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The relation of mantle heterogeneity to the bulk composition and origin of the Earth

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The heterogeneity of the mantle can be viewed in the context of models for accretion of the terrestrial planets from the solar nebula. Oxygen isotope ratios and mineralogy indicate the existence of hot planetesimals of diverse compositions. Assuming that nebular condensates range from a reduced state near the Sun to an oxidized state near Jupiter, a new model is proposed for heterogeneous accretion of the Earth beginning with hot, reduced condensates and ending with cool, oxidized condensates. The Ganapathy–Anders cosmochemical model for the bulk composition of the Earth was tested by summing measured compositions for the three outer zones and likely compositions for the inner zones. Revisions are suggested, including reduction of the content of the early condensate from that suggested by taking [U] ≈ 30 ng/g, as suggested by naïve interpretation of the heat flow. Elements that enter magma in preference to pyroxene or olivine are mainly confined to the outer 200 km. Elements that are chalcophilic under reduced conditions may be partly in the outer core. Hydrogen loss should result in an inward wave of oxidation, and may result in conversion of carbon to CO_2.

INTRODUCTION

The other papers in this volume amply demonstrate that the upper mantle is heterogeneous, but it is far from clear what the causes were and when they operated. Answers to these questions are of fundamental importance to speculations on the bulk composition of the Earth and on the origin of the terrestrial planets, especially of the Earth–Moon doublet. This paper was not scheduled in the original announcement for the symposium, but was added to give an introduction to current cosmochemical and cosmophysical ideas. Such ideas are subject to temporary enthusiasms, often fed by a charismatic leader, and readers should be wary. A review of the mineralogy of the planets (Smith 1979) ends with a new model for heterogeneous accretion of the terrestrial planets, and readers should make a point of reading papers with a different point of view, especially Clark *et al.* (1972) and Hutchison (1976) for different models of heterogeneous accretion, and Ringwood (1975, 1977) for a model of hot, homogeneous accretion of the Earth. Very brief summaries are now given on important factors for the origin of the Earth, particularly those relevant to models of its chemical composition and radial heterogeneity.

ORIGIN OF THE EARTH AND OTHER INNER PLANETS

Essentially all thinking on the origin of the solar system is based on condensation of a mass of gas dominated by H and He. For two decades, chemical homogeneity was assumed, and the chemical composition was modelled from direct analysis of C1 meteorites for the less volatile elements and indirect interpretation of light emitted by the Sun, especially for the more volatile elements. The assumption of chemical homogeneity has been destroyed by the observations of isotopic differences between the various types of meteorites, and especially in some inclusions in a C2 meteorite (reviewed by Clayton 1978). There can be little doubt that supernova debris carrying exotic isotopes was injected into the Solar System, and that the oxygen isotopic ratios of meteorites require explanation in terms of addition of various proportions of ^{16}O as well as of expected mass fractionation from gas–solid processes. But how much heterogeneity was produced in the solar nebula, and in particular for the inner region where the terrestrial planets accreted?

Undoubtedly there will be fierce debate on the original place of origin of the meteorites, especially those with highly unusual isotopic ratios. I assume that most of the 'differentiated' meteorites (i.e. those that have undergone crystal–liquid differentiation) and the non-carbonaceous chondrites were resident in the inner part of the asteroid belt before journeying to Earth (Anders 1975), and that most of them accreted in that region while a few were perturbed outwards from the region of the terrestrial planets or inwards from the region of the giant planets. I assume that the dark asteroids, which tend to populate the outer part of the asteroid belt, mostly accreted there, and that some, but probably not all, carbonaceous meteorites derive therefrom. But what is the role of comets in supplying meteorites? Did they supply a range of meteorites, or merely some carbonaceous ones, or none at all?

