



the IRON bypothesis





The Royal Society of New Zealand Southern Ocean Iron Release Experiment (SOIREE) Why would 26 scientists load the research vessel *RV Tangaroa* with 10 tonnes of iron sulphate and sail 1200 nautical miles south into heavy seas and winds up to 55 knots? Then they tipped their precious cargo into the wild Southern Ocean! These modern-day scientist adventurers must have had a good reason. They did – they wanted to test the iron (Fe) hypothesis.

What is the Fe hypothesis?

The Fe hypothesis suggests that:

- (i) the concentration of dissolved Fe limits phytoplankton (plant plankton) growth and biomass in a large proportion of the nutrient-rich regions of the world's oceans including the Southern Ocean; and
- (ii) an increased Fe concentration in the Southern Ocean in the last glacial maximum resulted in increased movement of carbon into the deep ocean.



Fig. 1 Physical and biological pumps for CO₂ between the atmosphere and the ocean.

This hypothesis was first proposed by John Martin of the Moss Landing Laboratory in the USA in the late 1980s, after the development of technology which enabled the measurement of CO₂ concentrations in ancient air trapped in ice cores. This allowed scientists to show that CO₂ concentrations as low as 200 parts per million (ppm) occurred during the last glacial period. This should be compared to the interglacial period of 280 ppm CO_2 . This represents a change of approximately 170 billion tonnes of carbon in the earth's atmosphere. For a change of this magnitude to occur it was suggested that changes in the CO_2 in the ocean must have also occurred as there is approximately 60 times more CO_2 in the ocean than in the atmosphere.

Why is silicon a major nutrient requirement for some phytoplankton?

Silicon (Si) is a major nutrient requirement for some phytoplankton. The diatons, a common and significant group in many phytoplankton populations, require Si for growth. The diatoms use Si to form a hard external shell (frustule). The frustule is composed of two sections, with the edges sitting one inside the other like a pill box. The frustules often have intricate patterns on the outside and these patterns along with the shape of the frustule are used as key features to identify species of diatons. Often the frustules are joined together so that chains of diatons are formed. The amount of Si required for the frustule varies from species to species. Many of the species found in the Southern Ocean have very heavy frustules requiring lots of Si. These may have evolved to help protect the cells from zooplankton grazing.



How could such a large change in the CO₂ concentration in the ocean occur?

There are two pathways that control the movement of CO_2 from the atmosphere to the ocean. They are known as the physical pump and the biological pump (Fig. 1). When the activity of the biological pump is high, then atmospheric CO_2 concentrations are likely to decrease as CO_2 is pumped into the ocean.

Why was the biological pump so active in the last glacial period?

Large areas of the world's ocean, including the Equatorial Pacific and the Southern Ocean have high concentrations of major nutrients such as nitrogen (N), phosphorus (P) and silicon (Si) (Box 1) to support phytoplankton (plant plankton) growth, yet phytoplankton biomass is low.

The Fe hypothesis proposes that the phytoplankton growth and biomass in these areas of the ocean are limited by the concentration of dissolved Fe in the water. Analysis of Fe concentrations in the Vostok ice cores showed Fe-rich dust concentrations were 10 to 20 times higher during the last glacial period than now. These elevated dust concentrations could have supported higher phytoplankton growth and biomass during this period. This means the biological pump would have been stronger and this would have resulted in lower CO_2 concentrations in the atmosphere.

Testing the Fe hypothesis

Bottle experiments

Initial testing of the hypothesis was conducted in small containers (1–30 litre) with natural populations of phytoplankton collected from the ocean, and in laboratory-based experiments. These experiments showed that phytoplankton growth and biomass could be limited by a lack of dissolved Fe and hence supported the Fe hypothesis. The problem with these types of experiments is that they do not reflect response of the whole planktonic community due to the small size of the containers and the experiments only last a few days. These experiments were a first step but more compelling evidence was needed to support the Fe hypothesis.

