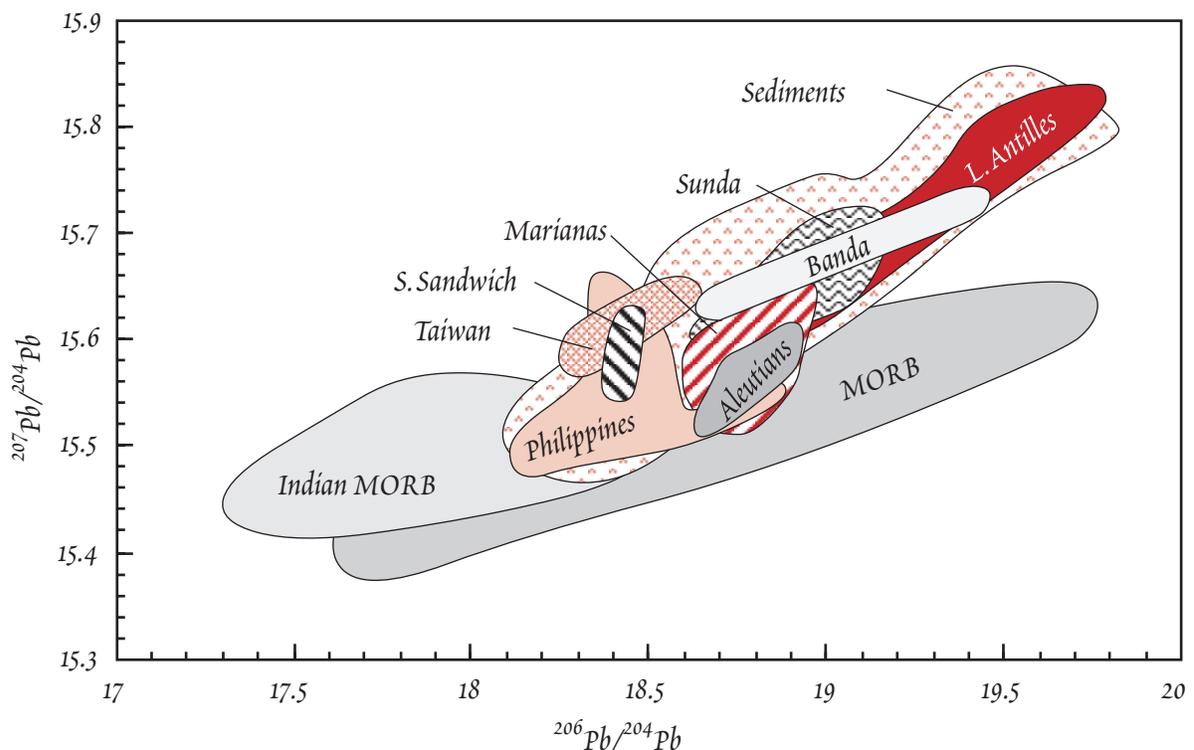
Figure 12.13. Pb isotope ratios in island arc volcanics. Fields for the South Sandwich, Lesser Antilles, Aleutians, Marianas, Philippines, Taiwan, Banda and Sunda arcs are shown and compared with fields for Atlantic and Pacific MORB (field labeled MORB) and Indian Ocean MORB (IMORB), and modern marine sediments.

OIB), there is a slight tendency for IAV to have higher Sr isotope ratios for a given Nd isotope ratio and hence plot to the right of the oceanic basalt array on a Nd–Sr isotope ratio plot. This shift to higher Sr isotope ratios appears to result from a contribution of subducted oceanic crust to IAV magma sources. This conclusion is based on the observation that during weathering and hydrothermal alteration of the oceanic crust, isotopic exchange with seawater shifts Sr isotope ratios of the oceanic crust to higher values. Nd isotope ratios, are virtually unaffected by these processes because of the extremely low concentration of Nd in seawater.

$^{206}Pb/^{204}Pb$ isotope ratios overlap values of oceanic basalts, but generally having a more restricted range. $^{207}Pb/^{204}Pb$ ratios are typically higher IAV than most oceanic basalts. They tend to form steeper arrays on $^{207}Pb/^{204}Pb$–$^{206}Pb/^{204}Pb$ plots, and overlap the field of marine sediments (Figure 12.13). For most island arcs, Pb isotope ratios in the arc volcanics lie between sediment local to the arc and the MORB field (Karig and Kay, 1980). We pointed out in the last chapter that Indian Ocean MORB have lower $^{206}Pb/^{204}Pb$ and higher $^{207}Pb/^{204}Pb$ than do MORB from the Atlantic and Pacific. This presumably reflects a difference in the isotopic composition between the

Figure 12.14. Pb isotope ratios in volcanics of the Lesser Antilles island arc and on the Atlantic Plate subducting beneath it. Contours show the $^{206}Pb/^{204}Pb$ ratios in the sediment, which increases from north to south due to the increasing contribution of Orinoco River sediment. The average $^{206}Pb/^{204}Pb$ for each island, which is shown beside the island, also increases from south to north. From White and Dupré (1986).

upper mantle beneath the Atlantic and Pacific on the one hand and the Indian on the other. Interestingly, the Pb isotope arrays for Indian and southwestern Pacific arcs (Sunda, Banda, Philippines, and Taiwan) are elongate toward the Indian Ocean MORB field rather than Atlantic and Pacific MORB. On the whole then, Pb in island arc magmas appears to be a mixture Pb from local sediment and local upper mantle.

The Lesser Antilles arc illustrates this particularly well. The Lesser Antilles arc lies on the Caribbean Plate just to the north of South America. The Orinoco River, which drains the Archean Guiana Highland, delivers sediment that contains particularly radiogenic Pb to the front of the arc. As a result, the Pb isotope ratios in sediments of the Demerara Abyssal Plain decrease systematically from south to north (Figure 12.14). A similar pattern of decreasing Pb isotope ratios can be seen in the volcanics of the arc, apparently reflecting the changing isotopic composition of the sediment being subducted.

Pb isotope ratios are particularly sensitive to the presence of subducted sediment because the concentration of Pb in sediment is so much higher, well over two orders of magnitude, than in the mantle. In a mixture of sediment and mantle, the Pb isotope ratios of the mixture are virtually identical to those of the sediment when as little as 2 to 3% sediment is present in the mixture. This is not true of Sr and Nd isotope ratios.

^{10}Be is an even more sensitive indicator of the presence of sediment in IAV magma sources than Pb, because it is present in young sediment, but entirely absent from the mantle. As we found in Chapter 8, ^{10}Be is a cosmogenic isotope; it is produced in the atmosphere by cosmic ray spallation of ^{14}N. It has a half-life of only 1.5 million years, so we would not expect to find significant amounts of ^{10}Be in the Earth's interior; any created before the solar system formed has long since decayed away. ^{10}Be created in the atmosphere is purged by rainfall and is strongly absorbed by clays of sediment and soil.
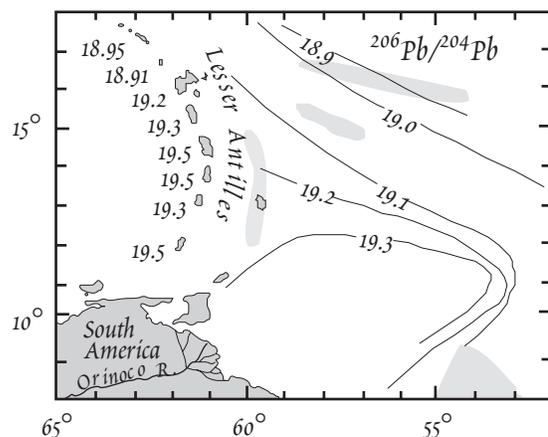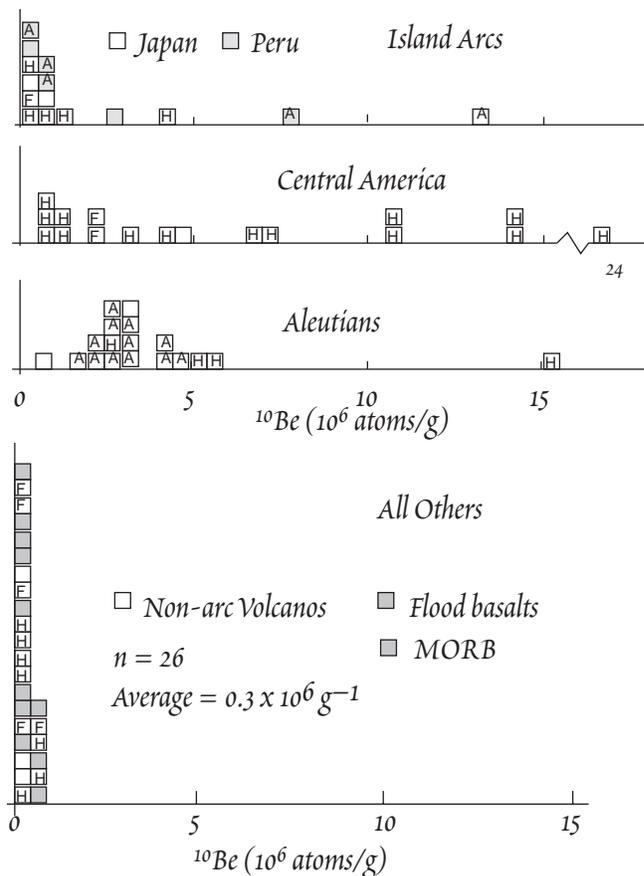
Figure 12.15. [10]Be in arc and non-arc lavas. "A" indicates sample from active volcano, "H" a historic eruption, and "F" (fresh) indicates collected during eruption. From Tera et al., 1986.

Workers at Carnegie Institution of Washington turned to [10]Be when they were seeking a means of determining subduction rates. They decided to attempt to determine the amount of [10]Be in island arc volcanics on the assumption that sediments containing [10]Be were subducted, and by comparing the amount in arc volcanics with the amount of sediment, they hoped to determine how much had decayed away, and thereby how much time had elapsed since the sediment left the surface. The problem proved to be too complex to determine subduction rates quantitatively. However, in the course of this attempt, they produced by far the best evidence that sediment is indeed subducted in island arcs. Figure 12.15 compares the amount of [10]Be in arc lavas with that in non-arc lavas. [10]Be has not been found in measurable quantities (10^6 atoms per gram) in non-arc lavas, but has been found in lavas of some arcs. The interpretation is that the [10]Be originates from sediment subducted to the magma genesis zone. The absence of [10]Be in other arc lavas does not mean sediment is not subducted in those arcs. Only very young sediment, < 10-15 Ma, will contain appreciable amounts of [10]Be, so if the uppermost sediment is removed in an accretionary wedge, no [10]Be will be delivered to the magma genesis zone even though deeper, older sediment is being subducted.

Figure 8.36 showed that IAV have higher and more variable $\delta^{18}O$ than either MORB or OIB. This may also be attributed to a contribution of subducted oceanic crust and sediment. Indeed, as we have said before, oxygen isotope ratios can be changed only at or near the surface of the Earth, so this is the only way the $\delta^{18}O$ of IAV can be readily explained.

MAGMA GENESIS IN SUBDUCTION ZONES

Now that we have an overview of the composition of arc magmas, let's consider in more detail the processes that lead to the unique geochemistry of island arc magmas. Figure 12.16 summarizes petrogenesis in the subduction zone environment.

Most geochemists and petrologists believe that arc magmas are produced primiarily within the mantle wedge[‡] (e.g., Hawkesworth et al., 1991; Kay and Kay, 1994). The evidence for this is: (a) Primary arc magmas differ only slightly in their major element chemistry from oceanic basalts, which are definitely mantle-derived. The andesitic nature of many arc magmas probably results from fractionation crystallization in a crustal or subcrustal magma chamber. It is therefore most

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[‡] The *mantle wedge* is the part of the mantle overlying the subducting slab; because the slab descends at an angle, this region in triangular, or wedge-shaped.
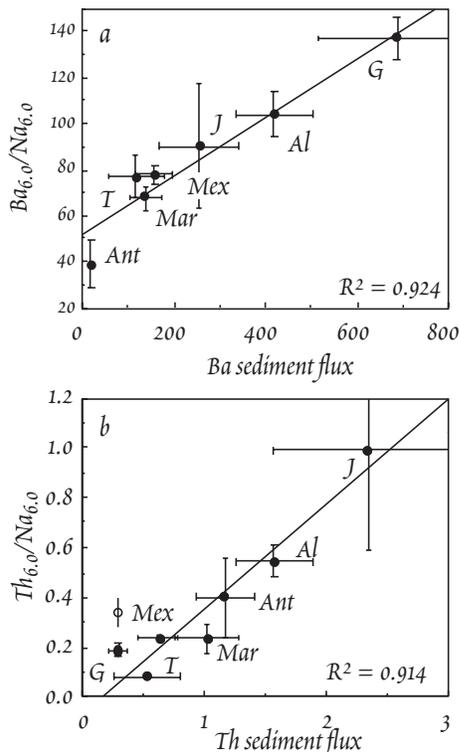
Figure 12.16. Cross-section of a subduction zone illustrating island arc magma genesis.

likely they are partial melts of peridotite rather than subducted basalt or sediment. (b) Radiogenic isotopic and trace element systematics generally allow only small fraction of sediment (generally a few percent or less) to be present in arc magma sources. Relatively high $^3He/^4He$ ratios in arc lavas confirm this. (c) Rare earth patterns of island arc magmas are consistent with these magmas being generated by partial melting of peridotite, but not by partial melting of eclogite, which would be the stable form of subducted basalt at 100 km depth (the subducting lithosphere is typically located at about 100 to 120 km depth beneath island arc volcanos). Because the heavy rare earths partition strongly into garnet (e.g., Figure 6.15), melts of eclogite should show steep rare earth patterns, with low concentrations of the heavy rare earths. This is not generally the case. Rare high magnesium andesites, sometimes called "adakites" (after a well documented occurrence on Adak Island in the Aleutians) with steep rare earths patterns may represent exceptions to this rule and may indeed by generated by small extents of melting of subducted oceanic crust (Kay, 1978; Defant and Drummond, 1990). It is possible that such "slab melts" were more common several billion years ago. We discuss this possibility later in the chapter. Finally, we should point out that some scientists believe arc magmas are indeed generated in the subducting slab (e.g., Brophy and Marsh, 1986).

