



Peter Schickel/Still Pictures

Has the sea always been so salty?

Has the composition of sea water always been the same? This article looks at the factors which affect it.

If you have ever swallowed a mouthful of sea water you will know only too well that it contains a lot of dissolved salts. Sea water from all over the world is remarkably similar — it has 3.5% dissolved salts. The taste tells us that sodium chloride is the main dissolved salt, but significant amounts of several other elements contribute to the salt in the sea: in descending order, magnesium, sulphur, calcium, potassium, bromine and carbon.

How did the sea gain its salt?

In 1714, Edmond Halley (of comet fame) noted that landlocked seas such as the Dead Sea and the Caspian Sea, which are fed by rivers but have no outlets, were very salty. He concluded that the rivers brought the salt to these seas and that the evaporation

of water from their surfaces left the seas salty. He deduced that the water in the world's oceans had similarly been fed its salt by the rivers which flowed into them.

He also proposed that if we could determine the annual rate at which the world's rivers supplied the seas with salt, and the total mass of salt in the oceans, we could work out the age of the Earth, assuming that the oceans had begun as bodies of fresh water.

However, there were a couple of flaws in Halley's proposition:

- we don't know that the oceans were ever fresh water
- we now know that the ocean basins do not retain all the salt that is fed into them

Above: Salt at the shore of the Dead Sea

After Halley died other people used his assumption to calculate the Earth to be 100 million years old.

GCSE key words

Sea water composition
Radioactivity
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Although Halley's method gives a rather young age for the Earth, it is still used by geochemists to find out how long different substances last in the oceans.

What affects the composition of sea water?

Halley rightly highlighted two vital factors that affect the composition of sea water:

- he saw the need to identify and quantify the input of dissolved salts to the sea
- he recognised the importance of the world's great rivers as the most obvious suppliers

However, there are other important processes which add chemical constituents to sea water and extract elements from it. Some of them have only been discovered in the last 20–30 years.

The effect of hydrothermal systems

In each of the world's great ocean basins (Atlantic, Pacific, Indian and Southern Oceans) there are mid-ocean ridges – the spreading centres of tectonic plates. These ridges are the sites of invisible volcanic activity: basaltic lavas are erupted onto the ocean floor, approximately 2.5 km below sea level. Large volumes of cold sea water are drawn into the hot basalt lavas in an enormous hydrothermal convection system. This cools the recently erupted basalts.

The sea water is rapidly warmed up by the hot rock and reacts chemically with the basalt. Some elements in the basalt are dissolved into the hot sea water (iron, manganese, copper, nickel, cobalt, zinc), while other elements originally in the sea water (like sodium,

chlorine and a trace of uranium) are given up to the basalts. Halley had not envisaged that elements could be extracted from sea water in this way.

Eventually, the hydrothermal system discharges very hot brines back into the cold ocean water through chimney-like structures called **black smokers**. Many of the dissolved elements in the brines precipitate immediately on contact with the cold ocean water, forming a thin sedimentary layer on the ocean floor. Others remain in solution and are effectively a new chemical input into sea water.

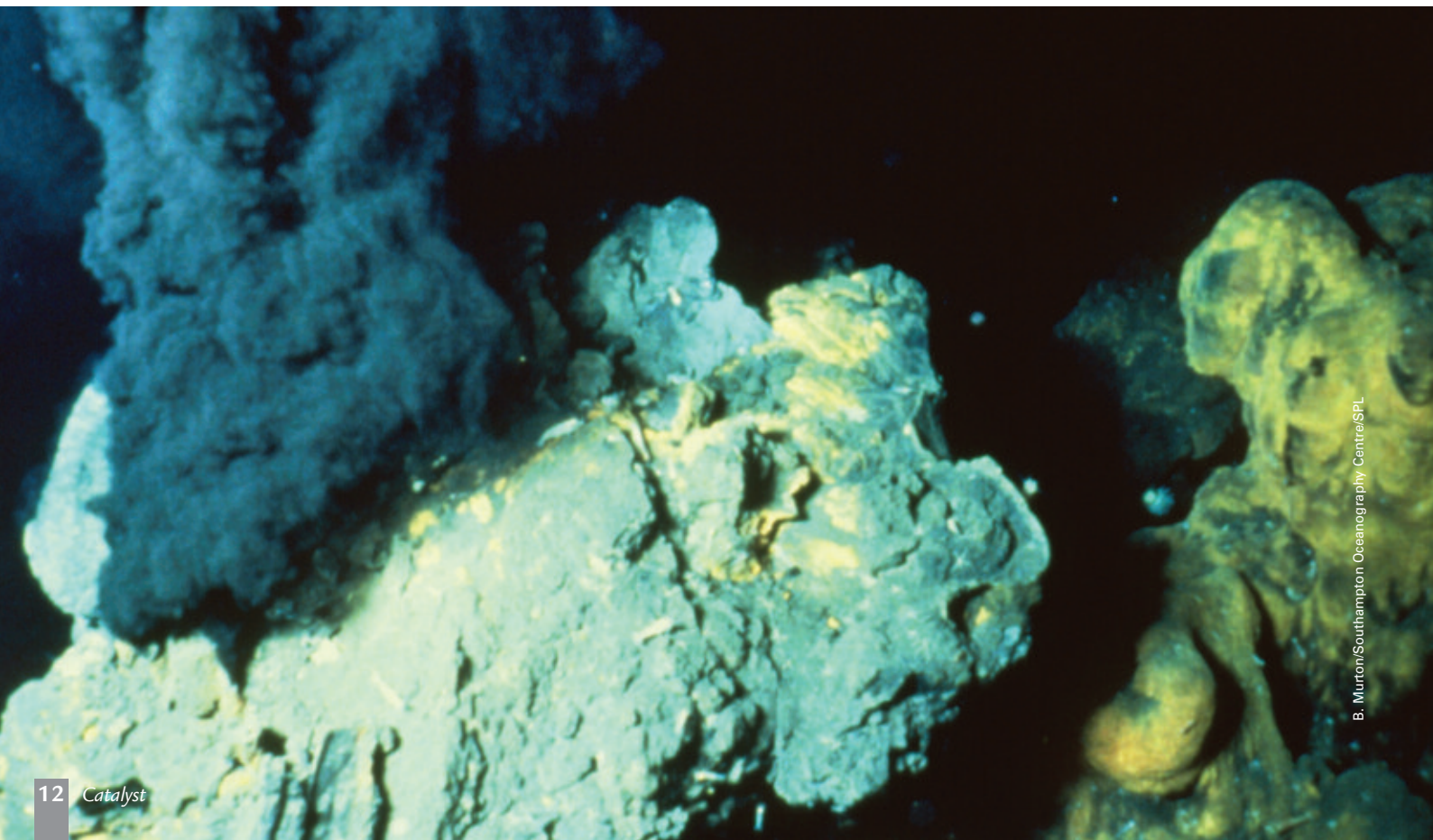
In what other ways are elements extracted from sea water?

