



Chemical Composition and Element Distribution in the Earth's Crust

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GLOSSARY

Anorthosite Essentially monomineralic intrusive igneous rock composed almost entirely of plagioclase feldspar.

Diagenesis Chemical, physical, mineralogical, and biological transformations undergone by a sediment between the time of initial deposition and metamorphism.

Differentiation The separation of chemical elements during crystallization into different mineral phases.

Europium anomaly and Eu^* The element europium is

divalent on the moon and is mostly separated from the other trivalent rare earth elements because it is concentrated in plagioclase feldspar. The degree of enrichment or depletion is given by Eu/Eu^* , where Eu is the measured abundance and Eu^* is the abundance expected if Eu had the same relative concentration as the neighboring rare earth elements, Sm and Gd.

Ignimbrite A rock formed from the deposition of volcanic ash flows.

Lithosphere The cool outer rigid layer of the Earth, including the crust and uppermost mantle, and separated

from deeper layers of the mantle by a relatively weak zone, the asthenosphere. Lithosphere thickness varies from zero at active mid-ocean ridges to as much as 200 km or more beneath continents.

Model age Age of a rock or mineral that is determined by radiogenic isotope methods in which the initial isotopic ratio of the sample is assumed.

Normative mineralogy Theoretical mineralogical composition of a rock that is determined from the chemical composition by assuming standardized mineral compositions and crystallization under equilibrium conditions.

Planetesimals The building blocks of the planets. Small rocky or icy bodies formed in the primordial solar nebula. They range greatly in size from one kilometer up to the size of small planets.

P-wave velocity (V_p) Seismic body wave velocity associated with particle motion (alternating compression and expansion) in the direction of wave propagation.

Shield Tectonically stable, low lying Precambrian nucleus of continents, commonly containing the metamorphosed roots of ancient orogenic activity.

TWO PRINCIPAL TYPES of Earth's crusts have formed. These are the oceanic and the continental crusts that differ in composition, age, and evolution. The oceanic crust is effectively a conveyor belt that transfers the chemical elements, derived from melting in the mantle beneath the mid-ocean ridges, to the plate margins where they are subducted back down into the mantle. The composition is dominated by basalts with a veneer of sediment derived from biological activity in the oceans and weathering of the continents. Intraplate basaltic volcanoes from a deeper mantle source that involves some of the subducted oceanic crust, make a minor contribution to the oceanic crust.

In contrast to the transient nature of the oceanic crust that currently is younger than 200 million years, the continental crust grew slowly and episodically through geological time from melting and dehydration, of the downgoing slab and the mantle immediately above the slab. About 60% of the crust was formed mostly in the late Archean 3000–2500 million years ago. Growth continues today through island arc volcanic activity. The continental crust, in contrast to the oceanic crust, is buoyant and is only subject to surficial erosion. The upper crustal composition is arrived at by using the abundances of immobile elements in sedimentary rocks, coupled with large-scale sampling of the surface, while heat-flow data are used to constrain bulk crustal composition. The bulk continental crust is approximately andesitic in composition. Subsequent melting within the crust has produced an upper crust dominated by granites, rich in elements such as K, U, Th, Ba, and

Rb and leaving a depleted lower crust. The end result of about 4 billion years of this activity is that the continental crust now contains up to 50% of the total Earth budget of these elements. The continental crust is unique compared to the dominantly basaltic crusts on other planets in the inner solar system. Along with the operation of the unique plate tectonic cycle this is a consequence of the presence of abundant free water on the Earth.

Here we summarize their composition and the distribution of the chemical elements and explain how these two contrasting crusts arose on the planet.

I. TWO CRUSTS ON A MOBILE EARTH

There are two major and quite distinct types of crust on the Earth. This is in contrast to most other bodies in the solar system. The oceanic crust, mainly basalt, is derived from melting within the mantle at mid-ocean ridges. Coated with a veneer of sediment, it is subducted back into the mantle at the site of the great trenches. This process has continued for around 4 billion years, so that about 10% of the mantle comprises recycled oceanic crust. The oceanic crust resembles a conveyor belt continuously extracting melts of basaltic composition from the mantle, and mostly returning them back to the mantle on timescales of 100–200 million years. At any stage, therefore, its composition has a transitory quality as elements are extracted from one mantle reservoir (usually labeled as the mid-ocean ridge basalt, hereafter MORB, source) and mostly return back into the mantle. A small percentage of elements emerge back on the surface later as lavas erupted from intraplate volcanoes. These are customarily referred to as oceanic island basalts (OIB)

The continental crust, in contrast, forms slowly over geological time by processing of the subducting oceanic crust at the sites of the downgoing slabs (Fig. 1). At these locations, dehydration and melting releases a small fraction of elements that emerge at the surface in various manifestations of island arc activity as tonalites, trondhjemites, or andesites that eventually form the continental crust. Remelting of such mantle-derived rocks within the crust gives rise to more silica-rich derivatives of which varieties of granites and ignimbrites are most familiar. These, overlaid by a veneer of sedimentary rocks, are the major components of the upper 10 km or so of the continental crust. The end result of several stages of melting over a few billion years is to produce an upper crust that is strongly enriched in incompatible elements such as K, U, and Th, so that the continental crust, and the upper crust in particular, contains significant proportions of the total Earth budget for these elements. The continental crust thus becomes strongly zoned with an upward enrichment

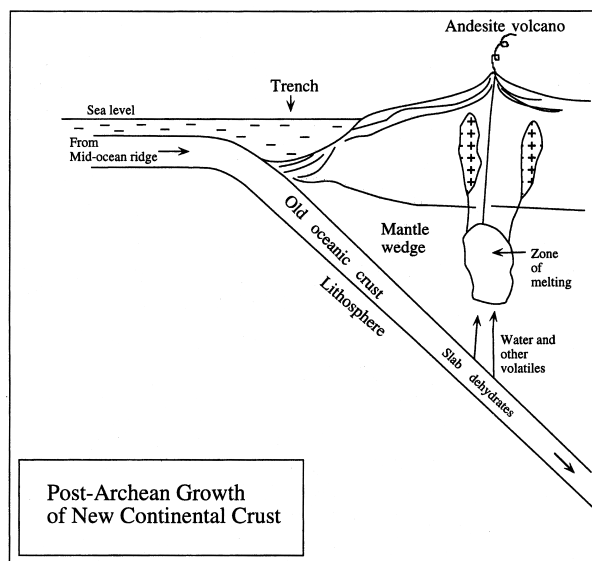


FIGURE 1 Schematic model of Post-Archean crustal growth at subduction zones.

of incompatible elements and a somewhat depleted lower crust. However, its production is so inefficient that after 3 or 4 billion years, it now constitutes only about 0.40% of the mass of the Earth. Unlike the oceanic crust that is rapidly recycled, the continental crust remains buoyant, subject only to destruction by the geological processes of surficial erosion.

II. SAMPLING THE CRUSTS

Establishing the composition of the oceanic crust has been carried out by a combination of dredging, drilling by the Ocean Drilling Program, sampling of oceanic island volcanoes, and some detailed examination by submersibles. The relative uniformity of the composition of MORB that makes up the bulk of the crust, apart from the veneer of sediments that are mostly derived from continental sources, makes the task of estimating the bulk composition of the oceanic crust somewhat easier than that of the very diverse continental crust. Isotopic studies delineate various distinctions among the MORB sources, but these have only a minor effect on the compositions of the major elements. The volcanoes that make up oceanic islands are somewhat more varied in composition, due to magma chamber fractionation, but are dominated by OIB that come from a source distinct from MORB and point to long-term mantle heterogeneities.

The continental crust is especially diverse and heterogeneous. Major compositional changes occur, sometimes on a scale of meters. Arriving at a reliable average composition might be thought to be difficult, if not impossible.

Nature, however, through the processes of erosion and sedimentation, has carried out its own overall sampling of the exposed crust and this information is stored within the sedimentary rock record.

The average composition of the bulk crust down to 40 km is a more complicated issue and the various geophysical approaches (e.g., seismology, heat flow) are not in complete agreement. Accordingly, there is considerably less of a consensus about both bulk crustal composition and mechanisms of crust formation. Constraints from geochemistry and continental heat flow appear more reliable and, though model-dependent, provide reasonable estimates of the average K, Th, and U content of the bulk crust. In turn these data limit models of bulk crustal composition. Reading the sedimentary and geophysical records have helped to resolve the sampling problem and have provided detailed information about the composition and evolution of the continental crust.

Geological, petrological, geochemical, and geophysical observations each provides important constraints on the composition and evolution of the continental crust and combine to allow some broad generalizations. Thus the heat-flow data indicate that the composition of the readily observable upper crust cannot persist below about 10 km, so that the lower crust is in many ways a distinct geochemical entity.

There is much evidence to suggest a basic difference between the crust generated during much of the Early Archean (before about 3000 million years) and that which developed during the Late Archean and subsequently during the Proterozoic and Phanerozoic. The nature of the earliest crust, though the subject of intense interest, remains largely a mystery. There has been a continuing debate over the growth rate of the crust, the scale of recycling of the crust into the mantle, and of course its ultimate origin.

A. Sedimentary Rocks as Crustal Samples

Some elements possess the desirable property of having extremely low concentrations in natural waters and so have short residence times in the oceans (Fig. 2). Such elements, of which the rare earth elements (REE) are a prime example, are thus transferred quantitatively during erosion and sedimentation from the parent rocks into clastic sediments. The most important among these elements are the REE, Y, Sc, and Th (other insoluble elements, such as Zr, Hf, and Sn, have similar properties but the chemistry of these elements in clastic sediments is totally dominated by heavy minerals, such as zircon and cassiterite that are readily segregated in geological processes). Mixing and homogenizing effects of sedimentary processes should produce uniform REE patterns in sedimentary rocks, especially for fine-grained clastic sedimentary rocks such as shales and that these should reflect the abundances in the upper

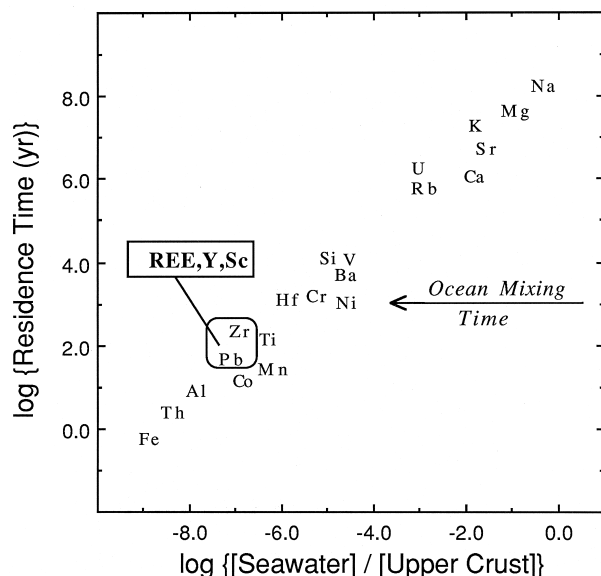


FIGURE 2 Plot of Residence Time against the ratio of concentrations in average seawater to that in the upper continental crust, for selected elements. Elements with very low concentrations in seawater and very low residence times (e.g., REE, Th, Sc) are transferred nearly quantitatively into terrigenous sediments and thus record their distributions in the upper crustal provenance. Some elements with low residence times are less useful due to complex behavior during sediment transport (e.g., Zr, Hf, Sn) or diagenesis (e.g., Fe, Mn, Pb).

continental crust. Shales and their relatives are volumetrically the most important sedimentary rock types (constituting about 70% of the sedimentary mass) and so effectively the abundances of these insoluble elements in shales can be closely related to that of the upper crust (Fig. 3).

Although some diversity exists in REE patterns, especially in first-cycle sediments (particularly those from volcanically active continental margins), the average REE pattern is very similar for most shales. These REE patterns are enriched in the light REE (LREE = La–Sm) relative to chondritic patterns, that are taken as representative of the bulk Earth, and have a depletion in Eu relative to the neighboring REE, Sm, and Gd (usually referred to as a “negative Eu anomaly”). The converse enrichment in Eu is often referred to as a “positive Eu anomaly.”

