

ORIGIN OF THE OCEANS

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Introduction

The oceans and the salts dissolved in them probably all formed early in the Earth's history. Although planetary degassing is occurring, as evidenced by studies of rare gases in rocks, the oceans, and the atmosphere, there is also a loss of water to the mantle via subduction. Supply from and loss to the mantle may be roughly equal at present.

Acquiring an Ocean

The oceans can be conceived of either as a feature established in the earliest history of the planet or as the result of a continuing supply of water and the constituents of sea water by degassing from the Earth's interior.

In 1951 W.W. Rubey, in his Presidential Address to the Geological Society of America, took the latter point of view. His arguments were colored by the knowledge available at that time of the age of the Earth and the age of the oldest rocks. Based on the analysis of lead isotopes in galenas, it was determined in the late 1940s that the Earth was about 3.2 billion years old. Some continental rocks, presumed to be relicts of ancient terrains, dated at about the same time also gave ages of about 3.2 billion years. On this basis it was assumed that the oldest rocks preserved a record of the dawn of Earth history. The contemporary oceans and ocean-derived sediments contain chemical species in quantities far in excess of those available from the weathering of crustal rocks (Table 1). These components were called 'excess volatiles' by Rubey, but Harold Urey suggested that they were really better characterized as 'excess solubles'. If these species all arrived with an early ocean, the early ocean would have had a radically different composition. It would dissolve rocks and also precipitate compounds different from those depositing from the present ocean.

If that were indeed the case, Rubey argued, the initial rocks should show the effects of a sudden supply of ocean water and hydrochloric and sulfuric acids, and carbon dioxide that ultimately dissolved rocks and formed the saline sea. The ancient rocks,

however, do not look appreciably different from younger rocks; thus the absence of a difference in composition indicates that the oceans with their attendant excess anionic species have grown slowly with time. Indeed, it was argued that if a small fraction of the flux of water from fumaroles and hot springs were primary (from the Earth's interior) rather than meteoric or surface recycled water, then, over time, the oceans could be added to the surface from the interior so that the volume was increasing with time.

The discovery in 1955 that the Earth as a member of the solar system was really about 4.55 billion years old, and that the oldest rocks were considerably younger, ruled out having a record of the earliest days of the Earth's existence. In addition, from measurements of the hydrogen and oxygen isotopes of hot springs and in some cases tracking radioactive tritium from nuclear tests in hot springs, it was clear that all or most of the water in hot springs, and fumaroles was meteoric, and therefore determining a primary water flux was virtually impossible.

There is evidence, however, that there is planetary degassing, as revealed in the flux of radiogenic ^{40}Ar (Figure 1) and primordial ^3He (Figure 2) to the atmosphere. When these fluxes are used to model the flux of other gases (or their condensation products), two results are obtained. Gases that behave like ^{36}Ar (the nonradiogenic argon isotope) appear to have arrived at the Earth's surface in the earliest days of Earth history, while carbon dioxide and its condensation products, limestone and organic compounds, are being recycled via the processes associated with plate tectonics. One can assume that other chemically reactive analogues like water, behave in the same way. Like ^{36}Ar water may have been at the Earth's surface early in its history, and like carbon dioxide it is being recycled.

Table 1 Components of the oceans, atmosphere, and sedimentary rocks not derivable by weathering of primary silicate rocks

<i>Chemical species</i>	<i>Amount on Earth's surface not derived by weathering ($\times 10^{20}$ g)</i>
Water	16600
Total carbon as carbon dioxide	910
Chlorine	300
Nitrogen	42
Sulfur	22

After Rubey (1951).

