The history of an atmosphere of impact origin

Bruce M. Jakosky and Thomas J. Ahrens
Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125

Abstract—Most of the mass accreting onto the Earth and terrestrial planets impacted at sufficiently high velocities to release their volatiles into the atmosphere by impact-heating. However, based on models of planetary growth by accumulation from solid bodies, the time-scale for accretion was sufficiently long that the average surface temperatures could not have been above 350 K. Using measured frictional rates, the released volatiles should have been re-impacted onto the planet by hydrating the surface minerals and were subsequently buried during accretion. Rapid hydration of impact products precludes the formation of a thick atmosphere on the planet accreted. Thus, only the subsequent differentiation and evolution of the terrestrial planets determined the size and composition of each planet’s atmosphere.

INTRODUCTION

The terrestrial planetary atmospheres are generally believed to have resulted from the release of gases originally contained within the solid material from which the planets accreted (Brown, 1952). The time-history of the release into the atmosphere of the volatiles has been the subject of much debate. Rubey (1951) suggested that the earth’s supply of volatiles accumulated at the surface throughout geologic time as the result of volcanic activity. Female (1971) explained the early upward concentration of lead and uranium in the earth as resulting from differentiation within the first 100 m.y. after formation, accompanied by an early catastrophic degassing of the planet. The idea of early outgassing was extended by Ozima (1975; Hamano and Ozima, 1978) using the Ar$^{36}$/Ar$^{39}$ ratio to place constraints on the differentiation of volatiles and the timing of the outgassing of the earth’s mantle. Assuming that the ratio Ar$^{36}$/Ar$^{39}$ for the initial earth was the same as the solar value requires that most of the atmosphere was formed very early in the earth’s history.

Antheunis et al. (1974) and Benlow and Meadows (1977) argued that the large increase in temperatures which occurred during the impact of accreting planetesimals onto the surface of the forming earth was sufficient to melt or vaporize the material, releasing the volatiles into the atmosphere. Kingwood (1966, 1975, 1977) proposed a positive feedback mechanism, whereby the protoplanet formed in this manner is sufficiently thick to vaporize the later-accreted material, placing still more material into the atmosphere. It becomes sufficiently thick to effectively
hinder the radiative loss of energy and stays hot enough to keep all of the accreted material gaseous.

In this paper, we will examine the thermal state of the accreting earth and place constraints on the spatial average of the surface temperature during accretion. This will allow us to determine the fate of an atmosphere formed by impact-heating: that is, whether it remains as an atmosphere or can be re-incorporated into the planet as accretion occurs. This can serve as an important boundary condition for models of the initial temperature profile of the earth. These models determine the heating upon impact which occurs assuming that no atmosphere was present (e.g., Safranov, 1979; Käpka, 1979) or allowing modification by the atmosphere (Ringwood, 1966, 1975, 1977).

ACCRETION OF THE EARTH

The terrestrial planets are thought to have formed by the collisional accretion of solid planetesimals into large bodies. These continue to accrete material in their region of the solar system until each region is left with one planet-sized object (e.g., Safranov, 1972; Weidenschilling, 1974, 1976).

The composition and the accretion rate was probably not constant either with time or with location in the solar system. A variation in composition with time can occur as a result of the rapid accretion of material which condenses early in the cooling of the solar nebula while the lower-temperature condensates are still in the gaseous phase (Turekian and Clark, 1969; Clark et al., 1972). Also, gravitational scattering of material from one region of the solar system to another may occur as the planets grow, leading to homogenize the accreting material throughout the inner solar system towards the end of accretion (Hartmann, 1976). Spatial variations of composition may result from differential condensation of the solar nebula (Lewis, 1972) or from some fractionation with distance from the sun of the nebula itself.

We assume here that each of the terrestrial planets formed from a uniform mixture of material with constant composition. An inhomogeneous formation, as proposed by Turekian and Clark (1969) and Clark et al. (1972), is unlikely because the time-scale for cooling and condensation of the solar nebula (<0.1 years; Cameron and Pine, 1973) is much less than the time-scale for accretion of the planets from planetesimals (<10^6 years; Safranov, 1972; Weidenschilling, 1976; Käpka, 1979). No currently-known meteorite has the same composition as the overall earth (see Ringwood, 1977; Anders and Owen, 1977). We assume an accumulation from a mixture of materials which results in the current composition of the earth, the bulk composition of the accreting material remaining constant with time.