Since the REE are not readily fractionated in sedimentary processes (except that Ce^{3+} may be oxidized to Ce^{4+} and separated as the insoluble phosphate in marine environments, or less frequently as the hydroxide in terrestrial environments), this pattern is recording a previous signature of igneous events involving partial melting (or crystal fractionation) and removal of Eu by plagioclase as a residual phase.

Modern sediments (Table I) mostly display REE patterns similar to those of the Post-Archean shales (Fig. 3).

The REE patterns of most suspended particulate matter in some of the world's major rivers are also very similar to average Post-Archean shales, although slightly enriched in total REE due to their finer grain size (REE are concentrated in the clay fraction and in heavy minerals).

About 10% of the Earth's land surface is covered with Pleistocene loess. The origin of most loess by aeolian transport from glacial outwash, particularly during cold dry climatic regimes is well established. This combination of widespread production of silt-sized rock flour, and its transport by wind over hundreds of kilometers thus provides geochemists with a natural sampling of comparatively unweathered material from the exposed crust. Loesses from North America, Europe, China, and New Zealand show very uniform REE abundances (although sometimes diluted by quartz or carbonate), with Eu depletions equivalent to those observed in other clastic sedimentary rocks, indicating that they are providing a reasonable sample of the upper continental crust.

The similarity of REE patterns for the widely scattered loess deposits to those of shales from widely separated continental areas indicates that loess also provides the same information on the composition of the upper crust as that provided by clastic sediments. There is little evidence these sediments have been affected by significant weathering. This demonstrates that upper crustal provenance is the prime control on REE patterns of clastic sedimentary rocks rather than the effects of sedimentary processes.

Important to these interpretations of sedimentary REE patterns is an understanding of possible effects of various

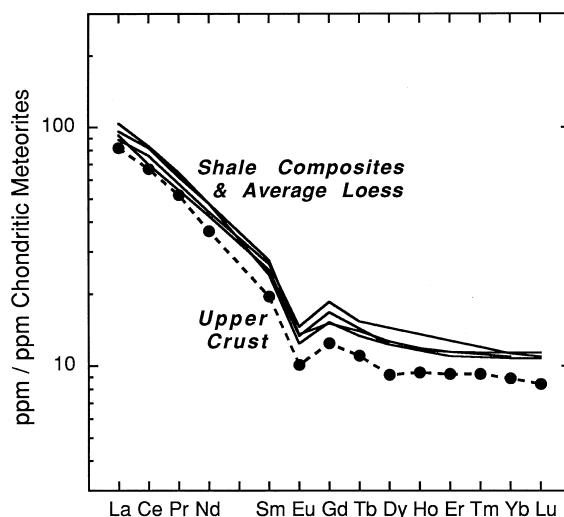


FIGURE 3 Rare earth element (REE) diagram showing compositions of various shale and loess averages and composites. Shown for comparison is the REE pattern for the average upper continental crust.

TABLE I Estimates of the Average Chemical Composition of Various Sedimentary Reservoirs

Element	Average sediment ^a	Average mud ^b	Average river particulate ^c	Loess ^d	Average Pelagic clay ^e	Deep sea carbonate ^f
Li (ppm)	21	30	25	30	57	5
Be (ppm)	2.2	3	—	2	2.6	—
B (ppm)	75	100	70	—	230	55
Na (wt.%)	1.25	0.89	0.71	1.4	4.0	0.2
Mg (wt.%)	1.85	1.4	1.2	0.68	2.1	0.4
Al (wt.%)	7.10	10.3	9.4	6.9	8.4	2.0
Si (wt.%)	30.0	29.9	28.9	35.7	25.0	3.2
P (ppm)	665	700	1150	—	1500	350
K (wt.%)	2.35	3.2	2.0	1.9	0.5	0.3
Ca (wt.%)	6.40	0.93	0.2	0.79	0.93	31.24
Sc (ppm)	14	16	18	8	19	2
Ti (wt.%)	0.45	0.60	0.56	0.41	0.46	0.08
V (ppm)	110	140	170	73	120	20
Cr (ppm)	74	100	100	44	90	11
Mn (ppm)	680	850	1050	560	670	1000
Fe (wt.%)	4.00	5.1	4.8	2.4	6.5	0.90
Co (ppm)	16	20	20	11	74	7
Ni (ppm)	40	60	90	20	230	30
Cu (ppm)	40	50	100	18	250	30
Zn (ppm)	65	85	350	60	200	35
Ga (ppm)	16	20	25	4	20	13
Ge (ppm)	1.5	2	—	—	2	0.2
Rb (ppm)	110	160	100	85	110	10
Sr (ppm)	385	200	150	192	18	2000
Y (ppm)	21	27	28	25	40	42
Zr (ppm)	210	210	—	375	150	20
Nb (ppm)	17	19	—	20	14	—
Mo (ppm)	—	1.0	3	—	27	—
Cd (ppb)	—	—	1000	—	300	—
Sn (ppm)	5	6	—	5	3.0	—
Cs (ppm)	4.5	6	6	4	6	0.4
Ba (ppm)	480	650	600	625	2300	190
La (ppm)	28.3	38.2	46	35.4	42	10
Ce (ppm)	58.9	79.6	88	78.6	80	—
Pr (ppm)	6.52	8.83	9.0	8.46	10	—
Nd (ppm)	24.9	33.9	33	33.9	41	—
Sm (ppm)	4.23	5.55	7.0	6.38	8.0	—
Eu (ppm)	0.86	1.08	1.5	1.18	1.8	—
Gd (ppm)	3.61	4.66	5.4	4.61	8.3	—
Tb (ppm)	0.60	0.774	0.89	0.81	1.3	—
Dy (ppm)	3.61	4.68	5.4	4.82	7.4	—
Ho (ppm)	0.76	0.991	1.1	1.01	1.5	—
Er (ppm)	2.19	2.85	3.1	2.85	4.1	—
Tm (ppm)	0.31	0.405	0.44	0.40	0.57	—
Yb (ppm)	2.14	2.82	3.2	2.71	3.8	—
Lu (ppm)	0.33	0.433	0.52	0.42	0.55	—
Hf (ppm)	5.5	5.0	6	11.4	4.1	—

Continues

TABLE I (continued)

Element	Average sediment ^a	Average mud ^b	Average river particulate ^c	Loess ^d	Average Pelagic clay ^e	Deep sea carbonate ^f
Ta (ppm)	1.5	2	1.25	—	1	—
W (ppm)	2.1	2.7	—	1.6	1	—
Pb (ppm)	17	20	150	13	30	9
Bi (ppb)	—	250	—	—	550	—
Th (ppm)	10.4	14.6	14	11.3	13.4	—
U (ppm)	2.3	3.1	3	2.5	2.6	—

^a Average sediment: Procedure is to take average of distinctive sedimentary lithologies and form weighted average based on relative distribution of lithologies during the Cenozoic. Proportions adopted are mud : sand : carbonate : evaporite : siliceous : volcanogenic = 59 : 16 : 13 : 2 : 1 : 9. Volatile free.

^b Average mud: Volative-free, carbonate-free basis; assumed to be equivalent to average shale.

^c Average river particulate: Note that concentrations of some elements are affected by anthropogenic factors (e.g., Cd, Pb).

^d Average loess: On a carbonate-free basis.

^e Average pelagic mud: Estimate includes 1300 ppm F and 2.1% Cl.

^f Deep sea carbonate: Note that composition includes a small terrigenous component (e.g., Al = 2.0%).

[Adapted from McLennan, S. M., and Murray, R. W. (1999). In "Encyclopedia of Geochemistry," (C. P. Marshall and R. W. Fairbridge, eds.), pp. 282–292, Kluwer Academic, Dordrecht.]

sedimentary processes on REE distributions in sedimentary rocks. Recent studies of granite weathering indicate that substantial fractionation may take place within weathering profiles resulting in, among other things, significant cerium anomalies associated with formation of Ce⁴⁺ and stable cerium hydroxides. In most situations, such fractionation does not translate into unusual sedimentary rock REE patterns because the weathering profile is well mixed during subsequent erosion and transport although a few exceptions may exist.

Sedimentary transport may also result in changing sedimentary REE patterns due to heavy mineral (notably zircon and monazite) fractionation. Such effects can be modeled with some confidence and are most likely to be a significant influence in clastic sediments such as quartzites with low REE abundances. Recent studies have also demonstrated that REE may be significantly affected during certain conditions of diagenesis. Redistribution of REE among newly formed diagenetic minerals, without significant transport, appears to occur in most cases.

The bulk of the REE elements reside both in trace minerals (such as zircon, monazite, apatite, etc.) and the fine-grained (clay and silt) fraction (but that there is no correlation with specific clay mineralogy). There is some indication that significant fractions of REE in clay minerals may also occur as microinclusions of resistate minerals such as apatite.

Sand fractions within a sedimentary rock have significantly lower total abundances and slightly lower La/Yb

ratios (due to heavy mineral concentrations) than finer grained fractions, but Eu anomalies are similar in all size fractions.

Coarse-grained sedimentary rocks typically have REE patterns essentially parallel to those of shales, but with lower total abundances than shales, due mainly to the diluting effect of quartz. The overall shape of the patterns (Eu/Eu*, La/Yb) is generally similar for sandstones and shales. The REE abundances in quartz-rich sedimentary rocks are typically very low. The potential of heavy minerals to distort REE patterns in sedimentary rocks is well recognized. However, these minerals are only rarely concentrated in amounts sufficient to cause perceptible effects on the REE patterns. Thus the resistant mineral zircon, typically enriched in heavy REE, affects the bulk rock patterns only when zircon constitutes more than about 0.06% (or Zr abundances exceed about 300 ppm), since every 100 ppm of Zr as zircon adds only about 0.25 times the chondritic levels of Yb (typical shale patterns are about 10–15 times chondritic levels for that element).

III. HEAT PRODUCTION AND HEAT FLOW

It is important to realize that the sedimentary rock data provide information only on that portion of the crust exposed to weathering and erosion, that is mostly the upper 10 km. Evidence from heat-flow data shows that the upper crust (about 10 km thick) is strongly enriched in the heat-producing elements (K, U, and Th). Simple mass balance

calculations show that a 41-km thick crust with K, Th, and U abundances equal to the upper continental crust would require about 80–90% of the entire Earth's complement of these elements to be present in the continental crust. Thus the upper crust is not representative of the entire 41-km thickness of the continental crust.

There are two primary sources of heat: radioactive decay, principally from ^{40}K , ^{238}U , ^{235}U , and ^{232}Th , contributing up to 80% of the terrestrial heat flow, and secular cooling of the Earth, responsible for at least 20%. Some estimates place the radiogenic component of terrestrial heat flow as low as 50% and the relative importance of the various sources of the Earth's heat remains an important outstanding question. The average heat flow at present from continental areas is about 65 mWm^{-2} compared to 101 mWm^{-2} for the oceans and 87 mWm^{-2} for the whole Earth. Temperatures at the base of the crust are typically $300\text{--}400^\circ\text{C}$ in shield areas, $500\text{--}600^\circ\text{C}$ in young orogenic areas, and $650\text{--}750^\circ\text{C}$ in rift regions. This heat is derived from three main sources.

The first is the “reduced” heat flow that is heat from the deep interior transmitted mainly by conduction across the crust-mantle boundary. Then there is additional heat associated with tectonic activity within the lithosphere (mountain building and denudation). This component decays rapidly over periods of about 400 million years and so is unimportant except in regions that experienced Phanerozoic tectonic activity. The third component is heat generated by radioactive decay within the lithosphere; this is dominated by upper crustal heat production. This component is estimated at 29 mWm^{-2} . For a 41-km thick crust, this gives an average heat production of about $0.7 \mu\text{Wm}^{-3}$.

This value enables bulk crustal values for K, U, and Th to be estimated. Using the well-established values of $\text{Th}/\text{U} = 3.8$ and $\text{K}/\text{U} = 10^4$, we arrive at crustal abundances of $\text{K} = 1.1\%$, $\text{U} = 1.1 \text{ ppm}$, and $\text{Th} = 4.2 \text{ ppm}$.

