Clues from isotopes indicate a hybrid parentage for earth, its waters and atmosphere

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The current view holds that earth was formed approximately 4.6 billion years ago through accretion of solid materials, which condensed gravitationally from a viscous disk of gas and dust orbiting the protosun[1]. These, the 'building blocks' of earth, are identified with a class of meteorites or chondrites called carbonaceous chondrites. Considered most primitive remnants of the circumstellar disk, these chondrites are a mechanical mix of grains of assorted composition populating this disk. They were never subjected to gravitational heating and melting, a process, which in some planets had led to formation of core and mantle[2]. They are hence considered to preserve in 'pristine' state most of the elements in the same ratios as in the Sun, a feature that has made these carbonaceous chondrites the choice of geochemists as a reference standard in their studies probing earth's chemistry. Such a choice obviously assumes that earth had a carbonaceous chondritic bulk chemistry originally. Now, several recent contributions have highlighted the inappropriateness of such a model to assess earth's chemical evolution. This appears justified if we take into account earth's prolonged accretionary phase during which several compositionally distinct classes of chondrites that were generated could also have accreted besides carbonaceous chondrites. Actually, the 'heterogeneous accretion theory' on origin of earth advanced some twenty years ago[3] is based on such significant temporal changes in composition and oxidation-state of materials forming in this disk.

Three classes of accreting materials are most common. Increasing in their degree of oxidation, they are the enstatite chondrites, ordinary chondrites, and carbonaceous chondrites. Carbonaceous chondrites and ordinary chondrites are alike except that the former type has retained volatiles like C, Pb, and Bi. Based on the properties of these depleted elements, it is inferred that the ordinary chondrites must have been subjected to heating at 450 K at some time and according to the thermal gradient in the solar system, this volatilization must have taken place at a distance of 2.6 AU (1 AU = earth–Sun distance) from the protosun[4,5]. This distance marks the junction between the ordinary chondrites and zone of carbonaceous chondrites, water-rich bodies, water-snow condensates, and icy comets (Figure 1). At the place where protoearth formed, between 0.8 and 1.3 AU, the accreting bodies must have experienced temperature between 900 K and 1400 K, high enough for them to get degassed, leaving a material rich in silicates and reduced iron. But this degassing, according to some planetologists, was a late event, taking place after earth was formed[6].

Geochemical explanations for various discrepancies in earth's composition have often led to unending discussions due to lack of precise knowledge about the planet's accretionary history and chemical evolution. Immense heat from impacts, combined with heat from radioactivity and gravitational compression produced a molten protoearth. Core separation followed through extraction of iron and 'iron loving' elements, better known as the 'siderophiles' (essentially Co, Ni, Mo, noble metals Ru, Rh, Pd, Os, Ir, Pt, Au and Re). In this manner, relative to the chondrites, earth's primitive mantle came to be depleted in iron and the siderophiles and the crust enriched in Al, Na, and K. Even after the formation of the core, which took place around 10–50 million years after protosun developed[7], impacts by chondrites continued, many of which by then had grown to large-sized bodies. It is probable that some of these earth-impactors could have come from regions beyond 2.6 AU also, gravitationally pulled from their distant orbits by huge planets, particularly Jupiter[5,8]. One such giant impact, when earth was hardly 40–50% of its present mass, led to the formation of the moon[7,9,10]. Such giant-sized impacts are believed to have generated magma-oceans which effectively re-homogenized earlier mate-

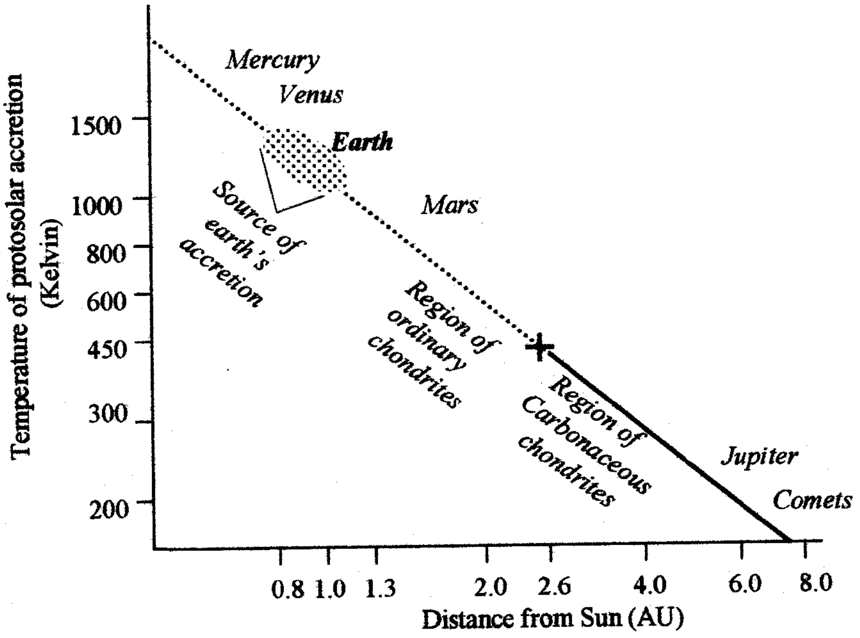

Figure 1. Diagram showing decreasing temperature with increasing distance from sun and the positions where some of the planets formed. Dotted line represents the region of ordinary chondrites and solid line that of carbonaceous chondrites, water-rich bodies and icy comets (adapted from refs 4, 5).