The non-carbonaceous chondrites can be split into the 'ordinary' chondrites, which are moderately oxidized with Fe-bearing pyroxene, and the enstatite chondrites, which are highly reduced with Fe-free pyroxene and unusual minerals such as oldhamite, carbide and nitride. If both types accreted in the inner Solar System, there must have been a strong variation of oxidation state. Actually the enstatite chondrites and achondrites have oxygen isotopic ratios that fall on the mass-fractionation trend through the Earth and Moon, whereas the ordinary chondrites are displaced. I propose that the enstatite chondrites and achondrites provide clues to the planetesimals that accreted nearer to the Sun than the asteroid belt, and that the rare E-type asteroids are surviving planetesimals that were thrown outwards into the asteroid belt. I further assume that the oxidized chondrites represent accretion conditions in part of the asteroid belt, and that some carbonaceous chondrites represent other stages in that region, probably at a greater distance from the Sun. Differentiated meteorites result from hot planetesimals of various primary compositions.

This leads to the possibility that condensation produced an overall trend of increasing oxidation state with increasing distance from the Sun, but there is no fundamental explanation. Perhaps some mechanism can be found to give a trend of the C/O ratio from 0.6 to more than 1, since thermochemical data would then provide the required change of oxidation state (Larimer 1975) from oxidized to reduced conditions.

There is so much evidence in differentiated meteorites for crystal–liquid fractionation and high-grade metamorphism that it is easiest to assume that the terrestrial planets accreted principally from hot planetesimals, probably heated by radionuclides with a short half-life (e.g. ^{26}Al). Furthermore, this makes it easier to develop models for early melting of the small planets Mercury and Mars, as is required to explain their surface morphology. Ironically, accretion of the Earth from hot planetesimals makes it easier to end up with a cool Earth because early crystal–liquid differentiation pumps the radioactive species to the surface where the heat can be radiated away.

I prefer not to accrete planets as fast as material condensed from the gaseous nebula, and therefore do not accept the heterogeneous accretion model of Clark *et al.* (1972).

If accretion proceeded via planetesimals, following the physical processes reviewed by Safronov (1972), the Earth would begin to grow from low-speed planetesimals in near-circular orbits. Other proto-planets would be growing simultaneously, and some planetesimals would be lucky enough to capture their neighbours. Near-misses would result in deflexion into non-circular orbits, and proto-planets would increasingly capture material from greater distances. Jupiter would be much more effective than the inner planets in perturbing nearby planetesimals, and it not only stopped accretion of the main-belt asteroids into a planet, but also stunted Mars. Much of the material in this region was ejected into the outer Solar System, but a considerable amount would go inwards.

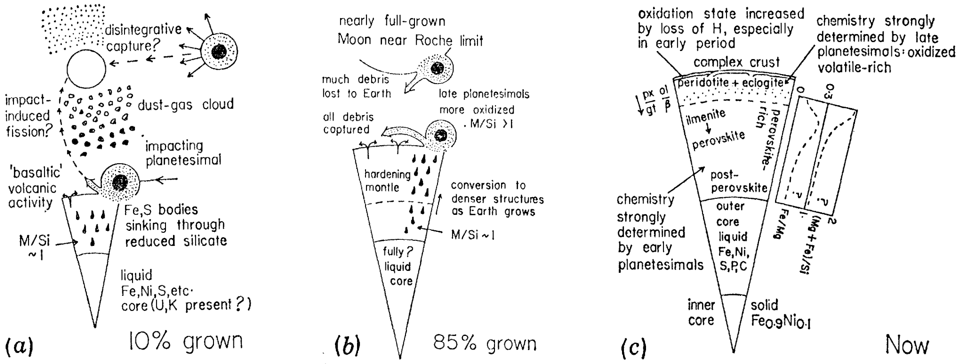

FIGURE 1. A new heterogeneous accretion model of the Earth (Smith 1979).

