

# What was the Volatile Composition of the Planetesimals that Formed the Earth?

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**Abstract** Is there an asteroid type or meteorite class that best exemplifies the materials that went into the Earth? Carbonaceous chondrites were once the objects of choice, and in the minds of many this choice is still valid. However, the origin of primitive chondritic meteorites is unclear. At the extremes they could either be fragments of very small parent bodies that never became hot enough to undergo geochemical modification other than mild lithification, or remnants of the uppermost layers of a body that had undergone a significant degree of internal differentiation, while the top layers remained cool due to radiative heat loss or loss of volatiles to space. This latter case is problematic if one considers these objects as precursors to the Earth since the timescale for the evolution of such a small body could be longer than the timescale for the accretion of the Earth. Large-scale circulation of materials in the primitive solar nebula could greatly increase the diversity of materials near 1 AU while also making the entire inner solar system both more homogeneous and much wetter than previously expected. The total mass of the nebula is an important, but poorly constrained factor controlling the growth of planetesimals. There is also a selection effect that dominates our sampling of the planetesimals that may have existed 4.5 billion years ago; namely, small fragile bodies are more likely to be lost from the system or ground down by collisions between small bodies, yet these are precisely those that may have dominated the population from which the Earth accreted. The composition of these aggregates could have played a very important role in the early chemical evolution of the Earth. In particular, the Earth may have been much wetter and richer in hydrocarbons and other reducing materials than previously suspected.

**Keywords** Accretion · Earth · Planetesimals · Water · Organics · Oceans · Volatiles

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## 1 Introduction

There are many reasons to worry about the chemical composition of the building blocks from which the terrestrial planets were assembled. The standard model is to postulate that the terrestrial planets formed from carbonaceous chondrites or even enstatite chondrites, yet this view has been questioned (Drake and Righter 2002; Righter et al. 2006; Righter 2007) on grounds that no known meteorite type appears to satisfy the observed compositional and isotopic constraints posed by the Earth's primitive upper mantle. From a geological perspective the chemical compositions of the Earth's core and lower mantle are important factors in understanding the workings of the deep interior of our planet. From an astrobiology perspective, the quantity of organic molecules and water that was accreted into the early Earth could have been a controlling factor in the origin of life, as these will have a major effect on the evolution of the oceans and on the oxidation state of the terrestrial atmosphere. These same considerations apply to the reconstruction of the early histories and evolution of Venus and Mars as well as to the potential that life might evolve in other protoplanetary systems. The origin of the terrestrial oceans is still a matter of debate, especially the relative contribution of water (Drake 2005) that may have outgassed from the Earth's interior compared to the quantity that may have been contributed by comets or even asteroids as a late arriving planetary veneer.

Unfortunately gathering an unbiased sample of the materials that accreted to form the Earth may be nearly impossible. The surface of the Earth has certainly been affected by planet building processes, including core formation, volcanic eruptions and chemical weathering to the point that nothing remains of the original building blocks. The great impact that formed the Moon certainly would have erased virtually any trace of the original material left at the Earth's surface. We also know that the surface of the Earth was changed significantly during the Late Heavy Bombardment (Levison et al. 2001, 2006) that peaked approximately 3.9 billion years ago and emplaced more than 20,000 craters with diameters greater than 20 km and more than 40 impact basins with diameters greater than 1000 km on the surface of the Moon. Because of the greater gravitational cross section of the Earth one should expect much larger fluxes of impactors on Earth than on the Moon. These planetesimals impacting the Earth and the moon evolved for more than 600 million years. Over this time period considerable chemical change could have occurred, especially to the concentrations of the more volatile elements.

In what follows I will examine factors responsible for the evolution of the planetesimals from which the Earth formed, and the likely timescales for their evolution based on a range of reasonable assumptions. I will also examine a generalized scenario for planetesimal accretion based on the comet accretion scenario of Weidenschilling (1997) and will then look to the current meteorite population as well as to their parent bodies to examine any bias(es) that might preclude the use of this data set as a starting point in modeling the formation and evolution of the Earth. Finally I will present the most likely candidate for a generalized model for the average primitive body aggregated into the growing Earth and discuss the implications of this choice for its early history, especially the oxidation state of the early atmosphere, the origin of the oceans and the conditions leading to the origin of life.

