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Thermal evolution of the Earth: effects of volatile exchange between atmosphere and interior

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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. 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. 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 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.

1. Introduction

Parameterized models of whole mantle convection have been used to study the thermal history of the Earth and to infer some physical properties of the mantle such as radiogenic heat source content [1–8]. These models generally show that mantle temperature and heat flow decrease with time, while mantle viscosity increases with time, all in accordance with a cooling Earth. Furthermore, heat flow exceeds radiogenic heat generation at the present day so that the Urey ratio, the ratio of internal heat generation to surface heat flow, is less than unity at present.

An essential feature of these parameterized

convection thermal history models is their inclusion of the strong temperature dependence of mantle viscosity. The thermostat effect of temperature-dependent mantle viscosity regulates the rate of mantle cooling [9,10]; early in the Earth's thermal evolution, when the mantle is very hot, the viscosity is low, convection is highly vigorous, and the mantle cools rapidly. The rapid reduction in mantle temperature increases mantle viscosity and reduces the vigor of convection and the rate of mantle cooling. Throughout most of the Earth's thermal history, cooling is gradual, about 100 K/Gyr.

Mantle viscosity is not only a strong function of temperature, but it depends sensitively on man-

the volatile content as well. Dissolved volatiles in the mantle lower the creep activation enthalpy and thus reduce the viscosity at a given temperature. Thus, a loss of volatiles from the mantle (degassing or outgassing) would stiffen the mantle and require an increase in mantle temperature to maintain a requisite vigor of convection. However, with one exception [11], none of the previous parameterized convection thermal history studies have included the dependence of mantle viscosity on volatile content. The inclusion of a volatile-dependent as well as a temperature-dependent mantle viscosity into thermal history modelling is important not only for a correct simulation of mantle evolution, but also for its implications regarding the evolution of the atmosphere [12].

The dependence of mantle viscosity on both temperature and volatile content produces a strong coupling between mantle thermal evolution and the degassing/regassing history of the mantle [12]. (Regassing refers to the volatile recharging of the mantle by tectonic processes such as subduction, overthrusting, and delamination.) In the thermal history study of Jackson and Pollack [11], the degassing history of the mantle was *a priori* specified by assuming explicit functional forms for the dependence of activation enthalpy (or temperature) on time. In the present paper we self-consistently solve for the evolution of both mantle temperature and the mantle degassing/regassing rate.

2. Model

The basic equations of parameterized convection are developed in detail in previous references [2,10]; we will only briefly review the key concepts and equations. The kinematic viscosity of the mantle is assumed to have the following temperature dependence:

$$\nu = \bar{\nu} \exp(A/T) \quad (1)$$

where A is the activation temperature for solid-state creep, T is a characteristic mantle temperature, and $\bar{\nu}$ is a constant. Decaying radiogenic heat sources are assumed to produce energy in the mantle at a rate Q per unit volume, where:

$$Q = Q_0 e^{-\lambda t} \quad (2)$$

and Q_0 and λ are constants, and t is the time.

The Rayleigh number Ra for a convecting mantle is:

$$Ra = \frac{g\alpha(T - T_s)(R_m - R_c)^3}{\kappa\nu} \quad (3)$$

where g is the acceleration of gravity, α is the coefficient of thermal expansion, T_s is the surface temperature, R_m and R_c are the mantle outer and inner radii, respectively, and κ is the thermal diffusivity. Mantle heat flow q is parameterized in terms of Ra by [2]:

$$q = \frac{k(T - T_s)}{(R_m - R_c)} \left(\frac{Ra}{Ra_{cr}} \right)^\beta \quad (4)$$

where k is the thermal conductivity, Ra_{cr} is the critical value of Ra for the onset of convection, and β is an empirically determined dimensionless constant found to be around 0.3. Conservation of energy gives an equation for the time rate of change of the characteristic mantle temperature \dot{T} :

$$\rho c (R_m^3 - R_c^3) \dot{T} = -3R_m^2 q + Q (R_m^3 - R_c^3) \quad (5)$$

where ρ is the density and c is the specific heat. Equations (1) to (5) give a first-order non-linear differential equation for the mantle temperature T , which, when given the temperature T_0 at time $t=0$, is easily solved by numerical integration. (We have chosen an adaptable stepsize Runge-Kutta algorithm [13] to integrate (1) to (5)). This differential equation for T has been the subject of several studies. For example, Schubert et al. [2] and Jackson and Pollack [3] used a constant value for A , and Jackson and Pollack [11] assumed a specific function for the time dependence in A . In this study we provide a parameterization of A that self-consistently determines mantle temperature and degassing/regassing rate as a function of time.

