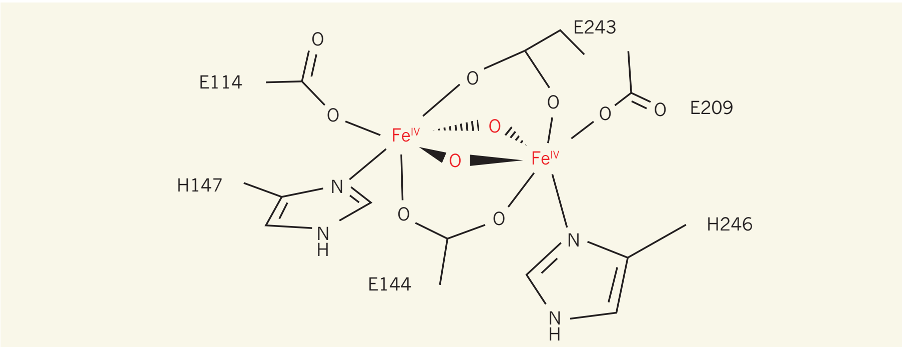

Figure 1 | The structure of Q. Banerjee *et al.*[1] report the structure of compound Q, a key intermediate in the conversion of methane to methanol by an enzyme called soluble methane monooxygenase. Their results indicate that Q's structure contains a 'diamond core' (red) in which two iron ions in the +4 oxidation state (Fe^{IV}) are bridged by oxygen atoms. The numbered groups in black surrounding the diamond core are the side chains of amino-acid residues. H, histidine residues; E, glutamate residues.

fingerprint for how the iron and oxygen atoms are bonded. This experiment is challenging for several reasons. First, intermediate Q forms only transiently, so the spectrum must be acquired in a time-resolved fashion. Second, signals from Q are expected to be weak because solutions of sMMO can be prepared at only low concentrations for analysis, and because of other experimental difficulties.

Banerjee *et al*. overcame these obstacles using a specially designed and optimized Raman instrument. In their set-up, a continuous stream of the diiron(II) enzyme was mixed with a second continuous stream of dioxygen-saturated buffer, and spectra were then acquired at different time points to capture the largest possible quantity of the short-lived Q. By comparing the spectra generated when both atoms in dioxygen were oxygen-18 isotopes ($^{18}O_2$) with those obtained using two oxygen-16 isotopes ($^{16}O_2$), they were able to isolate Q's vibration from the sea of other signals. A comparison of the frequency of this vibration with those observed for various iron–oxygen species in model complexes and enzymes gives only one match: the diamond core (Fig. 1). Importantly, the vibration does not correspond to a terminal Fe^{IV}=O species, as would be expected for an open core structure.

To probe how the apparent diamond core forms, Banerjee and colleagues conducted experiments using a mixed isotopic form of dioxygen (^{16}O–^{18}O). They observed a new frequency in the spectrum of Q, which can be explained only by a diamond core that contains one ^{16}O and one ^{18}O atom, and which indicates that both atoms of dioxygen end up in Q. The spectra also reveal a vibration attributable to the product complex T, which contains one of the dioxygen atoms as a single unprotonated oxygen (an oxygen without a hydrogen atom attached) bridging the two iron ions. Further consideration of the results sheds light on how sMMO breaks the O–O bond to form intermediate Q. The data are most consistent with a mechanism in which the two electrons of the bond are distributed one to each oxygen atom (homolytic cleavage), although it is not possible to completely rule out a mechanism in which both electrons go to the same oxygen atom (heterolytic cleavage).