## 2 Thermally Driven Evolution of Planetesimals

There are many factors that influence the thermal evolution of a planetesimal ranging from the relative concentrations of radioactive elements and water, to proximity to the heat and

magnetic field of the sun, to the sheer size of the body itself. I will briefly examine each of these factors below and will conclude that if all other factors are roughly equal, then a larger ( $\sim 1000$  km) body (protoplanet) will evolve much more rapidly than a smaller ( $\sim 10$  km) body (planetesimal).

## 2.1 Radioactive Heating

Although potassium, thorium and uranium decay are now responsible for heating the interior of the Earth, the short lived radioactive elements  $^{26}\text{Al}$  and  $^{60}\text{Fe}$  most likely provided the energy that drove geological processing of the earliest stages of planetary history (Chabot and Haack 2006). While  $^{60}\text{Fe}$  can only be produced in a supernova explosion,  $^{26}\text{Al}$  and other short-lived elements can be made in the winds of massive stars as well as by spallation reactions due to irradiation of heavier elements by protons and alpha particles produced in an intense, active, early sun (Gounelle et al. 2001). There is considerable controversy over the sun's birthplace. Was the sun formed in a quiescent environment such as is found in the modern Taurus Auriga star-forming region (Hartmann et al. 1998; 2001), or as was more recently suggested did the sun form in the presence of one or more massive stars such as is seen in the Orion Nebula (Hester et al. 2004)?

In the traditional view the solar nebula would be reasonably homogeneous and all planetesimals would contain roughly the same proportion of all of the radioactive elements. In such a star-forming region the concentration of short-lived spallation-produced nuclides might have increased sporadically due to solar flares, but most of this material would remain concentrated near the protostar with limited but steady, outward transport (Boss 2004; Ciesla 2007). In such a scenario the earliest formed planetesimals could experience slightly less radioactive heating than later-formed bodies since they would contain fewer radioactive nuclei and might therefore evolve a bit more slowly.

In a star formation region such as the Orion Nebula, the nebula could have been seeded with  $^{26}\text{Al}$  over time by nearby stellar winds before being injected with  $^{60}\text{Fe}$  due to one or more supernova explosions (Wadhwa et al. 2006). In regions of massive star formation where short-lived radioactive elements could be injected well after some planetesimals had already formed, those formed after the nebula was seeded with short-lived radioactive nuclei could evolve much more rapidly than the earliest formed bodies. A complicating factor is the distribution of the radioactive elements, that is, if early formed planetesimals accreted large fractions of calcium-aluminum rich inclusions (CAIs), and thus more  $^{26}\text{Al}$ , then even small (5 km radius) bodies could rapidly ( $10^6$  years) melt (Das and Srinivasan 2007).

## 2.2 Water

The temperature in the solar nebula decreased with increasing heliocentric distance, which causes a snow line where water condenses to ice at some distance from the sun. Most planetesimals that begin to accrete outside the snowline will contain some water as ice grains become trapped together with silicates and other more refractory materials within these kilometer-scale bodies. Only those bodies that accreted completely inside the snowline might be devoid of ice or water. Such planetesimals could still contain substantial quantities of hydrated silicates and it is possible that dust grains inside the snow line could carry substantial quantities of adsorbed water (Stimpfl et al. 2006a, b). There is likely to be a gradient in water content in planetesimals orbiting in the region of the nebula where the

Earth formed (Ciesla and Cuzzi 2005, 2006) ranging from some small percentage of hydrous silicates nearest the sun to substantial quantities of internal ice in the outermost regions of the asteroid belt. If the orbital eccentricities of these bodies are excited by the formation of a giant planet (Wetherill 1985, 1996) this gradient could become disturbed due to the penetration of ice-bearing planetesimals deep into the innermost nebula. Yet it is unlikely that this gradient could be completely erased. If all other factors are equal, lower water content should lead to more rapid heating of a primitive planetesimal, since the same amount of radioactive decay will lead to higher internal temperatures without the moderating effects of melting rocks (dissolved water lowers the melting point of magmas), subliming ices or the escape of steam from the hot interior.