3. Activation temperature and regassing/degassing parameterizations

Experiments on the deformation of candidate mantle minerals have revealed that dissolved volatiles such as water weaken the minerals by reducing the activation energy E^* for solid-state creep [14–16]. Activation energy is related to activation temperature by the equation:

$$A = E^*/R \quad (6)$$

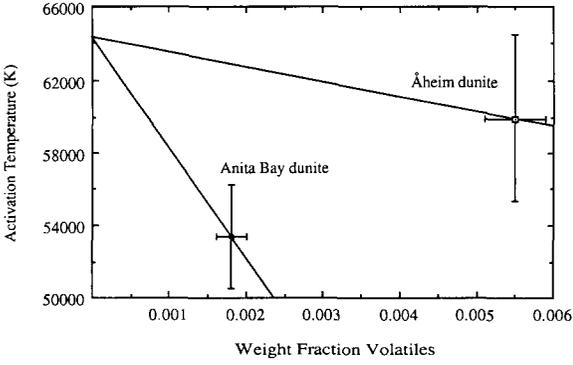


Fig. 1. Activation temperature (K) vs. weight fraction volatiles for two samples of dunite. Data are from [15]. The straight lines connecting the wet and dry activation temperature values provide a simple parameterization for the dependence of A on weight percent volatiles (the dry values are identical for both samples).

where R is the universal gas constant. Chopra and Paterson [15] give values for the activation energy and weight fraction of water for two samples of “wet” dunite as well as the activation energy for both “dry” samples (plotted in Fig. 1). The parameterization we use for activation temperature as a function of volatile weight fraction is a simple straight line drawn through the wet and dry points for each type of dunite. Uncertainties in the data and the lack of additional data preclude a more complicated parameterization. Accordingly, we write:

$$A = \alpha_1 + \alpha_2 x \quad (7)$$

where x is the volatile weight fraction and α_1 , α_2 are constants determined by the straight lines in Fig. 1. The values of α_1 and α_2 according to Fig. 1 are $\alpha_1 = 6.4 \times 10^4$ K, α_2 (Anita Bay dunite) = -6.1×10^6 K/weight fraction, and α_2 (Åheim dunite) = -8.1×10^5 K/weight fraction. The smaller value of α_2 is representative of a mantle with a weak dependence of rheology on volatile content; the larger value of α_2 typifies a strong dependence of mantle viscosity on the percentage of volatiles. Fig. 2 shows the dependence of mantle viscosity on x and T obtained from (1), (6) and (7) together with the values of α_1 and α_2 (Anita Bay) given above. Mantle viscosity decreases with increasing T and volatile weight fraction.

Our model requires a prescription for determining the mass of dissolved volatiles in the mantle as a function of time. We have identified the major

mechanisms of mantle degassing and regassing and have parameterized them to provide equations for the degassing and regassing rates. Fig. 3a shows a schematic of the degassing of the mantle at a mid-ocean ridge. The rate of mantle degassing $[\dot{M}_{mv}]_d$ is given by:

$$[\dot{M}_{mv}]_d = \rho_{mv} d_m S \quad (8)$$

where ρ_{mv} is the density of volatiles in the mantle, d_m is the average depth from which volatiles are released from the mantle (assuming complete outgassing to this depth), and S is the areal spreading rate for the Earth’s mid-ocean ridges. The parameter d_m can be thought of as an “equivalent depth”, combining the actual depth of melting with an efficiency factor for the release of volatiles. Fig. 3b shows the situation at a subduction zone, where volatiles are recycled back into the mantle. The rate of regassing $[\dot{M}_{mv}]_r$ is given by:

$$[\dot{M}_{mv}]_r = f_{bas} \rho_{bas} d_{bas} S \chi_r \quad (9)$$

where f_{bas} is the mass fraction of volatiles in the basalt layer, ρ_{bas} is the density of the basalt, d_{bas} is the average thickness of the basalt, and χ_r is an efficiency factor representing the fraction of volatiles that actually enters the deep mantle instead of returning to the surface through back-arc volcanism. The value of d_{bas} can be varied to reflect the added contribution of a subducted sediment layer.

To obtain the spreading rate S as a function of known quantities we use the relation between heat

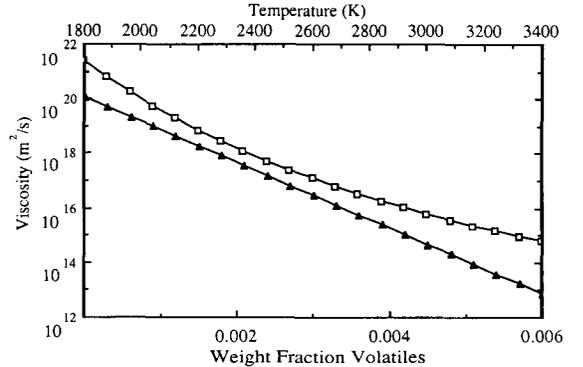


Fig. 2. Mantle viscosity as a function of x and T for the Anita Bay dunite with the activation temperature dependence of x given in Fig. 1. The upper curve (squares) shows viscosity as a function of T with x held constant at 10^{-3} , while the lower curve (triangles) shows viscosity as a function of x with T held constant at 2200 K.