rials and in this way earth is supposed to have gone through a molten state more than once[11].

Considering earth's long formative phase (> 100 million years since solar system formed) (refs 4, 7) during which accretion by a variety of materials could have altered earth's initial chemistry, the suitability of carbonaceous chondrites for modeling earth's composition is now questioned by Michael Duke and Kevin Righter of Lunar and Planetary Laboratories, Tucson, Arizona[8]. According to them, the present day mantle is quite different from the one that formed out of the original accreted materials and distinctly different from any of the presently existing meteorite types and that today there is no uniquely 'chondritic' or average solar system object. They have based these observations on certain major element ratios, oxygen isotopes, ^{187}Os/^{188}Os, D/H and ^{84}Kr/^{130}Xe ratios in the meteorites and earth. They point out that in earth's primitive mantle, immediately after core formation, the Mg/Si and Al/Si ratios were distinctly different from those of undifferentiated meteorites (carbonaceous chondrites) which are supposed to represent 'average solar system' composition. Similarly, oxygen isotopes indicate that only enstatite meteorites (chondrites and achondrites) share a common oxygen source with earth, and it is unlikely that any large percentage of carbonaceous-chondrite-like material could have formed part of earth's accretionary materials[8,12].

The anomalous excess of certain highly siderophile elements (HSE) like the noble metals in the mantle, all of which should have been drained into the core along with iron, is now attributed to their introduction through late accretion of carbonaceous chondrites ('late veneer' concept)[8,11,13] after core formation. However, the noble metal ^{187}Os/^{188}Os ratios in earth's primitive upper mantle (0.1296 ± 0.008) represented by mantle xenoliths collected from around the globe (North and Central America, Europe, South Africa, Asia and the Pacific region) differ from those of carbonaceous chondritic ratios (0.1260 ± 0.0021) (ref. 14). This rules out any dominant contribution through late additions of such types of chondrites. They feel that the 'late veneer' contribution is a complex issue since the processes that collected HSE in chondrites are, as yet, unclear and further there is no one single set of HSE chondrite abundance to which other planetary abundance can be compared.

While the carbonaceous chondritic parentage of solid earth is doubted, studies on earth's atmospheric gases, particularly the noble gases like krypton and xenon, also lead to this view. These gases, being inert, are expected to preserve their primordial or pristine ratios, but the observed patterns in atmosphere are different and indicate that they must have come from distinct source materials. Each of them exhibited unique elemental, isotopic and abundance patterns, which were easily recognizable because they never got well mixed[15]. Thus, one could identify in the atmosphere both the solar as well as planetary (carbonaceous chondrite) patterns.

The pattern shown by ^{130}Xe is another example indicating mixed source materials. Its abundance in atmosphere is solar while in carbonaceous chondrites it is ten times the solar value, a figure that discounts such a chondritic source for earth's xenon[4]. Similarly, ^{84}Kr/^{130}Xe ratio (12×10^{-2}) also does not compare with that of present day carbonaceous chondrites (5.1×10^{-2}). Geochemists, in fact, have long been puzzled about ratios of these isotopes in earth's atmosphere. While xenon is enriched in the heavier isotope, krypton does not exhibit a similar behaviour, a feature considered to be a case of decoupled fractionation, a poorly understood mechanism[15]. One cosmic explanation ascribes the Kr and Xe differences to delivery through comets from far away Uranus-Neptune zone. Here, comets can carry these gases within crystalline clathrate-hydrates at the prevailing low temperature (30–75 K) inside amorphous ice[4,16].