## 2.3 Heating Mechanisms

### 2.3.1 Solar Heating

The protosun heats the innermost regions of the nebular accretion disk to sufficiently high temperatures ( $>1500$  K) to evaporate silicates and other refractory grains (Woolum and Cassen 1999). Directly heated regions will naturally conduct some fraction of this energy into the interior of the disk where it will add to the gravitational energy dissipated during infall from the molecular cloud. This heating leads to a compositional gradient of small dust grains in the nebula ranging from highly refractory calcium and aluminum bearing minerals nearest the sun, to silicates, and even ice-coated silicates and ices farther out in the disk. One might assume that the larger planetesimals ( $>10$  km) would be effectively immune from solar heating, after the dissipation of the gaseous disk, except for the net energy conducted from their surfaces due to the emission of infrared radiation or the conduction from the tenuous residual nebular gas.

### 2.3.2 Magnetic Induction Heating

A more viable way to heat planetesimals is magnetic induction. The large magnetic flares observed by the Chandra Mission (Feigelson et al. 2006) and especially by the COUP project (Feigelson et al. 2005) imply the presence of a very strong magnetic field associated with young stars. If a planetesimal is conductive, then the Hall effect will heat it to some degree; e.g., moving a conductor in the presence of a magnetic field induces electrical current flow and the resistance of the medium leads to power dissipation—and heating—within the planetesimal (Sonett and Colburn 1968; Sonett et al. 1968). Nearly all primitive meteorites and chondritic aggregate interplanetary dust particles (for a petrologic review see Rietmeijer 1998) contain metals and sulfides, which are very good natural conductors. Melting ice could lead to the dissolution of some mineral species that would greatly enhance the electrical conductivity of some meteorite parent bodies and leave as evidence veins of aqueous minerals, mostly various salts, that chemically precipitated from hot evaporating fluids: Such reactions could also destroy metal and sulfide particles, leading to local decreases in heating. In bodies free of ice, heating of carbonaceous grain coatings could lead to the deposition of graphitic material at grain boundaries, possibly forming large conductive networks that would also lead to more efficient magnetic induction heating of the interior of the body. However, such a mechanism generally favors heating the outer portions of most asteroids.

## 2.4 Planetesimal Mass

Despite the potential importance of the factors discussed above, the most important single consideration controlling the loss of volatiles from a planetesimal is undoubtedly its size. A larger body will contain more radioactive elements per unit of surface area, will release more energy from each accretional impactor, will have a larger gravitational cross-section, thus attracting impactors at a higher rate, and will also release internal energy more slowly to space due to a smaller surface to volume ratio. Once the planetesimal grows sufficiently large ( $>1000$  km), geological forces such as core-mantle formation based on density will release gravitational energy to drive volatile loss. From this point of view, the larger a planetesimal grows, the faster it changes from an undifferentiated planetesimal to a fully differentiated planet (Kleine et al. 2002). Therefore an important question to consider is “Do all planetesimals accrete and grow at the same rate?”

## 3 Planetesimal Accretion

One of the most reasonable models of planetesimal accretion, starting from dust grains, was published by Weidenschilling (1997) and based on the assumption of a minimum mass solar nebula. The minimum mass nebula is the lowest mass from which the solar system could possibly form and it is highly probable that our nebula was more massive (Weidenschilling 1997). In this model individual dust and ice grains aggregate slowly because they are closely tied to the ambient gas, and grain diffusion via Brownian motion is the dominant cause of collisions among these grains. As the aggregates increase in size, and depending on their fractal dimension (Meakin and Donn 1988), they slowly begin to decouple from the gas and gently spiral inward, collecting more grains and aggregates via increasingly energetic collisions. In this model comets begin to accrete at  $\sim 100$ – $200$  AU and complete their growth to  $\sim 10$ – $15$  km scale bodies near  $5$ – $10$  AU. At this size they orbit independent of the ambient solar nebula gas.