We have seen that isotope systematics, particularly Pb and ^{10}Be, provide evidence of subducted sediment in the sources of most arcs. Subducted sediment appears to influence the trace element compositions of arc lavas as well. Plank and Langmuir (1993) carried out careful study of the composition of volcanics from 8 arcs and the sediments being subducted beneath them. By analyzing representative samples from the sediments and considering the proportions of sediment types being carried beneath the arc, they estimated the flux of elements being carried by sediment beneath the arc. They found they could relate the degree of enrichment of most incompatible elements to the sediment flux of that element. For example, the Ba/Na and Th/Na ratio (after correction for fractional crystallization to 6% MgO) correlate strongly with the Ba and Th sediment fluxes (Figure 12.17). Different arcs are enriched to different degrees in these elements: for example, the Lesser Antilles arc has moderate Th/Na ratios but low Ba/Na ratios. The difference appears to be due to the difference in the sediment flux.

The trace element geochemistry of island arc magmas cannot, however, be explained solely by partial melting of simple bulk mixtures of mantle, sediment and subducted oceanic crust. In particular, the characteristic enrichment of the alkalis and alkaline earths cannot be accounted for in this way. This is illustrated in Figure 12.18, which compares the observed enrichment of Lesser Antilles low-K basalts in incompatible elements with the enrichment predicted assuming the source was a mixture of depleted mantle and sediment. White and Dupré (1986) calculated the fraction of sediment in the mixture from Nd isotope ratios of the basalts, and assumed simple batch melting. This simple model

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Figure 12.17. Relationship between $Ba/Na_{6.0}$ and $Th/Na_{6.0}$ in volcanics from 8 arcs and Ba and Th sediment flux beneath those arcs. Horizontal bars represent uncertainty in the amount of sediment subducted; vertical bars reflect the variance of the ratio in the arc volcanics. G is Guatemala, M: Mexico, J: Java, T: Tonga, Mar: Marianas, Al: Aleutians, Ant: Lesser Antilles. From Plank and Langmuir (1993).

rine basalts from the Marianas. As mentioned above, water concentrations correlated with those of mobile trace elements (as well as those of several less mobile, but incompatible trace elements, such as La). However, water concentrations correlated inversely with the concentrations of moderately incompatible elements, such as Ti, Zr, and Na. These observations at first seem contradictory. To explain them, Stolper and Newman (1994) developed a model in which a mantle source consisting of a mixture of depleted mantle (i.e., a composition that would melt to produce average MORB) and an H_2O-rich component melts to varying degrees. Their calculated H_2O-rich

predicted the concentrations of the rare earths and Th reasonably well, but the enrichment of Pb, Cs, Rb, U, K, Ba, and Sr was greater than predicted. The elements that are over-enriched are those most soluble in aqueous solution, so the excess abundance of these "mobile" elements suggests they are enriched due to preferential transport in aqueous fluids. Particularly strong enrichment of these elements is characteristic of virtual all arc magmas, not just those of the Lesser Antilles. Thus it is widely believed that water released by dehydration of the subducting oceanic crust and sediment transports mobile elements from the slab to the overlying mantle wedge. This idea is supported by the positive correlation observed between concentrations of these elements and water contents of submarine basalts from the Marianas (Stolper and Newman, 1994).

A long standing and key question is why magmas are generated at all in an area where cold lithosphere is descending. Decades of experimental work has shown that water lowers the solidus of rock and leads to enhanced melting at any given temperature compared to dry conditions, hence water released by the subducting slab may induce melting in the wedge. The best evidence of this comes from work of Stolper and Newman, 1994) on subma-
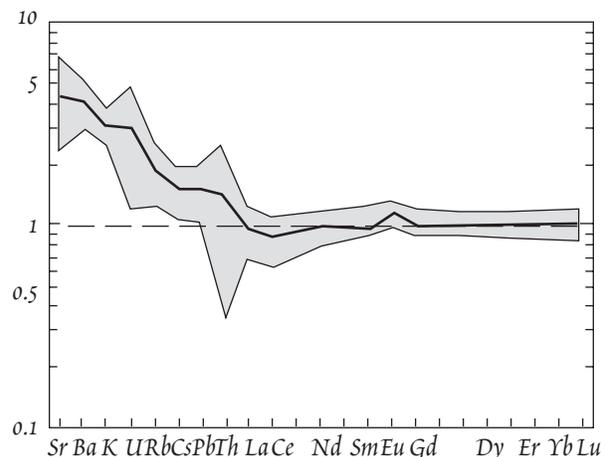

Figure 12.18. Ratio of observed enrichment of incompatible elements in Lesser Antilles low-K basalts compared to enrichment calculated from a sediment-depleted mantle mixing model based on Nd isotopic composition. Enrichment of the rare earths and Th can be accounted for by this model, but the enrichment of Pb, Cs, Rb, U, K, Ba, and Sr is greater than predicted, probably due to preferential transport of these elements in fluids. Gray area is 1 standard deviation of the basalts used in the average. From White and Dupré (1986).

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component was strongly enriched in incompatible and mobile elements, including Na. To explain the inverse correlation between Na and H_2O in the basalts, they found that the extent of melting must vary inversely with the amount of H_2O-rich component in the source mixture. The smallest extents of melting (about 5%) occur in H_2O-poor sources and give rise to incompatible element-poor basalts, while the highest extents (over 20%) give rise to H_2O and incompatible element-rich basalts. The large extents of melting producing that latter leads to their being poor in elements such as Na and Ti, which are only moderately incompatible. Thus Stolper and Newman's results suggest water induces melting in the mantle wedge.

The origin of the Nb-Ta depletion remains unclear, though there are a variety of ideas: (a) In part, this depletion may reflect the low abundance of these elements in sediments, but it seems unlikely this alone can account for this depletion. (b) The high charge to radius ratios of these elements makes them relatively insoluble in the aqueous solutions, and hence they may be transported to the mantle wedge less efficiently. (c) They may be retained in specific phases, such as ilmenite, stabilized by unusual conditions or composition of the slab or the web. (d) Finally, these elements may have the same abundances in the mantle wedge as in the source of MORB, but higher degrees of melting involved in the generation of IAV compared to MORB lead to lower abundances in the former. These possibilities are not mutually exclusive; several factors may contribute to Nb-Ta depletion.

Why island arc magmas are more silicic and appear to have experience more fractional crystallization than oceanic basalts is also unclear. Again, there are several possibilities: (a) Retardation of plagioclase crystallization and early onset of oxide crystallization due to high concentrations of water in IAV may drive island arc magmas to more silicic compositions than water-poor magmas such as MORB. (b) Island arc crust is generally thicker than oceanic crust, providing a greater opportunity for stagnation and fractional crystallization. This will certainly be true of continental margins such as the Andes. It would be particularly difficult for basaltic magmas to ascend through such thick, low density continental crust. (c) Subduction zones are fundamentally compressional environments, which may make it more difficult for magmas to ascend to the surface, again causing magmas to stagnate and crystallize. (d) Primary magmas may be more silicic and less mafic, though not necessarily andesitic, due to generation under "wet" conditions. Again, these possibilities are not mutually exclusive.

CRUST–MANTLE INTERACTION: ASSIMILATION

Some of the characteristics of island arc magmas that have been ascribed to sediment subduction can also be produced when mantle-derived magmas assimilate continental crust. When mantle-derived magmas encounter continental crust, the basalt heats the crust. If temperatures are high enough, the crust may melt. The temperature reached will depend on the size of the magma body: a relatively thin dike will cause partial melting only very locally; a larger body will cause partial melting at greater distances (Figure 12.19). The melt produced can be assimilated by the intruding magma. Assimilation of crust is a pervasive phenomenon and affects most, though certainly not all, magmas erupted through continental crust, both in subduction and other tectonic environments. For this reason, we need to devote special attention to the problem.

GEOCHEMISTRY OF TWO-COMPONENT MIXTURES

In the simplest case, the resulting magma becomes a two component mixture of the crustal and mantle melts. If homogenization in not complete, there will be some compositional variation. If we plot the concentration of any two elements in different samples of this mixture against each other, they must lie on a straight line between the two end members. However, if we plot ratios of elements, or isotope ratios, they need not lie on a straight line. Indeed, in the general case they do not; rather they will define a curve whose equation is:

$$Ax + Bxy + Cy + D = 0 \qquad\qquad 12.1$$

where x and y are the variables of the abscissa and ordinate respectively (Langmuir et al., 1978). If end members are designated 1 and 2 and have ratios x_1 and y_1, and x_2 and y_2 respectively, then
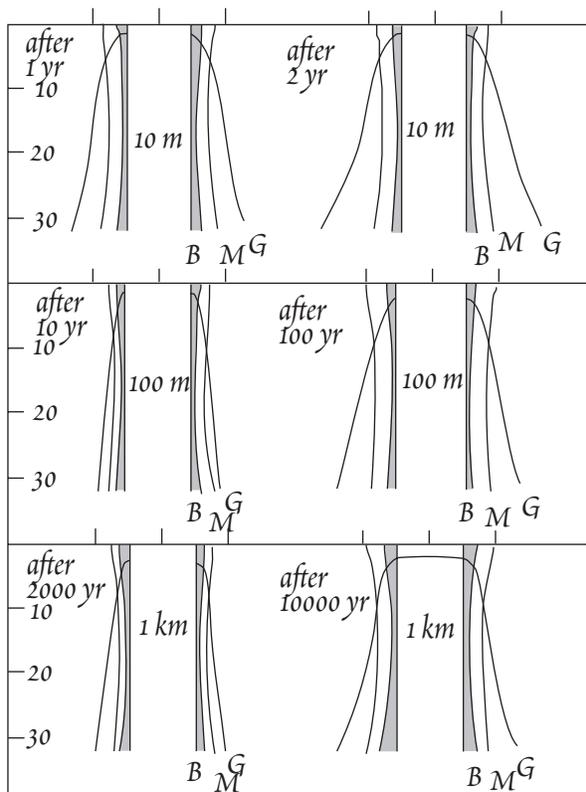
Figure 12.19. Temperatures as a function of time and distance surrounding basaltic dikes of various thickness. Lines B, M, and G are the temperatures of biotite breakdown, muscovite breakdown and granite minimum melting respectively. Gray area is region of partial melting. From Patchett (1980).

$$A = a_2b_1y_2 - a_1b_2y_1 \qquad 12.2$$

$$B = a_1b_2 - a_2b_1 \qquad 12.3$$

$$C = a_2b_2x_1 - a_1b_2x_2 \qquad 12.4$$

$$D = a_1b_2x_2y_2 - a_2b_1x_1y_1 \qquad 12.5$$

where a_i is the denominator of y_i and b_i is the denominator of x_i. The curvature of the mixing line will depend on the ratio r:

$$r = a_1b_2/a_2b_1 \qquad 12.6$$

The greater the value of r is, the greater the curvature. Only in the special case were $r=1$ is the line straight. This is illustrated in Figure 12.20. This result is completely general and applies to mixing of river water and seawater, etc. as well as mixing of magmas.

Taking the example of $^{143}Nd/^{144}Nd$ versus $^{87}Sr/^{86}Sr$, the curvature depends on the ratio of $(^{144}Nd_1{}^{86}Sr_2)/(^{144}Nd_2{}^{86}Sr_1)$. Since to a very good approximation the amount of ^{144}Nd and ^{86}Sr are proportional to total Nd and Sr respectively, r is approximated by Nd_1Sr_2/Nd_2Sr_1. If we express this ratio as $r = (Nd/Sr)_1/(Nd/Sr)_2$ we see that the curvature depends on the ratio of the Nd/Sr ratio in the two end members. In mantle-derived rocks Sr/Nd does not deviate greatly from 10, so mixing curves will be close to straight lines. In crustal rocks and sediments, deviations fr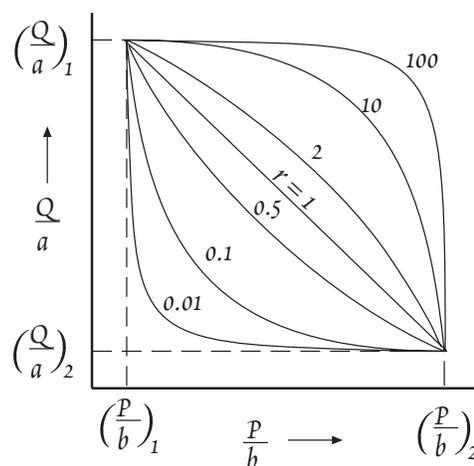om $r = 1$ are more likely and curved mixing lines therefore more common. Note that on a $^{207}Pb/^{204}Pb$—$^{206}Pb/^{204}Pb$ plot, mixing curves will always be straight lines because the denominators are the same (i.e., $a = b = {}^{204}Pb$).

Two component mixtures will also form straight lines on isochron plots (e.g., $^{87}Sr/^{86}Sr$—$^{87}Rb/^{86}Sr$ such as Figure 7.6), because the denominators are the same. Thus mixing lines can be mistaken for isochrons and visa versa. One way to distinguish the two is a ratio-element plot. A ratio-element plot, for example $^{87}Sr/^{86}Sr$ vs. Sr, will also be a curve described by equation 12.1, but a ratio plotted against the inverse of the denominator, for example $^{87}Sr/^{86}Sr$—$1/Sr$, will be a straight line. Such a plot can be a useful discriminator between isochrons and mixing lines because only in the latter case will $^{87}Sr/^{86}Sr$—$1/Sr$ necessarily define a straight line (Figure 12.21). Again, this result is completely general, and while the general prin-

Figure 12.20. Plots of ratios of elements or isotopes, Q/a versus P/b for mixing of end members 1 and 2. The numbers along the curves are the values for r. From Langmuir et al. (1978).
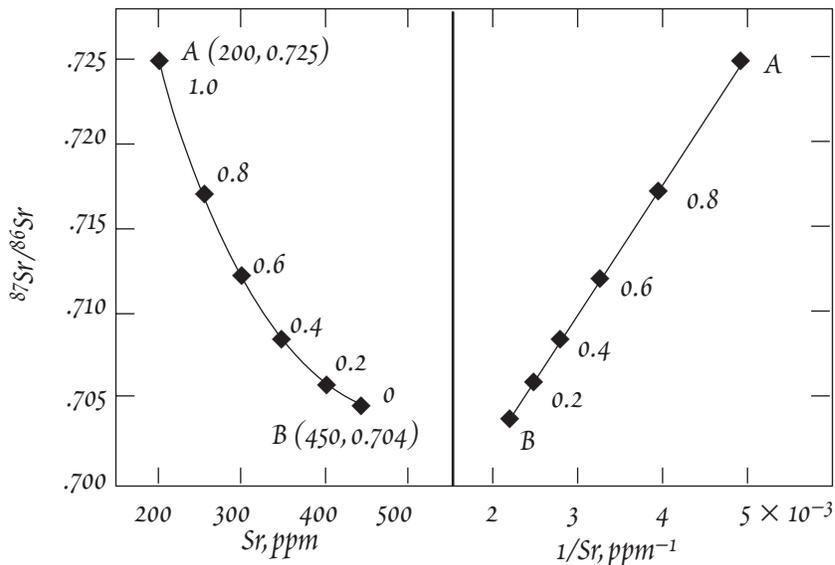
Figure 12.21. Mixing hyperbola formed by components A and B. After Faure (1986).

cipals have been illustrated with isotope ratios, they apply equally well to ratios of concentrations.