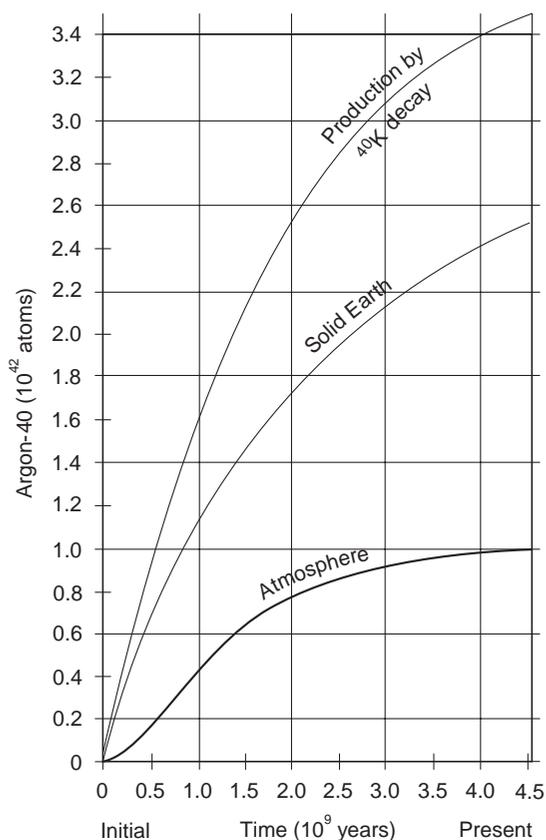


Figure 1 The degassing of radiogenic ^{40}Ar (from the radioactive decay of ^{40}K) from the solid Earth can be expressed by the equation $dX_{\text{SE}}^{40}(t)/dt = \lambda K_0 \exp(-\lambda t) - \alpha \exp(-\beta t) X_{\text{SE}}^{40}(t)$, where $X_{\text{SE}}^{40}(t)$ is ^{40}Ar in the solid Earth, λ is the radioactive decay constant for ^{40}K , α is the first-order degassing constant, and β is a measure of the exponential decrease in the efficiency of degassing over time as the result of the decrease in heat production from radioactive decay and loss of initial heat. K_0 is the amount of ^{40}K in the planet 4.55×10^9 years ago that will decay to ^{40}Ar . The lowest curve represents the growth of ^{40}Ar in the atmosphere over the past 4.5 billion years. The application of the values of α and β derived from the ^{40}Ar record when applied to the nonradiogenic isotope of argon (^{36}Ar) indicates that the nonradiogenic rare gases in the atmosphere largely had to be supplied to the atmosphere early in the Earth's history. $\alpha = 1.4 \times 10^{-9}$, $\beta = 1.2 \times 10^{-9}$, $K_0 = 3.85 \times 10^{42}$ Present-day flux of ^{40}Ar to atmosphere = 1.5×10^{31} atoms per year.

We are thus left with the possibility that the oceans, including both the water and the soluble salts found therein, were present at the Earth's surface right at the beginning and subsequently have been subjected to recycling between crust and mantle via the plate tectonic cycle.

The Loss of Water from the Earth's Surface

If the oceans were effectively at the surface at the beginning, what processes could diminish the

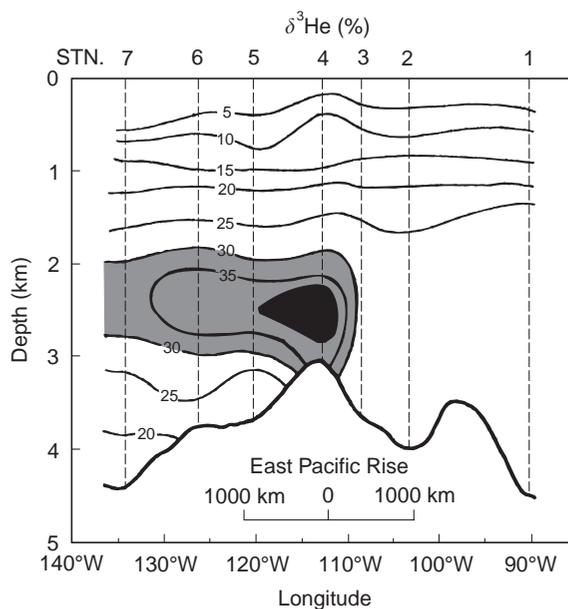
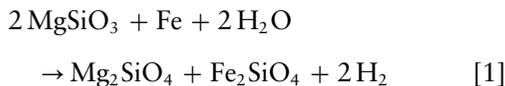