The interpretation of the heat-flow data is not without problems. These will be discussed more fully when we come to consider the constraints that the data place on the bulk composition of the Archean crust. There is a well-established difference between the heat flow in Archean and later Precambrian terrains. Originally, these differences were attributed to differing crustal abundances between Archean and Post-Archean stabilized crust. It appears that the principal controlling factor is not only the crustal abundances of the heat-producing elements but also the thickness of the subcrustal lithosphere.

IV. GEOCHEMICAL DATA

Problems that face both geochemists and other scientists in dealing with the abundance and distribution of the ele-

ments lies both in their wide range in concentrations and in the large number of elements. Weight percentages are the units that are used for the major elements with concentrations above about 0.1% (1000 ppm). Below that level parts per million (10^6), or ppm, are used. One percent is 10,000 ppm. Parts per million is a useful unit for comparing the abundances of trace elements, because many elements have concentrations at that level in rocks and minerals. It also enables the use of small numbers and avoids long strings of zeros. Parts per billion (10^9), or ppb, are employed for abundances 1000 times less than ppm. Thus the amount of the element iridium in the Earth's crust is only one-tenth of a ppb. Finally parts per trillion (10^{12}), or ppt, are employed for concentrations 1000 times less than ppb. These useful units have become firmly entrenched in the geochemical literature.

The large number of elements may be usefully divided into various classes. For the purpose of this article that deals with elements in the crust of the Earth, the principal criterion is their distribution between melts and crystalline phases that are dominated by silicates. Thus we deal here mainly with lithophile elements that form mainly ionic bonds with oxygen. These may be broadly divided into “compatible” and “incompatible” elements. These terms arose during geochemical studies of the mantle. Compatible elements are those that enter the Fe and Mg sites in olivine and pyroxene, minerals that dominate the mineralogy of the upper mantle. Incompatible elements are those whose size or valency exclude them from such minerals. They concentrate in residual melts during crystallization of magmas. They are of most interest here as they are finally concentrated in the crust. A useful diagram for our purpose is Fig. 4a, that clearly separates the lithophile elements on the basis of size and valency. The position of an element in this diagram explains much about its distribution and abundance in the crust. In the wider sphere of planetary compositions, volatility is a major factor, whereas chalcophile (sulfur-loving) and siderophile (metal-loving) properties are more significant in dealing with the formation of the core and mantle.

V. THE OCEANIC CRUST

At the mid-ocean ridges, lavas are erupted from the mantle as the crustal plates are pulled apart due to the drag of the down-going slabs at subduction zones. The mid-ocean ridge (essentially a mountain range) usually has a median valley where most of the igneous activity is concentrated. The active zone is extremely narrow, just a few kilometers wide. At these locations where the new crust is forming, there is little sediment and the crust consists of a few kilometers of basalt. The production of new crust at the

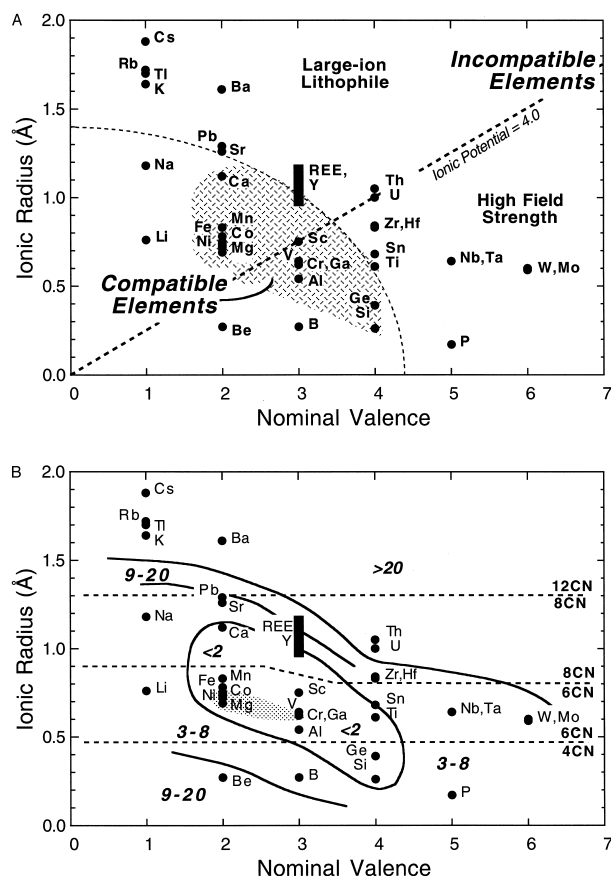


FIGURE 4 Plot of ionic radius versus nominal valence for selected elements. (a) Elements are divided into incompatible and compatible (shaded region) with incompatible elements being further divided into Large Ion Lithophile (LIL) and High Field Strength (HFS) depending on the ratio of Valence/Ionic Radius (Ionic Potential). (b) Same diagram as (a) showing enrichment factors of lithophile elements (divided by solid lines) and depletion of compatible elements (stippled region) in continental crust relative to abundances in the primitive mantle. The degree of enrichment/depletion is a function of the level of incompatibility. Horizontal dashed lines show the coordination with oxygen that was used in calculating the ionic radii.

ridges is about 20 km³ per year. Although hidden from view this constitutes the major expression of volcanism on the globe. Away from the ridges, the crust becomes progressively older. The spreading rates are usually a few centimeters per year. The oldest identified oceanic crust is Jurassic in age, about 200 million years old, but the composition of the lavas is indistinguishable from their modern counterparts at the ridges. The oceanic crust sinks as it ages and cools and the lithosphere thickens.

Out in the ocean between the ridges and the subduction zones, the crust is composed of three main parts. The top layer, Layer 1, is sedimentary cover up to 1 km thick

derived from continental weathering, erosion, volcanic ash, and biological activity that contributes dominantly siliceous material and carbonates. The seismic velocities (V_p) are variable up to 2 km/sec. Layer 2 is varied in thickness around 2.5 km and is composed of basalt with intercalated lenses of sediment. The upper portions of this layer, with $V_p < 4$ km/sec, are mostly of low density, with high porosity due to alteration by reaction with seawater. The lower parts have higher seismic velocities, with V_p around 5 km/sec. Layer 3 is about 4.5 km in thickness. Seismic velocities range from 6.9 km/sec in the upper parts to 7.0 or 7.5 km/sec nearer the Mohorovicic Discontinuity, marked by the change to mantle (V_p) velocities of 8.1 km/sec. Layer 3 is thought to be composed principally of MORB-type basalt. However, the role of underplating or intrusion of serpentinized mantle peridotites at its base is unclear. Although layer 3 may contain gabbros and cumulate rocks developed in magma chambers at mid-ocean ridge sites, the continuous injection of fresh batches of magma at the ridge sites will maintain a uniform MORB-type composition. Thus our estimates of the composition of the oceanic crust are dominated by the MORB component.

There are, however, a number of complicating features. The oceanic islands are mostly composed of OIB, significantly enriched in large ion lithophile elements. These OIB rocks are mostly derived from plume sources that originate deep in the mantle. They contain a substantial component of subducted recycled oceanic crust together with elements apparently from a more primitive mantle component. There are, in addition, a large number of seamounts or guyots resulting from intraplate volcanism that are mostly expected to be of alkali basalt composition. The total production of intraplate volcanism is about 1.5 km³ per year and, although more visible, is minor compared to the massive eruption of MORB at the mid-ocean ridges. Thus in addition to MORB that is depleted in large ion lithophile elements, the OIB will contribute an uncertain amount of these elements to the overall composition of the oceanic crust, that is eventually subducted back into the mantle. Large basaltic plateaus, of which the Ontong Java Plateau in the Western Pacific is the type example, add to the complexity of the oceanic crust.

There is a major interaction between the oceanic crust and circulating seawater. This has substantial effects on the distribution of soluble elements like the alkalis and uranium. Uranium is both leached from basalt and adsorbed on altered basalt. Of interest here is the behavior of the REE. They remain immobile during the alteration of basaltic glass to palagonite and the low concentrations of the REE in seawater percolating through the basalt are rapidly equilibrated so that significant changes in REE patterns or isotopic systematics are not expected, in contrast

to uranium. The depth of penetration of seawater into the crust is probably restricted to the upper portions of the crust.

Table II gives the composition of layer 3 and is essentially that of MORB. Other minor components are variable amounts of pelagic clay (Table I) and OIB (Table II) that contribute to the bulk composition of the oceanic crust.

VI. THE CONTINENTAL CRUST

The mass of the continental crust comprises only 0.40% of that of the Earth. Although it might thus seem so small that it could be ignored to a first approximation, the crust contains over 30% and perhaps up to 50% of the bulk Earth budget for several of the most incompatible elements, such as Cs, Rb, K, U, Th, and La (Fig. 4b). Accordingly the crust is a major geochemical reservoir and its composition is an important constraint on all geochemical models of bulk earth composition and evolution, particularly since the crust is not easily recycled back into the mantle. Any significant temporal change in either the composition or mass of the crust will have important implications for understanding the evolution of the Earth.

A. Size and Mass

The continental crust covers 41.2% of the surface area of the Earth or $2.10 \times 10^8 \text{ km}^2$ of which 71.3% or $1.50 \times 10^8 \text{ km}^2$ lies above sea level. There are four submerged microcontinents and ten major continental blocks. The average elevation of the continents above the mean sea floor (oceanic crust) is about 5 km. The elevation of the area which lies above the 200-m isobath (i.e., the shelf/slope break) is 690 m. The mean elevation of the continental crust above present sea level is 125 m. Crustal thickness varies between 10 and 80 km, correlating with the size of the continental block and the age of the last tectonic event. The average thickness is about 41 km. The volume of the crust is about $8.61 \times 10^9 \text{ km}^3$. This includes both the volumes of the submerged continental masses and sediment on the ocean floor derived from the continents, and has an error of at least $\pm 10\%$ because it depends on the variations in crustal thickness. The base of the crust is defined as the Mohorovicic Discontinuity. At this boundary, compressional wave velocities (V_p) increase from about 7 to about 8.1 km/sec. The Moho may be absent locally and is often not sharp. Thus the crust is usually defined as material with seismic shear wave velocities $V_s < 4.3 \text{ km/sec}$ or $V_p < 7.8 \text{ km/sec}$. Because of the possibility of underplating by basic or ultramafic material, and because of probable interlayering of high-velocity mantle material

with lower velocity crustal material, the base of the crust is likely to be very complicated in detail.

A mid-crustal boundary, the Conrad Discontinuity, is occasionally observed at a depth of about 10–20 km. Where present, it represents a discrete increase in seismic velocity with V_p increasing from about 6.1 km/sec to about 6.4–6.7 km/sec. It is often absent, or poorly constrained by seismic data, especially in shield areas. Sometimes it is gradational over several kilometers. Curiously, the super-deep drill holes have failed to identify many of the discontinuities that were based on interpretations of the geophysical evidence.

Estimates of crustal density range from 2.7 to 2.9 gm cm^{-3} increasing with depth. If an average density of 2.83 gm cm^{-3} is adopted, a crustal mass of $2.44 \times 10^{25} \text{ gm}$ ($\pm 7\%$) is obtained. On this basis, the continental crust forms 0.40% of the mass of the whole Earth and 0.62% of the mass of the crust and mantle, excluding the core.

B. Age

The continental crust, on average, is of great antiquity when compared to oceanic crust which is everywhere less than about 200 million years old. The most robust approach available is based on the Sm–Nd isotope system since in bulk rock samples this is least prone to resetting during later metamorphism. The most important episode of fractionation of Sm from Nd takes place at the time of mantle melting to form continental crust and so the Nd model age of crustal igneous rocks is thought to reflect the age of mantle extraction. Estimates of average crustal age based on the Nd isotope system, while superior to other isotopic approaches, are still likely to represent a minimum due to the effect of intracrustal melting, metamorphic resetting, and assimilation of older material. On the basis of Nd model age provinces in North America and Australia an average age of continental crust is about 2.0 Ga. These data indicate that only 40% of the continental crust was in place by 2.7 Ga (Table III). A mean age of about 2.4 Ga for the continental crust is obtained if about 60% of the crust was in place by 2.7 Ga, as is suggested here.