When a magma or series of magmas appear to reflect mixing, we are often faced with having to decide whether (1) two mantle-derived magmas are mixing, (2) two distinct mantle sources are mixing before melting, or (3) a mantle-derived magma is mixing with assimilated crust. In case (2), plots involving an elemental concentration will not fall on mixing lines because partial melting and fractional crystallization will change element concentrations. Isotope ratios will not be changed by magma genesis so a plot of two isotope ratios will describe a mixing line in case (2) as well as cases (1) and (3). As we pointed out in Chapter 9, stable isotopes are particularly useful in recognizing assimilation. This is so because mantle materials have comparatively uniform stable isotope ratios and crustal rocks very often have stable isotope ratios that are different from mantle values.

Recognizing crustal assimilation in subduction zones magmas can be particularly difficult because many of geochemical effects characteristic of crustal assimilation can also result from the presence of subducted sediment component in such magmas. For example, the $\delta^{18}O_{SMOW}$ of sediment is generally greater than +15 whereas the mantle value is about +5.6. Island arc magmas derived from a source having a component of subducted sediment will thus have slightly $\delta^{18}O$ higher than mantle values. However, high $\delta^{18}O$ can also result from assimilation of crust during magma ascent. Similarly, elevated values of $^{87}Sr/^{86}Sr$ could result from either the subducted sediment in the magma source of assimilation of continental crust.

By combining O isotope analyses with radiogenic isotope analyses, it is possible to distinguish between these two processes. Virtually all silicate rocks, including sediments, magmas, and peridotite, have similar O concentrations (generally close to 50%), whereas concentrations of the radiogenic elements Sr, Nd, Hf, Pb, etc. vary widely. In particular, since these elements (except Os) are incompatible to some degree, their
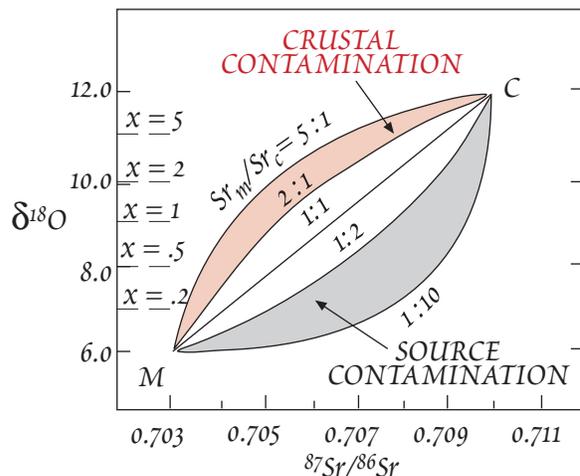

Figure 12.22. O—Sr isotope plot showing the difference is mixing curves produced by contaminating magma with crust ("crustal contamination") as opposed to contaminating the magma source with subducted material ("source contamination"). x is the fraction of end member "C" (crust or subducted sediment) in the mixture. After James (1981).

concentrations in magmas will be higher than in the mantle. Many island arc magmas have Sr concentrations that are greater than those typical of continental crust, but the mantle has much lower concentrations of Sr than sediment. This means mixing curves for sediment-mantle mixing will look very different from for magma-crust mixing.

In the case of sediment-mantle mixing, the value of $r = Sr_M/O_M/Sr_S/O_S$ (where the subscripts M and S denote the concentrations in mantle and sediment respectively) will be typically much less than 1. In the case of magma-crust mixing, the value of $r = Sr_M/O_M/Sr_C/O_C$ (where the subscripts M and C denote the concentrations in magma and crust respectively) will typically be 1 or greater. On a plot of $\delta^{18}O$ vs. $^{87}Sr/^{86}Sr$, this produces a convex curve in the case of assimilation and a concave curve in the case of subducted sediment mixing with mantle (Figure 12.22).

Assimilation–Fractional Crystallization

As we pointed out in Chapter 9, assimilation will inevitably be accompanied by fractionation crystallization, because heat released during crystallization provides the energy for melting surrounding crust. Where fractional crystallization also occurs, assimilation will not produce simple mixing curves. Let's consider this in more detail.

The change in concentration of an element, C, in a magma undergoing assimilation and fractional crystallization (AFC) is given by:

$$C_m/C_m^o = F^{-z} + \left(\frac{R}{R-1}\right)\frac{C_a}{zC_m^o}(1 - F^{-z}) \quad 12.7$$

where C_m is the concentration in the magma, C_m^0 is the original concentration in the magma, F is the mass of magma remaining as a fraction of the original magma mass, R is the ratio of mass assimilated to mass crystallized, D is the solid-liquid partition coefficient of the element, and C_a is the concentration in the assimilated material, and

$$z = \frac{R + D - 1}{R - 1} \quad 12.8$$

(this treatment follows DePaolo, 1981a). These equations are invalid if R = 1, but as we found in Chapter 9, R will generally be less than 1. The variation of concentration as a function of F for R = 0.2 and various values of D is shown in Figure 12.23.

The variation of an isotope ratio in assimilation-fractional crystallization (AFC) is given by:

$$\varepsilon_m = \frac{\frac{R}{R-1}\frac{C_a}{z}(1 - F^{-z})\varepsilon_a + C_m^0 F^{-z}\varepsilon_0}{\frac{R}{R-1}\frac{C_a}{z}(1 - F^{-z}) + C_m^0 F^{-z}} \quad 12.9$$

where ε_m is the isotope ratio in the magma, ε_a is the isotope ratio in the assimilated material, ε_0 is the isotope ratio in the original magma and other variables are as defined above. We derived an equation for the behavior $\delta^{18}O$ during assimilation in Chapter 9. That equation (8.67)
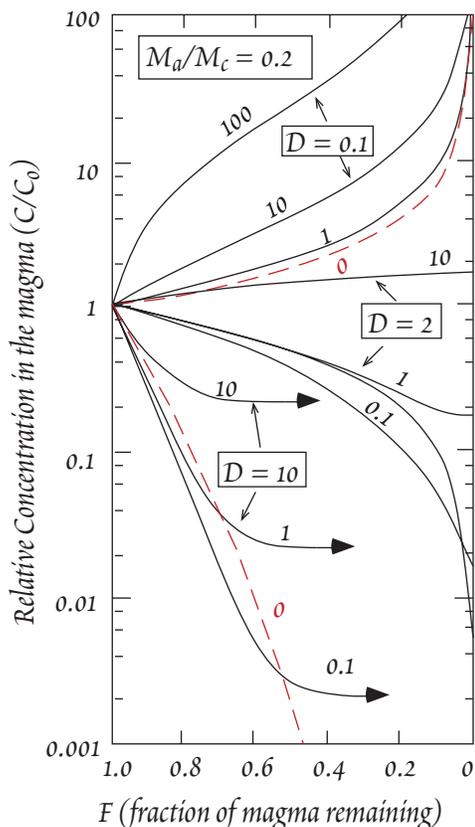

Figure 12.23. Variation of concentration during assimilation-fractional crystallization. Short dashed red lines are for simple fractional crystallization. Numbers on the curves refer to values of C_a/C_m^o, the ratio of the concentration in the assimilant to the original concentration in the magma. After DePaolo (1981a).
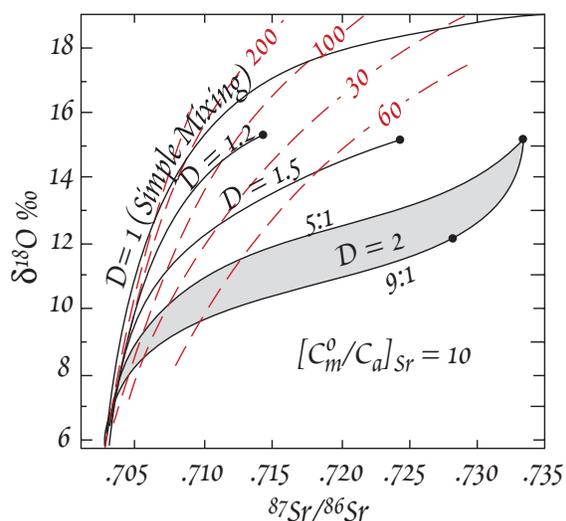
Figure 12.24. Variation of $\delta^{18}O$ with $^{87}Sr/^{86}Sr$ during AFC for a magma with an initial $\delta^{18}O$ = 5.7 and $^{87}Sr/^{86}Sr$ = 0.703, and an assimilant with $^{87}Sr/^{86}Sr$ = 0.735 and $\delta^{18}O$ = +19. All curves are for R = 0.2 (5:1), except for one with D = 2 for which R = 0.11 (labeled 9:1). dashed lines are calculated Sr concentrations (ppm) assuming an initial concentration of Sr in the magma of 500 ppm. In the case where D = 1, the problem simplifies to one of simple mixing. From Taylor (1980).

is somewhat simpler because the concentration of oxygen does not vary. AFC will produce curves on plots of $\delta^{18}O$ vs. radiogenic isotope ratios that can be quite different from the simple mixing curves in Figure 12.23. Figure 12.24 shows some examples of such curves for $\delta^{18}O$ vs. $^{87}Sr/^{86}Sr$.

COMPOSITION OF THE CONTINENTAL CRUST

The continental crust is extremely heterogeneous, thus 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 borehole, drilled by the Russians in the Kola Peninsula has reached only 12 km and the average thickness of the continental crust is about 35 km. Therefore, 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), and Shaw et al. (1986). Two very recent estimates are those of Rudnick and Fountain (1995) and Wedepohl (1995). These estimates are not entirely independent. For example, Weaver and Tarney (1984) rely on an early version of Taylor and McLennan's upper crustal estimate; Rudnick and Fountain (1995) also rely on Taylor and McLennan's upper crustal estimate. 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), Rudnick and Fountain (1995), and Wedepohl (1995). In doing so, we want both to learn of the composition of the crust and to understand how these estimates are made.

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

TABLE 12.3. ABUNDANCE OF IGNEOUS AND SEDIMENTARY ROCKS IN THE UPPER CRUST

Plutonic Rocks	Volume %	Sedimentary Rocks	Volume %
Granite, Granodiorite	77	Shales	72
Quartz Diorite	8	Carbonates	15
Diorite	1	Sandstones	11
Gabbros	13	Evaporites	2
Syenites, anorthosites, peridotites	1		

From Taylor and McLennan (1985).

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 (i.e., 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 Upper Crust

Historically, three approaches to estimating the composition of the upper continental crust have been used. The first is to estimate the volume of various rock types and then use typical or average compositions of each to derive a compositional estimate. Table 12.3 gives such an estimate of the relative volumes of various igneous and sedimentary rocks in the upper crust. Continental sediments constitute about 8% of the mass of the crust; if pelagic sediments are added the total sediment mass is about 11%.

A second approach 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, 1967; Eade and Fahrig, 1971; Shaw et al., 1986; Wedepohl, 1995). Studies of these kinds consistently produce an average upper crustal composition similar to that of granodiorite. This is encouraging since 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, as can be seen in Figure 12.25.

A third 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 melt-water 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.
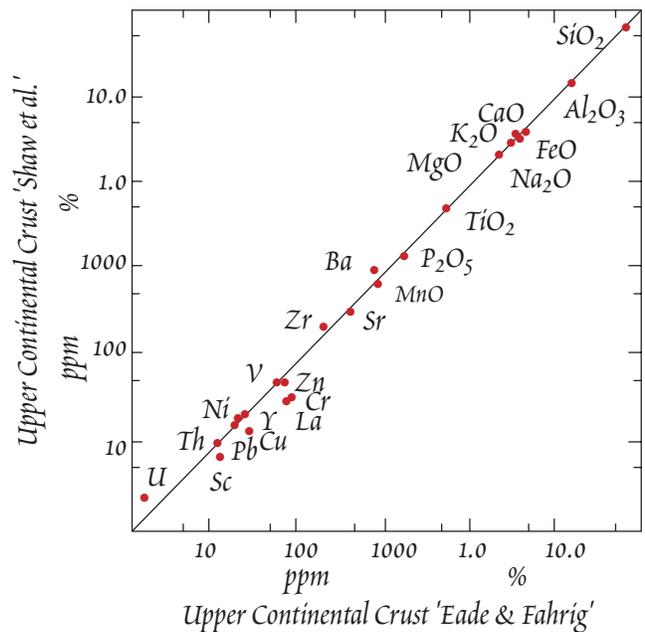

Figure 12.25. Comparison of estimates of the average composition of the upper crust by Eade and Fahrig (1971) and Shaw (1967). Both were based on studies of the Canadian shield, but different areas. From Taylor and McLennan (1985).
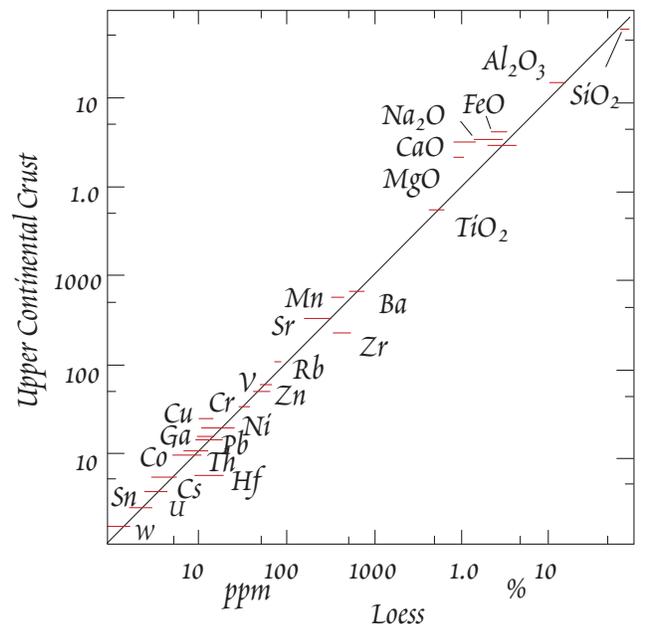

Figure 12.26. Comparison of elemental concentrations in loess with estimated upper crust. From Taylor and McLennan (1985).

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One advantage of sediments over glacial material is that whereas most glacial deposits are of Pleistocene age (but there are various 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.

Figure 12.27. Rare earth patterns of Post-Archean Australian Shale (PAAS) composite, the North American Shale Composite (NASC) and the European Shale (EC) composite. From Taylor and McLennan (1985).