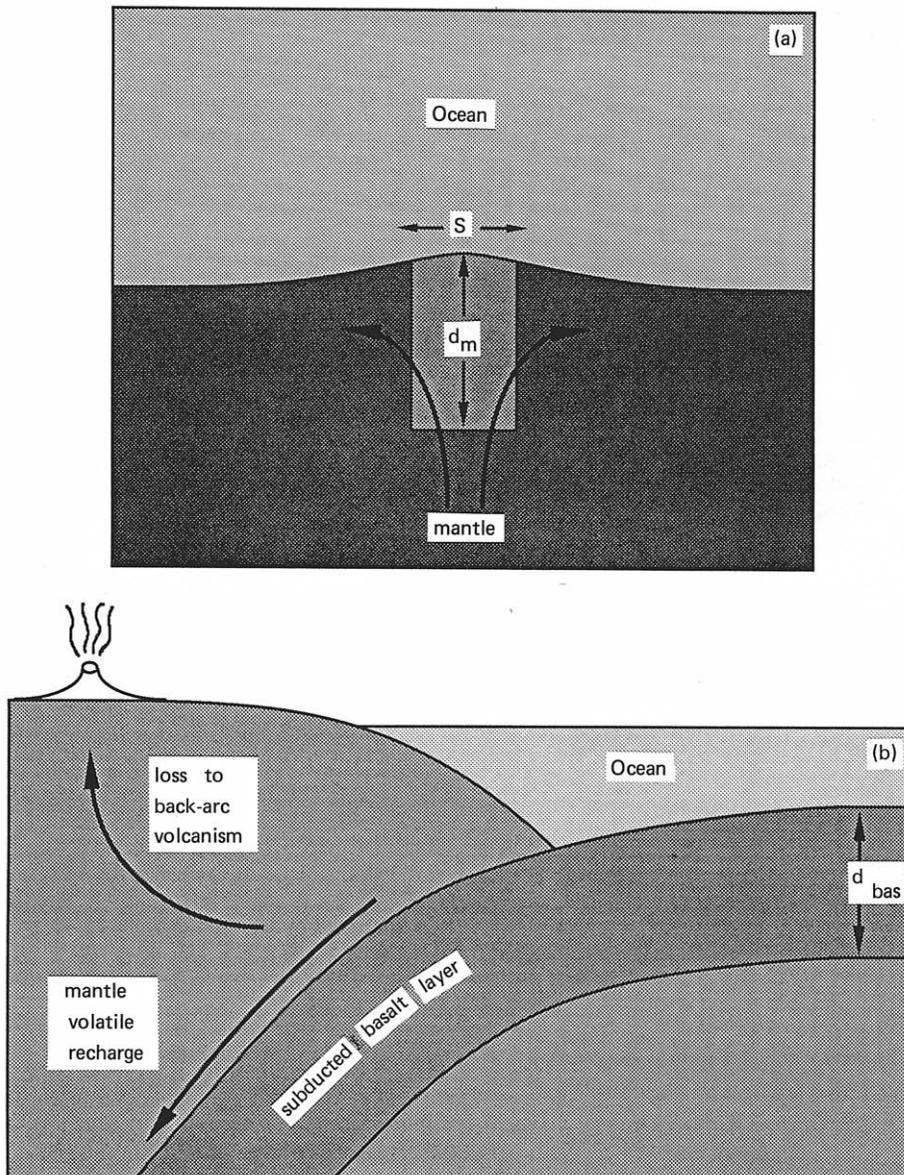


Fig. 3. (a) Schematic view of mantle degassing from mid-ocean ridges. The ridges create new surface area at a rate S (area/time). The quantity d_m represents a typical depth from which volatiles are released. The product of these two quantities gives a volume rate of flow through the shaded box from which volatile outgassing is calculated. (b) Schematic view of mantle regassing at a subduction zone. Volatiles present in the basalt layer (of thickness d_{bas}) are subducted along with the rest of the oceanic plate. An efficiency factor determines the amount of volatiles that actually reaches the deep mantle.

flow q and the average age of subduction of oceanic crust τ [17, eq. 4-128]:

$$q = \frac{2k(T - T_s)}{\sqrt{\pi\kappa\tau}} \quad (10)$$

where τ is given by:

$$\tau = \frac{A_o(t)}{S} \quad (11)$$

and A_o is the area of the ocean basins at time t .

The solution of (10) and (11) for S is:

$$S = \frac{q^2 \pi \kappa A_o(t)}{[2k(T - T_s)]^2} \quad (12)$$

Reymer and Schubert [18] provide a formula for $A_o(t)$ based on the assumption of approximately constant continental freeboard over the last 500 million years:

$$A_o(t) = A_o^* \left[\frac{V_{oa}^*}{V_o} + \frac{V_{ob}^* q^*}{V_o q(t)} \right]^{-1} \quad (13)$$

where V_o is the total volume of water in the oceans (assumed constant in time), V_{oa} is the volume of the ocean basins above the peak ridge height, V_{ob} is the volume of the ocean basins below the peak ridge height, and asterisks denote present-day values.

The differential equation for the mass of mantle volatiles is simple:

$$\dot{M}_{mv} = [\dot{M}_{mv}]_r - [\dot{M}_{mv}]_d \quad (14)$$

This equation assumes that no other fluxes of volatiles (such as impact degassing) are significant.

