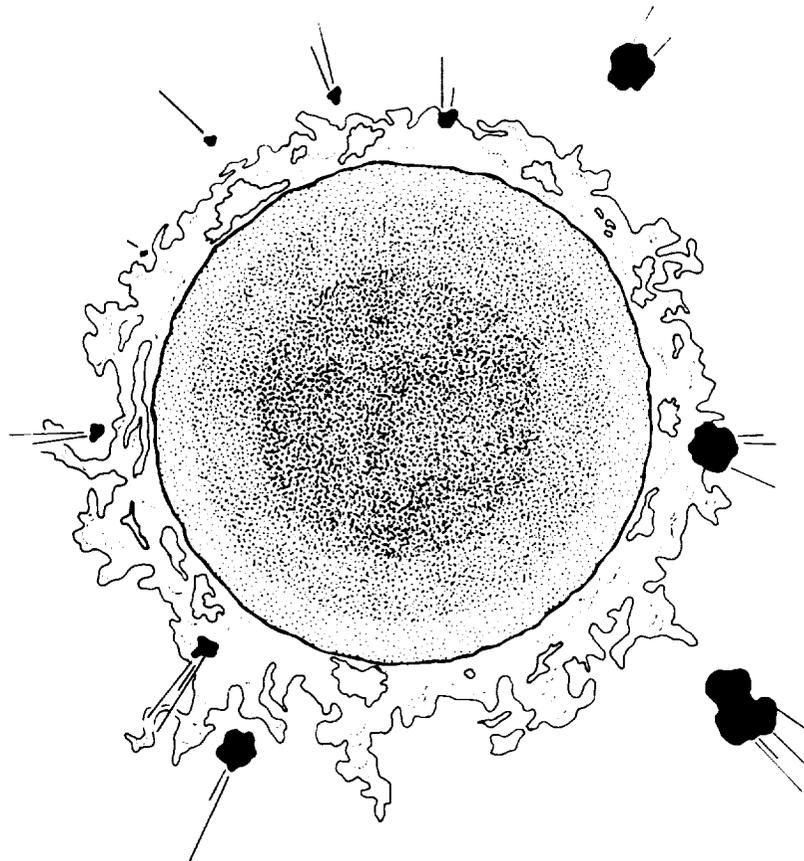


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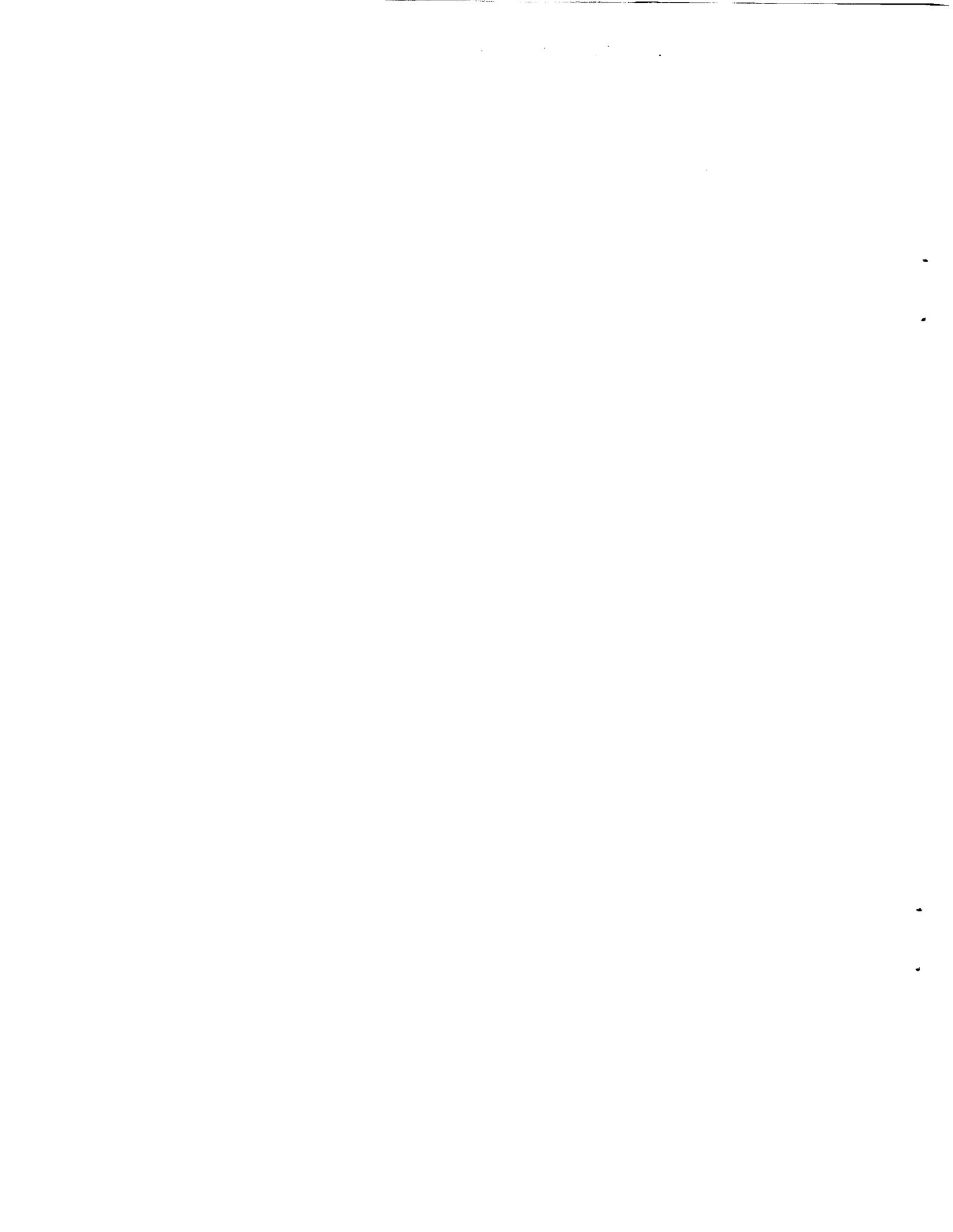
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**December 1 - 3, 1988**

**Berkeley, California**

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**Abstracts Presented to the Topical Conference**  
**Origin of the Earth**

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## PREFACE

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## Geochemical Constraints on Early Earth Melting

CARL B. AGEE (Bayerisches Geoinstitut, Universität Bayreuth, Postfach 10 12 51, 8580 Bayreuth, West Germany)

Early Earth melting scenarios can be tested by referring to recent high pressure phase equilibria results [1,2,3] since crystal fractionation should control the connection between the initial state of a partially molten Earth and the differentiated products. For the major elements (Si,Al,Fe,Mg,Ca) a remarkably good mass balance exists [4] which produces the present average upper mantle peridotite composition from a combination of C1 chondrite minus Mg-perovskite plus olivine. This combination possesses a real physical meaning in a C1 mantle which is molten to depth of at least 1000 km. In such a mantle dense perovskite is fractionated from the C1 liquid at high pressures (>700 km) by crystal settling downward. Addition of olivine occurs in the shallow mantle and can be understood in the context of crystal flotation in compressible mantle melts at 250 km depth [5]. The major element mass balance predicts that the residual liquid which would be trapped at depth in the mantle after initial differentiation to be komatiitic, a consistent result with respect to komatiite volcanism recorded in the Archean [6].

Minor element geochemistry data collected at high pressure can in principle provide an additional constraint to the mass balance. Results from a recent high pressure study [7], in which samples were doped with trace elements ( $\approx 1000$  ppm), argue that even small amounts of Mg-perovskite fractionation would perturb some of the chondrite-like element ratios estimated for the primitive upper mantle. But comparison of Mg-perovskites synthesized at 25 GPa [2,3,7] from a range of experimental bulk chemical compositions and temperatures (from 1400 to 2500°C) shows for example, that significant variation can exist in Mg-perovskite Ca/Al ratios (ranging from 0.740 [2] to 0.177 [3]) and in the Mg-perovskite/silicate liquid distribution coefficient for Ti (values from 0.83 measured [3] to 10 calculated [7]). These divergent results indicate that the composition of Mg-perovskite produced at high pressure is sensitive to choice of starting chemistry and experimental conditions. More work is needed to pin down perovskite/liquid trace element partition coefficients before they can be confidently used to constrain the Earth's thermal history. Acquisition of *near liquidus* perovskite/liquid trace element data at *chondritic abundance levels* should be a high experimental priority.

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COMPOSITION OF THE EARTH'S CORE REFLECTS CONDITIONS AT THE SURFACE DURING ACCRETION, Thomas J. Ahrens, Seismological Laboratory 252-21, California Institute of Technology, Pasadena, CA 91125

As the earth accreted from the infall of planetesimals, both impact-induced shock heating of surface materials and the blanketing effect of a coaccreting atmosphere resulted in sufficient surface heating that melting of both silicates (magma ocean) and metallic components, mainly iron plus sulfides, resulted in core fluid droplet formation and core formation. This event began to occur at  $\sim 0.5$  times the present earth radius and probably continued during the formation of the balance of the earth (Safronov, 1972; Kaula, 1979; Ringwood, 1979; Stevenson, 1981; Lange and Ahrens, 1982, 1984; Abe and Matsui, 1986; Zahnle et al., 1988). As pointed out by Stevenson (1987) and Rintoul and Stevenson (1988) the continuous existence of a magma ocean critically depends on the virtually unknown size spectrum and flux rate of planetesimals impacting and hence accreting on the earth, as well as the rate of release of gravitational energy from core formation (Sasaki and Nakazawa, 1986).

It has become increasingly clear upon modelling the chemistry of an earth, partially or completely covered with a magma ocean and retaining a blanketing atmosphere (containing a large fraction of the H, C, N, and the noble gas element complement of the earth) that the chemical environment evolved from a very reducing (e.g. iron-wüstite buffer) to quite oxidizing (fayalite-magnetite-quartz buffer) as accretion of the earth proceeded from a lunar-sized object to the present size.

Over this range, minimum planetesimal infall velocities increased from 2.5 to the present 11 km/sec. This resulted in impact temperature increases. Recently, laser impact simulations on chondrites demonstrate that devolatilization products evolve from  $\text{CH}_4$ , CO, and  $\text{H}_2\text{O}$  at low laser fluxes, and presumably low temperatures, to  $\text{CO}_2$ ,  $\text{H}_2$ , and  $\text{O}_2$  at higher temperature (Gerasimov, 1987). Consideration of the gaseous assemblage of C, H, S, and O at equilibrium with a chondritic-like mineral chemistry (Holloway, 1988) tends to verify this result. Moreover, consideration of both the constraints on the FeO and  $\text{H}_2\text{O}$  content of the earth (Lange and Ahrens, 1984) and the siderophile content of the upper mantle (Ringwood, 1979; Wänke, 1981, and Jones and Drake, 1986), as well as, consideration of the carbon content of the atmosphere during accretion (Abe, 1988) all point to the gradual transition of the surface conditions from reducing to oxidizing.

Light elements which we know are present in the liquid outer core of the earth and reduce the density of iron by  $\sim 10\%$  must reflect this accretion history. Although a detailed chemical model of the molten core during accretion is not available the three elements, C, S, and O are expected to be present, all at abundance levels lower than ordinary chondrites, carbonaceous chondrites, or estimated solar abundances (Table 1).

Carbon is expected to be dissolved in the earliest core forming liquid on account of the high solubility of liquid iron in the presence of  $\text{CH}_4$  and  $\text{CO}_2$  in the early coaccreting atmosphere. Although it is unclear that most of the earth's budget of C is sequestered in the core, the earth's crust and mantle are very depleted in C relative to noble gas (solar or meteoritic) abundances. A strong case for an appreciable sulfur content of the liquid outer core can be made because of the drastically lowering of the melting point of iron at low pressures which sulfur provides. Because recent experimental data indicate that FeO metallizes at high pressures (700 kbar) (Knittle and Jeanloz, 1986) it is expected to also become increasingly soluble in liquid Fe at high pressures of the earth's interior (Kato and Ringwood, 1988). Although only a small amount of O is soluble in Fe at low pressures, solution of O in Fe may occur continuously at the core-mantle boundary.

Table 1. Light Element of the Earth's Core, Earth, and Cosmochemical Abundances

Light Element (X) in the Core	Reuss Mixtures from shock wave data	Wt.% Core	(X/Si) Atomic Fraction, Earth	(X/Si) Atomic Fraction, Chondritic (1) Abundance	(X/Si) Atomic Fraction, Carbonaceous Chondrites (2) Abundance (3)	(X/Si) Atomic Fraction, Solar Abundance (4)
C	Fe <sub>3</sub> C(hpp)+C (diamond)	11	0.44-0.63	0.006	0.32	5.9-14.5
S	Fe <sub>9</sub> S(hpp)+Fe(hpp) also	9-12	0.14-0.29	0.11	0.49	0.24-0.52
O	FeS <sub>2</sub> (hpp)+Fe(hpp) Fe <sub>0.94</sub> O(hpp)+Fe(hpp)		3-4	3.5	4.3	13.8-21.4
						6.4±0.3
						0.46
						22.9

- (1) Ganapathy and Anders, 1974
- (2) Anders and Ebihara, 1982
- (3) Ross and Aller, 1976
- (4) Breneman and Stone, 1985

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## BULK CHEMISTRY AND COMPOSITIONAL STRATIFICATION OF THE EARTH

Don L. Anderson, Seismological Laboratory, California Institute of Technology, Pasadena, CA 91125

The Earth is the largest available piece of condensed matter in the solar system. Its chemistry is therefore relevant to the chemistry of at least the inner part of the solar system and, perhaps, to the chemistry of the refractory part of the solar nebula. CI chondrites are falling out of favor as unaltered primitive material but solar abundances are becoming more precise.

New estimates of solar composition, compared to previous measurements, are enriched in Fe and Ca relative to Mg, Al, and Si. The Fe/Si and Ca/Al ratios are 30-40% higher than chondritic values. This necessitates a revision in the so-called "cosmic abundances" and in the composition of the nebula from which the planets accreted. Geophysical data for the Earth can accommodate these new values but they imply a mantle containing 15 wt.% FeO and more  $\text{CaMgSi}_2\text{O}_6$  than previously supposed. Seismic data is consistent with an FeO-rich lower mantle and a  $\text{CaMgSi}_2\text{O}_6$  (diopside)-rich transition region.

It is generally assumed that the Sun, planets and chondritic meteorites are all derived from the solar nebula and that they contain approximately the same ratios of the refractory condensable elements. Carbonaceous chondrite abundances are usually taken as an appropriate guide to the composition of the condensable material in the solar system and the planets. Chondritic and solar values are both used in compilations of the so-called "cosmic" or solar system abundances<sup>1</sup>. Satisfactory models of the Earth can be obtained from these cosmic abundance tables<sup>2</sup>.

Recently, the composition of the corona and photosphere of the Sun have been redetermined<sup>3</sup>. The Fe abundance is about 40% higher than previous measurements and Fe, Ca, and Ti, relative to Si, Al and Mg, are 30-40% higher than chondritic values. This suggests that chondritic meteorites may not be undifferentiated or representative samples of the solar nebula, and that the terrestrials planets may be more Fe, Ca and Ti rich than previously supposed. The differences from conventional values are so large that major contradictions with geophysical data might be expected. In particular, with these new values the mantle of the Earth would have a higher FeO-content and more  $\text{CaMgSi}_2\text{O}_6$ , the diopside component of clinopyroxene (cpx).

I have calculated the composition of the terrestrial mantle from these new solar values. The procedure is as follows. The core is assumed to be  $\text{Fe}_2\text{O}$ . This is close to the inferred eutectic composition of the Fe-O system at high pressure and also has about the right density. The relative mass of the core is 32.5% and this determines the total amount of FeO remaining for the mantle. It is then assumed that all of the remaining Fe, as FeO in silicates, along with fully oxidized Mg, Si, Al and Ca are in the mantle. The composition of the mantle, so determined, is given in Table 1. The inferred FeO content of the mantle is about 15 wt.%. This is much greater than the 8-12% of upper mantle lherzolites and basalts. The lower mantle represents 70% of the mantle and the implication is that the lower mantle is enriched in FeO compared to samples from the upper mantle. This high

inferred FeO content of the mantle is similar to estimates of the lunar and Martian mantles and about twice as high as usual estimates of the terrestrial mantle. The upper mantle and transition region may also be enriched in FeO compared to available samples.

The density of the Earth's mantle is constrained by the mass, moment of inertia and periods of free oscillation. The uncompressed high temperature density is about  $4.0 \text{ g/cm}^3$ .<sup>4</sup> The mineralogy of the lower mantle is primarily (Mg,Fe)SiO<sub>3</sub>-perovskite structure and (Mg,Fe)O-rocksalt structure, with the FeO strongly partitioned into the (Mg,Fe)O phase. If we assume a mean temperature of 1700°C for the uncompressed adiabat and a mean coefficient of thermal expansion of  $(30-40) \times 10^{-6}/^\circ\text{C}$ , the inferred (metastable) density of the lower mantle is 4.21 to 4.28 g/cm<sup>3</sup>.

The density of the lower mantle with 15.7 wt.% FeO (Table 1) and solar ratios of the major elements distributed amongst perovskites, magnesiowüstite and corundum is 4.26 to 4.28 g/cm<sup>3</sup>. This agrees with the inferred zero-pressure density of the lower mantle calculated above from the geophysical data.

The close correspondence of the "solar" mantle with komatiites is remarkable. The oldest komatiites (~3.5 Ga) have the highest CaO/Al<sub>2</sub>O<sub>3</sub> and FeO. The rarity of komatiites since the Archaean is probably due to their high density and the currently thick lithosphere.

Table 1 Estimate of mantle composition and comparison with mantle lherzolites, komatiites and pyrolite

	(1)	(2)	(3)	(4)	(5)	(6)
SiO <sub>2</sub>	52.5	45.0	44.2	44.9	44.8	45.1
Al <sub>2</sub> O <sub>3</sub>	3.8	3.2	2.0	3.1	3.6	4.6
FeO	3.3	15.7	8.3	13.5	12.0	7.8
MgO	37.7	32.7	42.3	33.0	34.9	38.1
CaO	3.0	3.4	2.1	3.8	3.7	3.1
CaO/Al <sub>2</sub> O <sub>3</sub>	0.79	1.08	1.07	1.21	1.02	0.67
MgO/(MgO+FeO)	0.92	0.68	0.84	0.71	0.74	0.83

- (1) Chondritic
- (2) Solar
- (3) Average of 301 continental spinel lherzolites
- (4) Komatiite, Barberton, South Africa
- (5) " "
- (6) Pyrolite

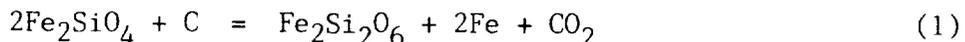
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DEVELOPMENT OF  $Mg/(Mg + Fe)$  ( $Mg^*$ ) = 0.9 IN THE EARTH'S MANTLE

R.J.Arculus (Dept. Geol.Sci., Univ. of Michigan, Ann Arbor, MI 48109),  
 R.Powell (Dept. Geology, Univ. of Melbourne, Parkville, Victoria, 3052)

The widespread development in the Earth's upper mantle of a  $Mg^* = 0.9$  is a well established fact, based on direct analysis of the most abundant peridotite xenolith types, slices of upper mantle preserved in alpine peridotites, and the maximum value of this ratio commonly observed in terrestrial basalts. The prevalence of this value throughout the mantle is in dispute. A clear understanding of the processes giving rise to this non-chondritic ratio in the upper mantle at least has not been obtained. Success in this direction should provide useful constraints in the development of models of the Earth's formation and early evolution. Recognizing that within the silicate fraction of meteorite samples a range of  $Mg^*$  from about 0.5 to 1.0 exists, it is clear that the process of reduction of FeO to core-forming metal must have been arrested in the case of the Earth before proceeding to completion. The fact that a similar  $Mg^*$  is characteristic of the silicate portion of the Main Group Pallasites (and by O isotope fingerprinting perhaps the eucrite parent body (EPB)) suggests that this arrest was not necessarily a function of high pressure (greater than a few kbar) conditions. A similar argument can be made to discount the importance of metal formation through FeO disproportionation as the dominant core-forming event. Rather the availability of reductant seems to be the most significant factor for the arrest of the core-forming process. For example, equilibria involving carbon such as:



serve to illustrate the type of reaction involved. The  $dT/dP$  of this reaction probably changes from +ve to -ve with increasing pressure, and therefore can proceed in a growing planet even at relatively low temperatures.  $X_{CO_2}$  is obviously important as the equilibrium pressure at T will drop under  $H_2O$  (or  $CH_4$ )-rich conditions. Some of the complications in investigating this type of reaction are: i) the availability of high PT fugacity polynomials; ii) selective loss of volatiles from the reaction horizon leading to migration of the reaction in P-T space as a function of  $X_{CO_2}$ ; and iii) the  $f_{O_2}$ -dependence of carbonate-forming,  $CO_2$ -silicate reactions which are important in a relatively large terrestrial planet (internal P's greater than 15 kbar) but not in the EPB. If the availability of C as a primary reducing agent was responsible for the change of  $Mg^*$  in the proto-mantle from 0.5 to 0.9, then the subsequent loss of most of the terrestrial C endowment seems required, perhaps as the result of atmospheric erosion in the Moon-forming Big Splash. Two other possible coincidences with respect to  $Mg^* = 0.9$  are worth noting. Cell volumes along the forsterite-fayalite join show a maximum deviation from ideal mixing (with cell contraction) at a  $Mg^*=0.9$ . However, the small magnitude of the change in partial molar volumes involved requires cycling of silicate mantle through a large P range to be significant relative to equilibria such as (1). In the case of high-P silicate phase relations,  $Fo_{0.9}$  is within the relatively narrow olivine compositional band in equilibrium with the denser beta- and spinel-structured phases over a considerable temperature range. Thus the existence in at least the upper mantle of a  $Mg^*=0.9$  may be indicative of density stratification of the growing Earth undergoing simultaneous reduction. Since these are high-pressure phenomena, no analogy with the EPB can be made and may be misleading.

**3D SOLAR NEBULA MODELS: IMPLICATIONS FOR EARTH ORIGIN.** Alan P. Boss, DTM, Carnegie Institution of Washington, 5241 Broad Branch Road N.W., Washington DC 20015.

Formation of the solar nebula through the collapse of a dense interstellar cloud has been studied through a set of 16 three dimensional (3D) numerical models [1]. This abstract summarizes the implications of these models for the dynamics and thermodynamics of terrestrial planet formation.

The solar nebula models are produced by calculating the collapse of initially uniform density and rotation, spherical clouds, onto protosuns of variable mass. The calculations involve solutions of the three dimensional equations of hydrodynamics, gravitation, and radiative transfer in the diffusion approximation. Improvements over previous calculations [2] include updated opacities, enhanced spatial resolution for thin disks, a central sink cell to simulate the growing protosun, and initial densities sufficiently high to reach phases where the protosun has formed and is surrounded by a growing solar nebula. The detailed thermodynamical treatment means that the temperature of the nebula is self-consistently determined. Forming the nebula from a collapsing cloud means that *ad hoc* initial conditions for the nebula (e.g., strongly unstable disks) are avoided.

Three parameters have been varied in the 16 models: the initial mass of the protosun (0.0 to  $1.0 M_{\odot}$ ), the initial mass of the nebula (0.10 to  $1.0 M_{\odot}$ ), and the initial specific angular momentum of the nebula ( $2.0 \times 10^{18}$  to  $6.2 \times 10^{19} \text{ cm}^2 \text{ s}^{-1}$ ). The final models have protosun masses ranging from 0.001 to  $1.8 M_{\odot}$  and nebula masses ranging from 0.002 to  $1.02 M_{\odot}$ . Hence the models represent a wide range of possible solar nebula models (from minimum mass to massive nebula models) as well as a considerable range of evolutionary phases (both through the time evolution of each model as well as through the different total masses in each model).

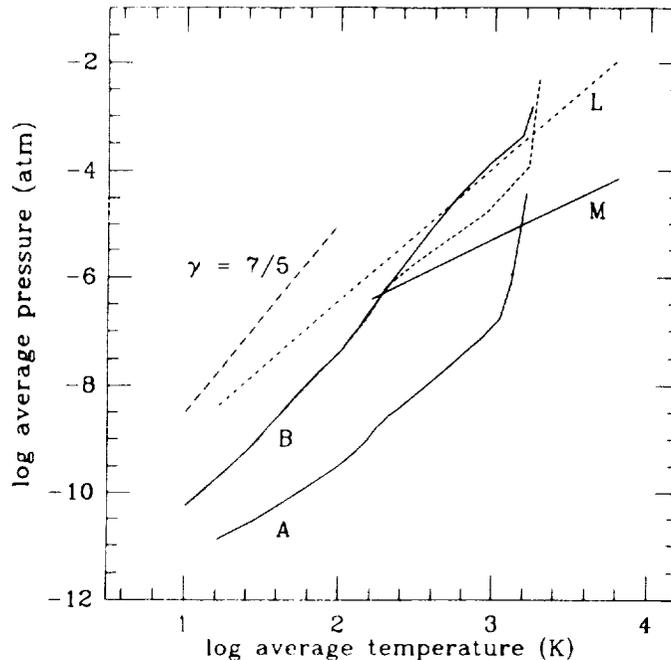
#### DYNAMICAL IMPLICATIONS:

- (1) The solar nebula may have been significantly nonaxisymmetric, i.e., bar-like, and gravitational torques within a nonaxisymmetric nebula may have been responsible for nebula evolution and partial clearing on time scales of  $10^6$  to  $10^7$  years. If so, this would obviate the need for ascribing nebula evolution to viscous torques.
- (2) Surface densities in the inner solar nebula are high enough in essentially all the models to account for terrestrial planet formation through the gravitational instability of a dust sub-disk [3,4]. However, in the outer solar nebula densities are insufficient for a similar rapid formation of rocky cores [5], unless the nebula is quite massive ( $\approx 1 M_{\odot}$ ).

#### THERMODYNAMICAL IMPLICATIONS:

- (1) Compressional energy produced by the collapse of the presolar cloud was trapped within the nebula for time scales on the order of  $10^5$  years. Midplane temperatures at 1 AU could well have reached 1500 K or more during this phase [6]. In addition, if the nebula was strongly nonaxisymmetric, temperatures at 1 AU could have varied substantially in azimuth, opening up the possibility of periodic thermal cycling of solids moving on Keplerian orbits.
- (2) High temperatures in the inner solar nebula imply that sequential condensation of solids as the nebula cooled may well have occurred [7]. However, maximum temperatures may have been regulated to  $\sim 1500$  K by the thermostatic effect of the opacity (see Figure). Because the nebula opacity at high temperatures is primarily provided by iron grains, which vaporize around 1420 K [8], the opacity drops precipitously when temperatures reach  $\sim 1500$ K, leading to enhanced radiative cooling. When temperatures drop below  $\sim 1500$ K, the iron grains reform, the opacity rises, and radiative losses drop, effectively regulating the temperature. This means that equilibrium condensation sequences may have to be recalculated in order to take into account finite initial temperatures and hence survival of the most refractory interstellar grains.
- (3) While cooling from high temperatures implies equilibrium condensation sequences were operative, condensation need not have led to a strong compositional gradient in the terrestrial planet region, because of the thermostatic effect previously noted. That is, if the thermal gradient is nearly zero because of the thermostat effect, condensation sequences may have been similar throughout the inner solar nebula. Furthermore, stochastic orbital evolution of large planetesimals (leading to large scale radial mixing) tends to erase the effects of any primordial compositional gradients [9].
- (4) High temperatures in the inner solar nebula may have been directly responsible for the depletion of volatile species (C, N,  $\text{H}_2\text{O}$ ) in the terrestrial planets by factors of order  $10^4$  or more compared to solar abundances [10]. The volatiles may have been removed from the terrestrial planet region along with the rest of the gaseous portion of the nebula through dynamical evolution of the nebula itself or through the enhanced early solar wind.

(5) While temperatures around 1500K imply that equilibrium chemistry is likely to have occurred in the inner solar nebula and that thermochemistry was the dominant energy source [10], vaporization of iron grains at the midplane may have limited the effectiveness of the Fe catalysis (Fischer-Tropsch-type reactions) suggested as a means of converting CO to CH<sub>4</sub> [10] and of forming other organic compounds found in carbonaceous chondrites, at least during these hot early phases. The question then becomes, how much cooling occurred prior to inner solar nebula removal?



Pressure as a function of temperature for two 3D models of the solar nebula [6]. Model A has a protosun of mass  $1.0M_{\odot}$  and a nebula of mass  $0.06M_{\odot}$ . In model B the protosun has not formed yet, and the nebula is bar-like with a mass of  $1.0M_{\odot}$ . The pressures and temperatures are averaged in azimuth, except for the dashed line of model B, which shows the variation along the bar. An arbitrary adiabat for molecular hydrogen ( $\gamma = 7/5$ ) is shown, as well as the Larson (L) adiabat [11] and a generic viscous (M) accretion disk profile [12]. Note the convergence of the 3D model profiles at  $\sim 1500\text{K}$ .

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## XENON FROM CO<sub>2</sub> WELL GASES

Marc W. Caffee, G. Bryant Hudson, and Carol Velsko, *Lawrence Livermore National Laboratory, Livermore, CA 94550 USA.*

E. Calvin Alexander, Jr. and Gary R. Huss, *Dept. of Geology and Geophysics, Univ. of Minn., Minneapolis, MN 55455 USA.*

Allan R. Chivas, *Research School of Earth Sciences, Australian Natl. Univ., Canberra, A. C. T. 2601, Australia.*

Much of our understanding of the early history of the solar system comes from extensive studies of the elemental and isotopic composition of the noble gases in meteorites and lunar samples. Analyses of Xe, for example, demonstrated the presence of <sup>244</sup>Pu and <sup>129</sup>I in the early solar system. We have also learned that there are several distinct reservoirs of noble gases (solar and planetary) found in extra-terrestrial material. This knowledge is accessible because several classes of meteorites are, when compared to terrestrial material, largely unaltered. Studies of the early history of the Earth, on the other hand, are hampered owing to 4.5 Gyr of extensive geologic activity. This is especially true for the noble gases, whose abundances are exceedingly low and likely to be altered by such activity. Indeed, the relationship between the noble gases found in meteorites and those found in terrestrial reservoirs is not well understood. From a noble gas perspective, a key to understanding the early history of the Earth is identifying noble gases whose composition may yet contain vestiges from a more primordial source. A candidate for such a source is presumed to be the mantle, although it is likely that even noble gases from the mantle are altered.

A particularly interesting example of a presumably mantle-derived gas is the Harding Co. CO<sub>2</sub> well gas, originally studied by Boulos and Manuel (1) and later reanalyzed by Phinney *et al.* (2). These investigators found excesses, relative to atmospheric Xe, of <sup>129</sup>Xe. As in the case of meteorites, these excesses were attributed to the decay of <sup>129</sup>I. Unlike meteorites and lunar material there is no clear-cut evidence for Xe from the spontaneous fissioning of <sup>244</sup>Pu in conjunction with the <sup>129</sup>I decay. Subsequent studies of MORB samples have also shown excesses of <sup>129</sup>Xe (3), but again, show no clear-cut evidence for <sup>244</sup>Pu-derived Xe.

We have undertaken a study of several CO<sub>2</sub> gas deposits. To date, we have analyzed noble gases from two deposits in Colorado, McElmo Dome and Sheep Mtn., and one from Australia, Caroline (4). All three samples show clear excesses of <sup>129</sup>Xe. Also present are excesses, relative to air Xe, of <sup>132-136</sup>Xe. The observed Caroline Xe composition represents a mixture of different Xe compositions. Air Xe and Xe from the spontaneous fission of <sup>238</sup>U are likely sources. Other possible sources are solar Xe, represented by SUCOR (5), and planetary Xe, represented by Kenna (6), and <sup>244</sup>Pu fission Xe. In addition, mass fractionation of the Xe might occur. Table 1 summarizes these possibilities and gives a value of  $\chi^2$  which measures the goodness-of-fit of the particular mixture. From Table 1 we conclude two reasonable possibilities exist: 1) the underlying composition is mass-fractionated atmospheric Xe where the fractionation favors the light Xe isotopes or 2) the underlying composition is a mixture of atmospheric Xe and a meteoritic component. Table 2 expands the results of Table 1 for these two cases.

1) *Mass-fractionated atmospheric Xe:* How much fractionation is required to explain the deviations from air in the Caroline data? As noted in Table 1, about 40‰/mass is required. The remainder of the heavy Xe isotopes could then be attributed to decay of <sup>238</sup>U. In this instance, the salient observation is the lack of <sup>244</sup>Pu-derived Xe in conjunction with the I-derived <sup>129</sup>Xe. This circumstance is troublesome given the longer half-life of <sup>244</sup>Pu and is a topic of controversy (7).

2) *Two-component mixing:* Figure 1 is a graph showing <sup>128</sup>Xe/<sup>130</sup>Xe vs. <sup>129</sup>Xe/<sup>130</sup>Xe. It seems that the amount of excess <sup>129</sup>Xe is correlated with the amount of excess <sup>128</sup>Xe. Owing to the small size of the data set of we believe at this time that this correlation can only be described as qualitative. Within the confines of the previously discussed hypothesis, there is no reason to suppose that such a correlation should exist at all. We would, however, expect such a correlation if the Xe in these CO<sub>2</sub> well gases were a mixture of atmospheric Xe and a more primitive meteoritic component, such as solar- or planetary-Xe. In such a model the excess <sup>129</sup>Xe would also be attributed to a meteoritic source, hence the correlation between <sup>128</sup>Xe and <sup>129</sup>Xe. For the Xe from the Caroline sample a mixture of ~10% meteoritic Xe and the remainder atmospheric Xe would be required. Again, there are excesses at the heavy Xe isotopes which are attributable to <sup>238</sup>U and/or <sup>244</sup>Pu decay. These remaining heavy Xe isotopes are fit best with a combination consisting of ~30% <sup>244</sup>Pu fission and 70% <sup>238</sup>U fission (Table 1). This hypothesis requires the existence a source of meteoritic Xe in the mantle. Other investigators have observed Ne isotopic ratios higher than the atmospheric ratio and from these ratios have inferred the presence of a source of solar-like Ne in the mantle (8). We have analyzed the Ne isotopic ratios of all

three CO<sub>2</sub> gases and have found that the <sup>20</sup>Ne/<sup>22</sup>Ne ratio is higher than that of atmospheric Ne.

The demonstration of a source of non-atmospheric Xe in the mantle has far-reaching implications for the early history of the Earth. In particular, it has always been reasonably assumed that the <sup>129</sup>Xe excesses resulted from the decay of <sup>129</sup>I in the solid Earth. If, on the other hand, the mantle contains a primitive meteoritic noble gas reservoir, the most likely explanation for these excesses is that the material from which the mantle accreted already contained <sup>129</sup>Xe from <sup>129</sup>I decay. In this instance the presently observed <sup>129</sup>Xe excesses contain little chronometric information about the early Earth. Indeed, the small size of the <sup>244</sup>Pu-Xe excess argues for a slow (with respect to 10<sup>8</sup> yr) degassing of the mantle to form the present atmosphere.

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Table 1. Goodness-of-fit for various mixtures of Caroline Xe

Mixture	$\chi^2$ <sup>a</sup>	Pu/U <sup>b</sup>	non-air/ <sup>c</sup> air	mass- <sup>d</sup> fractionation
air + <sup>238</sup> U	115.4	0	0	0
fractionated air + <sup>238</sup> U	5.6	0	0	3.97
fractionated (air + <sup>238</sup> U)	5.9	0	0	3.95
air + SUCOR + <sup>238</sup> U	8.2	0	0.081	0
air + Kenna + <sup>238</sup> U	9.0	0	0.084	0
air + SUCOR + <sup>238</sup> U + <sup>244</sup> Pu	1.6	0.27	0.088	0
air + Kenna + <sup>238</sup> U + <sup>244</sup> Pu	1.9	0.32	0.094	0

<sup>a</sup>  $\chi^2$  = sum over all isotopes except <sup>129</sup>Xe of (meas. - calc.)<sup>2</sup>/σ<sup>2</sup>.

<sup>b</sup> <sup>132</sup>Xe due to <sup>244</sup>Pu / <sup>132</sup>Xe due to <sup>238</sup>U.

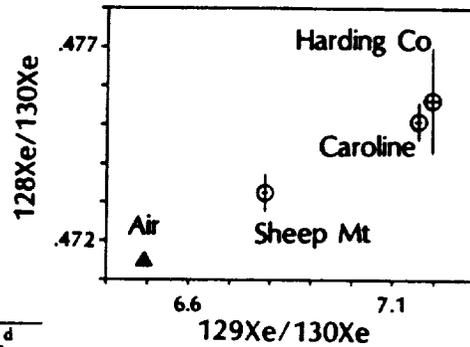
<sup>c</sup> <sup>132</sup>Xe due to SUCOR or Kenna / <sup>132</sup>Xe due to air.

<sup>d</sup> expressed in units of *per mil/mass unit*.

Table 2. Deviations of "best" mixtures from Caroline composition

<sup>130</sup> Xe = 1	<sup>124</sup> Xe	<sup>126</sup> Xe	<sup>128</sup> Xe	<sup>131</sup> Xe	<sup>132</sup> Xe	<sup>134</sup> Xe	<sup>136</sup> Xe
Caroline	0.0239 ±0.0001	0.0223 ±0.0001	0.4751 ±0.0005	5.223 ±0.007	6.708 ±0.008	2.729 ±0.002	2.376 ±0.002
air + Kenna + <sup>238</sup> U + <sup>244</sup> Pu	0.0239	0.0222	0.475	5.223	6.705	2.730	2.375
deviation from Caroline	-0.19	1.21	-0.17	0.08	0.35	-0.40	0.26
frac. (air + <sup>238</sup> U)	0.0239	0.0221	0.475	5.215	6.699	2.731	2.375
deviation from Caroline	-0.21	1.35	-0.33	1.20	1.05	-1.02	0.54

\* This work was performed under the auspices of the U.S. Dept. of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.



**EFFECTS OF THE GIANT IMPACT ON THE EARTH.** A. G. W. Cameron and W. Benz, Harvard-Smithsonian Center for Astrophysics.

We have been carrying out a series of investigations of the largest collision that the Earth would have encountered during its accretionary history: that with the second most massive body in its region of accumulation. Our objective in these calculations has been to see what the characteristics of the collision must have been if one outcome of the collision would have been the formation of the Moon.

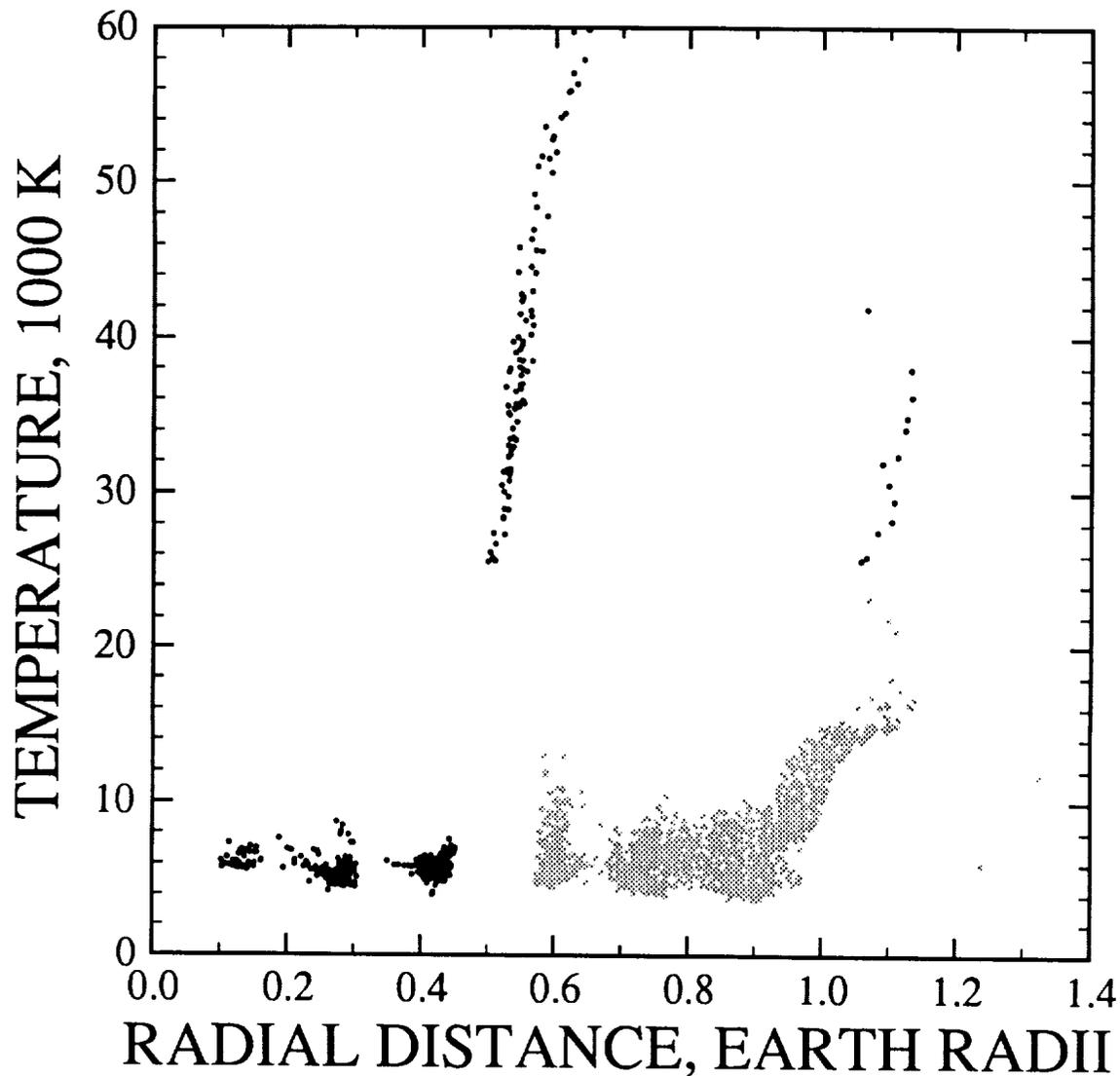
The calculations have been carried out using three-dimensional smooth particle hydrodynamics. In this method a mesh is not used, but rather the masses of the Protoearth and the Impactor are divided into a number of particles (3008 for each of the cases investigated here). These particles are extended in space (their shape is called their kernel), so that they overlap under normal conditions. Pressure and density are bulk properties of the medium obtained by averaging over the particles. The particles move in response to the forces exerted on them by gravity and by pressure gradients. Both the Protoearth and the Impactor have been modelled with iron cores and dunite mantles, and on the assumption that they would have been heated by their prior accumulation, we assumed that they were both initially isothermal with a temperature of 4,000 K. This assumption also made it easy to see how much heating the various particles received in the collision. So far we and our collaborators have prepared three principal articles on these collisions (1,2,3).