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. This is illustrated in Figure 12.26. Loess is enriched in SiO_2, Hf, and Zr relative to estimated concentrations in the upper crust. This reflects the enrichment of loess in mechanically and chemically stable minerals, such as quartz and zircon, because the lighter clays are carried further from their site of origin by wind and water. Loess is also depleted in Na 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 all the rare earths are concentrated in the clay fraction, which ultimately form 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 12.27, which compares three shale composites from three continents. Because of these properties of the rare earths, S. R. Taylor and colleagues at the Australian National University used them as a point of departure for estimating the composition of the upper continental crust.

Though rare earth patterns in shales are representative of their sources, their absolute concentrations are not. Because some elements are lost to the sand fraction and others to solution (and ultimately to chemical sediments such as evaporites and carbonates), the REE are enriched in shale by about 20%. Thus Taylor and McLennan (1985, 1995) reduced REE (and Sc, Y, and Th) concentrations by 20%, in making their estimate of upper crustal composition. Elements other than the REE, Sc, Th, and Y were estimated either from known ratios of elements to one of these, or were borrowed from the estimates based on analysis of large numbers of samples. For example, Taylor and McLennan (1985) obtained the K concentration from the Th concentrations by assuming a Th/U of 3.8 and a K/U ratio of 10^4. Their Sr concentration, on the other hand, is an average of Eade and Fahrig (1968) and Shaw (1967).
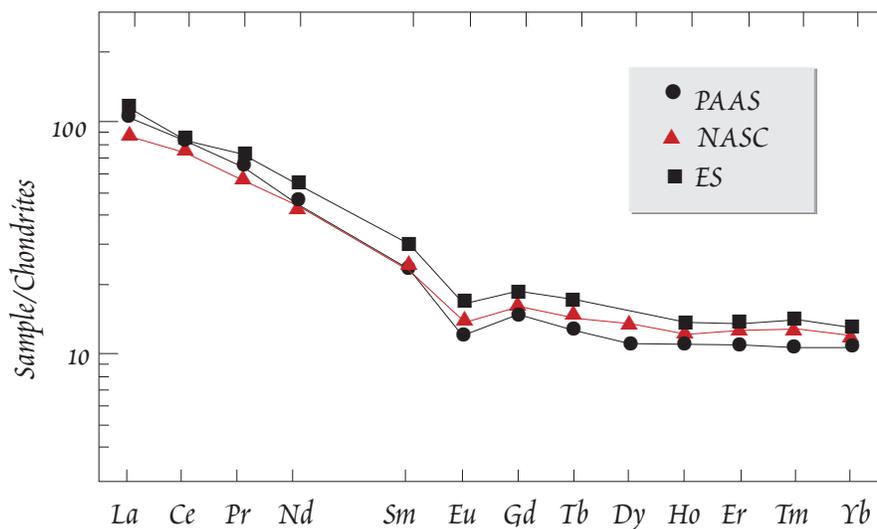
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Table 12.4 lists the upper crustal compositions estimated by Taylor and McLennan (1985, 1995) and Wedepohl (1995). The estimates are broadly similar, and they agree on the concentrations of many elements within 10%. Both indicate an upper crust of "granodioritic" or "tonalitic" composition. For some elements, however, the good agreement simply reflects the reliance of both papers on the previous work of Shaw (1967), but this is not true of all elements. For example, the two estimates agree closely on the concentrations of the light rare earths despite having used completely different approaches in estimating these concentrations. For a few elements, the agreement is poor. For example, Taylor and McLennan's estimate of the copper concentration is 75% greater than that of Wedepohl's.

Plank and Langmuir (in press) suggested several revisions to Taylor and McLennan's values for Cs, Nb, Ta, and TiO_2 based on their study of marine sediments. Their values are shown in parentheses in Table 12.4. Notice that these are substantial changes: Cs increases by over 50%, while Nb and Ta de-

TABLE 12.4. COMPOSITION OF THE UPPER CONTINENTAL CRUST

Major Oxides (wt %)	T& M	Wedepohl			Normative Mineralogy (T & M)	
SiO_2	66.0	64.9			Quartz	15.7
TiO_2	0.5 (0.76)	0.52			Orthoclase	20.1
Al_2O_3	15.2	14.6			Albite	13.6
FeO	4.5	3.97			Diopside	6.1
MgO	2.2	2.24			Hypersthene	9.9
CaO	4.2	4.12			Il	0.95
Na_2O	3.9	3.46				
K_2O	3.4	4.04				

	T & M	Wedepohl		T & M	Wedepohl		T & M	Wedepohl
Li ppm	20	22	Ga ppm	17	14	Nd ppm	26	25.9
Be ppm	3	3.1	Ge ppm	1.6	1.4	Sm ppm	4.5	4.7
B ppm	15	17	As ppm	1.5	2	Eu ppm	0.88	0.95
C ppm		3240	Se ppm	0.05	0.083	Gd ppm	3.8	2.8
N ppm		83	Br ppm		1.6	Tb ppm	0.64	0.5
F ppm		611	Rb ppm	112	110	Dy ppm	3.5	2.9
Na %	2.89	2.57	Sr ppm	350	316	Ho ppm	0.8	0.62
Mg %	1.33	1.35	Y ppm	22	20.7	Er ppm	2.3	
Al %	8.04	7.74	Zr ppm	190	237	Tm ppm	0.33	
Si %	30.8	30.35	Nb ppm	25 (13.7)	26	Yb ppm	2.2	1.5
P ppm	700	665	Mo ppm	1.5	1.4	Lu ppm	0.32	0.27
S		953	Pd ppb	0.5		Hf ppm	5.8	5.8
Cl		640	Ag ppb	50	55	Ta ppm	2.2 (0.96)	1.5
K %	2.8	2.87	Cd ppb	98	102	W ppm	2	1.4
Ca %	3	2.94	In ppb	50	61	Re ppb	0.4	
Sc ppm	11	7	Sn ppm	5.5	2.5	Os ppb	0.05	
Ti ppm	3000 (4560)	3117	Sb ppm	0.2	0.31	Ir ppb	0.02	
V ppm	60	53	Te ppb			Au ppb	1.8	
Cr ppm	35	35	I ppm		1.4	Hg ppb		56
Mn ppm	600	527	Cs ppm	3.7 (7.3)	5.8	Tl ppb	750	750
Fe %	3.5	3.09	Ba ppm	550	668	Pb ppm	20	17
Co ppm	10	11.6	La ppm	30	32.3	Bi ppm	127	123
Ni ppm	20	18.6	Ce ppm	64	65.7	Th ppm	10.7	10.3
Cu ppm	25	14.3	Pr ppm	7.1	6.3	U ppm	2.8	2.5
Zn ppm	71	52						

T&M: Taylor and McLennan (1985,1995), Wedepohl: Wedepohl (1995). Values shown in parentheses are revisions of Plank and Langmuir (in press) to Taylor and McLennan's estimates.

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crease by over 50%. Taylor and McLennan's values for these elements are poorly constrained so Plank and Langmuir's values should be considered superior. Wedepohl's concentrations for these elements are intermediate between the original Taylor and McLennan values and Plank and Langmuir's revised values. The values in Table 12.4 will undoubtedly be further refined in the future.

THE MIDDLE AND LOWER CRUST

Rocks metamorphosed deep within the crust are called *granulites*; an important characteristic of such rocks is that they are anhydrous, with pyroxene replacing amphibole and biotite. They are sometimes exposed at the surface by tectonic processes and hence can provide insights into the nature of the lower crust. However, these granulite terranes have often been subjected to retrograde meta-morphism (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 heavily on indirect inference and geophysical constraints. There are two principal geophysical constraints:

- Heat flow in the continental crust. A portion of the heat flowing out 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 are low abundances). The concentrations of these elements can be related to rock type, as indicated in Table 12.2.
- Seismic velocities in the continental crust. Seismic velocities depend on density, compressibility and the shear modulus, 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) with depth. Let's consider them in greater detail.

Heat is transported conductively through the lithosphere. The equation governing heat conduction is identical to that governing diffusive chemical transport (Fick's First Law, equ. 5.90):

$$Q(z) = -k \frac{\partial T}{\partial z} \qquad 12.10$$

where Q is the heat flow at some depth, z, k is the thermal conductivity, and $\partial T/\partial z$ is the change in temperature with depth. The thermal conductivity of rocks can be measured in the laboratory and averages about 2 $Wm^{-1}K^{-1}$. Thus by measuring the thermal gradient, in boreholes and mines for example, the heat flow can be calculated. The average heat flow of the continents is about 60 mW/m^2. This heat has two components: heat conducted out of the mantle, which is about 20 mW/m^2, and 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

TABLE 12.5. U, TH, AND K CONCENTRATIONS AND HEAT PRODUCTION IN VARIOUS ROCK TYPES.

Igneous Rock Type	U (ppm)	Th (ppm)	K (%)	Th/U	K/U	Density g/cm³	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

decrease with depth. The concentrations of these elements are related to rock type, as is illustrated in Table 12.5. The problem is complicated, however, by variations in the "mantle" heat flow. Heat flow varies significantly with tectonic age, as is illustrated in Figure 12.28. 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, the variation seen in Figure 12.28 may represent different thickness of the lithosphere (Vitorello and Pollack, 1990; 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.

Seismic velocities increase with depth in the crust: P-wave velocities increase from about 6 km/sec in the upper crust to about 7 km/sec in the lower crust. The dependence of the velocity of P waves (compressional-waves) on physical properties is:

$$v_P = \sqrt{\frac{K + \frac{4}{3}\mu}{\rho}} \qquad 12.11$$

and that for velocity of shear waves (S-waves) is:

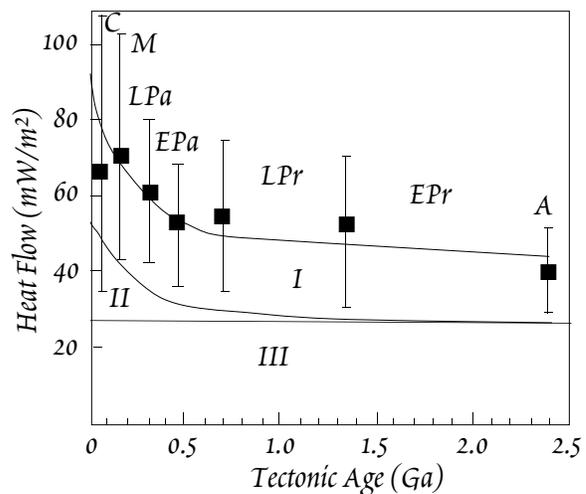$$v_S = \sqrt{\frac{\mu}{\rho}} \qquad 12.12$$

Figure 12.28. Heat flow as a function of tectonic age. Component I is radiogenic heat produced in the crust, II is heat from a transient thermal perturbation associated with tectonism, and III is background heat from deeper sources. A is Archean, EPr is Early Proterozoic, LPr is Late Proterozoic, EPa is early Paleozoic, LPa is late Paleozoic, M is Mesozoic, and C is Cenozoic. From Vitorello and Pollack (1980).
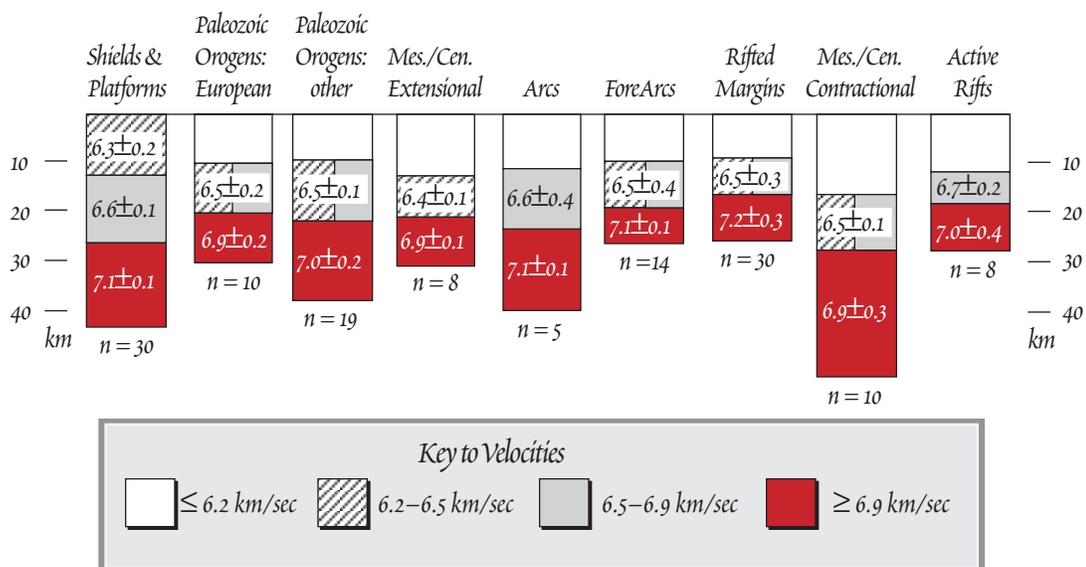
Figure 12.29. Seismic velocity structure of the continental crust, illustrating its 3-layered nature. Velocity structure falls into 9 types. The number of profiles used to construct each type is shown below each type. From Rudnick and Fountain (1995).

where K is the bulk modulus (inverse of β, compressibility), μ is the shear modulus, and ρ is density. Thus the increase in seismic velocity with depth implies increasing density and decreasing compressibility with depth. Some, but not all, of the increase in density results merely from compression. The remainder represents changing composition. The real problem is to understand precisely how seismic velocity depends on composition.

Seismic velocity profiles vary widely from place to place, as does crustal thickness. Rudnick and Fountain (1995) examined a global database of seismic cross sections and found that they can be divided into 9 classes, which are illustrated in Figure 12.29. One must next relate seismic velocity to composition. This can be done by making measurements of seismic velocity in the laboratory on samples of known composition. For example, Figure 12.30 shows the relationship between SiO_2 and seismic velocity in a variety of rock types.

Figure 12.30. Correlation between measured seismic velocity (v_P) and SiO_2 concentration. From Rudnick and Fountain (1995).

To produce an estimate of crustal composition, Rudnick and Fountain assigned an average lithology to the seismic sections shown in Figure 12.29. They then assigned a composition to each lithology using a database of the composition of lower crustal xenoliths. Then by estimating the aerial extent of each type of crustal section, they produced the compositional estimate in Table 12.6. 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 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 3 lithologies to 3 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 their characteristic seismic velocities were observed in the European Geotraverse. His estimate of the composition of the lower crustal is also listed in Table 12.6.