Figure 2 A section across the East Pacific Rise in the South Pacific showing ^3He in excess over that expected from the atmospheric ^3He dissolved in sea water when scaled to the more common ^4He . The difference between the dissolved isotopic ratio and atmospheric ratio is represented by $\delta^3\text{He}$ in percentage difference. ^3He is assumed to be primordial and indicates degassing of the mantle at the divergent plate boundaries featured as oceanic ridge systems. STN = station number of the sampling. (Reprinted with permission from Lupton and Craig 1981, copyright American Association for the Advancement of Science.)

original inventory? There are two ways to lose water from the Earth's surface: (1) the photolytic dissociation of water vapor in the atmosphere with subsequent loss of hydrogen to space and the utilization of the released oxygen to oxidize reduced iron and sulfur compounds from the mantle; and (2) the loss of water, as well as of the oxidized components, to the mantle by way of hydrated minerals (such as clay, minerals, micas, and amphiboles) and minerals with oxidized iron and sulfur.

Although the first process is occurring today, it is not very efficient because of recombination with the abundant oxygen in the atmosphere as well as the fact that the supply of solar hydrogen to Earth may compensate for the loss of hydrogen. In the early history of the solar system, the flux of high-energy photons from the sun is thought to have been much greater than it is today, resulting in a very efficient conversion of water to hydrogen and oxygen. The stream of hydrogen from the atmosphere to outer space may have entrained heavier gases and caused the mass fractionation of the rare gases relative to each other and the fractionation of the isotopes of individual rare gases relative to solar composition.

We can estimate how much water was dissociated by considering the oxidation of the mantle. If the Earth started out with the oxidation state of chondrites (although not necessarily of total chondritic composition), it would take the oxygen from about one present-day ocean volume to reach the oxidation state of the mantle inferred from mantle-derived rocks. Alternatively, if we start with a more reduced ensemble, suggested by condensation calculations from a solar nebula, we will have primarily enstatite (MgSiO_3) and metallic iron as the original source to be oxidized. The oxidation reaction would then be as shown in eqn [1].



To oxidize the mass of the Earth with this initial make-up to the present oxidized level would require the dissociation of 60 present-day ocean volumes. Clearly, the results indicate hydrogen loss and planetary oxidation, although the exact starting material is not precisely defined.

In either case, the oxidation of the planet is the consequence of the photodissociation of water vapor and loss of hydrogen to space. In order to fractionate the rare gases by entrainment in the hydrogen streaming from Earth, this process must have occurred almost instantaneously in the early history of the Earth. Therefore, it is reasonable to assume that both water and rare gases were at the Earth's surface virtually at the time of formation of the Earth.

Sources of Water

Water reached Earth by one of two processes. The first is by way of the capture of water from the solar nebula as it cooled down. There is evidence from neon isotopes (Figure 3) that the initial imprinting of Earth with gases was likely to have been of solar composition. If this were the case, then the amount of water trapped by the accreting planet would have been large and provided the fundamental source of water. A second source is cometary impacts. Comets have often been described as dirty snowballs. They are rich in organic compounds and ice. Carbonaceous chondrites may be related to comets and, if so, their rare gas isotopic signatures are characteristically different from solar abundances and isotopic compositions owing to adsorption processes. Therefore, if water tracks the rare gases and if the neon isotope signature of mantle rocks indicates a solar origin for the terrestrially accumulating gases