In order to account for the unique compositional properties of the Moon, we have defined a promising outcome of a collision as one in which there is more than one Moon mass beyond the outermost orbiting iron particle, if there is one. We have limited our investigations to collisions in which the angular momentum is in the range 1.0–1.7 times the angular momentum of the present Earth-Moon system. This allows for some loss of angular momentum due to solar tides. The outcome of the collision is a sensitive parameter of the geometry of the collision, and, since we are unsure that the radius of the model would represent accurately that of the Protoearth, there is in any case a related uncertainty in the appropriate angular momentum to use. We have looked closely at the damage done to the Protoearth in our recent series of *Definicon* and *Compaq* runs at Harvard, 11 so far, having Impactor/Protoearth mass ratios of 0.14, 0.16, and 0.25, and having velocities at infinity of 0–7 km/sec.

The characteristics of the collisions fall into a recognizable pattern. In the collision itself the Impactor is destroyed by being drawn out into a long arc or bar. Its iron core lies within that part of the arc or bar closest to the Protoearth, so that all or nearly all of it falls out onto the mantle of the Protoearth. This iron falls through the mantle and wraps itself around the core of the Protoearth. The arc or bar is very effective in transferring angular momentum to the outermost rock within it; this rock can go into orbits at both large and small radial distances. Usually there is some rock beyond the Roche lobe, more than a Moon mass of it for the larger angular momentum cases. In those cases where there is a lot of material beyond the Roche lobe, we find that much of it clumps into one or more bodies, in some cases one of these bodies approaches the mass of the Moon. In such cases a protolunar body can accumulate from these clumps and extract angular momentum from the disk, which will be driven onto the Protoearth. In other cases the disk would have to spread by viscous dissipation before a similar process can begin. Where several clumps are formed, some are likely to be ejected, carrying away some of the angular momentum.

In all cases the damage to the Protoearth is extensive and major. All of the cases give very similar results. The set of results for our case DEF3 is shown in the Figure, which plots the temperatures of all the particles in the Protoearth (in thousands of degrees K) against the radial distance in units of the present radius of the Earth. Iron particles are plotted as small black filled circles, and rock particles as small gray filled circles. It may be seen that the particles tend to be clumped near particular values of the radial distance. This is an artifact of the modelling: in the initial models the particles tended to sort themselves out onto concentric spherical shells; much of this original structure survives the collision (less so in the more energetic collisions).

All particles in the Protoearth suffered some rise in temperature; those in the original Protoearth were heated by amounts varying from 300–5000 degrees. The iron from the Impactor which accreted around the core of the Protoearth has been heated into the range 25,000–60,000 degrees. Because all particles have the same mass, and higher density for the iron particles can be felt only when two or more of them overlap, the iron particles that become isolated do not fall through the mantle and can be seen just beyond one Earth radius; this behavior is an artifact of the calculation. The rock particles within the mantle have been heated typically into the range 5,000–10,000 degrees, but those accreting onto the surface (originally both from the Protoearth and the Impactor) lie in the range 6,000–18,000 degrees, with a tendency for the temperature to



increase outwards. This very hot gaseous material (a rock vapor atmosphere) extends outwards to 1.1 Earth radii. Over a period of thousands of years much material from the orbiting disk will accrete onto the surface as a result of disk dissipation and tidal interactions with the forming Moon, maintaining a very high surface temperature during this period.

The mantle will thus be strongly heated both at its base and at the top. The high surface temperature will maintain the orbiting disk as rock decomposition vapor products, which will reduce its viscosity and prolong its dissipation. The disk, being heated from the surfaces, is unlikely to be thermally convective, so that the lighter gases can diffuse outwards and can escape at the Roche lobe. This includes practically all of the primordial terrestrial atmosphere.

Some time later an adiabatic gradient will be established from the base of the mantle to the surface. This will maintain vigorous thermal convection of the molten mantle for an extended time. The cooling time of the Earth from the Giant Impact will be determined by the effective temperature of the Earth, which can be quite low if the Earth reaccretes enough volatiles to form an atmosphere with an outer cloud layer.

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MAGMA OCEANS, OCEAN RIDGES, AND CONTINENTAL CRUST:  
 RELATIVE ROLES IN MANTLE DIFFERENTIATION. R.W. Carlson and S.B. Shirey,  
 Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad  
 Branch Road N.W., Washington DC 20015.

Processes acting during the formation and differentiation of the Earth have resulted in a present upper mantle that has element abundances decidedly different from the chondritic meteorites. In some cases, these differences can be related to obvious features of chemical stratification in the Earth, such as the low Fe and siderophile element abundances in the mantle resulting from core formation. A characteristic of mantle composition with a less clear-cut explanation is the higher than chondritic Mg/Si [1] and Ca/Al [2] of the upper mantle. To explain this characteristic, recent models have proposed that the upper mantle formed either as an extensive partial melt of mantle in the majorite stability field [3] or as the residual liquid from the crystallization of a magma ocean hundreds of kilometers deep [4,5]. Judging from the evidence for an early magma ocean on the Moon (e.g. [6]), extensive melting of the Earth should have been a possible, if not probable consequence of its accumulation. However, the pattern of elemental abundances in the upper mantle, as determined primarily by data for incompatible element depleted mid-ocean ridge basalts (MORB), is most consistent with clinopyroxene being the dominant phase controlling the abundances of highly to moderately incompatible lithophile elements [7]. Based on the only available partition coefficient data for majorite and perovskite [8], fractionation of either of these high-pressure phases would have produced an upper mantle composition with trace element distributions unlike those actually observed [8]. Rather, the composition of the upper mantle appears to have been affected primarily by low-pressure ( $\approx 1 - 3$  GPa) partial melting and the fractionation caused by melt removal to form oceanic and continental crust.

Reliance purely on the extraction of continental crust to create the elemental distributions characteristic of the upper mantle suffers two problems. 1) Most Archean mantle derived rocks have initial Nd isotopic compositions greater than chondritic (e.g. [9]) indicating that the upper mantle was depleted in incompatible elements long before continental crust began to be preserved beginning about 3.8 Ga ago. If significant volumes of continental crust were present prior to 3.8 Ga, they should have been preserved at the Earth's surface because of their low density and low melting temperature which would have caused their rapid return to the surface if subducted. 2) Compared to the mantle, the continental crust is small in volume, but is capable of causing incompatible element depletions in large volumes of mantle because of its extreme enrichment in these elements [10]. In contrast, extraction of the continental crust would have minimal effect on the Si, Mg, Ca, and Al abundances of the mantle unless the portion of mantle depleted by crust removal is very small compared to the total mantle volume. Simple mass balance calculations suggest that a section of depleted mantle only 100 to 200 km thick beneath continents is all that is necessary to supply the inventory of all but the most highly incompatible elements in the continental crust [11]. The calculated volumes of mantle residue required to form the continental crust thus are on the order of the volume of the continental lithosphere observed to be strongly depleted in basaltic components [12]. If most of the residues of crust formation are trapped in the continental lithosphere, continental crust formation would have little effect on the major element and moderately incompatible element ( $D's > 0.1$ ) abundances in the mantle.

We suggest that both of the problems presented above can be solved if the composition of the upper mantle is determined by a combination of oceanic *and* continental crust formation. Removal of a quantity of basalt approximately equal to 7 to 10% of the mass of an initially "chondritic" mantle composition would increase the Mg/Si and Ca/Al, and create sufficiently high Sm/Nd, in the residuum to evolve the observed Nd isotopic composition in the Archean mantle if basalt extraction began to occur prior to

4.0 Ga [13,14]. If a mass equal to that of the mantle above 650 km depth is assumed to be the residue of basaltic oceanic crust extraction, then the mass of basalt needed to explain the composition of the upper mantle is about half to a third of the total oceanic crust created over Earth history assuming the present crust production rate was constant through time. This amount of basaltic crust is roughly 18% of the mass of the transition zone (for a depleted layer 400 km deep), 26% of the mass of the D" layer, or only about 2% of the mass of the lower mantle. If stored exclusively in one of these regions, the basalt would significantly modify the composition of the transition zone or D" layer, but would lower the  $Mg/(Mg+Fe^{2+})$  of the lower mantle by only 0.005. The recycling time of oceanic crust into the upper mantle appears presently to be 1.8 Gyr based on the Pb-Pb isotopic model age for modern oceanic basalts (e.g. [11]). Reassimilation of this basaltic component will limit the maximum extent of differentiation of the depleted mantle and, if occurring in the early Archean, might provide an explanation for the nearly constant chondrite normalized initial Nd isotopic compositions ( $\epsilon_{Nd}$ ) of 3.8 to 2.7 Ga old mantle derived rocks if the mantle had reached a steady-state between the rates of extraction of new oceanic crust and the assimilation of old subducted crust.

Removal of basaltic oceanic crust alone, however, cannot match the degree of depletion of the MORB source in highly incompatible elements such as Rb and Ba, nor can it lead to its apparent enrichment in Nb and Ta and depletion in Pb [7] compared to estimates of primitive mantle compositions. The clear complementarity in the abundances of these elements between continental crust and depleted MORB-mantle [7] shows that some elemental transfer has taken place between the upper mantle and the continental crust. This ongoing exchange most likely occurs at continental-oceanic convergent margins by the transfer of incompatible element rich fluids or very small volume partial melts from the subducting oceanic plate to the overlying continental lithosphere. Nb/Th for Archean komatiites and some Archean basalts, however, are similar to primitive mantle values [15]. This supports the idea that the mantle in the Archean did not yet bear the chemical signature of continental crust extraction either because the volume of pre-Archean crust was too small to create a resolvable effect or the nature of the crustal extraction process changed after the Archean. The relative Nb enrichment typical of the present upper mantle [7] and the increase in  $\epsilon_{Nd}$  for mantle derived rocks between the Archean and Proterozoic may record the chemical changes in the mantle caused by the extraction of large volumes of continental crust during the Archean. The major element and moderately incompatible element abundances in the upper mantle, however, may have been controlled throughout Earth history by the plate-tectonic cycle of basaltic oceanic crust formation accompanied by a significant time lag before the subducted basaltic crust is rehomogenized back into the mantle.

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### HEAT AND MASS TRANSPORT IN THE EARLY EARTH

Geoffrey F. Davies, Research School of Earth Sciences, Australian National University, Canberra ACT 2601, Australia.

Heat and mass transport have been intimately related throughout earth history. We can identify three main processes: impact stirring, chemical segregation and thermal convection. These processes most likely overlapped in time, with thermal convection coming to predominate as the earth attained its final size. Advection, the transport of heat by mass motion, has exerted a dominant control on the thermal regime of the earth's interior except in the early stages of accretion.

In the early stages of the growth of the earth, impacts of accreting bodies served as the main source of heating and the only significant source of mass transport. The depth of penetration of the largest impacts defines the outer zone of impact stirring. The impacts deposit heat to significant depths and stir the adjacent material, thereby enhancing heat removal over removal by pure conduction. They might also cause considerable chemical homogenization. Despite the seemingly large uncertainties in these processes, it is likely that the result of the competing heat deposition and removal was the attainment of temperatures near melting in the outer parts of the earth by the time it had attained about half of its final radius. As the impact stirring zone progressed outwards to this point, it would leave below it a static zone with the lowest temperatures at the center of the earth. Assuming homogeneous accretion, this cool proto-core would have been a fairly intimate mixture of rock and metal.

Probably the greatest uncertainty associated with impact-related processes concerns the effects of the largest impacts, which might dominate the collective effects of smaller impacts.

Segregation of the core and mantle was undoubtedly second only to accretion in magnitude. Although there are large gaps in our knowledge, several things can be said with reasonable certainty. If the earth started from a fairly homogeneous mixture, then the energy released by core segregation would have been sufficient to heat the earth by about 2000 C, although much of this heat may have been removed during the process. Segregation would probably have begun in the outer parts of the earth at about half of its final radius, when the melting temperature of the metal phase was reached. A catastrophic overturn, replacing the proto-core with a growing metal core, would have quickly ensued; this would transport heat down as well as causing dissipative heating. Thereafter, core segregation would have been contemporaneous with and rate limited by accretion. The metal phase may have chemically equilibrated near the surface, but may have descended rapidly in large (km+ ?) bodies, preventing equilibration under prevailing internal pressures.

Mantle convection would have begun soon after segregation of the core and mantle materials, under the combined heating effects of impacts and segregation, and would have been the dominant regulator of the earth's thermal state ever since. The strong temperature-dependence of silicate rheology (viscosity drops by about an order of magnitude for each 100 degrees increase in temperature) ensures that temperatures are strongly buffered on the high side. This means, for example, that highly unstable temperature profiles would not have been able to develop and that melting of most of the mantle would not have been possible, even, it would seem, in the event of a late giant impact.

Extensive near-surface melting undoubtedly occurred in the late stages of

accretion due both to impact heating and to removal of internal heat. However, ultramafic melts have low viscosities and would have cooled and solidified very quickly. Accumulation of melts into a magma ocean requires either a very rapid input of heat or insulation from surface heat loss. A late, giant impact could certainly have supplied heat rapidly and produced a near-surface magma ocean, possibly of order one hundred kilometers deep, but this would have cooled to mush within a few hundred years. A buoyant, insulating, lunar-type anorthositic crust does not seem likely for the earth, but melts may be denser than coexisting solids 200-300 km deep in the mantle and might have accumulated there. A massive atmosphere might insulate the surface sufficiently to keep it molten, but this is not a popular scenario and it involves great uncertainties in physical properties and processes. Thus a transient magma ocean following a giant impact seems quite plausible while a more persistent magma ocean due to other effects is uncertain.

Whether any compositional stratification due to melting and solidification (local or global, transient or persistent) might have survived late impact bombardment and vigorous mantle convection driven by both thermal and chemical buoyancies seems to be completely open from the physical point of view. Recent high pressure trace element partitioning experiments indicate that the upper mantle is not the product of melting in the lower mantle. On the other hand, if the mantle has uniform major element (pyrolite) composition, its silic content is low compared with chondritic meteorites. While the notion that the present mantle is compositionally layered has been popular, current geophysical arguments weigh rather strongly against this and inferences to this effect from isotopic evidence have been based on unjustified assumptions about the physical process of convective stirring.

The mantle of the early post-accretion earth was probably several hundred degrees hotter than at present and vigorously convecting with extensive melting over upwelling areas. The thermal transient resulting from accretion and core segregation would have been dissipated within a few hundred million years, after which the thermal state would have tracked the decay of internal radioactive heat sources. Without the organising effect of large, strong plates, mantle convection would have been multiscale (100-5000 km?) and time-dependent (1-50 m.y.?).

Post-accretion transitions in convection style may have occurred. Subduction in the modern sense probably could not have occurred in the early earth because the thermal boundary layer was too thin, too weak and too buoyant. The onset of subduction would have enhanced the efficiency of heat transport and caused another thermal (and tectonic) transient to a cooler mantle. Since layering impedes the efficiency of convective heat transport, the breakdown (or accumulation) of any compositional layering would also have caused a transient. It is tempting, but conjectural, to identify such transitions with the onset of the rock record at about 4 b.y. and the Archean-Proterozoic boundary at about 2.7 b.y.

The continental crust is relatively small in mass but records a large fraction of earth history. If little of it had been recycled back into the mantle by subduction, then its present age distribution would record its differentiation from the mantle. However, some recycling seems likely, in which case the present age distribution would be the result of competing processes of generation and removal and the early rates and modes of generation become very uncertain, as does the crustal volume as a function of time.

MICHAEL J. DRAKE, DANIEL J. MALVIN, AND CHRISTOPHER J. CAPOBIANCO.

(Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721, U.S.A.)

Theoretical considerations of planetary accretion suggest that terrestrial planets should begin to melt by the time they achieve about one tenth of an Earth mass [1]. Hypotheses for the origin of the Moon involving giant impacts suggest that the Earth would have been substantially melted or even vaporized as a result of the impact [2]. Recent high pressure experimental phase equilibrium studies [3,4] have shown a convergence of the liquidus and solidus for candidate upper mantle compositions, and may be interpreted in terms of a substantially molten Earth during and subsequent to accretion. In contrast, experimental trace element partitioning studies [5] have shown *that at* most minor amounts of majorite and perovskite fractionation are consistent with the approximately chondritic ratios of most refractory lithophile elements inferred for the upper mantle. It has also been proposed that the superchondritic Mg/Si ratio of 1.12 relative to CI in the upper mantle [6] is a consequence of flotation of olivine at high pressure on a buried magma ocean, with subsequent mixing of that olivine into the upper mantle [7]. Mixing of approximately 30% olivine is required.

This proposal may be tested against the approximately chondritic ratios of Sc/Sm, Ni/Co and Ir/Au in the upper mantle (e.g. [8]). Under all experimental conditions [e.g. 9,10], olivine/liquid partition coefficients for Ni,  $D(\text{Ni})$ , are greater than for Co, with  $D(\text{Ni}) > 2 \times D(\text{Co})$ . Estimates of partition coefficients obtained from abundances [11] of Au and Ir in mantle nodules and basalts indicate that Ir is compatible and Au indifferent or incompatible in magmatic processes. Whether these contrasting geochemical behaviors are due to silicate mineral/silicate melt partitioning or to sulfide mineral/silicate melt partitioning is presently uncertain. However, estimates of  $D(\text{Ir})$  and  $D(\text{Au})$  from olivine fractionation in komatiites also suggest that Ir is compatible and Au incompatible [12]. While both Sc and Sm are incompatible elements, Sc appears to be only moderately incompatible while Sm is highly incompatible.

Absolute values of partition coefficients for these elements are not known under appropriate mantle conditions. Thus, calculations have been carried out for a variety of partition coefficient values. For example, for plausible values of  $D(\text{Sc}) = 0.3$ ,  $D(\text{Sm}) = 0.01$ ,  $D(\text{Ni}) = D(\text{Ir}) = 2$ , and  $D(\text{Co}) = D(\text{Au}) = 0.6$ , upper mantle ratios of Sc/Sm, Ni/Co, and Ir/Au will be raised by in excess of 10% above chondritic ratios. Thus, it seems difficult to reconcile extensive melting of the Earth's upper mantle with refractory lithophile, moderately siderophile, and highly siderophile element systematics.

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## OXYGEN PRODUCTION BY LARGE IMPACTS IN THE EARTH'S EARLY ATMOSPHERE

B. Fegley, Jr. and R.G. Prinn, Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139

Bombardment of the Earth by large extraterrestrial bodies leads to the shock heating and chemical reprocessing of the ambient atmosphere (1-3). Impact induced shock chemistry in the present oxidizing atmosphere leads to the production of large amounts of NO (and subsequently NO<sub>2</sub> and HNO<sub>3</sub> acid rain) which at sufficiently high concentrations can lead to a wide range of harmful environmental effects including the destruction of the ozone layer, essentially quantitative extinction of sunlight at the Earth's surface, accelerated chemical weathering and leaching of continental rocks, and neutralization of the alkalinity in the upper-most mixed layers of the oceans with consequent increases in atmospheric CO<sub>2</sub> levels (1,2). In contrast, impact induced shock heating in (hypothesized) oxygen-poor atmospheres on the primordial Earth is predicted to have led to the synthesis of copious amounts of HCN, which is a crucial starting material for complex organic syntheses (3).

However, another important consequence of impact induced shock heating and chemical reprocessing of the Earth's primordial atmosphere is the abiotic production of oxygen. Although the Earth's primordial atmosphere is generally acknowledged to have been deficient in molecular oxygen (O<sub>2</sub>) relative to the present terrestrial atmosphere (4), O<sub>2</sub> was certainly not totally absent in the primitive atmosphere. Photodissociation of CO<sub>2</sub> and H<sub>2</sub>O, as in the present-day atmosphere of Mars, may have produced small amounts of O<sub>2</sub> (volume mixing ratios less than or equal to 10<sup>-9</sup>) in the Earth's early atmosphere (5). In this abstract we argue that an even larger source of O<sub>2</sub> in the Earth's primordial atmosphere was O<sub>2</sub> produced by impact induced shock heating and chemical reprocessing of the early terrestrial atmosphere.

This point is illustrated in Figures 1 and 2 which display calculated equilibrium abundances of important H-C-N-O gases as a function of temperature in cooling parcels of shocked atmospheric gas. The two figures are for two different plausible models for the composition of the Earth's early atmosphere; in one case the initial atmospheric composition is the same as the present-day atmosphere (without oxygen) and in the second case the initial atmospheric composition is that of Hawaiian volcanic gases (minus condensable components such as sulfur and chlorine). In both cases it is apparent that significant amounts of O<sub>2</sub> can be produced if quenching of chemical reactions in the shocked air parcels occurs at sufficiently high temperatures. In particular, we note that production of O<sub>2</sub> volume mixing ratios greater than 10<sup>-9</sup> occurs for quenching at temperatures greater than 1480 K in the N<sub>2</sub>-rich atmosphere illustrated in Figure 1 and occurs for quenching at temperatures greater than 1430 K in the CO<sub>2</sub>-rich atmosphere illustrated in Figure 2. Production of significant amounts of oxygen at an early stage in the Earth's history is important for several reasons: (A) O<sub>2</sub>-bearing atmospheres are ineffective for the synthesis of complex organic molecules via abiotic routes, (B) O<sub>2</sub> is a poison for primitive anaerobic organisms, and (C) sufficiently large amounts of O<sub>2</sub> would have led to the production of large amounts of NO via the same impact induced shock heating and chemical reprocessing. These considerations, the relative chemical reactivities of O<sub>2</sub> and by-products such as H<sub>2</sub> and CO, and the quantitative quenching calculations for O<sub>2</sub> production in a range of plausible model primitive atmospheres will be described at the meeting.

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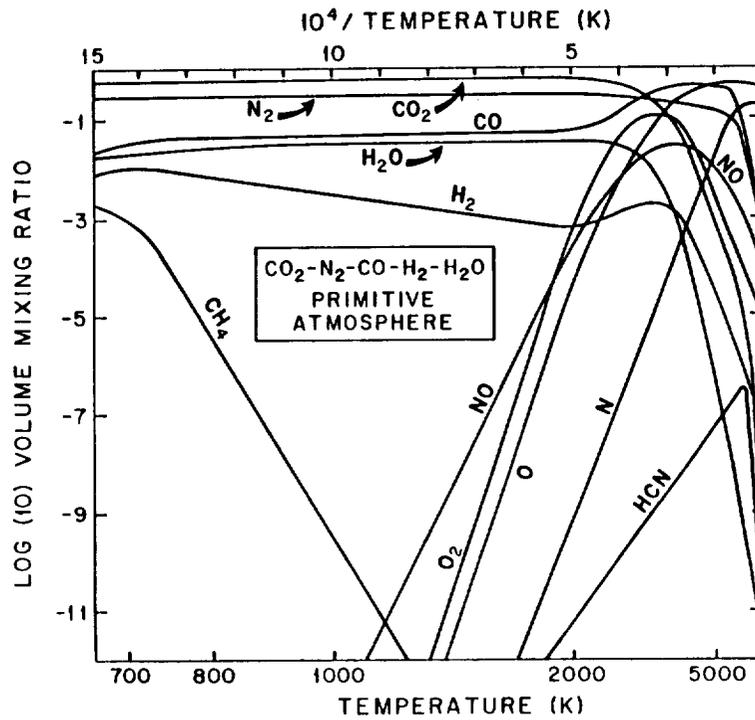


Figure 1. Calculated equilibrium abundances of important H-C-N-O gases in a cooling parcel of a shock heated neutral atmosphere. The initial composition is 98.4%  $N_2$ , 1.5%  $H_2O$ , 0.1%  $H_2$ , 300 ppm  $CO_2$ , and 30 ppm CO which is taken from Pinto et al. (1980). The total pressure is 1 bar.

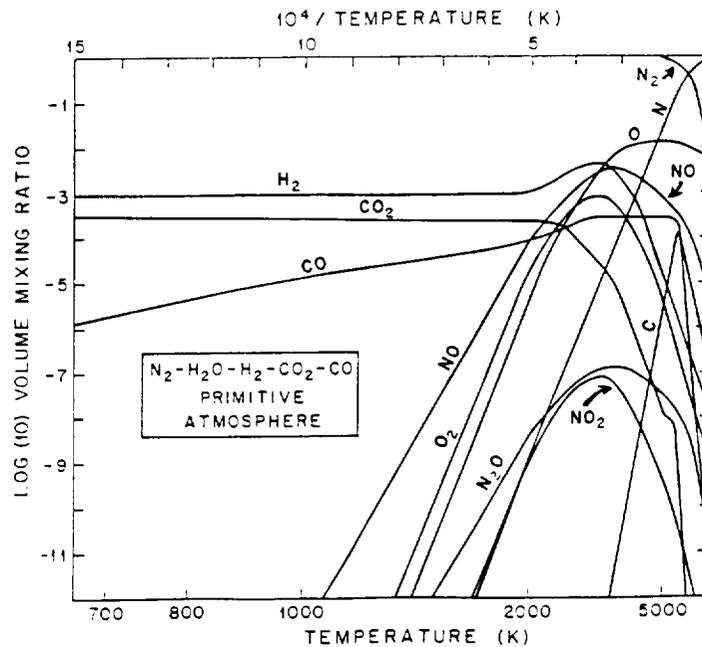


Figure 2. Calculated equilibrium abundances of important H-C-N-O gases in a cooling parcel of shock-heated  $CO_2$ -rich atmosphere. The initial composition is 66.4%  $CO_2$ , 26.4%  $N_2$ , 2.3%  $CO$ , 2.2%  $H_2$ , 1% Ar, and 1%  $H_2O$ . This composition is the average Hawaiian volcanic gas composition of Rubey (1951) minus condensibles with  $H_2O$  at 1%. The total pressure is 1 bar.

THERMAL HISTORY OF INNER SOLAR SYSTEM PLANETESIMALS PRIOR TO TERRESTRIAL PLANET ACCRETION. Michael J. Gaffey, Department of Geology, Rensselaer Polytechnic Institute, Troy, New York 12180-3590.

On geochemical and cosmological grounds, the Earth and other terrestrial planets are generally assumed to have accreted from a population of chondritic planetesimals [1-4]. This "chondritic" assumption actually includes two independent inferences concerning the properties of the accreting flux. The strictly proper use of "chondritic" in these models, indicating a bulk composition with approximately solar proportions of the non-volatile elements, appears well justified based on the compositional information available for the Earth, Moon, and other terrestrial planets. However, "chondritic" is also a textural/genetic definition when applied to meteorites, a usage denoting an undifferentiated assemblage. Accretionary models have not generally distinguished between the explicit compositional assumption and the implicit textural/temperature assumptions.

Two end-member accretionary models have arisen depending upon assumptions concerning the retention of the accretional energy within the growing planet. The "iron catastrophe"-type model (no significant retention of accretional energy) assumes that the accreted body is composed of an intimate metal-silicate mixture at subsolidus temperatures. The decay of long-lived radionuclides eventually raises the internal temperature to above the Fe-FeS eutectic, producing a dense melt phase which migrates downward converting gravitational potential energy to heat in a positive feedback process which rapidly raises the temperature of the Earth's interior by 1500-2000°K. In such models the Earth "turns on" approximately 0.5-2.0Gyr after its formation, initiating core-mantle segregation and volcanic outgassing as a significant contributor to the atmosphere and ocean. The "magma ocean"-type model assumes that after a nucleus has grown to some critical size, the retention of accretional energy is sufficient to melt or partially melt the near surface regions, resulting in primordial terrestrial planets with cold cores beneath hot differentiated mantles. Outgassing would begin during the late stages of accretion, providing early atmospheres and/or oceans on the larger bodies. Most recent models belong to the latter type, and are largely concerned with the mechanisms and relative efficiency of accretional energy retention.

Both classes of models have generally presumed cool planetesimals whose internal heat did not contribute to raising the temperature of the accreting planet. Based upon what was inferred about the planetesimal population from meteorite studies, this was a reasonable and plausible assumption. However, recent asteroid studies indicate that most - if not all - of inner solar system planetesimals underwent strong early heating. Thus, the Earth and other terrestrial planets would have accreted from a population of differentiated planetesimals with chondritic compositions.

The asteroids are the remnants of a system-wide planetesimal population from which the satellites and terrestrial planets accreted. More than 600 of the larger asteroids have been classified into a variety of types based upon color and albedo data[5]. Analysis of visible and near-infrared spectral reflectance data obtained for individual members of each type has produced general mineralogical characterizations for these asteroid classes. These classes can be broadly divided into a "heated" group and an "unheated" group.

The differentiated [heated] asteroids exhibit surface mineral assemblages produced by magmatic processes ( $T > 1000^{\circ}\text{C}$  to produce melting in the initial chondritic materials and to permit gravitational segregation of different phases) within their parent planetesimals. The surface assemblages

of these asteroids are analogous to meteorites formed by igneous processes (i.e. the irons, stony-irons, and achondrites). The undifferentiated [unheated] asteroids show surface assemblages consistent with some type of chondritic mineral assemblage. Among the fourteen asteroid types, six are differentiated: types A, V, R, M, E and S. There is a general consensus among asteroid investigators that the types A, V, R, M and E are differentiated. There has been considerable controversy on whether the S-type is differentiated. While there are meteoritic and dynamical reasons to suggest that the the S-asteroids are similar to the undifferentiated ordinary chondrites[6], all available direct evidence on the S-asteroids indicates that they are predominantly differentiated [7-9].

The relative proportion of these differentiated types among classified asteroids shows a steep, nearly linear decrease in the fraction of parent planetesimals subjected to post-accretionary heating above the Fe-FeS solidus from 100% at 1.8-2.0AU to 0% at >3.5AU[10]. This heating event was superimposed upon and modified any compositional gradient inherited from the solar nebula. The location and slope of this distribution should provide an important test of the proposed heat source models[11], but at present it favors a sun-centered heating mechanism having a strong falloff with increasing heliocentric distance such as T-Tauri inductive heating[12].

It is most probable that all planetesimals formed inside 2AU were subjected to similar strong heating and differentiation prior to incorporation into the Earth and other terrestrial planets. The nature of plausible heat sources in small bodies and the chronology of the differentiated meteorites constrains the heating event to the first few million years of solar system history[11,12], prior to or at the very onset of terrestrial planet accretion [13]. Since the time for significant internal cooling of planetesimals in this size range is long compared to the probable duration of planetary accretion[14], the bulk of the material contributed by the planetesimals will be near or above 1000°C, and substantial fractions of the accreting material should be in the form of magma and liquid metal.

Models for the accretion and early evolution of the terrestrial planets should consider hot planetesimals as the baseline case. Most of the accreting material will have undergone at least some degree of degassing prior to incorporation in the terrestrial planets, and the exposure of planetesimal magmas during impacts onto the embryonic planets may preferentially incorporate gases from any ambient atmosphere. The rare gas inventory of the Earth thus may represent the net effects of several different processes.

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**SOME CHEMICAL AND THERMAL CONSEQUENCES OF EARLY MANTLE DIFFERENTIATION;** S.J.G. Galer<sup>1</sup> & S.L. Goldstein<sup>2</sup>, <sup>1</sup>Scripps Institution of Oceanography, UC-San Diego, La Jolla, CA 92093-0212, USA; <sup>2</sup>Max-Planck-Institut für Chemie, Mainz, FRG.

The presence of a substantially depleted mantle in the early Archean requires a counterbalancing 'enriched' reservoir to exist contemporaneously somewhere on the Earth. To generate  $\epsilon_{Nd}=+3.0$  in the depleted mantle by 3.8 Ga mass balance dictates that the 'enriched' region contained ~0.3-0.5 of the total Nd, assuming its Sm/Nd ratio lay between 20 and 40% less than chondrites and it formed at 4.55 Ga. If its Sm/Nd ratio was less fractionated or differentiation was more protracted an even greater inventory of Nd needs to have resided there. Even this lower limit is comparable to the proportion of Nd currently in the continents. This was probably accompanied by >0.9 of the highly incompatible elements (*e.g.* Rb, Pb), including the heat-producing elements (Th, U, K).

Both the initial positive  $\epsilon_{Nd}$  (*cf.* [1]) and low  $^{87}Sr/^{86}Sr$  ratios [2] of continental crust at this time suggest that the enriched region did not directly contribute to growing continental crust. This is also substantiated by the near coincidence of Nd model ages ( $T_{DM}$ ) and stratigraphic ages of Archean sediments [3]; nor is its presence evident in the clastic sedimentary mass as a whole today [4]. Some fundamental tectonic reason must underlie its failure to contribute to surviving Archean rocks. Inasmuch as sedimentary cannibalism and crustal reworking (*e.g.* [2]) characterize both Archean and modern "continental crust" the enriched region is unlikely to be comprised of continental crust *per se*. An enriched basaltic layer would be more compatible with the geological constraints and would need to be located at the Earth's surface from a consideration of heat dissipation (*cf.* below). Assuming it had a Sm/Nd ratio 20% less than chondrites it would need to be at least ~30 km thick for an upper mantle 'system' to produce the observed depleted mantle  $\epsilon_{Nd}$  by 3.8 Ga, or about four times as thick for the whole mantle. Moreover, because it does not survive in tangible form today it must have been destroyed in the interim by recycling to the mantle. In this way it would (1) not contribute Nd or Sr directly to the continents, and (2) indirectly supply the growing continents with highly incompatible elements. However, its lifetime has to be >0.5 Ga to preserve positive  $\epsilon_{Nd}$  of the depleted mantle throughout the Archean.

Irrespective of the form it took, the heat-producing elements would have resided predominantly in the enriched region early on and then the continental crust. This localization of heat production in the Earth's exterior profoundly affects the interpretation of (1) the Earth's thermal evolution, (2) Archean "tectonics", and (3) the imbalance between heat produced and currently lost from the Earth (the Urey ratio, [5,6]). It can be expected that intrinsic heat production in the depleted mantle has remained <0.1 of the global average since the early Archean. This is perfectly in accord with the apparent secular constancy of the continental geotherm [6,7] and palaeomagnetic rates of continental drift [8]. Archean heat dissipation was probably mediated by the enriched region and not the uppermost mantle. Therefore enhanced plate spreading (*e.g.* [7]) does not follow *a priori* from greater Archean radiogenic heat production. Because the thermal time constant of mantle-wide convection is <1 Ga [5], the present-day Urey ratio of  $0.48 \pm 0.12$  [1] requires sources of heat in the deep Earth and retention of this heat for >1 Ga. Radiogenic heating is the only viable source implying that (1) the mantle is chemically layered with respect to the heat-producing elements, and (2) convective transport of the deeper mantle to shallow levels is inefficient, as a consequence of layering or rheological properties (*e.g.* [5,9]).

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COMMENTS ON THE BULK COMPOSITION OF THE EARTH  
K.A. Goettel, Lyman Laboratory of Physics, Harvard University,  
Cambridge, MA 02138

There are two complementary approaches to understanding the bulk composition of the Earth: one based on the wide variety of geophysical and geochemical data from the Earth's interior and one based on comparative planetology. The terrestrial data base (e.g., seismology, petrology) is invaluable in placing rigorous bounds on the composition of the Earth. These data, however, are insufficient to specify precisely some of the key aspects of the composition of the Earth, including questions about the light element(s) in the core, the FeO content of the lower mantle, and the volatile content of the deep interior. In this context, insights gleaned from the collective wisdom of the comparative planetology of the entire terrestrial planet group can contribute to a better understanding of the bulk composition of the Earth.

Substantial differences in the uncompressed (zero-pressure) mean densities of the terrestrial planets demonstrate unambiguously that the planets differ appreciably in bulk composition. Early models for the compositions of the terrestrial planets (e.g., (1)) postulated clear trends of varying composition with heliocentric distance. However, as understanding of the dynamics of the accretion process has advanced it has become clear that mixing processes must have muted the compositional differences between the terrestrial planets (e.g., (2) and references therein). In the extreme case (3) it is possible that the silicate fractions of the terrestrial planets are virtually identical and that the differences in mean density are explainable by physical mechanisms of Fe/Si fractionation (e.g. (4)). More plausible (i.e., non-end-member) models suggest that mixing did not completely homogenize the terrestrial planets (cf (3)). The abundance of FeO in silicates is a key indicator of the extent to which planetary compositions were determined by heliocentric gradients or by mixing.

For the large terrestrial planets (i.e., Earth and Venus) the effects of high pressure complicate interpretation of the bulk compositions. The high pressures in these planetary interiors introduce substantial model-dependent uncertainty in deducing the zero pressure densities and compositions. Furthermore, pressure effects, including metallization of FeO (5), on differentiation processes may result in time-dependent evolution of the compositions of the mantle and core (e.g., gradual incorporation of FeO into the core).

Unlike Earth, Mars is small enough and central pressures are low enough (below 400 kilobars (6)) that pressure effects do not introduce significant uncertainty in interpretation of the

planet's zero pressure density or bulk composition. Thus, in some respects, the composition of Mars is better understood than the composition of Earth. Models for the composition of Mars which are based on the petrology of the SNC meteorites (7) and models based on condensation in the solar nebula (8) agree substantially.

If mixing processes during accretion have markedly flattened the composition gradient previously expected (1) among the terrestrial planets, then the present composition of Mars may be quite similar to the initial composition of the Earth (prior to incorporation of FeO into the Earth's core). I postulate, therefore, a Mars-based, initial composition of the Earth which differs from conventional wisdom in two main respects. First, the silicate fraction of the Earth would have initially had substantially higher FeO content (perhaps up to 15 weight percent) than the present upper mantle. Second, the initial volatile inventory of the Earth may have been substantially higher than previously postulated. Both of these postulated modifications to estimates of the Earth's bulk composition would affect significantly the quantitative modeling of the geophysical and geochemical evolution of the Earth's interior.

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STABLE ISOTOPE STUDIES OF THE ARCHEAN NORTH POLE DOME, PILBARA BLOCK: IMPLICATIONS FOR THE ARCHEAN HYDROSPHERE. R.T. Gregory, Department of Earth Science, Monash University, Melbourne 3168, Australia.

The North Pole dome of the Pilbara block, Western Australia covers some 700 km<sup>2</sup> and provides an opportunity to examine a well-preserved, essentially undeformed  $\approx 3.5$  Ae greenstone succession. A long standing controversy is the conflict between the interpretation of chert  $\delta^{18}\text{O}$  signature and the  $^{18}\text{O}$ -buffering of seawater hypothesis suggested by studies of Phanerozoic ophiolite sequences and recent oceanic crust [1, 2]. The chert  $\delta^{18}\text{O}$  values have been interpreted in terms of either warmer oceans or oceans with much lower  $\delta^{18}\text{O}$  [3, 4]. These issues have important implications for Archean climates and global geochemical cycles (e.g. carbon and  $^{18}\text{O}$ ).

*Geologic setting:* The North Pole dome contains a thick (>6 km) section of interlayered cherts and basalt and is the site of a prominent barite marker horizon that has interlayers of chert preserving some of the oldest algal mat structures [5, 6]. The section consists from the core of dome upwards: a) hornfels, gabbro, dolerite, pillow lava and locally, mafic schist; b) silicified volcanics cut by numerous cross-cutting silica and minor barite veins; c) silicified clastic sedimentary rocks interbedded with stratiform barite; d) interlayered pillow lavas and chert, cut locally by gabbroic sills; e) massive basalt and pillow lava; f) pillow lava interlayered with chert and clastic sediments, g) overlain by pillow lava, sedimentary chert, and finally h) unconformably overlain by Fortescue Basalt. The mafic rocks of the core of the dome are cut by the North Pole adamellite covering 32 km<sup>2</sup>.

The metamorphic assemblages in the greenstones are remarkably uniform above the stratiform barite horizon (albite-calcite-chlorite-quartz). The carbonation of the lowest grade rocks is prominent throughout the Pilbara block with carbonate contents up to 30 volume percent. A kilometer below the barite zone, epidote-actinolite assemblages become common. Hornfelsic rocks in contact with the North Pole adamellite exhibit a range of plagioclase compositions from albite to labradorite at the contact. The hornfelsic assemblage is clearly superimposed on the earlier greenschist alteration. The North Pole Adamellite has a porphyritic border zone, and dikes and sills of porphyritic material similar to the border zone rocks cross cut the barite horizon and extend as much as 4 km upward in the section appearing as isolated stocks with sericitic haloes into the greenstones. The extensive zone of hydrothermal alteration and silification (continuous along a >15 km strike) that underlies the stratiform barite horizon, does not affect the basalts overlying the barite marker horizon, and is itself crosscut by porphyritic dikes similar to the North Pole adamellite suggesting at least three episodes of fluid-rock interaction.

*Stable isotopic results:* Over 140 samples from whole-rocks, vesicles, and veins have been analysed for either oxygen or carbon isotopic composition. The range in greenstone-silicate fraction  $6 < \delta^{18}\text{O} < 12$  is similar to that of the carbonate fraction  $7.5 < \delta^{18}\text{O} < 13.5$ . The similarity in the ranges of the  $\delta^{18}\text{O}$  values of coexisting carbonate and silicate fractions of greenstones (70 pairs) is consistent with an approach to isotopic equilibrium with  $\Delta^{18}\text{O}_{\text{carbonate-silicate}} \approx 2$ . 50 chert analyses give an average  $\delta^{18}\text{O} = 13.8$ . This gives  $\Delta^{18}\text{O}_{\text{chert-carbonate}} \approx 3$ , which would correspond to equilibrium at  $\approx 300^\circ\text{C}$ . The  $\delta^{18}\text{O}$  of cherts are not sensitive on local lithologic relationships within the cherts themselves but rather on the 10-100 meter-scale chert to greenstone ratio (never >10%). Cherts located in the greenstone dominated portions of the section have  $\delta^{18}\text{O} \approx 12$  whereas in the section where chert is most abundant the  $\delta^{18}\text{O}$  values are mainly between 13.5 and 14.5 with values as high as +16.6. The lowest  $\delta^{18}\text{O}$  values for mafic rocks are found within the hornfelsic contact

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aureole ( $4.8 < \delta^{18}\text{O}_{\text{hornfels}} < 7.2$ ) of the North Pole adamellite ( $7.8 < \delta^{18}\text{O}_{\text{quartz}} < 8.4$ ; mean  $\Delta^{18}\text{O}_{\text{qtz-feld}} \approx 2$ ).

