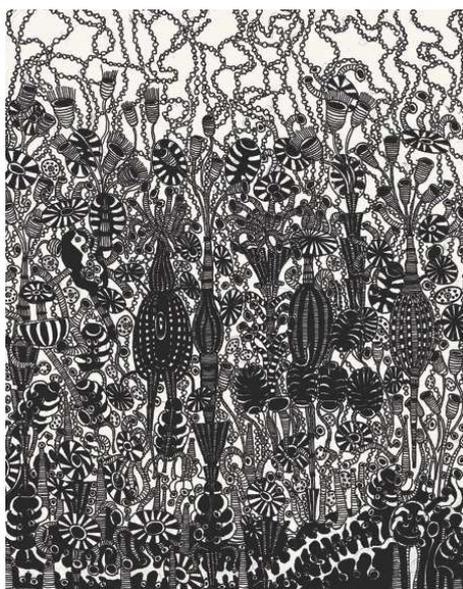


the smell of the sea

Vivienne Baillie Gerritsen

The chances a cloud will remind you of the ocean are slim. Yet without oceans, there would be fewer clouds drifting above our heads. This is because these huge stretches of sea are full of tiny creatures that produce a gas known as dimethyl sulphide, or DMS, which under certain circumstances has the faculty of initiating the beginnings of a cloud. These creatures – algae or bacteria – do not synthesize DMS for sculpting clouds; DMS happens to be the side product of a metabolite known as dimethylsulfoniopropionate, or DMSP, that phytoplankton probably require for buoyancy or protection, or perhaps even both. The air-borne DMS is responsible for the sometimes unpleasant pungent smell that is characteristic of the sea. The enzyme that is at the heart of this distinct sea scent was recently discovered in the marine phytoplankton *Emiliania huxleyi* and baptised DMSP lyase 1 – an algal enzyme that cleaves DMSP and in so doing releases the perfumed DMS into the earth's atmosphere.



Pen and ink drawing by Sue Bartfield

Courtesy of the artist

Emiliania huxleyi is the most abundant marine phytoplankton to float on the earth's oceans, and forms the massive green patches – or blooms – that can be seen from space. It is happy both in tropical and subarctic waters and is an important part of marine food webs. *E.huxleyi* is a single-celled eukaryotic phytoplankton surrounded by what is known as a coccolith, a term coined by the British comparative anatomist Thomas Huxley (1825-1895). Coccoliths are made of calcite. Their architecture is extraordinary and intricate, more

often than not transparent and colourless. *E.huxleyi* coccoliths are made of calcite disks that were first described by Huxley and an Italian microbiologist Cesare Emiliani (1922-1995) – hence the name, *Emiliania huxleyi*. These calcite shells suggest some sort of protective role, yet no one knows it for sure. Coccoliths are perhaps a way of preventing zooplankton from grazing, or may just act as a physical barrier against viral or bacterial invasion and even harmful UV light. They could also simply be part of the physics that keeps the phytoplankton afloat or, in deep-dwelling species, a means of gathering and concentrating light for photosynthesis. These calcite shells are shed continuously and sink to the bottom of the sea where they form an important part of the deep-sea sediment. The white cliffs of Dover are an example of such sediment, deposited about 65 million years ago.

Besides its unique calcite shell, *E.huxleyi* produces – along with its fellow phytoplankton species and other marine microalgae – one of the most important and most abundant organic molecules in the world: DMSP. One billion metric tons of this organic compound are not only poured into the oceans every year but also turned over! DMSP is in fact so plentiful that it has become a signature molecule for life at sea. If so much is produced, surely it must have an important role in the life-cycle of phytoplankton and marine algae. No doubt. But to date nobody knows which. It could serve to protect organisms against osmotic stress. It could have a role in buoyancy. It could also be a means of communication in predator-prey interactions. First identified in 1948 in the red alga *Polysiphonia*, scientists recognised it to be the progenitor of DMS

which was already known to waft from seaweed. In 1956, a first enzyme able to cleave DMSP was discovered – one of many that were to follow, the most recent of which is DMSP lyase 1.

The ocean is awash with many different beasts able to split DMSP into DMS and acrylate by way of hordes of different enzymes. In the same way DMSP is a major compound of the ocean's sulphur sink, DMS is a major component of atmospheric sulphur – and together they represent key components of the ocean's sulphur cycle. DMSP lyases exist both in eukaryotes and bacteria, however *E.huxleyi* DMSP lyase 1 bears no resemblance to any other. It is tetrameric and belongs to the aspartate racemase superfamily while in marine bacteria, for instance, DMSP lyase belongs to the M24 peptidase family. DMSP lyase 1 cleaves DMSP, releasing in the process DMS – a gas – and acrylate. Crystal structures of various DMSP lyases suggest two active-site cysteines. The enzyme's activity is equally thought to be dependent on algal symbiosis or associated bacteria.

DMS let loose in the atmosphere plays a key role in the earth's sulphur cycle. Its tangy aroma serves as a chemical attractant which guides a variety of marine animals – such as sea birds, invertebrates and even mammals – to possible food supplies. Atmospheric DMS is a huge part of the global cycle of sulphur from the sea into the air, and then back into the sea or onto land when it rains. DMS even has a part to play in cloud formation, and hence in the world's weather. How? When the gas is flung into the atmosphere, it is *per forza* prone to oxidation. DMS oxidation products – DMSO – act as condensation nuclei causing water molecules to coalesce, leading to cloud formation or enhancing it. And where there are clouds, there are consequences on the local climate – or perhaps on an even more global scale. Clouds increase the reflection of solar radiation,

sending it back where it came from, thereby influencing the earth's atmospheric temperature.

DMS has this particular tangy smell to it. Some say cabbage-like. Others, more poetically, refer to it as the smell of the sea. The characteristic scent is also released when cooking beetroot, asparagus and sea foods for example. An amusing anecdote: twenty years ago, a French chemist, Thierry Talou, was the first to identify DMS as the chemical responsible for the tangy scent, and used truffles and pigs to support his theory. Today, DMS is in fact used – in very small concentrations – as a food additive to impart a savoury flavour. Oxidised DMS is an important industrial solvent.

There is something hugely lyrical in a chemical component that is capable of creating a cloud. However, clouds spell climate change – a particularly sensitive subject today. Getting to know DMSP lyases better, the way they contribute to atmospheric DMS – which is dependent on the global distribution of bacteria and eukaryotes – and how they are affected by environmental parameters, or indeed how they affect the environment, are all important issues in our day and age. What is more, there are no doubt other forms of enzymes that act as DMSP lyases which are still unknown.

Understanding the physiological and signalling roles of DMS in the phytoplankton's resistance to viral infection, its fight against predators or its symbiotic interaction with other organisms will also help to give a fuller picture of a form of life that is so essential in the marine sulphur cycle besides having such a large impact on the earth's atmospheric conditions and hence the planet we are part of too. *E.huxleyi* was actually the creature that inspired Lovelock's famous Gaia hypothesis claiming that the earth's biochemistry and geochemistry are intimately intertwined.

Cross-references to UniProt

DMSP lyase 1, *Emiliania huxleyi* (Pontosphaera huxleyi) : P0DN21

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