VII. THE POST-ARCHEAN CRUST

The continental crust is particularly heterogeneous as a glance at a geological map illustrates. Compositional changes may occur on a scale of meters. However, the processes of erosion and sedimentation have carried out an efficient sampling of the upper crust and this information

TABLE II Estimates of the Average Chemical Composition of the Mid-Ocean Ridge Basalt (MORB) and Ocean Island Basalt (OIB) Reservoirs

	MORB	OIB				
SiO ₂	49.5	49.0				
TiO ₂	1.5	2.4				
Al ₂ O ₃	16.0	14.5				
FeO	10.5	11.8				
MgO	7.7	8.0				
CaO	11.3	9.6				
Na ₂ O	2.8	2.8				
K ₂ O	0.15	0.83				
SUM	99.5	99.9				
	MORB	OIB		MORB	OIB	
Li (ppm)	10	6	In (ppb)	72	—	
Be (ppm)	0.5	—	Sn (ppm)	1.4	2.0	
B (ppm)	4	—	Sb (ppb)	17	30	
Na (wt.%)	2.08	2.08	Te (ppb)	3	—	
Mg (wt.%)	4.64	4.82	Cs (ppb)	20	600	
Al (wt.%)	8.47	7.67	Ba (ppm)	15	300	
Si (wt.%)	23.1	22.9	La (ppm)	3.7	19	
K (ppm)	1250	6890	Ce (ppm)	11.5	43	
Ca (wt.%)	8.08	6.86	Pr (ppm)	1.8	4.9	
Sc (ppm)	40	30	Nd (ppm)	10.0	21	
Ti (wt.%)	0.90	1.4	Sm (ppm)	3.3	5.4	
V (ppm)	250	200	Eu (ppm)	1.3	1.8	
Cr (ppm)	270	450	Gd (ppm)	4.6	5.5	
Mn (ppm)	1000	1200	Tb (ppm)	0.87	0.9	
Fe (wt.%)	8.16	9.17	Dy (ppm)	5.7	5.3	
Co (ppm)	47	50	Ho (ppm)	1.3	1.0	
Ni (ppm)	140	120	Er (ppm)	3.7	2.7	
Cu (ppm)	80	90	Tm (ppm)	0.54	0.32	
Zn (ppm)	85	100	Yb (ppm)	3.7	1.9	
Ga (ppm)	17	19	Lu (ppm)	0.56	0.28	
Ge (ppm)	1.5	—	Hf (ppm)	2.5	4.0	
As (ppm)	1.0	—	Ta (ppm)	0.2	—	
Se (ppb)	160	—	W (ppm)	0.01	0.6	
Rb (ppm)	1.5	20	Re (ppb)	0.9	—	
Sr (ppm)	115	400	Os (ppb)	<0.004	—	
Y (ppm)	32	23	Ir (ppb)	0.02	—	
Zr (ppm)	80	150	Pt (ppb)	2.3	—	
Nb (ppm)	2.2	20	Au (ppb)	0.23	—	
Mo (ppm)	0.5	—	Hg (ppb)	20	—	
Ru (ppb)	1.0	—	Tl (ppb)	12	100	
Rh (ppb)	0.2	—	Pb (ppm)	0.5	3.0	
Pd (ppb)	<0.2	—	Bi (ppb)	7	—	
Ag (ppb)	26	—	Th (ppm)	0.22	2.7	
Cd (ppb)	130	—	U (ppm)	0.10	0.7	

TABLE III Age Province Distribution Based on Neodymium Isotope Model Ages

Age province (Ga)	North America ^a (%)	Australia ^b (%)	Weighted average (%)	Average growth rate (%/Ga)
1.0–0.0	19	6	16	16
1.7–1.0	12	12	12	17
2.7–1.7	23	58	32	32
3.8–2.7	46	24	40	36
Total	100	100	100	—

^a [Adapted from Nelson, B. K., and DePaolo, D. J. (1985). *Geol. Soc. Amer. Bull.*, **96**, 746–754.]

^b [Adapted from McCulloch, M. T. (1987). *Amer. Geophys. Union Geodyn. Ser.*, **17**, 115–130.]

is contained in the sedimentary rock sequences. The REE abundance patterns in Post-Archean clastic sedimentary rocks show extreme uniformity on a global scale. Thus REE patterns for composite shale samples from Europe (ES) and North America (NASC) are similar to those for the Post-Archean Australian average shale (PAAS). These patterns are distinguished by relatively flat heavy REE abundances about 10 times chondritic, by light REE enrichment and with a quite uniform depletion in Eu ($\text{Eu}/\text{Eu}^* = 0.65$). This uniformity extends both within and between continents. It is thus interpreted to represent the REE abundances in the upper continental crust exposed to weathering (Fig. 3). The concentrations of other insoluble elements, such as Th and Sc, are also a measure of upper crustal abundances like the REE. Scandium, although trivalent and a member the same group (III) of the periodic table as the REE, is a much smaller ion, and is concentrated in basic rocks, entering early crystallizing pyroxenes. In contrast, thorium is typically concentrated in granitic rocks. The Th/Sc ratio in sedimentary rocks thus forms an index of the relative proportions of granitic and basic rocks.

By using elemental ratios that either are constant across a wide range of igneous compositions (e.g., K/U) or vary systematically with bulk composition (e.g., K/Rb), it is possible to extrapolate to obtain the upper crustal abundances of a number of other elements (Table IV). In this manner the abundance of Rb can be obtained from K/Rb (250); Sr from Rb/Sr (0.3), while U can be obtained from the upper crustal Th/U ratios (3.8) and K from K/U ratios (10,000). The rapidly increasing database for sedimentary rocks has recently permitted upper crustal estimates for a variety of other elements (e.g., Nb, Ta, Zr, Hf, Cr, Ni) from the sedimentary data.

The normative mineralogy of the upper crust based on its major element composition is given in Table V. Thus the composition of the Post-Archean upper crust is well

established, with several estimates converging on a composition close to that of granodiorite.

Modeling of heat-flow/heat-production measurements indicate that this composition cannot be representative of the entire crust (Fig. 5). Evidence for an intracrustal origin of the upper crust is provided by the Eu depletion in Post-Archean sedimentary rocks. Eu anomalies rarely occur in igneous rocks derived from the mantle. No primitive mantle-derived volcanic rock shows a relative depletion in Eu. The depletion of Eu that characterizes chondrite-normalized REE patterns in clastic sedimentary rocks is not due to surficial processes of oxidation or reduction. This element is present as the trivalent ion in sediments. Under the reducing conditions typical of magmas, much of the Eu is divalent. Thus the depletion in Eu is the signature of an earlier igneous event. The origin of the Eu-depleted, K-rich granites and granodiorites, that now dominate the upper crust, is due to formation by intracrustal melting. The depletion of Eu observed in the upper crust is due to the retention of Eu in residual Ca-rich plagioclase in the lower crust (Fig. 6). Plagioclase is only stable to a pressure of 10 kbars (a depth of 40 km on the Earth). This sink for Eu is thus consistent with the experimental studies of intracrustal melting for granite origin. Two sources of heat are available to initiate intracrustal melting. One is the heat generated by radioactive decay of K, U, and Th. The second source is underplating of the crust by basaltic magmas and mantle plumes. The process of underplating is less easily evaluated, but may be needed since the crustal radioactive sources are probably inadequate.

Information about how long this process has been operating can be obtained from the sedimentary record. Loess, derived from source rocks that extend back almost 2 billion years, has uniform REE patterns. This indicates that during the period represented by the source regions of the loesses, the processes producing the upper crust have not changed. Thus the composition of the upper continental crust has been uniform and produced by similar processes well back into the Proterozoic.

There are two sources of heat available to induce intracrustal melting. The first is the heat generated by radioactive decay of K, U, and Th. The second source, underplating of the crust by basaltic magmas, is less easily evaluated, but appears to be required since the crustal radioactive sources are generally considered to be inadequate for the task.

A. The Lower Crust

Geophysical data show the very diverse nature of the lower crust. It appears to be at least as heterogeneous as the upper crust and is likely to be very complex in detail, an example of which appears to be the Ivrea Zone in Northern Italy.

TABLE IV Chemical Composition of the Continental Crust

Element	Upper continental crust	Bulk continental crust	Lower continental crust	Average andesitic crust	Lower crustal granulites	Archean upper crust	Archean bulk crust
Li (ppm)	20	13	11	10	6	—	—
Be (ppm)	3.0	1.5	1.0	1.5	—	—	—
B (ppm)	15	10	8.3	—	—	—	—
Na (wt.%)	2.89	2.30	2.08	2.60	1.9	2.45	2.23
Mg (wt.%)	1.33	3.20	3.80	2.11	4.3	2.83	3.56
Al (wt%)	8.04	8.41	8.52	9.50	8.78	8.10	8.04
Si (wt%)	30.8	26.8	25.4	27.1	24.4	28.1	26.6
P (ppm)	700	—	—	—	400	—	—
K (wt%)	2.80	1.1	0.53	1.25	.50	1.5	1.0
Ca (wt%)	3.00	5.29	6.07	5.36	6.7	4.43	5.22
Sc (ppm)	13	30	36	30	31	14	30
Ti (wt%)	0.39	0.54	0.59	0.48	0.5	0.50	0.60
V (ppm)	110	230	270	175	195	195	245
Cr (ppm)	85	185	218	55	215	180	230
Mn (ppm)	600	1400	1700	1100	800	1400	1500
Fe (wt%)	3.50	7.07	8.24	5.83	6.5	6.22	7.46
Co (ppm)	17	29	33	25	38	25	30
Ni (ppm)	50	128	154	30	88	105	130
Cu (ppm)	25	75	90	60	26	—	80
Zn (ppm)	71	80	83	—	78	—	—
Ga (ppm)	17	18	18	18	13	—	—
Ge (ppm)	1.6	1.6	1.6	—	—	—	—
As (ppm)	1.5	1.0	0.8	—	—	—	—
Se (ppm)	50	50	50	—	—	—	—
Rb (ppm)	112	37	12	42	11	50	28
Sr (ppm)	350	260	230	400	348	240	215
Y (ppm)	22	20	19	22	16	18	19
Zr (ppm)	190	100	70	100	68	125	100
Nb (ppm)	12.5	11	10	11	5	—	—
Mo (ppm)	1.5	1.0	0.8	—	—	—	—
Pd (ppb)	0.5	1	1	—	—	—	—
Ag (ppb)	50	80	90	—	—	—	—
Cd (ppb)	98	98	98	—	—	—	—
In (ppb)	50	50	50	—	—	—	—
Sn (ppm)	5.5	2.5	1.5	—	—	—	—
Sb (ppm)	0.2	0.2	0.2	—	—	—	—
Cs (ppm)	4.8	1.5	0.4	1.7	0.3	—	—
Ba (ppm)	550	250	150	350	259	265	220
La (ppm)	30	16	11	19	8	20	15
Ce (ppm)	64	33	23	38	20	42	31
Pr (ppm)	7.1	3.9	2.8	4.3	2.6	4.9	3.7
Nd (ppm)	26	16	12.7	16	11	20	16
Sm (ppm)	4.5	3.5	3.17	3.7	2.8	4.0	3.4
Eu (ppm)	0.88	1.1	1.17	1.1	1.1	1.2	1.1
Gd (ppm)	3.8	3.3	3.13	3.6	3.1	3.4	3.2
Tb (ppm)	0.64	0.60	0.59	0.64	0.48	0.57	0.59
Dy (ppm)	3.5	3.7	3.6	3.7	3.1	3.4	3.6

Continues

TABLE IV (continued)

Element	Upper continental crust	Bulk continental crust	Lower continental crust	Average andesitic crust	Lower crustal granulites	Archean upper crust	Archean bulk crust
Ho (ppm)	0.80	0.78	0.77	0.82	0.68	0.74	0.77
Er (ppm)	2.3	2.2	2.2	2.3	1.9	2.1	2.2
Tm (ppm)	0.33	0.32	0.32	0.432	—	0.30	0.32
Yb (ppm)	2.2	2.2	2.2	2.2	1.5	2.0	2.2
Lu (ppm)	0.32	0.30	0.29	0.30	0.25	0.31	0.33
Hf (ppm)	5.8	3.0	2.1	3.0	1.9	3	3
Ta (ppm)	1.1	1.0	1.0	—	0.6	—	—
W (ppm)	2.0	1.0	0.7	—	—	—	—
Re (ppb)	0.4	0.4	0.4	—	—	—	—
Os (ppb)	0.05	0.05	0.05	—	—	—	—
Ir (ppb)	0.02	0.1	0.13	—	—	—	—
Au (ppb)	1.8	3.0	3.4	—	—	—	—
Tl (ppb)	750	360	230	—	—	—	—
Pb (ppm)	16	8.0	5.3	10	4.2	—	—
Bi (ppb)	127	60	38	—	—	—	—
Th (ppm)	10.7	4.2	2.0	2.5	1.2	5.7	3.8
U (ppm)	2.8	1.1	0.53	1.0	0.2	1.5	1.0

Adapted from [Taylor and McLennan \(1995\)](#) with additional alterations. Values for average lower crustal granulites from [Rudnick and Fountain \(1995\)](#).