Interpretation of (14) requires an assumption about the initial value of M_{mv} . We let:

$$M_{mv}(t=0) = n_m M_{ocean} \quad (15)$$

where M_{ocean} is the mass of the Earth's oceans and n_m is the number of ocean masses initially in the mantle. We similarly express the initial value of the mass of volatiles starting out on the surface as:

$$M_s(t=0) = n_s M_{ocean} \quad (16)$$

where n_s is the number of ocean masses originally in surface volatile reservoirs.

4. Model parameter values

To provide a starting point from which to begin our study we established a nominal case using the parameter values given in Tables 1 and 2. Table 1 list the values of the parameters pertaining to the basic convection equations. Table 2 lists the values of the parameters used for the degassing/regassing part of the calculation. Both tables provide references for the assumed parameter values. The value of the depth of melting d_m is derived from an estimate of the depth of the basalt eutectic in the Archean [19, fig. 1]. This value is too large to

TABLE 1

Nominal case convection parameter values

Parameter	Value	Source
$\bar{\nu}$	$2.21 \times 10^7 \text{ m}^2/\text{s}$	[11]
λ	$3.4 \times 10^{-10} \text{ yr}^{-1}$	[3]
g	9.8 m/s^2	[11]
α	$3 \times 10^5 \text{ K}^{-1}$	[2,11]
κ	$10^{-6} \text{ m}^2/\text{s}$	[2,11]
R_m	6271 km	[2,11]
R_c	3471 km	[2,11]
T_s	273 K	[2,11]
k	4.2 W/m K	[11]
Ra_{cr}	1100	[2,11]
ρc	4.2 MJ/m ³ K	[2,11]
β	0.3	[2,11]

reflect present conditions, but it is intended to model conditions prevalent in the early history of the Earth when convective vigor was much greater. Since rates of volatile exchange in the model (and presumably in the Earth) are much greater in the early part of a calculation than they are toward the end of a calculation, the value of d_m should represent conditions early in Earth's evolution. Ringwood [20,21] has estimated that the mass of dissolved water in the mantle is approximately three times that currently in the oceans. With the assumption that the total amount of water in the mantle–hydrosphere–atmosphere system is conserved, we set $n_m = 4$. The value of Q_0 is iteratively adjusted so that the heat flow q at $t = 4.6$ Gyr is equal to the present day value, $q^* = 70 \text{ mW/m}^2$.

TABLE 2

Nominal case degassing/regassing parameter values

Parameter	Value	Source
M_{mantle}	$4.06 \times 10^{24} \text{ kg}$	[2]
d_m	100 km	[19]
f_{bas}	0.03	[12]
d_{bas}	5 km	[12]
ρ_{bas}	2950 kg/m ³	[17]
χ_r	0.8	–
M_{ocean}	$1.39 \times 10^{21} \text{ kg}$	[27]
n_m	4.0	[21,20]
n_s	0	–
A_o^*	$3.1 \times 10^{14} \text{ m}^2$	[18]
V_{oa}^*	$7.75 \times 10^{17} \text{ m}^3$	[18]
V_{ob}^*	$3.937 \times 10^{17} \text{ m}^3$	[18]
V_o	$1.1687 \times 10^{18} \text{ m}^3$	[18]
q^*	70 mW/m ²	[17]

TABLE 3
Summary of computations

Calculation	Conditions (modifications to nominal case)
1	nominal
2	Åheim dunite parameterization
3	constant A , $\alpha_1 = 5.60199 \times 10^4$ K, $\alpha_2 = 0$
4	$d_{\text{bas}} = 6$ km, $d_{\text{melt}} = 50$ km, $n_m = 4$, $n_s = 2$
5	$n_m = 10$ ($n_s = 0$)
6	$T(0) = 2000$ K
7	$\bar{\nu} = 1.65 \times 10^2$ m ² /s [2]
8	$\lambda = 4.5 \times 10^{-10}$ yr ⁻¹ [3]

Table 3 summarizes how the nominal case parameters were modified to consider other evolutionary scenarios. The nominal case is intended to demonstrate the effects of a strongly volatile-dependent viscosity. Calculation 2 uses a weaker rheological volatile dependence, and case 3 has a volatile-independent rheology. The first three calculations all resulted in net outgassing from the mantle. Thus for case 4, parameters were adjusted to diminish degassing and promote regassing. Case 5 starts with a highly volatile-charged mantle. Case 6 demonstrates the effects of an initially cool mantle. Computations 7 and 8 test the effects of alternate values for $\bar{\nu}$ and λ used in other parameterized convection models.

5. Results

Table 4 lists the final values (at $t = 4.6$ Gyr) of mantle temperature, volatile loss, Urey ratio, viscosity, and Rayleigh number for each of the calculations. Also listed is the value of the param-

eter Q_0 which was determined to result in a heat flow q of 70 mW/m² at $t = 4.6$ Gyr.