Iron addition experiments in the Equatorial Pacific Ocean

In October 1993, a group of scientists added Fe to a small patch of ocean 500 km south of the Galapagos Islands. This is an area of the ocean with high nutrient and low chlorophyll *a* concentrations. Unfortunately, four days after the Fe was added to the patch of water the scientists lost the patch. Before this happened, measurements in the patch showed phytoplankton biomass doubled, and growth increased four-fold. However, in May 1995, a second Fe addition experiment was conducted in the Equatorial Pacific. Over a three week period phytoplankton biomass had increased 85 times and growth 10 times. The results of both of these experiments supported the Fe hypothesis.

The big question left to answer was, would the addition of Fe to waters in the Southern Ocean have the same effect? The Fe hypothesis would certainly have greatest significance in the Southern Ocean where most of the world's high-nutrient, low-phytoplankton biomass waters are found. It is also the region where

there is the greatest evidence of a link between dissolved Fe concentrations and increased activity in the biological CO_2 pump. The team of scientists from the second experiment in the Equatorial Pacific concluded that "the extreme turbulence and variability in the Southern Ocean posed a tantalising yet formidable challenge". It was this challenge that the SOIREE team took up.



NIWA research vessel RV Tangaroa.

SOIREE

Planning for SOIREE

The first question was, where should the experiment be conducted?

The key properties for the experimental site were:

- (i) physical, chemical and biological properties typical of the Southern Ocean;
- (ii) water with low ambient (<0.1 nM) dissolved Fe concentrations, low phytoplankton biomass and sufficient N, P and Si in the mixed layer (Box 2) so that these nutrients would not limit phytoplankton growth;
- (iii) a physical environment away from major currents so that the patch would be easier to track;
- (iv) a mixed layer that was shallower than 90 m so that the Fe and tracer added did not become too dilute and the phytoplankton received enough light for growth; and
- (v) summer weather patterns that would enable the experiment to be completed.



Fig. 2 TOPEX/POSEIDON satellite image of mean winds and wave heights. NASA JET PROPULSION LABORATORY, PASADENA, CALIFORNIA

The mixed layer

A very important feature of the ocean is the depth of the mixed layer. This is the depth of the surface water that mixes freely. This means the water in the mixed layer is of similar density. The density of sea water is a function of temperature and salinity.

Chemically the mixed layer will be similar throughout; however, below the mixed layer there are generally increased concentrations of nutrients such as N, P, Si, Fe.

Biologically, the mixed layer depth is important as it determines the amount of light the phytoplankton receive. The deeper the mixed layer the less light on average the phytoplankton receive.

Two key factors that control the mixed layer depth are wind and sunlight. High winds are likely to increase the depth of the mixed layer. Sunlight heats the surface waters and creates a less dense layer near the surface and reduces the mixed layer depth.



Approximately 18 months before the experiment was to be conducted, a team of scientists gathered as much information as possible about the Southern Ocean south of New Zealand and Australia. This included satellite images of the region (Fig. 2). They concluded that the area south of Tasman at approximately 61°S, 140°E (Fig. 3) was the best site. They were fortunate to receive data from a French ship, which had made measurements in this region about two weeks before they were due to sail. The French data confirmed the region of 61°S, 140°E as a good site for the experiment.

The science team

The science team for SOIREE included chemists, physicists, and biologists. There were a large number of scientists to choose from as lots of scientists from around the world were very keen to be involved in such a new and exciting experiment. The final team was truly multinational with scientists from New Zealand, Australia, England, the Netherlands, Canada and the USA.

The SOIREE experiment

The scientists sailed from Wellington on board the NIWA research ship *RV Tangaroa* on 1 February after three very busy days preparing the ship. This included installing a container on the deck to provide extra laboratory space, and securing two 6000 litre tanks with stirrers for mixing the Fe solution and two 4000 litre tanks for making the sulphur hexafluoride (SF₆) solution (Box 3). The first night was very uncomfortable, with 55 knot southerly winds, this was not a good start to the month in the Southern Ocean as many of the scientists were sick.