Rare earth patterns of upper, middle and lower crust as estimated by Rudnick and Fountain (1995) are compared in Figure 12.31a. 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 features of these patterns. Eu is strongly held in plagioclase (Chapter 7). The presence of plagioclase in the melting residue would produce a negative Eu anomaly in the melt and a positive one in the residue. Thus these anomalies suggest that crustal has differentiated to form distinct layers at least partially through partial melting, with granitic melts forming the upper crust and granulitic residues forming the deeper crust. Figure 12.31b displays the estimated composition of the middle and lower crust relative to the upper crust. The lower and middle crust are depleted in incompatible elements and enriched in compatible elements relative to 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.
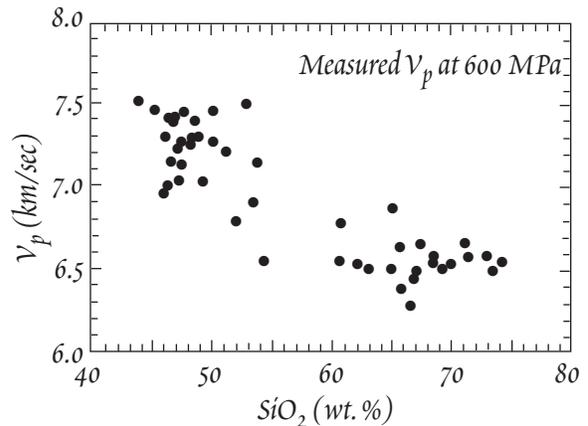
Table 12.6. Composition of the Middle and Lower Continental Crust

Major Oxides, %

	R & F Lower	R & F Middle	Wedepohl Lower
SiO_2	52.3	60.6	58.05
TiO_2	0.8	0.7	0.84
Al_2O_3	16.6	15.5	15.52
FeO	8.4	6.4	7.34
MnO	0.1	0.1	0.12
MgO	7.1	3.4	5.23
CaO	9.4	5.1	6.80
Na_2O	2.6	3.2	2.86
K_2O	0.6	2.01	1.85
P_2O_5	0.1	0.1	0.20

Trace Elements, ppm

	R & F Lower	R & F Middle	Wedepohl Lower		R & F Lower	R & F Middle	Wedepohl Lower
Li	6	7	13	Sn			2.1
Be			1.7	Sb			0.3
B			5	I			0.14
C			588	Cs	0.3	2.4	0.8
N			34	B a	259	402	568
F			429	La	8	17	26.8
S			408	Ce	20	45	53.1
Cl			278	Pr	2.6	5.8	7.4
Sc	31	22	25.3	Nd	11	24	28.1
V	196	118	149	Sm	2.8	4.4	6.0
Cr	215	83	228	Eu	1.1	1.5	1.6
Co	38	25	38	Gd	3.1	4	5.4
N i	88	33	99	Tb	0.48	0.58	0.81
Cu	26	20	37.4	Dy	3.1	3.8	4.7
Zn	78	70	79	Ho	0.68	0.82	0.99
Ga	13	17	5.4	Er	1.9	2.3	
As			1.3	Tm			0.81
Se			0.17	Yb	1.5	2.3	2.5
Br			0.28	Lu	0.25	4.1	0.43
Rb	11	62	41	Hf	1.9	4	4.0
Sr	348	281	352	Ta	0.6	0.6	0.84
Y	16	22	27.2	W			0.6
Zr	68	125	165	Tl			0.26
Nb	5	8	11.3	Hg			0.21
Mo			0.6	Pb	4.2	15.3	12.5
Ag			0.08	B i			0.037
Cd			0.101	Th	1.2	6.1	6.6
In			0.052	U	0.2	1.6	0.93

R & F: Rudnick and Fountain (1995), Wedepohl: Wedepohl (1995).
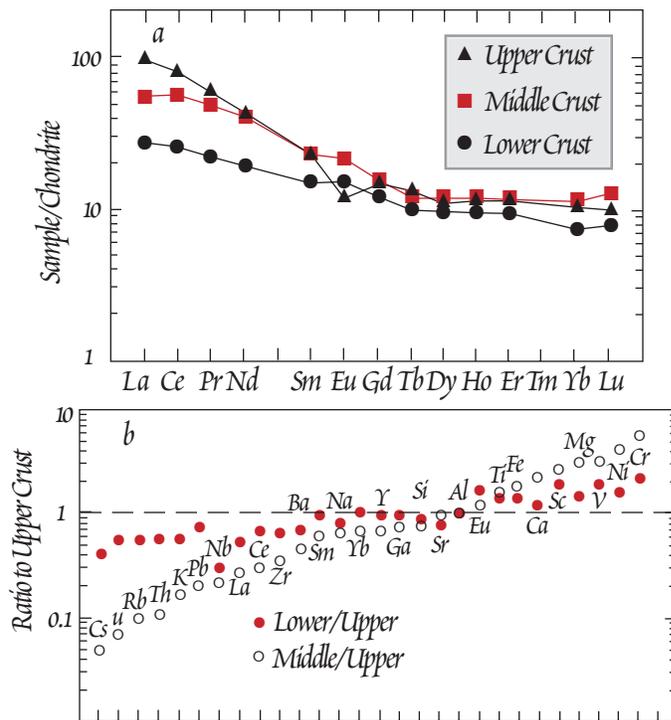
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Figure 12.31. (a). Comparison of chondrite-normalized in upper, middle and lower crust. (b). Elemental enrichment or depletion of the middle and lower crust relative to the upper crust. From Rudnick and Fountain (1995).

THE TOTAL CONTINENTAL CRUST

The approach used by most workers to estimate the composition of the total continental crust is simply to calculate an average of two or three crustal sections, weighting each by its mass. 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. Both Weaver and Tarney (1984) and Rudnick and Fountain (1995) 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. All use geophysical constraints for this.

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 modify 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 Fountain (1995) are given in Table 12.7. Also listed are estimates of trace element concentrations by Taylor and McLennan (1995), Rudnick and Fountain (1995), and Wedepohl (1995). Since Rudnick and Fountain (1995) rely on the Taylor and McLennan upper crustal estimates in calculating the total crust composition, the revisions to the Taylor and McLennan upper crustal values for TiO_2, Cs, Nb, and Ta of Plank and Langmuir (in press) affect the Rudnick and Fountain total crustal values of these elements. These revisions have been made in the Table.

The ranges of estimates for SiO_2 and Al_2O_3 in Table 12.7 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 siliceous 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 com-

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* The Lewisian, which outcrops in Northwest Scotland, is perhaps the classic exposure of lower crust.

position 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).

The Th/U ratio in both Taylor and McLennan's and Rudnick and Fountain's estimate (3.85 and 3.94 respectively) is probably too low. The Th/U ratio of the depleted mantle is well constrained by $^{230}Th/^{232}Th$ ratios in MORB to be <2.5. If the bulk Earth value is 3.9–4.2 (as would be the case if the terrestrial Th/U is chondritic), then mass balance requires the crustal ratio to be higher than the bulk Earth value, yet both Taylor and McLennan's and Rudnick and Fountain's Th/U ratios are close to bulk Earth. Wedepohl's Th/U ratio of 5 may be more appropriate.

Figure 12.32 shows the primitive mantle-normalized incompatible element concentrations in the total continental crust. All these estimates show the continental crust to be enriched in incompatible elements. This is consistent with the view that the crust was created by partial melting of the mantle. The elemental enrichment pattern is not smooth, however. First, Nb (and Ta, not shown), and to a lesser degree Ti, are not as enriched as elements of similar incompatibility. Second, Pb is anomalously enriched. As we found earlier in the chapter, these are features of island arc magmas and their presence here strengthens the notion that island arc volcanism has

Table 12.7. Composition of the Continental Crust

Major Oxides, wt. %

	R & F	T & M	W & T	We	Shaw
SiO_2	59.1	57.3	63.2	61.5	63.2
TiO_2	0.75	0.9	0.6	0.68	0.7
Al_2O_3	15.8	15.9	16.1	15.1	14.8
FeO	6.6	9.1	4.9	5.67	5.60
MnO	0.1	0.18	0.08	0.10	0.09
MgO	4.4	5.3	2.8	3.7	3.15
CaO	6.4	7.4	4.7	5.5	4.66
Na_2O	3.2	3.1	4.2	3.2	3.29
K_2O	1.88	1.1	2.1	2.4	2.34
P_2O_5	0.2		0.19	0.18	0.14

Trace Elements (in ppm unless otherwise noted)

	R & F	T & M	We		R & F	T & M	We
Li	11	13	18	Sb		0.2	0.3
Be		1.5	2.4	Te, ppb			5
B		10	11	I, ppb			800
C			1990	Cs	3	1	3.4
N			60	Ba	390	250	584
F			525	La	18	16	30
S			697	Ce	42	33	60
Cl			472	Pr	5	3.9	6.7
Sc	22	30	16	Nd	20	16	27
V	151	230	98	Sm	3.9	3.5	5.3
Cr	119	185	126	Eu	1.2	1.1	1.3
Co	25	29	24	Gd	3.6	3.3	4.0
Ni	51	105	56	Tb	0.56	0.6	.65
Cu	24	75	25	Dy	3.5	3.7	3.8
Zn	73	80	65	Ho	0.76	0.78	0.8
Ga	16	18	15	Er	2.2	2.2	2.1
Ge		1.6	1.4	Tm		0.32	0.3
As		1	1.7	Yb	2	2.2	2.0
Se		0.05	0.12	Lu	0.33	0.3	0.35
Br			1.0	Hf	3.7	3	4.9
Rb	58	32	78	Ta	0.7	1	1.1
Sr	325	260	333	W		1	1.0
Y	20	20	24	Re, ppb		0.4	0.4
Zr	123	100	203	Os, ppb		0.005	0.05
Nb	8.5	11	19	Ir, ppb		0.1	0.05
Mo		1	1.1	Pt, ppb			0.4
Ru, ppb			0.1	Au, ppb		3	2.5
Rh, ppb			0.06	Hg, ppb			40
Pd, ppb		1	0.4	Tl, ppb		360	520
Ag, ppb		80	70	Pb	12.6	8	14.8
Cd, ppb		98	100	Bi, ppb		60	85
In, ppb		50	50	Th	5.6	3.5	8.5
Sn		2.5	2.3	U	1.42	0.91	1.7

R & F: Rudnick and Fountain (1995) as revised by Plank and Langmuir (in press), T & M: Taylor and McLennan (1985, 1995), We: Wedepohl (1995), Shaw: Shaw et al. (1986), W & T: Weaver and Tarney (1984).
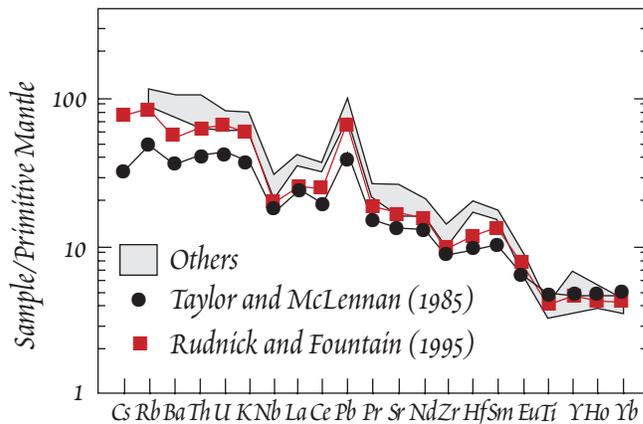
Figure 12.32. Comparison of incompatible element enrichment of estimated bulk crustal composition of Taylor and McLennan (1985), Rudnick and Fountain (1995) with other estimates (Weaver and Tarney, 1984; Shaw et al., 1986; Wedepohl, 1995). From Rudnick and Fountain (1995).

played an important role in creation of the continental crust.

Rudnick and Fountain's (1995) or Wedepohl's (1995) estimated compositions are significantly more enriched in incompatible elements than the estimated composition of Taylor and McLennan (1985, 1995). Since the former two estimates are based on observations while the Taylor and McLennan estimate is based on assumptions about how the crust formed, the former estimates should probably be preferred. This strong enrichment of the continental crust in incompatible elements has important implications for the evolution of both the crust and the mantle. Based on Rudnick and Fountain's (1995) or Wedepohl's (1995) estimates, the crust is more enriched in incompatible elements than typical island arc andesite. Thus subduction-related magmatism alone is inadequate as a mechanism for creation of the continental crust. Based on these estimates, a substantial proportion of the Earth's total inventory of lithophile incompatible elements are in the crust. For example, using the primitive mantle values listed in Chapter 11, we can calculate that 50% or 67% of the Earth's total Rb is in the Earth's crust using Rudnick and Fountain's and Wedepohl's crustal estimates respectively. Similar fractions of other highly incompatible elements such as Cs, Ba, and Th are also concentrated in the crust. This implies that the melt must have been extracted from over half the mantle to create the crust, and therefore that at least half the mantle is incompatible element depleted. Thus differentiation of the Earth's has been remarkably efficient.

Growth of the Continental Crust

The composition of the crust gives us important clues as to how it was created. For example, one possible model for the formation of the continental crust is that it was produced by late accretion of a volatile-rich veneer when the Earth formed. But the composition given in Table 12.7 is clearly inconsistent with this view: the crust is not systematically enriched in volatile elements. The crust *is* systematically enriched in incompatible elements; this leads to the hypothesis that the crust was created by partial melting of the mantle. However, even here there are some inconsistencies, since a partial melt of the mantle is unlikely to have as much SiO_2 as the crust (~60%).
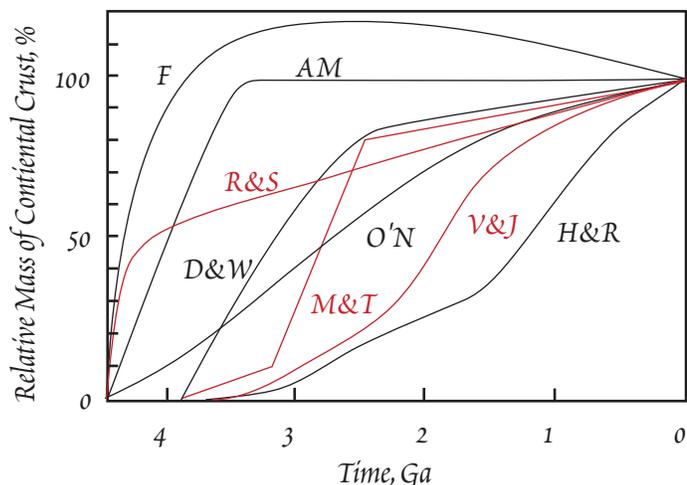

Figure 12.33. Models of the rates of crustal growth. AM: Armstrong (1981a), R&S: Rymer and Schubert (1984), F: Fyfe (1978), D & W: DePaolo and Wasserburg (1979), M & T: McLennan and Taylor (1982), O'N: O'Nions and Hamilton (1981), V & J: Veizer and Jansen (1979), H & R: Hurley and Rand (1969). Adapted from Taylor and McLennan (1985).