The  $\delta^{13}\text{C}$  values of the greenstones show limited variability,  $-3.7 < \delta^{13}\text{C} < 1.55$  (average  $\delta^{13}\text{C} = -0.8 \pm 1.2$ ). Samples from the core of the dome exhibit the greatest range in  $\delta^{13}\text{C}$  with values down to  $-3.7$ . Based on  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of carbonates, the section divides into three major groupings: the core of the dome where  $\delta^{13}\text{C}$  is slightly depleted as  $\delta^{18}\text{O}$  increases, sections d ( $\delta^{13}\text{C} \approx 0.55\delta^{18}\text{O} - 6.5$ ) and sections f and g ( $\delta^{13}\text{C} \approx 0.55\delta^{18}\text{O} - 5.6$ ).

*Significance of the stable isotopic data:* The abundance of carbonate in the metabasalts requires a large uniform reservoir of carbon (average modal calcite  $> 10\%$ ). If production of greenstone in the Archean matched or exceeded current production rates of altered basalt, the flux of  $\text{CO}_2$  from seawater into the crust would be comparable to the rates at which carbonate rocks accumulate in modern oceans. The spread in  $\delta^{13}\text{C}$  values for carbonates in these Archean greenstones is virtually the same as carbonates formed during the seafloor weathering of modern basalts [7]. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values when considered together are lower in  $\delta^{18}\text{O}$  than the modern seafloor-weathering products of basalt. The  $\delta^{13}\text{C}$  vs.  $\delta^{18}\text{O}$  relationship is similar to that observed for carbonates that have exchanged isotopes during metamorphism suggesting a low temperature weathering event followed by re-equilibration during burial. If the carbonate  $\delta^{13}\text{C}$  values really reflect Archean seawater carbonate  $\delta^{13}\text{C}$  values, then there was no major departure from modern values of the  $\delta^{13}\text{C}$  of the atmosphere-seawater system even in the Archean.

The dependence of chert  $\delta^{18}\text{O}$  on the local ratio of greenstone/chert suggests that all of the cherts are  $^{18}\text{O}$ -depleted relative to their primary  $\delta^{18}\text{O}$  values and indicates that these cherts have no paleoclimatic significance. Re-examination of their relatives, the Proterozoic siliceous iron formations [4] suggests that high- $\delta^{18}\text{O}$  cherts ( $> +16$ ) are typically associated with other chert, shale, or carbonate assemblages. Low- $\delta^{18}\text{O}$  ( $< +15$ ) cherts are clearly associated with greenstone successions. This suggests that all Precambrian cherts need to be examined in terms of the "mode effect" before any attempt at interpreting their significance to the seawater/paleoclimate problem.

The apparent  $\Delta^{18}\text{O}$  values for chert-carbonate and greenstone silicate-carbonate fractions on a terrane scale suggest equilibration at  $300^\circ\text{C}$ . Waters in equilibrium with such rocks have  $\delta^{18}\text{O}$  values around  $+5 \text{ ‰}$ . If this fluid was Archean seawater, then the bulk  $\Delta^{18}\text{O}_{\text{crust-seawater}}$  would have been  $+1$  instead of a value close to  $+6$  for the Phanerozoic [2]. This would imply an alteration temperature regime not supported by the alteration assemblages normally encountered in Archean greenstones. Rather, the similarity of the alteration assemblages, the inferred temperatures of alteration, and the range of  $\delta^{18}\text{O}$  values of  $\approx 3.5$  Archean greenstones (here and in the Barberton, [8]) that are virtually identical to modern greenstones, all suggest that the  $\delta^{18}\text{O}$  composition of seawater has remained near constant back to the earliest preserved sections of the Archean. REFERENCES: [1] K. Muehlenbachs and R.N. Clayton (1976) *J. Geophys. Res.* 81, 4365-4369. [2] R.T. Gregory and H.P. Taylor, Jr. (1981) *J. Geophys. Res.* 86, 2737-2755. [3] L.P. Knauth and D.R. Lowe (1978) *Earth and Planet. Sci. Lett.* 41, 209-222. [4] E.C. Perry and S.N. Ahmad (1983) *Geol. Soc. Amer. Mem.* 161, 253-264. [5] J.S.R. Dunlop, M.D. Muir, V.A. Milne, D.I. Groves, 1978, *Nature*, 274, 676-678. [6] R. Buick, J.S.R. Dunlop, D.I. Groves (1981) *Alcheringa*, 5, 161-181. [7] K. Muehlenbachs (1987), *Mineral. Assoc. Canada Short Course* 13, 162-187. [8] H.S. Smith, J.R. O'Neil, and A.J. Erlank (1984) in: A. Kroner et al., *Archean Geochemistry*, Springer-Verlag, 115-137.

### INTENSE EARLY BOMBARDMENT AND ITS EFFECTS ON PRIMORDIAL EARTH

David H. Grinspoon, Lunar and Planetary Lab., Univ. Arizona, Tucson, Arizona, 85719, and William K. Hartmann, Planetary Science Institute, Tucson, AZ 85719.

The integrated mass flux necessary to accumulate the Earth in the permitted formation interval of some 10-100 My yields an initial mass flux 4.55 Gy ago of the order  $10^9$  x the present flux (1). Studies of the lunar cratering record at dated Apollo and Luna landing sites indicate that 4.0 Gy ago, the impact rate was roughly  $10^3$  x the present rate (2). These figures correspond to a half-life of some 24 My, averaged over the first few hundred My, in the planetesimal population, and slowly lengthening.

Coupling these results, we investigate the possibility that this dramatically declining flux represents a relatively smooth sweepup of planetesimals left over after Earth's formation. Wetherill (3) studied the dynamical properties of leftover planetesimals in an effort to explain a hypothetical terminal catastrophe, or short, sudden bombardment that was once hypothesized to have occurred 4 Gy ago. Although Wetherill's models were aimed at explaining the supposed cataclysm, one of the models showed the plausibility of a relatively smooth decline with an early half-life of 20-30 My, just as we observe. The analysis suggests that the half-life would slowly increase, as bodies are pumped up into more inclined and eccentric orbits due to close encounters with Earth. This matches the observations.

Based on these consistencies between the observed record and the dynamical analysis of planetesimal calculations, we attempt to reconstruct a plausible impact rate for primordial Earth as a function of time during its first few hundred My.

The extremely high impact rates have numerous possible consequences, some of which have already been discussed elsewhere. These include: a) a giant impact of the second- largest body in Earth's zone, dislodging the material that formed the moon (4); b) disruption of any early homogeneous crust that was forming, with impact basins causing thin spots in some areas and piling up crustal debris in pseudo-continental masses in other areas (5); c) exposing the hot mantle and helping to initiate convection and plate tectonic motions (6); d) severe climatic consequences due to the constant dust pall of ejecta (7); e) impact frustration of the origin of life until the impact rate declined (8).

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## STABILISATION AND EVOLUTION OF THE CONTINENTAL LITHOSPHERE

**C.J. Hawkesworth**, Department of Earth Sciences, The Open University, Milton Keynes, MK7 6AA, U.K.

**R.M. Ellam**, Department of Earth Sciences, University of Oxford, Parks Road, Oxford, OX3 1PR, U.K.

**F. McDermott and N.W. Rogers**, Department of Earth Sciences, The Open University, Milton Keynes, MK7 6AA, U.K.

An extensive trace element and radiogenic isotope database has been compiled for Archaean to Recent continental rocks, and it is used to constrain models of lithosphere generation and recycling in the development of chemical heterogeneities in the upper mantle.

Studies of recent destructive plate margin rocks indicate that new continental crust is on average basaltic in composition<sup>(1)</sup>, and that it is characterised by relatively low Rb/Sr ( $\sim 0.03$ ) and low Th/U. The LIL element contents of island arc tholeiites are dominated by the contribution from the subducted slab, whereas those of continental margin rocks are dominated by that from the mantle wedge. Data from both oceanic and continental plate margins have been integrated in a model which proposes that the flux from subducted crust is best estimated from arc rocks in areas where the mantle wedge was exceptionally depleted prior to the onset of subduction<sup>(2)</sup>. It is argued that the major site of recent crust generation is within the mantle wedge, and that subducted crust contributes  $\sim 25\%$  of the Sr and  $< 15\%$  of the K, Rb and Ba in average new continental crust. Sr isotope arguments further suggest that  $< 5\%$  of the Sr in new crust is from recycled continental material with average crustal  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.716). Finally, in this model, as little as 3% of the Sr in subducted crust is required for the slab-derived flux, so that most of the LIL elements in oceanic crust are recycled deep into the upper mantle.

The consequences of such models for recent subduction zone magmatism are: (i) destructive plate margins as observed today are not the site of significant crust/mantle fractionation of Rb/Sr, Sm/Nd or U/Pb; and (ii) subducted sediments may preserve both their trace element and radiogenic isotope ratios beyond the site of arc magmatism. The evidence from both upper and lower crustal suites is that crust generation, and intracrustal differentiation processes were different in the Archaean and Early Proterozoic<sup>(3)</sup>. Specifically, Archaean suites typically exhibit elevated Rb/Sr ( $\sim 0.12$ ) prior to the appearance of plagioclase as a significant fractionating phase, consistent with models of remelting basalt at depths greater than the stability field of plagioclase<sup>(4,5)</sup>. Secondly, basic lower crustal granulite suites are a feature of mid-Proterozoic and younger terrains indicating that crust generation processes changed prior to the mid-Proterozoic, and that they may not have changed significantly since. This change in the nature of new continental crust clearly affects the nature of the continental material available for recycling into the upper mantle at different stages in earth history.

One aspect of the upper continental crust which appears to have remained uniform is its Th/U ratio, either measured, or inferred from Pb-isotopes. This is in contrast to the range of time integrated Th/U ratios calculated from MORB, OIB and mantle xenoliths, and it has been used to argue that recycled sediment, for example, is not the primary cause of the so-called DUPAL anomaly in the upper mantle<sup>(6)</sup>. Figure 1 summarises selected Pb- and Sr-isotope data on Mesozoic continental flood basalts (CFB), and it is clear that high Ti CFB plot on an extension of the MORB array. They are therefore similar to, but with slightly higher  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  and  $\epsilon_{\text{Sr}}$  than DUPAL OIB. The low Ti CFB are significantly

displaced to both higher  $\epsilon_{Sr}$  and lower  $^{208}Pb^*/^{206}Pb^*$ . The mantle source regions of the high Ti CFB thus exhibit many similarities to those of particularly DUPAL OIB, in that they have experienced similar Rb/Sr, Sm/Nd and Th/U fractionation. The source regions of the low Ti CFB, by contrast, are apparently unique to continental areas, and their inferred trace element fractionation patterns (as, for example, from Figure 1) are most simply explained by the introduction of subducted sediment.

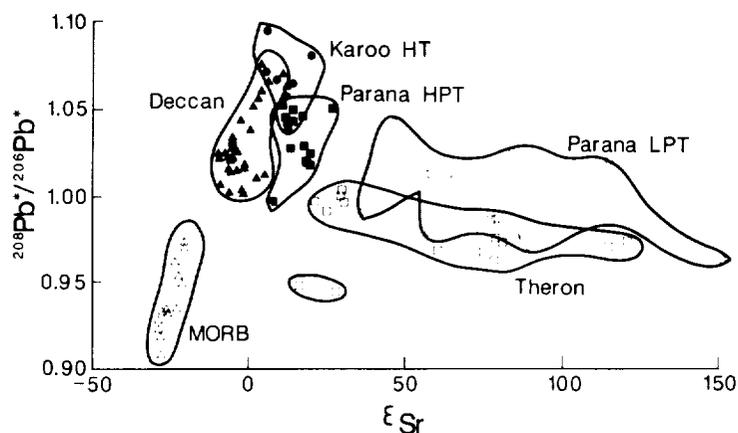


Figure 1  $^{208}Pb^*/^{206}Pb^*$  versus  $\epsilon_{Sr}$  for high and low Ti continental flood basalts. Typical continental sediments have  $^{208}Pb^*/^{206}Pb^* \approx 1$  and a range of  $\epsilon_{Sr}$  with  $\epsilon_{Sr} > 50$ (6).

In the same way that Archaean and post-Archaean crust appear to reflect different processes of formation and differentiation, there is increasing evidence for systematic differences between Archaean and post-Archaean mantle lithosphere(7). The former is highly depleted in major elements, reflecting the extraction of komatiite, and is thus less dense and probably thicker than post-Archaean lithosphere. The latter has a higher average density and is both sufficiently fertile to contribute significantly in the generation of CFB (which only exhibit Proterozoic and younger source ages), and it may be more readily delaminated into the convecting upper mantle. Such mantle lithosphere has been invoked as the cause of chemical heterogeneities in the source of DUPAL type OIB(8,9), and as indicated above, sediments are likely to have influenced the composition of low Ti CFB. In general, however, it now appears that chemical heterogeneities may be relatively shallow level features in the Earth's upper mantle.

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**EXPERIMENTAL CONSTRAINTS ON THE FORMATION OF THE EARTH'S UPPER AND LOWER MANTLE** C.T. Herzberg and M.D. Feigenson, Department of Geological Sciences, Rutgers University, New Brunswick, NJ 08903

**EXPERIMENTAL DATA**

Crystal-liquid phase equilibrium relations to 25 GPa (250 kilobars) for peridotite, komatiite, and chondrite compositions have been explored in a large number of experiments done since 1985 (Japan, ANU, and now Stony Brook; 1,2,3,4,5,6,7). The results show a high degree of internal consistency (8) largely because equilibrium occurs in less than 3 minutes at temperatures typical of most experiments (2000°C); this is based on a recent reversal experiment done at the Stony Brook lab. The following is a summary of these observations:

1) the liquidus phase changes in the following sequence at the approximate pressures indicated: olivine - (13-16 GPa) - majorite - (25 GPa) - perovskite. For chondrite compositions the sequence is predicted to include pyroxene between olivine and majorite (ie., Ol-Px-Mj-Pv), but this has not been observed in the experiments from Japan (we are testing this at Stony Brook, and will report the results).

2) isobaric and polybaric crystallization sequences for peridotites and komatiite in the system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS) and KLB1 can be used to topologically constrain the compositions of liquids produced on the anhydrous solidus. The results show that mantle peridotite is compositionally very similar to liquids formed at ultrahigh pressure eutectic-like equilibria involving olivine + garnet + pyroxene (L + Ol + Gt + Px), and thermal minima involving majorite + olivine (modified spinel) (L + Mj + Ol/Sp). Peridotite liquids with more than 39 % MgO and CaO/Al<sub>2</sub>O<sub>3</sub> > .96 are stable on the anhydrous solidus at pressures exceeding 14 GPa. Very primitive peridotite liquids having 36 to 39 % MgO are stable in the 11 to 14 GPa range. A world data base of over 1000 samples (8,9) demonstrates unambiguously that CaO/Al<sub>2</sub>O<sub>3</sub> for upper mantle peridotite averages around .96, an excellent match with the experimental data, but in stark contrast to .79 for chondrites and pyrolite.

3) for chondrite, CaO/Al<sub>2</sub>O<sub>3</sub> in majorite coexisting with peridotite liquid and modified spinel near the solidus is close to but somewhat less than chondritic.

**IMPLICATIONS OF THE EXPERIMENTAL DATA**

Upper Mantle

Liquid peridotites are definitely stable on the anhydrous mantle solidus at pressures greater than 11 GPa, and they have compositions very similar to spinel-type peridotites. The upper mantle formed from the crystallization of these liquids (10). Upper mantle peridotite is therefore more magnesian than a chondritic bulk Earth because of ultrahigh pressure crystal-liquid phase equilibrium relations, first proposed by Herzberg and O'Hara (10), not because of silica volatilization (Ringwood, 11), nor because of olivine flotation (Walker and Agee, 12).

### Lower Mantle

Mass balance holds for a chondritic Earth with about 37 % upper mantle peridotite + 50 % majorite + 12 % modified spinel. Fractionation of majorite + modified spinel near the solidus would have produced a lower mantle enriched in SiO<sub>2</sub> (8). Recent objections to majorite fractionation based on Ca/Al (7) are invalid because they are based on mass balance arguments that do not apply to thermal minima on the anhydrous solidus. Objections to majorite fractionation, which presumably occurred 4 to 4.5 billion years ago, based on REE of modern-day upper mantle peridotite (7) are also invalid because corrections for the effect of some 4 billion years of partial remelting have not been considered. Indeed, we have modelled the primordial upper mantle to be LREE-enriched and HREE-depleted; second stage melting with garnet stable yields a depleted residuum with patterns that range from flat and chondritic-looking to LREE-depleted, matching those seen in typical spinel-lherzolites and the modern-day MORB source region.

Fractionation of pyroxene with some olivine at pressures below the stability of majorite (11 to 14 GPa) is another good possibility that we are currently exploring.

### A Magma Ocean?

The ultrahigh pressure phase diagrams do not permit firm conclusions to be drawn on the extent of melting in the early differentiating Earth. The possibilities that emerge are:

1. **Upper mantle peridotite formed as residual liquids in a differentiating "magma ocean"**. For this model to work, majorite on the liquidus would have remained suspended in vigorously convecting cells (equilibrium crystallization), fractionating only at the solidus when the degree of crystallization was advanced and convective velocities were lowered (fractional crystallization). This model would be compatible with hypotheses that advocate collision of the Earth with another large object, resulting in wholesale melting of the Earth during the formation of the moon.

2. **Upper mantle peridotite formed as a partial melt in differentiating "magma seas/floods/puddles/etc"**. Melting was regulated by the heat of fusion along the solidus. This mode of melting is very similar to that which occurs during the formation of basaltic magmas, the main difference being higher pressures which yield peridotite magmas rather than basaltic magmas. The degree of partial melting would not have exceeded 50 % but, time- and space- averaged, would have been global in extent. This model would be compatible with non-collisional accretionary hypotheses.

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## NOBLE GAS ISOTOPES IN HAWAIIAN XENOLITHS

E. Heusser, T. Kirsten, A. Rocholl\*, H. Richter

Max-Planck-Institut für Kernphysik, Heidelberg, W. Germany

\*Max-Planck-Institut für Chemie, Mainz, W. Germany

A series of 15 Hawaiian ultramafic xenoliths from Salt-Lake- and Aliamanu-crater, Oahu, Hawaii, has been analyzed for all rare gas isotopes, including high precision  $^3\text{He}/^4\text{He}$ -determinations. This was made possible by a tandem-arrangement of two mass-spectrometers. One spectrometer was specially tuned for He and had a mass resolution of 720. The second spectrometer was optimized to measure small amounts of Xe-isotopes ( $10^{14} \text{ cm}^3 \text{ STP}$ ).

The analyzed samples comprise a group of 3 spinel-lherzolites, 10 garnet-pyroxenites, 1 spinell-olivine-clinopyroxenite and 1 gabbro. Of major interest was the group of spinel-lherzolites, since they are in general interpreted as representing residues of partial melting of a primitive mantle source and are related to the Hawaiian tholeiites. Extraction of the gases occurred by melting in a Mo-crucible of an inductive-heated furnace. Most samples were degassed in one temperature step at 1500 C, but also two step degassing has been performed, to distinguish the amount of atmospheric gases from the mantle gases. For almost all samples duplicate measurements have been performed, to improve the isotopic signatures and to check reproducibility. Further we analyzed cpx, opx and ol minerals, in order to find out the amount of gases held in the matrix of the major minerals.

Element abundance patterns are similar to the "planetary"-pattern of ordinary CII-chondrites. He concentrations are lower than in MORB-glasses ranging from  $5 \times 10^{-9}$  to  $1 \times 10^{-6} \text{ cm}^3 \text{ STP}$ . With one exception all samples showed isotopic signatures, which are typical for tholeiitic MOR-basalts, i.e.  $^3\text{He}/^4\text{He} = 8-11 \times R/R_{\text{atm}}$ ,  $^{40}\text{Ar}/^{36}\text{Ar} = 10^3-10^4$  and  $^{129}\text{Xe}_{\text{exz}}$ . One spinel-lherzolite showed indications for a higher contribution of primitive mantle gases, resulting in  $^3\text{He}/^4\text{He} = 40 \times R/R_{\text{atm}}$  and  $^{40}\text{Ar}/^{36}\text{Ar} = 340$ . Isotopic systematics and possible implications for the origin of these gases will be discussed.

MANTLE RESERVOIRS; A. W. Hofmann, Max Planck Institut für Chemie,  
Postfach 3060, 6500 Mainz, F.R. Germany

Isotopic heterogeneity in oceanic island basalts (OIB) has led to the concept that the mantle contains several distinct source reservoirs which contribute in varying proportions to the various OIB. The reservoir concept contrasts with the recurring idea that the chemical heterogeneities are distributed randomly in lumps, layers, or veins, and that the isotopic chemistry of a given volcano depends mostly on the effective degree of melting in the source region. This idea, though plausible in theory, has never been confirmed in any of the studies where relative degrees of melting could be assessed and correlated with the isotopic and chemical composition of the basalts. Rather there is overwhelming evidence that large-scale chemical and isotopic mantle heterogeneities are mapped quite effectively by oceanic basalts.

As the amount of available data has multiplied over the past ten years, the number of apparently distinct reservoirs has risen from two (primitive and depleted mantle, respectively) to five (primitive or "prevalent" = "PREMA," depleted, "HIMU" = high-U/Pb, and two types of "EM" or enriched-mantle reservoirs) (1,2). The depleted reservoir produces "normal" (= N-type) MORB, i.e. probably more than 90% of all MORB. The other four reservoirs are sampled by "enriched" or "plume-type" (= E- or P-type) MORB and by ocean island volcanism. Some ocean islands have nearly uniform compositions, but most sample two or more source reservoirs and may encompass a wide range of isotopic compositions. The compositional diversity and the universal Nb,Ta excess and Pb deficit in all OIB demonstrate that their sources cannot lie in a primitive reservoir (3,4). Rather, these basalts must come from comparatively small source regions which have been subjected to variable mutual mixing.

The non-primitive nature of OIB sources invalidates the mass balance models based on Nd (and Sr) isotopic compositions of two mantle reservoirs plus one crustal reservoir. A new mass balance (3) based on Nb/U and Ce/Pb ratios, which are uniform and higher than primitive in MORB and OIB, and lower than primitive in the continental crust, yields a combined mass fraction of MORB plus OIB sources ranging from 30 to 80% of the total mantle, depending on assumptions about the composition of the continental crust. Overall, it is marginally possible but unlikely that the upper mantle above 670 km depth can accommodate the entire MORB and OIB source(s).

It is proposed that a single general mechanism, subduction, produces all four types of OIB source reservoirs in spite of their distinctiveness. It introduces substantial amounts of material with varied, and apparently appropriate isotopic and chemical compositions into the mantle. A tentative unified model identifies the different OIB source reservoirs as follows:

**(1) HIMU or St.Helena-type: recycled N-type MORB.**

HIMU basalts have MORB-like isotopic compositions of Sr, Nd, Hf, and  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  and Ba/La ratios, but much higher  $^{206}\text{Pb}/^{204}\text{Pb}$ . Therefore, their sources have similar depletion patterns as MORB, except for U/Pb (and Th/Pb). Thus, these sources have lost Pb in preference to U and Th, probably during subduction when island arc volcanics extracted Pb preferentially, acquired very low U/Pb (as well as low Ce/Pb ratios), and left a high-U/Pb residue in the mantle. Evidence for this Pb loss is provided by anomalously high Ce/Pb ratios in the HIMU samples so far analyzed (Chauvel, pers. comm.). In addition, it is likely that the original N-type oceanic crust received some uranium during ridge-crest hydrothermal uptake. This would contribute to the low Th/U ratios and the slightly lower-than-normal Nb/U ratios found in St. Helena basalts.

**(2) PREMA or Hawaii-type: recycled P-type MORB, OIB, or oceanic plateaus.**

Common characteristics of these are: relatively high Rb/Sr and Th/U ratios, but low Sm/Nd and Lu/Hf ratios. During partial melting under a thickened crust (e.g. under Hawaii, Iceland or oceanic plateaus), these element ratios are fractionated because of the presence of residual clinopyroxene and sometimes garnet. When such thick (10 to 20 km) oceanic crust is subducted, its chances to survive convective mixing and thus to retain its isotopic identity are higher than

those of thin, N-type MORB crust. When it is incorporated into a new plume, the above element ratios are fractionated again. In this way, repeated recycling of plume-type mantle produces a correlated pattern of mother-daughter element ratios, which form the main isotopic "mantle array" of correlated Sr, Nd, Hf, and  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  isotope ratios. Because of its relatively high absolute trace element concentrations, this P-type material is much less subject to the alterations that affect the depleted N-type MORB during its generation and subduction. The repeated re-enrichment process through partial melting normally leaves garnet in the residue, causing Lu/Hf ratios to be fractionated, and this accounts for the correlated  $^{176}\text{Hf}/^{177}\text{Hf}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios in OIB. The process does not fractionate (Nb,Ta)/U and Ce/Pb ratios, because the participant elements have similar bulk partition coefficients during purely magmatic fractionation.

**(3) EM I or Kerguelen type: Recycled P-type oceanic crust with small additions of old crustal material.**

The main enrichment trend is the same as that seen in PREMA sources. EM I sources deviate from these by having relatively low  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  but high  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios. The exact nature of the continental crust component is not well understood. It might be old sedimentary material from a former continental margin or it might be derived directly or indirectly from the lower continental crust. The enrichment patterns of EM I sources are such that some EM Is (e.g. Koolau tholeiites) have isotopic compositions of Sr, Nd, Hf, and Pb close to primitive mantle values. However, this match is fortuitous because both Nb/U and Ce/Pb ratios of these basalts and their sources have been fractionated and are clearly not primitive. The locus of possible primitive compositions does lie within the broad field of actual, variously enriched isotopic compositions of OIBs, but this is a consequence of the source enrichment therefore has no special significance.

**(4) EM-II or Society Island type: recycled N-type MORB with variable but small additions of sediments of relatively young age.**

The sediments add components high in  $^{87}\text{Sr}$  and  $^{207}\text{Pb}$ , high in Pb and low in Nb and Ta concentrations. This causes the isotopic trends to deviate from the Nd-Sr mantle array and from the so called northern hemisphere correlation of  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios. Low Nb concentrations and Ce/Pb ratios are correlated with high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios on Society Island volcanics (6), but the amount of sedimentary material is sufficiently small to keep Nb/U ratios between present-day mantle values of about 47 and the primitive mantle value of 30. Thus the overall source enrichment of EM-II basalts is dominated by recycled oceanic crust, the bulk composition of which has been modified not only by possible hydrothermal effects noted for the HIMU sources but also by the addition of small amounts of sediments.

In summary, the variety crustal rocks that are known to be subducted are capable of providing the entire range of enrichment patterns actually observed in various OIBs. On many islands, two or more of these types of enrichment are found to be closely associated. This makes it all the more likely that a single basic mechanism accounts for all of them, as proposed earlier (6).

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DOES THE MOON HAVE THE SAME COMPOSITION AS THE TERRESTRIAL UPPER MANTLE? J. H. Jones\* and L.L. Hood\*\*. \*SN2, NASA Johnson Space Center, Houston, TX 77058; \*\*Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721.

Any theory for the origin of the Earth must at some point deal with the historic difficulties in finding a suitable theory for the origin for the Moon. Recent theories of the origin of the Moon tend to fall into one of two categories: giant impact or coaccretion [1]. In either case, the similarity of oxygen isotopic compositions of the Earth and Moon [2] suggests that the material which now comprises the Moon shared some common chemical characteristics with the Earth. In particular, it has been argued both that the Mg# [Mg# = Mg/(Mg+Fe), by moles] of the Earth and Moon are nearly identical [3] and that the giant impact (or a series of smaller impacts) incorporated no more than about 20 percent of the material from the impactor(s) [4]. We have asked whether it is possible to place any constraints on these theories using known geophysical parameters. In particular, can a Moon with the bulk silicate composition of the Earth's upper mantle satisfy the Moon's measured density and moment of inertia criteria? To this end, we have employed the differentiation models of Hood and Jones [5] using the composition of the terrestrial upper mantle [6]. For comparison we also investigated a second composition, a "typical" lunar composition from Jones and Delano [7] which is very similar to the preferred lunar composition of Ringwood et al. [8].

**Method.** The differentiation models of [5] fall into four categories (I-IV): (I) removal of a lunar crust composition [9], 70 km thick, with subsequent homogenization at all depths below the crust; (II) removal of a crustal composition from the upper 500 km with pristine material below 500 km; (III) removal of crust to a minimum depth  $d$  with pristine material below  $d$ ; and (IV) same as (III) but with complete homogenization below 500 km. The depth  $d$  of models (III) and (IV) is determined by choosing the minimum depth necessary to remove enough  $Al_2O_3$  to form a 70 km thick lunar crust. For the compositions investigated here, no solutions to model (II) were possible because depths  $d$  in model (III) were 645 km and 582 km for the terrestrial and model lunar compositions, respectively.

To calculate density as function of depth, the chemical compositions of the various regions of the differentiated model Moons are transformed into mineralogies and coupled with a (P,T) model for the lunar interior [5]. Previously we have used three very different thermal models [10,11,12] to assess the sensitivity of the model to temperature. Here we have retained this method but no viable solutions using the third thermal model [12] were found for either set of compositional models.

Once density has been calculated as a function of depth, both bulk density and moment of inertia can be computed. If the Moon is less dense than it should be, then a small metallic core is added and the process repeated until either both the calculated density and moment of inertia agree within the error of the measured values or it is clear that no solution is possible.

**Results and Conclusions.** In the case of the terrestrial upper mantle composition, we have viable solutions only for the Toksöz et al. [10] thermal model. The Schubert et al. [11] thermal model is marginally hotter on average and no solutions are possible. The core sizes necessary to allow solutions to the Toksöz model are rather large (>500 km) and approach sizes that are prohibited by other geophysical considerations (see, e.g., [13]). In fact these core sizes are larger than would be required to deplete siderophiles to observed lunar concentrations -- even starting with chondritic siderophile element abundances [14]. Consequently, we conclude that it is not physically possible for the Moon to have the same composition as the upper mantle of the Earth. If the Moon formed, either by fission or by giant impact, from terrestrial materials, then either a second component is necessary or the composition of the Earth's upper mantle has changed over time.

A corollary of this conclusion is that the Moon is unlikely to have the same Mg# as the Earth -- a conclusion that could not be determined unambiguously from analysis of lunar samples [1]. The main problem with using the terrestrial upper mantle as a source for the Moon is that the Earth is apparently more depleted in FeO than the Moon. The consequence for our calculations is that the Moon is not dense enough. Thus, more core is added to raise the density, which then lowers the moment of inertia until an unacceptable limit is reached. As pointed out by Taylor [9], a Moon with ~13 wt.% FeO (or FeO equivalent) is necessary to meet bulk density constraints. For example, using the comparison model that we investigated (i.e., the "typical" model of [7]), which has ~12 wt.% FeO, there was never a problem finding solutions to the Toksöz et al. and Schubert et al. thermal models. In our previous modeling we have found acceptable solutions with compositions as low in FeO as ~11 wt.%, but ~8 wt.% (the value for the terrestrial upper mantle) is apparently too low. Of course, there is a certain tradeoff between FeO and Al<sub>2</sub>O<sub>3</sub>. If there is more alumina then there can be more garnet, which is dense and can partially make up for a lack of FeO. However, the terrestrial upper mantle composition of Jagoutz et al. [6] has comparatively low concentrations both of FeO and Al<sub>2</sub>O<sub>3</sub>.

If we accept the constraints that non-terrestrial materials comprise <20% of the Moon [4] and that the Moon contains ~12 wt.% FeO, then we may calculate the FeO content of the second component. Assuming that the FeO content of the upper mantle has not changed over time, the abundance of FeO in the impactor is calculated to be >~28 wt.%. The only chondritic samples in our collections that contain such large amounts of oxidized iron are carbonaceous chondrites -- none of which has an oxygen isotopic composition similar to the Earth's [2]. Conversely, if we assume that the Earth's upper mantle has become depleted in FeO over geologic time, then it is puzzling that Ni and Co, which have very different siderophile tendencies, are present in approximately chondritic relative abundances in the upper mantle today [6]. Thus, neither alternative is geochemically attractive. We have no solution to this conundrum except to reiterate that the Moon cannot be comprised entirely of material from the terrestrial upper mantle.

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## AXIAL SYMMETRY OF HOTSPOT ISOTOPIC COMPOSITIONS: A PRODUCT OF CORE-MANTLE CHEMICAL INTERACTIONS?

J.S. Kargel<sup>1</sup> and K.A. Foland<sup>2</sup>; <sup>1</sup>Lunar and Planetary Lab, University of Arizona, Tucson, AZ 85721; <sup>2</sup>Department of Geology and Mineralogy, The Ohio State University, Columbus, OH.

A quarter century of isotopic analyses have established that the Earth's mantle is geochemically structured on kilometer, regional, and hemispheric scales. This work builds on that of Hart (1) and shows that the Southern Hemisphere "Dupal" isotopic anomaly is preserved and becomes more tightly defined in terms of latitude after plate tectonic corrections are made to the locations of hot spot volcanics with significant ages. When the Dupal Anomaly is considered together with other significant isotopic groupings of hotspots, it appears that hotspot isotopic signatures are symmetrical about the Earth's rotation axis. This paper presents a preliminary summary of the evidence for symmetry and its geodynamic implications.

The great lateral extent of the largest mantle structures was graphically demonstrated by Hart (1); he mapped the Sr and Pb isotopic compositions of hot-spot volcanics and found that Northern and Southern Hemisphere hot-spots are isotopically distinct. A broad region of the Southern Hemisphere was termed the "Dupal anomaly". Isotopic ratios indicate that this region of the mantle has had extreme time-integrated enrichments in Rb/Sr ratios and moderately enriched Th/Pb and <sup>235</sup>U/Pb ratios relative to Northern Hemisphere hotspots.

Some hotspot isotopic signatures in portions of the Southern Hemisphere are themselves anomalous with respect to the prevailing Dupal Anomaly. Particularly, volcanic rocks from the South Atlantic island of St. Helena and from the South Pacific islands of Tubuai and Mangaia (2) collectively have the least radiogenic Sr and the most radiogenic Pb of all oceanic island hotspots; these isotopic characteristics indicate extreme time-integrated depletions in Rb/Sr and relatively extreme enrichments in U/Pb and Th/Pb (or simply depletions in Pb). This mantle component has been termed "HIMU" for "high mantle Uranium" (3). In addition to its unique isotopic characteristics, the HIMU component has low present-day Rb/Th, Rb/Nb, and Pb/Ce ratios relative to the Dupal component (2); this is consistent with the isotopic ratios and indicate an event which extracted Pb and Rb from the HIMU source and enriched these elements in the Dupal source.

Southern Hemisphere hotspots have correlated isotopic and trace element ratios which span the range between the HIMU and Dupal components (2). This correlation suggests wholesale mixing between the end-members or variable degrees of enrichment and depletion of Pb and Rb. Northern Hemisphere hotspot compositions fall on a different regression line in Pb-Pb and Pb-Sr isotopic space (1). High northern latitude hotspots (Iceland, the Pribilofs, and Nunivak Island) are isotopically similar to each other and to Northern Hemisphere mid ocean ridge basalts, namely, they have relatively unradiogenic Pb and Sr; hotspots from the mid latitudes of the Atlantic Ocean (Azores, Canaries, and New England Seamounts) plot at the more radiogenic end of the Northern Hemisphere line. Recently acquired data for mantle xenolith-bearing basalts from the Western USA (Lunar Crater Volcanic Field, Nevada; Foland et al., in prep) and alkaline to sub-alkaline intra-plate (non-orogenic) Mesozoic intrusives from New England look isotopically nearly identical to the mid-latitude Atlantic Ocean hotspots (4).

These observations indicate that hotspot mantle sources, as indicated by their Sr and Pb isotopic signatures, may be organized into global-scale axially symmetric structures. The origin and depth of these structures is uncertain, but geochemical and geodynamic considerations suggest some connection to the core of the Earth.

The geochemical arguments have been debated extensively in the last several years: Common igneous processes usually fractionate Rb/Sr, U/Pb, and Th/Pb ratios coherently; therefore, one must develop some scenario which may explain the antithetical fractionations of these element ratios. A commonly discussed scenario holds that much of the isotopic variation in the mantle is the result of the subduction of ancient crust or lithosphere altered by seawater interaction or various other crustal processes (i.e. 2, 5). Alternatively, these fractionations and the long-debated "lead paradox" may be explained by the partial extraction of Pb and Rb from the mantle in sulfide melts and the deposition of these melts in the core (6-8); as will be discussed below, other types of core/mantle open system behavior are also conceivable.

## CORE-MANTLE CHEMICAL INTERACTIONS

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The analysis of Kargel *et al.* (9) indicates that over half of the Earth's Pb and Rb apparently reside in the core; apparently there is virtually no U or Sr in the core. On the basis of this analysis it is impossible to determine when or how Pb and Rb entered the core. However, the lead paradox argues strongly that Pb was extracted from the mantle significantly after the origin of the Earth but still sometime in the first billion years (7). Considering the core's infinitesimal U/Pb ratio, core Pb should be highly unradiogenic relative to mantle Pb.

The inferred Rb content of the core suggests that over half of Earth's radiogenic  $^{87}\text{Sr}$  should have been generated in the core (9). The partitioning behavior of Sr and the short mixing time-scale of the liquid outer core indicate that the core's radiogenic Sr should have entered the lower mantle nearly as rapidly as it was produced.

Several models of the core's convective structure suggest that the core exhibits axially-symmetric zonal flow near the core-mantle boundary (10, 11); this flow pattern may be similar to those of other internally heated, rotating fluid bodies including Jupiter (12) and the sun. Theoretical models indicate that a convecting body of this sort will display large latitudinally-correlated variations in heat flow.

It is reasonable to assume that the silicate/liquid metal partitioning behavior of Pb, like other chemical equilibrium constants, is temperature-dependent. It also appears that there is an approximately equilibrium abundance of Pb in the core and mantle (9). If the core-mantle boundary exhibits an axially symmetric thermal structure then this raises the possibility that Pb may be leached from some latitude belts and re-precipitated elsewhere. Zonal flow also offers the potential for homogenizing the isotopic composition of the lower mantle along a given latitude belt. Therefore, it is possible that core-mantle chemical interactions may change the U/Pb ratio of the lower mantle in a non-uniform, axially symmetric fashion.

Unlike the case with Pb, no experimental data are available on the silicate/metal partitioning behavior of Rb; therefore, we have not been able to determine whether or not the core is near saturation with respect to Rb. A working hypothesis might assume that Rb and Pb are leached and re-precipitated more or less together along the core/mantle boundary, thereby explaining the antithetical correlations of time-integrated and present-day U/Pb and Rb/Sr ratios in Southern Hemisphere hotspots. Since the Sr abundance in the core is very likely to be near the equilibrium value (or possibly supersaturated), the deposition rate of  $^{87}\text{Sr}$  may also be laterally variable.

In summary, the axially symmetric belt-and-zone thermal-convective structure of the core may manifest itself in a belt-and-zone Sr and Pb isotopic structure of the lower mantle. Given this, the present hypothesis requires the convective destabilization of the lower mantle and the formation of hotspot plumes originating near the core-mantle boundary. This hypothesis predicts that the Sm-Nd and Lu-Hf systematics of the lowermost mantle should be unaffected by core solution and re-precipitation, since neither parent nor daughter isotopes are significantly soluble in the core. Indeed, the Nd isotopic composition of the HIMU component falls near the average composition of hotspots, in contrast to its extreme Sr and Pb isotopes. However, if mechanical zonal mixing occurs along the core/mantle interface, Nd and Hf isotopes may be mixed or homogenized.

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**COMPOSITION OF EARTH'S INNER AND OUTER CORE AND PRIMITIVE MANTLE**  
**J.S. Kargel, D. Musselwhite, J.S. Lewis, and T. Swindle; Lunar**  
**and Planetary Laboratory, University of Arizona, Tucson, AZ 85721**

There have been numerous efforts to infer the average compositions of the Earth and other terrestrial planetary objects. This abstract is the first in a series evaluating and synthesizing these and our own compositional estimates. This paper is concerned strictly with the composition of the Earth and its constituent chemical reservoirs.

We have compiled several published Earth composition estimates (1-8) together with our own compositional estimates based on trace elements in alkali basalts from Nevada (9) and Liberian dolerites (10), and halogens in mid-ocean ridge basalts (11). After comparing and critically evaluating these compositional estimates we determined a "best bulk silicate Earth" (BBSE) composition. The BBSE values represent straight averages of the individual estimates if there is close agreement. Grossly deviant values are generally excluded from the average. For compatible elements the xenolith-based estimates are weighted more heavily than the volcanic rock-based estimates.

Figure 1 shows the average composition of ordinary chondrites (12), normalized to Type CI carbonaceous chondrites (13), plotted against a volatility index; the latter consists of the solar nebular condensation temperatures appropriate for 50% condensation in a solar-composition nebula at  $10^{-4}$  bars total pressure (14). This figure shows that these nominal condensation temperatures provide a useful volatility index, even if they ignore the details of the temporally and spatially variable nebular and accretion environments.

Figure 2 plots the BBSE composition against the volatility index. Unlike the ordinary chondrites, there has clearly been some process in addition to volatility that has depleted the concentrations of many elements in the silicate Earth. It has long been believed that this process was the separation of an Fe-Ni-S core (6, 15, 16).

Figure 2 and similar plots for the Moon and for the Shergottite and eucrite parent bodies show that the elements Mg, Na, F, Zn, and In are consistently among the least depleted elements for a given volatility index. These element abundances appear to be controlled principally by volatility; these element abundances describe a linear "volatility trend" for each planet. For a given element, one may infer a siderophile/chalcophile depletion factor by normalizing the element abundance to the abundance predicted by the volatility trend.

Figure 3 shows the volatility-compensated depletion factors (presumably due to core formation) on a periodic table of the elements. There are four groups of elements which have apparently been partitioned significantly into the core: the siderophiles, the chalcophiles, the heavier alkali metals, and the heavier halogens. The estimated core composition is given in Table 1.