Collecting seashells on the beach provides a quick answer. Many animals (and other organisms) extract calcium and carbon from sea water (as calcite and/or aragonite) to make their shells. Some beaches consist almost entirely of shell sand. Features like the Great Barrier Reef off the coast of Australia are enormous areas of living limestone factories, which extract their construction materials from the sea water around them. The Cretaceous chalk of southern England is composed almost entirely of the tiny calcium carbonate shells of billions and billions of microorganisms.

But biological extraction does not account for all the calcium carbonate taken out of sea water. On the shallow Bahama Banks very fine calcite needles are precipitated as a result of the sun warming the ocean water, and probably breaking down the hydrogen carbonate (HCO_3^-) ions in the water. In other areas of very shallow warm sea, different minerals are extracted

Below:

A 'black smoker'





Corel

Left: Coral reefs have been important sites of calcium carbonate extraction and limestone formation for most of the last 500 million years of the Earth's history

from sea water as a result of evaporation. In the Persian Gulf temperatures are so high that sea water which infiltrates beaches is evaporated, leaving calcium sulphate crystals (gypsum) and building up **sabkha** deposits.

Does the composition of sea water change over time?

How can we answer such a question? A very useful approach is to look at the isotopic composition of the element strontium in fossil marine shells. Strontium has four isotopes (^{88}Sr , ^{87}Sr , ^{86}Sr and ^{84}Sr). Of these, ^{87}Sr is in part the product of the radioactive decay of ^{87}Rb , an isotope much more abundant in the continental crust than in mid-ocean ridge basalts or their source in the mantle.

Strontium isotopic compositions are reported as the ratio $^{87}\text{Sr}/^{86}\text{Sr}$. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in river water draining the continents is markedly higher than the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for mid-ocean ridge basalts and the hydrothermal brines discharging from them.

Figure 1 shows the variation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seashells through time (effectively the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of sea water at the time when the organism that made the shell was living). If there had been no variations in the proportions contributed by rivers and mid-ocean ridge hydrothermal systems, we should expect the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio to be stable through time. However, Figure 1 shows that the ratio has fluctuated over the last 500 million years. There were particularly high values in the Cambrian period (500 million years ago) and values are high again now. There were very low values at the end of the Permian era (250 million years ago), and again at the end of the Jurassic era (140 million years ago).

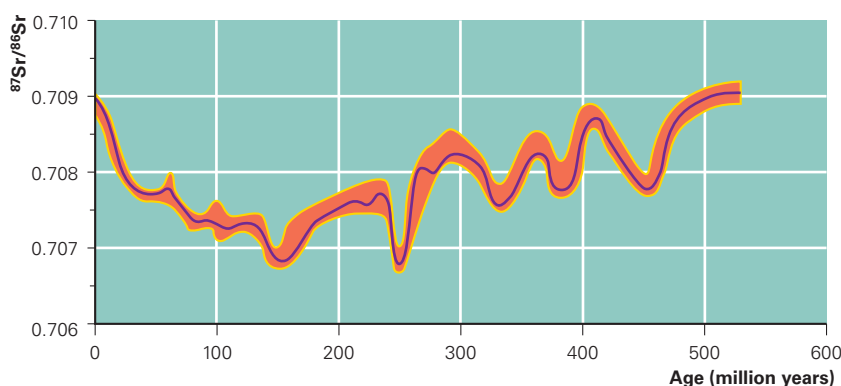


Figure 1 Variations in the strontium isotope composition of sea water over the last 500 million years

High $^{87}\text{Sr}/^{86}\text{Sr}$ values reflect a high salts input into the sea from rivers, whereas low values show periods when mid-ocean ridge hydrothermal activity may have been more important — or the input from rivers much reduced.

Conclusion

Variation in the strontium composition of sea water through time is well-documented. It is much harder to get direct evidence about other ways that sea water has changed in the past, but it is unlikely that strontium is the only element that fluctuates through time. We are still learning about the flow of chemical substances through the oceans, but questions which may have seemed unanswerable in the past can now start to be tackled.

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All elements have isotopes — different forms of the element with the same number of protons but different numbers of neutrons.