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Also, the trace element composition of the crust is not like that of any single type of mantle-derived magma. This suggests the growth of the crust has been a complex process. The details of this process are not yet fully understood. In this section, we examine what is known about crustal growth.

THE PACE OF CRUSTAL GROWTH

The first question we might ask is how has the crust grown with time? A variety of answers to this question have been suggested. These are illustrated in Figure 12.33. They can be broken into three types: (1) growth rate increasing through time, e.g., curve V & J (=Vezier and Jansen) and H & R (Hurley and Rand), (2) approximately linear growth through time, such as the curve marked O'N (= O'Nions), and (3) early rapid growth followed by later slow growth or no growth, e.g., curves Am (=Armstrong) and F (Fyfe).

Early studies favored accelerating crustal growth through time. Age provinces for North America based on radiometric dates compiled by Hurley and

Figure 12.34. Age provinces of the North American continent (after Hurley and Rand, 1969).

Rand (1969) are shown in Figure 12.34. Based on this, Hurley suggested most of the crust was produced in the last 1 or 2 Ga. However, subsequent work utilizing U-Pb dating of zircons and Sm-Nd model ages has substantially changed this view. U-Pb zircon ages are not so easily reset by metamorphism as are the Rb-Sr ages relied on by Hurley. Zircon dating has revealed large areas of the continental crust that were created more than 2.7 Ga ago. Zircon dating as also identified limited areas of crust that are old than 3.5 Ga. The oldest dates are from two localities in Australia. Zircons from Mt. Narryer, Western Australia give ages of around 4.15 Ga (Frounde et al., 1983). Slightly older ages (4.2-4.3 Ga) were determined on zircons from a second, nearby locality, the Jack Hills. These zircon analyzes were done by ion probe rather than conventional mass spectrometry and were initially controversial for that reason, but they ages are now generally accepted. In both cases, the zircons are found in metasedimentary rocks of much younger age (3–3.5 Ga), and only a handful of the zircons in these rocks are this old. While these ancient zircons have been preserved, the rocks in which they crystallized apparently have not. Nevertheless, the zircons are relatively U-rich, suggesting they come from silica-rich rocks typical of true continental crust rather than more mafic rocks.

More recently, zircons in the Acasta gneisses from the Slave Province in Canada have been dated at 3.96 Ga by this method (Bowring et al., 1989). These ages are interpreted as the age of crystallization of protoliths of these gneisses. Interestingly, their initial ε_{Nd} are negative, indicating derivation from a light rare earth-enriched source, which could be even older crust. Thus there is evidence that at least some continental crust formed very early in Earth's history.

In Chapter 11, we found that the many very ancient rocks have positive initial ε_{Nd} ratios. For example, the Isua rocks of East Greenland, which have crystallization ages around 3.8 Ga, have initial ε_{Nd} around +1 to +3; rocks of similar age from India have similar initial ε_{Nd} values. This implies their sources had high Sm/Nd ratios, and therefore were LRE-depleted for a substantial amount of
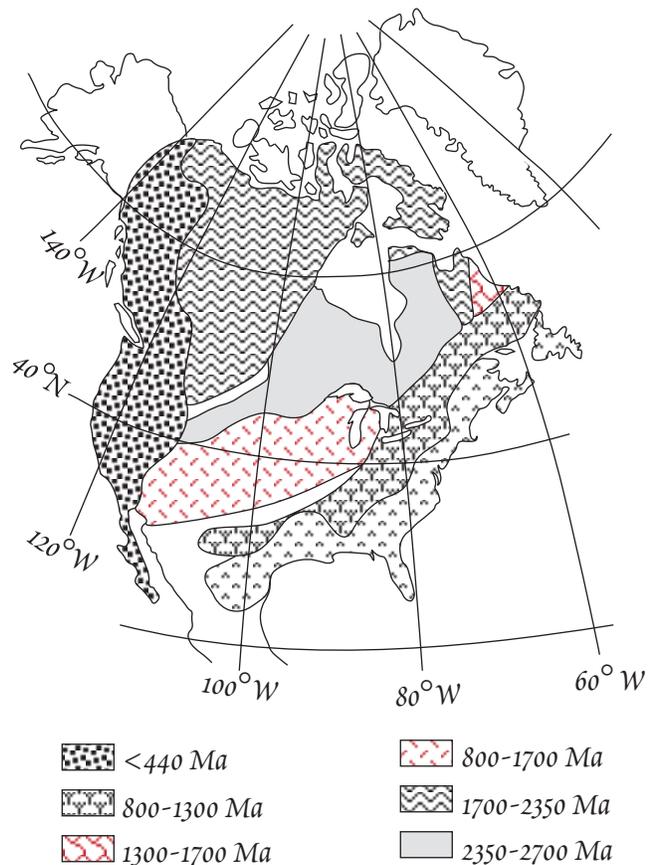
time, hundreds of millions of years, before the crystallization of these rocks. This requires that a complimentary LRE enriched reservoir, possibly an early continental crust, formed before 4.0 Ga. How large this crust reservoir was, however, depends on how large the volume of depleted mantle was, which is not constrained (McCulloch and Bennett, 1994). Nevertheless these data provide indirect evidence that at least crust formation began well before 4.0 Ga.

Sm-Nd model ages also have the power to "see through" metamorphism and establish "crust formation ages", as we found in Chapter 8. The example of the

Figure 12.35. Isotopic provinces, based on crustal residence times (τ_{DM}) of the Western U.S. From Bennett and DePaolo (1987).

western U. S. illustrates this point. Figure 12.35 is a map of the Western U. S. showing contours of Nd crustal residence times (τ_{DM}). The data define 3 distinct provinces and suggest the existence of several others. There is a general similarity to Hurley's map (Figure 12.34), but there is greater detail, and the ages are generally older.

Figure 12.36 shows the initial ε_{Nd} values of the granites from the three numbered provinces of Figure 12.35 plotted as a function of their crystallization age. Despite the variations in crustal residence times, the crystallization ages indicate Provinces 1-3 all formed between 1.65 and 1.8 Ga. Only the ε_{Nd} from Province 3 plot close to the depleted mantle evolution curve. From this we can conclude that only Province 3 was a completely new addition to the crustal mass at that time. Initial ε_{Nd} for the remaining provinces plot below the depleted mantle evolution curve, suggesting they are mixtures of new mantle-derived material and older crust. The crustal residence ages of these provinces are older than the crystallization ages because they are mixtures of mantle and older crust.

In each province there have been subsequent episodes of magmatism. However, the initial ε_{Nd} lie along the same growth trajectory as the older rocks. This suggests that magmatism in these subsequent episodes simply recycled pre-existing crustal material and there were no new additions to crustal mass from the mantle. Thus Hurley's map (Figure 12.34) must reflect orogeny in which the radiogenic clocks are reset rather than new crustal additions.

At the other extreme of the continental growth question, Armstrong (1968, 1981a) argued that the mass of the crust has remained nearly constant of the past 4 Ga or so. Armstrong recognized that new crust has been continually created through time, but he argued that the rate of crustal creation was balanced by an equal rate of crustal destruction through erosion and subduction of sediment. Three lines of evidence support this view. First, Armstrong cited the absence of ancient pelagic sediment anywhere on the Earth's surface and argued that most sediment must therefore be subducted. In support of this, he cited estimates of sediment subduction rates by several workers that are sufficient to balance crustal growth. Second, he pointed out that neither sea level nor the average thickness of stable continental cratons have changed with time, and therefore that continental volume also must not have changed. Finally, he pointed out that positive ε_{Nd} in the earliest rocks requires a very early depletion of the mantle (Figure 10.19), most likely through generation of continental crust. Further-
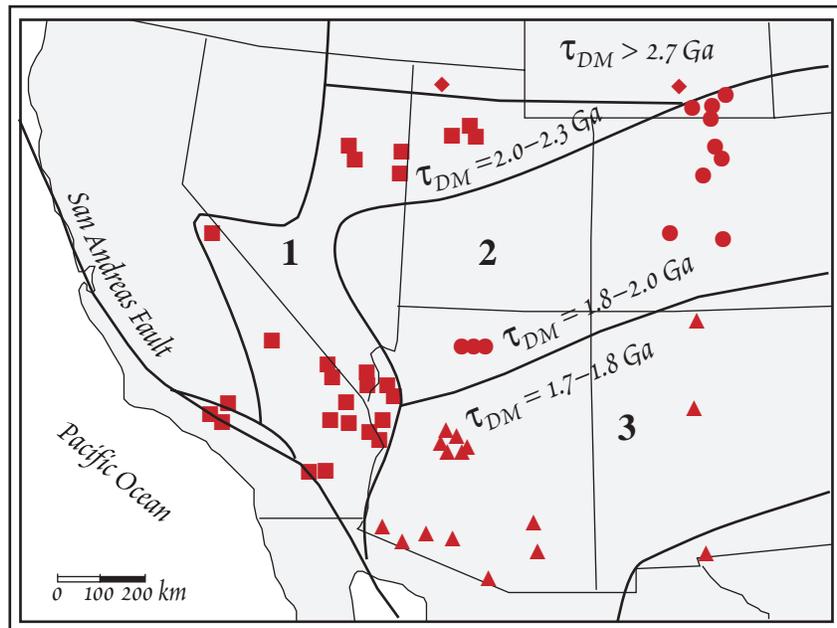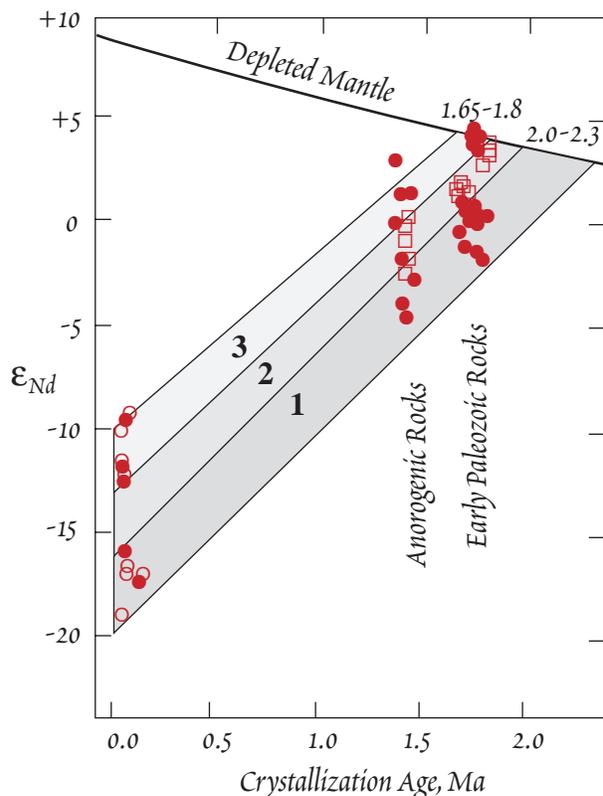
CHAPTER 12: THE CRUST

Figure 12.36. ε_{Nd} (initial) as a function of crystallization age of Western U.S. Groupings 1 2, and 3 refer to provinces shown in Figure 12.35. From Bennett and DePaolo (1987).

more, the subsequent nearly linear growth of ε_{Nd} is consistent with constant continental mass and inconsistent with continental growth (Armstrong, 1981b, DePaolo, 1981b).

Because sediments effectively sample rocks of a wide variety of ages, isotope ratios in sediments provide a means of studying crustal evolution. By studying sediments of various ages, we should be able to draw some inferences about the rates of continental growth. Goldstein et al. (1984) found that the mean crustal residence time (τ_{DM}) of the modern river particulates was 1.7 Ga, which they interpreted as the mean age of the crust now being eroded. However, they estimated the mean crustal residence time of the entire sedimentary mass to be about 1.9 Ga. Figure 12.37 compares the stratigraphic age[*] of sediments

with their crustal residence ages. We expect that crustal residence ages will be somewhat older than the stratigraphic ages. Only when a rock is eroded into the sedimentary mass immediately after its derivation from the mantle will its stratigraphic (τ_{ST}) and crustal residence age (τ_{CR}) be equal.

The top diagram illustrates the relationships between τ_{ST} and τ_{CR} that we would expect to see for various crustal growth scenarios, assuming there is a relationship between the amount of new material added to the continents and the amount of new material added to the sedimentary mass. If the continents had been created 4.0 Ga ago and if there had been no new additions to continental crust since that time, then the crustal residence time of all sediments should be 4.0 Ga regardless of stratigraphic age. This is illustrated by the line labeled "No New Input". If, on the other hand, the rate of continent growth through time has been uniform since 4.0
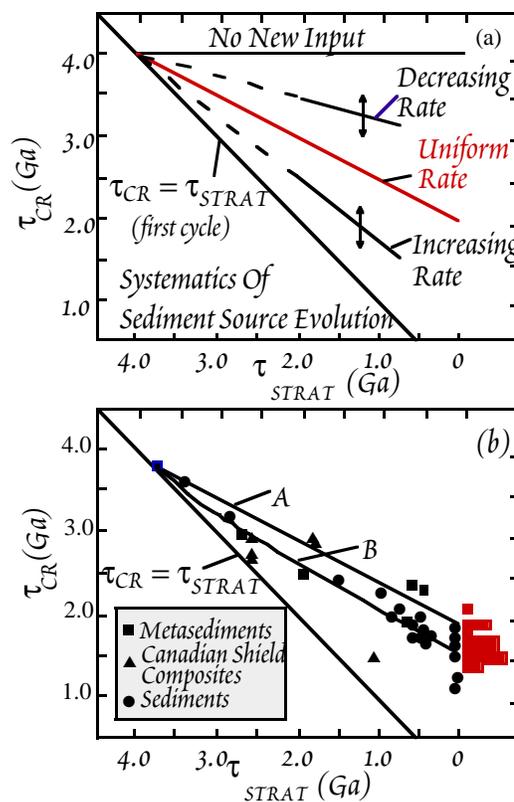

Figure 12.37. Relationship between stratigraphic age of sediments and the crustal residence age of material in sediments. From Goldstein et al., 1984).

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[*] The stratigraphic age is the age of deposition of the sediment determined by conventional geochronological or geological means.