This analysis supports the published concepts of significant quantities of S, K, and Pb in the core (15-18). The core apparently contains about 98% of Earth's S, 93% of P, 65% of Rb, 60% of Pb, and possibly 45% of K. The apparent core and mantle abundances of Pb yield a core/mantle partition coefficient for Pb of about 3.3, assuming equilibrium; this is close to the nominal 2.5 obtained in partitioning experiments (19); this inferred partition coefficient also argues for early extraction of Pb into the core during the Earth's first 300 million years (20). The inferred K content in the core is about the same as the absolute solubility of K in Fe-FeS liquid (21); however, the K/S ratio of the core is an order of magnitude greater than obtained in the same experiments.

This analysis finds total low-mass components in the core make up about 3.7% of its mass. This estimate is insensitive to errors in the BBSE S and P contents; it is, however, sensitive to the slope of the volatility trend in Figure 2; this uncertainty could contribute a factor of two error in the estimated impurities content. Nevertheless, the estimated content of impurities is considerably less than the 15% estimated earlier based on the assumption that the whole Earth contains a full chondritic complement of S (15). This level of impurities appears to be insufficient to account for all of the "light" component (22); the remainder could be Si (17, 19) or O; C could probably constitute only a few tenths of a percent of the core (23).

The core has extremely low U/Pb and extremely high Rb/Sr ratios; therefore, the core should have evolved unusually unradiogenic Pb and nearly pure radiogenic  $^{87}\text{Sr}$ . Chemical interactions between the core and lower mantle should result in unusual and very diagnostic lower mantle Pb and Sr isotopic compositions. Some of these isotopically anomalous regions may be tapped by ocean island basalts (Kargel, this volume).

A fractional crystallization model, utilizing the partition coefficients of reference 6, was applied to the core to derive the compositions of the solid inner and the liquid outer portions of the core (the solid core constitutes 5% of the core's mass). The Pt group elements are strongly concentrated in the solid inner core. Co and Ni are abundant in both the inner and outer core. The chalcophiles and alkalis are abundant in the outer core only (Table 1).



ACCRETION PROCESSES IN THE EARLY SOLAR SYSTEM ON DATA OF TRACK STUDIES OF ORDINARY CHONDRITES. L.L.Kashkarov, N.N.Korotkova, A.Ya.Skripnik, A.L.Lavrukhnina; V.I.Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, Moscow, USSR.

It is inferred now (e.g.[1]) that the universal accretion process includes a great many of stages of cosmic matter aggregation—from dispersive dust through the grain aggregates to the primary planetesimals and then to the larger bodies and planets. The silicate mineral grain aggregates which entered into chondrules and matrix of chondrites during accretion can provide a unique source of information about the pre-compaction environment conditions and radiation of primitive matter (e.g.[2,3]). It is necessary to distinguish clearly the preaccretion stage from the later regolith evolution history during of which the gas-rich meteorites have stored both SF<sub>VH</sub>-nuclei tracks and SW noble gases simultaneously.

The paper presents the results of pre-accretion track study of olivines from Nikol'skoe L4-5 and Elenovka L5 ordinary chondrites containing no solar gases [4]. Firstly the chondrules and crystals from Nikol'skoe chondrite were selected by a special method taking into account the accretion structure of chondrites [5]. The method includes sample structure analysis and rather exact mapping of picked grain positions. This allowed to localize the regions (Fig.1) enriched in pre-irradiated chondrules (black spots) up to order of value as compared to bulk sample [6]. At first 21 chondrules from different parts of the fragment (dark field) have been studied in attempt to search for CR track-rich regions and then 117 chondrules from revealed localization (white field) have been investigated more detailly. Pre-accretion irradiation tracks have been found in 32 of a 70 chondrules containing large olivine crystals (>50 μm). Textures of most irradiated chondrules are microporphyrific. There are from one to a few olivine grains with  $\rho_{VH} \sim 10^6 - 10^7 \text{ cm}^{-2}$  in a whole chondrule section. The localization revealed by us accords with the morphology and texture of meteorite fragment rather well and can be interpreted preliminarily as accretionary shell containing the admixture of chondrules with another radiation and/or thermal history.

The possible influence of accretion process on track characteristics was elucidated by comparative scanning of chondrule and matrix olivine crystals (sizes  $\geq 30 \mu\text{m}$ ) from Elenovka L5 chondrite. Distributions of track densities ( $\rho$ ) measured in ~260 matrix grains and in ~320 grains from 46 chondrules are shown in Fig.2. The clear difference between two distributions is observed. The percentage of chondrule crystals with  $\rho > 7 \cdot 10^5 \text{ cm}^{-2}$  is of ~10% only. The only chondrule crystal has  $\rho > 10^7 \text{ cm}^{-2}$  and the track density gradients are quite absent. At the same time the part of matrix crystals with  $\rho > 7 \cdot 10^5 \text{ cm}^{-2}$  exceeds ~60%. However there are no

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crystals with  $\rho > 10^7 \text{ cm}^{-2}$  and with gradients in the matrix. The observed essential exceeding of the average  $\rho$  value for matrix olivine grains in comparison with that for chondrules can be explained by a partial track annealing in crystals entered into chondrules. The formation of chondrules most of which had microporphyrritic and fine-grained textures [7] could supposedly take place at the accretion stage in the gas-dust nebula.

Thus our data indicate the storage of pre-accretion VH-nuclei cosmic ray tracks in olivines from two ordinary chondrites containing no solar gases. It was obtained also: 1) a preliminary confirmation of reality of the primary accretional structure in the Nikol'skoe L4-5 chondrite fragment; 2) a clear difference between track characteristics in chondrule and matrix crystals of Elenovka L5 chondrite which can be explained by higher degree of thermal influence on chondrule precursor.

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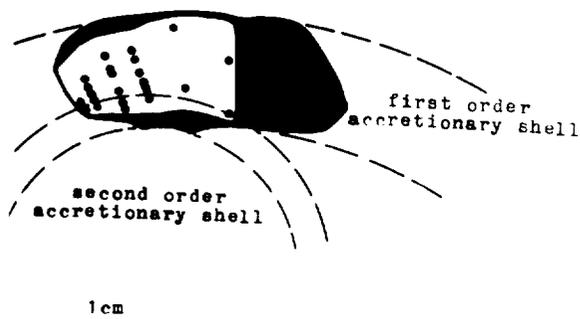


Fig. 1. Reconstruction of accretional structure in Nikol'skoe L4-5 chondrite fragment on the track data. Dotted lines show assumed structural boundaries.

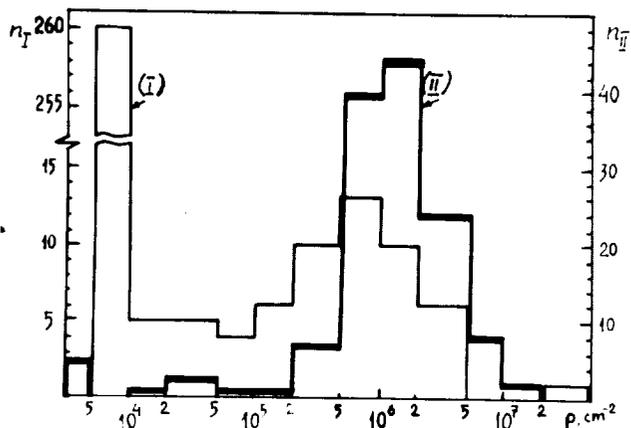


Fig. 2. Frequency distributions of track densities ( $\rho$ ) measured on polished surfaces of the olivine grains from chondrules (I-curve) and matrix (II-curve) of Elenovka L5 ordinary chondrite. n-Number of crystals under investigation.

EFFECT OF HEAVY BOMBARDMENT ON THE CHEMICAL COMPOSITION OF THE EARLY ATMOSPHERE; James F. Kasting, Department of Geosciences, The Pennsylvania State University, University Park, PA 16802

Current models of the Hadean atmosphere (3.8 to 4.5 Ga) suggest that it consisted mostly of  $N_2$ ,  $CO_2$ , and  $H_2O$ , along with smaller amounts of more reduced species, primarily  $H_2$  and  $CO$  (1,2,3,4). Hydrogen is thought to have been provided by volcanism and by photooxidation of iron in the ocean and to have been lost by escape to space;  $CO$  would have been produced by outgassing and by photolysis of  $CO_2$  (1,5,6). Bombardment of the early Earth by late-arriving planetesimals (or comets) could conceivably have altered the balance in favor of these more reduced gases by providing an additional source of reducing power. If the impactors were similar in composition to ordinary chondrites, Fe and FeS would have constituted some 10 to 20% of their mass (7). Carbonaceous chondritic, or cometary, material would have been more highly oxidized, but may still have contained some percentage of reduced compounds. During impact, a significant fraction of this reduced material would have interacted with the atmosphere at very high temperatures. The likely effect would be to strip off oxygen atoms from  $CO_2$  and  $H_2O$ , creating an impact source for  $CO$  and  $H_2$ . One can estimate the magnitude of this source by using impact flux estimates derived from the lunar record. A reasonable figure, based on the crater Orientale and several other craters of similar age, is  $\sim 5 \times 10^{21}$  g of material per  $10^6$  years at 3.8 Ga (8). If the impacting material contained on average about 1% elemental iron, and if all of this iron was oxidized to  $FeO$ , the equivalent hydrogen source would be about  $3 \times 10^9$  ( $H_2 + CO$ ) molecules  $cm^{-2} s^{-1}$ . This is comparable in magnitude to other sources of hydrogen on the early Earth (1,6). The flux of impactors, however, may have been much larger than this prior to 3.8 Ga; Maher and Stevenson (9) suggest that the frequency of impacts decreased exponentially during the Hadean with a time constant of about 70 Ma. The impact flux at 4.5 Ga could thus have been some  $10^4$  times higher. This additional influx of reducing power would almost certainly have overwhelmed the capacity of the atmosphere to convert  $CO$  back into  $CO_2$  by photochemistry (10). An early atmosphere dominated by  $CO$  would be the likely result. ( $H_2$  would still have been lost rapidly by escape to space.)

The chemical effects of such impacts will be studied by incorporating them into a one-dimensional photochemical model of the primitive atmosphere. The goal of this study will be to determine if and when the atmosphere changed its composition from  $CO$  to  $CO_2$ . Possible implications for prebiotic synthesis and the origin of life will be considered.

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PLANETESIMAL EFFECTS ON PLANET ORBITS, SPIN, AND HEATING  
W. M. Kaula, Department of Earth & Space Sciences, U. C. L. A.

A major problem of the origin of the Earth is why it became so different in secondary properties from Venus, the body by far the most nearly similar in primary properties: the two planets differ less than 30 percent in mass, mean density, and solar distance. Several of the secondary differences-- the surface temperature, the absences of water, magnetic field, and plate tectonics in Venus-- are explicable as consequences of evolution. But there are two great differences that must depend on formation: the states of spin + satellite, the Earth being prograde with a satellite, and Venus being retrograde; and the retention of heavy primordial inert gases, especially  $^{36+38}\text{Ar}$ , of which Venus has about 80 times as much as the Earth. Dissipative processes must evolve and maintain Venus's very slow spin (1), but primordially Venus must start retrograde (2): the more so, the lower the  $1/Q$  required to slow down (3). Regarding the argon difference, attempts to explain it by nebula or solar wind effects (4,5) have remained unpersuasive. The obvious hypothesis for the two differences is the late stage impact history, as suggested by Cameron (6): the Earth got hit by a big body, degassing it and knocking off the protolunar matter, while Venus was not hit by anything nearly as large.

Hence the question is what was the population of bodies-- masses and orbits-- characterizing the penultimate stage of terrestrial planet formation: what constraints can be placed on it by these differences in secondary properties of Venus and Earth (as well as the primary properties of all four planets)? Wetherill (7,8) showed that, given a suitable confinement in semi-major axis of a starting swarm of 500 planetesimals, about four planets will be obtained, with the final stages entailing impacts of bodies of about  $0.3 M_{\oplus}$  at velocities of about 9 km/sec. Hence his Monte Carlo models support Cameron's (6) conjecture, but he did not calculate the spins resulting from collisions in the model, and did not explore in any detail the implications of the observed outcomes in spin and volatile retention for the planetesimal population.

Earlier discussions of the implications of planet spin rates and obliquities (9,10) concluded that they limited the size of the forming planetesimals. Indeed, Safronov's (9) main observational argument for the runaway growth of the largest body in a zone was the obliquities. This problem has been reexamined by Hartmann & Vail (11) with a model defined by distributions in mass and approach velocity & offset of impactors with the conclusion that impactors could have had masses 20% of the planet's.

We have adapted an Opik algorithm, developed for another purpose, to this problem. The main difference of the algorithm from Wetherill's is that a priori four bodies are designated as "planets"; the remainder, as "planetesimals"; and only planet-planetesimal interactions are taken into account. The application discussed here is essentially a combination of the later stages of the modelling by Wetherill (8) with the impact: spin modelling of Hartmann & Vail (11). In addition to spin orientation and magnitude, energy dissipation upon collision is calcu-

lated, since variation therein would pertain to the hypothesis of an impact-generated volatile difference (6).

The starting conditions for the runs already made approximate those of the 31 My, or 81% accreted, stage of Wetherill [p. 537 of (8)]: four planets, 81% as massive as the final, plus fifty planetesimals of masses  $m$  randomly selected from a distribution  $n(m) = k m^{-1.5}$ , with a maximum not more than 200 times the minimum, and a total mass 23.5% of the total mass of the planets. Random selections were also made of the action elements from distributions of similar form, with negative correlations of  $-0.3$  of the eccentricities and inclinations with masses. The starting spins were all prograde, with magnitudes in accord with the empirical rule that the angular momentum densities were proportionate to  $M^{5/6}$  (3): i.e., LOD's of 19 hours for proto-Earth and proto-Venus, 27 hours for proto-Mars, and 30 hours for proto-Mercury.

In the thirty runs made to date, there were no significant differences in the averages of the outcomes for Venus and Earth, but appreciable variations about these averages in individual cases for these two planets: 1. retrograde spins for 15% of cases; 2. slow downs of spins for 15%; 3. speed ups of spins to angular momenta of the Earth + Moon (i.e., LOD of less than six hours) for 10%; 5. summed energy dissipations/unit mass ranging from  $3 \times 10^6$  to  $2 \times 10^7$  J/kg (equivalent to 3,000 to 20,000 C temperature rise); and 6. orbit eccentricities ranging from 0.001 to 0.039. These effects may be too low because the  $m^{-1.5}$  formula for masses gave maxima too low: .02 to .05  $M_{\oplus}$ , less than suggested by Wetherill's (8) figure.

The results for Mercury were fragmentation in 90% of cases: i.e., spin ups to instability ( $LOD < 2.6^h$ ), with energy dissipations of  $10^7$  to  $2 \times 10^8$  J/kg. Mars was fragmented in 50% of cases, and had dissipations of  $2 \times 10^6$  to  $4 \times 10^7$  J/kg.

The modellings are thus consistent with the hypotheses that the spin + satellite states of Venus and Earth; a greater outgassing of the Earth; the stunted growths of Mars and Mercury; and the predominantly iron composition of Mercury are all results of the late stages of their growths being impacts by planetesimals with masses ranging up to well above the Moon's. However, an appreciably greater range of parameters needs to be explored, and better physical models of impact effects on fragmentation, satellite formation, and outgassing need to be developed.

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## The Formation and Evolution of the Earth's Core: Constraints from High-Pressure Experiments

Elise Knittle, Quentin Williams, *Earth Sciences Board, University of California, Santa Cruz, CA 95064* and Raymond Jeanloz, *Dept. of Geology and Geophysics, University of California, Berkeley, CA 94720*

High-pressure, high-temperature experiments using the laser-heated diamond cell provide an important and unique dataset constraining the temperatures of the Earth's core, the incorporation of light-alloying components into the core and the chemical evolution of the core-mantle system. Melting studies to over 100 GPa on Fe, FeS, FeO and two model core compositions containing 10 weight percent of oxygen and sulfur,  $\text{Fe}_{0.61}\text{O}_{0.39}$  and  $\text{Fe}_{0.84}\text{S}_{0.16}$ , document that temperatures in the Earth's core are greater than 4500 (+/-500) K: higher than most previous estimates. The high temperatures suggest that either significant radiogenic element enrichment occurs at depth in the Earth (perhaps as a contaminant in the liquid outer core) or that the deep Earth retains heat from the accretion process or from core formation. In addition to constraining core temperatures, high P-T experiments document fundamentally different chemical behavior for oxygen and sulfur when alloyed with iron at high pressures. The Fe-FeO system exhibits solid-solution behavior above the metallization pressure of FeO at 70 GPa, whereas the Fe-FeS system has a eutectic composition to pressures greater than 100 GPa. The metallization of both solid and liquid FeO at ~ 70 GPa itself represents a dramatic change in the bonding properties of oxygen with iron at high pressure. In particular, the metallic behavior of FeO liquid at high pressures shows that oxygen will alloy with iron under these extreme conditions. This is in contrast to the behavior of the Fe-O system at low pressure, where oxygen has very limited solubility in liquid iron (<0.2 percent). The ability of oxygen to alloy with liquid iron at high pressure supports the idea that oxygen could be an important, if not dominant, light alloying constituent of the Earth's core. Our results suggest that because oxygen and sulfur alloy with liquid Fe under different physical conditions, the incorporation of these important light alloying components into the core depends on the pressure at which core formation initiated and the chemical composition of the core began to evolve. Sulfur is a likely candidate for the dominant light-alloying component in the outer core if molten iron segregated from the silicates in the early Earth when pressures in the planet's interior were low. However, the incorporation of oxygen could only begin at higher pressures. If 70 GPa was the required pressure (noting that lower pressures may have been sufficient), this implies that the Earth must have accreted to 4500 km in diameter before this interior pressure was reached and oxygen could alloy with liquid iron. Therefore, the incorporation of oxygen into the core would be more characteristic of a late stage in the core-formation process. An additional scenario for the incorporation of oxygen into the outer core comes from the experimental observation that chemical reactions occur between silicates and liquid iron at pressures greater than 40 GPa. This observation suggests that chemical reactions between the Earth's core and the mantle may be an important process in the evolution of the chemical composition of the core. Specifically, in accord with experimental results, chemical reactions between the core and mantle will 1) dissolve components of silicates (particularly oxygen) into the outer core and 2) create regions at the core-mantle boundary which are enriched in silicate components ( $(\text{Mg,Fe})\text{SiO}_3$ , and  $\text{SiO}_2$ ) and regions enriched in the metallic component (FeO and FeSi alloys). Therefore, chemical reactions have been experimentally shown to provide a mechanism for incorporating light alloying components into the outer core. In fact, these reactions suggest that oxygen will inevitably be present in the outer core and that the chemical composition of the outer core continues to evolve even to the present day.

## GIANT IMPACTS AND THEIR INFLUENCE ON THE EARLY EARTH.

Christian Koeberl\* and Virgil L. Sharpton, *Lunar and Planetary Institute, 3303 NASA Road One, Houston, TX 77058, USA* (\* also at: *Institute of Geochemistry, University of Vienna, A-1010 Vienna, Austria*).

In the early solar system cratering was a very important process, even more important than now, since planetesimals were much more abundant than today. It is not easy to draw an exact line between the accretionary process, when planetesimals collide and merge to build up larger planets, and a later stage, when remaining planetesimals impacted on the planets. It can be assumed that even after the main accretionary stage large impacts continued to be important for the growth of the early planets, adding a few percent of mass over several hundreds of millions of years. Although the major phase of the buildup of the terrestrial planets required only a few million years, the final accretion stages continued over a much longer time, in excess of 100 my (e.g., [1]). The orbital evolution of remaining planetesimals leads to an increase in the relative velocities and thus to hypervelocity impacts that are no longer accretionary (in the sense of simple "merging" of bodies), but catastrophic. The giant impactor hypothesis of lunar origin (e.g., [2]) would lead to numerous smaller bodies and fragments travelling in a similar orbit as the earth and the moon. These fragments will eventually impact on the earth and, to a lesser extent, also on the moon.

It is well known from lunar studies that the cratering rate during the first billion years of lunar history was very high. Dating of lunar rocks has demonstrated the virtual absence of rocks older than 4.0 Gy, which led to the concept of a terminal lunar cataclysm [3]. The normal cratering rate declined in the form of an almost exponential curve since about 4.6 Gy, and, taken alone, would make it difficult to understand the absence of older rocks. In addition, the dating of several large lunar basins (Orientale, Imbrium, Serenitatis) yielded ages of about 3.8 Gy, which is additional evidence for a terminal cataclysm. There seems to be ample evidence for unconformities (spikes) in the simple impact rate decay curve, with shorter periods of intense impact bombardment (probably resulting from the breakup of larger planetesimals) up to about 3.8 Gy ago (e.g., [4]).

Considering the larger geometrical and gravitational cross section for the earth it is obvious that the impact rate was higher on earth than on the moon by a factor of at least 2 [5]. If the late bombardment observed on the moon is a physical reality we would expect a considerable temporary increase in the impact rate on earth, too. The size frequency of the impacts is not well known. As on the moon there are two major possibilities, one where only large bodies are responsible for the spikes, and another one with a normal size distribution of planetesimals and meteorites. Although the second possibility would add a large mass to the earth, only the impact of large bodies is relevant for global evolution. Part of the kinetic energy of the impacting body is transferred into thermal energy, which adds significant amounts of heat to an already hot system. The late bombardment, which has also been effective on earth, was probably responsible for a constant disruption, breakup, and reworking of the terrestrial crust. It is not clear if the energy was sufficient for sustaining a global magma ocean over longer periods of time, but any crust that was forming at that time was reworked.

No terrestrial rocks with ages  $>3.8$  Gy have been preserved, with the exception of some relict minerals (zircons) from earlier lithologies. Although these rocks are not necessarily pristine, they indicate that most probably no crust has survived before that time. This hiatus coincides very well with the terminal lunar cataclysm. There are geochemical arguments, based on trace element contents of lherzolites (e.g., the enrichment in siderophile elements as well as their ratios, [6,7]), that the primitive upper mantle of the earth suffered a late stage bombardment after the formation of the core. The inferred chemistry of the planetesimals (projectiles) is chondritic and similar to the chemistry of the ancient lunar meteoritic component of Apollo 17 [7]. The discovery of indications for a late stage bombardment adds significantly to the probability of a terminal cataclysm. Since then tectonic processes have been important for reworking the terrestrial crust, but the fact that some rocks as old as 3.8 Gy have survived may be considered important.

There is a very good chance that the late stage bombardments left some scars on the terrestrial surface which may still be found. One way to deal with this question would be to look for shock effects in selected 3.8 Gy old rocks. Although we (and other workers) have so far been unable to find shock signatures in a preliminary study of Amitsoq gneisses, we conclude that it is very likely that the record of the late bombardment may still be present in some of these old rocks. Most Archean rocks have been subject to metamorphic events, but severe shock effects are not readily destroyed. An example would be the Vredefort

structure, or the Sudbury structure, where a shock event was followed by tectonic events without completely erasing the indications of shock. If carefully selected Archean rocks are studied for shock effects it seems probable that some features will be discovered. We feel that impact processes have been of great importance during the first several hundred million years of the history of the earth, and that the oldest rocks of the earth may contain evidence of early large scale impacts.

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NOBLE GASES IN OCEANIC VOLCANIC ROCKS AND IMPLICATIONS FOR THE TERRESTRIAL MANTLE; Mark D. Kurz, Chemistry Department, Woods Hole Oceanographic Institution, Woods Hole, MA 02543

The isotopic compositions of the noble gases, particularly He, Ar, and Xe, in oceanic basalts can provide important constraints on the evolution of the earth's mantle. The highest  $^3\text{He}/^4\text{He}$  ratios are found in basalts from oceanic islands such as Hawaii and Iceland (Kurz et al., 1982). These data suggest that the mantle sources for these islands have had a higher time-integrated  $^3\text{He}/\text{Th}+\text{U}$  ratios, and hence are less degassed than mid-ocean ridge basalts (MORB) or other islands. The argon and xenon isotopes in the samples that have the highest  $^3\text{He}/^4\text{He}$  (i.e., Loihi seamount near Hawaii) are close to the atmospheric composition, suggesting either atmospheric contamination, or that the undegassed mantle is similar to the atmosphere in these parameters (Allegre et al., 1983). Noble gas data from MORB glasses have less variable  $^3\text{He}/^4\text{He}$  ratios than those from oceanic islands, and include the highest ratios of  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{130}\text{Xe}$ . These data can best be explained by a heterogeneous mantle which retains a significant mass of relatively undegassed material.

One of the most important constraints on the the origin of mantle heterogeneity and the degassing history of the early earth are the xenon data from MORB glasses. The difference in  $^{129}\text{Xe}/^{130}\text{Xe}$  between MORB and the atmosphere, and the short half-life of extinct  $^{129}\text{I}$ , require that the upper mantle and atmosphere were separated within 100 my of accretion (Staudacher and Allegre, 1982). This can be explained by early outgassing of the atmosphere, or by heterogeneous accretion of the earth (Ozima et al., 1985). If the atmosphere was produced by outgassing, the xenon data also suggest that the mantle has retained heterogeneity in the noble gases since accretion.

One significant problem in interpreting the noble gas data is evaluating the relationship between measured values and the inferred mantle reservoirs. In particular, data from MORB and oceanic islands can be extremely variable on a local scale, which may relate to small scale mantle heterogeneity, magma migration processes, or surficial contamination processes. Helium, strontium and lead data from Mauna Loa volcano in Hawaii (Kurz et al., 1987, and unpublished) demonstrate that noble gases in volcanic systems can evolve significantly with time, and that detailed sampling is required to properly use the noble gases as mantle tracers.

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## EVIDENCE FOR A VERY ANCIENT CRUSTAL FRAGMENT IN THE ARCHEAN SLAVE PROVINCE

*T.M. Kusky*, Department of Earth and Planetary Science, The Johns Hopkins University, Baltimore, Maryland 21218 U.S.A., *S.A. Bowring*, and *C. Isachsen*, Department of Earth and Planetary Science, Washington University, St. Louis, Missouri, 63130, U.S.A.

A growing body of evidence indicates that a large ancient crustal fragment occupies the western part of the Slave Craton in Canada's North West Territories. The western Slave Province, or Anton Terrane (Kusky, 1988), is characterized by a mixed suite of meta-igneous and meta-sedimentary gneisses, intruded by voluminous quantities of granitoids. The gneisses are in places structurally overlain by mixed mafic/felsic volcanic sequences, and by graywacke turbidites. Other meta-sedimentary sequences containing quartzites and metapelites appear to unconformably overlie the gneisses (Easton, 1985). The eastern margin of the Anton Terrane is marked by a complicated structural zone coincident with a strong Bouger anomaly. Younger meta-sedimentary and meta-igneous rocks of the eastern Slave Province are interpreted to have been thrust over the Anton Terrane along this zone (Kusky, 1988). In the west the Anton Terrane dips under Proterozoic rocks of the Wopmay orogen. Evidence for the age of the Anton Terrane comes from several independent studies, and is summarized here (Figure 1). Zircons separated from a tonalitic gneiss in a basement culmination of Wopmay Orogen have yielded Pb-Pb ages in excess of 3.5 Ga, and have a strongly negative  $\epsilon_{Nd}$  value at 3500 Ma, implying derivation from even older rocks. Chamberlain et al. (1984) report U - Pb zircon ages in excess of 2900 Ma for tonalitic gneisses occupying 200 km<sup>2</sup> east of the Wopmay fault. Frith et al (1986) obtained a three point concordia intercept age of 2989 Ma for basement in the Grenville Lake area. Nikic et al (1980) have obtained a 3210 Ma Pb-Pb age on tonalitic boulders from a diatreme near Yellowknife, and Bibikova et al. (1988) suggest 3340 and 3390 Ma Nd model ages for the same rocks. Shärer and Allègre (1982) have analyzed detrital zircons from the Contwoyto Formation on Point Lake and have shown several source ages; three fractions correlate with the age of volcanism in the Slave Province (2660 - 2710 Ma), but two fractions are significantly older. These include upper-intercept ages of 3250 +110/-90 Ma, and 3530 +200/-160 Ma, suggesting derivation from the Anton Terrane. Franklin and Thorpe (1982) suggest, from an analysis of lead-isotope data on volcanogenic massive sulfide deposits, that Slave Province lead has been variably contaminated from a crustal source. Assuming a reasonable age for the sulfide deposits of 2670 Ma, they further calculated an age for the contaminant of 4017 +/- 60 Ma. Rocks of the Sleepy Dragon terrane, which have been correlated with the Anton Terrane (Kusky, 1988), yield a similar set of ages. For instance, Krogh and Gibbins (1978) obtained an U-Pb age of 3152 Ma for a chloritic granite on Point Lake. In the south, the Sleepy Dragon Complex yields U-Pb ages of 2829 +40/-31 Ma (Henderson et al., 1987), and Nd model ages of 3300 Ma have recently been reported from here (Dudas et al., 1988). There is thus a growing body of evidence which suggests that there are protoliths in the Anton terrane with ages in the 3.2 - 3.5 Ga interval, and there is some indication that an even older crustal component exists in the western Slave Province. The Anton Terrane of the western Slave Province should thus be considered as yet another remnant of continental crust which formed in the earth's first billion years.

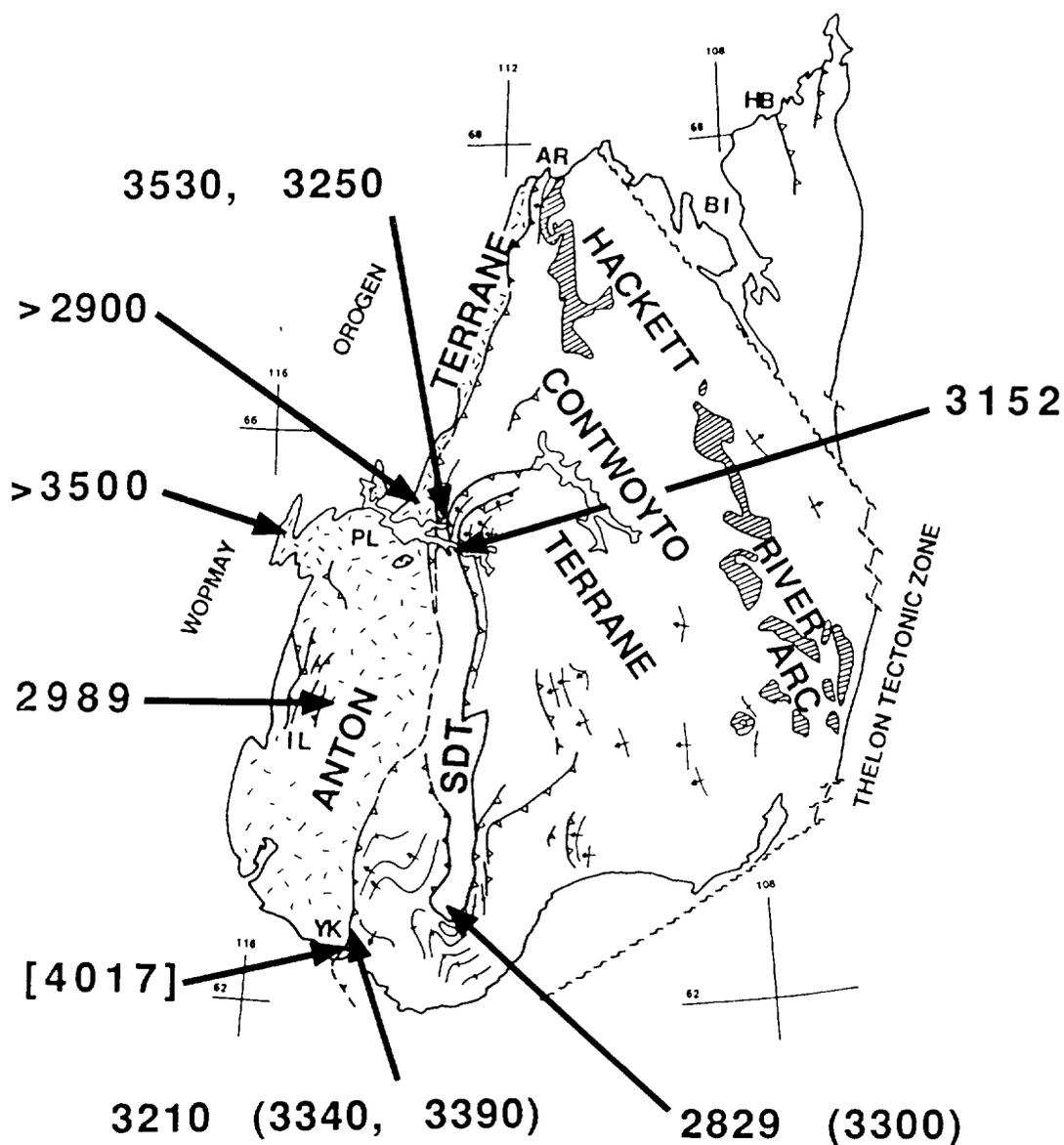


Figure 1. Terrane map of the Slave Province (from Kusky, 1988) showing the locations of dated samples discussed in text. Sm-Nd dates in parentheses, U-Pb and Pb-Pb dates are unornamented, and other age estimates in square brackets.

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NUMERICAL SIMULATION OF THREE-BODY INTERACTIONS WITH AN ENERGY DISSIPATION SUBROUTINE FOR CLOSE ENCOUNTERS BETWEEN TWO BODIES: IMPLICATIONS FOR PLANETARY ACCRETION AND PLANETOID CAPTURE PROCESSES; R. J. Malcuit, Dept. of Geology and Geography, D. M. Mehringer and R. R. Winters, Dept. of Physics and Astronomy, Denison University, Granville, Ohio 43023.

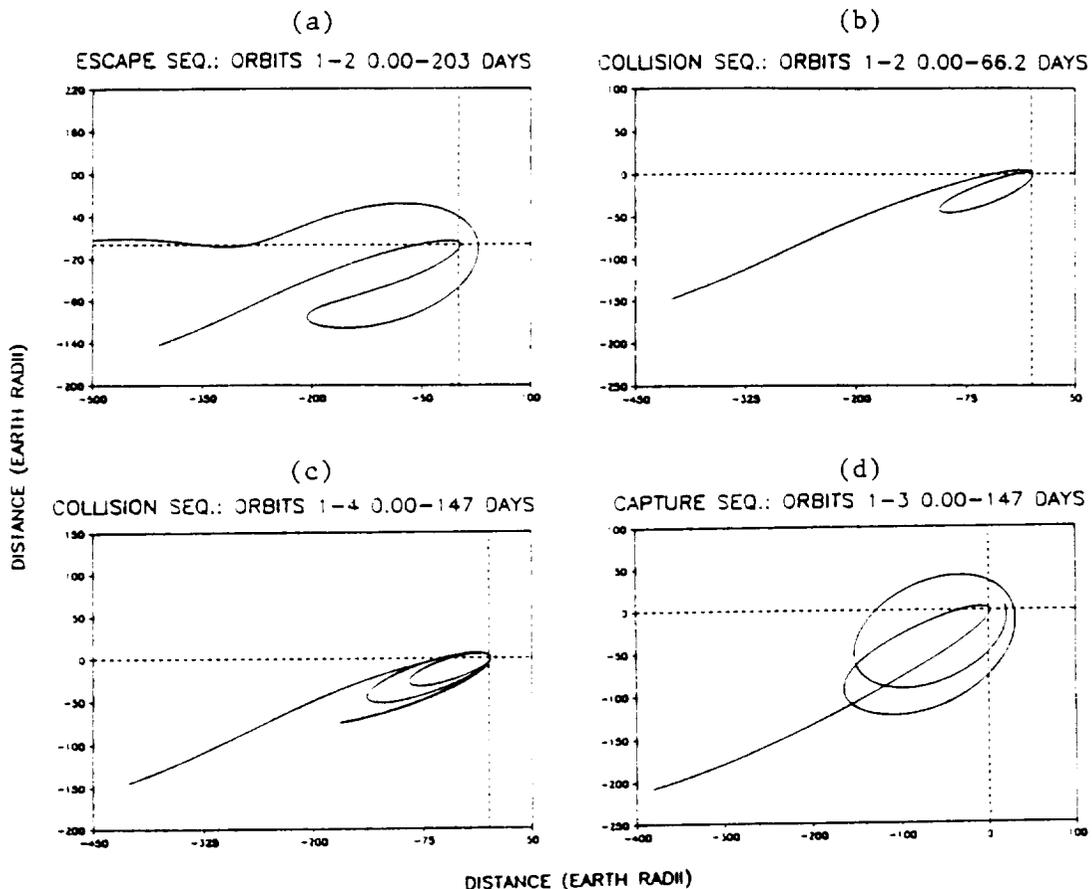
A three-body (Sun, Earth, planetoid) numerical code with an energy-dissipation subroutine [using equations from (1)] has been devised to study the effects of close gravitational interactions between Earth-like planets and large planetoids (lunar-mass and Mars-mass) in Earth-like, co-planar heliocentric orbits. The major variables for the two interacting bodies are: (1) the perigee distance ( $r_p$ ) of close encounters, (2) the displacement Love number ( $h$ ) for each body, (3) the specific dissipation factor ( $Q$ ) for each body, (4) the Earth anomaly (the position of the Earth-like body relative to the Sun at the beginning of the calculation), and (5) the planetoid anomaly (the position of the planetoid relative to the Earth-like body at the beginning of the calculation). The results of these simulations can be placed into five categories: (1) close non-capture encounters in which the encountering body is deflected in a near-parabolic orbit by the Earth-like body and then continues on a heliocentric orbit; (2) non-capture geocentric orbital scenarios in which the encountering body goes into geocentric orbit for a few orbits and then returns to heliocentric orbit; (3) stable gravitational capture scenarios in which the encountering body is inserted into a geocentric orbit because of radial tidal energy storage and subsequent dissipation within the two encountering bodies; (4) grazing collision scenarios in which the closest approach distance is greater than the sum of the planet-planetoid radii but less than the grazing limit when the equilibrium tidal bulges are considered; and (5) collision scenarios in which the distance of closest approach is less than the sum of the planet-planetoid radii. For lunar-like bodies (Moon-mass and density) characterized by a displacement Love number ( $h$ ) of 0.5 and a  $Q$  of 1 and an Earth-like planet with  $h_e = 0.7$  and  $Q_e = 1$ , the grazing encounter limit at perigee (for equilibrium tidal deformations of the interacting bodies) is about  $1.36 R_e$  and the stable capture limit is about  $1.45 R_e$ . For a Mars-mass body with lunar density and the same displacement Love number and  $Q$  values used in the case of the lunar-like body and interacting with an Earth-like body with the deformational properties stated above, the grazing encounter limit at perigee is about  $1.71 R_e$  and the stable capture limit is about  $1.88 R_e$ . Using the traces of the two-body parabolic trajectories associated with the  $r_p$  limits as a measure of the "capture" window, we find that this window is larger for Mars-mass bodies than for lunar-mass bodies of the same density.

Calculations for planetoids in geocentric orbits in an elastic system (no energy dissipation) suggest that orbits with apogee distances beyond about  $200 R_e$  are unstable relative to solar perturbations. The total energy for a lunar-mass body in an orbit with a major axis of  $200 R_e$  is about  $-2.0 \times 10^{35}$  ergs and that for a Mars-mass body is about  $-23.0 \times 10^{35}$  ergs. Thus, about that much energy must be dissipated within the interacting bodies during a close encounter for stable capture, if we assume that the relative velocity at infinity ( $v_\infty$ ) is near 0. Fig. 1 shows plots of calculated scenarios for Mars-mass (and lunar density) bodies interacting with an Earth-like planet.

Some tentative conclusions from our limited set of calculations (all co-planar) are (1) that all retrograde runs within the "capture" window have resulted in either escape or collision, (2) that most encounters within the

prograde capture window result in stable capture, (3) that collisions from geocentric orbit (mainly from the retrograde direction) are about equally distributed between retrograde and prograde directions at impact, and (4) that the prograde capture window diminishes as  $h$  decreases and/or  $Q$  increases relative to the values given above. Reference: Peale and Cassen (1978) *Icarus*, 62, 245-269.

Figure 1. Plots of orbital scenarios for the case of a Mars-mass (lunar-density) planetoid encountering an Earth-like planet. Earth is at the origin, the curved line is the path of the planetoid. For all scenarios:  $h_e = 0.7$ ,  $Q_e = 1$ ,  $h_{p1} = 0.5$ ,  $Q_{p1} = 1$ , Earth anomaly =  $0^\circ$  (Sun starts to left of diagram), Earth orbital eccentricity = 0.0170, planetoid orbital eccentricity = 0.0230, path of planetoid begins at  $450 R_e$  from Earth-like planet, non-rotating reference frame. (a) Retrograde Encounter-Escape Sequence: planetoid anomaly =  $199.2^\circ$ , energy dissipation on first encounter =  $11.3 \times 10^{35}$  ergs,  $r_p = 2.12 R_e$ . (b) Retrograde Collision Scenario: planetoid anomaly =  $199.8^\circ$ , energy dissipation on first encounter =  $29.5 \times 10^{35}$  ergs,  $r_p = 1.80 R_e$ , collision in retrograde direction at  $0.74 R_e$ . (c) Complex Collision Scenario: planetoid anomaly =  $199.4^\circ$ , energy dissipation on first encounter =  $15.3 \times 10^{35}$  ergs,  $r_p = 2.01 R_e$ , collision on fourth perigee passage is in prograde direction at  $1.36 R_e$ . (d) Stable Capture Scenario: planetoid anomaly =  $208.1^\circ$ , energy dissipation on first encounter =  $18.8 \times 10^{35}$  ergs,  $r_p = 1.95 R_e$ , close encounter on fourth perigee passage (not shown) causes stable capture.



## Evolution of the Terrestrial Environment from the Impact-induced Steam Atmosphere to the Present N<sub>2</sub> Rich Atmosphere

Takafumi Matsui\*, and Eiichi Tajika\*\*

\*Department of Atmospheric, Oceanic and Space Sciences, Ann Arbor, Michigan 48109-2143

\*\*Geophysical Institute, University of Tokyo

It has been widely accepted that the terrestrial planets were formed by accretion of planetesimals. If this were the case, the surface of proto-Earth and -Venus would have been covered by magma ocean due to the blanketing effect of an impact-induced steam atmosphere (1). In the case of Earth, the steam atmosphere becomes unstable with decreasing impact flux thus forming the proto-ocean. This, however, is not the case for Venus due to higher solar flux (2). Then the proto-atmosphere just after the the formation of the Earth is mainly composed of CO<sub>2</sub> which is the second abundant volatile species of the present Earth's surface environment. The question is how such CO<sub>2</sub> rich atmosphere evolves to the present N<sub>2</sub>-rich atmosphere. In this paper we discuss this long-term evolution of the Earth's environment by using a simple geochemical modeling of CO<sub>2</sub> cycle between four reservoirs: atmosphere, ocean, oceanic plate and continent.