Fig. 3 Site of SOIREE.



Sulphur hexafluoride (SF₆)

Use of the inert gas SF_6 as a tracer has enabled experiments like SOIREE to be conducted. SF_6 is an excellent tracer as it is inert and can be measured down to a concentration of 10^{-16} M.

To use SF_6 as a tracer it is bibbled into sea water until a saturated solution is achieved. This occurs at approximately 3 nmol 1⁻¹. In SOIREE the saturated solution was made in 4000 litre tanks and when the first Fe addition was made the saturated solution of SF_6 was pumped into the dissolved Fe solution as it was pumped over the stem of the ship into the ocean. The initial concentration of SF_6 in the patch was 300 fmol1⁻¹. This concentration dropped to 30 fmol 1⁻¹ during the experiment. This was well above the lowest concentration that can be measured.

During SOIREE, the SF_6 concentrations were measured every 7 minutes, 24 hours a day. This meant the position and size of the patch could be tracked effectively.



Survey

After arriving at the site the scientists spent 3 days surveying a 115 km long and 30 km wide area to make sure the conditions at the site were what had been predicted and met the conditions for the experiment. They particularly checked the concentrations of nutrients N, P, Si, Fe, and the depth of the mixed layer.

Addition of Fe

On 9 February the scientists decided the site was right and it was time for the Fe and SF_6 addition. Preparation for this involved filling the Fe tanks with 6000 litres of seawater, and adding 120 litres of HCl to drop the pH to dissolve the Fe. The SF_6 solution was also prepared by bubbling SF_6 into the two 4000 tanks of seawater. A large pump was used to mix the Fe and SF_6 solutions as they were pumped over the stern of the ship into the water approximately 15 m below the surface. The mixture was initially added at the centre of the



Fig. 4 Rossette sampler for collected water samples.

patch and steamed in ever-increasing hexagonal patterns around a buoy, which was placed in the centre of the patch. As water in the ocean is always moving, the navigation to make sure the Fe was added in the right area to give a coherent patch was tricky. To add Fe to the 50 km² patch 24 000 litres of Fe solution containing 3813 kg of FeSO₄ was required. Once the patch was established it was very important to check its location and map it. The key issue in mapping the patch was the measurement of the SF₆ concentration. Over the next 13 days keeping track of where the patch was, and how large it was, was very important and took almost 12 hours each day. To maintain the high Fe concentration in the patch 1550 kg of FeSO₄ was dissolved and added to the patch on days 4, 6, and 8 of the experiment.

Measurements conducted

Two basic types of measurements were made during SOIREE, those that were made continuously, i.e., 24 hours a day, on water pumped onto the ship and measurements that were made on discrete water samples taken with Niskin bottles (Fig. 4). The measurements that were made continuously included; SF_{c} for



tracking the patch, the concentration of CO_2 in the water, dissolved Fe, chlorophyll *a* as an estimate of phytoplankton biomass, and water temperature and salinity, which were used to track the movement of the patch.

Fig. 5 Underway measurements of the SF₆, chlorophyll *a* (a measure of phytoplankton biomass), and CO₂ concentration over the period of the experiment.

From the discrete water samples the measurements made included: nutrient concentrations (N, P, Si); the biomass of phytoplankton, bacteria and zooplankton; the growth rates of phytoplankton and bacteria, the grazing rates of zooplankton; and a range of chemical and phytoplankton physiological measurements.

What happened when dissolved Fe was added to the Southern Ocean?

Over the first three days of the experiment, the only measurement taken that indicated a biological change was the photosynthetic ability of the phytoplankton cells, which increased in the first 48 hours. This is a result of the phytoplankton cells taking up Fe into the cell to be used for vital cell functions (Box 4). Over the 13 days of the experiment the phytoplankton biomass increased 6 times and growth 4 times (Fig. 5). The types of phytoplankton

also changed during the period of the experiment. At the beginning of the experiment the very small phytoplankton made up over 50% of the biomass, during the experiment the larger cells such as the diatom (Box 1) *Fragilariopsis kerguelensis* became dominant, and by the end of the experiment the small cells only made up about 20% of the phytoplankton biomass. This change is important as the larger heavier diatom cells are more likely to sink into the deep ocean removing carbon from the surface waters.