Further verification of the Q structure is now desirable, and might be obtained from high-level computational studies and additional spectroscopic work. Diiron diamond cores have been previously observed in model complexes that cannot oxidize methane[10], so what is it about Q that enables methane oxidation? One possibility suggested by Banerjee *et al.* is that a different arrangement of the valence electrons of the iron(IV) ions in Q (a high spin state) confers increased reactivity, compared to the low spin state of synthetic complexes. This difference is probably just one of many ways that the enzyme micro-manages the oxidation chemistry to ensure Q's potency. ■

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CLIMATE SCIENCE

The future of coastal ocean upwelling

An ensemble of climate models predicts that winds along the world's coasts will intensify because of global warming, inducing more ocean upwelling — a process that will affect the health of coastal marine ecosystems. **See Letter p.390**

EMANUELE DI LORENZO

At the ocean surface, where light is abundant, microscopic photosynthetic phytoplankton are the primary producers of organic material and the main source of energy for the oceanic food web. Phytoplankton growth depends on essential nutrients, which are typically depleted at the ocean surface but abundant in the deep ocean. Upwelling ocean currents carry these nutrients to the surface and thus support marine life. On page 390 of this issue, Wang *et al.*[1] report that many climate models predict that coastal upwelling will intensify in three of the most productive marine ecosystems of the world: the Canary, Benguela and Humboldt Eastern Boundary Upwelling Systems (EBUSs). This result comes at a time when scientists are still debating the evidence supporting an increase in coastal upwelling, and its effects on coastal ecosystems and global carbon cycling.

Along the oceans' eastern boundaries, winds flowing along the coast drag surface waters out to sea. These displaced surface waters are replaced by water from lower down — the upwelling current. In 1990, the climate scientist Andrew Bakun realized that rising surface temperatures caused by the greenhouse effect would not be uniform: land will heat up faster than the ocean[2] (Fig. 1). Bakun proposed that this would create an ocean–land contrast in atmospheric pressure, which would drive stronger upwelling-favourable winds.

Wang and colleagues show that climate-model projections for the year 2100 support

Bakun's hypothesis by predicting a strong relationship between the strengthening of the land–ocean surface-temperature gradient and the intensification of the alongshore winds in most EBUSs. Furthermore, they find that this intensification will occur mostly at higher latitudes, where coastal upwelling is generally weaker. This in turn suggests that differences between the amount of upwelling at low and high latitudes will be reduced, causing homogenization of coastal upwelling habitats at different latitudes.

Is there observational evidence that winds have already increased along the coast? Scientists have debated this issue for the past 20 years, but there is a growing data-driven consensus that alongshore winds are indeed intensifying in EBUSs[3]. However, the future of coastal upwelling portrayed by Wang and co-workers comes with important caveats. Indices of coastal upwelling derived from alongshore winds are not the only indicators of upwelling strength[4] and ecosystem impacts. The dynamics controlling the upward flux of nutrients (and therefore productivity) in the coastal ocean are complex and include processes that are not driven by alongshore winds.

For example, changes in upper-ocean stratification and deep-ocean nutrient concentrations[5], changes in the energy of oceanic vortices[6], extreme weather events and wind-stress gradients near the coast[7] all affect coastal upwelling and marine ecosystems. Unfortunately, some of their effects are hard to predict in future scenarios of climate change, because they involve regional-scale ocean-transport dynamics that are not well represented in climate models.

Furthermore, upwelling systems undergo strong decadal climate-related fluctuations[8], which might increase in amplitude as the climate changes, giving them a bigger effect than the long-term trends. Such decadal fluctuations occur in the California EBUS[9], where Wang *et al*. found no significant increase in upwelling winds. Nevertheless, Wang and colleagues' study provides an invaluable starting point to think about the response of coastal upwelling systems to greenhouse forcing.

What are the potential ecological and societal impacts of increased coastal upwelling? It is estimated that phytoplankton growth in EBUSs already supports more than 20% of wild fisheries[10]. Most of this productivity occurs in the higher-latitude portions of the upwelling systems, where Wang and colleagues predict the strongest increase in upwelling. Increased upwelling in these regions might increase productivity and boost food production.