Thus I conceive of the Earth accreting heterogeneously (figure 1). At an early stage (e.g. 10% grown), it would be capturing nearby planetesimals at low velocity. These planetesimals would have melted from short-lived radionuclides, and the growing Earth would already be differentiating into a liquid core rich in Fe, Ni, S and metal-loving and sulphide-loving elements, and a shell of reduced silicate perhaps dominated by Fe-poor pyroxenes. Volcanic activity would be driving U, Th and K to the surface. It is just possible that a little U and K would go into the sulphide component of the core if the conditions were highly reducing, but it is perhaps better to assume initially that the radionuclides were mostly pumped to the surface where their heat could be radiated away. The growing Earth would be surrounded by a huge dust–gas cloud resulting from disintegrative near-capture of a significant fraction of incoming planetesimals. A proto-Moon might arise either from accretion of the debris, or perhaps by fission of the Earth induced by fortuitous off-centre collisions of large planetesimals arriving at fairly high velocity.

At the 85% stage (achieved over *ca.* 25–50 Ma?), accreting planetesimals would be arriving at greater velocity, and would tend to have grown from dust at a greater distance from the Sun. They would be more oxidized and contain more volatiles. Some iron would have reacted from the metallic to the ferrous state, producing Fe-bearing pyroxene and olivine. The growing Earth would be large enough to retain all collision debris, even for planetesimals perturbed by Jupiter, but the Moon would be too small to retain collision debris from high-speed impacts. The growing Earth is not envisaged as being completely molten at this stage, and certainly is not envisaged as a cloud of vapour. In order to explain (i) the near-cosmic ratio of Fe/Ni in present peridotite xenoliths from the upper mantle, (ii) the substantial presence of noble metals in such xenoliths, (iii) the occurrence of H_2O and CO_2 in the present Earth, and (iv) the present-day emission of rare gases from the Earth, it seems easiest to assume that the Earth was developing a fairly rigid mantle to (i) protect the late accreted material from reacting with the core and (ii) allow H_2O and CO_2 to be locked up in minerals rather than going into the atmosphere where they could be swept away by a solar gale. To achieve the rigidity of the mantle, most of the radioactive and accretion heat must have been radiated away, and catastrophic core formation at a late stage cannot be allowed.

The late planetesimals would tend to be oxidized and volatile-rich, probably derived mainly from the region of the main-belt asteroids and Jupiter. Intense volcanic activity would continue after accretion had been 99.9% completed. The last substantial planetesimals would arrive in synchrony with those that produced the lunar basins, and only a few smaller bodies would arrive after -3.9 Ga.

Particularly important for this symposium is the possibility that the late impacts caused such intense volcanic activity that the outer part of the Earth would be effectively 'stirred' to produce a rim of nearly constant composition. Perhaps this region might be *ca.* 200 km thick, and be the principal source for subsequent differentiation into a crust and a depleted upper mantle. Another alternative is that ghostly relics remain of the last few large projectiles, but this seems very unlikely in view of the intense volcanic activity needed to dissipate heat.

If the present model of an early hot Earth is correct, essentially all the K, Rb, U, Cl, Ba, H_2O and CO_2 would be in the outer zone, and these elements would be transported rapidly during melting events: for example, hydroxylated minerals would be capturing and releasing H_2O as they moved in and out of pressure–temperature stability zones. Ultimately an unstable crust would develop from rocks rich in plagioclase feldspar and amphibole, which would lie over differentiated peridotitic rocks. The crust would slowly stabilize as granulitic rocks developed, and plate tectonic processes would control later stages. Although there is a strong similarity between surviving Archaean rocks from W Greenland and recent rocks from continental margins, such as that of the eastern Pacific, earlier rocks might be different.