Fig. 4 shows the results of the thermal history model for the nominal case. The decline of mantle temperature with time (Fig. 4a), the increase of viscosity over the history of the Earth (Fig. 4a), and the decrease of Rayleigh number (Fig. 4b) and heat flow (Fig. 4c) with time are all in qualitative accord with the results of previous parameterized convection calculations. The degassing history of the mantle (Fig. 4b) is characterized by an early period of rapid outgassing (more than one ocean mass in the first 500 million years), followed by a gradual levelling-off in the outgassed mass for the remaining several billion years. The change in activation temperature A exhibits similar behavior due to its dependence on mantle volatile content. A comparison of Fig. 4a and b shows that the timescales for degassing and for rapid initial cooling are approximately the same.

Fig. 4c plots the parameterization of the area of the Earth's ocean basins A_o (normalized to the total surface area), as a function of time. Although the assumption of constant freeboard is known to be valid only for the last 500 million years [18,22], this parameterization results in a monotonic decrease in ocean basin area (increase in continental area) over geologic time, in qualitative agreement with many crustal growth models [18, fig. 6]. By (13) and our requirement that the present heat flow q^* matches the measured value, the present value of A_o necessarily agrees with today's area of the ocean basins. Also, (12) shows that S , the quantity dependent on A_o , is proportional to the square of the heat flow q . Since q changes by more than an order of magnitude over the range

TABLE 4
Model results

Calculation	Q_0 (J/m ³ s)	T (K)	Mantle volatile loss	Urey ratio	Viscosity (m ² /s)	Rayleigh number
1	1.43093×10^{-7}	2480.0	1.48	0.743	4.953×10^{17}	2.876×10^7
2	1.40006×10^{-7}	2635.3	1.25	0.727	6.651×10^{17}	2.297×10^7
3	1.43508×10^{-7}	2372.1	1.56	0.745	3.986×10^{17}	3.398×10^7
4	1.43540×10^{-7}	2313.0	-0.81	0.745	3.522×10^{17}	3.738×10^7
5	1.45181×10^{-7}	2447.1	7.03	0.754	4.641×10^{17}	3.024×10^7
6	1.46151×10^{-7}	2434.5	0.86	0.759	4.526×10^{17}	3.082×10^7
7	1.63900×10^{-7}	1762.2	1.82	0.851	9.007×10^{16}	1.067×10^8
8	2.15071×10^{-7}	2490.9	1.63	0.673	5.060×10^{17}	2.829×10^7