The following discussion of the thermal state of the accreting planets' surfaces is restricted for the most part to the earth, with some speculations to the other terrestrial planets. The maximum average surface temperature of the accreting earth can be obtained by equating the energy supplied from the kinetic energy of
the incoming planetesimals to that lost to heating up the incoming material and radiating energy to space. Hanks and Anderson (1966) did this to determine the initial temperature profile of the earth. The implicit assumption in their work is that all of the energy is deposited directly at the surface as heat. This is equivalent to assuming that all of the matter accreted as very small particles. Determinations of the partitioning of impact energy (Gault and Hettewitt, 1963; O'Keefe and Ahrens, 1977) and the flow-fields of material during cratering (Shoemaker, 1963; Gault et al., 1968; O'Keefe and Ahrens, 1978) show that large impacting bodies will emplace much of their energy as heat at some depth beneath the surface, with only a small amount going to kinetic energy of ejecta and becoming then placed at or near the surface. Thus, the method outlined above yields the maximum temperature, above which the actual average surface temperature cannot rise.

We equate the potential energy of falling through the proto-earth's gravitational field to the energy radiated thermally from the surface at a given time during accretion:

\[ \frac{dM(t)}{dt} \frac{dM}{r} = 4\pi r^2 \varepsilon \sigma (T_s^4 - T_e^4) \delta \]

where:
- \( G \) = gravitational constant
- \( r \) = radius of proto-earth at time \( t \)
- \( M(t) \) = mass of proto-earth at time \( t \)
- \( \varepsilon \) = surface emissivity
- \( \sigma \) = Stefan-Boltzmann constant
- \( T_s \) = average surface temperature
- \( T_e \) = average temperature of space.

Here, \( \delta \) is the fraction of the impact energy which is actually placed at the surface \( (\delta = 1 \text{ in the Hanks and Anderson (1969) model; } \delta = 0.2 \text{ if } 5.8 \text{ of the energy goes either as heat buried deep beneath the surface or as plastic work). For simplicity, this ignores the energy which actually heats the planetesimals to the average temperature.}

Estimates for \( \frac{dM}{dt} \) and the total accretion time \( \tau \) are based upon dynamic models for the gravitational sweeping of material from the region of the solar system into the earth's vicinity. Differing values can be obtained using different assumptions concerning the particle velocity distribution and size of the planetary "feeding zone". Safronov (1972) and Weidenschilling (1976) both estimate that \( \tau \) is about \( 10^9 \) years; Kasta (1979) obtains a \( \tau \) of about \( 5 \times 10^9 \) years. The factional form we use for \( \frac{dM}{dt} \) is obtained from the work of Weidenschilling (1976) and is shown in Fig. 1. \( \tau \) is left as an independent variable.

Figure 2 shows the average surface temperature as a function of the size of the growing earth for several values of \( r \) in the case \( \delta = 1.0 \) (all the accretion energy
is supplied as heat directly at the surface. The maximum of the surface temperature coincides in time with the maximum accretion rate. If all the energy was actually entrapped right on the surface, these curves would also show the initial temperature profile of the earth, ignoring radiogenic and compressive heating. The temperatures shown here are less than those obtained by Hanks and Anderson (1969) only because of the different time-scales of accretion used.

A more reasonable value for \( \delta \), based on the energy-partitioning calculations of O'Keefe and Ahrons (1977), would be 0.2. The average surface temperatures
for this case are shown for several values of \( \tau \) in Fig. 3. Interestingly, for accretion times in the range predicted by the models, the average surface temperature does not rise above about 330 K. For the longest plausible accretion times predicted by models, temperatures are not above about 270 K, at which point the temperatures are controlled by evaporation, and ambient surface conditions are quite mild.

**HISTORY OF THE VOLATILES**

The volatiles budget of the earth, shown in Table 1, is dominated by water and carbon dioxide. They comprise over 99% of the total volatiles that have been removed from the interior. The amount of volatiles remaining in the interior today is unknown. Craig and Lupton (1976) have shown that juvenile gases are being removed from the mantle today, Luthe (1971) constrains the mantle to have

<table>
<thead>
<tr>
<th>Species</th>
<th>Present Earth atm* (%</th>
<th>Total abundance including oceans and sediments** (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>&lt;3</td>
<td>427</td>
</tr>
<tr>
<td>CO₂</td>
<td>5.63</td>
<td>75.8</td>
</tr>
<tr>
<td>N₂</td>
<td>76</td>
<td>3.87</td>
</tr>
<tr>
<td>**Ar</td>
<td>0.08</td>
<td>3.2 × 10⁻³</td>
</tr>
<tr>
<td>*Ar</td>
<td>1</td>
<td>0.41</td>
</tr>
</tbody>
</table>

* from Paule (1971)
** from Roade and Yarkovsky (1967)
less than 50% of the earth's total water to account for the water abundance in oceanic basalts. Although the amount of CO₂ in the mantle is not known, the fact that diamond pipes are emplaced by CO₂ gas drive from greater than 200 km depth (Kennedy and Noide, 1986) indicates its presence. It will be of interest to try to account for the water and carbon dioxide throughout the accretion process.