Due to its inaccessibility and to the absence of some averaging technique, such as provided for the upper crust by sediments, it is much more difficult to arrive at a representative composition for the lower crust than for the upper crust. Current understanding of the petrogenesis of the majority of granitic rocks and the ubiquitous presence of negative Eu anomalies in sedimentary rocks indicate that intracrustal partial melting must be a fundamental process governing the composition and chemical structure of the lower continental crust. Xenoliths and exposed granulite facies rocks are available as potential samples.

Xenoliths are frequently found in volcanic pipes and flows and record P–T conditions indicative of derivation from the lower crust. They are commonly much more basic in composition than the granulite facies regions. They frequently show a relative enrichment in Eu. The positive Eu anomaly is mostly related to the accumulation of cumulate phases rather than to simple residues from partial melts.

Granulite facies regions are possible samples of the lower crust and they commonly possess positive Eu anomalies; however, these are typically found in the more acidic compositions rather than in mafic material that could represent residues after partial melting. Many such terrains appear, on compositional grounds, to be upper crust that has been buried in Himalayan-type collisions.

Possibly most regional granulites formed in mid-crust regions so they are not a good model on which to base lower crustal compositions. A caveat is whether the present locations of upper and lower crusts have persisted throughout geological time or whether horizontal decoupling has occurred, so that the present locations have no connection with past history.

In summary, the lower crust appears to be essentially the basic residue left after extraction of the granodioritic upper crust together with additions from underplating by basaltic magmas. Measurements of Poisson's ratio (V_p/V_s) provide strong support for the basic nature of the lower crust. On at least a local scale, delamination and sinking of heavy residual material may also be expected, adding to the complexity and to the variable nature of the Moho. Estimates of the average composition and normative mineralogy are presented in [Tables IV](#) and [V](#).

B. The Archean-Proterozoic Boundary

The Archean-Proterozoic transition marks a major change both in the volume of crust and of intracrustal differentiation. The crustal processes responsible for these changes took place during the Late Archean and are recorded in Early Proterozoic sedimentary rocks. The presence of large masses of unobductable continental crust changed the tectonic regime from the multiplate Archean crust and

TABLE V Mineralogical Composition of the Continental Crust

	Upper crust ^a	Exposed crust ^b	
<i>Upper crust mineralogy</i>			
Quartz	23.2	20.3	
Plagioclase	39.9	34.9	
Glass	0.0	12.5	
Orthoclase	12.9	11.3	
Biotite	8.7	7.6	
Muscovite	5.0	4.4	
Chlorite	2.2	1.9	
Amphibole	2.1	1.8	
Pyroxene	1.4	1.2	
Olivene	0.2	0.2	
Oxides	1.6	1.4	
Other	3.0	2.6	
Total	100.2	100.1	
	Upper crust	Bulk crust	Lower crust
<i>Normative mineralogy</i>			
Quartz (Q)	16.1	6.6	3.7
Orthoclase (Or)	20.1	6.5	2.0
Albite (Ab)	33.0	26.2	23.7
Anorthite (An)	13.9	26.2	30.4
Diopside (Di)	5.8	8.7	9.8
Hypersthene (Hy)	10.0	24.1	28.6
Ilmenite (Il)	1.0	1.7	1.9
Total	99.9	100.0	100.1

^a Assumes metamorphic/intrusive rock ratio of 1.9.

^b Represents exposed crust surface.

[Adapted from upper crust mineralogy from Nesbitt, H. W., and Young, G. M. (1984). *Geochim. Cosmochim. Acta*, **48**, 1523–1534.]

produced the present linear (e.g., South America) or arcuate subduction zones (e.g., Western Pacific arcs).

This change reflects an episodic change in upper crustal composition and related to a massive emplacement of K-rich granitic rocks, depleted in Eu, in the upper crust toward the close of the Archean. This process (“cratonization”) produces massive intracrustal melting to produce granites, transfers heat-producing elements to the upper crust, and generally “stabilizes” the crust (Fig. 5). It was nonsynchronous over the globe, and extended over several hundred million years. Abrupt changes in the REE patterns in clastic sedimentary rocks are observed but it was non-synchronous over the globe, and extended over several hundred million years around the Archean-Proterozoic Boundary.

Many geological events correlate with a major change at the Archean-Proterozoic Boundary. The widespread oc-

currence of uranium deposits in basal Proterozoic sediments can be attributed to the enrichment of the upper crust in incompatible elements due to intracrustal melting. The dramatic increase in ⁸⁷Sr in marine carbonates from that period is similarly due to an upper crustal enrichment in ⁸⁷Rb in the K-rich granites that came to dominate the upper crust (and a reduction of mantle flux of Sr resulting from a cooling Earth).

VIII. THE ARCHEAN CRUST

The composition of the Archean upper crust as revealed in the sedimentary record stands in marked contrast to that of the Post-Archean crust. A significant difference is shown by the REE patterns in the Archean sedimentary rocks, which relative to those of the Post-Archean crust, typically show no Eu anomalies and lower enrichment in the LREE.

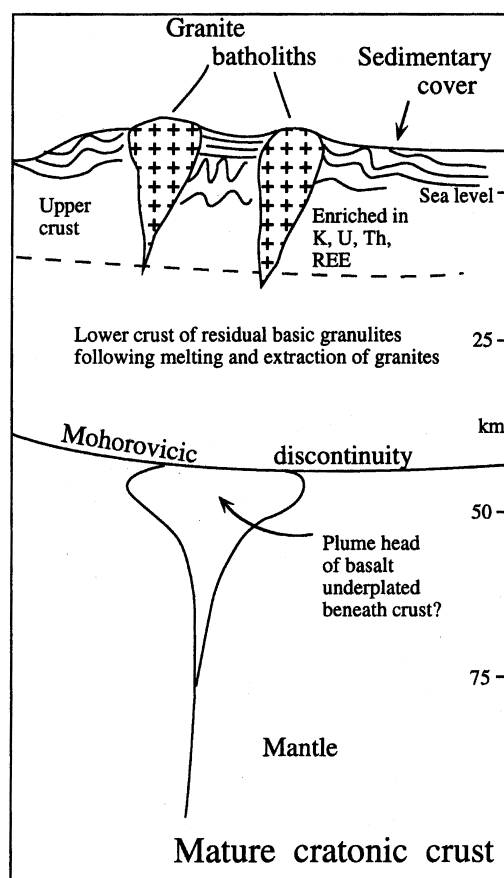


FIGURE 5 Schematic diagram illustrating the process of crustal stabilization to form cratons. Melting within the crust to produce granitic rocks, due to the buildup of heat from radioactive decay and possibly the intrusion of basaltic magmas at the base of the crust causes the transfer of incompatible element, including heat-producing elements, to the upper part of the crust.

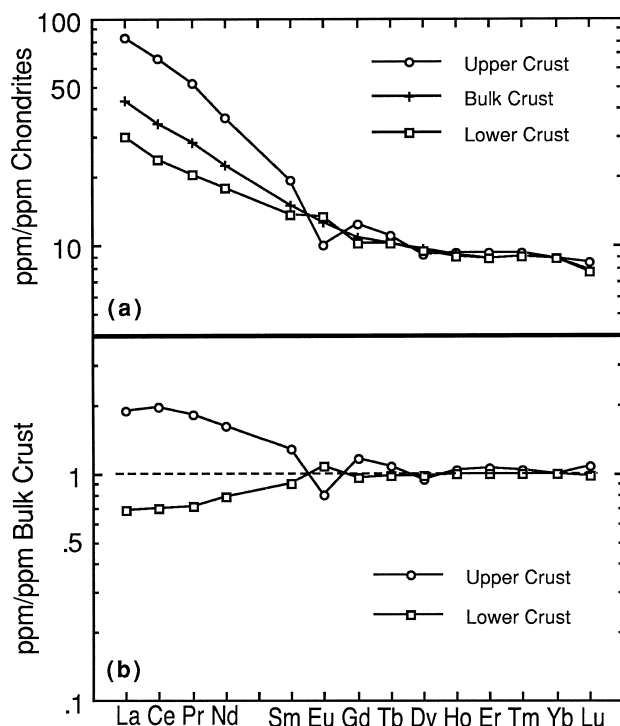


FIGURE 6 Rare earth element (REE) patterns in the continental crust. (a) Values normalized to average chondritic meteorites (taken to be representative of the bulk earth); (b) values normalized to the bulk continental crust abundances. The upper crust is enriched in the light rare earths, La-Sm, and exhibits a negative Eu anomaly. The lower crust has a complementary pattern with an overall slight enrichment in Eu resulting from the separation of plagioclase during partial melting and crystal fractionation within the crust.

These differences in REE patterns between Archean and Post-Archean clastic sediments have been documented in many studies. They form a crucial observation for models of the evolution of the continental crust.

In detail, there is a great variation in REE patterns in Archean sediments. This stands in contrast to the very uniform Post-Archean sedimentary REE patterns. Both very steep and flat patterns are locally abundant. The flat patterns are derived from basaltic precursors to first-cycle sediments. The steep patterns occur in first-cycle sediments derived directly from tonalites, trondhjemites, and granodiorites (TTG igneous suites). Both REE patterns come from the Archean “bimodal igneous suite,” which largely dominates the Archean upper crust. The most common patterns bear a superficial resemblance to the REE patterns of island-arc volcanic rocks such as andesites. This similarity is the result of derivation largely from a mixture of the ubiquitous bimodal suite of felsic igneous rocks (tonalites, trondhjemites, granodiorites or the

“TTG suite” and their volcanic equivalents) and basaltic rocks which are dominant in many Archean terrains.

Most of the crust as sampled by the greenstone belt terrains was derived from areas where the bimodal suite of basalt and TTG dominated the land area being eroded to supply the sediments. It is sometimes suggested that granites with Eu anomalies were widespread in the Archean, although now missing due to erosion. However, despite the close association of greenstone belts with “granitic” terrains the limited extent of these Archean granitic terrains with “Post-Archean” REE signatures is indicated by the absence in the greenstone belt sediments of such signatures. Wind-borne dust should have been widespread in the Archean due to the absence of land-based vegetation. Any granitic terrain should have contributed the characteristic signature of Eu depletion to the greenstone belt sediments. The absence of this signature in the majority of Archean sediments means that such high-grade terrains represented less than 10% of the exposed Archean crust.

In modern environments such as arcs or Pacific deep-sea environments, where volcanic provenances dominate, there is ubiquitous evidence for upper crustal material with negative Eu anomalies. In contrast to the situation in Post-Archean time, the isolation of small Archean cratons enabled the survival of distinct suites of sedimentary rocks with much variation in REE patterns.

