G R E S H A M

C O L L E G E

WATER, WATER, EVERYWHERE

A Lecture by

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Water, water everywhere

It is very easy to be blasé about water. It is the most obvious compound to be produced on the grounds of the availability of the elements. Hydrogen is by far the most abundant element in the Universe, left over from the Big Bang, and oxygen, rather than carbon, is top of the list of species most likely to be produced in stellar nucleosynthesis. Only the noble gas helium is more prolific but it is inert and does not combine with other members of the periodic table. Hydrogen reacts explosively with oxygen, when the two come together, so by rights we ought to be literally up to our necks in water. And indeed we are 70% of the human body is water; even the brain is nearly 90% of the stuff. Its not just having water which is important, it has to be continuously turned over. At least 2.5 litres into and out of our bodies every day. You can survive without food for 3 months, a couple of days without water and ....!

Viewed from space it appears that Earth literally is flooded, 75% of its surface is covered with water. But Earth is unique amongst the planets in that it is situated just the right distance from the Sun to allow water to be able to exist in all its three states: solid, liquid and vapour. However, it is liquid water which is the essential basis of life as we understand it. Without water as a solvent life would be impossible, chemical reactions would be too slow and complicated substances needed for the biochemistry could not develop. Plants also have to cycle water in and out of their systems. Without the benefit of privatised water supplies, a cereal plant might develop 300 miles (!) of root network to obtain access to the absolute necessity for growth water. Some leaves have 300,000 stomata to respire what they do not need. Specially adapted plants such as cacti have water in them which is 200 years old.

Despite its predicted universal abundance, evidence for water is decidedly lacking in astronomical situations. Touring through our own solar system it is immediately obvious that Mercury has none, its size and proximity to the Sun is incompatible with retention of water at the surface. Venus ought to behave more like the Earth but studies of its atmosphere by the Pioneer space probe suggest an abundance of less than 1ppm. Anyway, there is strong evidence for the existence of sulphuric acid in the atmosphere of Venus, a compound which has a tremendous affinity for water, so what there is is pretty comprehensively unavailable.

Mars is a much better bet. Pictures of the surface of the red planet show very pronounced features which can only be due to the presence of liquid water sometime in its past. The major debate concerns how much was there and where is it now. Some of it is locked up in polar ice caps, but not all of this can be water, they must also consist of frozen out carbon dioxide. It has been calculated that there might be enough water at the martian north pole to cover the surface of Mars to a depth of 1cm, not much by terrestrial standards. But there is indisputable evidence from martian meteorites that water has existed on the planet since these objects contain hydrated minerals and features which suggest deposition of carbonates under hydrothermal conditions.

The giant planets with their vast quantities of hydrogen and helium are not a very good location for seeking the presence of liquid water, but it has been known for some time that at least two of the satellites of Jupiter, Ganymede and Europa, host water ice at their very surface. Europa is an intriguing case because the latest pictures acquired by the Galileo probe shows unambiguous features in the ice which suggest it is in motion. This leads to the idea that it may be a solid crust on top of a liquid which could be produced by internal or external heating of the satellite. An internal heat source would be volcanic eruptions under the ice and external one would require interactive tidal forces from the giant planet. With the possibility of ancient life on Mars having been postulated from martian meteorite studies in recent times, it is very much in vogue to suggest Europa as the best chance of contemporary life in the solar system. An irony in this situation is that water is very unusual in that ice is less dense than liquid water so that it floats. If water was like most other liquids, ordered hydrogen bonding its structure cause expansion on freezing instead of contraction, then there would be no chance of possible havens for life on Europa.