Nebular mass (and the higher pressure of gas in the nebula) affects the scale of the zone of growth for a planetesimal, the timescale for planetesimal growth and determines the smallest planetesimal size of a given density that will orbit the sun unaffected by the drag of the ambient gas. Yet a higher nebular mass does not change the general picture described above. At higher nebular pressures, growth occurs faster, the distance traveled during the growth process is smaller and the final planetesimal will be larger, denser, or both. Yet the vast majority of planetesimals could start accumulating well outside the snowline (Lunine 2006; Ciesla and Charnley 2006) and should thus contain some quantity of water and organics. Planetesimals in a massive nebula would not travel as far and might be devoid of water if they started aggregating well within the snowline. Although planetesimals in a higher mass nebula would accrete grains and collide with similar sized aggregates at slightly higher velocities, they would still be only moderately compacted bodies that had yet to experience significant internal changes via typical geological processes (Donn 1991, and references therein).

While the vast majority of planetesimals remain small (kilometer scale) a few stochastically “runaway cores” quickly grow to planetary scale bodies many hundreds to thousands of kilometers in radius (Wetherill and Stewart 1989, 1993). These runaway cores grow at the expense of the existing planetesimal population; e.g. they grow by accretion of unprocessed planetesimals, mostly by virtue of their ever-increasing gravitational cross-sections. As they grow larger, they evolve faster; differentiating a core, mantle and crust,

outgassing volatiles to form an atmosphere and possibly a hydrosphere as at least some of these volatiles should condense around the largest of these bodies.

## 4 Implications for the Chemical Composition of the Earth

If mass is the single most important factor controlling the heating of a planetesimal, and if models of planetary formation are correct about the prevalence of runaway accretion in aggregation of the terrestrial planets, then the Earth accreted largely from planetesimals that had just barely begun to get warm due to radioactive heating and had no chance to evolve into the “dead” parent bodies of modern meteorites (asteroids). Some questions logically arise. What differences exist between the initial unaltered planetesimals that accreted into the runaway Earth and the rest of that same population of planetesimals that evolved due to internal heating and volatile loss for several hundred million years? What differences exist between a population of initially unaltered planetesimals that had evolved for several hundred million years and the modern asteroid population from which our meteorite collection is derived?

### 4.1 Changes on Half-Billion Year Timescales

As small planetesimals slowly heat due to the decay of short lived radioactive elements (e.g. La Tourette and Wasserburg 1998), water ice and clathrates melt or sublime, lost to the vacuum of a nebula that has already lost most of its gas. Depending on the ratio of rock to ice, and the composition and character of the dust, heating could leave planetesimals almost completely hydrated, including intercalated water in clay minerals. At lower water to rock ratios (less than 1–1), all internal water could be lost with enough radioactive energy left over to melt large fractions of the interior. At high water to rock ratios some small degree of gravitational and collisional settling and consolidation occurs, as water is lost from the interior, yet blocky aggregates could become cemented together due to hydrous alteration. Such processes could leave large voids in the interior of the planetesimal. At water to rock ratios so low that the higher radiation concentration causes silicates to melt, the surface tension of the melt will lead to compaction and, upon cooling, the planetesimal will be solid throughout. This leads to chemical and textural differences in planetesimals on timescales of roughly 500 million years. Depending on the concentration of radioactive elements, planetesimal size and the radius of its orbit, most ten kilometer scale planetesimals should stop increasing in temperature within much less than 500 million years (Ghosh et al. 2006). Further change in such small bodies is driven more by physical processes.

Planetary bodies—the products of runaway accretion—evolve on faster timescales than the ten kilometer scale planetesimals from which they are derived. The earth was fully-grown within 10 million years and core formation occurred within 30 million years of nebular collapse (Jacobsen 2003; Nichols 2006). Total melting within even water-free 10-kilometer scale planetesimals may not have occurred for several tens of million years (Huss et al. 2006), though much shorter timescales are possible if the concentration of  $^{26}\text{Al}$  is enhanced (Das and Srinivasan 2007). Planetesimals accreting into growing planetary embryos were much less evolved than the embryos themselves.