The Archean crust probably consisted of many small fast-spreading plates. The tonalite-trondhjemite suite was produced by rapid subduction of warm basaltic crust (Fig. 7). The steep REE patterns of the Archean TTG suites indicate that garnet was in the residue during partial melting. An origin by melting at mantle depths for the TTG suite is thus indicated, because garnet is only stable in mafic-ultramafic systems at depths below about 40 km. The Archean crust thus formed as a mixture of piled-up basalt-komatiite and tonalite-trondhjemite intrusions and extrusives. Sedimentary data suggest that in the upper crust the ratio of basalt to TTG was about equal. Probably this ratio was typical of the Archean bulk crust. In the Southern Andes where rapid subduction of young hot oceanic crust occurs today, the slab reaches melting temperatures before complete dehydration occurs, and “Archean-like” tonalites are produced.

Only minor intracrustal melting occurred in the Archean. Areas of the crust that had undergone such melting, generating upper crustal negative Eu anomalies, formed cratonic regions of limited extent. Perhaps they were only slightly larger than the present extent of Early Archean terrains, such as those in West Greenland-Labrador and the Minnesota River Valley. The limited extent of Post-Archean shale type REE patterns in

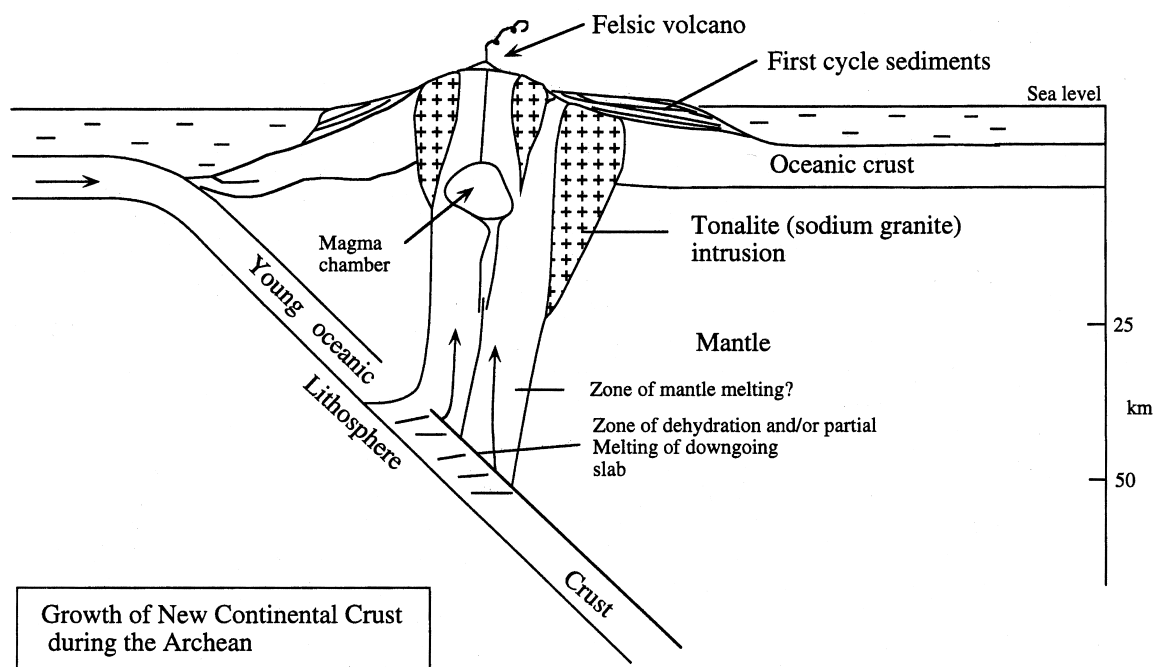


FIGURE 7 Schematic model of Archean crustal growth at subduction zones. Archean crustal growth likely differed from Post-Archean crustal growth (see Fig. 1) in that the subducting ocean crust was younger and hotter and thus melting took place prior to complete dehydration of the subducting lithosphere (see text for further discussion).

the Archean sedimentary record show that the cratonic regions were very localized. In contrast, the Post-Archean crust is highly stratified into upper and lower crust, due to extensive intracrustal partial melting.

difference between the heat flow in Archean and later Precambrian terrains. There appears to be a steep offset in the data at the Archean-Proterozoic Boundary. Because erosional levels are not significantly deeper in Archean

IX. COMPOSITION OF THE BULK CRUST

In comparison with the well-established composition of the upper crust, there is less of a consensus about bulk crustal composition as arriving at the average composition of the bulk, rather than the exposed crust is complicated (Fig. 8). The most important constraint on models of bulk crustal composition relies on the interpretation of continental heat-flow data (Fig. 9).

The sedimentary rock data provide information only on that portion of the crust exposed to weathering and erosion, but the upper crust is not representative of the entire 41-km thickness of the continental crust. Mass balance calculations show that a 41-km thick crust with K, Th, and U abundances equal to that of the present upper continental crust would require about 80–90% of the entire Earth's complement of these elements to be present in the continental crust. The heat-flow data show that the upper crust (about 10 km thick) is strongly enriched in the heat-producing elements (K, U, and Th).

Even when the effects of a tectonic heat contribution are removed for younger crust, there is a well-established

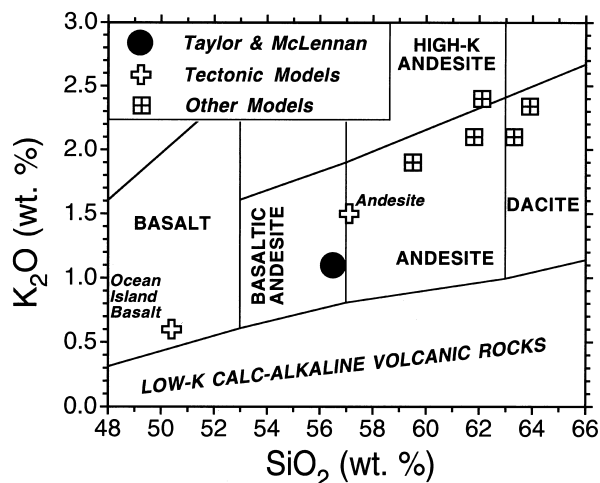


FIGURE 8 Plot of K_2O versus SiO_2 for various models of bulk continental crustal composition, superimposed on the classification of calc-alkaline volcanic rocks. The model favored here is shown in the heavy black circle. A variety of other compositions have been proposed on the basis of plate tectonic models (e.g., andesite, ocean island basalt; open crosses) and various seismic and geological models (open squares). These various models predict a wide range of heat-producing element abundances (K, Th, U) and thus can be tested from heat-flow data.

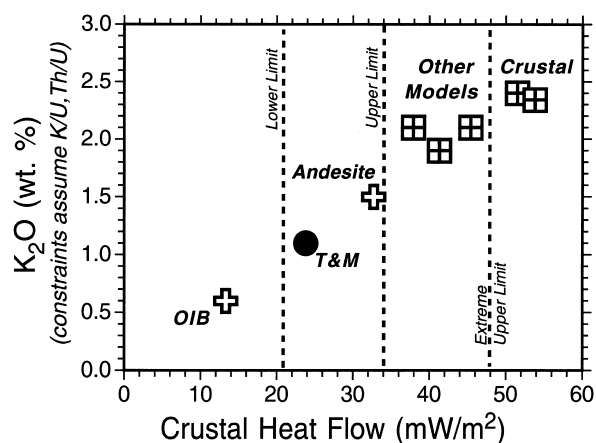


FIGURE 9 Plot of K_2O versus crustal heat flow, comparing various estimates of bulk continental crust composition. Heat-flow constraints are shown in the vertical dashed lines. The lower limit assumes that the lower crust contributes no heat and all heat-producing elements are contained within the upper crust. The absolute upper limit is given by the total average heat flow from stabilized continental crust and thus assumes no mantle contribution to heat flow. A more realistic upper limit is model-dependent and adopts modest mantle heat-flow contributions suggested by detailed geochemical studies of deeply exposed crustal cross sections.

terrains, this is not due to deeper erosion of the Archean crust, removing a surficial hot layer, or an upper granitic layer. This difference in heat flow results from an increase in the thickness of the subcrustal lithosphere under Archean cratons. This results in a lower surface heat flow by deflecting mantle heat flow around the Archean cratons. On this basis, the bulk Archean crustal values for the heat-producing elements are 1.0% K, 3.8 ppm Th, and 1.0 ppm U.

Most of the crust is generated in the Late Archean, with lesser additions from later island-arc volcanism, to make up the present crust. The overall crustal bulk composition was calculated from a 60/40 mixture of the Archean bimodal and the Post-Archean andesitic compositions. These result in the following concentrations for the heat-producing elements in the bulk continental crust: 1.1% K, 4.2 ppm Th, and 1.1 ppm U, which give the crustal component of the heat flow of 29 mWm^{-2} , or slightly over half of the total heat flow measured in the continental crust. Thus there may be little difference in bulk composition between the Archean and Post-Archean bulk crust despite a significant difference in their upper crustal compositions. The bulk crustal compositions in fact are quite similar (Post-Archean values of 1.1% K; 4.2 ppm Th, and 1.1 ppm U compared with bulk Archean crustal values of 1.0% K, 3.8 ppm Th, and 1.0 ppm U). These differences are probably within the error limits. Nevertheless, there are some minor differences between Archean and Post-

Archean crustal compositions that have important implications for crust/mantle evolution. For example, HREE depletion is a common feature in Archean crustal rocks but virtually absent from rocks formed during the Post-Archean. In contrast, other recent estimates of bulk crustal composition exceed the heat-flow constraint. In contrast, models that propose a basaltic crustal composition produce too little heat in the crust to account for the observed values.

Archean terrains lack positive gravity anomalies, suggesting either that basaltic underplating is absent or perhaps has been removed by delamination. The possible absence of basaltic underplating would further imply that intracrustal melting had not occurred, and is possibly the reason why the Early Archean crust has not undergone much intracrustal melting but has mostly remained in its undifferentiated state.

X. THE SUBCRUSTAL LITHOSPHERE

The mantle up to several hundred kilometers beneath the continents, particularly under the older cratons, forms deep keels characterized by fast seismic velocities, is Mg-rich, and depleted in Fe. It is less dense than the surrounding mantle, a factor that imparts stability to the keels, which thus “float” under the continents. Although the low Fe/Mg ratio and low Ca and Al contents are generally attributed to the extraction of a partial melt, this “subcontinental lithospheric mantle” (SCLM) is apparently enriched in incompatible elements such as Ba, Th, U, Ta, Nb, La, Ce, and Nd and depleted in HREE, Ti, Sc, V, Al, and Ca relative to average abundances in the mantle. This element pattern indicative of both enrichment and depletion indicates that multistage processes must have occurred, with an initial extraction of a partial melt, followed by at least one stage of a secondary enrichment, often referred to a “metasomatic” event. Curiously, this event has apparently not affected the Fe/Mg ratios.

Many models have been proposed to account for this enigmatic composition. The first constraint is the serious sampling problem. The geochemical evidence comes from data from xenoliths. Because of secondary alteration from the enclosing lavas, considerable caution is warranted in interpreting the data. Median values, rather than averages that can be distorted by a few anomalous values, seem more reliable. But it is unclear how representative the xenoliths are, and whether they represent refractory survivors of multiple extractions of partial melts.

Data for Sm-Nd, Rb-Sr, and Th-U-Pb isotopic systems are readily affected by contamination from the enclosing lavas and by the secondary enrichment events. Only the Re-Os system seems capable of giving reliable ages for the

partial melting events in which Re is strongly partitioned into the melt, while Os remains in an Re-poor environment in the residual mantle. There the Re-Os ratio is so low, and the ^{187}Re half-life so long that the Os isotopic ratios are not readily influenced by later metasomatic episodes. The ages so recorded are typically late Archean and indicate that such regions can remain isolated from the rest of the mantle for periods exceeding one billion years. Clearly, rehomogenization of the subcontinental lithospheric mantle is an inefficient process. Although it is sometimes debated whether these keels are firmly linked to the cratonic masses above or whether their present location is accidental and decoupled from the continental crust, the Re-Os isotopic systematics indicate a correlation between the subcontinental lithosphere and the overlying continent.