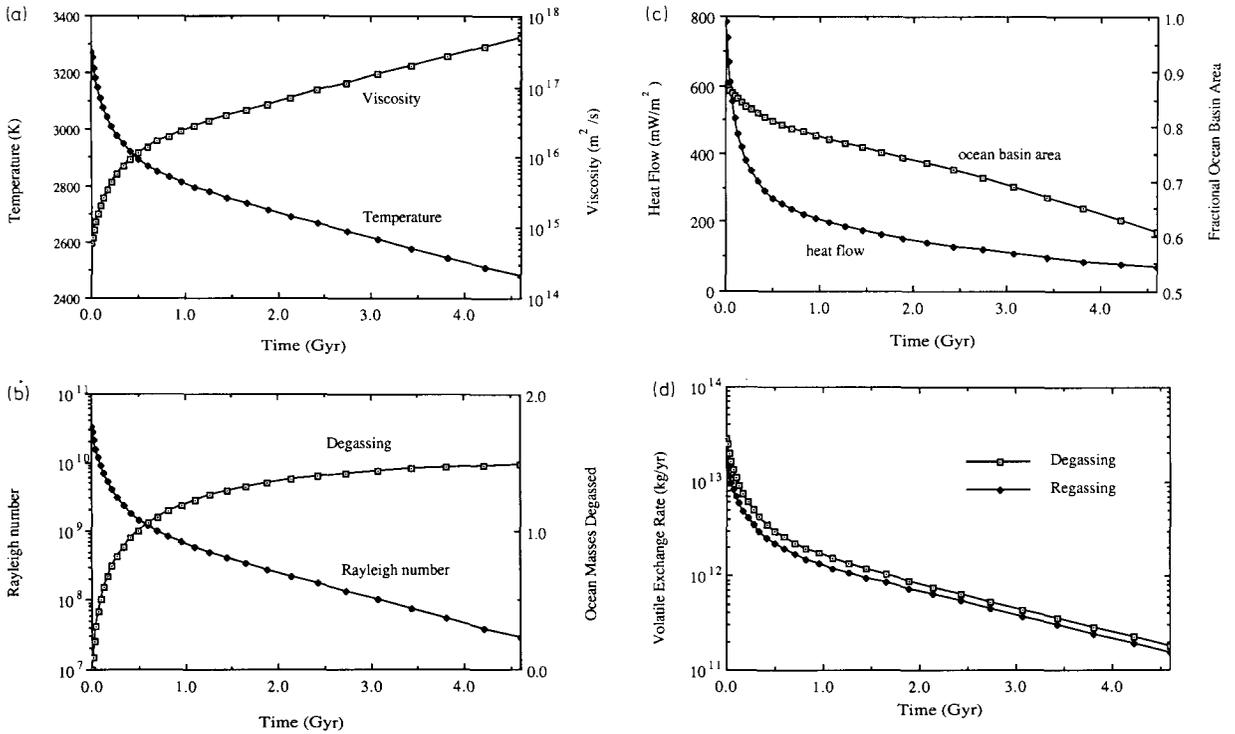


Fig. 4. (a) “Average” mantle temperature T and mantle viscosity ν as functions of time for the nominal case (calculation 1). (b) Mantle Rayleigh number and amount of outgassing from the mantle (in units of ocean masses) as functions of time for the nominal case. (c) Heat flow from the mantle and the normalized area of the ocean basins (from the parameterization of the spreading rate S) as functions of time for the nominal case. (d) Mantle degassing and regassing rates as a function of time for the nominal case.

of all the computations, this variation has much greater influence on the value of S than uncertainties in the value of A_0 .

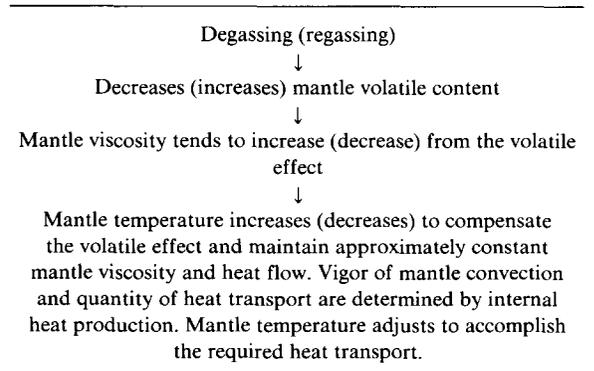
Fig. 4d shows the mantle degassing and regassing rates (from (8) and (9)) for the nominal case, as functions of time. The degassing curve of Fig. 4b is simply the integral of the area between these two curves. As implied by Fig. 4b, these values start out with a significant difference (83%), but converge as $t \rightarrow \infty$ (15% difference at $t = 4.6$ Ga).

Case 2, which uses the less volatile sensitive rheology of Åheim dunite (with larger values of A for a given volatile content), exhibits a similar though more sluggish thermal history compared to the nominal calculation. Thus, at any time, viscosity and temperature are higher, and Rayleigh number and mass of degassed volatiles are lower than in the nominal case. Case 2 does not show an early period of rapid adjustment of volatile content (and A) (case 2 takes about two billion years to outgas one ocean mass).

Comparison of the results of the nominal case with the results of calculations 3 (volatile-independent rheology) and 4 (volatile-dependent rheology, net regassing of the mantle), serves to identify the

TABLE 5

Rheological influence of mantle devolatilization/revolatilization on interior thermal history



major effect of mantle degassing/regassing on the thermal evolution of the Earth. Table 5 summarizes how the dependence of mantle viscosity ν on volatile content combines with the temperature dependence of ν to influence the thermal evolution of a convecting mantle in a degassing/regassing scenario. Outgassing dries out the interior and tends to increase its viscosity. However, the tendency for devolatilization to increase ν is compensated by the effect of temperature on viscosity. A higher viscosity tends to reduce heat flow. Thus heat generated by radiogenic sources builds up and tends to increase mantle temperature. A higher temperature tends to reduce viscosity and enhance heat flow. Thus, the mantle tends to maintain the required rate of heat loss by increasing temperature, reducing viscosity, and maintaining the level of convective vigor. The net result is a hotter mantle as a consequence of degassing, but mantle heat flow, viscosity and convective vigor are essentially the same as in a mantle with volatile-independent rheology. These effects are shown in Fig. 5a, which compares the evolution of temperature with time for the nominal case (dotted curve) and case 3 (solid curve). With degassing and a volatile-dependent rheology the mantle is hotter and cools more slowly than for a mantle with a volatile-independent rheology.

Regassing increases the volatile content of the interior and tends to decrease its viscosity. However, as in the degassing case, the tendency for re-volatilization to decrease ν is compensated by a reduction in mantle temperature so as to maintain viscosity, heat flow, and convective vigor approximately constant. These effects are shown in Fig. 5b, which plots mantle temperature vs. time for case 4 (volatile-dependent rheology, dashed curve) and case 3 (volatile-independent rheology, solid curve). In addition, the figure shows the amount of water regassed into the mantle. The evolution, in terms of the amount of cooling and the quantity of water reabsorbed into the mantle, is rapid during the first several hundred million years, becoming more gradual afterwards. In case 4 about 3/4 of an ocean mass of volatiles (water) is reinjected into the mantle over geologic time, with the bulk of this occurring in the first billion years. The main effect of the volatile-dependent mantle viscosity is a cooler mantle, compared to case 3 where ν depends on temperature only. As