Of the observed meteorite types, carbonaceous chondrites are the richest in volatiles. If one were to choose the single meteorite type which could best supply the earth's volatiles, any of the classes of carbonaceous chondrites would suffice. Asders and Owen (1977) obtain the best fit to the bulk and isotopic data if they assume that about 6% of the earth's mass was derived from the CIIV chondrites. Volatiles are bound up in these meteorites in several species. Water is obtained from H₂O is hydrated minerals and also from H in the carbonaceous matrix e.g., Kasla, 1968, Ch. B. Carbon is present in the carbonaceous matrix (Anders and Owen, 1977). The location of the noble gases is not currently known (e.g., Summaer et al., 1977).

In our model for the earth's formation, CO₂ and H₂O are accreted in a low-temperature, volatile-rich component, and are present in the same form as they are in carbonaceous chondrites. As pointed out by Arthensius et al. (1974) and Penlow and Meadows (1977), the energy retained as heat upon impact is sufficient to vaporize the volatile species from the planetesimal, releasing the H₂O and CO₂ to the proto-atmosphere. This will be true for impacts at velocities greater than about 3 km/sec (see Fig. 6 of O'Keefe and Ahrens, 1977). Impact velocities onto the planets (Fig. 4) are larger than this during the accretion of the earth and Venus for greater than 90% of the mass accreted and during the accretion of Mars for about 80% of the mass accreted. Mercury presents a special case due to its proximity to the sun and will be ignored here. Any non-volatile solids melted or vaporized will rapidly cool and condense onto the surface. The volatiles, however, include H₂O, CO₂, and the noble gases, will probably remain gaseous and stay in the atmosphere (although the water may liquefy into an ocean, depending on the ambient conditions).

The question then arises as to the course which the volatiles may follow. Consider the atmospheric water: (1) it may be photodissociated by sunlight followed by escape of the hydrogen into space; (2) it may itself escape from the atmosphere; (3) it may oxidize the surface aided by photo-stimulation (as can occur today on Mars; see Huguenin, 1976a); (4) it may re-hydrate the surface minerals; or (5) it may remain in the atmosphere or ocean. The ambient conditions at the surface of the forming earth will determine the rates of some of these processes and thus determine the fate of the volatiles.

The rates of photodissociation and atmospheric escape of H₂O are negligible in terms of removing the entire budget, assuming upper-atmospheric conditions similar to the present earth. Brinkmann (1969) estimates that photodissociation is sufficient over geologic time to remove only about a bar of water, thus, being insignificant during accretion. Based on the theory of atmospheric escape (Levin, 1923), H₂O escapes with a lifetime of greater than 10⁹ years during most of the
formation of the earth. Non-thermal mechanisms of escape may increase the H2O escape rate, but not enough to make loss of H2O significant. If the solar output were very different 4.6 b.y. ago from what it is now, these results would be modified, but extremely large factors would be required to make the H2O loss during accretion non-negligible.

The reaction of water with the surface via photo-stimulated oxidation has been discussed in detail by Huguenin (1974, 1976a, 1976b) and applied to Mars. In this case, the regolith becomes a sink for atmospheric water. The mechanism involves oxidation of magnetite and ferrosilicate in the presence of water. For instance, magnetite oxidizes by the overall reaction $3\text{Fe}_2\text{O}_3 + 16\text{H}_2 \rightarrow 6\text{FeO}_2 + 8\text{H}_2\text{O}$. For the latter, H+ ions are incorporated into the surface to maintain charge balance upon removal of Fe+ ions during formation of $\text{FeO}_2$. This, in effect, stores water in the regolith. On Mars, the rate is sufficient to remove $10^6$ to $10^7$ water molecules per square centimeter of planet each second, equivalent to removing up to about $10^9$ g/cm$^2$ over geologic time (Huguenin, 1976a). Scaling this to the earth’s larger surface area and lesser distance from the sun allows removal of up
to 8 \times 10^3 \text{ g/cm}^2 \text{ of water (equivalent to about 77 bars on earth if it were all in the vapor phase)} over geologic time. Thus, this will be an ineffective mechanism for placing significant amounts of water into the regolith on the time-scale of the accretion of the earth.