Model: Geochemical model of the CO<sub>2</sub> cycle between the four reservoirs used in this study is summarized in Fig. 1. For the sake of simplicity we neglect the biological effect on this cycle.

Mass balance equations: Mass balance of carbon, calcium and magnesium between the four reservoirs is expressed by the following equations.

$$\begin{aligned} d L_C/dt &= -F_W^C + F_{ac} \\ d P_C/dt &= -F_m - F_{ac} + F_p^{Ca} + F_p^{Mg} \\ d M_{Ca}/dt &= F_W^C + F_W^{CaSi} + F_{v-sw} - F_p^{Ca} \\ d M_{Mg}/dt &= F_W^{MgSi} - F_{v-sw} - F_p^{Mg} \end{aligned}$$

where  $F_W$ ,  $F_{ac}$ ,  $F_{v-sw}$ ,  $F_m$  and  $F_p$  are the fluxes due to weathering, accretion, volcanic-seawater reaction, metamorphic magmatism and precipitations, respectively.

Numerical results: The above equation are numerically solved. We assumed that chemical equilibrium is always achieved between the atmosphere and ocean and the distribution of C between them is dependent on the pH of the Ocean. An example of the numerical results is shown in Fig. 2. This model is characterized by the ratio ( $F=0.75$ ) of the precipitated oceanic CaCO<sub>3</sub> between accreted and subducted plates, and pH of ocean (pH = 8) As is evident in this figure, the predicted present abundance of each reservoir matches well with the observed one. The results are highly dependent on  $F$ . When  $F$  is lower, most of

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C is stored in the oceanic plate and much higher values of C content are found in the atmosphere. When F is largest, most of C is concentrated into the continent and the surface temperature stays around 0°C or below. To arrive at the present environment it is necessary that the distribution ratio F of the precipitated CaCO<sub>3</sub> between the continent and the mantle is around 0.75. This suggests that the Earth should have both ocean and granitic continent to become a habitable planet.

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Abe Y. and Matsui T. (1987) J. Geophys. Res. 90, C545-C559.
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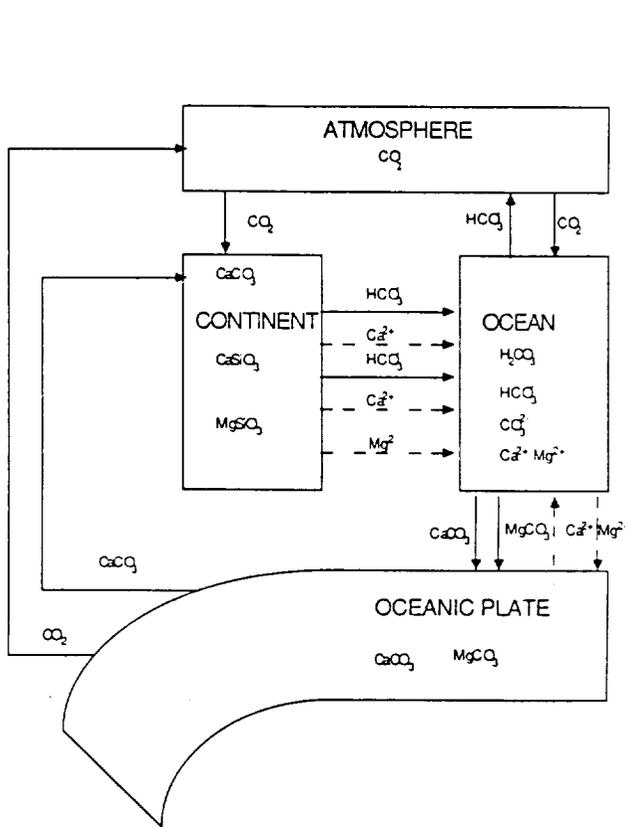


Fig. 1. A geochemical model of model of CO<sub>2</sub> cycle between reservoirs.

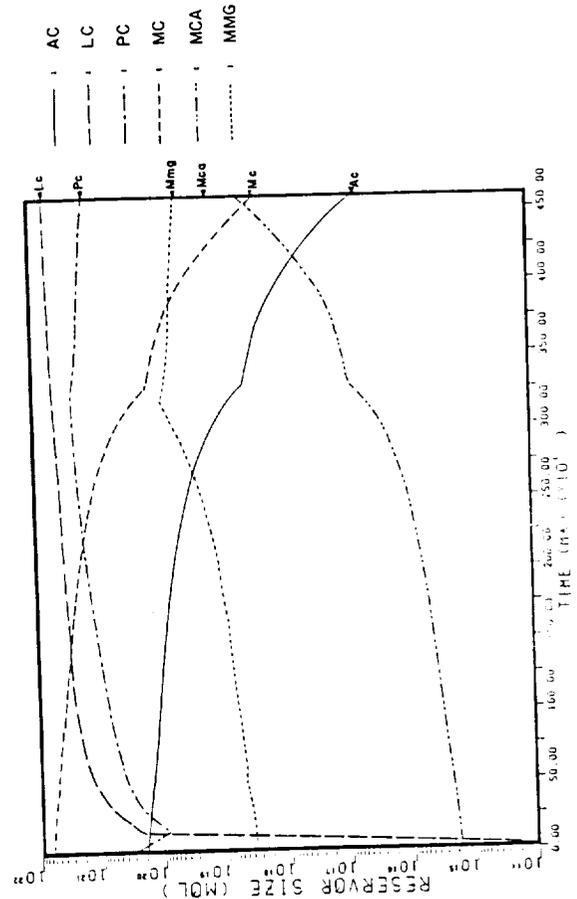


Fig. 2. Temporal variation of C, Ca and Mg content in each reservoir. A, L, P and M represent the atmosphere, continent, oceanic plate and ocean reservoirs, respectively. The arrows on the right ordinate represent the present abundance.

THERMAL EVOLUTION OF THE EARTH: EFFECTS OF VOLATILE EXCHANGE  
BETWEEN ATMOSPHERE AND INTERIOR; P. J. McGovern and G. Schubert,  
Department of Earth and Space Sciences, University of California,  
Los Angeles, CA 90024

A parameterized model of mantle convection that includes the effects of volatile exchange between the mantle and the surface reservoir and the softening of the mantle by the dissolved volatiles is used to study the thermal history of the Earth. Based on the deformation data of Chopra and Paterson (1984), it is assumed that the activation energy for temperature-dependent solid-state creep is a linear function of weight percent of volatiles. The mantle degassing rate is taken to be directly proportional to the rate of seafloor spreading which depends on the mantle heat flow. The rate of regassing also varies with the seafloor spreading rate, but it depends on other factors as well, including the mass of the atmosphere-hydrosphere system and the efficiency of volatile recycling through island arc volcanoes. Thus, because the degassing/regassing rates are a function of convective vigor which is regulated by mantle volatile content (through the volatile dependence of viscosity), the devolatilization/revolatilization of the mantle is self-consistently calculated. Model results indicate that mantle degassing and regassing rates quickly equilibrate during an early stage of rapid Earth cooling and adjust to regulate a more gradual cooling of the Earth over most of geologic time. These adjustments occur in the first several hundred million years of Earth's history. Most of the net volatile release from the mantle (or, in some cases, net volatile absorption into the mantle) occurs early, in accord with isotopic evidence for rapid formation of the atmosphere. The net mass of volatiles released from the mantle is easily comparable to that of Earth's oceans. When mantle viscosity depends on both volatile content and temperature, changes in volatile content are compensated by changes in temperature so that the mantle evolves with the viscosity and convective vigor required to transfer its internally generated heat. Thus, the mantle is hotter (colder) as a consequence of degassing (regassing) compared to a mantle with a volatile-independent rheology. The ratio of internal heat generation to total heat flow (the Urey ratio) is regulated by the temperature dependence of viscosity; models with high initial Urey ratios build up high temperatures very rapidly, thereby enhancing heat flow and reducing the Urey ratio. Early volatile loss from the mantle leads to a more rapid buildup of high temperature; thus, the 'corrective' heat flow occurs even faster. Due to these feedback effects, the present value of the Urey ratio cannot exceed unity.

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**GIANT IMPACT THEORY OF THE MOON'S ORIGIN: IMPLICATIONS FOR THE THERMAL STATE OF THE EARLY EARTH;** H. J. Melosh, Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721, and M. E. Kipp, Sandia National Laboratory, Albuquerque, NM 87185.

Ideas on the early thermal structure of the earth have evolved rapidly over the last few decades. Most of this evolution is ultimately traceable to the size of the planetesimals from which the earth is believed to have formed. Less than twenty years ago most authors (eg. 1,2) supposed that the earth accreted from myriads of small planetesimals that, upon impacting the surface of the growing proto-earth, proceeded to radiate most of their heat to space. Under such conditions the earth would have had to accrete over the remarkably short interval of 0.5 Myr (1) if melting temperatures were to be reached anywhere within its interior. Less than ten years ago, Kaula (3) realized that if most of the planetesimals are in the 30-100 km diameter range, then a large fraction  $h$  (where  $h \approx 0.5$ ) of their original kinetic and gravitational energy would be buried below the earth's surface at depths too large for conduction or radiation to easily dissipate it to space. Kaula's model predicts that the temperature distribution in a growing planet is a parabolic function of radius  $R$  in the planet, increasing from the inside of the planet toward the surface as  $R^2$  until the solidus is reached, at which point liquid convection holds the temperature between the liquidus and solidus. This initial temperature inversion would have been wiped out by core formation as density-driven convection mixed the initially cool interior with the hotter external regions (as well as released more gravitational energy). This model permits the earth to grow over the much longer interval of ca. 50 Myr, which is more in consonance with the predicted dynamical growth timescales.

Most recently it has been suggested that the moon formed as a result of a collision between the proto-earth and a Mars-size planetesimal (4). Computations by Wetherill (5) show that large impacts of this kind are plausible events near the end of planetary accretion, about 100 Myr after accretion began. The chemistry of the moon, particularly its low abundance of metallic iron, suggests that the earth's core had already formed at the time the putative giant impact event took place. The initial state of the earth's mantle is unknown, although the  $10^{31}$  J released by core formation (if the earth was initially homogeneous) would have been enough to raise the mean temperature of the earth 1,500 °K. Thus, the earth's early mantle was probably already molten at the time of the impact. Even if it was not, we will show below that an impact energetic enough to have ejected the moon would certainly have left the entire mantle molten (and some of it vaporized!) afterwards.

The idea of a Mars-size impactor was first suggested by the anomalously large angular momentum of the earth-moon system. It is easy to show the present angular momentum could have been imparted only by the impact of a body with a mass in the vicinity of that of Mars, although other factors such as impact velocity and impact parameter (a measure of the obliquity of the impact) also play a role. The *total* energy that such an impact would add to the earth is the sum of the projectile's gravitational potential energy, ca.  $6.7 \times 10^6$  J/kilogram of the earth, and the projectile's kinetic energy,  $0.054 v^2$  per kilogram of the earth, where  $v$  is the encounter velocity between the projectile and the proto-earth. Taking a typical silicate heat capacity of 700 J/kg°K and a latent heat of melting of  $4.2 \times 10^5$  J/kg, this implies that even if the entire earth's mantle started out cold, the distributed energy of the impact would raise the earth's mean temperature nearly 9,000 °K for  $v=0$ . For  $v=10$  km/sec the mean temperature would rise by more than 16,000 °K. Given a mantle liquidus in the neighborhood of 3000 °K (6), it is clear that melting, even vaporization, must be widespread in such a collision.

Although the total energy available from the collision of a Mars-size projectile with the proto-earth is impressive, the *distribution* of the energy within the earth is equally important. If, as has been suggested by Stevenson (7), this energy is mainly expended in vaporizing the projectile, the earth may acquire a transient silicate vapor atmosphere without strongly heating the deeper mantle. Some simple considerations of the physics of impact cratering makes this situation unlikely, however. When two bodies collide at high speed, strong shock waves propagate from the point of the impact into the adjacent target and projectile. These shock waves weaken as they spread, with

the maximum pressure falling off approximately as  $P_0(r/r_p)^{2-3}$ , where  $P_0$  is the pressure at the contact between projectile and target,  $r_p$  is the projectile radius and  $r$  is the distance from the impact site. Although the complex geometry in a planet-sized collision makes this relation difficult to apply exactly, it suggests that if  $r_p$  is roughly half the earth's radius, the shock pressure at the earth's center is at most a factor 5 less than  $P_0$ . But even in the lowest velocity impact, when the projectile strikes at the earth's escape velocity, 11.2 km/sec,  $P_0$  is on the order of 240 GPa, so that the shock pressure perturbation deep in the earth generally exceeds about 50 GPa. This is close to the shock pressure needed to cause melting in initially cold rocks.

To address the temperature rise in the earth more exactly, we have performed a series of 2-dimensional numerical hydrocode computations designed to simulate the impact between the proto-earth and a Mars-size protoplanet. We used the code CSQ II, implemented on the Cray II supercomputers of the Sandia National Laboratory. This computation uses realistic equations of state for dunite in the mantles and iron in the cores of the two colliding planets. The earth has a central gravitational field, and is initially adjusted so that it has a temperature profile similar to that of the present-day earth. These models thus start out relatively cold, with the mantle temperatures initially below the solidus of dunite. We have performed computations at a variety of initial velocities and impact parameters, including pairs that give the earth-moon system its present angular momentum.

At the lowest velocity ( $v=0$ ), for impact parameters of 0.5, 0.88, 1.0, and 1.25 times the earth's radius, the strongest heating upon impact is initially confined to the hemisphere on which the projectile strikes. Temperatures rise typically 3,000 to 4,000 °K between the site of the impact and the earth's core. Unfortunately, our computations do not extend to long enough times for the entire projectile to merge with the earth in the high impact parameter runs. In these cases we had to stop the computation while some of the projectile was still falling on portions of the earth more distant from the impact site. In these cases we believe that more than half the mantle will be strongly heated, so the quoted results must be seen as a lower limit.

The results for the higher impact velocity  $v = 7.8$  km/sec are more spectacular. For all the impact parameters studied (0.5, 0.59, 1.0, and 1.25 earth radii) the mantle was heated nearly uniformly by 3,000 to 4,000 °K. The projectile's core was almost entirely vaporized, being heated to more than 8,000 °K after release from high pressure. A fast, much hotter vapor plume also carries several lunar masses of material out along trajectories that eventually take up elliptical orbits about the earth.

These computations, in conjunction with the more general considerations described above, indicate that a moon-forming impact would have had a profound effect on the earth's thermal state. The shock produced by the impact would have heated the earth to great depths, raising at least the hemisphere adjacent to the impact above the melting temperature. There seems to be no way to avoid the conclusion that a large moon-forming impact is inevitably accompanied by widespread melting of most or all of the earth's mantle. This scenario raises implications for the geochemistry of the earth that will be dealt with in an accompanying abstract (8).

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EFFECT OF TOTAL PRESSURE AND OXYGEN FUGACITY ON CONDENSATION AND EVAPORATION BEHAVIOR OF HIGH-TEMPERATURE REFRACTORY PHASES IN THE EARLY SOLAR NEBULA. B. O. Mysen, Geophysical Laboratory, 2801 Upton St., N.W., Washington, D.C., 20008, USA.

Evaporation, condensation and melting behavior in the system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> has been determined experimentally to 2000°C between 10<sup>-2</sup> bar and 10<sup>-10</sup> bar pressure. The pressures were determined with the weight-loss technique in Knudsen cells<sup>[1]</sup>, calibrated for the present experiments by<sup>[2]</sup>. The pressure uncertainties are ±0.3-0.4 log units. The oxygen fugacity was controlled with the Mo-MoO<sub>2</sub> (MMO) and C-CO-CO<sub>2</sub> (CCO) buffers, which yield f(O<sub>2</sub>) in the range from 1-1.5 orders of magnitude above and 3-3.5 orders of magnitude below, respectively, that of the iron-wüstite f(O<sub>2</sub>) buffer. Temperatures were monitored with W-W74Re26 thermocouples.

Phase relations involving enstatite, forsterite, silica, hibonite, calcium dialuminate, corundum and spinel have been determined. At pressures above 10<sup>-4</sup>-10<sup>-7</sup> bar (depending on composition), melt occurs in the condensates. All phases except corundum, silica and forsterite melt incongruently. For the aluminates, initial melting produces corundum+liquid, whereas for enstatite, initial melting results in forsterite + liquid. With dilution of the gas phase appropriate for the early solar nebula, melt + crystals will condense in the subsystems MgO-SiO<sub>2</sub> and CaO•2Al<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> at pressures above ~10<sup>-1</sup> bar, whereas for MgAl<sub>2</sub>O<sub>4</sub>, melt is stable only at total pressures above 10<sup>1</sup> bar. Fractional distillation of liquid will result in forsterite + corundum + spinel in the residue with total pressure between 10<sup>-1</sup> and 10<sup>1</sup> bar, whereas at higher pressures, the residues will be essentially forsterite+corundum.

The evaporation phase relations at pressures below that where liquid is stable are strongly dependent on oxygen fugacity. Whereas at the f(O<sub>2</sub>) of the MMO buffer, all phases except enstatite evaporate congruently, at the f(O<sub>2</sub>) of the CCO buffer, hibonite and spinel evaporate incongruently to corundum and an Mg- or Ca-rich gas, respectively. The corundum, spinel and hibonite vaporous volumes are, therefore, sensitive to f(O<sub>2</sub>). Enstatite evaporates incongruently under all conditions to forsterite+Si-rich vapor.

The enthalpies of evaporation derived from experimentally-determined vapor pressure versus temperature curves;

$$\ln P_v = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (1)$$

have been used to construct vaporous phase diagrams for the system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (Fig. 1). In the pressure range 10<sup>-1</sup>-10<sup>-4</sup> bar, the earliest phases to condense from solar nebula gas are forsterite+spinel+calcium dialuminate (CA2) with the condensation sequence spinel→forsterite→CA2 at P>10<sup>-3</sup> bar and forsterite→spinel→CA2 at P<10<sup>-3</sup> bar. At the f(O<sub>2</sub>) of the MMO buffer, the latter sequence remains to lower pressure, whereas at the f(O<sub>2</sub>) of the CCO buffer, the earliest phases are forsterite+corundum+hibonite+spinel to pressures

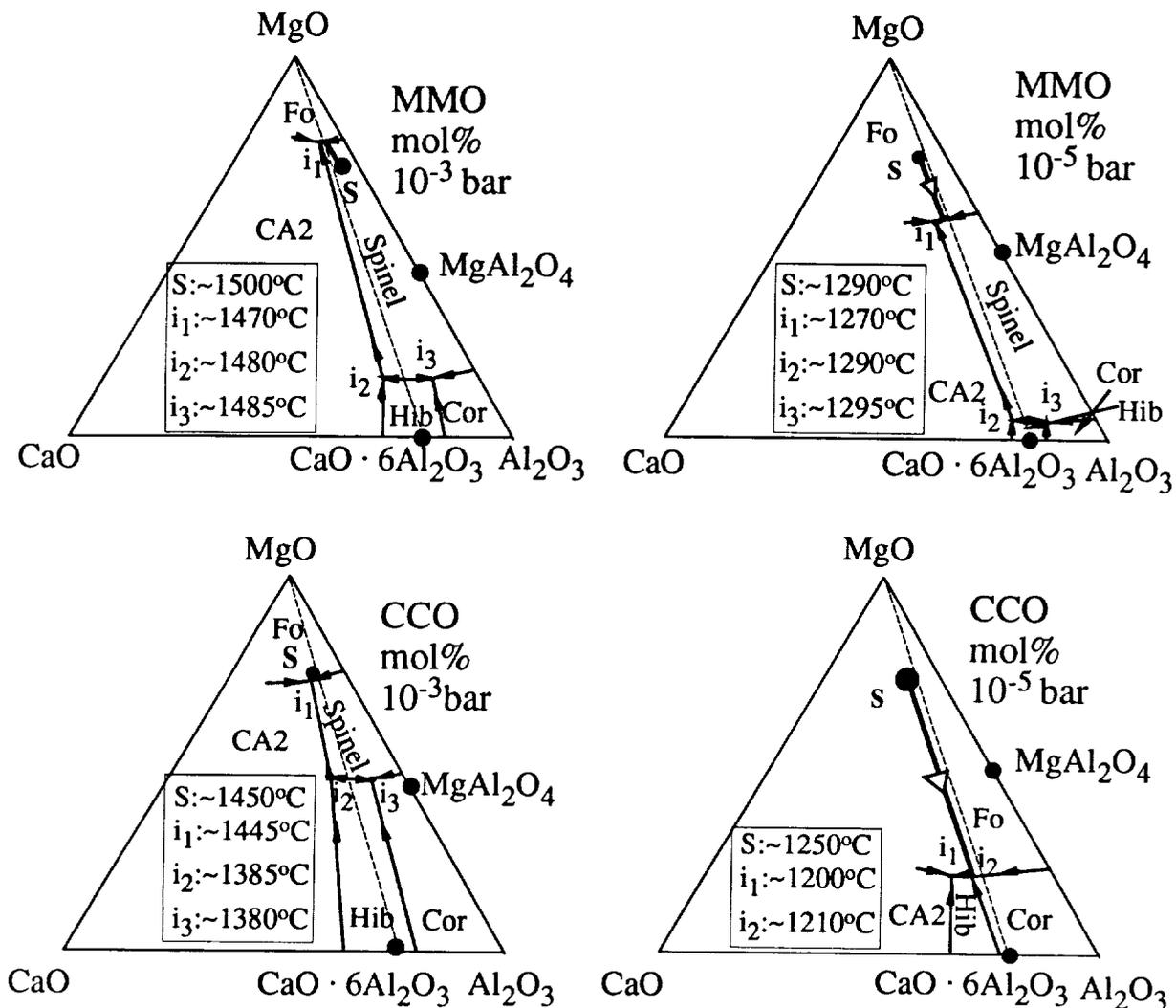


Figure 1 - Vaporous phase relations in the system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> at pressure and oxygen fugacities as indicated. Abbreviations: Fo = forsterite, CA2 = calcium dialuminate, Hib = hibonite, Cor = corundum. Inserts indicate temperatures as reaction points and S.

above about 10<sup>-5</sup> bar, and forsterite+corundum+hibonite at lower pressure. The absence of spinel on the vaporous at P<10<sup>-5</sup> bar is controlled by the reaction relationship between vapor and corundum at the f(O<sub>2</sub>) of the CCO oxygen buffer. Because of the reaction relationships between enstatite and vapor, enstatite will condense later than forsterite under all conditions investigated.

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HETEROGENEOUS ACCRETION OF THE EARTH: EVIDENCE FROM  
SIDEROPHILE ELEMENTS AND THE COMPOSITIONS OF ASTEROIDS AND METEORITES.  
H.E. Newsom, Dept. of Geology and Institute of Meteoritics, Univ. of New Mexico, Albuquerque,  
NM 87131, U.S.A.

Several types of geochemical evidence suggest that the Earth did not accrete from a single reservoir of material with a unique composition and oxidation state. Evidence for heterogeneous accretion of the Earth comes from siderophile elements, volatile elements, and the chemical and isotopic composition of the atmosphere. The variability in the composition of meteorites and asteroids may provide clues to the nature of the early solar system, which allowed for different sources of material to contribute sequentially to the accretion of the Earth.

The siderophile elements provide evidence for heterogeneous accretion involving a large fraction of the Earth's mass. The depletion of siderophile elements in the Earth's primitive mantle (i.e. the Earth's silicate portion) can be divided into two groups [1, 2]. The moderately siderophile elements are 0.1 to 0.01 of chondritic abundances, while the highly siderophile elements are all approximately 0.002 times chondritic. New data for the moderately siderophile elements Mo and W [3], and As and Sb [4] are consistent with this conclusion (Fig. 1). Wänke [5] explained this pattern in terms of a two component model, with the Earth accreting initially from a highly reduced volatile-free component, followed by a volatile-rich oxidized component after approximately two thirds of the Earth had accreted. During this second phase of accretion, the concentrations of the moderately siderophile elements built up to their present levels, but the abundances of the highly siderophile elements must have remained below their present levels due to a small amount of metal or sulfide segregation [3]. The final stage of accretion, amounting to less than 1% of the mantle, brought in the so-called late veneer after all core formation had ceased, and established the observed chondritic relative abundances of the highly siderophile elements. The composition of the accreting material as a function of the percent accretion of the Earth for this model is shown in Fig. 2.

The accretion of a late veneer on the Earth has been criticized due to the possible lack of evidence for such a veneer of material on the Moon [6]. The important questions include, the depth to which the veneer is mixed on the Earth and Moon, and the relative accretion rates for the Earth and Moon. Morgan et al. [7] has shown that the veneer material could be accounted for in the lunar regolith, for the restrictive assumptions that the veneer was only mixed to a depth of 670 km on the Earth, and that about 33 times as much material accreted to the Earth, as to the Moon, due to gravitational focusing [8]. Another possibility is that the late veneer is due to material from the core of an impactor connected with the origin of the Moon [6,9].

An alternative model for the abundances of siderophile elements in the mantle, inefficient core formation, has been explored by Jones and Drake [10]. They suggest that small amounts of Fe-metal and S-rich metallic liquid containing siderophile elements could have been left behind in the mantle during core formation. Heterogeneous accretion, however, is also consistent with the volatile element evidence, including the existence of liquid water on the Earth's surface [11]. Liquid water would not be stable in the case of homogeneous accretion of material containing approximately 30% Fe-metal.

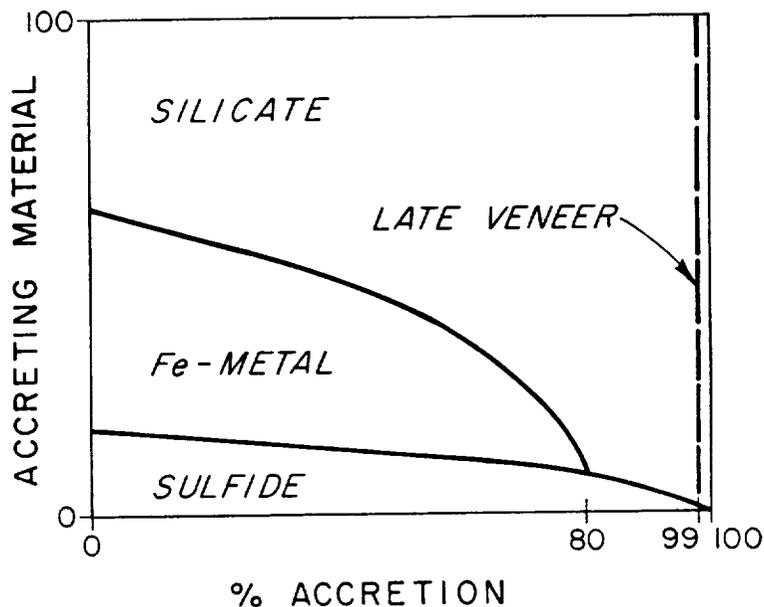
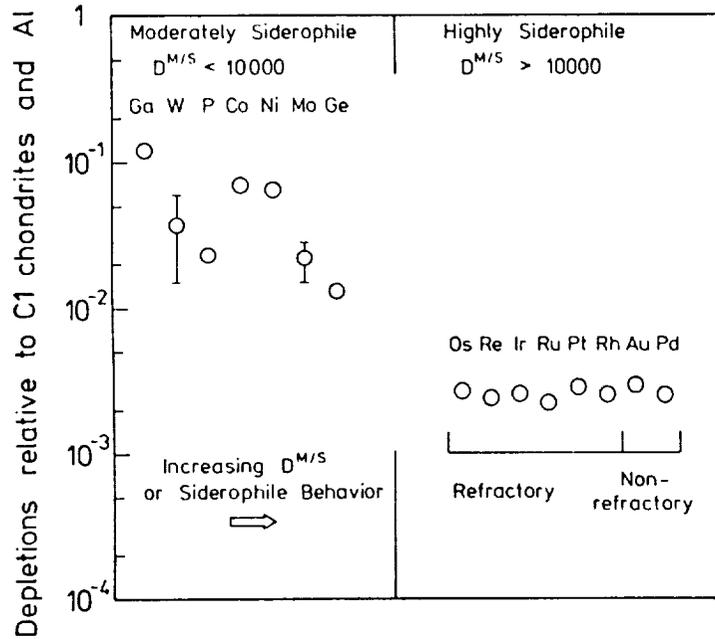
Both heterogeneous accretion and inefficient core formation models have problems explaining the low sulfur abundance and the chondritic Ni/Co ratio in the mantle [10]. Another problem with both models is the remarkable homogeneity of siderophile elements in mantle derived samples. This homogeneity in the mantle could be explained by melting and rapid convection due to giant impacts, if differentiation of the mantle can be avoided.

The assumption that the Earth accreted heterogeneously from several different reservoirs of material raises the question of the location of these reservoirs. The origin of this material can be explained by widespread transport of material across large heliocentric distances, including from the asteroid belt [12], but an alternative hypothesis is the accretion of the Earth from planetesimals with variable compositions that formed in the vicinity of the proto-Earth, analogous to the highly variable asteroid spectral types in the asteroid belt [13]. Spectral observations of asteroids reflect the diversity of materials in the asteroid belt, with 14 distinct classes in different regions of the main belt. Recent theoretical and observational evidence suggests that the meteorites are derived from the asteroid belt at 2 to 3 A.U.. As an example of the variability in meteorite compositions, the metal content of the 8 primitive chondrite groups and the primitive meteorites Bencubbin, Kakangari and ALH 85085 ranges from 0-35 wt%, and they are all presumably derived from the inner asteroid belt. Therefore the composition of the Earth may be due in part, to the stochastic order of assembly of the components available in the vicinity of the Earth.

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Fig. 1. Depletion of siderophile elements in the primitive mantle [3].

Fig. 2. Schematic illustration of the composition of accreting material during the formation of the Earth.



6 Ga  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  'AGE' OF ZAIRE CUBIC DIAMONDS: PRE-SOLAR OR EXCESS  $^{40}\text{Ar}$ ?. M. Ozima<sup>1</sup>), S. Zashu<sup>1</sup>), Y. Takigami<sup>1</sup>), G. Turner<sup>2</sup>),  
<sup>1</sup>Geophysical Institute, The University of Tokyo, Tokyo 113, JAPAN; <sup>2</sup>Department of Physics, The University of Sheffield, Sheffield, U. K.

Zashu et al. (1) reported that ten cubic diamonds from Zaire yielded excellent linear correlations in both  $^{40}\text{Ar}$ - $K$  and  $^{40}\text{Ar}/^{36}\text{Ar}$ - $K/^{36}\text{Ar}$  diagrams. If the linear arrays are assumed to be isochrons - which is the basic premise in  $K$ - $\text{Ar}$  dating - the ages would be about 6 Ga which is older than the age of the Earth. As possible interpretations of the extraordinary age, they suggested (i) that experimental artefact, (ii) that the  $^{40}\text{Ar}$  in the diamonds is excess  $^{40}\text{Ar}$  and has no age meaning, (iii) that the basic assumptions underlying the  $K$ - $\text{Ar}$  dating method, such as the constancy in  $^{40}\text{K}/K$  isotopic ratio and of the decay constant  $\lambda_e$  of  $^{40}\text{K}$ , were not satisfied, or (iv) that the diamonds or the inclusions in the diamonds are pre-solar.

As the experiments were repeated with different mass spectrometers, gas extraction lines and calibration systems both for argon and potassium to yield the identical results, the experimental artefact can be safely dismissed. As to the third possibility, Podosek et al. analysed two Zaire cubic diamonds from the same group used for the  $K$ - $\text{Ar}$  dating, and found normal  $K$ -isotopic composition (2). This result also rules out the possibility of change in  $\lambda_e$ . Consequently, we are left with the remaining two possibilities, (ii) excess  $^{40}\text{Ar}$  or (iv) a pre-solar origin. We therefore applied the  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  stepheating dating on four Zaire cubic diamonds from the same group as in the previous  $K$ - $\text{Ar}$  dating(1) and  $K$  isotopic studies(2) to examine whether the  $^{40}\text{Ar}$  is excess or in situ decay radiogenic.

In an  $^{40}\text{Ar}/^{36}\text{Ar}$ - $K/^{36}\text{Ar}$  diagram where  $K$  was measured as  $^{39}\text{Ar}$ , there is an excellent linear correlation (Fig.1). Thermal release patterns for  $^{40}\text{Ar}$  and  $^{39}\text{Ar}$  are identical. Both the experimental results suggest strongly that the  $^{40}\text{Ar}$  is in situ decay radiogenic, and therefore the correlation line represents 'an isochron'. The calculated 'isochron age' is 5.7Ga which agrees well with the  $K$ - $\text{Ar}$  isochron 'age' of the diamonds.

However, the  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  stepped heating experimental data also show that  $^{38}\text{Ar}$  derived from  $\text{Cl}(^{37}\text{Cl}(n, \gamma, \beta^-)^{38}\text{Ar})$  correlates excellently with the  $^{40}\text{Ar}/^{36}\text{Ar}$ - $\text{Cl}/^{36}\text{Ar}$  diagram (Fig.2), and a thermal release pattern for  $^{38}\text{Ar}$  is identical with those for  $^{39}\text{Ar}(K)$  and  $^{40}\text{Ar}$  (Fig. 3). The observed excellent correlations and also the identical thermal release patterns among  $^{40}\text{Ar}$ ,  $K(^{39}\text{Ar})$  and  $\text{Cl}(^{38}\text{Ar})$  can be most reasonably explained by fluid inclusions which leached  $K$ ,  $\text{Cl}$ , as well as  $^{40}\text{Ar}$  from environmental rocks and were trapped in the diamonds, since trace elements, once leached in fluids, would be well homogenized to give rise to uniform elemental ratios. They would also give an identical thermal release pattern, because they were trapped as fluid inclusions at the same sites. Na analysed by INAA for five Zaire diamonds from the same group as those for this study also correlates excellently with  $K$ , of which  $K/\text{Na}$  ratio is about 3. The supposed fluid inclusions are very likely to

correspond to sub-micron fluid inclusions recently found in several cubic diamonds including two from Zaire and attributed to pristine mantle fluids by Navon *et al.*(3)

Other noble gases ( $\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $\text{Kr}$ ,  $\text{Xe}$ ) show thermal release patterns quite distinct from  $^{40}\text{Ar}$ ,  $^{39}\text{Ar}$  and  $^{38}\text{Ar}(\text{Cl})$  (Fig. 3), indicating that they are of a different origin from the  $^{40}\text{Ar}$ . Since these noble gases are quite tightly trapped in the diamonds judging from the thermal release patterns, and also  $\text{Ne}$  has non-atmospheric but solar-like isotopic ratios (4), they must have been trapped in the diamonds during crystallization in the mantle. The two distinct residing sites for noble gases can be best explained on the basis of a two stage growth model for cubic diamonds concluded by Boyd *et al.*(5); while the most of the  $^{36}\text{Ar}$  and other noble gases were trapped in the core of cubic diamonds,  $^{40}\text{Ar}$  was later trapped as fluid inclusions in the coat of diamonds in the upper mantle. The solar like  $\text{Ne}$ (4) which resided in the core then represents the mantle region where the core of the diamonds crystallised, possibly in the deeper mantle.

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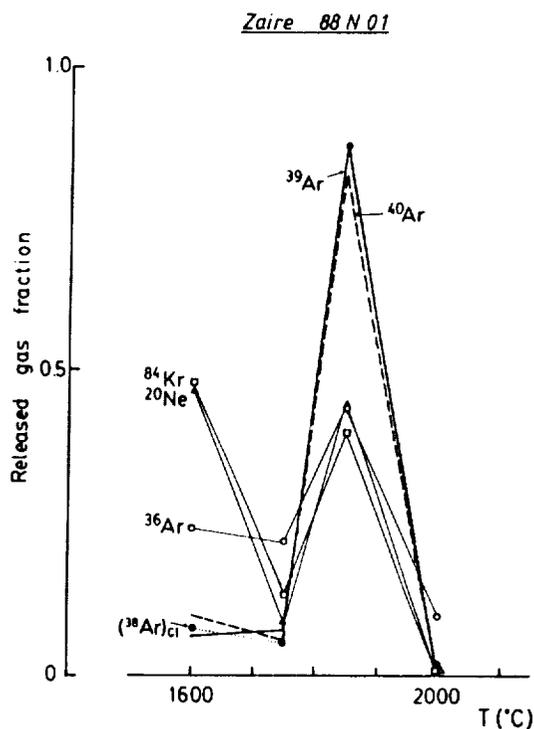
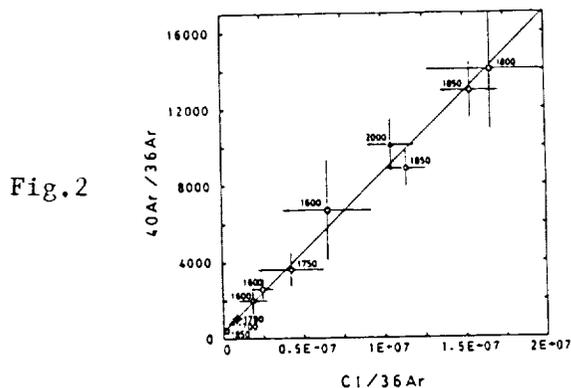
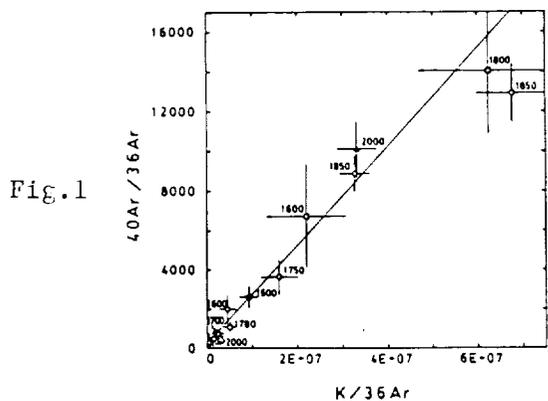


Fig.3

THE CHEMICAL COMPOSITION OF THE EARTH

H. PALME AND H. WÄNKE, Max-Planck-Institut für Chemie, Saarstr. 23, D-6500 Mainz, F.R. Germany

A Major Elements

The major element composition of the Earth is essentially chondritic: The elements Si, Mg, Al, Ca, and Fe occur in the bulk Earth in the same proportions as in chondritic meteorites and in the photosphere of the Sun i.e. in the average solar system. This can be demonstrated by simple mass-balance equations, assuming 32% of the mass of the Earth to be in the core.

Mass balance equation for the mantle (only major components):

$$\text{MgO} + \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{CaO} + \text{FeO} = 100$$

By inserting chondritic ratios of  $\text{SiO}_2/\text{MgO}$ ,  $\text{Al}_2\text{O}_3/\text{MgO}$  etc. one obtains an equation relating MgO of the upper mantle to FeO. Such relationships are plotted in Fig. 1 for different types of chondritic meteorites. If, for example, the bulk Earth had a CI-chondritic composition, the composition of its mantle must plot along the line labeled CI.

Mass balance for the core:

$$\text{Fe}_{\text{core}} \times X_{\text{core}} + \text{Fe}_{\text{mantle}} \times (1 - X_{\text{core}}) = \text{Mg}_{\text{mantle}} \times (1 - X_{\text{core}}) \times (\text{Fe}/\text{Mg})_{\text{bulk}}$$

Assuming a chondritic Fe/Mg-ratio for the bulk Earth (Fe/Mg is constant in different types of carbonaceous chondrites, in contrast to Si/Mg) and 32% by weight for the core, it is possible to calculate a second relationship between FeO and MgO with opposite slope. This is also shown in Fig. 1 where two cases for the amount of Fe in the core are considered: 80% (A) and 75% (B). The intersection of these lines with the FeO-MgO-mantle correlation lines define the MgO and FeO (and thus the composition) of the mantle. The composition of the mantle of a CV-chondrite Earth with 32% core and 75% iron in the core is given in Tabl. 1. Estimates from upper mantle rocks are also listed in this Table and plotted in Fig. 1. The good agreement of the CV-model composition with those derived from upper mantle rocks demonstrates that the Earth is basically chondritic in composition.

Fig. 2 shows the Earth's mantle compositions in a Mg/Si vs. Al/Si diagram (1). Both ratios are higher in the mantle of the Earth than in most meteorites classes. Two possibilities exist: 1.) The mantle of the Earth is inhomogeneous; The lower mantle has a lower Mg/Si ratio thus compensating for the high upper mantle ratio and the bulk Earth could have a CI-ratio.

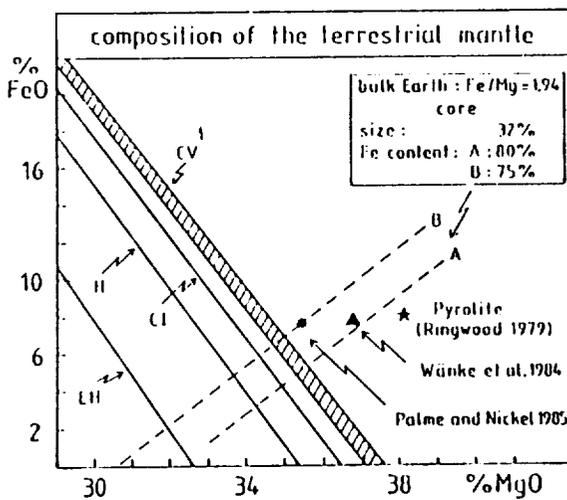


Fig. 1

Fig. 2

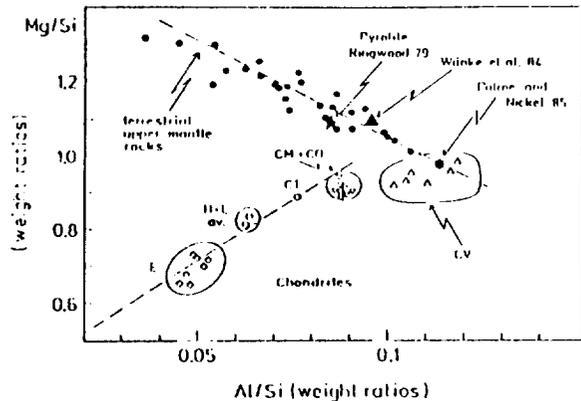


Table 1: Composition of the Earth's mantle

	Based on analyses of upper mantle rocks			Chondritic Earth (CV)
	(A)	(B)	(C)	
SiO <sub>2</sub>	45.1	46.3	45.9	48.0
MgO	38.1	35.5	36.9	37.0
Al <sub>2</sub> O <sub>3</sub>	3.3	4.8	4.2	4.2
CaO	3.1	4.4	3.5	3.4
FeO	8	7.7	7.6	7.4

(A) Pyrolite, Ringwood (4); (B) Wänke et al. (2); (C) Palme and Nickel (5).