Ga, then τ_{ST} and τ_{CR} of the sedimentary mass should lie along a line with slope of 1/2, which is the line labeled "Uniform Rate". The reason for this is as follows. If the sedimentary mass at any given time samples the crust in a representative fashion, then τ_{CR} of the sedimentary mass at the time of its deposition (at τ_{ST}) should be $(4.0-\tau_{ST})/2$[†], i.e., the mean time between the start of crustal growth (which we arbitrarily assume to be 4.0 Ga) and τ_{ST}. A scenario where the rate of crustal growth decreases with time is essentially intermediate between the one-time crust creation at 4.0 and the uniform growth rate case. Therefore, we would expect the decreasing rate scenario to follow a trend intermediate between these two, for example, the line labeled 'Decreasing Rate'. On the other hand, if the rate has increased with time, the τ_{CR} of the sedimentary mass would be younger than in the case of uniform growth rate, but still must be older than τ_{ST}, so this scenario should follow a path between the uniform growth rate case and the line $\tau_{ST} = \tau_{CR}$, for example, the line labeled "Increasing Rate".

Line A in Figure 12.37b is the uniform growth rate line with a slope of 1/2. Thus the data seem to be compatible with a nearly uniform rate of growth of the continental crust, such as the line labeled "O'N" in Figure 12.33 or even with an increasing growth rate. However, Goldstein et al. noted sedimentary mass is cannibalistic: sediments are eroded and redeposited. Line B represents the evolution of the source of sediments where crustal growth is constant but erosion and re-deposition of old sediments occurs. The situation is further complicated when crust is destroyed through erosion and subduction of marine sediments. Goldstein et al. (1984) concluded their data could be consistent with either nearly constant continental growth rate or a nearly constant continental mass if the rate rate of continent-to-mantle recycling decreased through time.

In summary, formation of the continental crust began 4.0 Ga ago or earlier. The rarity of rocks of this age, however, suggests either that crustal growth was initially quite slow, or that much of this early continental crust may have been destroyed and recycled into the mantle. Since then, there have been continued additions to the continental crust. The degree to which destruction of crust through erosion and subduction may have balanced these additions is unclear and remains highly controversial. The average age of the presently existing continental crust is around 2.2 Ga. Models, such as that of Hurley, in which the rate of crustal growth is increasing cannot be correct. Reconnaissance Sm-Nd studies of the sort illustrated in Figure 12.35 show that the crust is created in large blocks, and that the rate has been somewhat episodic. Judging from these kinds of studies, the late Archean and early Proterozoic (the period between roughly 3.0 and 1.8 Ga) appears to have been a time of relatively rapid crustal growth (e.g., Patchett and Arndt, 1986; McCulloch, 1987). On the other hand, crustal growth rates in the Phanerozoic (the last 550 Ma) appear to be lower than during earlier times.

Mechanisms of Crustal Growth

We have seen how the composition of the continental crust is qualitatively consistent with the crust having been created by partial melting of the mantle. But what are the details of this process? In what tectonic setting has the crust been produced? We can identify a number of possible mechanisms for the creation of the continental crust. These are as follows:

[†] One way to rationalized this equation is to think of newly deposited sediment at τ_{ST} as a 50-50 mixture of material derived from the mantle at 4.0 Ga and τ_{ST}. The equation for the τ_{CR} of this mixture would be:

$$\tau_{CR} = \frac{4.0 + \tau_{ST}}{2} \ .$$

At time of deposition, its crustal residence age would have been: $\tau_{CR} = \frac{4.0 + \tau_{ST}}{2} - \tau_{ST} = \frac{4.0 - \tau_{ST}}{2} \ .$

You could satisfy yourself that a mixture of material having τ_{CR} of all ages between 4.0 Ga and τ_{ST} would have the same τ_{CR} as given by this equation.

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Table 12.8. Comparison of Continental Crust with Andesite

	Continental Crust	Average Andesite
SiO_2	57.3-63.2	59.7
TiO_2	0.6-0.9	0.7
Al_2O_3	14.8-16.1	17.1
FeO	5.6-9.1	6.3
MnO	0.08-0.18	0.12
MgO	2.8-5.3	3.2
CaO	4.7-7.4	6.6
Na_2O	3.1-3.2	3.3
K_2O	1.1-2.4	1.5
P_2O_5	0.14-0.20	0.19

Continental Crust from Table 12.7. Average medium-K orogenic andesite from Gill (1981).

• Subduction-related volcanism. The Andes Mountains with their magnificent and very active andesitic volcanos represent a modern example of how the crust grows above a subduction zone.

• Accretion of oceanic crust and oceanic plateaus. Oceanic crust is usually subducted and returned to the mantle, but anomalously thick crust, such as that of the Ontong-Java Plateau of the Western Pacific may be difficult to subduct. The alternative is that is accretes to continental margins, becoming part of the continental mass.

• Continental volcanism. Rifting and mantle plumes are two causes of volcanism unrelated to subduction. Flood basalts, probably produced by the start-up phase of mantle plumes, have occasionally been erupted in tremendous volumes.

• Underplating. Magmas erupted on continents may represent only the tip of the iceberg so to speak. Because of the low density of the continental crust, basalt magma may stagnate at the crust-mantle boundary. In this scenario, the crust primarily grows from the bottom down.

• Intrusion by small-degree melts. Small degree melts of shallow mantle under the continents that are highly enriched in incompatible elements, such as kimberlites and lamprophyres, may not contribute significant volumes to the continents, but may contribute a disproportionate fraction of the incompatible element inventory.

Of course, all these mechanisms have contributed to crustal growth to varying degrees. The real question is which mechanism is most important?

There are a number of cogent arguments favoring subduction-related magmatism as the principal mechanism of crustal growth. First, in a qualitative way, the continental crust has a major element composition similar to andesites erupted on continental margins and in island arcs. This point is made in Table 12.8, which compares average "orogenic" (i.e., island arc or continental margin) andesite to the estimates of crustal composition in Table 12.7. The resemblance is strong; only the Al concentration lies outside the range of estimated concentrations in the crust.

The similarity in composition also extends to incompatible elements. This point is made in Figure 12.38, which compares the composition of a siliceous andesite from the Banda arc (Indonesia) with the range of estimates of crustal composition. While the match is not an exact one, the continental crust shares the strong enrichment in highly incompatible elements, the relative depletion in Nb and Ta, and the excess enrichment in Pb observed in most island arc magmas. We should point out, however, that to some extent, the incompatible element enrichment of island arc magmas results from a "continental component" in them, originating either through sediment subduction or assimilation of crust. Thus in trying to understand the incompatible element enrichment of the crust, postulating an origin by subduction zone magmatism begs the question in a certain sense.

Finally, as we noted earlier, subduction-related magmatism is the most important mechanism of crustal growth at present, and probably throughout the Phanerozoic as well. Many igneous and meta-igneous rocks of Proterozoic age also have chemical features suggesting they were produced in subduction settings. Bennett and DePaolo (1987) concluded the provinces in the Southwest U.S. shown in Figure 12.35 formed by successive accretion or growth of island arcs on the edge of the pre-existing Archean Wyoming Craton to the north. Judging from their older Sm-Nd model ages, the northeastern arcs contain a substantial component of older crust derived from the craton. This could have occurred through erosion and subduction, or, if the volcanos were built directly on the continent, through assimilation of crust. As new Proterozoic crust was built outward from the continent, it screened subse-
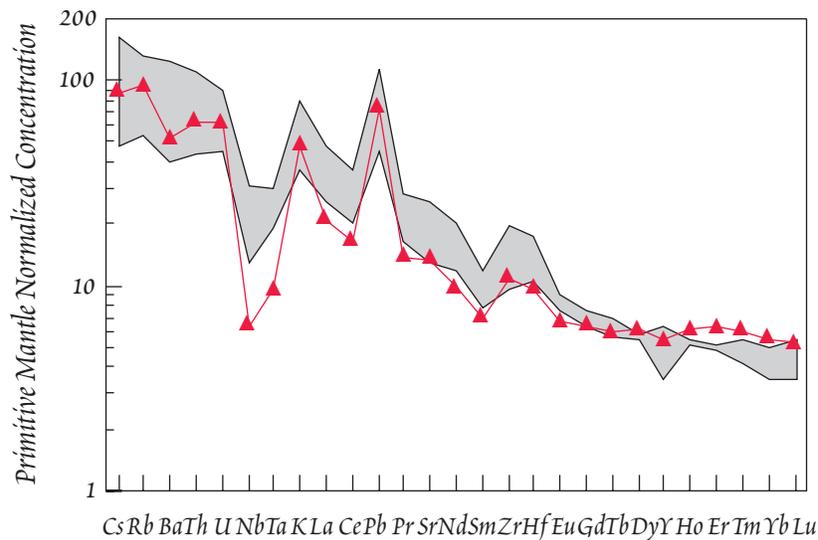
Figure 12.38. Comparison of incompatible element concentrations in a siliceous andesite from the Banda arc (red triangles) with the range of estimated concentrations in the continental crust (gray field). Both share a relative depletion in Nb and Ta and a relative enrichment in Pb.

quent arcs from the contribution of material from the Archean crust. A similar effect has been observed in the Proterozoic provinces of Canada.

Accretion of intra-oceanic arcs, modern examples of which include the Marianas and the Aleutians, may also contribute to crustal growth. Indeed, major segments of continental crust appear to have grown so rapidly that the could not have been created in a single arc (Rymer and Schubert, 1986); they therefore may have originated as several simultaneously active arcs subsequently accreted to a continental margin. Even in this case, however, global magma production rates at subduction zones during at least some parts of the Proterozoic must have been 6 to 10 times higher than during the Phanerozoic (Rymer and Schubert, 1986). These high growth rates may mean some mechanism other than subduction-related volcanism was responsible for growth of much of the crust.

Though subduction-related volcanism may have been the dominant mode of crustal growth in the Proterozoic and Phanerozoic, other mechanisms have played a role. The Wrangalia Terrane in NW British Columbia and Alaska, is widely considered to consist in part of oceanic plateaus. The plateaus were produced over a mantle plume in Paleozoic time and later accreted to the North American continent by plate tectonic processes. The Coast Ranges of Oregon represent an example of more recently accreted oceanic crust. Mantle plumes surfacing beneath continents also produce magmas that add mass to the continents. The most voluminous eruptions occur in the initial stages of the plume, when the large buoyant plume head approaches the surface. Under these circumstances, enormous volumes of basalt erupt. Examples of such flood basalts include the Siberian Traps, the Karoo of South Africa, the Deccan of India, the Parana of Brazil, and the Columbia River of the NW U. S. Gravity anomalies suggest even greater volumes of basaltic magma were trapped at deep crustal levels.

Continental rifts can also be sites of voluminous eruption of basaltic magma. A well-documented example is the Proterozoic Keweenawan or Mid-Continent Rift of the U. S., which formed some 1 to 1.2 Ga ago. Though now mostly covered by Phanerozoic sediments, where it is exposed the rift consists of a trough 150 km wide and 1500 km long filled with up to 15 km of volcanics, primarily basalt, and clastic sediments derived from them. Modern examples of continental rifts include the Rio Grande Rift of New Mexico and the East African Rift.

CRUSTAL GROWTH IN THE ARCHEAN

The case for crustal growth through subduction-related volcanism is much less strong in the Archean. While andesites dominate island-arc volcanism at present, andesites seem to be relatively rare in the Archean. Taylor and McLennan (1995) remarked that "the composition of the Archean upper crust stands in marked contrast to that of the post-Archean crust." This suggests the Archean-

Proterozoic boundary marks a change in the manner in which crust was generated. Since nearly half the continental crust was created by the end of the Archean, understanding the genesis of Archean crust is important.

There are two principle types of Archean terranes. The first is greenstone belts, of which the Abitibi Belt in the Superior Province of Canada is a classic example. They consist of thick sequences of volcanic and sedimentary rocks in elongate basins punctuated by circular or elongate granitic batholiths. They have experienced only low grade metamorphism (hence the term greenstone: chlorite-serpentinite is the typical metamorphic grade).

Figure 12.39. REE patterns of typical Archean tonalites and trondhjemites. From Taylor and McLennan (1985).

Tholeiitic basalt and komatiite are the predominant volcanics, but more siliceous ones are also common. The combination of mafic volcanics and granitic intrusives makes greenstone belts distinctly bimodal in composition.

The presence of komatiites is significant. They are ultramafic lavas erupted at temperatures of 1400 to 1600° C, much hotter than basalts, whose eruption temperatures are typically 1100 to 1200° C. Their chemistry indicates they are products of large extents of melting, perhaps up to perhaps 40%. Komatiites are largely restricted to the Archean; there are a few early Proterozoic occurrences and only one documented Phaner-ozoic occurrence. The absence of komatiites in the latter part of Earth's history undoubtedly reflects secular cooling of the mantle.

The other type of Archean crust, the high-grade gneiss terranes, such as West Greenland, is much different. They typically consist of felsic gneisses and sedimentary and volcanic rocks metamorphosed at amphibolite to granulite grade. These terranes do not seem to be simply a highly metamorphosed version of the greenstone belt terranes as they differ in structure and in sedimentary facies. The felsic gneisses consist of metamorphosed plutonic rocks of the so-called "TTG" (Tonalite*–Trondhjemite[†]–Granodiorite) suite, characterized by higher Na/K ratios than are found in most post-Archean granitoids. Many have steep REE patterns (Figure 12.39) and no Eu anomalies. These rare earth characteristics indicate they formed by partial melting at great depth (>60 km), where garnet, rather than plagioclase, was present in the residua. The presence of garnet would account for their steep heavy rare-earth patterns and the absence of plagioclase would explain the lack of Eu-anomalies. Positive initial ε_{Nd} values of many of these gneisses, particularly the oldest of them, indicates they formed directly from the mantle, or more likely, by partial melting of basalts that had them-
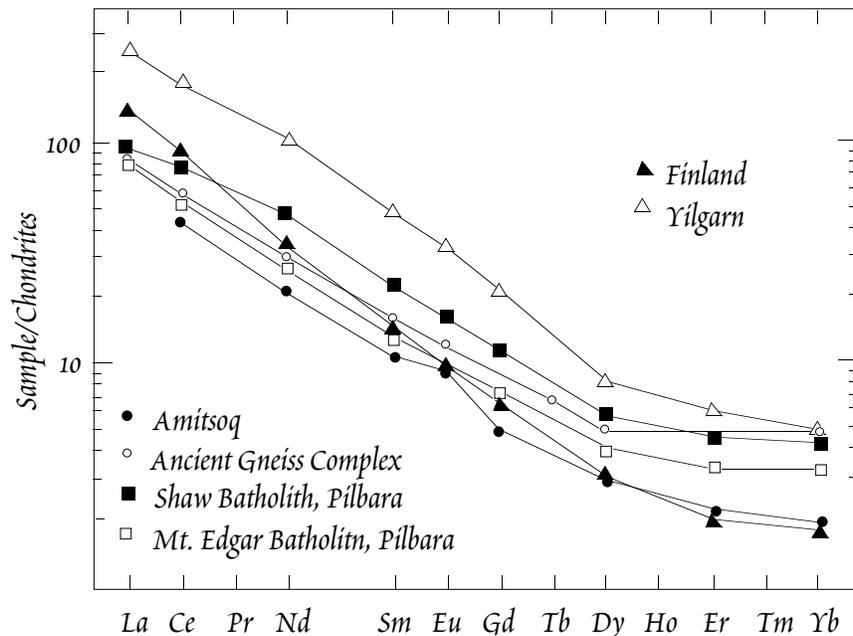
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* Tonalite, or quartz diorite, is a plutonic rock of more or less andesitic composition, having a predominance of plagioclase over orthoclase (i.e., K-poor diorite).