Finally, consider the hydration of surface minerals. Species such as serpentine (Mg,Si,O,OH) and brucite (Mg(OH)\(_2\)) can form from the hydration of forsterite (Mg,Si,O\(_4\)) and enstatite (Mg,Si,O\(_3\)) (e.g., via 2Mg,Si,O\(_4\) + 3H\(_2\)O \rightarrow Mg(OH)\(_2\) + Mg,Si,O\(_3\)OH\(_2\)). Other hydrations can occur, for instance the formation of tremolite (Ca\(_2\)Mg,Si,O\(_4\)OH\(_2\)) or micas, but these involve more complicated systems and will not be considered here. In a homogeneously-accreting earth, sufficient amounts of forsterite and enstatite will be present to completely remove the water from the atmosphere if the hydration reaction is fast enough.

The kinetics and mechanisms of the hydration reactions of forsterite and enstatite were determined by Martin and Fyfe (1970) for temperatures between 323 K and 832 K and pressures between 700 and 2700 bars. Extrapolation of their results to lower temperatures is done via an Arrhenius-type law. Extrapolation to very low pressures is not as doable as might first appear. The reaction is initially surface-controlled, such that it is the rate at which water molecules adsorb onto active sites of the reactant which controls the rate of hydration. Only after hydration of the near-surface region is the reaction rate determined by the rate of diffusion into the crystal. Thus, the reaction rate should initially be independent of pressure above the water saturation pressure. Therefore, the hydration rate at the saturation pressure appropriate for a given temperature will be the same as the rate determined at that temperature and higher pressure. For lower water vapor pressures, a first-order estimate is obtained by interpolating linearly to zero rate at zero pressure. However, our conclusions will not depend strongly on this last assumption. The reaction rate constants are shown in Table 2, along with the rates of incorporation into the mica. At a temperature of 350 K, the forsterite hydration rate in units of grams of water per square centimeter per second is approximately (J/P) \times 10^{-5}, where P is the water vapor pressure and J, the saturation pressure. Over the range of temperatures expected for the surface of the accreting earth (see previous section), the reaction rate will vary by approximately an order of magnitude. Notice that this is the rate per surface area of particles, rather than per surface area of the planet, such that a regolith consisting of fine particles will incorporate water much faster than a solid surface.

We conclude that the only viable sint for water on the time-scale of accretion is re-incorporation into the surface by hydration of surface minerals. If we equate the rate of supply of water to the atmosphere from accretion planetesimals to the rate of loss of water due to hydration (averaged over the entire planet), assuming that all the water is released upon impact and that the earth's total supply of water is currently in the surface, we can estimate the partial pressure of water vapor during accretion. Allowing water to interact only with the top 1 m of a regolith composed of 50-\(\mu\)m particles results in a maximum water vapor pressure
The history of an atmosphere of impact origin

Table 2. Hydration rate constants for silicate and FeS.

<table>
<thead>
<tr>
<th></th>
<th>Eosinite</th>
<th>Fresnolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydration, reaction rate constant* (sec⁻¹)</td>
<td>(8 \times 10^5)</td>
<td>(6.5 \times 10^7)</td>
</tr>
<tr>
<td>Incorporation rate of H₂O into crystal (NH₂O - cm²/sec⁻¹)</td>
<td>(1.9 \times 10^{11})</td>
<td>(6.0 \times 10^{12})</td>
</tr>
<tr>
<td>Incorporation rate of H₂O onto planet (NH₂O - cm²/cycle)</td>
<td>(2.9 \times 10^8)</td>
<td>(9.2 \times 10^8)</td>
</tr>
</tbody>
</table>

\* at T = 350 K
\*\* From Narte and Dyke, 1971

Maximum rate, assuming interaction of a neutral atmosphere with 1 cm thick regrets composed of 50-μm particles. The rates scale linearly with regolith thickness and as the inverse cube of particle size. Compare these to the maximum rate of supply of H₂O during accretion at \(7.9 \times 10^7\) g.H₂O/sec (for \(a = 1.4 \times 10^9\) yr).

of about 0.009 bars. Surface temperatures lower than 373 K will not result in significantly larger water partial pressures.

Thus, essentially all of the water released into the atmosphere can be re-incorporated into the planet quickly enough to prevent building up a thick water atmosphere. The fate of CO₂ released into the atmosphere will not be addressed in detail. Carbonater will be stable at the low temperature and with small amounts of atmospheric water present (Golding, 1978). Also, experiments on the rates of carbonate growth under conditions similar to those considered here obtain growth of \(10^3-10^4\) molecules of CaCO₃/cm²/sec (Bosch and Kieffer, 1978), which is more than sufficient to remove CO₂ from the atmosphere on the time-scale of the earth's accretion.