## CHEMICAL COMPOSITION OF THE EARTH

Palme H. and Wanke H.

## 2.) The mantle of the Earth is homogeneous in composition.

This either implies a bulk composition of the Earth similar to CV-chondrites, or it may reflect loss of Si from the upper mantle.

Si may be lost either by volatilization or by partitioning into the core (see 2 and references therein). There is at present no convincing evidence to strongly favour any of the above mentioned possibilities.

B Trace Elements

Refractory elements occur in chondritic relative abundances in the upper mantle of the Earth. It is therefore not to be expected that they are grossly different in the lower mantle. The absolute contents of refractory elements (i.e. Al/Si-ratio) is somewhere between the CV and the CI ratio (Fig. 2).

The most volatile among the refractory element, V, as well as Cr and Mn are considerably depleted in the upper mantle rocks. It is difficult to explain these depletions by volatility alone. Some fraction of these elements may have partitioned into the core in an early more reducing stage of the evolution of the Earth. Simultaneously some Si could have entered the core.

Moderately volatile lithophile elements (Na, K, Rb, Li, F) are depleted in the upper mantle of the Earth. This may either be a characteristic property of the material that made up the Earth or it may reflect loss of volatile and moderately volatile elements during accretion (perhaps loss of an early hot atmosphere containing some fraction of these elements).

The pattern of siderophile and chalcophile elements is complicated and cannot easily be explained by a single process. The contents of Ni, Ir, etc. in the upper mantle rocks are far too high to record equilibrium between metal (core) and silicate (mantle). It is possible, although unlikely, that equilibrium occurred at greater depths where metal/silicate partition coefficients would be lower. It has also been suggested that the high content of siderophiles in the upper mantle reflects incomplete separation of metal to the core (3). Another possibility is some type of inhomogeneous accretion, where the accreting material becomes more and more oxidized as accretion proceeds. The last spike of matter is so oxidized that metallic Fe is no more stable and siderophile elements are quantitatively retained. The highly oxidized crust of the Earth as well as the uniform enrichment of highly siderophile elements (Ir, Pt, Ru, Os, etc.) in the upper mantle speak in favour of this model. Before this final stage of accretion, conditions were still fairly oxidizing therefore only very Ni-rich metal and/or sulfide was able to segregate to the core. In fact, the high Ni-content of the upper mantle olivine (3000 ppm) records the equilibrium with Ni-rich metal. Only metal with 80 to 90% Ni could coexist with such an olivine. Under these conditions only elements with high metal (sulfide)/silicate partition coefficients can be extracted to the core, primarily highly siderophile elements. Other elements would be less affected, depending on their metal (sulfide)/silicate partition coefficients.

In summary, the Earth is, in a broad sense, chondritic, but it is not clear if the Earth composition is identical to any of the groups of chondritic meteorites. The CV-chondrites, for example, would come closest to the major element composition of the Earth. There are, however, differences in oxygen fugacity and oxygen isotopic composition that exclude this type of meteorite as a parent material for the Earth. For a more detailed understanding of the bulk composition and the accretion history the following questions need to be answered:

- 1.) What is the light element(s) in the core?
- 2.) Is the lower mantle different in composition from the upper mantle?
- 3.) Were volatile elements lost during the accretion of the Earth?
- 4.) What processes were responsible for establishing the presently observed pattern of siderophile and chalcophile elements in the upper mantle?
- 5.) What fraction of the mantle has the typical upper-mantle pattern of these elements?

Furthermore, additional data are required to obtain better upper mantle abundances, as the abundances of some of these elements are only poorly known.

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## PLANETARY ACCRETION BY RUNAWAY GROWTH: FORMATION OF THE EARTH

Chris Patterson, Los Alamos National Laboratory, Los Alamos, NM 87545, and  
Dominique Spaute, PSI, 2030 E. Speedway, Tucson, AZ 85719

The outcome of runaway growth is examined in the Earth's accretion zone. It is found that runaway growth of a few planetary embryos quickly leads to high relative velocities ( $>10$  m/sec) of the 1- to 10-km diameter swarm planetesimals due to gravitational stirring. Such velocities cause the swarm planetesimals to fragment by mutual collisions. This fragmentation of swarm planetesimals during runaway growth leads to a size distribution with most of the mass in fragments less than 10-m diameter independent of the initial planetesimal size.

In the presence of solar nebula gas, these fragments will have reduced relative velocities and enhanced accretion cross sections with the embryos, thereby aiding in their rapid runaway growth. Orbital decay due to gas drag enables fragments to be continuously fed to the embryos and greatly expands their feeding zones. It seems likely that much of the Earth accreted from fragments originally at much farther distance from the Sun, possibly including fragments originally in the asteroid belt.

**ON THE LOSS OF EARTH'S PRIMORDIAL ATMOSPHERE.** R. O. Pepin, School of Physics and Astronomy, University of Minnesota, Minneapolis, MN 55455

It is possible, perhaps probable, that a preexisting atmosphere would have been largely lost in a Moon-forming collision of a very large body with Earth (1). Thus it is of interest to consider evolutionary scenarios in which the Earth's primary atmosphere, coaccreted prior to the collision from volatiles captured from the nebula and degassed from impacting planetesimals, was ejected in this way. Loss of primary volatiles in an appropriately timed giant impact event turns out to be an attractive way to deal with an intrinsic problem in the nebular capture hypothesis when applied to both Earth and Venus. It could also explain why a 15% carbonaceous chondrite (CI) accretional component, invoked for Earth on geochemical grounds (2,3), has left no detectable signatures in contemporary noble gas distributions.

Hunten's expression  $p_s = p_n e^{\lambda}$  (4) for the surface pressure of gravitationally condensed nebular gases, together with equations for radial temperature (T) and pressure ( $p_n$ ) profiles from a current accretion disk model (5), are taken to approximately describe isothermal capture of nebular matter by planets. The exponent  $\lambda$  is  $GM_p \mu / kTr = [1.845 \times 10^{-15} (M_p/r)^{2/3}] / T$  with nebular molecular weight  $\mu = 2.3$  amu and present planetary mass  $M_p$  and radius  $r$  in cgs;  $f$  is the fraction of  $M_p$  accumulated at the time of capture. The column mass of an accreted species of molecular weight  $M$  is  $(1.013 \times 10^6) S_M (M/2.3) p_s / g f^{1/3}$  g/cm<sup>2</sup>-planet, where  $S_M$  represents the nebular partial pressure of  $M$ ,  $p_s$  is in atm, and  $g$  = present surface gravity.

Now suppose that all of the solar-composition gases in a primary atmosphere derived from nebular capture. Then on Venus, using Ar for illustration, the accreted amount is 6.05 g<sup>36</sup>Ar/cm<sup>2</sup>-planet in one example model. From the equations above  $p_s \approx 59$  atm and  $\lambda = \ln(p_s/p_n) = 1.484 \times 10^4 / T$ , assuming  $f = 1$  for the moment. In Wood and Morfill's (5) model of the solar accretion disk, temperatures and pressures are both proportional to  $(dm/dt)^{2/3}$ , where  $dm/dt$  is the rate of mass flow into and out of the disk. Self-consistent values of T and  $p_n$  at Venus' radial distance that satisfy these expressions for  $\lambda$  can be found for a particular value of  $dm/dt$ . In the present example they are  $T = 930$  K and  $p_n = 7.0 \times 10^{-6}$  atm for  $dm/dt = 0.59$  (in units of solar masses/10<sup>6</sup> yr). Capture of the primary solar gas component on Venus thus requires a somewhat cooler and more tenuous nebula than in the illustrative example given by Wood and Morfill, where their nominal choice of  $dm/dt = 1$  yields  $T = 1325$  K and  $p_n = 1.0 \times 10^{-6}$  atm at 0.72 AU. With  $dm/dt = 0.59$ , the Wood-Morfill formulation yields (T,  $p_n$ ) values at 1.0 and 1.52 AU of (570 K,  $3.4 \times 10^{-6}$  atm) and (305 K,  $1.3 \times 10^{-6}$  atm) respectively, and with these the predicted concentrations of <sup>36</sup>Ar on Earth and Mars from nebular capture are readily calculated using the above equations. They are very high for Earth and negligible for Mars. The  $f = 0.6$  case, as expected, requires a significantly cooler nebula and lower mass flux through the disk for equivalent gas capture by planets that were only 60% accumulated.

The enormous amount of accreted <sup>36</sup>Ar predicted for Earth is largely an artifact of the breakdown of the isothermal assumption in Hunten's (4) equation under conditions of high capture. Atmospheric heating by release of accretional energy leads to hydrostatic equilibrium at much lower surface pressures. However, more realistic estimates, calculated from a detailed treatment of nebular capture on Earth (6), still exceed the model abundances of <sup>36</sup>Ar in the primary terrestrial atmosphere by factors of  $\approx 50$ -500. Thus if temperature and pressure in a Wood-Morfill nebula were such that the full complement of primary solar gases required for Venus was accreted from the nebula, Earth would have captured far too much of these gases and consequently its original primordial atmosphere must have been almost completely removed.

Stripping of this atmosphere might have left behind the "correct" amounts of solar-composition gases on Earth; or, alternatively they were later resupplied as a second-generation primary atmosphere. Incomplete loss probably cannot account for the solar gas component, since one would expect impact-erosion residues of a few percent or less to be

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fractionated (7). It seems more likely that a primary atmosphere reaccumulated on the planet, principally from the nebula. If so, there are consequences relating to the timing of a giant impact and the subsequent physical state of the proto-Earth. Resupply from ambient gases would require an early collisional event, prior to nebular dissipation at  $t_0 \approx 1-10$  myr. In addition, the abundances of gases recondensed after the event must have been lower, compared to amounts captured prior to impact, by factors of  $\approx 50-500$  as noted above. Important considerations in addressing this latter requirement are the thermal state of the post-impact proto-Earth, its collisional spinup to high angular velocity, and the consequences of this environment for Hunten's (4) simple barometric law for isothermal nonrotating atmospheres. While not yet studied in detail, the combined effects of higher temperature and possibly rapid atmospheric rotation (4) could have limited the efficiency of post-impact nebular gas capture.

A giant collisional event would also have removed the volatiles accumulated in Earth's original primary atmosphere from impact-degassing of planetesimals accreted prior to the event. This poses a problem in accounting for the presence at  $t_0$  of the isotopically solar but elementally fractionated noble gases (the "P"-component) needed in the models to match observed distributions. But it also allows us to address the issue of how the large contribution of CI-type volatiles implied by a 15% CI accretional component in Earth might be accommodated.

There are several possible *ad hoc* explanations for the presence of P-type gases in the regenerated post-impact primary atmosphere: accretion of refractory carriers of adsorbed P-component gases after the impact but prior to  $t_0$ ; accretion of P-carrying cometary matter in the same time interval; or survival of a remnant of the earlier atmosphere. The latter may be the most plausible way to account for this component in the context of the giant impact hypothesis. It requires post-impact retention of  $\sim 0.4 - 4\%$  of pre-impact xenon abundances, and progressively smaller fractions of the lighter noble gases, consistent with the elemental fractionation expected in a surviving residue of collisional atmospheric ejection.

As to the possibility of a large volatile component in the original primary atmosphere from accretion and degassing of CI material, let us assume it was there. In the case of total atmospheric expulsion by impact, there would be no survival of CI isotopic signatures in present-day terrestrial noble gas compositions, as observed, and therefore no problem. But suppose instead that a fraction of this atmosphere remained as the "P-component". Isotopic compositions of P-gases are required to be solar or nearly so in the present models, but with this origin as atmospheric residues they are sensitive to the pre-impact mixing ratios of CI and solar components, and so there is a constraint on these ratios. It turns out, however, that the gases contributed by a 15% CI mass fraction in the planet are marginally allowed: residual "P-component" Xe compositions are only slightly heavier than solar, and all final Xe isotope ratios calculated for Earth are within  $< 2\sigma$  of expected values.

It appears that gravitational condensation of nebular gases is a feasible way to supply solar-composition noble gases to the primary atmospheres of Earth and Venus. The process is very inefficient for Mars, in agreement with atmospheric modeling. Required accretion disk temperatures are on the cool side of many estimates, but not unreasonably so. The particularly interesting result, with respect to the giant Moon-forming impact theory, is that nebular conditions leading to accretion of the Venus solar inventory imply a large oversupply on Earth. If capture models are to be viable most of this excess must be ejected from the planet.

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## IRON ORES AND EARTH EVOLUTION

J.A. Philpotts, MS 923, U.S. Geological Survey, Reston VA 22092

Olympic Dam, Australia; Kiruna, Sweden; Bayan Obo, China; and the Missouri ferroan felsic association, are all examples of billion-ton concentrations of iron oxides considered to be of mid-to late-Proterozoic age (1). Although these deposits differ in many characteristics, their large size, unusual features, and approximate contemporaneity suggest that they may be differing manifestations of similar processes. At the very least, the deposits appear to reflect unusual conditions in the crust and/or mantle. Iron enrichment also occurs in iron-titanium deposits and ferro-syenites in rocks of the anorthosite association, many of which are of similar age (2) and could be a related phenomenon. Most of the deposits appear to be internally derived, and several show highly enriched light rare-earth abundance patterns.

Large-scale hydrothermal circulation or igneous processes involving contamination or extreme fractionation, perhaps with liquid immiscibility enhanced by phosphorus or carbon content, are among possible genetic processes for these iron ores. For some igneous ores, the high-level emplacement of high-specific-gravity oxides would seem to require extensive fractionation at low pressure or transport of the iron from depth as silicate, carbonate, or volatile-rich fluid. Some deposits show little crustal geochemical signature; mantle contributions (in addition to any thermal contribution) are indicated. The deposits do not seem related, in general, to either immediate subduction or extensive basaltic volcanism. Plumes appear to be a more likely mantle source. If it is of mantle origin, high iron content might come from extensive fractionation; scavenging by volatiles; recycling of subducted 2 Ga sedimentary banded iron formation (BIF) or carbonate; or oxidized (C-Ti-P bearing?) iron from the D" layer at the core-mantle interface.

Some BIF may have an origin similar to that of the internally derived iron deposits. The concentration of BIF around 2 Ga has been ascribed to increased oxygenation of the atmosphere/hydrosphere to levels leading to the formation of iron oxide (3). However, this requires a fine balance through time of iron, oxygen, and sulfur in diverse environments. The similarity of Archean and Proterozoic BIF (4) in spite of likely environmental changes, favors a volcanogenic source of the iron. The relative paucity of volcanics associated with Proterozoic BIF might be explained in terms of transport of iron by fluids. The currently observed dearth of internally derived 2 Ga iron ores could be due to their destruction following emplacement in oceanic regimes.

The increasing oxygenation of the atmosphere at about 2 Ga, as evidenced by disappearance of placer uraninite and appearance of red beds, etc., is generally attributed to photosynthesis. Phosphorus is an essential constituent of the fuel providing energy for living organisms. Phosphates are common accessory phases of internally derived iron ores. The iron-enrichment activity may have added significant amounts of phosphorus to the hydrosphere at about 2 Ga, leading to increased photosynthesis and a more oxygenated atmosphere. Similar addition at about 1.5 Ga may have facilitated the emergence of eukaryotic organisms (5).

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## FORMATION OF THE EARTH AS A MULTIDIFFUSIVE CONVECTION MECHANISM

A. Rice, Dept. of Physics, University of Colorado Denver, 1200 Larimer St., Denver, CO

Early gravitational sorting of a prot-stellar nebula will yield both temperature and concentration gradients from the outer reaches of the nebula in toward the axis of rotation: mass and temperature increasing inward. The temperature gradient would impose convection in a radial direction as well as normal to the plane of the disk of the nebula. Convection in systems that also have concentration gradients imposed on them show a propensity to break up into layers of uniform density such that each layer is well mixed and of uniform concentration and temperature. Gradients occur only at the boundaries separating the layers. These gradients are quite sharp and are conducive to significant Soret fractionation if there are many such boundaries in place for a long period of time. If the concentration and temperature gradients along the radius of the disk of the proto-stellar nebula induce a similar type of layering, several interesting possibilities arise: 1) the layers will be concentric around the proto-sun, 2) the innermost layers will be hottest and will contain heavier and more refractory components, the outermost layers will be coldest and contain lighter components, therefore inner planets will be composed of heavy material, outer planets of light material, 3) Coriolis components in both out and ingoing convective streams will yield cyclonic motion in the shear zones of each boundary with sense the same as the rotation of the proto-stellar cloud. Pressure lows at the center of these vortices in the boundary layers facilitate accumulation of debris, i.e., planetary formation with rotation in the same sense as the forming star, 4) the above dynamics remove angular momentum from the condensing cloud, 5) planets formed in such fashion will be slow rotators if they are inner planets, fast rotators if they are outer planets, 6) boundary layers will be thin in the inner regions, thick in the outer regions, facilitating formation of small planets in the inner regions and large planets in the outer regions, 7) convective heat transfer will modulate boundary layers to minimize eccentricity, 8) orbits formed in this fashion will all be coplanar, 9) within the low pressure zones of the vortices in the boundary layers, much smaller analogs of the original proto-stellar nebula can form which evolve in a similar manner yielding a planet surrounded by satellites, all coplanar, all with orbital and rotational motion in the same sense as the sun, 10) assuming quasi-steady heat flux out through the layers in the radial direction requires that the distance between boundaries separating each layer be given by  $r_i = C2^i$  which has the form of the Titius-Bode relationship. This convective mechanism for solar system formation is far removed from that proposed by Von Weizsacker and should not be confused with it. As the earth possesses the characteristics indicated above, it's formation may have proceeded from a multi-layered, multi-diffusive convective process.

## EARLY HISTORY OF THE EARTH-MOON SYSTEM

A.E. Ringwood, Research School of Earth Sciences, Australian National University, Canberra, 2601

Currently, there is widespread support for a model of planet formation (1) which implies that accretion was a hierarchical process and that the Earth was formed largely by the coagulation of a population of intermediate-sized bodies, some of which were themselves of planetary size. For example, it was proposed that 1-2 Mars-sized bodies, 3 Mercury-sized bodies and many lunar-sized bodies participated in the formation of the Earth (1). The Moon is believed to have formed as a byproduct from the collision of a Martian-sized planetesimal with the growing Earth, eg (2). It is recognized that this accretion scenario would lead to complete melting of the Earth (2); hence a test of the hypothesis is possible.

Complete melting of the Earth's mantle would have been followed by extensive crystallization differentiation. New high pressure experimental measurements of partition coefficients of many minor and trace elements between liquid silicate perovskites, garnets and melts permit the consequences of a differentiation process of this type to be modelled (3). These results show that it would have led to the development of a primitive crust strongly enriched in Ba, K, Rb and Cs, and relatively depleted in U, Th, Pb, Sr, Zr and Hf. Moreover, gross fractionations between Sc, Zr, Hf on the one hand and the REE on the other, would have been caused. There is no sign of these fractionation patterns in the Earth's earliest crustal rocks (~ 3.9 Ga) and zircons (~ 4.20 Ga). If a primitive crust of this type had formed and had then been consumed by subduction, prompt remelting and re-formation of new crust would have occurred because of the high buoyancy and low melting point of the subducted crust. The heat generated by  $^{40}\text{K}$  strongly concentrated in crustal rocks would have facilitated upward segregation of recycled crust. The overall result of these processes would have been the formation of a smaller "steady-state" primitive crust, and strong contamination of the upper mantle by material possessing the primitive crustal geochemical signature described above (3).

The absence in the earliest crustal rocks and minerals of geochemical signatures that would have been caused by melting and differentiation of the mantle provides strong evidence that extensive melting and differentiation did not in fact occur. This, in turn, suggests that the Safronov-Wetherill scenario for accretion of terrestrial planets and formation of the Moon (1) is seriously flawed.

Additional problems with this hypothesis arise from the demonstration that ferroan anorthosites crystallized in the lunar crust at  $4.44 \pm .02$  Ga (4), only ~ 100 m.y. after the commencement of accretion of terrestrial planets. According to Wetherill's accretion model (1), about 2 percent of the planetesimals in the terrestrial planet region of the solar nebula remained to be swept up after 100 m.y. These should have caused massive meteoritic contamination of the upper 20 km of primitive lunar crust on a scale which is considerably greater than observed.

These problems might be alleviated if:

- (a) accretion of the terrestrial planets occurred on a much shorter timescale ( $< 10^7$  y) than the  $\sim 10^8$  yr timescale proposed by (1).
- (b) the largest accreting bodies were closer to lunar than to Martian size,
- (c) a large proportion of accreting material was present in the form of bodies smaller than 10 m and,
- (d) accretion was largely completed before the gases of the primitive solar nebula had been dissipated, as proposed by (5).

Accretion from a smaller-sized population of planetesimals could have provided a hot but not totally molten Earth in which core-formation proceeded simultaneously with accretion, whilst most of the mantle remained unmelted (6). Gas friction would have imposed low eccentricities

upon the orbits of small planetesimals and caused them to spiral inwards towards the sun. This would have resulted in preferential capture of planetesimals by the Earth in prograde circumterrestrial orbits (5), thereby providing an efficient means of converting orbital angular momentum of planetesimals to rotational angular momentum of the Earth. The presence of a hydromagnetically coupled and co-rotating primitive terrestrial atmosphere extending to about 3 Earth-radii would have increased the radius of capture by the Earth, thereby enhancing the effectiveness of this process (5). Protolunar material may have been ejected from Earth's mantle by multiple impacts from a series of medium-sized planetesimals (eg. 0.1-1 lunar masses). The co-rotating primitive terrestrial atmosphere is believed to have played an important role in trapping ejected material in circular coplanar orbits. In this way, a disc of Earth-orbiting planetesimals or moonlets may have formed and subsequently coagulated to form the Moon (7).

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THE ROLE OF LARGE INFREQUENT IMPACTS IN THE THERMAL STATE OF THE PRIMORDIAL EARTH. Danny Rintoul, (Physics Department, Caltech) and David Stevenson (Division of Geology and Planetary Science, Caltech) Pasadena, CA 91125.

INTRODUCTION. The Earth is thought to have reached its present mass in the first 5 to  $10 \times 10^7$  years of its existence. This has often been modeled as a steady continuous accretion of mass. If this is the case, then it has been shown by Abe and Matsui [1] that this continuous depositing of energy would have kept the Earth's mantle molten for most of the Earth's accretion. However, it is now increasingly believed that most of the mass arrived in large discrete bodies, some as large as the moon or even Mars. These impacts would have caused large amounts of energy to be deposited in the Earth over a very short period of time which in turn would have caused a very non-uniform thermal evolution. It is then possible that the Earth was cool for large portion of its accretional stage. An understanding of these thermal processes is necessary to better understand the physical state of the early Earth, which affected the origin and early evolution of the Earth's atmosphere, hydrosphere, and mantle, and perhaps even the origin of life.

METHOD. In this model, I assume a mass spectrum of projectiles defined by  $n(m) \propto m^{-\alpha}$ , where  $\alpha=1.6, 1.7, 1.8, 1.9,$  and  $1.95$ , and  $n(m)$  is the number of bodies with mass between  $m$  and  $m+dm$ . With this, I assume a maximum projectile size of .2 Earth masses and generate masses down to a lower limit which is a function of  $\alpha$ , but is on the order of .001 Earth masses. I then start with an initial body of .1 Earth masses and start taking projectiles from my distribution and impacting the Earth with them. After the impact I calculate the heating of the Earth's mantle (assuming a uniform heating) and the time needed for the Earth to cool down to 1200 °K, at which point a solid skin forms over the magma ocean and prevents cooling of all but the outer skin of the magma ocean. The time difference between the impacts is determined by assuming the projectiles collide with the early Earth at a rate determined by  $dm/dt \propto R^2(1-M/M_f)$ , where  $M_f$  is the final Earth mass.

IMPACT HEATING AND COOLING. The change in temperature is determined by setting  $.5mv^2=4\pi\epsilon R^2D\rho C_p\Delta T$  where:

$m$  = mass of the projectile

$v$  = is the velocity of the projectile which is assumed to be the escape velocity of the Earth at the time of impact

$\epsilon$  = efficiency of the conversion of kinetic energy into deposited heat

$R$  = radius of the Earth at the time of impact

$D$  = depth of the magma ocean

$\rho$  = density of the magma ocean

## LARGE IMPACTS OF THE PRIMORIDIAL EARTH

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$C_p$  = Specific heat of the magma ocean

$\Delta T$  = Change in temperature of the magma ocean

The efficiency factor is the proportion of kinetic energy not lost by heat immediately radiated out into space. The tail end of the mass spectrum, which contains smaller projectiles is approximated as a constant heat flux and taken into account when the Earth was cooled. To calculate the rate of cooling, I have used the model given by Zahnle et al [2], which relates the heat flux of the early earth to the surface temperature. I have approximated this curve by a function of the form  $-a+bT^4$  for temperatures above 1361 °K and a constant for temperatures lower than that. This model assumes a constant H<sub>2</sub>O abundance at 46.4 bars.

**RESULTS.** My standard parameter values for my program were a magma ocean depth of 300 km, a total accretion time (.95 Earth masses) of  $5 \times 10^7$  years, and a heating efficiency of .5 for both the background and discrete impacts. For these values, I found that for values of  $\alpha \geq 1.75$ , the background flux was large enough to prevent cooling of the Earth's mantle to 1200 °K. Whether or not the Earth's mantle cooled was a strong function of the efficiency for the conversion of the smaller particles to deposited heat, and not so much the larger ones. This was due to the fact that the high temperatures caused by the infrequent larger projectiles cooled very quickly due to the  $T^4$  cooling, and the steady low temperature heating by the background particles caused a heating that didn't cool so rapidly compared to the rate that the particles were coming in. If less of the kinetic energy of the smaller projectiles was deposited in the Earth's mantle, then the Earth could have easily been cool for approximately 99% of its accretion period. Also notable is the fact that at times during the middle of the accretion, the Earth could have been hotter than at the beginning of end due to the collision rate being greater then. I also found that if the accretion time for the earth dropped below approximately  $3.5 \times 10^7$  years then the rate at which the background flux would have come in at a high enough rate to keep the Earth's mantle molten.

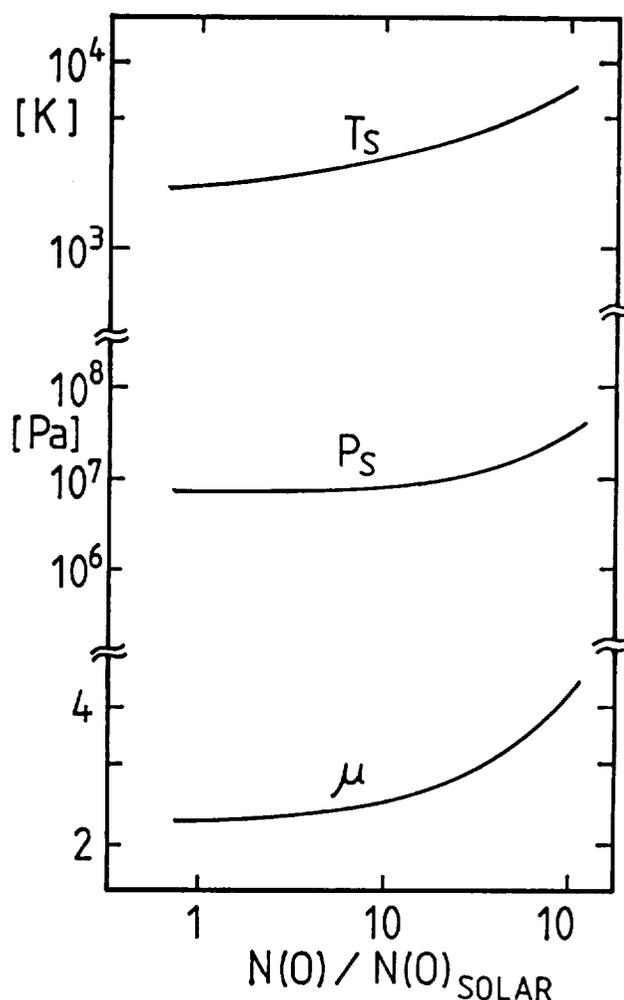
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**STRUCTURE OF THE PRIMORDIAL H<sub>2</sub>-HE ATMOSPHERE:  
POSSIBLE HIGH SURFACE TEMPERATURE OF THE ACCRETING EARTH**  
Sho SASAKI, Lunar and Planetary Laboratory, Univ. of Arizona,  
Tucson, AZ85721

Timing of dissipation of the solar nebula divides theories on formation process of terrestrial planets into two categories (or stages): the gaseous (1) and the gas-free (2) accumulations of planetesimals. In the course of gaseous accretion, the terrestrial planets as well as jovian planets gravitationally attract the nebular gas and the primordial H<sub>2</sub>-He atmospheres are formed surrounding them. The optically-thick solar-type atmosphere should prevent rapid escape of the accretional energy and enhance the surface temperature of a protoplanet (3). When the planetary mass  $M_p$  reaches  $0.2M_E$  ( $M_E$  being the present Earth's mass), temperature at the planetary surface  $T_s$  exceeds melting temperature of silicates and planet-forming materials start to differentiate during the accretion.

Figure: Temperature, pressure, and mean molecular weight at the bottom of the primordial atmosphere (i.e. planetary surface) for relative number density of oxygen atom (which is nearly proportional to H<sub>2</sub>O abundance). The planetary mass is  $1M_E$ , mass accretion rate of planetesimals is  $1M_E/10^7$  [yr], dust abundance is equal to interstellar value (0.003 [kg/kg]), and average size of dusts is  $1 \times 10^{-5}$  [m].



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The structure of the primordial atmosphere is determined by opacity and mean molecular weight as well as energy outflow. In the outer region of the atmosphere, dust materials from incoming planetesimals are the main source of the opacity, and in the bottom region where dusts should evaporate because of high temperature, gas species such as H<sub>2</sub> and H<sub>2</sub>O are the principle source. The previous study (4) suggested that evaporation of dust materials should suppress the temperature gradient in the atmosphere and suppress the surface temperature to be around 2200[K] (at  $M_p = 1M_E$ ) (see case N(O)/N(O)solar = 1 in Figure). In the present numerical study of the primordial atmosphere, we newly take into account a rather detailed expression of dust opacity (5) and the effect of additional H<sub>2</sub>O.

When  $M_p > 0.2M_E$  and the surface temperature is high enough (>1500[K]), iron oxide or silicate of surface or floating materials should oxidize the atmospheric H<sub>2</sub> to supply the additional H<sub>2</sub>O into the atmosphere. The additional H<sub>2</sub>O increases gas opacity; the surface temperature increases to be higher than that in the previous results and the bottom region of the atmosphere becomes convectively unstable. If the H<sub>2</sub>O production proceeds rather effectively according to a probable oxygen buffer system (QIF: SiO<sub>2</sub>-Fe-Fe<sub>2</sub>SiO<sub>4</sub> or IW: Fe-Fe<sub>x</sub>O),  $P_{H_2O}/P_{H_2}$  would be enhanced to be 0.3 at the planetary surface (the relative number of oxygen atoms being about 100 times larger than the solar value). Then increase in gas mean molecular weight  $\mu$  enhances the surface temperature largely (3000[K] at  $M_p = 0.5M_E$  and more than 6000[K] at  $M_p = 1M_E$ , see Figure) since  $T_s \propto \mu$ . Such high surface temperature promotes the evaporation of the surface materials (7, 8, 9). The lower convective zone extends to the Roche radius (2.8R<sub>E</sub>) just overlapping with the condensing zone of silicates; there is a possibility that the evaporated silicates are transported upward by convection and recondense to be source materials of the moon.

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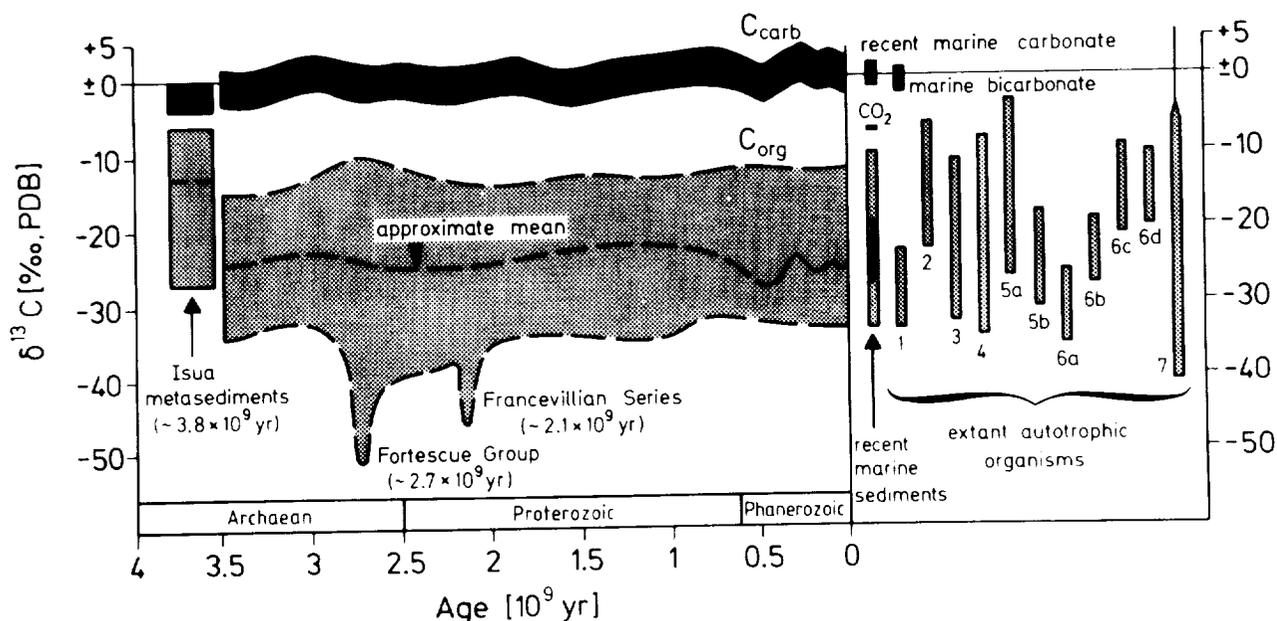
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## A 3.8 GYR ISOTOPIC RECORD OF AUTOTROPHIC CARBON FIXATION FROM CARBON IN SEDIMENTARY ROCKS

M. SCHIDLOWSKI

Max-Planck Institut für Chemie (Otto-Hahn-Institut), Mainz, FRG

During the last decade, disparate lines of evidence have merged to indicate that the Earth was inhabited by life as from almost 4 Gyr ago [1]. In particular, the isotope age curve of sedimentary carbon can be best explained as an index line of autotrophic carbon fixation, with  $^{13}\text{C}/^{12}\text{C}$  fractionations between organic carbon and carbonate largely consonant with the isotope-discriminating properties of RuBP carboxylase as the principal  $\text{CO}_2$ -fixing enzyme of the photosynthetic pathway. Allowing for a secondary metamorphic overprint of the oldest (>3.5 Gyr) sedimentary  $\delta^{13}\text{C}$  values, biologically mediated carbon isotope fractionations have persisted rather uniformly over the hitherto known record, attesting to an extreme degree of evolutionary conservatism in the biochemistry of autotrophic carbon fixation [2].



**Fig. 1.** Isotope age functions of carbonate ( $\text{C}_{\text{carb}}$ ) and organic carbon ( $\text{C}_{\text{org}}$ ) over 3.8 Gyr of recorded geological history as compared with the isotopic compositions of their progenitor materials in the contemporary environment (marine bicarbonate and biogenic matter, see right box). Numbered groups of extant autotrophic organisms are (1) C3 plants, (2) C4 plants, (3) CAM plants, (4) eukaryotic algae, (5) cyanobacteria (natural and cultured), (6) photosynthetic bacteria other than cyanobacteria, (7) methanogenic bacteria. The envelope shown for fossil organic carbon covers an update of the data base originally presented by Schidlowski et al. in [1]; conspicuous negative offshoots such as at 2.7 and 2.1 Gyr indicate the involvement of methane-utilizing pathways in the formation of the respective kerogen precursors. Note that the isotope spreads of extant primary producers have been transcribed into the record with just the extremes eliminated, the resulting isotope age functions thus representing an index line of autotrophic carbon fixation over almost 4 Gyr of Earth history.

Accordingly, autotrophy -- and notably photoautotrophy as the quantitatively most important process of carbon assimilation -- had been extant as a biochemical process and as a geochemical agent since at least 3.8 Gyr ago. There is good reason to believe that the potential of the biosphere to generate economic energy deposits dates back to the same time. The demonstrable absence from the record of such deposits before the dawn of the Phanerozoic is most probably due to the small mass half-age of coal- and hydrocarbon-hosting strata rather than to an inherent incapability of a microbially dominated biosphere to give rise to economic-grade carbon accumulations.

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THE ROLE OF AQUEOUS SOLUTIONS IN THE ORIGIN OF ORGANIC COMPOUNDS ON THE EARTH, Everett L. Shock and Mitchell D. Schulte, Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130, USA

Fischer-Tropsch and Miller-Urey mechanisms for synthesis of organic compounds from mixtures of inorganic gases may accurately describe the formation of carbonaceous material on interplanetary dust or reactions in the atmospheres of the outer planets but are difficult to apply to prebiotic synthesis on the Earth. Numerous lines of evidence from geochemistry and atmospheric chemistry suggest that early in the Earth's history the necessary gas mixtures were either evanescent or nonexistent (1,2). Nevertheless, considerable research into the origin of life continues on the assumption that a steady source of organic compounds was available for subsequent reactions. Evaluating the significance of this substantial body of work awaits identification of terrestrial environments in which organic compounds could have formed. This, in turn, can only be accomplished by analyzing prebiotic synthesis within a geochemical framework. As a first step in this analysis we are considering the role of aqueous solutions in the synthesis of organic compounds from a wide variety of starting materials.

Volatile elements would have been incorporated into the Earth during its formation from a variety of sources including: ices, carbonates and other salts, hydrated silicates, and condensed organic phases such as those found in carbonaceous chondrites and interplanetary dust. Depending on the response of these materials to accretionary events, a wide variety of reactants, from reduced gases to complex, condensed organic phases, may have been available for prebiotic synthesis. Alteration of these compounds by aqueous solutions would have led to different suites of products owing to differences in temperature, pressure, oxidation state, composition of the aqueous phase and coexisting minerals, and differences in initial composition. It is not clear from the outset which of these variables would have had the greatest impact on prebiotic synthesis, but the complexity of these problems makes a theoretical approach attractive in order to narrow the list of possibilities before performing laboratory studies.

Recent advances in theoretical geochemistry allow calculation of the standard molal thermodynamic properties of a wide variety of aqueous organic species as functions of temperature and pressure (3). These species include: alkanes, alkenes, alkynes, alkylbenzenes, alcohols, ketones, amines, carboxylic acids, and amino acids. By combining calculated equilibrium constants for reactions involving these species with mass balance constraints, the distribution of aqueous organic species in stable and metastable states can be evaluated. In the current study we have considered two vastly different environments, a hydrothermal system and low-temperature surficial weathering.

The hydrothermal system is similar to a modern submarine vent environment in which aqueous solutions move mixtures of reduced inorganic species (for example,  $\text{CH}_4$  and  $\text{NH}_3$ ) through an oxidation gradient imposed by various mineral assemblages (iron-wüstite (IW), fayalite-magnetite-quartz (FMQ), pyrrhotite-magnetite-pyrite (PMP), magnetite-hematite (MH)). It is proposed that rapid oxidation of the reduced starting materials leads to metastable states in which aqueous organic species form rather than the stable assemblages dominated by  $\text{CO}_2$ ,  $\text{N}_2$ , and graphite. Metastable states of this type are ubiquitous in nature at temperatures  $< 600^\circ\text{C}$  (4). The process we envision is similar in many respects to Miller-Urey synthesis except that all reactions occur in aqueous solution at explicit oxidation states and at higher temperatures and pressures where reaction rates are fast and an external source of energy, such as an electric discharge, is likely to not be required. Distri-

bution of species calculations allow evaluation of the activities of aqueous organic species as functions of temperature, pressure, oxygen fugacity, and activities of aqueous methane and ammonia. The dependence of these variables on one another can be interpreted with a series of two-dimensional activity diagrams contoured for activities of the aqueous organic species. Calculations at 350°C, 500 bars, and constant activities of methane and ammonia indicate that the activities of aqueous organic compounds are strong functions of oxygen fugacity. The dominant species from a list of ~80 aqueous organic species include: formic acid, acetic acid, propanoic acid, methanol, ethane, methanamine, glycine, and glutamine. The activities of these species increase with increasing oxygen fugacity corresponding to the FMQ, PMP, and MH buffers. As an example, at log activities of methane and ammonia of -1, the log activity of glutamine varies from -16.1 at FMQ to -2.7 at MH. These activities can be used to estimate the contribution of submarine hydrothermal vents to prebiotic synthesis. Given a log activity of glutamine of -8, a flow rate of 1 liter sec<sup>-1</sup> vent<sup>-1</sup>, and an average spacing of 100 km between vents on 60,000 km of ridge during the Archean, the global production of glutamine would have been  $27.6 \times 10^9$  g (10<sup>6</sup> yr)<sup>-1</sup> or  $27.6 \times 10^5$  metric tons (10<sup>8</sup> yr)<sup>-1</sup>. These calculations provide a framework for evaluating the efficiency of sequestering agents and catalysts such as clay minerals and zeolites.