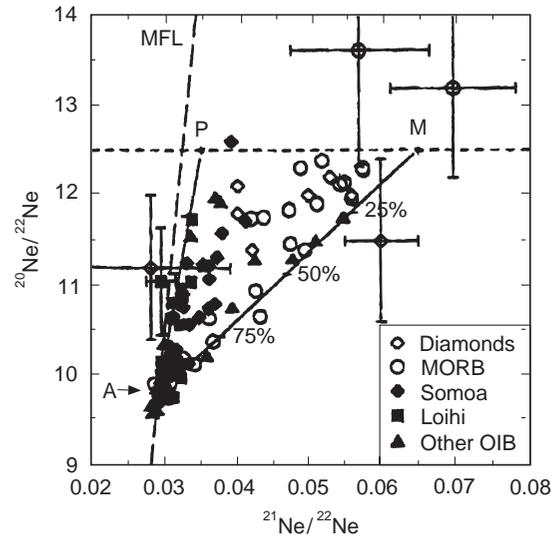


Figure 3 The distribution of neon isotopes in mantle-derived rocks, indicating the presence of an atmospheric component, a radiogenic component adding ^{21}Ne (produced by neutrons from uranium fission acting on oxygen and magnesium), and a solar component. It is this latter that indicates that gases in the mantle were derived from the capture of solar material in the early history of the Earth. M = MORB (mid-ocean ridge basalts); P = plume or ocean island basalts (OIB); A = atmosphere. Solar neon is represented by the horizontal line at $^{20}\text{Ne}/^{22}\text{Ne} = 12.5$; MFL is the mass fractionation line. The presence of solar neon in ocean basalts was first identified by Craig and Lupton (Craig H and Lupton JE (1976) *Earth and Planetary Science Letters* 31: 369–385). (Reprinted with permission from Farley and Poreda (1993).

rather than a cometary origin, then most of the oceans owe their origin to direct capture of gases in the solar nebula cooled sufficiently to allow the production of water molecules.

There have been claims that absorption spectra of sunlight indicate house-sized blocks of cometary ice entering our atmosphere. If the claim were substantiated the calculated rate of influx of these blocks of ice would be sufficient to provide the present volume of the oceans. However, these claims have not been independently substantiated and the consensus is that such blocks of ice are not responsible for the observations. Unless new measurements support this suggestion, we are constrained to accept the hypothesis of an initial ‘watering’ of the planet rather than a gradual accumulation.

The Composition of the Oceans

If indeed the oceans were present virtually from the day the Earth was formed, there is a further question: Was it salty like the present ocean? The salts dissolved in the ocean were probably dissolved from the original materials composing the Earth if

low-temperature condensation compounds such as the chlorides, sulfates, and carbonates were present. Indeed, salts of these anions have been leached from primitive meteorites such as the carbonaceous chondrites as well as some other meteorites that have undergone some reheating. On the basis of theoretical calculations, similar compounds should have been present in the accreting Earth. With leaching of these compounds by the original water released from the Earth early in its history, it can be assumed that the oceans were always salty.

Indeed, the argument that oceans over several hundred million years ago might actually have been twice as saline as the contemporary ocean is based on the fact that there are many geological salt deposits and deep brines, often associated with oil fields. The assertion is based on a reasonable premise that salt deposits became important about 400 million years ago. The salt prior to that time had to be stored in the oceans, thus increasing its salinity by a factor of about two higher than the contemporary ocean.

The Future of the Oceans

If most of the water found on Earth was primarily in the oceans, with some dissolved in a molten mantle existing in the early days of the history of the Earth, then as we have seen, there was a decrease in the size of the original oceans. This decrease occurred because of photolysis of water vapor and subsequent loss of hydrogen from the atmosphere or the entrapment of water in hydrated minerals that were then subducted into the mantle.

The rate of photolytic loss must be considerably smaller at present compared to that on the early Earth because of the decrease in the extreme ultraviolet flux from the Sun. Also, the rate of subduction of the hydrated crust must be less now than it was early in the Earth's history because the driving forces for mantle convection and thus plate

tectonics are gravitational heat from accumulation and fractionation and heat production by radioactive nuclides, both of which are waning with time. Therefore, the rate of supply of water to the mantle is now diminishing and there may actually be a release of the water stored in the mantle from previous times. As in the case of carbon dioxide, we may be in a steady-state of water supply from the mantle and return of water to the mantle, thereby maintaining the size of the oceans. At any rate, changes in the volume of water will probably not be large in future.

See also

Conservative Elements. Elemental Distribution: Overview. Hydrothermal Vent Fluids, Chemistry of. Mid-ocean Ridge Geochemistry and Petrology. Volcanic Helium.

Further Reading

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OVERFLOWS AND CASCADES

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Introduction

When dense water enters an ocean basin it often does so at a shallow depth passing through a

narrow strait or over a sill from a neighboring basin or marginal sea, or flowing down the continental slope from a shelf sea. The dense water flow is affected by the Earth's rotation and so does not flow directly down slope but instead turns to flow partly along the slope. Large-scale, continuous flows from one ocean basin or large sea down into another are referred to as 'overflows,' while smaller scale, intermittent flows of dense water from shelf seas down