The accretion of planetary bodies is much more energetic than similar processes in kilometer scale aggregates, especially when two large bodies collide, such as during the moon forming event (Cameron and Benz 1991; Canup and Asphaug 2001; Canup 2004).

Such processes can result in the loss of all volatiles from the surfaces of both bodies and to degassing of the mantle of the largest body. It is likely that the moon formed from material that had been dispersed as small particles around the Earth at very high temperatures, and was thus completely degassed (Jacobsen 2005). The fraction of the proto-Earth that may have been degassed during this collision has yet to be well determined, though mantle depth magmas can hold up to 3% water by mass (Righter 2007).

#### 4.2 Changes on Longer Timescales

Roughly 3.9 billion years ago a Lunar Cataclysm or Late-Heavy Bombardment was responsible for creating several impact basins and more than 20,000 craters on the moon (Hartmann et al. 2000; Levison et al. 2001, 2006). The much higher mass of the Earth, and the greater gravitational cross section for impactors due to gravitational focusing, would bring a much higher impactor flux to the surface of the Earth than was experienced by the Moon. If the Late Heavy Bombardment was triggered by the rearrangement of the outer solar system (Gomes et al. 2004, 2005) then impactors would be a mixture of unprocessed comets and evolved asteroids, neither of which would be representative of the building blocks of the Earth. Comets rarely migrated to the inner solar system during the planetary accretion phase, being effectively stopped by Jupiter, Saturn, Uranus and Neptune. The asteroids had already evolved according to their size, internal complement of radioactive elements and proximity to the sun; they were considerably different from the primitive, volatile-rich aggregates available less than 30 million years after nebular collapse.

The current asteroid belt has evolved considerably over the last 3.5–4.0 billion years of relative stability throughout the rest of the system. Change is driven primarily by resonant orbital interactions with giant planets, especially Jupiter. Resonant interactions increase orbital eccentricity causing asteroids to interact with others in nearby orbits. Even slight changes in stable systems can lead to catastrophic collisions that disrupt kilometer scale objects. It is easier to disrupt a fluffy, loosely bound, aggregate of hydrous silicate than to break stony iron rocks. All asteroids are gradually worn away, but the volatile rich, loosely aggregated, less cohesive bodies are destroyed more rapidly.

Meteorites in today's collection arrived on Earth within the last few hundred thousand years, after having spent a few tens to hundreds of millions of years in slowly evolving orbits after ejection from parent asteroids via collisions. Our collection is a sample of the modern asteroid population, and may not be complete, let alone representative. The most volatile rich and least structurally sound asteroids were long ago ground into dust and lost from the system. Those that remain are much more cohesive. There are also severe selection effects in the terrestrial atmosphere where ram pressure disrupts low shear strength objects (Chyba et al. 1994).

Unless a volatile rich bolide is seen to fall (such as Tagish Lake), it may be overlooked as a meteorite. Even if such an object were collected in the field, unless special precautions were taken, volatiles could be lost due to melting and sublimation (e.g. Brown et al. 2000). The true fraction of volatile rich asteroids is therefore likely to be under-represented in our meteorite collection.

#### 4.3 Chemical Implications

From the arguments discussed above, no modern meteorite type is likely to be representative of the primary building blocks of the Earth (Drake and Righter 2002). While the



refractory content of CI chondrites provides a reasonable starting point to estimate the chemical composition of the core, mantle and crust, even such a primitive specimen will not contain sufficient water and volatile carbon to match the majority of planetesimals available 4.5 billion years ago. Thermally driven processing of modern asteroids and loss of the most fragile and primitive specimens to collisional disruption over the lifetime of the solar system severely biases our perceptions of the volatile content of the bodies that went into the Earth. Even the mild heating experienced by ordinary chondrites of metamorphic grade 3.6 has been shown to result in loss of all pre-solar carbonaceous grains (Huss 1990; Huss and Lewis 1994, 1995) due to reactions between diamond, graphite and silicon carbide and the oxide components that dominate meteorites. If such robust forms of carbon can be destroyed then more reactive materials, possibly in closer contact with oxide grain surfaces (e.g. organic grain coatings) would also be lost at low temperatures (400 K) on billion year timescales.