**DISCUSSION**

This paper has suggested that the rates of incorporation of water and carbon dioxide into the repat of the accreting earth are large enough to prevent formation of a thick atmosphere at the planet form. This conclusion is based on the low average surface temperatures of the earth form long times scales of accretion. For dynamically plausible times of \(7 \times 10^4\) to \(10^5\) years, in fact, the average surface temperature will not rise above about 320 K. An accretion time shorter than \(8 \times 10^5\) years is required to yield surface temperatures that are high enough to make the hydrated products unstable and allow the buildup of a thick water atmosphere.

Therefore, the assumptions in the thermal accumulation models that the atmosphere does not play a large role in modifying the thermal behavior is justified. The initial-temperature calculations by Safinov (1973) and Kaula (1975) ignore the
effects of an atmosphere, while those by Longwood (1966, 1972, 1977) require extensive modification by the atmosphere.

Some processes occurring during accretion may significantly affect our results. Implicit in the model is the assumption that once the volatiles in the regolith are buried they are retained in the interior of the planet. With much of the energy of accretion being deposited beneath the surface, the temperatures at depth may be sufficiently high to make the volatile-rich phases unstable, releasing the volatiles. If they were able to migrate back to the surface, a thick atmosphere would result. However, just as the impact-stirring caused by the accretion of large bodies is insufficient to diffuse buried heat to the surface (Safaviyeh, 1978; Kaula, 1979), so will it be insufficient to cause the released volatiles to diffuse to the surface. Non-impact-related diffusion to the surface and volcanism are other means of replacing volatiles back into the atmosphere. At the low surface temperatures prevalent during accretion, however, the vapor pressure of water is less than 1 bar and water reaching the surface will condense out to form a standing ocean rather than a thick water atmosphere.

Differentiation of the homogeneous planet will probably provide enough energy to melt much of the planet and release the volatiles. This would likely result in the formation of a thick atmosphere unless a vapor-liquid equilibrium kept much of the volatiles dissolved in the planet (Fischel, 1971). If not, our model is valid so long as differentiation does not occur during accretion. That the volatiles are still at the earth's surface is a result of ongoing tectonic processes, which serve to recycle the volatiles back to the atmosphere. The current thermal state of the mantle does not allow the reaction products to remain stable at depth.

An inhomogeneous accretion of the type envisioned by Turekian and Clark (1969) would result in the late addition of volatile-containing components. Gases released from this material would not be an easily re-incorporated into the surface, since less exposed surface would be capable of binding up the volatiles.

Compare now the behavior of the other terrestrial planets with that of the earth. Venus, with an accretion time about the same as the earth (Weidenschilling, 1976) should behave similarly. Mars, which takes a factor of ten longer to accrete (Weidenschilling, 1976), would be significantly colder at the surface and would be even more prone to retaining its volatiles in its interior.

The question arises as to the cause of the current differences between the terrestrial planetary atmospheres. Since the major volatiles are incorporated within the planets during accretion, the present atmospheres result from a later outgassing, and the differences between them result from either different abundances or different histories.

One way of estimating the relative outgassing histories is through a comparison of the noble gas abundances (see Owen et al., 1977). The non-radiogenic isotopes abundances determine the total amount of volatiles present, while the radiogenically-produced isotopes determine the time-history of outgassing. This type of analysis seems to indicate that Mars is depleted in volatiles relative to the earth by a factor of about 100 (Anders and Owen, 1977) and that Venus is enriched relative to the earth by the same factor (Hoffman et al. 1975; Oyama et al.,
1979). This is exactly opposite from what would be expected on the basis of solar nebula condensation models, which predict a greater abundance of volatiles on planets forming further from the sun (e.g., Lewis, 1972). The model that we present here does not explicitly consider the fate of the noble gases, and therefore cannot explain this discrepancy. Whether or not noble gases are released into the atmosphere during accretion will depend on the volatility of the specific isotope containing them. If they are released into the atmosphere, reaction with surface materials is unlikely, but adsorption into the soil may be important (Fameau et al., 1978).

Ultimately, the volatile release may be related to the degree of differentiation of the planet. Mars, with the smallest current atmosphere, would seem to have undergone the least differentiation. Venus, with the greatest volatiles, may have had the strongest subsequent differentiation. Walker (1979) has suggested a similar explanation, that the differences are due to the degree to which each planet has re-incorporated the volatiles subsequent to the complete release into the atmosphere, with differences due to the differing internal thermal states of the planets.

REFERENCE


Ringwood A. E. (1977) Composition and origin of the Earth. Phil. Soc. 1209 of Research School of Earth Science, Australian National University, Canberra.