Whereas magmaphile elements would tend to concentrate into the outer 200 km, elements that enter pyroxenes would tend to be distributed throughout the entire mantle. It will be difficult or impossible to place limits on these elements (which include Ca, Al, Ti, Cr and Na), except by cosmochemically based models which are the subject of the next section. Furthermore, if most of the Earth accreted under highly reducing conditions, some elements (including Cr, V and Ti) might be chalcophilic and become sequestered in the outer core. Complications arise from the possibility of high-temperature disproportionation of transition elements into two valence states, of which the reaction $3Fe^{2+} \rightarrow 2Fe^{3+} + Fe^0$ is particularly important.

Finally it is necessary to consider the possibility of an inward wave of oxidation resulting from upward transfer of H_2O through the atmosphere and preferential loss of H over O. How much of the ferric iron results from reaction of ferrous iron with the resulting oxygen? Even more speculative is the possibility that elemental carbon was incorporated into the early part of the Earth as graphite or carbide, and that mantle convection is resulting in transfer of carbon into a region where a downward wave of oxidation causes production of CO_2 which then escapes from the mantle.

Whatever the merits of these ideas, it is obvious that there is plenty of scope for heterogeneity of the upper mantle since Archaean times.

Towards the chemical composition of the Earth

The following ideas are based on Smith (1977, 1978, 1979). Equilibrium condensation of a solar nebula, originally gaseous with C/O (atomic) < 1 and $P < 10^{-3}$ atm (10^2 Pa), should yield the sequence of condensates summarized by Grossman & Larimer (1974). Refractory metals (Os, W, Zr and Re) would condense at *ca.* 1800 K, Ca–Al–Ti oxides at 1600–1400, and Fe–Ni–Co metal and Mg–Si oxides at 1400–1300 K. Some metallic Fe would react to sulphide at 700 K and some to oxide at 500. Hydroxylated silicates would form at 400 K and water ice at 150 K. Ganapathy & Anders (1974) capitalized on this theoretical scheme to produce a seven-component model for the Earth, Moon and parent bodies of meteorites (Anders 1977). In general, the higher the condensation temperature, the greater the accretion efficiency: this could be explained by progressive dispersal of the solar nebula and volatile-rich collision debris by the solar wind while accretion was proceeding.

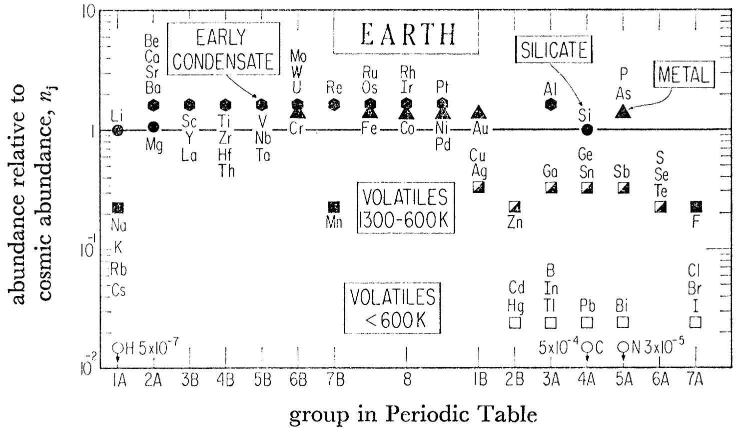

Figure 2. Chemical model for the Earth based on cosmochemical analogy (Ganapathy & Anders 1974).

Figure 2 shows the G.A. (Ganapathy–Anders) model for the Earth in which each element is referenced to a table of cosmic abundances (mostly based on C1 meteorites) and plotted against the column number in the Periodic Table (note convenient choice of position for A and B subgroups). Elements of the *early condensate* (hexagons; including Ca, Al, Ti, r.e.e.) were assumed to have accreted on to the Earth with equal efficiency, and were modelled by the assumption that the U content of the Earth could be obtained from the heat flow. The *metal* group (Fe, Co, Ni, Au, P, As, Cr) was modelled from the assumed Fe content of the Earth, which is constrained fairly well by the density. The volatiles 1300–600 K were split up into lithophile and siderophile elements. The lithophile elements (Na, K, Rb, Cs, Mn, F) were modelled by K/U = 9440. The volatiles less than 600 K were modelled by Tl/U = 0.27. Space forbids discussion of details for siderophile elements and H, C and N. Of course, these groups look rather bizarre when set in the context of crystal–liquid differentiation, and it must be remembered that the coherence was developed in a gas dominated by hydrogen.