If complex, condensed organic phases survived accretionary reprocessing, it is likely that polyaromatic hydrocarbons, heteroatomic compounds, and other higher molecular weight species were present in solid phases at or near the surface of the early Earth. By analogy to CM carbonaceous chondrites, in which pervasive low-temperature aqueous alteration is apparent (5,6), weathering processes could have led to the aqueous alteration of these compounds on the Earth. In preliminary calculations we have used pyrene, a polyaromatic hydrocarbon with the formula C<sub>16</sub>H<sub>10</sub>, as a model compound and consider an alteration process at 25°C and 1 bar in which pyrene reacts with aqueous solutions containing variable activities of ammonia at several oxidation states. The distribution of aqueous organic species in the metastable assemblages resulting from this alteration depends dramatically on oxidation state. As an example, at log a NH<sub>3</sub> = -2 and log a pyrene = -2 and values of log f<sub>O<sub>2</sub></sub> below about -75, the alkanes are the predominant species, with lesser but significant activities of carboxylic acids. Between log f<sub>O<sub>2</sub></sub> values of -75 and -72.3 (MH) the carboxylic acids displace the alkanes and glycine and alanine attain log activities > -12. At oxidation states above the magnetite-hematite assemblage, carboxylic acids and amino acids become the predominant species, and are the only significant species above log f<sub>O<sub>2</sub></sub> = -66, with log activities in the range -2 to -6. This implies that the prevailing oxidation state during aqueous alteration of polyaromatic hydrocarbons will dictate whether hydrocarbons or amino acids form. Although these calculations refer to a simplified system, they suggest that significant amounts of amino acids and carboxylic acids could be produced at 25°C and 1 bar during aqueous alteration at mildly oxidizing conditions.

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**ABUNDANCES OF AS, SB, MO AND W IN THE CRUST AND MANTLE: IMPLICATIONS FOR TERRESTRIAL ACCRETION AND CORE FORMATION THROUGH GEOLOGIC TIME.** K.W. Sims<sup>#</sup>, H.E. Newsom<sup>#</sup>, E.S. Gladney<sup>\*</sup> and K. Keil<sup>#</sup>; <sup>#</sup> Dept. of Geology and Institute of Meteoritics, Univ. of New Mexico, Albuquerque, NM 87131; <sup>\*</sup> Los Alamos National Laboratory, Health and Environmental Chemistry Group MS K-484, Los Alamos, NM 87545.

**INTRODUCTION** The depletion of moderately siderophile elements in the Earth can be interpreted in terms of a two component model [1] suggesting heterogeneous accretion of the Earth, with an initial reduced component giving way to an oxidized component. The alternative metal retention model [2], involves an incomplete core formation event. We are determining the abundances of As and Sb in the mantle and crust, and improving our knowledge of the abundances of Mo and W. The abundances in the primitive mantle of compatible siderophile elements, such as Ni and Co, are well known from mantle nodules, because they are retained in olivine during partial melting. The abundances of incompatible siderophile elements such as P, W, Mo, Sb and As, must be determined by normalizing the abundances of these elements to lithophile elements of similar geochemical behavior in both mantle reservoirs and crustal reservoirs.

The siderophile depletion data can also be used to constrain the possibility of core formation through geologic time. Newsom et al. [3] showed that the depletion of Mo in the Earth was independent of the Pb isotope variations that have been interpreted as due to continual core formation [4]. This work has been expanded by examining the abundance of Mo in the crust to confirm the earlier conclusions [3] based only on data from mantle derived oceanic rocks.

As, Sb, W, and Mo in four loess samples and an Australian post-Archean shale were determined in triplicate by Radiochemical Epithermal Neutron Activation analysis [5]. Previously unpublished As and Sb abundances in oceanic rocks were determined in the same metal extraction experiments as the Mo and W determinations reported in Newsom et al. [3].

**RESULTS AND DISCUSSION** Newsom et al. [3] showed that Mo is correlated with the light rare earth element Pr in mantle derived oceanic rocks. Our new crustal data fall within the uncertainty for the Mo/Pr ratio from the oceanic rocks, suggesting that this Mo/Pr ratio represents the ratio in the primitive terrestrial mantle. The W data agree precisely with earlier analyses [6,7].

Sb is similar in geochemical behavior to Pb and Ce during igneous fractionation (Fig. 1). The crustal derived materials appear to be enriched in Sb relative to Ce by a factor of 5, similar to Pb [3]. This enrichment is possibly due to hydrothermal processes during crustal formation. Compared to previous estimates of the depletion of Sb in the primitive mantle [8,9], our data suggests that the primitive mantle is more depleted, perhaps by a factor of 5.

As behaves somewhat like the heavy rare earth elements such as Yb, especially regarding the similar As/Yb ratios in mantle nodules and mantle-derived oceanic rocks (Fig. 2), but the data are more scattered than for Mo, W or Sb. The crust appears to be enriched by a factor of 5 in As relative to Yb, compared to the mantle-derived samples. This data suggests that the As/Yb ratio in the crust is actually a factor of 3 greater than previous estimates [8]. The primitive mantle abundance is much less constrained and may be similar to the estimate of Sun [9] or as much as a factor of 2 lower.

As and Sb are more volatile than Mo and W, and their depletion in the Earth's mantle is due to both volatility and core formation. The depletion due to core formation is estimated by assuming their original abundance was similar to lithophile elements of similar volatility. The resulting depletions for As and Sb are similar to the depletions for Ga and W respectively, qualitatively consistent with heterogeneous accretion of the Earth. Quantitative evaluation of their depletion will require the planned experimental determination of metal/silicate partition coefficients.

**CONCLUSIONS** This study has shown that the Mo/Pr ratio is the same for crustal derived loess and sediments, and mantle derived samples and probably represents the ratio for the primitive mantle. Additional data we are obtaining on archean rocks will help constrain the question of core formation throughout geologic time. New data on As and Sb for the crustal and mantle derived samples provides much improved estimates of the overall depletion relative to chondrites of these elements, and the portion of their depletion due to core formation. The preliminary analysis of the data suggests that the depletions are consistent with heterogeneous accretion of the Earth, but determination of metal/silicate partition coefficients is required. The new data also indicate that crustal formation has enriched Sb and As by an unknown process, possibly involving hydrothermal alteration, causing them to behave in a much more incompatible way than during oceanic volcanism.

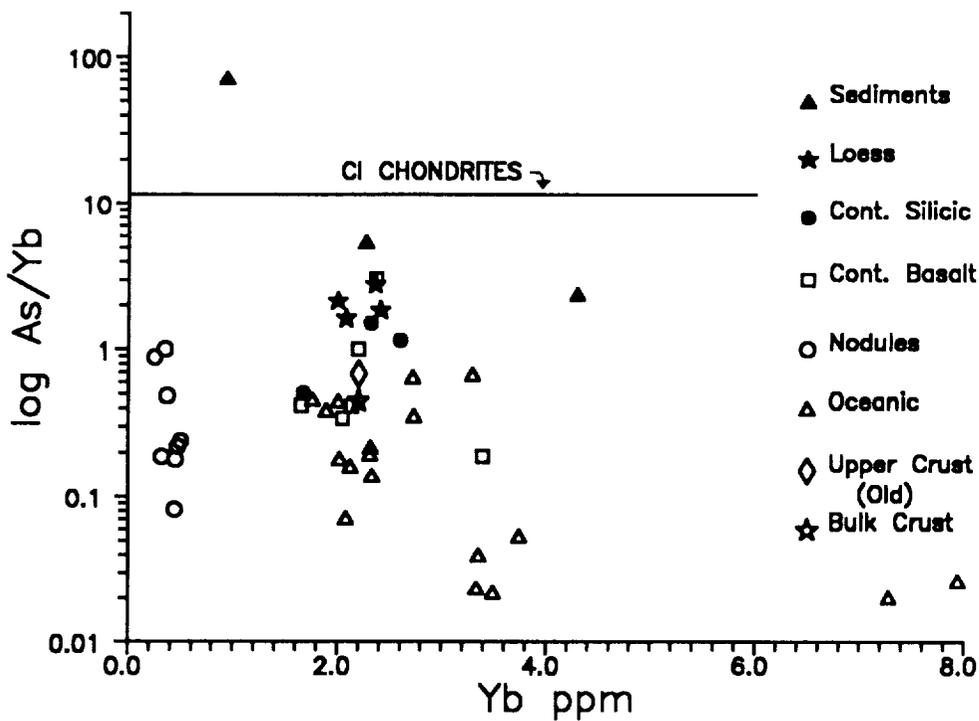
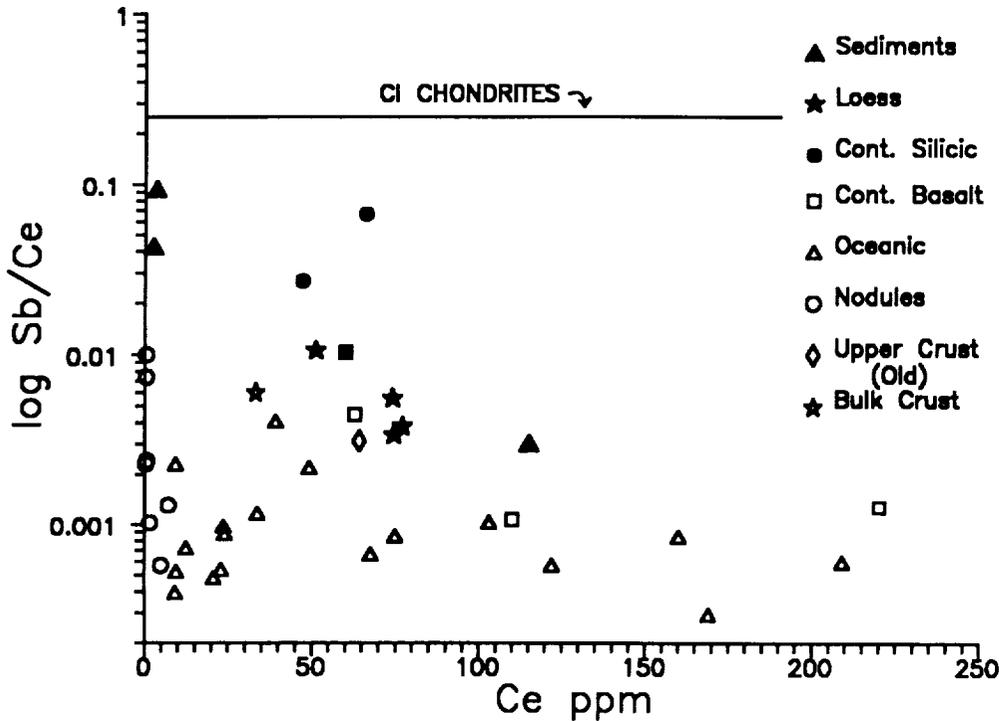
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Figs. 1,2. Data for As and Sb from this study with some additional data from geochemical reference standards. Data for Yb and Ce from refs. 3, 6 and 7. Crustal estimates from ref. 8. Nodule data from refs 10,11 and 12. As/Yb and Sb/Ce ratios for CI chondrites are also shown.



LARGE IMPACTS AND THE SURVIVAL OF ECOSYSTEMS ON THE EARLY EARTH, N. H. Sleep, Depts. Geology and Geophysics, Stanford University, Stanford CA 94305; J. Kast- ing, Depts. Geoscience and Meteorology, Penn. State Univeristy, University Park, PA 16802; K. J. Zahnle, NASA Ames Research Center, Moffett Field, CA 94035 and H. Morowitz, George Mason Univer- sity, Fairfax, VA 22030.

It is obvious that the earth experienced impacts during its accretion that would have wiped out any life forms. The size of later impacts until heavy bombardment ended around 3.8 B.Y. and their effects on lifeforms are less obvious, but can be quantified. The last impact to sterilize the planet was probably the last impact to fully evaporate the ocean. It is possible that no pre-existing complex organic chemicals would survive such an event. Lesser, but still dangerous, impacts evaporating the photic zone in the ocean would have been more frequent, and would have occurred later. It is possible that sterilization followed such a lesser impact if the global ecosystem were dependent on photosyn- thesis, and this capability was lost.

It takes  $5 \times 10^{27}$  J to vaporize the ocean. A significant fraction of the impact energy, conserva- tively estimated as 25%, is spent heating and evaporating water. For a typical asteroidal impact velo- city of 15-20 km/sec, a  $1-2 \times 10^{20}$  kg object is needed. The corresponding object, some 500 km in diameter, would have been comparable to, or somewhat smaller than, Pallas or Vesta. It added about 100 m to the diameter of the earth. The comparable mass for a comet would be much lower.

The number, energy, and mass of objects hitting the earth between the time of its accretion and 3.8 B.Y. ago must be obtained indirectly because no intact terrestrial rocks of that age are known. Use- ful constraints are obtained from the record of cratering on the moon, the geochemistry of the lunar highlands, from the chemistry of earth's mantle, and from the chemistry of shergottitic meteorites which are believed to come from Mars. Direct estimates of the energy of impact have been obtained only for Orientale, the youngest (ca. 3.8 B.Y.) and best preserved of the basins. Bratt et al. [1985a] estimate from thermal contraction of the basin an impact energy between  $4 \times 10^{25}$  J and  $3 \times 10^{26}$  J. A second estimate is obtained from the ejecta volume of  $3 \times 10^{19}$  kg [Bratt et al., 1985b]. As much of the ejecta is not melted, the thermal energy of the ejecta is less than  $4 \times 10^{25}$  J (assuming 1000° K of heating). If around 3/8 of the energy goes into heating ejecta, then the total energy is less than  $1.2 \times 10^{26}$  J, in the middle of the range for the first estimate. For typical asteroidal impact velocities, this corresponds to a  $1.3 \times 10^{18}$  kg object with a diameter of 90 km. Ejecta volumes [Spudis et al., 1988] and conventional diameter scaling indicate that the largest late basin, Imbrium (3.85 B.Y.), required twice this energy. There are numerous other older basins on the moon. Although the absolute chronology is in doubt, the larger surface area of the earth implies a basin forming impact about every million years.

The total mass of impactors is constrained by the total amount of meteoritic components present in the lunar crust. Ni and Ir abundances indicate a meteoritic component of 1-4% in the highland crust. The mixing depth is on the order of 35 km [Spudis and Davis, 1986]. This indicates an equivalent thick- ness of a kilometer. Similarly, the late chondritic component inferred from Shergottitic meteorites, about 0.1% of the mantle, is equivalent to a layer 1 km thick on Mars [Drake, 1987]. However, the late veneer component in the earth's mantle, 0.74% [Chou et al., 1983], is equivalent to a layer 18 km thick. Most probably the terrestrial thickness represents an earlier time before the lunar crust became a nearly closed system, about 4.4-4.5 B.Y. The rarity of large impacts after 4.35 B.Y. on the moon is indicated by the rarity of breaching of the KREEP layer deep in the crust.

The mass ( $1.5 \times 10^{21}$  kg) of an equivalent thickness of a kilometer implies a largest impactor of some  $3-5 \times 10^{20}$  kg on the earth assuming conventional mass distribution of objects. In the process of accreting this last kilometer the earth probably accreted 2-5 objects capable of vaporizing the oceans. Clearly, the impact history is difficult to deduce in detail because of the statistics of small numbers. As the impact rate decreased with time the last ocean vaporizing event may have been as early as 4.3 B.Y. However, simply scaling from Imbrium indicates there is some probability that it occurred as late as 3.8 B.Y.

The timescale for recovery from an ocean evaporating impact is at least 2000 years. The max- imum rate at which a planet with liquid water at the surface can radiate infrared energy to space defines

the "runaway greenhouse" threshold. This rate therefore determines the maximum rate at which water vapor can condense out of the atmosphere. For early Earth, this maximum rainout rate was around 150 cm/year [Kasting, 1988]. Accordingly, it took some 2000 years to rain out the oceans. Much of the balance of the energy released by the impact would also have to have radiated at this rate. Any additional delay in the onset of rainout, and any longer-term heat release from the impact, lengthens this time. The timescale for recovery from an Imbrium-scale impactor, which evaporates some 200 meters of water, is around 150 years.

The global lethality of an impact depends on the long term survival of ecosystems, rather than the immediate survival individual organisms and species. The key issue is the survival of primary producers which supply the energy to the rest of the ecosystem. It does no good to identify a survivable environment if some essential skill – most likely photosynthesis -- is irretrievably lost. For simplicity, we consider 3 types of ecosystems: (1) Primary productivity is by photosynthetic autotrophs; (2) Primary productivity is due to oxidation-reduction reactions of chemoautotrophs; and (3) The existence of combined photo- or litho-autotrophs and heterotrophs which can survive for long periods of no primary productivity using system reserves of organic compounds. The first type of ecosystem might be wiped out when the photosynthetic organisms die when the photic (top 200 m) of the ocean is boiled. Surface conditions remain untenable for hundreds of years. The Imbrium object would have done this had it hit the earth. The second type of system is harder to evaluate as modern hydrothermal vent communities ultimately depend on photosynthetic oxygen. In the third case the primary producers would survive by acting as heterotrophic anaerobes utilizing organic reserves. To survive an event that nearly boils the ocean, the reserves must last several thousand years.

The sedimentary column is the last refugium for organisms, but an unlikely one for primary producers. Colonization below 100 meters of marine sediment is imaginable in regions of low heat flow. Even in the event of complete evaporation of the ocean, the thermal pulse from the surface would not itself have been lethal much below 100 meters, given a typical sedimentary thermal conductivity. But photosynthesis is an unlikely attribute of any such survivors. It is possible that matters were analogous to the environment confronting the first life-forms, had they been heterotrophs; if so, one might imagine photosynthesis re-evolving among the survivors. But it is equally if not more likely that such organisms were too specialized to do so.

Hence (1) if anything survives anywhere it ought to be easy to recolonize the planet; however (2) the obscure environments in which survival of an ocean evaporating impact is possible may have been too specialized for RNA-based organisms to have been colonized in the first place.

Owing to the high opacity of seawater to infrared radiation, thermal radiation from the hot rock vapor would have been absorbed only in a very thin surface layer. Boiling would have been confined to this layer. Without mixing, the interior of the ocean would remain cool. Some photosynthetic organisms will survive the initial impact by being mixed into deeper waters. There is a good chance that photosynthesis would have survived an Imbrium-scale impact; especially if photosynthesis was not obligatory, or if the ability to form spores or akinetes had been developed.

Finally, mid-ocean ridge organisms appear particularly likely to survive an impact that partly boils the ocean. The conditions, contamination with rock, salinity variations, and higher temperatures basically extend the vent environment.

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FLUID DYNAMICS OF CORE FORMATION; David J. Stevenson  
(Division of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125).

INTRODUCTION. The mode(s) whereby core fluid drained from the mantle are poorly understood yet important for at least three reasons: (1) The dynamical processes determine the extent to which chemical equilibrium is established between core and mantle, and the pressures and temperatures of this equilibration. This determines the deviation of the core composition from "pure" Fe-Ni. (It is sometimes insufficiently appreciated that *fluid* dynamics may be just as important as *thermodynamics* in determining core composition.) (2) Core formation dynamics may influence the earliest thermal history because of the large associated gravitational energy release. (3) The incomplete drainage of core-forming fluid may strand some siderophiles in the mantle, creating a potentially important contribution to the present day mantle siderophile abundances [1].

Most past work has focused on macrosegregation models of core formation in which large blobs of liquid iron migrate through a solid or partially molten mantle (see review [2]). There are reasons to doubt that this is the complete story or even sometimes correct: (a) Very high temperatures may have prevailed during much of core formation so that *everything* is molten and some of the core fluid is emulsified in the mantle; (b) Even when the mantle is partly solid, segregation of core forming melt may not occur; percolative flow (if possible at all) may dominate. This contribution concentrates on the implications of these new considerations.

CORE FORMATION FROM AN EMULSION. During large impacts, extensive melting and very high temperatures are produced transiently [3]. Although some of the iron of the projectile's core may remain as an "intact" body (because of self gravity) much of the iron is emulsified in the mantle fluid. The subsequent rainout can be computed by the following considerations. Relative to neighboring mantle fluid, an iron-rich droplet of radius  $R$  has Stokes drift velocity  $V \approx \frac{2}{9}g\Delta\rho R^2/\eta$ , where the parameters have their usual definitions ( $\eta$  = viscosity of silicate mantle). However, droplets cannot be larger than the radius at which viscous drag forces overcome surface tension effects, i.e.,  $\eta V/R \lesssim \sigma/R$  ( $\sigma$  = liquid iron surface tension). The silicate liquid viscosity may be quite low at high pressure [4]. Solving, one finds  $R \lesssim 1$  cm and  $V \lesssim 10$  cm s<sup>-1</sup> (comparable to the convective velocity suggested by Kolmogorov scaling). Some recent experiments and simple theory designed for magma chambers [5] enable me to estimate the core drainage rate, given the expectation that most of the iron fluid is in large droplets. The characteristic mantle drainage time is a few times  $H/V \sim 10^2$  years, where  $H$  is the mantle depth. Thus, de-emulsification can be fast even when the liquid mantle is undergoing vigorous thermal convection. An important implication of this core formation mode is the excellent chemical equilibrium achieved, since the chemical diffusion time within and between droplets is even smaller than the settling time.

PERCOLATIVE CORE FORMATION. The high surface tension of pure iron liquid prevents the formation of an interconnected network of iron-rich liquid in a solid matrix of mantle minerals, at least at low pressures. Presence of alloying constituents (especially sulfur) and the effect of pressure [6] may eventually establish the same type of interconnection that occurs in basaltic melts and is responsible for the upward percolative flow leading to the dominant type of volcanism on Earth. The latter seems desirable since it is otherwise difficult to understand how core formation could have approached high efficiency. (Remember that there is nothing fluid dynamically wrong with a planet that has up to half of its total mass as dispersed metallic iron — solid or

liquid — in its mantle!) If percolation is achievable in the deepest mantle then convective transport of dispersed iron from higher up will guarantee good drainage. Using a simple Darcy's law approach in which the "melt" (iron) flux is  $u \sim 10^{-3} R^2 f^2 g \Delta \rho / \eta_c$  ( $f$  = melt fraction,  $R$  = grain size,  $\eta_c$  = core fluid viscosity) one predicts that  $f \sim \tau / t$  at long time  $t$ , where  $\tau \lesssim 10^2$  years. In fact, a compaction zone [7] will develop at the base of the mantle because of the possibly large bulk viscosity of the mantle, but this does not greatly change the conclusion that *very little* iron remains stranded in the mantle even during the accretion process itself, probably not enough to explain the siderophile abundances unless no other chemical assimilation process (oxidation) intervenes.

**SUMMARY.** Recent developments suggest that it is appropriate to move away from the old ideas of "diapiric" core formation modes. As a consequence, greater chemical equilibration with the deep mantle seems likely, including a primordial core that is saturated in mantle phases. This implies subsequent underplating of the mantle ( $D''$ ?) with implications for geochemical evolution. Highly efficient drainage of core fluid seems likely except for a thin boundary layer just above the core.

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U, Th, AND Pb ABUNDANCES IN HAWAIIAN XENOLITHS:  
 IMPLICATIONS FOR MANTLE DIFFERENTIATION.

M. Tatsumoto, U.S. Geological Survey, MS 963, Box 25046, Denver, CO 80225.

U, Th, and Pb abundances in minerals from xenoliths from Hawaiian volcanic rocks have been determined. The concentrations of the three elements are one order of magnitude lower for olivine, the same order for orthopyroxene, and one order higher for clinopyroxene compared to phenocrysts from basaltic volcanic rocks [1]. Choosing experimentally determined values for clinopyroxene of  $D^{Pb}$  [2] and  $D^U$  [3], and assuming  $D^{Th}$  is the same as  $D^U$ , partition coefficients of these three elements for other mafic minerals can be obtained from the abundance ratios in xenoliths (Fig. 1). It should be emphasized that  $D^{Pb}/D^U$  values calculated in this way are almost the same as those obtained from phenocrysts/matrix values, although the absolute D's are notably higher in the latter.  $D^{Pb}/D^U$  are >20 for plagioclase, ~10 for olivine, ~5 for orthopyroxene, and ~3 for clinopyroxene.

The high values of  $D^{Pb}/D^U$  for olivine and pyroxene are consistent with the idea that the Moon was extremely depleted in volatile elements from the outset. The  $^{238}U/^{204}Pb$  ( $\mu$ ) value for the Moon was 300-500 at its formation,  $\mu$  for early cumulates from the lunar primary magma ocean was lower (~50), and  $\mu$  of later cumulates gradually increased. With anorthosite floating to form the crust, late-stage cumulates had higher  $\mu$  values (~300), and residual liquids (the source for KREEP) consequently had tremendously high  $\mu$  values (>600). Because Pb is a chalcophile element and is partitioned into sulfides in preference to U and Th, the Pb evolution is probably more complicated. However, this scenario is also consistent with  $\mu$  values calculated from observed Pb isotopic compositions of KREEP (>700), mare basalts (~300), green glass (~20-55), and anorthosites (<50).

The abundance ratios for xenolithic garnet are still to be determined; however, garnet phenocrysts in volcanic rocks show a small  $D^{Pb}/D^U$  value (<0.1). The Pb paradox (enriched Pb isotopic signatures for the depleted mantle) observed for MORB has been explained in numerous ways; for example, Pb removal from the mantle to the core [4], a primitive Pb supply from the lower mantle to the upper mantle and a short residence time there [5], and a younger age for the Earth than chondritic meteorites [6]. If the D value of garnet phenocrysts can be applied to mantle chemistry, the Pb paradox may be explained

by the involvement of garnet during petrogenesis. Nearly constant  $\mu$  values of  $8 \pm 3$  for Pb of terrestrial rocks indicates that either the Earth's mantle and crust did not differentiate from a primary magma ocean into a layered mantle, convection has effectively homogenized the mantle, or the abundance ratio for garnet/pyroxene is well balanced in the mantle.

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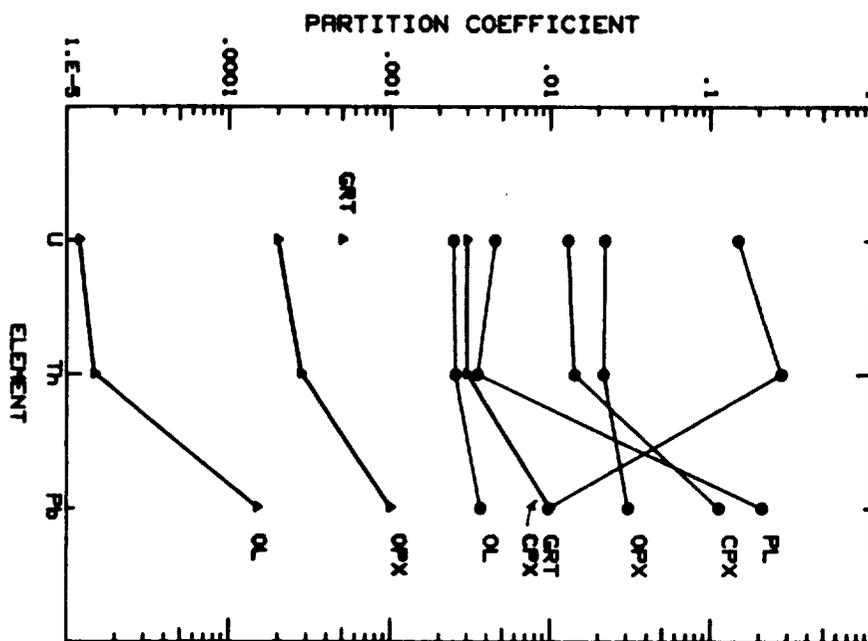


Fig. 1. Partition coefficients of U, Th, and Pb (● for phenocrysts; ▲ for xenolithic minerals)

## Geochemical Implications of Planetesimal Accretion

S.R. Taylor

Australian National University  
Lunar and Planetary Institute

The planetesimal hypothesis postulates that the Earth accretes from a hierarchy of bodies, the largest of which may approach Mars in size, during a period of  $10^7$ - $10^8$  years after  $T_0$  (4560 m.y.). What was the chemical and mineralogical composition of these planetesimals? Were they already differentiated into silicate mantles and metallic cores? What was the previous history of the materials? To address these questions, it is necessary to consider the initial state of material in the nebula. Two extreme models exist. In the first, condensation from a hot nebula produces the condensation sequence of oxides, silicates, Fe metal and sulfide. In the second, lower temperature scenario, the dust in the rotating disk of gas and dust was oxidised. A wide range of meteoritic evidence attests to a cool rather than a hot nebula. This includes preservation of isotopic anomalies, particularly for oxygen, rapidly cooled chondrules, presence of hydrated minerals in CI and multiple evaporation and condensation episodes to account for CAI.

Chondrule production occurs very early. Their total range in I-Xe ages is about 5 m.y. Chondrules form by melting of pre-existing dust in the nebula: volcanic and impact origins can be ruled out. Cooling times [ $<1$  hour] are too fast to allow for condensation from a hot nebula. Chondrules are dominantly silicate objects, depleted in siderophile and chalcophile elements. They are very variable in elemental and oxygen isotopic composition, but average compositions from differing groups are relatively uniform; the matrix accounts for the intra-group variations. Matrix and chondrules are complementary in composition, eg. in Fe/Si ratios.

Were the chondrules melted preferentially from pre-existing metal-poor silicate dust or from a dusty oxidised component closer to CI composition? The most likely scenario is that they were melted from oxidised pre-existing dust and that reduction of iron, depletion of siderophiles, chalcophiles and some volatiles occurred during this stage. In this scenario, metal-sulfide-silicate fractionation occurs effectively at  $T_0$ . The E, H, L, and LL chondrites, accumulated from this material, have similar whole rock ages of  $4,555 \pm 4$  million years. Pb-Pb and Rb-Sr ages give the time of U-Pb and Rb-Sr separation. Accordingly volatile depletion also occurred effectively at  $T_0$ .

Presumably these events correlate with early T Tauri solar activity, which cleared the inner nebula of gas. Nebular lifetimes are estimated at  $10^5$ - $10^6$  year. Accordingly, metal-sulfide-silicate phases were initially formed under low pressure conditions in the nebula.

There is a limit to how far we can pursue the meteoritic analogy; none of the present population of meteorites are candidates for left-over building blocks of the planets. All differ significantly in K/U ratios, oxygen isotopes and other parameters. Chondritic meteorites are generally less depleted in volatile elements (as shown by K/U ratios of  $6 \times 10^4$ ] than Mars [ $2 \times 10^4$ ], the Earth or Venus [ both about  $10^4$ ]. They are derived from the inner asteroid belt ; more primitive unfractionated compositions occur in the outer belt.

Volatile depletion apparently was thus greater in the inner solar system than in the region of the Asteroid Belt. If the Asteroid Belt is a relic of early nebular conditions, then its zoned nature indicates that the terrestrial planets probably accreted from rather narrow ( $<0.5$  AU) feeding zones in which the abundance of volatile elements varied; Mars appears to have about twice the volatile content of the Earth.

The planets thus appear to have accreted from planetesimals which were already volatile depleted. Melting in these parent planetesimals is likely to have produced further metal-silicate separation, in addition to that inherited from the meteoritic precursors. Igneous processing in asteroidal bodies began within a few million years of  $T_0$ . The basaltic achondrites have an average crystallisation age of  $4,539 \pm 4$  m.y., nominally only about 20 m.y. younger than the oldest dated material [Allende CAI:  $4,559 \pm 4$  m.y.]. The iron meteorites, of which over 60 differing types are known, also indicate the widespread occurrence of intra-asteroidal differentiation.

Material in planetesimals accreting to the Earth is thus likely to have experienced one or more stages of fractionation from an originally oxidised condition in the primordial nebula. As this fractionated metal-sulfide-silicate material accretes, there may be little further opportunity for metal silicate equilibration, assuming that core formation occurs rapidly.

Data source: Kerridge, J.F. and Matthews, M.S. 1988, Meteorites and the Early Solar System. Univ. Arizona Press.

**A WELL STIRRED MAGMA OCEAN: IMPLICATIONS FOR CRYSTAL SETTLING AND CHEMICAL EVOLUTION ; W. B. Tonks and H. J. Melosh, Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721.**

The cooling of a magma ocean is the generally accepted explanation of the observed dichotomy between the Europium-enriched anorthositic crust and the Europium-depleted basaltic source regions of the moon (i.e. Wood, 1970). Since the Earth does not have this distinctive signature, it has been argued by a number of workers (i.e. Kato et. al. (1988) and Drake et. al. (1988)) that it never had a magma ocean. However, the accretion models of Kaula (1979), together with the energetics of core formation strongly suggest that if the moon had a magma ocean the Earth should have had one also. This is especially true if the moon was formed by the giant impact of a Mars-sized body as noted in the works of Melosh and Kipp (1988) and Cameron and Benz (1988).

The cooling of a magma ocean was studied in detail by Hofmeister (1983). She assumed that crystals are removed from the magma when formed and modeled the chemical evolution as a batch fractionation process resulting in a layered structure very different than the present Earth. It seems, however, that the effect of convection in keeping the magma ocean well stirred has not been taken into account in the past. This work is a preliminary analysis of this effect. It is presumed (McBirney and Murase, 1984) that the magma behaves as an ordinary liquid until the concentration of crystals in the crystal-magma mush exceeds about 50%, at which point the mush locks up, the crystals and liquid are then unable to separate, and any further heat transfer must take place by subsolidus convection. The magma will thus solidify into the same chemical composition as the starting material since the liquid fraction and solid fraction remain intimately mixed. Note that in this study we explicitly exclude consideration of liquid-mush separation. We are well aware that this effect may be important, but limit our work to the question of crystal settling for reasons of practicality.

We investigated the suspension of crystals in a convecting magma ocean using the following relatively simple model, shown in figure 1.

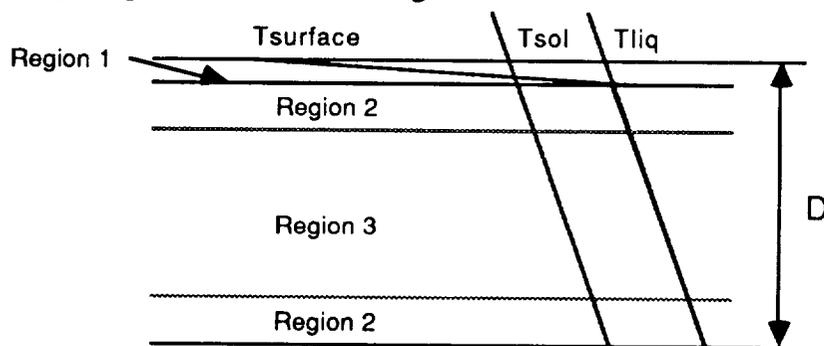


Figure 1. Basic model showing 3 distinct regions of behavior at the beginning of the computation.

It is assumed that the liquidus and solidus temperature profiles of the planet follow the adiabat. This is only strictly valid for a very small planet although recent experiments on the melting curves of peridotite at very high pressures (Takahashi, 1986) indicate that this simplification may not be too unrealistic. The planet is melted uniformly to depth  $D$ , and is originally at the liquidus. The temperature difference between the surface and the magma sets up free convection. The model considers only the effect of the cooling magma. After a time  $\Delta t$ , the ocean has lost an amount of energy equal to  $h\Delta t$ , where  $h$  is the heat flux. The heat flux  $h$  is derived from the Nusselt number  $Nu$  ( $h=h_c Nu$ , where  $h_c$  is the heat that would be conducted through a slab of thickness  $D$ ), which itself is related to the Rayleigh number of the convection through the following relationship:

$$Nu = 0.89 Ra^n$$

The magma ocean on both the earth and moon is initially convecting vigorously with an initial Rayleigh number (Ra) on the order of  $10^{27}$ , in a regime described by Kraichnan (1962). The flow is broken into 3 regions if the following condition is met:

$$35Ra^{1/3} > \sqrt{Pr}$$

where Pr is the Prandtl number.

Region 1 is a thin region where heat is transported by conduction, region 2 is a turbulent boundary layer where heat is transferred primarily by convection but in which viscosity dominates. Region 3 consists of highly turbulent fluid in which large eddies of spatial scale on the order of the depth of the ocean dominate. These eddies give rise to upward directed forces which have the potential to keep the crystals in suspension (Bagnold, 1965). In particular, if the effective frictional velocity arising from region 3 is about the same as the terminal velocity of settling crystals, the crystals should stay in suspension. Thus the ratio (S) of the frictional velocity to the terminal velocity was calculated, using Kraichnan's equations and a routine that calculated the Stoke's fall velocity if the local Reynold's number of the crystals was  $<1$  (which it was in all cases calculated thus far) and invoked the drag coefficient if the local Reynold's number was  $>1$ . Thus if  $S > 1$ , the magma ocean remains well stirred with a significant fraction of its crystals remaining in suspension. It is of interest to discover what factors, if any, cause  $S > 1$ . It should be noted that the only parameters that changed between the Earth and Moon models were the bulk compositions and the acceleration of gravity. The liquidus and solidus temperatures, among other parameters, were purposely kept constant in these calculations

The terminal velocity falls off as  $1/v$  but the frictional velocity falls off as  $1/v^{n/3}$  where  $v$  is the kinematic viscosity and  $n$  is the power in the Rayleigh-Nusselt number relationship. Thus  $S$  increases as the viscosity increases as crystallization proceeds as shown above. This also implies that  $S$  increases as the  $SiO_2$  content of the magma increases. The above models indicate that millimeter sized crystals are likely to be suspended in both lunar and terrestrial magma oceans, but crystals of size 1-10 cm will probably not stay suspended. Increasing the depth of the ocean enhances the likelihood that the crystals will be suspended, but the decrease of the acceleration of gravity between the Earth and Moon seems to have only a small effect. A potentially large effect not yet modeled is that of an increase in the liquidus and solidus temperatures with pressure. This may markedly enhance the terrestrial ocean's ability to keep crystals in suspension. Another aspect for study is the point at which region 3 disappears. If there is no region 3, the magma ocean's ability to keep crystals in suspension drops greatly. None of the models run thus far have had region 3 disappear even at 50% crystallization.

In spite of these uncertainties, it seems likely that crystals in a lunar magma ocean are more likely to sink (or float) than crystals in a deeper, more vigorously stirred terrestrial magma ocean. Although our initial runs show this effect to be smaller than we initially expected, we feel that a thorough discussion of the physics of crystal suspension in a convecting magma ocean may clarify some of the geochemical differences between the earth and the moon.

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**ORIGIN OF AN INHABITED PLANET; James C. G. Walker**

Space Physics Research Laboratory, Department of Atmospheric, Oceanic and Space Sciences and Department of Geological Sciences, The University of Michigan, Ann Arbor, Michigan 48109-2143

How does the existence and the history of life on Earth constrain theories of planetary origin? Something can be learned from the unambiguous record of the antiquity and continuity of life. The oldest clear evidence of life dates back to 3.5 billion years ago. By that time the processes of planetary growth had ameliorated enough to permit a habitable environment. It is not clear from the paleontological record, however, that the environment was permanently habitable as long ago as 3.5 billion years. A clearly continuous paleontological record of Archean life does not exist. Whole-Earth sterilizing impact events can not be ruled out on biological grounds until early in the Proterozoic period. The paleontological record of the antiquity and continuity of life sets upper limits on the sizes of objects with which Earth has collided over the course of geological history.

Organisms are uniquely able to unmix the constituents of the environment. In particular, photosynthetic organisms can generate reduced organic carbon compounds even in a strongly oxidizing environment. Their activities have resulted in accumulations of reduced compounds at the surface of the Earth, throughout the upper crust, and possibly at deeper levels also. Equivalent amounts of strongly oxidized compounds have also accumulated. The resultant heterogeneity makes it hard to determine the original oxidation state of Earth's outer layers. Life's unmixing activities have also obscured the original isotope ratios of several biogenic elements.

DENSITY WAVES AND PLANETESIMAL DISPERSION VELOCITIES. Wm. R. Ward, Jet Propulsion Laboratory, Pasadena, CA 91109. The most completely developed model for the accretion of the terrestrial planets is the gas-free, stochastic model (1,2). Accretion runaway in the early stages of accumulation (3,4) produces a small number [ $N \approx O(10^2)$ ] of large planetesimals,  $M$ , as the starting configuration for end-stage accretion. Orbital eccentricities and inclinations are excited by gravitational relaxation of the planetesimal disc but damped by inelastic collisions. Typical dispersion velocities are of order  $v_c \sim \sqrt{GM/\theta R}$ , where  $R$  is the object's radius and  $\theta \sim O(1)$  is the so-called Safronov number. Accretion time scales are long [i.e.,  $\tau_{acc} \approx O(10^7)$  yrs.] and the process exhibits considerable mixing.

The addition of aerodynamic drag - in the alternative assumption of an extant gaseous nebula (5) - does not appreciably change the outcome for the inner solar system because drag effects are relatively weak for large planetesimals with low surface to volume ratios. However, the effects of the gas disc are not limited to aerodynamic drag. A potentially much stronger coupling to the gas component can occur through the launching of density waves in the disc (6). A planetesimal will drive waves at various Lindblad resonances: positions where the local epicycle frequency of the disc is equal to the Doppler shifted frequency of a component of the planetesimal's Fourier decomposed disturbing function. These waves carry angular momentum and can significantly modify the orbit of the object generating them.

Variation of the eccentricity through Lindblad torques occurs within a characteristic time,  $\tau_e \sim \mu^{-1} \Omega^{-1} (M_0/\sigma r^2) (c/r\Omega)^4$ . There are two families of Lindblad resonances that contribute to eccentricity change: Resonances that lie inside or outside the perturber's orbit excite it (6), while resonances that fall at the perturber's orbit (co-orbiting) damp it (7). Recent calculations using a vertically averaged disturbing function indicate that co-orbiting resonances are slightly stronger and the eccentricity decays (7). We shall make that assumption here, although further study will be needed before this issue can be considered resolved.

Equating  $\tau_e$  to the gravitational relaxation time for the disc (8) yields a equilibrium dispersion velocity,  $v_{dw}$ , that is comparable to the gas sound speed,  $c$ , (9). This dispersion velocity is independent of planetesimal mass because both scattering and density wave time scales are proportional to the combination  $(\mu\sigma)$ . Should  $v_c$  rise above  $v_{dw}$ , "density wave drag", not collisions, will control the equilibrium state of the disc. This occurs when  $M \geq c^3 G^{-1} (3/4\pi G \rho_p)^{1/2} \sim O(10^{25} \text{ gm})$  which is itself comparable to the planetesimal size produced by runaway accretion.

When objects are few enough in number,  $N_c$ , that their characteristic differential semi-major axis  $\sim r/N_c$  exceeds their radial excursions,  $\sim v_{dw}/\Omega$ , orbits will no longer, in general, be crossing. The random walk assumption used to estimate a disc's relaxation time is not valid and mutual gravitational perturbations become increasing periodic in nature. The critical number for the inner solar system is  $N_c \sim O(r\Omega/c) \sim 40(T/100^\circ\text{K})^{1/2}$ ; for  $N < N_c$  the scattering strength quickly weakens and orbits become more circular.