The Earth accreted from much wetter, more carbon-rich planetesimals than any existing in our modern meteorite collections. During the Moon forming event internal water may have been lost from a proto-Earth but it is not clear that all water would have been lost from the deep mantle despite the catastrophic nature of such a collision. Water could have maintained oxidized iron in the Earth's crust and upper mantle, releasing large quantities of hydrogen that would migrate into the primitive and very hot, SiO-rich atmosphere. Hydrocarbons trapped in the terrestrial interior could have reacted with silicates to produce large amounts of CO, or might have escaped directly into the super heated atmosphere where reduced species would be stabilized by large quantities of hydrogen escaping from the interior. Escaping CO and hydrogen could have reacted at high pressures and temperatures on grain surfaces via Fischer-Tropsch type reactions to form simple hydrocarbons. Escaping nitrogen could also react to form ammonia via the analogous Haber-Bosch process. The net consequence of such a scenario is formation of a methane-, ammonia-, and water-rich atmosphere as postulated by Miller (1953) and Miller and Urey (1959) in experiments to understand chemical evolution leading to the origin of life on Earth. This atmosphere could persist as long as hydrogen, CO and hydrocarbons were escaping from the terrestrial interior. Loss of hydrogen from the top of the atmosphere combined with the attainment of a quasi steady state rate of exchange between the atmosphere, crust and upper mantle would gradually lead to the evolution of a less reducing system.

There has been speculation that comets may have provided sufficient water to account for the terrestrial oceans. This assumes that the Earth formed from CI chondrites. If the Earth accreted from primitive bodies that were wetter and more hydrocarbon rich than CIs, then this presents an interesting question, If a large impactor had *not* collided with the proto-Earth, thus drying out a considerable fraction of the material that became its crust and upper mantle, would the surface of the Earth have been completely covered by oceans? Would dry land exist on Earth today? Consequences for the natural history of the Earth and for the evolution of communicative civilizations on our planet are significant.

## 5 Summary

Models for the accretion of planetesimals tens of kilometers in diameter predict that they will grow from a wide feeding zone that could span the snowline in the primitive solar nebula. Our understanding of the evolution of isolated planetesimals of this size predicts that timescales on the order of tens to hundreds of millions of years are required to produce asteroids from which modern meteorites are derived, unless they contain enhanced levels



of  $^{26}\text{Al}$ . In contrast, the Earth accreted very rapidly, on the order of from ten to twenty million years maximum, as constrained from the time inferred for terrestrial core formation. The Earth must have therefore accreted from extremely primitive small bodies, many of which could have contained significant fractions of water and organics.

Heating of these primitive planetesimals leads to loss of water and volatile organics within the first few hundred million years. Remnants of the most volatile rich bodies would evolve into loosely bound aggregates of clay minerals and could contain large voids. Collisional evolution of the asteroid population over the last 3–4 billion years selectively destroys fragile bodies while preserving those that evolve into rocks. Atmospheric ram pressures experienced when bolides enter the atmosphere easily disrupt fragile meteoroids with high concentrations of organic materials, ices, or both. Their fragments are both unlikely to survive long on the surface of the Earth, or be identified as meteorites. We are forced to conclude that not only does our modern meteorite collection not contain samples of the primitive planetesimals that accreted to form the Earth, since they long ago evolved to much drier and less organic rich materials, but that it is unlikely that even the desiccated remnants of this population have been collected.

An exception could be the very primitive Orgueil carbonaceous chondrite meteorite that was a witnessed fall (Gounelle et al. 2006). Specimens that were subsequently recovered were still warm and could be cut with a knife and, when sharpened, could be used like a pencil, suggesting that many of its most volatile components were indeed lost during the bolide phase and during its very short terrestrial residence. Therefore no meteorite type adequately represents the chemical composition of the planetesimals that accreted to form the Earth. The intensifying research efforts on all aspects of meteors by traditional ground-based observers plus quantitative chemical data from spectral observations may lead to understanding of the fundamental differences between the meteorite database and the chemical properties of less-evolved material from different reservoirs in the solar nebula.

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