From what we have considered so far there seems to be a decided lack of water in the solar system. However, we have not yet considered comets. Current theories suggest that there may be as many as 10^{11} or 10^{12} comets in the Oort cloud which extends from us half way to the next star. Although most comets are only a couple of kilometres in diameter Halley (15 x 8km) and Hale-Bopp (40km) are exceptions, their combined mass may be up to twice that of the giant planets combined. Therefore comets are a very fundamental part of the solar system, the greatest repository for elements higher in mass than helium. They are also the place where presumably most of the volatile matter in the collapsing solar nebula ended up. From the one visit we have made to a comet so far, the ESA Giotto mission, we know that more than 80% astronomy's harbingers are water. We also know the flux of water molecules streaming from comets; a more typical one than Halley, the comet Wirtanen, which has just been closely monitored because of plans to send a mission called Rosetta to rendez-vous with and land on the nucleus, gave off between 10^{27} and 10^{28} molecules of water/second as it passed round the sun; an amount about the equivalent of emptying your bath. Its hard to comprehend that displays so magnificent as we are currently witnessing from Hale-Bopp are produced by about a petrol tanker of water being emptied into the vastness of space every second.

The origin of cometary water is something of great fascination and isotopic measurements are needed to address this question (the subject of a future lecture) but we may already have cometary water to hand. A small group of meteorites, the carbonaceous chondrites contain a relatively large proportion of water in their matrix, up to 20 wt%. So much that one of the earliest scientists to investigate light elements in meteorites, Berzelius almost threw away the sample of the Alais fall, when he found it was so wet. Another group of primitive meteorites, the unequilibrated ordinary chondrites also have water in their structure. The exact boundary between what is an asteroid ad what is a comet is a very grey area but volatile rich carbonaceous chondrites might very well represent that transition - that is, the carbonaceous chondrites could be the extinct cometary nuclei. We either have to except such a hypothesis or contemplate an alternative recent suggestion that type I carbonaceous chondrites are martian sediments deposited in martian seas, a very exciting possibility. We certainly can not have a 4.5 billion year old asteroid big enough to retain water throughout the history of the solar system.

A few years ago the isotopic composition of water from carbonaceous chondrites and unequilibrated ordinary chondrites provided a very interesting clue about contributions to the early solar system. The deuterium content of the water when measured turned out to be high, very high infact. In a subject where changes of a few percent get people very excited, obtaining an isotopic enrichment of over a factor of six, as was encountered for the Semarkona meteorite, is situation of, to use the appropriate word, astronomic proportions. The interpretation of the data is that the water has survived from times when it existed in dark interstellar clouds in space. In molecular clouds, isotopes can be very efficiently fractionated by a mechanism known as ion-molecule exchange, a process which can even led to the production of molecules with a D/H ratio of 1, from a starting point of 10^{-5}.

In recent months, there has been another reported occurrence of water in the solar system, that is on the Moon as indicated by radar measurements carried out by the space mission Clementine (very appropriate considering the popular song of the same name). Lunar rocks are almost entirely void of water suggesting that none existed on our satellite when the majority of the basalts were erupted. So if there is water on the Moon, where did it come from? Since the putative water is only found in very deep craters, areas in permanent shadow from the sun, one hypothesis is that it originated from comets or perhaps carbonaceous chondrite type meteorites. The water released by impacts would be partially trapped down by cryogenic cooling in these areas which are at temperature of -200°C, analogous to using a liquid nitrogen bath in the laboratory. This hypothesis, although plausible, provides only an intermittent source of water. There is actually a constant source of water, albeit small, on our satellite. The solar wind, mostly hydrogen, bombards the surface of lunar soil particles. As it does so, it chemically reacts with oxygen in the silicate to produce water in a fashion even more efficient than for the methane discussed in a previous talk. Water was in fact extracted from lunar samples and shown to be almost devoid of deuterium confirming a solar wind origin. Water from such a mechanism, constantly leaking out of the Moon's soil, could also migrate to cold traps. One day when we return to the Moon with space craft the existence of water for colonisation will be an important issue. Therefore it can be expected that isotopic measurements to understand the provenance of lunar water and its likely long term availability will be a priority investigation.