Smith (1977) tested this cosmochemical model by calculating the bulk composition of the Earth from (i) mass fractions of the various zones, (ii) the accurately known composition of the atmosphere and hydrosphere, (iii) a published estimate of the composition of the crust, (iv) an upper mantle (10%) based on a rag-bag of analyses of garnet peridotites, (v) a lower mantle (90%) with the same composition as the upper mantle except for exclusion of elements which would partition into magma instead of pyroxene and olivine, (vi) a sulphide component of the outer core with appropriate amounts of chalcophilic elements (including Cr) that enter meteoritic troilite, and (viii) a metallic component of the inner and outer core found in various iron meteorites. Figure 3 shows the S III model in which type III iron meteorites were used to model the metallic component of the Earth's core. This group of iron meteorites has undergone crystal–liquid fractionation of noble metals producing large concentration ranges (vertical lines).

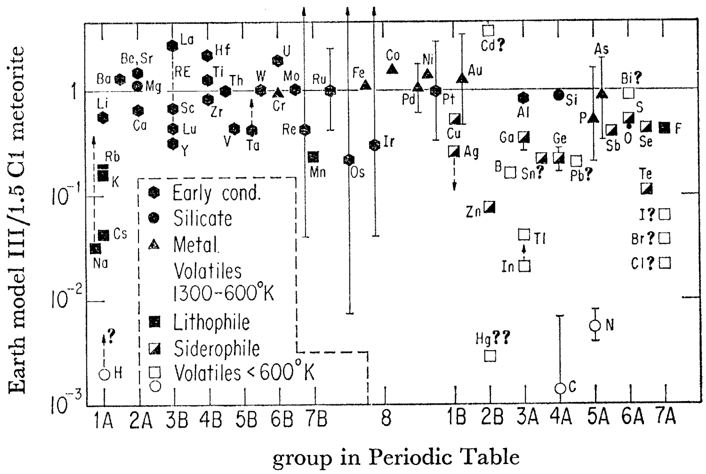

FIGURE 3. Chemical model for the Earth calculated from (i) direct evidence on the composition of the atmosphere, hydrosphere and crust, (ii) scattered data for peridotite nodules from the uppermost mantle, (iii) a similar composition for the deeper mantle except for absence of magmaphile elements, (iv) an outer core with sulphide component modelled after meteoritic troilite, and (v) metal component of the core modelled after type III AB iron meteorites (Smith 1977).

At first sight, the match with the G.A. model might be regarded as disappointing, but detailed study revealed plausible explanations for all of the major discrepancies, and showed that the G.A. model is indeed a reasonable starting point for estimating the bulk composition of the Earth. The abundances in the S III model are referenced to 1.5 times the abundance in C1 meteorites, with the factor of 1.5 covering loss of volatile elements.

Consider now the elements of the early condensate (hexagons) which scatter about the unit level. Uranium is high, but I suggested to F. Richter that the estimate of U from heat flow might need reducing if radioactive heat were not transported immediately to the surface, and indeed fluid-dynamical calculations (Daly & Richter 1978) allow possible reduction by twofold of the U content of the bulk Earth from above 30 ng/g to the calculated value of 14 ng/g (Smith 1978) for equal accretion efficiency of *early condensate*, *metal* and *silicate* elements. Furthermore, the Earth may retain accretional heat and develop heat from crystallization of the inner core. Calcium and aluminium can be raised to unit level by increasing the level in the mantle composition from the assumed 2.59% CaO and 2.80% Al_2O_3 in mantle peridotite. Barium must be confined essentially to the crust and uppermost mantle. The location of the rare earths requires detailed consideration because of strong partition coefficients between garnet, pyroxene, liquid and probable minor phases.