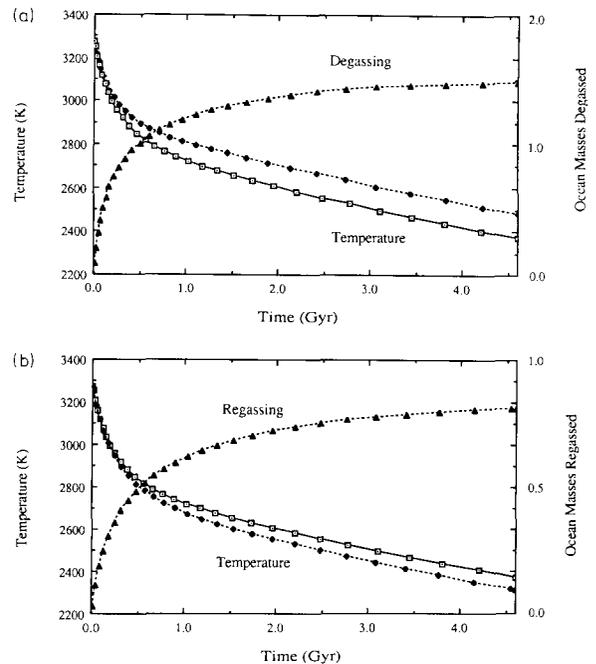


Fig. 5. (a) The effect of degassing on mantle temperature. Thermal histories for volatile-dependent (case 1, dotted line) and volatile-independent (case 3, solid line) rheologies are plotted along with the degassing history for case 1. Degassing with volatile dependence raises the present-day temperature of the mantle. (b) The effect of regassing on mantle temperature. Thermal histories for volatile-dependent (case 4, dotted line) and volatile-independent (case 3, solid line) rheologies are plotted along with the degassing history for case 4. Regassing with volatile dependence lowers the present-day temperature of the mantle.

in the degassing case, mantle viscosity and heat flow are essentially the same for both the volatile-dependent and volatile-independent viscosities. In both the regassing and degassing scenarios, the time rate of change of temperature eventually tends to the same value for the volatile-dependent and volatile-independent rheologies; during the latter stages of thermal evolution only a constant temperature offset distinguishes the volatile-dependent mantle cooling rate from the volatile-independent one.

6. Volatile history

Based on studies of noble gas depletion ratios (relative to the solar abundance; see [23]), it is believed that the Earth's atmosphere formed in an extremely rapid outgassing event early in Earth's

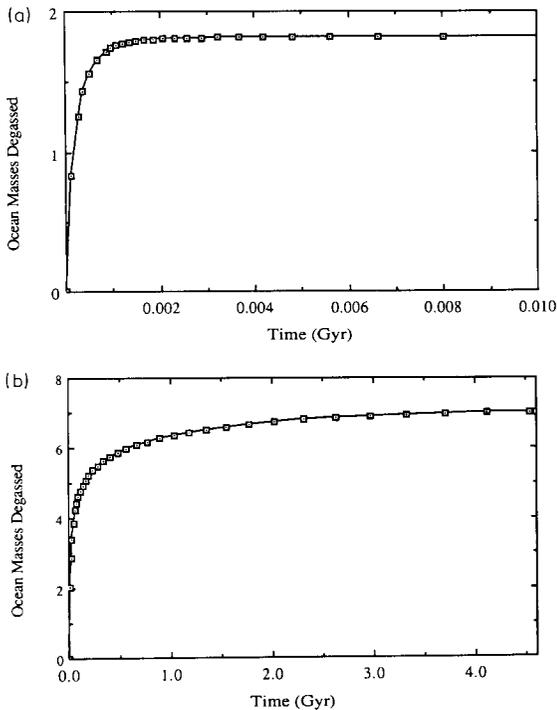


Fig. 6. (a) Degassing history for case 7 (lower value of $\bar{\nu}$). (b) Degassing history for case 5 (high initial mantle volatile content).

history. The timescale for this event is limited to tens of million years [23]. The timescale of degassing in calculations 1–3 is on the order of several hundred million years, too large to adequately provide the necessary episode. However, with different rheological properties, the mantle might be able to degas more rapidly. Fig. 6a shows the degassing history of calculation 7, in which $\bar{\nu}$ is more than five orders of magnitude lower than in the nominal case. With the reduced value of $\bar{\nu}$ the mantle responds practically instantaneously, discharging more than 1.8 ocean masses in less than 10 million years. The final value of viscosity in case 7 ($\nu = 9 \times 10^{16} \text{ m}^2/\text{s}$), however, is about a factor of 10 less than the generally accepted value of about $10^{18} \text{ m}^2/\text{s}$ for the present kinematic viscosity of the mantle [24,25]. The final temperature in case 7 ($T = 1762 \text{ K}$) is also below the accepted range of 2000–3000 K for the present mantle temperature [26]. Iterative adjustment of the rheological parameter values could undoubtedly yield an evolutionary scenario with the $O(10 \text{ Myr})$ early rapid outgassing event and more

reasonable present-day values of mantle viscosity and temperature.