A viable location both for enriching portions of the mantle in incompatible elements and for the extraction of partial melts would seem to occur above subduction zones, either by dehydration or partial melting of the downgoing slab. Thus the formation of the keels would be closely connected with the processes of the formation of the continental crust from the mantle in this model. The Late Archean Re-Os ages are consistent with other evidence for massive episodic continental growth at that time. The intrusion of kimberlites and similar magmas provides a second method of introducing incompatible elements. Among other effects, the keels apparently deflect heat, resulting in apparent low mantle heat flows in Archean cratons. The keels presumably also form barriers to underplating by rising mantle plumes. They would also place difficulties in the way of the popular model of sinking (delamination) of dense material from the base of the continents back into the mantle.

XI. EARLY PRE-3.9-Ga CRUSTS

In order to place this question in an appropriate perspective, it is necessary to consider the problems encompassing both the formation of this planet and some associated events.

The gaseous parts of the solar nebula were dispersed very quickly on time scales of a few million or less years following T_0 (4560 million years) by early violent solar activity. The Earth then accreted from a hierarchy of rocky planetesimals in a gas-free environment between 10 and 100 million years after T_0 . The moon was probably formed during the final stages of planetary accretion by the collision with the Earth of a body somewhat larger than Mars. High temperatures are a consequence of the formation of the Earth from planetesimals and total melting of the Earth seems unavoidable. Indeed the lunar-forming event was sufficiently energetic to have accomplished this

on its own. The subsequent crystallization history of the terrestrial mantle is less clear. The molten mantle was so large that conventional terrestrial analogies, derived from layered intrusions or the moon which is two orders of magnitude smaller, are inadequate to describe the solidification of a molten terrestrial mantle. Probably the mantle crystallized without producing separate mineral zones. Mantle temperatures during the Hadean (pre-3900 million years) were probably significantly higher due both to thermal inputs from impacts of large bodies, and a much higher heat flow. Over half the heat produced by the decay of ^{235}U to ^{207}Pb in the Earth was released during Hadean time alone adding up to several hundred degrees to the Earth's internal temperature.

It is often thought that, by analogy with the moon, the Earth formed an early anorthositic crust. Several reasons make this unlikely. First, the composition of the moon is richer in Ca and Al than that of the terrestrial mantle leading to the early appearance of plagioclase during crystallization of the lunar magma ocean. Secondly, plagioclase will transform to garnet at shallow depths (40 km) in the Earth, thus locking up Ca and Al in a dense phase. In contrast, plagioclase will be stable in the moon to depths of several hundred kilometers. Plagioclase will sink in a wet terrestrial basaltic magma. Finally there is no sign of an ancient reservoir of europium or of primitive $^{87}\text{Sr}/^{86}\text{Sr}$ that would have resided in an early Sr-rich, Rb-poor anorthositic crust.

Early granitic crusts were not formed. Two observations inform us that early "granitic" crusts were very limited in extent. There was no land vegetation in the Archean. Hence there must have been wide exposures of bare rock, with the consequent formation and wind transport of dust. Present-day mid-ocean sediments show the tell-tale signature of Eu depletion of the upper continental crust derived largely by wind transport. This signature of Eu depletion is missing from virtually all Archean sediments except for those found in the local cratonic areas discussed above. Most of the exposed crustal rocks from which the Archean sediments were derived were basalts and the TTG suite, rather than the granites and granodiorites.

The second crucial observation is the failure to find evidence of extensive pre-3.5-Ga recycled zircon populations that would have been indicative of large areas of old granitic crust. Zircon, being a highly durable mineral, survives through many cycles of weathering, erosion, and deposition of sediments. It also appears to be aerodynamically suited for large-scale wind transport as witnessed by enrichments seen in loess deposits and the presence of substantial exotic zircon in ancient soils. Thus if there was an early sialic crust, then a population of ancient zircons derived from it by erosion should have survived and be recycled into younger Archean sediments.

Zircon populations, dated by the ^{176}Lu - ^{176}Hf technique, in Early Archean quartzites, are mostly the same age as the terrain in which they are found, and there is a scarcity or absence of zircons of significantly older age, that could have been derived from preexisting crust. The conclusion from this study is that old sialic continental crust was rare and not much more extensive than the few remnants that are currently exposed.

There is almost no evidence on Earth of the Hadean Eon but the Nectarian (3850–?4200 million years) and Pre-Nectarian Systems (?4200–?4450 million years) on the moon cover this missing period of time in the terrestrial rock record. The Earth during this period was subjected to a heavy meteoritic bombardment. This bombardment was not the tail end of accretion but mostly due to a spike or “cataclysm” around 3850–4000 million years. Such an event is probably responsible for the effective absence of a terrestrial rock record before 3.9 Ga. What then was the nature of the crust of the Hadean Earth? Observations from Mars, the moon, Venus, and Vesta suggest that it was basaltic. Enigmatic isotopic evidence suggests that there was some extraction of incompatible elements from the mantle at this time, but the scale of this extraction was probably minor as the evidence is restricted to very small areas of outcrop of early Archean rocks. A few relict zircon crystals up to 4200 million years in age occur in younger sedimentary rocks. These zircons are the only surviving remnants that have been identified of the existence of surface rocks. The zircons appear to be derived from felsic igneous rocks. If so, small areas of such rocks presumably formed from remelting of basaltic crust that

sank back into the mantle. The oldest preserved terrestrial rock is the Acasta gneiss, 3960 million years old in the Northwest Territories of Canada.

The significant feature about the Earth, in contrast to the other terrestrial planets, appears to be the presence of liquid water at the surface that enables recycling of subducted basaltic crust through the mantle. It is this process that permits the slow production of the continental crust throughout geologic time. The conditions for the production of massive granitic crusts are probably unique to the Earth and require three or more stages of derivation from a primitive mantle composition.

XII. ORIGIN AND EVOLUTION OF THE CONTINENTAL CRUST

There is a basic distinction between the igneous activity that contributed to the formation of the continental crust in the Archean and Post-Archean Epochs (Fig. 10). There were probably many more plates in the Archean due to higher heat flow resulting in the rapid recycling of young hot oceanic lithosphere. Such basaltic crust reaches melting temperatures before dehydration has occurred. Under these conditions partial melting occurs leaving a hornblende-garnet residue. The resulting product is the TTG suite with a steep REE pattern and no Eu anomaly.

The Archean crust is formed from mixtures of the two dominant (“bimodal”) igneous lithologies: Na-rich igneous rocks such as tonalites, trondhjemites and granodiorites or the TTG suite (and their volcanic equivalents),

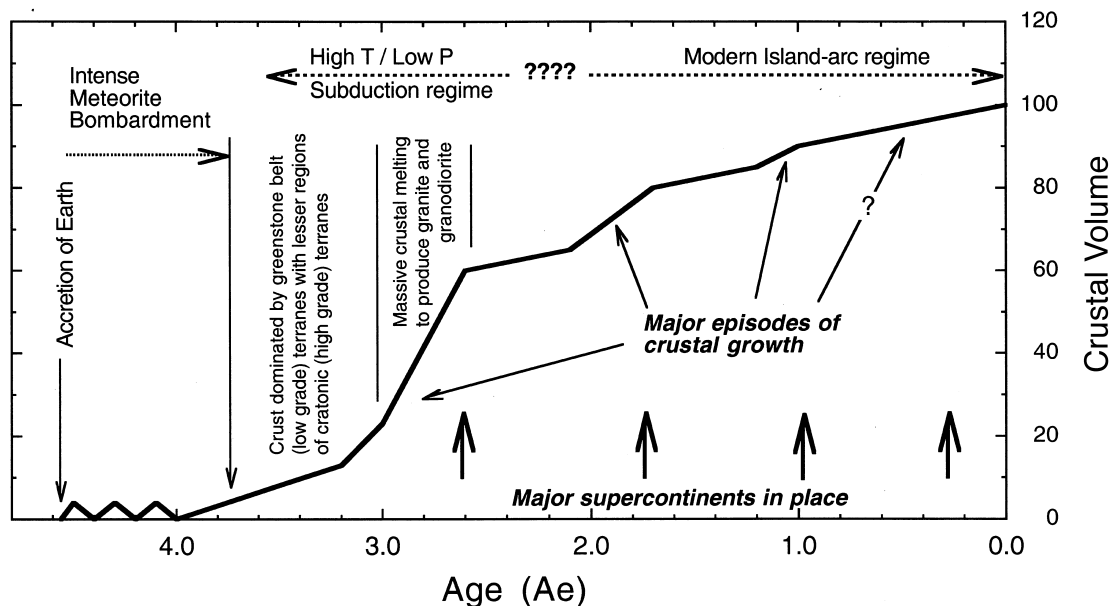


FIGURE 10 Generalized model of the growth and evolution of the continental crust.

and basalts. REE patterns with Eu depletion similar to PAAS are rarely observed in the sedimentary record. They are restricted to cratonic sediments preserved in high-grade metamorphic terrains. These are interpreted as being derived from minicratons that were forerunners of the major development of cratons in the late Archean.

A massive increase in the growth rate of the continental crust, well documented by the Nd isotopic evidence, occurred over an extended period between 3.2–2.6 Ga, differing for individual cratonic regions. Massive intracrustal melting of Late Archean crust produced an upper crust dominated by K-rich granodiorites and granites. This change is reflected in the REE patterns observed in the clastic sediments. These typically display a significant depletion in Eu. At this time, the upper crust assumed its present composition as Archean-type REE patterns are swamped.

Such intracrustal melting often occurs within 50–100 million years of the derivation of new crust from the mantle. Mantle plumes arriving beneath the crust are considered to be a prime cause inducing crustal melting. Possibly the lithospheric keel beneath older cratons deflects mantle heat flow or mantle plumes toward younger areas marginal to these areas.

The number of plates became fewer as global heat flow diminished in the Late Archean, and modern-style plate tectonics became the dominant tectonic theme. Oceanic crust was both older and colder by the time it reached the subduction zone. This older oceanic crust returns to the deep mantle without being remelted. Fluids from dehydration of the slab rise into the overlying mantle wedge, where they induce melting. This results in the production of the present subduction-zone calc-alkaline suite and in the addition of this material to the crust.

Evidence from ^{10}Be and Pb isotopes show that some sediments have been recycled into the mantle, but geological, geochemical, and isotopic constraints limit the amount of subducted sediments to a few percent. Those models which propose massive recycling of the crust through the mantle encounter various difficulties. Data from Pb isotopes, although sometimes cited in support, provide no independent constraints on this problem. During sedimentary recycling processes, the sedimentary mass is largely cannibalistic with little new material being added from the mantle. Thus the mass of sediment available for subduction is $<1.6 \times 10^{15}$ g/yr (about $0.5 \text{ km}^3/\text{yr}$ of crust). This amount does not provide sufficient material to support a steady-state crustal mass that is continuously recycled through the mantle.

In summary, the growth of the continental crust has proceeded in an episodic fashion throughout geological time with a major increase in the growth rate in the Late Archean. The contrast between Archean and Post-Archean

crustal evolution is almost certainly due to differing thermal regimes, but exactly how that expressed itself in terms of plate tectonic kinematics is less well understood. The crust continues to grow at present by island-arc volcanism and related magmatism, followed by episodes of intracrustal melting. Various geological, geochemical, and isotopic constraints limit the amount of subducted sediments to a few percent.

XIII. RELATIONSHIP TO OTHER PLANETARY CRUSTS

Planetary crusts may be divided into three types. Primary crusts form as a result of the initial melting of the body. The feldspathic crust of the lunar highlands forms this type of example (Fig. 11). Secondary crusts arise through later partial melting of solid planetary mantles and in the rocky inner planets of the solar system, produce basaltic melts. The lunar maria and the surfaces of Mars and Venus as well as our oceanic crust are examples (Figs. 11, 12). Remelting and reprocessing of the basaltic crust as it is returned to the mantle produces our familiar continental crust. This is an example of a tertiary crust, and it appears to be the sole example of this type in the solar system.

The familiar continental crust of the Earth on which most of us live is of unique importance because it formed the platform above sea level on which the later stages of evolution occurred leading to the appearance of *Homo sapiens*. The conditions for the production of massive granitic crusts are probably unique to the Earth and require three or more stages of derivation from a primitive mantle composition. The Earth has transformed less than 0.4% of its volume to continental crust of intermediate composition and less than 0.2% of its volume into granitic continental crust (i.e., upper continental crust) in over 4000 million years, so that the process is inefficient. The highland feldspathic crust of the Moon, about 12% of lunar volume, formed in contrast within a few million years.