For the metal elements, there is (i) a question about the amount of Fe in the lower mantle, which may be resolved when an accurate equation of state has been determined for each possible high-pressure phase, and (ii) a need to place most of the P and Cr deep in the Earth, perhaps with substantial amounts in the core.

For the silicate elements, the Mg/Si ratio of C1 meteorite can be obtained only if the lower mantle has Mg/Si ≈ 1 in contrast to the upper mantle with Mg/Si approaching 2 because of the dominance of olivine.

For the lithophile volatiles 1300–600 K, the Rb, K and Cs must be confined to the crust and uppermost mantle whereas most of the Na must occur below a 200 km depth. The Fe/Mn ratio of the bulk Earth can be modelled from the K content, and this in turn can be referenced to U by the K/U ratio of surface rocks.

For the siderophile volatiles 1300–600 K, setting their abundance equal to those of the lithophile volatiles would result in S accounting for only one-third to one-half of the light element(s) needed for the outer core. This may be the correct answer, but another possibility is that S-rich cores of planetesimals were better protected from destruction during collision of planetesimals than were lithophile-rich crusts, and hence that chalcophilic elements were not swept away by the solar wind as much as the lithophile volatiles.

For the volatiles less than 600 K, the similarity of level for Tl, I, Br and Cl suggests that all are in near-surface regions, and can be modelled from the Tl/U ratio. Analytical data for Cd, Hg and Bi are very uncertain.

Obviously there are many uncertainties and escape hatches, and very little that is definitive in these models. Fortunately the plausibility of the models is being strengthened by simultaneous consideration of the evolution of radionuclides, including the Sm and Nd species, as emphasized by O'Nions (this symposium). When effects of contamination of magmas have been removed, the isotope data indicate that for the accessible part of the Earth, the K, U, Pb, Rb, Sr, Sm and Nd isotopes are consistent with a Ganapathy–Anders type of model. If the further assumption is made that all of these elements except Sm and Nd have been swept out to the outer 200 km of the Earth, the bulk composition of most elements in the Earth can be constrained quite closely, and indeed are not far from the tables in Anders (1977) and Smith (1977, 1979). Lack of space forbids further details. There remain many interesting problems, as listed in the concluding section.

PROBLEMS FOR THE FUTURE

The following problems require study.

(i) Does the distribution of chemical elements in the Earth require heterogeneous accretion? Certainly it is necessary to accrete volatile-rich material at the end, but must the early material be volatile-poor? Would fission or even just high temperatures have resulted in loss of the early volatiles? I argue that many meteorites are sparse in volatiles such as H_2O and CO_2, and that the terrestrial planets must have accreted much volatile-poor or volatile-free material.

(ii) Was the material accreted early more reduced than the material accreted later? Definitive answers are not available, but the distribution of chalcophilic elements might be interpreted as favourable evidence; further discussion is needed.

(iii) Are the Ganapathy–Anders assumptions too simple? Yes. There must be gradations between the seven groups: for example, Cs is probably more volatile than the other alkalis in its group. But more serious is the likelihood that the model for progressive equilibrium condensation of the solar nebula is wrong in *detail* because of (*a*) sequestration of early condensate in clods and planetesimals, (*b*) *thermal* loss of volatiles from collision debris, (*c*) inhomogeneity of the solar nebula, perhaps involving really substantial amounts of supernova products, and (*d*) possible change of oxidation state in the solar nebula.

(iv) What are the geophysical constraints involving (*a*) the time–spatial distribution of energy sources and sinks and (*b*) the migration of material during crystal–liquid separation and solid-state convection?

(v) What are the mineralogical–petrological–geochemical constraints obtainable from study of xenoliths from the upper mantle and crust, and from volcanic rocks?

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