During the experiment there was a significant decrease in the CO_2 concentration in the water inside the patch compared to outside the patch (Fig. 6). This indicates that the biological pump (i.e., photosynthesis) had been stimulated and the CO_2 in the water used in photosynthesis. Over the period of the experiment the phytoplankton removed approximately 2000 tonnes of carbon from the water inside the patch.

What happened to this carbon?

If this carbon sinks into the deep ocean, it will be removed from the atmosphere for hundreds to thousands of years and result in a reduction of the CO_2 concentration in the atmosphere. If the carbon does not sink into the deep ocean it is likely to be released back into the atmosphere within 12 months. Which of these alternatives happened in SOIREE is the key to the Fe hypothesis in terms of increased dissolved Fe resulting in increased photosynthesis and in turn a decrease in the CO_2 in the atmosphere.





Fig. 6 Continuous measurement of the CO_2 concentration in the water. Notice how the difference in CO_2 concentration between inside and outside the patch increases over the period of the experiment.



Fig. 7 Deployment of sediment traps that were used to measure particles sinking in the water.

Why phytoplankton need Fe

Phytoplankton require very snall amounts of Fe for survival and growth. Fe is required for efficient photosynthesis, as photosystem II requires 2 atoms of Fe. In low dissolved Fe conditions inactivation of photosystem II can be as high as 50%. This leads to a marked reduction in efficiency with which light is photochemically converted to chemical energy. Fe is also required by a number of enzymes including nitrate reductase which is used to reduce NO₃ to a form that can be used by the cell. In cells with an adequate Fe supply the ratio of cell carbon:cell Fe is approximately 10 000:1, in comparison to a ratio of 100 000:1 when Fe is limiting growth.

SeaWiFS image of the SOIREE region, 23-March-1999



Fig. 8 Sea surface colour satellite image taken 32 days after the addition of Fe during SOIREE. The coloured ring indicates an area of increased phytoplankton biomass believed to be a result of the increased Fe concentrations in SOIREE. NASA DAAC/GSFC, © ORBITAL IMAGING CORPS & NASA SEAWIFS PROJECT, PROCESSED AT PLYMOUTH MARINE LAB, UK

During SOIREE the sinking of particles into the deep ocean was measured using sediment traps which have long tubes which capture particles sinking through the water (Fig. 7). The results showed that during the 13 days of the experiment there was no increase in carbon sinking into the deep ocean. However, this may have occurred after all the Fe added was used by the phytoplankton. As the scientists could not stay until this occurred they do not know if the CO_2 removed from the water by the phytoplankton eventually sunk into the deep ocean. This is a question to be answered in a future experiment.

How long did the Fe addition influence the patch?

Satellite images of sea surface colour enabled the scientists to estimate the biomass of phytoplankton in the surface waters. Images in the area that they predicted the patch would have moved to 32 days

after they left the patch showed a ring of increased phytoplankton biomass (Fig. 8). The scientists believe this ring is evidence that even 32 days after Fe was added to the patch, increases in plankton biomass as a result of the increased dissolved Fe concentrations were still apparent.

Conclusions

- The increased dissolved Fe concentrations in the patch resulted in increased phytoplankton biomass production.
- The increased dissolved Fe concentration resulted in a decrease in the CO₂ concentration in the water.
- The length of time the carbon will be removed from the atmosphere remains unknown.
- The increased phytoplankton biomas was still present in the surface waters 32 days after the initial addition of the Fe.

Ongoing question

Could/should Fe additions in the Southern Ocean be used to decrease the concentration of CO_2 in the atmosphere to reduce the greenhouse effect?

There is still a great deal of scientific data required to answer this question and also an ethical debate to be conducted.



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