[†] Trondhjemite is a plutonic rock of more or less granitic composition, but is poorer in orthoclase and richer in plagioclase than granite *senso stricto* (i.e., K-poor granite).

selves formed only shortly before. The oldest preserved crust (>3.5 Ga) invariably consists of high-grade gneiss terranes.

A number of tectonic models have been suggested for the origin of these two terranes. The greenstones themselves are clearly of mantle derivation, though there is evidence in a few cases of crustal contamination. Hypotheses for their origin include continental rifts, island-arcs or continental margins, back-arc environments, and oceanic plateaus formed over mantle plumes. Many have argued that the presence of komatiites precludes formation of greenstone belts in island arcs. Because komatiites require extremely high temperatures for their generation, the relatively cool subduction zone environment seems an unlikely setting for their production. It seems more likely they formed over a zone of mantle upwelling, such as a mid-ocean ridge or mantle plume. In the Abitibi Belt, which formed between 2730 Ma and 2690 Ma, the volcanics lack Nb-Ta anomalies characteristic of subduction related magmas. This, and the rapid production of great volumes of magma, led Vervoort et al. (1993) to argue this belt originally formed as an oceanic plateau produced by a mantle plume. The granitic intrusions, which are generally slightly younger, however, do possess Nb-Ta anomalies, and hence may have formed near a subduction zone. Vervoort et al. (1993) suggested these granites were generated over a subduction zone and intruded the greenstone belt as it was accreted to the growing Superior craton. Early Proterozoic greenstone belts of the West African Craton may also represent accreted oceanic plateaus (Abouchami et al., 1990). Volcanics of other greenstone belts do, however, have Nb-Ta anomalies, suggesting they formed in an island arc setting (Condie, 1989).

The origin of the high-grade gneiss terranes is perhaps more problematic. Some have argued that the TTG suites are mantle melts. While it is possible to create siliceous melts of peridotite under conditions of shallow depth and high water pressure, there are a number of problems with this idea, and it seems more likely the TTG suite represents melts of a basaltic precursor (Taylor and McLennan, 1985; Ellam and Hawkesworth, 1988; Rudnick, 1995). There are two basic variants of this idea. First, they could represent melts of basaltic lower crust. The basaltic precursor could have formed in any number of tectonic environments. Alternatively, they could represent melts of subducted oceanic crust (Martin, 1986; Drummond and Defant, 1990). Higher temperatures and more rapid plate movements in the Archean may have meant that melting of subducting oceanic crust, which is rare today, was common then. In either case, melting must have occurred under sufficient pressure that the basaltic source was metamorphosed to amphibolite or eclogite.

REFINING THE CONTINENTAL CRUST

We can summarize by saying that the continental crust has been created by partial melting of the mantle. Subduction-related volcanism appears to have been the principal environment in which new crust has formed. Rudnick (1995) estimates that 65 to 90% of the crust has been produced in this manner. Archean crust is compositionally distinct. This may reflect a greater proportion of crust produced by some other mechanism (e.g., melting of mantle plumes), a difference in the composition of subduction-related magmas due to higher temperatures, or both.

One serious problem remains, however, namely that the composition of the continental crust does not match that of a *primary* mantle melt. Primary mantle melts are, with rare exceptions, basaltic. If the continental crust were simply a melt of the mantle, it should have a basaltic composition, as does the oceanic crust. Compared to basalt, which is the principal melting product of the mantle, it is too rich in SiO_2, too poor in MgO and CaO (and probably FeO), has too low a Mg# and too high a Rb/Sr ratio, and is generally too rich in incompatible elements. This is true irrespective of the environment in which these melts are produced. Compared to typical island arc basalts, its Al_2O_3 is also too low, as is its Sr/Nd ratio. As we stated earlier, basalt, not andesite, is the primary melt produced in subduction zones, and intra-oceanic arcs have basaltic bulk compositions. Andesites, while abundant in island arcs and even dominant in continental margin settings such as the Andes, are products of intracrustal fractional crystallization of basaltic parents, which in the case of continental margins, is often accompanied by assimilation of pre-existing crust (e.g., Hawkesworth et al., 1982). Furthermore, andesites produced in this way have concentrations of highly compatible elements, such as Ni

and Cr, that are much lower than those of the continental crust. Similarly, mantle-derived magmas produced at rifts or over mantle plumes are predominantly basaltic. While some andesitic magmas can be produced by melting of mantle peridotite or by reaction of basaltic magma with peridotite (e.g., boninites), such melts are rare and require very special conditions for their generation. Furthermore, their compositions do not match that of continental crust. These observations have led to the suggestion that the continental crust has been "refined" in some way; that is, some other process or processes have operated to transform the composition of the crust.

One possible explanation for this problem is that lower continental crust, consisting of mafic cumulates or partial melting residues, detaches, or "delaminates", along with underlying subcontinental mantle lithosphere (Kay and Kay, 1991). The idea is that when the crust is thickened the 50 km or more in collisional zones such as the Andes or the Himalayas, mafic lower crust will be transformed to garnet granulite and eclogite, greatly increasing its density. Under these circumstances, it may simply detach from the overlying crust and be swept away in asthenospheric circulation along with the underlying mantle lithosphere. The lithosphere would be replaced by hotter, lower density asthenosphere, which would produce uplift and basaltic volcanism. Kay and Kay argued that precisely these phenomena are observed in the Puna of Argentina, where the crust was thickened to as much as 65 km in the Miocene. As we noted in the previous chapter, McKenzie and O'Nions (1983) suggested that detached subcontinental lithosphere could later form the source of mantle plumes.

Since the lower continental crust is clearly more mafic and poorer in incompatible elements than the bulk crust (compare Tables 12.6 and 12.7), loss of lower crust to the mantle clearly provides a mechanism for adjusting the composition of the crust in the desired direction. On the other hand, the great age of many xenoliths from the subcontinental lithosphere attests to it stability (it would be difficult to detach the lower crust without also detaching the underlying mantle lithosphere). As we noted in Chapter 11, peridotite xenoliths derived from the mantle lithosphere often have the same age as the overlying crust (however, none of these ancient xenoliths have been found in areas where lithospheric detachment is thought to have occurred). Furthermore, the distinctive Os–Nd isotope systematics of subcontinental lithosphere have not been found in any mantle plumes yet. Nevertheless, detachment of the lower crust is a viable and interesting hypothesis, and one that deserves further study.

Yet another possibility is that the composition of the crust has been refined through erosion and subduction of weathering products. During weathering, certain elements, most notably Mg, preferentially go into solution. Mg is carried to the oceans where it is removed from solution by reaction with the basaltic oceanic crust during hydrothermal activity at mid-ocean ridges (discussed in Chapter 15). Depending on the fluxes assumed, it would appear that this process has the potential for removing substantial amounts of Mg from the crust and hence make it less mafic (see Problem 12.8 at the end of the chapter). In the same way, other soluble elements, such as Ca and Na, would be removed from the crust.

While this process probably contributes to refining the composition of the crust, its effect is probably quite limited. If it were important, we would expect the major element chemistry of the crust to be enriched in the least soluble elements (Al, Si, and Fe) and systematically depleted in the most soluble ones (Na, Mg, Ca) compared to typical igneous rocks. This is not the case. Among trace elements, it would not increase the extent of LRE enrichment, nor is it clear that this mechanism could increase the Rb/Sr ratio of the crust as required (though it would decrease Sr/Nd).

O'Nions and McKenzie (1988) pointed out that the incompatible element abundances in the continental crust resemble that of a very small (~1%) degree melt of the mantle. They argued that such small degree melts will be generated during episodes of continental extension. The melts would migrate into the subcontinental lithospheric mantle or lower crust and freeze there. Subsequent melting of this lower crust would produce strongly incompatible element enriched granites, which are common components of the upper crust. Interestingly, if this mechanism does indeed have a significant influence on the incompatible element budget of the continents, it would mean that Sm-Nd model ages significantly underestimate the age of the continents. Relatively little testing of this interesting hy-

pothesis has been carried out, so it is difficult to judge the importance of this process. Even if the incompatible element abundances in the crust can be explained this way, they hypothesis does not address the problems with major element composition listed above.

References and Suggestions for Further Reading

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PROBLEMS

1. The adjacent table shows trace element data from three volcanic rocks, each erupted in a different tectonic environment. Plot the data on a "spider diagram". Make the y-axis logarithmic and order the elements as in Figure 12.32. "Normalize" the data to "Primitive Mantle" using the concentrations given in Table 10.3. Based on your plot, identify the tectonic setting in which each erupted.

2. In a sedimentary core, the surface sample had a ^{10}Be concentration of 100×10^6 atoms/g. Assuming steady state accumulation of ^{10}Be at the surface, what concentration of ^{10}B would you predict for a 10 million year old sample from lower in the same core? (*HINT: use the decay constant given in Table 7.5*).

3. The following Sr and Nd isotope data from St. Lucia show that these volcanics are mixtures of two components. Assuming that component A has $^{87}Sr/^{86}Sr$, ε_{Nd}, Sr, and Nd concentrations of 0.706, -0.5, 200 and 8.5 ppm respectively, and component B has $^{87}Sr/^{86}Sr$ and ε_{Nd} of 0.710 and -13.4, estimate the Sr and Nd concentrations of component B. (*HINT: Plot the data and superimpose a 2 component mixing model on the plot; adjust the concentrations by trial and error until you find the best fit*).

4. The adjacent table below shows concentrations of Sr and $^{87}Sr/^{86}Sr$ measured on river samples. These samples were taken just below the point where two major rivers join. Are data consistent with simple mixing between the waters of these two rivers? Why or why not.

5. Plot oxygen and strontium isotope ratios measured on lavas from Galeras Volcano (Colombia) in the following table, then decide whether mixing curve they define a result of sediment subduction ("source contamination") or assimilation ("crustal contamination")? Justify your answer.

DATA FOR PROBLEM 12.1

	A	B	C
Cs		1.07	0.015
Rb	34.00	17.96	1.33
Ba	389.47	353.83	12.30
Th	7.80	14.50	0.29
U	1.89	4.99	0.11
Nb	45.67	9.65	5.93
Ta	2.51	0.45	0.35
K	25921.00	5130.00	1160.00
La	42.78	31.38	6.93
Ce	93.76	66.73	23.10
Pb	4.14	7.86	0.68
Pr	11.96	7.41	4.31
Sr	717.87	798.75	92.60
Nd	48.20	28.21	22.80
Sm	10.36	5.29	7.89
Zr	300.91	121.92	227.00
Hf	6.97	3.86	7.15
Eu	3.06	1.45	2.50
Gd	8.90	4.83	10.90
Tb	1.36	0.69	
Dy	6.37	3.51	13.00
Y	30.34	19.73	69.10
Ho	1.06	0.68	2.89
Er	2.33	1.71	8.46
Tm	0.30	0.27	
Yb	1.63	1.58	7.94
Lu	0.22	0.23	1.19

SR AND Nd ISOTOPE DATA FROM ST. LUCIA

Sample	$^{87}Sr/^{86}Sr$	ε_{Nd}
STL220	0.70655	-3.02
SL124	0.70933	-11.76
SL125	0.70782	-8.74
SL51	0.70845	-10.26
SL52	0.70850	-10.09
SL121	0.70907	-11.26
SL48	0.70885	-10.90
SL42	0.70829	-9.71
SL40	0.70837	-9.99

DATA FOR PROBLEM 4

Sr, $\mu g/l$	$^{87}Sr/^{86}Sr$
45	0.71571
60	0.71305
78	0.71162
100	0.71073
123	0.71013
136	0.70969
161	0.70935
179	0.70909

DATA FROM GALERAS VOLCANO

$^{87}Sr/^{86}Sr$	$\delta^{18}O$	Sr, ppm
0.70414	6.79	503
0.70409	6.65	504
0.70453	7.65	545
0.70423	6.99	521
0.70434	7.51	521
0.70435	7.11	534
0.70419	6.72	514

6. Construct an AFC model of the data from Galeras Volcano in the accompanying table. Assume that the $^{87}Sr/^{86}Sr$ of the assimilant and original magma are 0.712 and 0.70375, respectively, the $\delta^{18}O$ of the assimilant and original magma are +10.5 and +5.8, respectively, and Sr concentrations of the assimilant and original magma were 100 and 470 ppm respectively. Find values of R (ratio of mass assimilated to mass crystallized) and D_{Sr} (bulk partition coefficient for Sr) that best fit the data (assume the partition coefficient for O is 1). (*HINT: plot both $^{87}Sr/^{86}Sr$ vs. Sr and $\delta^{18}O$ vs $^{87}Sr/^{86}Sr$, and adjust values of R and D until the line describing your model passes through the data*).

7. (a.) Assuming the Bulk Silicate Earth (BSE) has the "primitive mantle" Rb concentration given in Table 10.3, what fraction of the Rb in the BSE is in the crust according to the Taylor and McLennan, Rudnick and Fountain, and Wedepohl crustal compositions (Table 12.7)? (*HINT: use the volumes of crust and mantle given in the Appendix*).
 (b.) Assume that the silicate Earth consists of only three reservoirs: continental crust, depleted mantle and primitive mantle, that the depleted mantle has a Rb concentration that is 10 times lower than the average MORB concentration (Table 12.2), and that the primitive mantle has the Rb concentration given in Table 10.3. What fraction of the mantle would consist of depleted mantle when you use the Taylor and McLennan, Rudnick and Fountain, and Wedepohl crustal Rb concentrations (Table 12.7)?

8. Weathering and erosion remove Mg from the continents and transport it in dissolved form to the oceans. Dissolved Mg is removed from the oceans by hydrothermal activity at mid-ocean ridges. Assuming that the flux of Mg into the oceanic crust given in Chapter 15 has been constant through time over the past 2.5 Ga and that all this Mg is derived from the continental crust, how much has the crustal Mg concentration decreased as a result of this process? How might this result change if we make other "reasonable" assumptions about the flux of Mg into the oceanic crust through time?