This all brings us back to the Earth, since it is very likely that the Earth obtained its water by the kind of secondary process just discussed for the Moon. The water on Earth could have come from a late infall of volatile rich bodies such as comets. There is no real chance of demonstrating that Earth's water is isotopically different from the solid silicates because we live on such an active planet that any isotopic irregularities would have been exchanged out long ago as the hydrogeological cycle came to equilibrium. Water has always been an emotive subject in Britain. We used to worry about whether the rain would save England in the Test match now we are concerned about whether we are moving towards a subtropical Mediterranean climate. One should actually remember that it is the presence of water vapour in the atmosphere which causes the essential natural greenhouse warming of the planet. It is the addition of other minor components, many of them manmade which is threatening to disturb the delicate balance.

Water on Earth is distributed as set out in the Table and constantly circulates through a hydrogeological cycle (figure) which also involves all of life, including humans.

Distribution of water on Earth

	%	**km^3**
Oceans	97.2	1.3×10^9
Ice	2.15	2.9×10^7
Groundwater	0.63	8×10^6
Lakes	1×10^{-2}	0.8×10^5
Atmosphere	5×10^{-3}	1.3×10^4
Rivers	1×10^{-4}	0.3×10^3
Humans	ca 1×10^{-8}	0.12
Wine per year	ca 1×10^{-9}	0.01

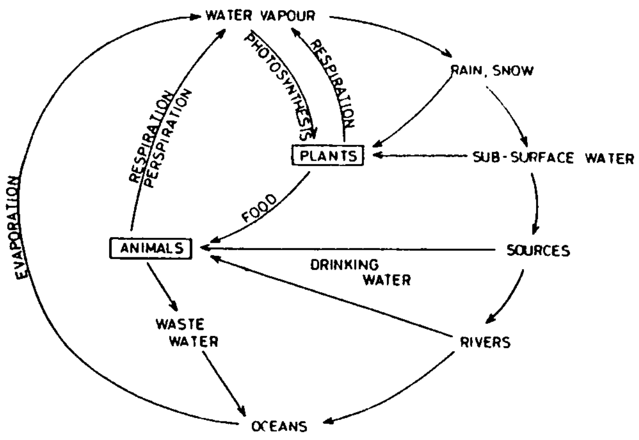

Fig. 1. The hydrological cycle, including the biological subcycles.

The cycle can be very carefully traced using the natural isotopic abundances of the elements of water, oxygen and hydrogen. As an aside here, we have only known that water was constituted this way for 200 years. The ancients, Aristotle stole the idea from Emperidocles (440BC), suggested four elements (Earth, Fire, Air and Water) and that everything was constituted from these. That water was a compound was demonstrated in the 1780s as part of the demise of the phlogiston theory of combustion. The men involved were Joseph Prestley, Henry Cavendish, James Watt (of steam engine fame) and Antoine Lavoisier. Who was to be given the credit caused a controversy at the time and it still exercising historical scholars over who should receive most credit. Something much more clear cut was that oxygen isotopes were discovered by investigating Earth's atmosphere and that Harold Urey (of the delta stable isotopic nomenclature) received the Nobel prize for finding deuterium. However, to return to the cycle, the isotopic composition of both hydrogen and oxygen is affected by the change of state in going from liquid to vapour. The lighter isotopes H and ^{16}O are more volatile and therefore enriched in the gas. When rain (or snow for that matter) condenses and falls, it is the heavy isotope (D and ^{18}O) waters which condense first. As rain clouds move across a continent the water which falls gets isotopically heavier. It is also a fact that the fractionation factor for separating one isotope from another increases as the temperature at which the process takes place decreases. This leads to precipitation at high latitudes becoming more and more isotopically light.

Everything else which subsequently happens to the water when it falls to Earth, its being taken up in plants or percolation into the water table and subsequently into the rocks themselves, has further isotopic effects. These subjects are very complicated but suffice it to say they can all be understood and used to our advantage, both academically and commercially. An example of the latter is the tracing of the origins of wines. Wines are 90% water but once the alcohol has been separated the isotopic signature of the region where they are made, which is a function of temperature, climate, geology etc., can be measured. The results are amazingly diagnostic. If you add in measurements of tritium then it is possible to make a measurement of a wine's age. So whilst isotope geochemists can not necessarily turn water into wine, they can at least ensure you get what you pay for.

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