If density waves damp the disc to an apparently collisionless state, what drives the system to its final configuration with  $N_c \ll N$ ? The same density wave torques will prevent permanent isolation of planetesimals by decaying their orbits. The time scale for orbital migration is  $\tau_a \sim \mu^{-1} \Omega^{-1} (M_0/\sigma r^2) (c/r\Omega)^2$ , (10). The drift direction depends on structural details

of the disc; but the most complete treatment to date indicates that orbits probably decay (11). Since  $\tau_a \propto \mu^{-1}$ , large objects drift faster, overtaking smaller ones. This produces a positive feed-back in the accretion rate resulting in a characteristic growth time independent of mass:  $\tau \sim (2\pi\Omega)^{-1} (\sigma/\sigma_d) (M_\odot/\sigma r^2)^2 (c/r\Omega)^2$ , where  $\sigma_d$  is the surface density of accreting material. This is much shorter than the estimate,  $\tau_{acc} \sim \Omega^{-1} (\rho_p R/\sigma_d)$ , for end-stage gas-free accretion; the ratio of these two time scales being  $\tau/\tau_{acc} \approx 3 \times 10^{-3} (T/100^\circ\text{K}) (\sigma/10^3 \text{ gm/cm}^2)^{-1} (M/M_\odot)^{-1/3}$ .

The protoplanet's orbital decay will stall if it can open a gap in the disc. Density wave torques can open and maintain a gap against gas diffusion when its mass exceeds  $\sim \alpha^{1/2} (c/r\Omega)^{5/2} \sim 0(10^{29} \alpha^{1/2} (T/100^\circ\text{K})^{5/4} \text{ gm})$ , where  $\alpha = \nu\Omega/c^2$  is a measure of the turbulent viscosity (10,12). For  $\alpha \sim 10^{-4}$  (13), this mass is comparable to the earth's. A protoplanet orbiting in a gap will then act as a barrier/sink for other drifting planetesimals.

The assumption that the nebula has not yet dissipated seems quite reasonable, considering the shorter formation time scales implied by this mechanism (i.e.,  $10^{5-6}$  yrs). Late impacting objects could be large, consistent with recent ideas concerning lunar origin. However, less mixing should occur, with the final planetary objects preserving some of the chemical gradient of the disc.

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## ORIGIN OF THE EARTH-MOON BINARY PLANET, 1: BULK COMPOSITION OF THE MOON

Paul H. Warren and John T. Wasson

Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90024

The origin of the Earth can only be understood in the context of the greater problem of the origin of the planets, and of the Moon in particular. Virtually all direct evidence regarding the earliest Earth has been obliterated by subsequent geologic activity. However, oxygen isotopic evidence [1] confirms a close genetic link between the Moon and the Earth. One recently popular model of lunar origin [review: 2] holds that a roughly Mars-sized planet collided with the nascent Earth; some of the liquid and vapor expelled from the impact site went into orbit, and eventually coalesced to form the Moon. This giant impact hypothesis has enjoyed bandwagon status since 1984. It implies that virtually all of the Earth was melted, and some of its outermost portion was vaporized, by the giant impact. In many versions of this model [3,4], the bulk of the Moon is derived from vaporized Earth material. In some recent versions, however, the bulk of the Moon is derived from the Mars-sized "impactor" planet. We will refer to these two versions of the giant impact hypothesis as model 1A and model 1B, respectively. Both models carry strong implications regarding the Moon's early thermal evolution, and almost equally strong (albeit in many respects contradictory) implications regarding its bulk composition.

Model 1A implies that the Moon and the Earth's mantle are compositionally related. Earliest versions [3,4] claimed that model 1A had the advantage of forming a Moon enriched several-fold in refractory lithophile elements (Al, Ca, Th, U, etc.), because the protolunar vapor cloud was predicted to undergo fractional condensation. However, this implication now appears more like a disadvantage. The hypothesis of a bulk-Moon enrichment in refractory lithophile elements received a serious setback when lunar heat-flow measurements were revised [5]. It was further weakened by a comprehensive assessment of (a) the geological and geochemical representativeness of the two heat-flow measurement sites (e.g., the site with the highest heat flow is in an anomalously Th-rich region), and (b) the implications of a U- and Th-enriched lunar composition for the present thermal state of the lunar interior, insulated as it is by a thick blanket of megaregolith [6]. The hypothesis was weakened yet further by the consistently low-Th compositions of the lunar meteorites [7]. A bulk-Moon enrichment in refractory elements is seldom mentioned in recent versions of the giant impact model. Stevenson [2] even argues that the orbiting "disk" of protolunar melt plus vapor was "essentially a closed system." However, his models assume that the mass of the disk was *two* Moon masses.

Another implication of fractional condensation of the protolunar material, as required by model 1, would be a depletion of volatile FeO (volatile, that is, compared to MgO, SiO<sub>2</sub>, and the other major elements) [8]. The bulk-Moon FeO concentration can be relatively well constrained, thanks to the consistent behavior of the ratio MgO/FeO during igneous differentiation. The MgO/FeO ratios of highlands samples imply that the bulk-Moon FeO concentration is impressively similar to that of the Earth's mantle [9] (however, it does *not* necessarily follow that the protolunar material therefore came out of the Earth's mantle). Most other estimations, derived mainly from the dubious assumption that many mare basalts formed by partial melting of little-differentiated portions of the lunar mantle, favor even *higher* FeO for the Moon vs. the Earth's mantle.

Ringwood et al. [10] have suggested that siderophile geochemistry shows that the Moon was derived mainly from the Earth's mantle, after the Earth's mantle had acquired its final siderophile element composition. Ringwood et al. [10] modeled Apollo-16 breccias as mixtures of near-nomineralic anorthosite, minor KREEP and meteoritic components, and a single indigenous mafic component. By assuming that KREEP and anorthosite have negligible siderophile element contents, and that the meteoritic debris has fixed, H-chondritic siderophile element ratios, measured breccia compositions are putatively "corrected" to the indigenous siderophile contents of the mafic component. Ringwood et al. [10] interpret the mafic component as lunar "komatiite." Ringwood et al. [10] found that the "residual" Ni contents of Apollo-16 breccias tend to be remarkably high, and display a strong correlation with mafic indicators, implying that the Ni content of the pure komatiite was  $\sim 1300 \mu\text{g/g}$ , i.e., virtually as high as typical Earth komatiite Ni contents. However, Apollo 16 does not appear to be representative,



## ORIGIN OF THE EARTH-MOON BINARY PLANET, 2: PHASED LUNAR DIFFERENTIATION

Paul H. Warren

Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90024

According to a recently popular model of lunar origin [1], a roughly Mars-sized planet collided with the nascent Earth, some of the liquid and vapor expelled from the impact site went into orbit, and eventually coalesced to form the Moon. This giant impact hypothesis implies that virtually all of the Earth was melted, and some of its outermost portion was vaporized, in the aftermath of the giant impact. Virtually all evidence regarding the earliest Earth has been obliterated by subsequent geologic activity. However, the giant impact model also implies that the Moon formed extremely hot. The model can thus be tested based on the early thermal evolution of the Moon. No consensus has yet emerged regarding the general validity of the lunar "magma ocean" (or magmasphere) hypothesis. However, during the past ten years a consensus *has* emerged that even if a major portion of the lunar crust formed by flotation over a magma ocean, at least a large part of the lunar crust did *not* form in such a mode, but instead formed by gradual differentiation of the deep, Mg-rich interior, throughout the first several hundred megayears of planetologic time. This "modern" hypothesis of lunar evolution, the evidence for which is reviewed below, implies that the earliest Moon was far from totally molten, because a totally molten Moon would probably have differentiated too thoroughly (i.e., concentrated feldspar and the incompatible-element heat sources K, Th and U too neatly into the crust) to allow such copious partial melting to occur in its post-magmasphere mantle.

Stevenson [1] has argued that even though the protolunar melt/vapor "disk" generated by the giant impact starts out at a temperature of several thousand K, by the time it coalesces into the Moon it is only partially molten. He also admits that this aspect of the model "has not been quantified." Efficient geochemical differentiation does not require that melting be total, only that it be sufficiently extensive, and sustained, for melts to migrate thoroughly apart from residual crystals. Even allowing for considerable cooling of the protolunar material prior to final accretion, the giant impact model predicts that all of the immediate precursor bodies of the Moon are already quite hot, *before* additional heat was generated from conversion of kinetic energy as the precursor bodies collided to form the Moon. This situation is radically different from that implied by most other lunar origin scenarios, in which heat generated from conversion of kinetic energy is a dominant factor, if not the only important factor, in primordial heating. Without the great stores of pre-existing heat implied by the giant impact model, substantial heating does not occur until the Moon reaches nearly its final mass. In short, the giant impact model implies that pervasive partial melting (if not total melting) is a factor throughout the volume of the Moon as it grows, whereas other models tend to predict pervasive, accretion-coeval partial melting only in the outer portion of Moon.

The primary evidence implying a complex, multistage origin for a major proportion of the lunar crust comes from geochemical studies of "pristine" nonmare rocks. In lunar parlance, a pristine rock is one that happened to avoid fine-scale impact-mixing during the intense meteoritic bombardment that afflicted the upper lunar crust, as recently as  $\sim 3.8$  Ga. In other words, only pristine rocks preserve unmixed compositions generated by internal lunar processes. Distinguishing pristine rocks from polymict impact breccias is generally feasible based on petrographic observations alone. Assuming the specimen is large enough to permit trace element analysis, the distinction can nearly always be confirmed by analysis of siderophile elements, because siderophile concentrations tend to be vastly higher in meteoritic impact debris than in pristine materials. Except for the extraordinarily young (and volumetrically almost negligible) mare basalts, the vast majority of materials found at the impact-scarred surface of the Moon are polymict (nonpristine). However, thousands of nonmare rock samples, including clasts within polymict breccias, have been examined over the years, and so far roughly 100 of them large enough to permit meaningful interpretation have turned out to be pristine. Nearly all of these pristine nonmare rocks appear to be igneous cumulates, sometimes thermally metamorphosed into coarse granulites, and very often mildly brecciated into monomict breccias; a few (i.e., most of those of "KREEP" affinity) are subophitic basalts.

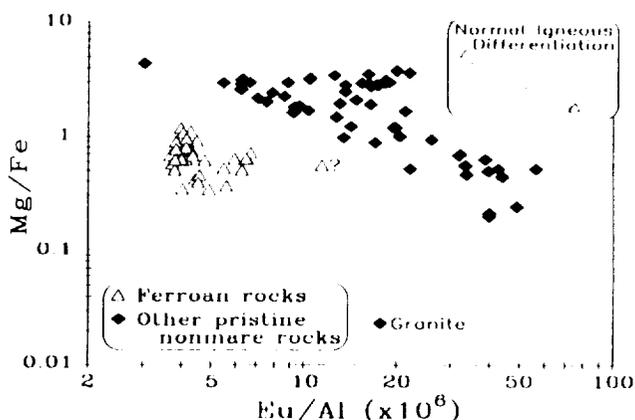
When the data base for Moon rocks is restricted to those of pristine nonmare affinities, a striking geochemical bimodality emerges. Most of the true anorthosites (and a few small fragments of moderate feldspar content) show

distinctly "ferroan" geochemistry in comparison to the remaining, generally less feldspathic, pristine nonmare rocks. In lunar parlance, "ferroan" geochemistry refers to a concurrence of relatively low Mg/Fe ratio with relatively high Ca/Na ratio. The Mg/Fe and Ca/Na ratios are extremely useful in studies of cumulates, especially lunar cumulates, because the Mg/Fe ratio is governed almost entirely by mafic silicates, and the Ca/Na ratio is governed almost entirely by feldspar. Thus, these ratios behave in relatively predictable ways, and a sample with just a few cumulus mafic silicate and feldspar crystals is likely to be reasonably representative of an entire large rock. Nonmare cumulates that are not of ferroan geochemistry are lumped into a category called "Mg-rich rocks." Substituting another feldspar-governed ratio, Eu/Al, for Ca/Na results in an even more pronounced expression of the bimodality (Figure). As might be inferred from the Figure, the Mg-rich (non-ferroan) rocks comprise a major proportion of the total crust. In fact, mass balance calculations for highlands regolith compositions imply that the overall proportion of Mg-rich material is probably at least close to 50 wt% (see [2] for the most recent and comprehensive, though slightly overstated, arguments along these lines).

Given this extreme geochemical bimodality, both the ferroan and the Mg-rich classes of ancient cumulates cannot be products of a single petrogenetic episode [3,4]. Either one or the other (or conceivably neither), but clearly *not* both, formed as flotation cumulates over the primordial magma ocean. Since the primary *raison d'être* for the magmasphere hypothesis has always been extreme concentration of feldspar into the early lunar crust [5], it is equally clear that, of the two main classes of pristine nonmare rocks, the ferroan class is the only one likely to have formed by magmasphere feldspar flotation. Except for the very youngest sorts of pristine nonmare rocks (i.e., a few KREEP basalts, which formed after the last intense meteoritic bombardment), ages for these rocks are problematical. Only about 10 have been measured reliably, and even when good isochrons are determined, they may in some cases date isotopic closure at the time a rock was excavated (by impact) from a slowly cooling region deep in the crust, rather than closure at the time when the rock crystallized from its parent melt. In short, both the greater extent of brecciation of the earliest crust, and its greater mean temperature, probably engender an inherent bias towards relatively low ages. However, it seems reasonably clear that the ferroan anorthosites are at least nearly as old as the Moon itself, and the Mg-rich rocks seem to have formed throughout the first 300 My of planetologic time [6]. The emplacement of the Mg-rich magmas as scattered intrusions into the older ferroan anorthosite crust left a distinctive imprint on the compositions of the KREEP basalts, which probably owe their origins ultimately to the last dregs of the primordial magma ocean, collected near the base of the crust (the putative "urKREEP"). The KREEP basalts have, along with the high incompatible element concentrations for which they are named, incongruously high Mg/Fe ratios, a paradox which can only be explained by systematic mixing between urKREEP and Mg-rich magmas rising out of the deeper interior [7].

Thus, the lesson from recent advances in lunar petrology is that a major proportion of the Moon's crust did *not* form by flotation over a primordial magma ocean. Major sources of heat and feldspar remained deep inside the Moon until after the magmasphere had expired. This conclusion implies a relatively cool origin for the Moon, and therefore seems only marginally consistent, at best, with the giant impact hypothesis.

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## ACCRETION OF THE EARTH

S.J. Weidenschilling, Planetary Science Institute, Tucson, Arizona

Earth's origin must be considered in the context of the formation of (at least) the terrestrial planets and the Moon. The present paradigm is accretion of  $\sim 10^{12}$  initial km-sized planetesimals into a few planets. Current debate concerns mechanisms and details of the accretion process. Some necessary conditions to be satisfied include:

(a) Accretion must proceed to production of  $\approx 4$  planets, although a larger number of smaller planets in more closely spaced orbits seems stable. The accreting bodies "communicate" over distances  $\gtrsim 0.1$  AU by acquiring large orbital eccentricities and/or evolution of semimajor axes by diffusion or systematic drift, e.g. by drag.

(b) Rotational obliquities require a large stochastic component of spin angular momentum presumably due to large impacts. A systematic prograde component does not appear to be necessary.

(c) Planetary compositions vary. Noble gas content decreases monotonically (systematically?) from Venus to Mars. Other variations (Fe) do not appear systematic.

(d) If SNC meteorites are from Mars, the oxygen isotope reservoir in the terrestrial planet zone was nonuniform, and preserved some variation, but Earth and Moon have identical O isotopic compositions.

Accretion scenarios divide on two major issues and their consequences: Was nebular gas present or absent during accretion of the terrestrial planets? Was the size distribution of accreted bodies dominated by large or small objects (relative to identifiable planetary embryos)? Four end-member permutations are possible:

I. Gas-free, Small Bodies. Sweeping up of small planetesimals by a dominant embryo was implicitly assumed by some early analytic models (1), and mentioned as a possible (but not inevitable) continuation of "runaway growth" of a small number of embryos (2). More elaborate numerical models (3) still require a single "designated embryo" in a "feeding zone"; (a) and (c) are assumptions rather than results. In the absence of gas, there seems to be no way for embryos to clear small bodies completely from the spaces between their orbits. Small impacts would not produce significant variation in obliquities. The lack of mixing between zones would satisfy (d), but lunar origin is difficult (4). Accretion timescales are  $\sim 10^7$ - $10^8$  y.

II. Gas-free, Large Bodies. Safronov's (5) analytic model derived a power-law size distribution dominated by the largest bodies. Emergence of dominant embryos was constrained by (b), with second largest bodies  $\sim 10^{-3}$ - $10^{-2}$  times the final planetary masses. Wetherill's (6-8) numerical simulations of a few hundred bodies on crossing orbits result in growth of many large bodies, with no clearly dominant embryos until very late in accretion. The last impacts involve very large mass ratios  $\gtrsim 0.1$ . Conservation of orbital angular momentum and energy imply an initially narrow swarm in the Earth-Venus region, with spreading yielding Mercury and Mars as "edge effects." There are no distinct feeding zones and much radial mixing; planetary compositions are correlated with location, but with large stochastic variations. This model can satisfy conditions (a,b), and (c) with possible exception of noble gases. It is consistent with origin of the Moon by giant impact, but seems to require coincidence to explain (d); the impactor and target must have the same O isotopic composition. Accretion timescales are  $\sim 10^7$ - $10^8$  y.

III. Gas-rich, Large Bodies. This scenario corresponds to the "Kyoto" model (9), which assumes presence of the solar nebular during accretion. The Kyoto scenario neglects collisional fragmentation. Gas drag induces radial

migration, but it is slow, due to the large sizes of planetesimals. Accretion timescales are  $\lambda 10^7$  y, which exceeds current astrophysical estimates of the nebular lifetime. Conditions (a,b) are not explicitly treated but may be satisfied. Earth and Venus would capture massive, temporary H-He atmospheres during accretion, causing extensive heating and melting of their outer layers. Their noble gas systematics may require complex fractionation processes (10). The Kyoto group assumes a capture origin for the Moon, but the impact model is not excluded.

IV. Gas-rich, Small Bodies. This scenario depends on gas drag to bring small ( $\ll$  km-sized) fragments of planetesimals to a growing embryo. Radial migration times can be very short, allowing rapid growth, in  $<10^6$  y. Patterson and Spaute (11) assume very weak planetesimals fragmented at low impact velocities due to gravitational stirring by a few early-formed embryos. Resonances can produce higher velocities over distances comparable to planetary spacings (12), possibly satisfying (a). In pure form, this model yields only small impacts, violating (b), but growth of  $>4$  embryos with some large late-stage impacts is not ruled out (13). Other conditions, including lunar origin, have not been addressed yet. This model depends on unknown mechanical properties of planetesimals.

Conclusions. Of the four basic scenarios, (II) appears to be the most self-consistent and successful at meeting the constraints. Scenario (IV) is relatively new and needs more development. The lifetime of the solar nebula is poorly constrained, so "hybrid" models, in which gas is present only at some early stage of accretion, are possible. Further work is needed to determine interactions of relatively rare large bodies with smaller bodies in the swarm, when "continuum" models for gravitational stirring (14) break down, and distant perturbations and resonances may become important. There is little justification for the canonical km-sized initial planetesimals (15); the effects of other starting conditions should be examined to determine effects on "runaway growth" of planetary embryos. Accretion probably involved large impacts or thermal blanketing by a massive captured atmosphere, or both. Thus, it is highly probably that the Earth formed hot (7).

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ACCUMULATION OF THE EARTH FROM RUNAWAY EMBRYOS; G. W. Wetherill,  
Dept. of Terrestrial Magnetism, Carnegie Institution of Washington,  
Washington, D.C. 20015.

Most earlier 3D simulations of the final stages of accumulation of the terrestrial planets assumed initial states based on the theories of embryo formation of Safronov (1) and Nakagawa et al (2). These are characterized by a "marching front" of a large number of sublunar-size bodies of nearly equal mass, followed by a power law tail of smaller bodies (3,4,5). It now seems more likely that terrestrial planet embryo formation involved runaway growth to form a smaller number of larger embryos (6). The principal cause of the runaway is energy equipartition that lowers the velocities of the largest bodies relative to those of the average mass bodies of the swarm (7,8).

Only a few simulations using runaway initial planetesimals have been reported (4). In the present work 42 new simulations of the growth of planets from 151 runaway embryos have been calculated for comparison with 38 "orderly growth" simulations reported earlier. An initial surface density of 20 g/cm<sup>2</sup> between 0.7 and 1.1 A.U. is assumed. This decreases uniformly inside and outside this range as described previously (4). Runaways were assumed to be limited to a spacing of 4 Hill sphere radii. The principal mass of the initial swarm consisted of 29 bodies ranging in mass from 6.4 X 10<sup>26</sup> g at 1.1 A.U. to 1.7 X 10<sup>26</sup> g at 0.7 A.U. The smallest bodies were closely spaced ( $\sim 10^{-3}$  A.U.) 7 X 10<sup>23</sup> g objects at 0.45 A.U. This distribution was not arbitrary, being constrained by the mass, energy, and angular momentum of the present terrestrial planets and the limits to runaway growth. The calculations were grouped into sets corresponding to different assumptions regarding the fractionation of impact energy into heating and fragmentation, and rate of completion of embryo growth as a function of semi-major axis.

In general the results are similar to those found for orderly non-runaway growth. In 60% of the calculations 2 final planets  $> 1.5 \times 10^{27}$  g were formed, and 3 final planets of this size were formed in 36% of the cases. The total number of final planets larger than one lunar mass ranged from 2 to 6 and averaged 3.6. The time scale for growth was the same as found before. Some differences in final mass distributions were found for variations in the initial conditions, but these were confined to the formation of the smaller planets.

In all cases the growth of the largest planets was punctuated by giant impacts. For those 25 cases where the number of large final planets was 2, the body with the greater heliocentric distance (usually  $\sim 1.0$ ) was designated "Earth". For that body the number of "catastrophic" events are tabulated below:

<u>Event</u>	<u>Average No./Simulation</u>
Mercury < impact mass < Mars	3.0
Mars < impact mass < 2 X Mars	1.2
2 X Mars < impact mass	0.8
Impact energy > 1/2 gravitational binding	0.2
Impact energy > gravitational binding	0
Rotational instability	0.04
Within 50% of rotational instability	2.1

Typically, "Earth" was totally melted by the time it grew to  $\sim 60\%$  of its final radius, requiring a time  $< 10^7$  years.

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## HISTORY OF U AND Pb IN THE EARTH'S MANTLE William M. White Department of Geological Sciences, Snee Hall, Cornell University, Ithaca, NY 14850 USA

Pb isotope ratios are a powerful tool for study of the chemical evolution of the Earth, but interpretation of Pb isotopes has proved more difficult than for simpler systems, as Pb isotope geochemistry has several well-known paradoxical features. These include: (1) both the depleted mantle and upper crust have  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  falling to the right of the geochron, indicating a time-averaged depletion of Pb relative to U in the mantle, even though U appears to be more incompatible than Pb; (2) though the time-averaged  $^{232}\text{Th}/^{238}\text{U}$  ratio ( $\kappa$ ) of the depleted mantle is quite high (3.6), the present ratio is low (2.6), (3) though Pb seems to have the same incompatibility as Ce in magmatic systems, it is a factor of 3 more depleted in the mantle than Ce.

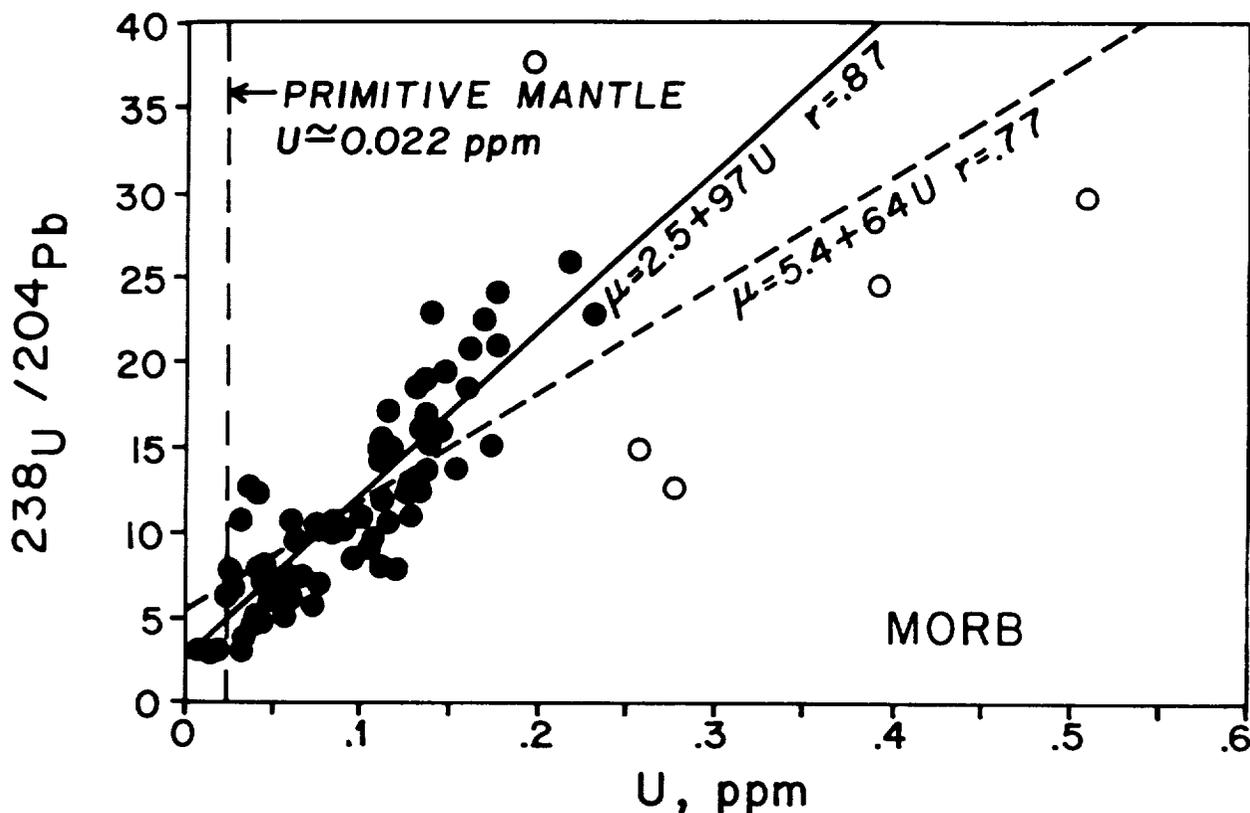


Figure 1. Variation of  $^{238}\text{U}/^{204}\text{Pb}$  and U in MORB. Open symbols are samples with E-type chemistries or with indications of secondary alteration. Dashed line is a regression line through all points, solid line is a regression line through solid points. Data compiled from the literature and from W. M. White (unpublished).

The present distribution of U and Pb in the Earth provides a useful boundary condition on Pb isotopic evolution. Up to now, this distribution has been poorly understood. However, there are sufficient data on mid-ocean ridge basalts (MORB), that some conclusions may be drawn. The relationship between  $^{238}\text{U}/^{204}\text{Pb}$  ( $\mu$ ) and U in 77 MORB samples is shown in Figure 1, which reveals a strong positive correlation between them ( $r = 0.77$  for  $n = 77$ ). The correlation improves to  $r = 0.87$  ( $n = 72$ ) when samples showing P- or E-MORB characteristics or indica-

tions of alteration are excluded. The value of  $r^2$  indicates 72% of the variation in  $\mu$  is related to variation in U. Variation in U in MORB, and hence in  $\mu$  as well, may be attributed to three causes: fractional crystallization, partial melting, and source heterogeneity. If the variations in  $\mu$  result from long-standing source heterogeneity, they should be related to variations in  $^{206}\text{Pb}/^{204}\text{Pb}$ . However, the correlation between  $\mu$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  is quite weak ( $r = 0.358$ , significant at the 1% level);  $r^2$  for this correlation indicates only 13% of the variation in  $\mu$  is related to variation in  $^{206}\text{Pb}/^{204}\text{Pb}$ . This suggests nearly all the variation in  $\mu$  (range: 3–26) results from magmatic processes such as partial melting and fractional crystallization. It is worth noting that the average  $^{232}\text{Th}/^{238}\text{U}$  ( $\kappa$ ) of this data set is 2.6, similar to values of  $\kappa$  estimated from  $^{230}\text{Th}/^{232}\text{Th}$ , but much lower than the time-integrated value estimated from  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  (3.6), and the bulk silicate Earth value ( $4.0 \pm 0.2$ ).

If we assume that all the variation in  $\mu$  and U results from fractionation during magma generation and evolution, then the correlation between them may be used to estimate a maximum value for  $\mu$  in the depleted mantle. A reasonable assumption is that the bulk silicate Earth, or primitive mantle, concentration of U, 22 ppb, is an upper limit to its concentration in the depleted mantle. An upper limit to the value of  $\mu$  in the depleted mantle is then given by the intersection of the  $\mu$ -U regression line with the bulk earth U concentration. This approach yields  $\mu \leq 4.6$ . A somewhat different approach is to assume that variation in  $\mu$  which is related to variation in U is due to magmatic fractionation, and that variation related to  $^{206}\text{Pb}/^{204}\text{Pb}$  variation is due to mantle heterogeneity. Under this assumption, an upper limit to the value of  $\mu$  in the depleted mantle may be estimated from multiple regression of  $\mu$  on U and  $^{206}\text{Pb}/^{204}\text{Pb}$ . This approach yields  $\mu \leq 4.4$  at the bulk earth U and the average  $^{206}\text{Pb}/^{204}\text{Pb}$  of MORB (18.4), an essentially identical result. If either approach is correct, the present-day average  $\mu$  in the depleted mantle is much less than the probable bulk silicate earth value of about 8. Taken alone, this result should not be surprising since U is more incompatible than Pb.

Time-integrated values of  $\mu$  in the depleted mantle may be derived from  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$ , which we shall term  $\mu_{206\text{Pb}}$  and  $\mu_{207\text{Pb}}$ . The average value of  $\mu$  for this data set estimated from  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  are 8.9 and 8.2 respectively. These estimates of  $\mu$  differ because the half-lives of  $^{238}\text{U}$  and  $^{235}\text{U}$  differ.  $\mu_{207\text{Pb}}$  and  $\mu_{206\text{Pb}}$  may be thought of as averages weighted over different times:  $\mu_{207\text{Pb}}$  is a measure of  $\mu$  over a relatively short time centered around 3.8 Ga, i.e., the early history of the Earth, while  $\mu_{206\text{Pb}}$  is a measure of  $\mu$  over a much longer time centered around 2.3 Ga, i.e., the whole history of the Earth. Thus the depleted mantle has experienced a complex history of an early increase in  $\mu$  and relatively recent large decreases in  $\mu$  and  $\kappa$ . The important conclusion to be drawn from this is that the relative behaviors of Pb and U were different in the early mantle that they are today. This in turn implies chemical processes in the early Earth must have differed in some fundamental way from present processes. A similar conclusion is suggested by the observation that Pb has become depleted relative to Ce, yet two elements are not fractionated by present-day magmatic processes. In the early Earth, Pb was extracted from the mantle more efficiently than U and Ce; more recently, U has been extracted from the mantle more efficiently than Pb and Ce.

There is an alternative interpretation, namely that the residence time of Pb in the depleted mantle is sufficiently short that the low  $^{238}\text{U}/^{204}\text{Pb}$  ratio of the depleted mantle is not significantly reflected in  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios. This interpretation was earlier proposed to explain the difference between the present value of  $\kappa$  in the depleted mantle and the time integrated on estimated from  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ . If this latter interpretation is correct, the source of Pb in the depleted mantle cannot be a primitive reservoir. Rather, it must be a reservoir enriched in U relative to Pb. One reservoir with this characteristic is the upper continental crust. However, efforts to produce a model of crust—mantle recycling that accounts for all the chemical and isotopic characteristics of the depleted mantle have so far not been successful.

WEATHERING AS A CONTROL FOR PRECAMBRIAN ATMOSPHERIC  
CONDITIONS; H. Wiggering, Essen University, F.R.G.

Numerous models of the degassing history of the Earth permit to infer a 'pre-oxidizing' Archean atmosphere, consisting of water vapor,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{H}_2\text{S}$ , and only minor amounts of more reducing components such as  $\text{H}_2$ .

Most models of the early atmosphere-hydrosphere system begin with an immediately outgassed and condensed ocean system equilibrated with  $\text{CO}_2$ . The most convincing models argue that weathering reactions were sufficiently rapid to keep up with the injection of acid volcanic gases into the atmosphere and hydrosphere. The initial pre-oxidizing system changed to an oxidizing system with the increase of  $\text{O}_2$  and the simultaneous decrease of  $\text{CO}_2$ .

In this context Precambrian paleosols have received considerable attention because they promise to yield semiquantitative answers to questions regarding the nature of early weathering processes. Since vascular landplants were absent at the time of their formation, the ancient paleosols are especially suitable to uncover inorganic subaerial weathering processes. These are controlled largely by partial pressures of  $\text{O}_2$  and  $\text{CO}_2$  in the primitive atmosphere.

Another way to shed light on the interactions of the primitive atmosphere and the Precambrian lithosphere is to carry out weathering experiments with different gas mixtures. Since mafic and ultramafic rocks have characterized the early Precambrian lithosphere pulverized ultramafic and mafic materials were given into perspex vessels, covered with  $\text{N}_2$  saturated water, and purged with different gases such as  $\text{N}_2$ - $\text{CO}_2$ - $\text{H}_2\text{S}$ - $\text{H}_2$  or pure  $\text{CO}_2$  etc.. Solution and precipitation of specific elements/minerals yield information of the probability of theories of Archean/Precambrian atmosphere.

In vessels purged with  $\text{CO}_2$  the pH remains stable at about 6 during the course of the experiments. In vessels purged with  $\text{N}_2$ - $\text{CO}_2$ - $\text{H}_2\text{S}$ - $\text{H}_2$  the pH varied between 6.5 and 5 if  $\text{N}_2$ -saturated water was added after each sampling, but dropped down to 3 where samples were removed only. Parallel with the pH decrease the colour of the samples and covering solutions changed continuously from green to black. The discolouration is due to the precipitation of sulphides. Since  $\text{Fe}^{+2}$  is below the detection limit in the discoloured solutions but present in fairly high amounts in the nondiscoloured solutions in vessels purged with  $\text{CO}_2$ , the discolouration can be explained in terms of iron sulphide precipitation. This is in agreement with solubility calculations for  $\text{FeS}$ . It can be concluded, if  $\text{H}_2\text{S}$  was present in the early atmosphere in such high amounts as discussed in literature, sulphides should be an important constituent in paleosols and analogous sediments.

INVENTORY OF TERRESTRIAL HELIUM-3, L. J. Wittenberg,  
Fusion Technology Institute, University of Wisconsin, Madison,  
WI 53706-1687

The nuclear fusion of He-3 with deuterium has the potential to be a major energy source in the 21st century. The radioactive waste produced from such a fusion power reactor is the lowest of any nuclear energy system being considered and its atmospheric pollution is minuscule. The major impediment to this type of fusion reactor has been the perceived scarcity of He-3. Recently, we identified an inventory of greater than a million tonnes of He-3 existing in the fine regolith on the lunar surface, as a result of solar wind implantation.

The earth is protected by a magnetosphere which shields it from the solar wind; consequently, nearly all of the He-3 presently on earth existed in the primordial material which formed the planet. This paper surveys the principal terrestrial reservoirs of He-3, namely: (1) the atmosphere, (2) crustal natural gas deposits, (3) tectonic plate, subduction zone gas deposits, and (4) mantle-derived gases. Each of these reservoirs has a characteristic He-3/He-4 isotopic ratio<sup>1,2</sup> which is combined with their total helium content in order to assess their He-3 inventories, Table 1.

One concept of the formation of the earth suggests that asteroids similar in volatile content to the chondritic meteorites accreted as a veneer on a previously formed core. This veneer constitutes the upper mantle which still contains many of the volatile components. Estimates based upon degassing models suggest that the mantle presently contains  $(1.4 \text{ to } 20) \times 10^{13}$  atoms of primordial He-4 per g. Using this value, I estimate that the mantle may contain  $10^6$  to  $10^7$  tonnes of He-3. Although a measurement of the mantle's He-3 content is not possible, its presence has been detected in gases emitted from volcanos in Hawaii and along mid-ocean ridge vents.

A deep-drilling project has been undertaken recently at the Siljan crater area of Sweden in an attempt to recover from the mantle non-biogenic natural gas, which would be accompanied by helium with a high He-3 content; however, no abiogenic gas<sup>3</sup> has been positively detected to a depth of 6 km.

Primordial He-3 in the terrestrial environment is diluted by  $\alpha$ -particles emanating from the radioactive decay of U and Th ores. Some He-3 is formed, however, by neutrons emitted from the spontaneous fission of U-235 which react with Li-6 to form H-3 which decays to He-3. The steady-state value for the He-3/He-4 ratio in the earth's crust is  $\sim 0.015$  at.ppm, as shown by many natural gas deposits in England and the North Sea. All natural gas wells in the USA with He contents  $> 0.1\%$  are routinely assessed for their He inventories.<sup>4</sup> The potential He-3 inventory in these wells is  $\sim 0.8$  tonnes based upon an average He-3/He-4 ratio of 0.2 at.ppm.

Natural gas wells along the tectonic plate subduction zones,<sup>5</sup> particularly in the Western Pacific Basin, have a helium content up to 180 ppm and He-3/He-4 ratios of 5-10 at.ppm. This helium may originate from the mantle and become trapped in the gaseous reservoirs as these plates recede into the mantle. Based upon the estimated sediment subducted during the present epoch, up to 1000 tonnes of He-3 may exist in these reservoirs. Subduction zones from past epochs could increase these reservoirs to 25,000 tonnes. In addition, the sea beds of the present epoch may contain up to 200 tonnes of He-3 due to the precipitation of interplanetary dust particles.<sup>6</sup>

The earth's atmospheric helium budget has apparently reached a steady-state between the out-gassing of helium from the earth and its escape from the atmosphere.<sup>7</sup> The atmospheric He-4 vol. fraction is 5.22 ppm. at a He-3/He-4 ratio of 1.39 at.ppm.

Table 1. Estimated Terrestrial He-3 Inventory

	He-3 Metric Tonnes			
	<u>Proved</u>	<u>Probable</u>	<u>Possible</u>	<u>Speculative</u>
Atmosphere	4,000			
Crustal Natural Gas (USA)	0.20	0.18	0.22	0.20
Subduction Zone Natural Gas	0.03		1,000	25,000
Mantle Gas				$10^6-10^7$
	$4 \times 10^3$	0.18	$10^3$	$10^6-10^7$

Conclusions: (1) The amount of He-3 in proved terrestrial reservoirs is small, ~ 4000 tonnes, chiefly residing in the atmosphere at a concentration of  $7.3 \times 10^{-12}$  vol. fraction. (2) Unproven, but predictable, natural gas reservoirs from crustal sedimentary and newly discovered subduction zone wells may contain up to 26,000 tonnes of He-3 in a concentration range of  $(1.4 \text{ to } 8.8) \times 10^{-10}$  vol. fraction. (3) Very large, but speculative amounts of He-3 still exist in the mantle; however, its measurement or recovery have been unsuccessful, thus far.

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H AND D ESCAPE FROM EARTH AND MARS: A COMPARATIVE STUDY; Yuk L. Yung, Calif. Institute of Technology, Pasadena, CA 91125, Mark Allen, Calif. Institute of Technology and Jet Propulsion Laboratory, Pasadena, CA 91109, and Joseph P. Pinto, G.F.D.L., Princeton University, Princeton, NJ 08540

A one-dimensional photochemical model was used to study the chemical and physical processes which control the escape of hydrogen and deuterium from the atmospheres of Earth and Mars. The escape of H from Earth is mainly by charge exchange, with smaller contributions from thermal and polar wind processes. The escape of D from Earth is dominated by polar wind, with a smaller contribution from charge exchange. The loss of H and D from Mars is mainly via thermal evaporation. Hunten's limiting flux condition is attained for H and D on both planets.

We find that if the present H and D loss rates for both planets were assumed to be representative over geological time, this would violate some geochemical constraints. An escape rate in the past about two orders of magnitude higher than the present rate is required to explain the observed D/H ratios on Earth and Mars. Thus, the atmospheres of the terrestrial planets may have evolved from initial states that are drastically different from the current atmospheres. An attempt is made to search for a common cause.



Neon Fractionation by Hydrogen Escape from a Steam Atmosphere, K. Zahnle and J.B. Pollack, NASA/AMES, MS 245-3, Moffett Field, CA 94035, and J.F. Kasting, Dept. of Geoscience, Penn. State University, University Park, PA 16802.

Atmospheric neon is isotopically heavier than some mantle sources of neon<sup>1,2</sup>. By contrast, mantle and atmospheric reservoirs of the nonradiogenic isotopes of argon, krypton, and xenon are isotopically the same<sup>2</sup>. Heavy atmospheric neon therefore indicates the preferential loss of the lighter neon isotope from Earth's atmosphere after it had decoupled from the mantle. The heavier noble gases indicate that this differential escape process was limited to neon and less massive gases.

Fractionation in hydrodynamic hydrogen escape from a polluted steam atmosphere offers an inherently plausible explanation. Hydrogen escape would have been driven by absorption of solar extreme ultraviolet (EUV) radiation at very high altitude<sup>3,4</sup>. Inferred EUV fluxes in the early solar system imply hydrogen escape rates high enough that other heavier atmospheric gases should have been dragged along with it<sup>5,6</sup>. However, abundant heavy molecules do not escape readily. Escape is throttled at the maximum hydrogen escape rate for which the abundant heavy molecule is retained. N<sub>2</sub> and CO are both heavier than neon but lighter than argon. They are also probable constituents of the earliest atmosphere. Hence it is possible for neon to escape while argon does not.

To address this question we extend the theory of mass fractionation in hydrodynamic escape to atmospheres in which hydrogen is not the only major constituent. The most interesting and relevant case is the "diffusion-limited flux", in which hydrogen escapes at the maximum rate for which abundant heavy atmospheric constituents are hydrostatically retained. An impure steam atmosphere during accretion<sup>7,8</sup> would have provided the right conditions for differential neon escape to take place. Escape of <sup>20</sup>Ne is greatly preferred over escape of <sup>22</sup>Ne, although neither escapes quickly. The required amount of neon fractionation could have been produced by a steam atmosphere lasting as little as five million years. Given a set of favorable assumptions, it is also possible that the observed neon fractionation was produced entirely from transient steam atmospheres formed in the aftermath of large impacts.

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