Isotopic composition of the waters of earth provides another line of approach to understand the problem of earth's parentage. Earth's waters, whether indigenous or exogenous in origin, has remained a baffling question for a long time. Recent answers to this have come from investigations on the deuterium-hydrogen (D/H) ratios in the waters. Many believe that earth accreted 'wet' and hence its waters are indigenous and released from a hydrous primordial magma–ocean. In support of this hydrous magma–ocean concept, existence of hydrogen in the core is cited as evidence. This core-lightening element, hydrogen, is released as a byproduct of reduction of water by Fe that settled at the bottom of such a hydrous magma–ocean in the lower mantle. This hydrogen is believed to have been incorporated into the core and not degassed into the early atmosphere as many believe[17,18]. An alternate explanation[19] conceives that considerable amounts of water can indeed be stored in the lower mantle within typical mantle-minerals – Mg-rich perovskite and magnesiowüstite (up to 0.2 wt%) as well as in Ca-rich perovskite (up to 0.4 wt%). Besides H_2O can also be added to lower mantle from hydrogen-saturated outer core[18]. Together, these sources account for five times earth's ocean waters[19].

Opponents of hydrous magma–ocean concept argue that at the distance of 1 AU where earth accreted, the temperature should be too high for hydrous phase to exist in the accreting materials and hence it is unlikely that earth's waters could be indigenous. These 'dry' accretionists believe that earth's waters are mainly exogenous brought by late accreting carbonaceous chondrites, ejected as collisional products of large asteroid-like objects from regions beyond 2.6 AU where temperature is quite low for retention of water. Impacts from such exogenous sources appear high judged from results of studies based on the size, age and density of impact cratering on moon and some of the inner planets. These testify to the intense scale of bombardment by large-sized bodies experienced by earth and its neighbourhood during its first half-billion years. But some doubt whether such a delivery could ever provide enough volume of water to form oceans even if the impactor was 1000 km wide[5].

Exogenous delivery of waters after our planet had achieved most of its mass is gaining acceptance and apart from water-rich asteroid-like objects, comets are the strongly favoured candidates. Most of them are more than 40% water by mass and it is argued that the heavy bombardment earth faced need to have been only ~ 10% cometary by mass to have delivered terrestrial oceans[20]. Such water-rich comets reside in far-flung orbits and they could be deviated out of their orbits in course of time by collisions or repeated gravitational pulls by giant planets. It has been estimated that as much as 10^{14} to 10^{18} tons of cometary material may have crashed within earth's first half-billion years[21].

The immense potential of comets as a major source for earth's waters is arrived after comparisons of deuterium/hydrogen (D/H) ratio in waters of our planet as well as in exogenous materials such as carbonaceous chondrites, comets, and gaseous planet like Jupiter[5]. Modelling studies of the evolution D/H in protosolar nebula have recognized an isotopic gradient – their ratio decreasing the closer they are to the sun and getting higher farther away. Based on this gradient, it is predicted that the D/H ratio for waters that condensed at 1 AU (where earth formed) should be close to the protosolar value of $\sim 80 \times 10^{-6}$. Earth, however, shows a ratio of $\sim 149 \times 10^{-6}$ which is close to the clay component within the carbonaceous chondrites. This suggests that the terrestrial waters must have been introduced from materials from the coldest regions of the solar system[22]. According to the proponents of this view, even though a small fraction of water may have come from water-rich bodies during earth's early accretion phase and hence indigenous, the main fraction was added exogenously by a few late giant-impactors[22]. A liberal calculation, however, puts this exogenous delivery around 10–15 per cent only and the rest may still be indigenous[8]. Present view is veering towards acceptance that earth's waters and atmosphere may have had mixed parentage – indigenous partly and exogenous in part through extra-terrestrial additions.

Many of the paradoxes and anomalies regarding the chemistry of earth, its waters and atmosphere have their roots in the first half billion year of earth's evolution when earth was still accreting through heterogeneous inputs of planetessimals, chondrites, asteroids, comets and the like. This was a turbulent phase of earth's evolution, a period notable for absence of reliable clues, many of which have been erased or reworked during earth's geological evolution. Apart from the question of earth's parentage, answers for many of the other events of earth's early history have also not been fully convincing and it appears explanations to these early events may have to come from astronomy rather than through geochemistry or geophysics. Hopefully, the ongoing unmanned research projects probing planets, near-earth asteroids, encounters with comets may help to demystify many aspects of earth's parentage and its chemistry.

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COMMENTARY

Cosmology – Facts and speculation*

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Cosmologists are often in error but never in doubt.

— *Lev Landau*

Among scientists (specially physicists), there has been a discussion for a long time about how much of a science is cosmology. The difficulty earlier (before 1920s) was the absence of any observations and the stronghold of mythology. Even broad observed features were highly ambiguous. Only in the twentieth century was it realized that what were thought of as nebulae were really distant galaxies. In 1927, Hubble observed faraway galaxies and their velocities and formulated Hubble's law which says, 'The farther a galaxy is, the faster it is running away from us'. This gave rise to the model of the expanding universe now known as the 'Big Bang'. Almost forty years later, in 1965, the cosmic microwave background radiation (CMBR) was discovered accidentally. The non-uniformity or anisotropy of CMBR was discovered only in 1992. It is only in the last two

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