The early rapid degassing of the mantle could alternatively be accommodated by a scenario in which the mantle initially has a high volatile content. Fig. 6b shows the degassing history for calculation 5, which has 10 ocean masses of volatiles initially in the mantle. This case simulates a very highly volatile-charged mantle with a strongly volatile-dependent rheology. These conditions result in an extremely rapid adjustment of mantle volatile content through discharge of more than 4 ocean masses in less than 70 million years. The final values for temperature and viscosity (Table 4) are in accord with present-day estimates for the mantle. Thus, scenarios with high initial mantle volatile content and low values of $\bar{\nu}$ allow for early rapid degassing of the mantle and formation of the atmosphere. Of course, atmospheric accumulation contemporaneous with accretion of the solid Earth by impact degassing also satisfies the noble gas evidence for early rapid degassing of the mantle.

7. Urey ratio

The Urey ratio Ur :

$$Ur = \frac{Q(R_m^3 - R_c^3)}{3qR_m^2} \quad (17)$$

is simply the ratio of the heat source term to the heat sink term in the heat balance equation of the Earth. A Urey ratio greater than unity implies a net gain of heat and a temperature increase in the mantle. A Urey ratio less than unity implies a net heat loss and temperature decrease in the mantle. The value of Ur for the Earth has been a subject of some debate. The models of Schubert et al. [2] suggest a value of around 0.8, as do those of Jackson and Pollack [3]. Jackson and Pollack [11] argue that Ur could exceed unity at the present day. They parameterized A as:

$$A(t) = A(t=0) \left[1 + \left(\frac{\Delta A}{A(t=0)} \right) \left(\frac{t}{4.6} \right)^\tau \right] \quad (18)$$

(with $0 \leq \tau \leq 1$ and $0 \leq t \leq 4.6 \text{ Gyr}$), where ΔA is the total change in activation temperature over the Earth's history, and τ is a parameter which describes the time dependence of A . For low values

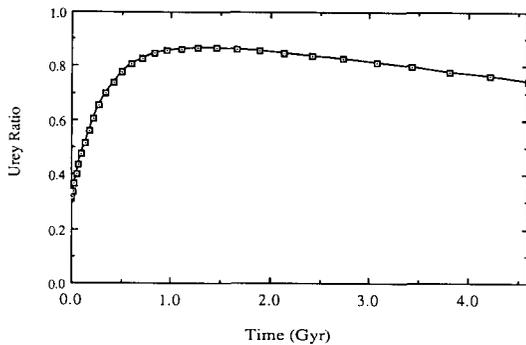


Fig. 7. Urey ratio for the nominal case (calculation 1) plotted as a function of time.

of τ , this parameterization results in an early rapid increase of A , corresponding to an early episode of rapid degassing from the mantle. Fig. 2. of [11] shows that for large enough values of τ (greater than about 0.25) and ΔA , the Urey ratio at present could exceed unity. However, large values of τ correspond to slow, steady, continuous degassing. When the time history of activation temperature is self-consistently calculated we find that the mantle adjusts its volatile content rapidly, corresponding to low values for τ . Even for the case with the slowest mantle response (calculation 2), the adjustment occurs rapidly enough such that the Urey ratio never exceeds unity. In addition, Jackson and Pollack consider values of ΔA that result in 20–100% changes in A over Earth's history. Such large changes in A are required for a Urey ratio greater than unity; we find, however, that our models in general result in smaller changes in A over time (about 5% for calculation 1, for example). Thus, our models are analogous to models in [11] with low values for τ and ΔA , for which the Urey ratio would be less than unity.

Fig. 7 shows the evolution of the Urey ratio for the nominal case. This variation of Ur with time is typical of all the calculations except case 6. The ratio starts with a relatively low value at $t = 0$ because of the dominance of the heat flow term in the initially hot mantle. The ratio quickly reaches a maximum and then slowly and steadily decreases as the mantle volatile exchange rates equilibrate and the value of A approaches its steady state value. Because of the decay of the radiogenic heat sources, Ur will tend to zero as $t \rightarrow \infty$. The only case in which Ur ever exceeded unity was

calculation 6, with a low initial mantle temperature. The Urey ratio started at about 18, due to the dominance of heat generation over heat flow in the initially cold mantle. The mantle then heated up until heat flow exceeded heat generation. Mantle temperature reached a maximum and declined steadily thereafter, in the same manner as in the other cases. With the eventual decline in mantle temperature Ur decreased below unity. We thus conclude that the dependence of viscosity on temperature and volatile content acts as a thermostat to regulate a slow steady cooling of the Earth at the present. For a wide range of parameters, rapid adjustment of temperature and volatile content ensure that $Ur(t = 4.6\text{Ga})$ is less than unity.

8. Conclusions

The dependence of mantle viscosity on volatile content has important effects on the thermal evolution of planetary interiors and the evolution of planetary atmospheres. A mantle with volatile-dependent viscosity quickly adjusts to reach equilibrium values of \dot{T} and volatile content. Degassing is compensated by an increase in temperature (over a volatile-independent case) and regassing by a decrease in temperature. Reasonable degassing scenarios can account for rapid early formation of Earth's atmosphere inferred from noble gas abundances. Volatile dependence of the heat production/heat flow (Urey) ratio by the temperature dependence of mantle viscosity. All of our results indicate that the present value of the Urey ratio is less than unity.

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