However, excessive productivity would generate heavier loads of organic matter that sinks into the deep ocean. Bacterial decomposition of this organic matter can deplete oxygen in the water column and, in extreme cases, generate deadly anoxic events at coastal upwelling sites[11]. In the past few decades, coinciding with reports of oxygen depletion in ocean basins, these ecological 'dead zones' have become more apparent along coasts[12], raising concerns for the well-being of coastal ecosystems. Unfortunately, humans add to the risk by discharging heavy loads of nutrients along coasts, mostly as run-off of fertilizers from farmland.

Coastal upwelling also leads to degassing of carbon dioxide from deep water into the atmosphere. Surface ecosystems can offset a rise of CO_2 degassing through increased photosynthesis, but the upwelling of carbon-rich water has other consequences. It is estimated that vertical mixing associated with oceanic physical processes has stored about half of the atmospheric CO_2 emitted since pre-industrial times in the deep ocean[13]. This has contributed to a progressive lowering of ocean pH and acidification of deep waters. Upwelling of these corrosive waters along the coasts has increasingly detectable effects on marine habitats and ecosystem functions[14].

The authors' study provides an invaluable starting point to think about the response of coastal upwelling systems to greenhouse forcing.

Increased upwelling currents will strongly affect marine ecosystems at EBUSs, but the long-term future of coastal acidification, dead zones and primary productivity probably depends on the properties of the water that comes to the surface. Observations and theories of deep ocean circulation show that nutrient, oxygen and dissolved-carbon concentrations naturally undergo large fluctuations on timescales of decades to centuries. This variability is superimposed on climate trends, making it difficult to separate natural and anthropogenic contributions to changes in coastal marine ecosystems. Even so, it might be possible to use the slowly varying timescales of the deep ocean to make decadal predictions of acidification and hypoxia in upwelling areas. ■

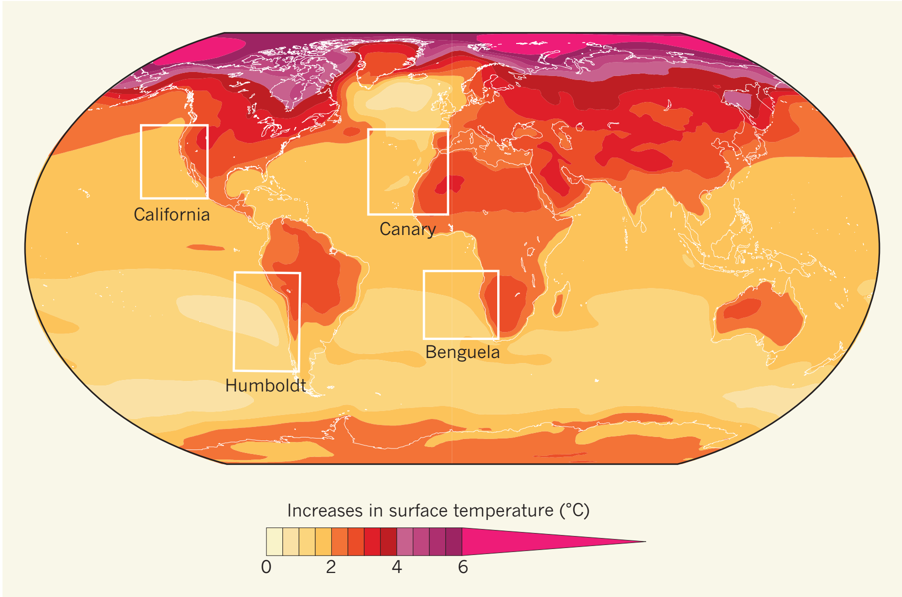

Figure 1 | Predicted changes in Earth's surface temperature. The map depicts differences in surface temperature between now and 2050, based on predictions from 27 climate models. The land heats up more than the ocean along major Eastern Boundary Upwelling Systems of the ocean (such as the California, Humboldt, Canary and Benguela systems). The resulting ocean–land temperature gradients have been hypothesized[2] to lead to stronger winds that favour upwelling along the coasts. Wang *et al.*[1] find support for this hypothesis using climate models. (Figure adapted from ref. 15.)

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