No crusts similar to the continental crust of the Earth appear to have formed on the other terrestrial planets, where the surface rocks are typically basaltic. The moon presents a special case of a primary crust composed essentially of anorthosite, which floated on an anhydrous magma ocean as a consequence of whole-moon melting at accretion. There is no evidence of a similar crust forming on the Earth as noted earlier, nor any sign of a granitic crust. The largest “lunar granites” are tiny fragments of siliceous differentiates (the largest is 1.8 gm).

Venus is the closest planet in size and composition to the Earth, and accordingly might be expected to have had a rather similar geological history. However, both planets

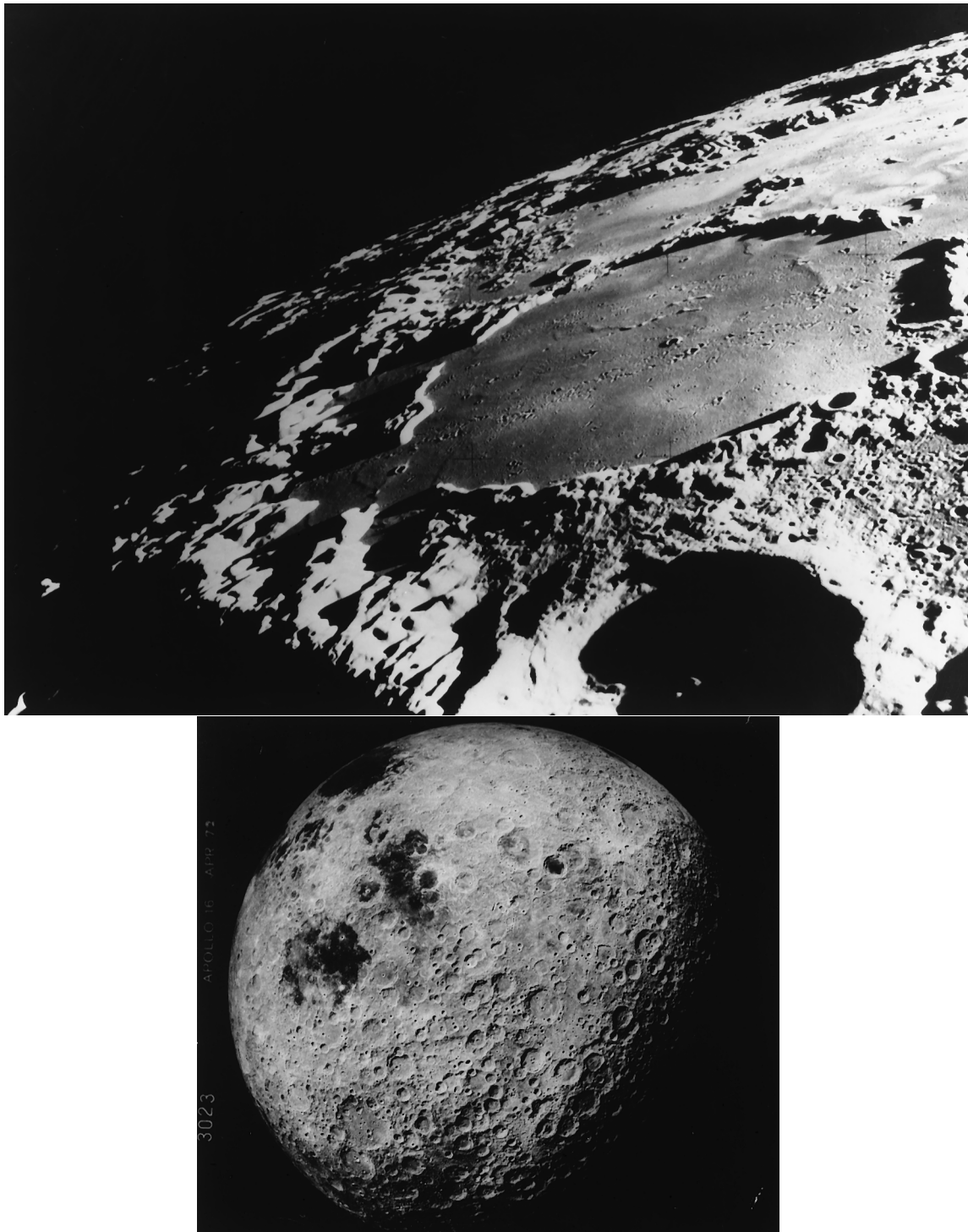


FIGURE 11 Top: Contrast between Primary and Secondary crusts on the farside of the Moon. The large crater is Thompson (112-km diameter) and is within the northeast sector of Mare Ingenii (370-km diameter). The crater in the right foreground is Zelinskiy (54-km diameter). Note that the large circular craters in the lunar highland (Primary Crust) are filled with mare basalt (Secondary Crust). Thus the stratigraphic sequence, from oldest to youngest is (1) formation of highland crust, (2) excavation of Ingenii basin, (3) formation of Thompson crater, (4) formation of Zelinskiy crater, (5) flooding of Ingenii and Thompson by mare basalt, and (6) formation of small craters on mare surface (NASA AS-15-87-11724). Bottom: A farside view of the lunar highland crust showing heavily cratered terrain. The lunar highland crust is an example of a Primary Crust. Scarcity of mare basalt, in contrast to the nearside, is attributed to the greater thickness of the feldspathic crust on the farside. (NASA Apollo 16 metric frame 3023.)

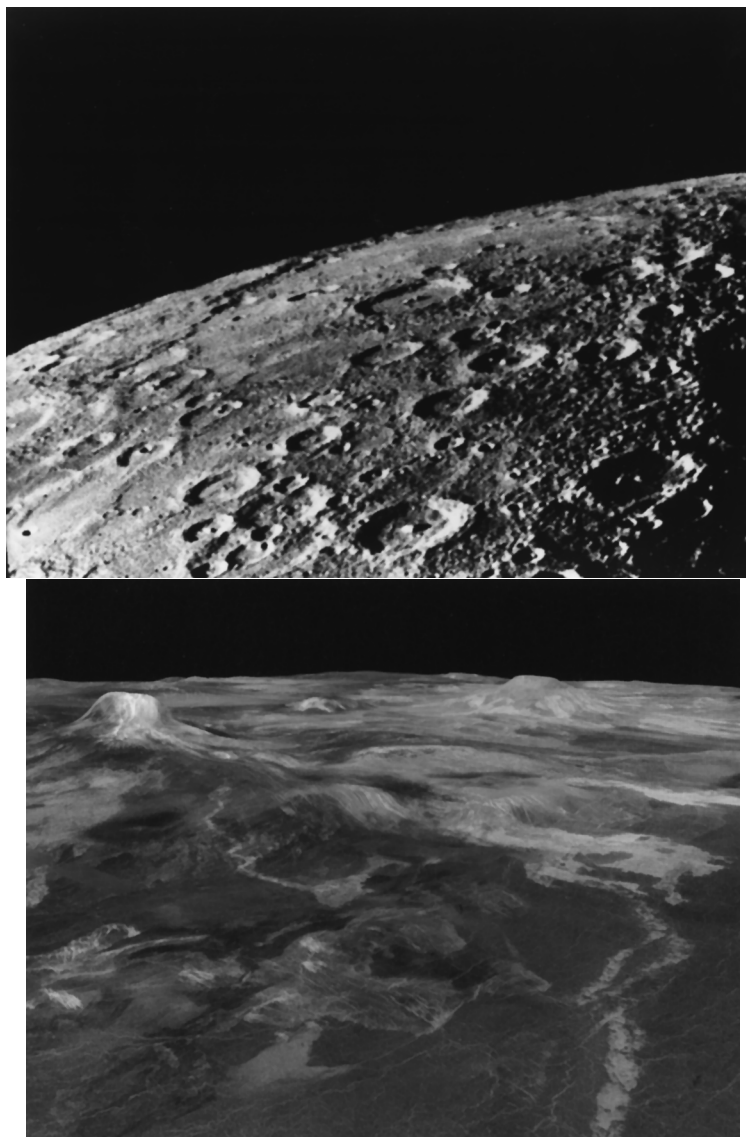


FIGURE 12 Upper left: Northern limb of Mercury showing heavily cratered terrain and prominent east facing scarp extending southward from limb near center of photograph. Horizontal dimension of base of picture is 580 km. This Mariner 10 photograph was taken at a distance of 77,800 km. Lower left: Three-dimensional perspective view of Venus generated from Magellan radar data. Vertical exaggeration is about 20 \times . Shown is the western Eistla Regio with two volcanoes, Gula Mons (left, 3-km altitude above plain) and Sif Mons (right, 2-km altitude above plain). Right: Northeast view across heavily cratered ancient crust of Mars. Large circular feature is Argyre basin (about 750-km diameter). Note the cloud haze above the horizon (NASA SP 76 27774).

show major differences and the Venusian surface appears to be mostly basalt, perhaps with a few scattered “pancakes” of more siliceous differentiates. The high-standing regions (e.g., Ishtar Terra, Aphrodite Terra) appear to consist of crumpled-up basaltic crust.

The northern crust of Mars appears to be basaltic, consistent with the geomorphic evidence for basaltic plains and volcanoes. The three landers (Viking 1 and 2,

Pathfinder), 4000 km apart in the northern hemisphere gave similar basaltic compositions for the fine-grained soils that were analyzed the fine material will contain a significant component from the ancient cratered terrain that dominates the southern hemisphere, where most of the global dust storms originate. However, no component more siliceous than basalt appears in the Martian compositions. At the Pathfinder site, more siliceous rock

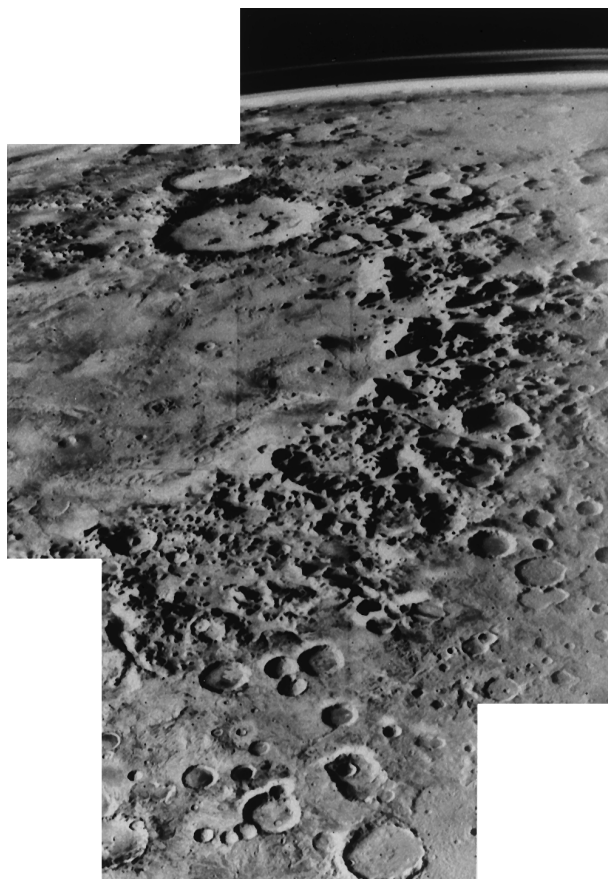


FIGURE 12 (Continued)

compositions were found but the origin of the high silica (primary igneous versus secondary) remains controversial. In any case, there is no evidence for a granitic terrain.

There is little evidence about the crust of Mercury, except that it has a reflectance spectra similar to that of the Apollo 16 highlands and hence is unlikely to be granitic.

The significant feature about the Earth, in contrast to the other terrestrial planets, appears to be the presence of liquid water at the surface, coupled with plate tectonics and

subduction, that enables recycling of subducted basaltic crust through the mantle. It is this process that permits the slow production of the continental crust. In other planets the absence of subduction leads to the persistence of barren basaltic plains such as we observe on other planetary bodies and the Moon.

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