dioxide (SO_2), which are poor oxygen buffers compared with the chemically reduced gases, such as hydrogen and hydrogen sulphide (H_2S) resulting from the earlier, mainly submarine eruptions. The GOE followed in response.

Gaillard *et al.*[1] now give us a way to think about continents, volcanoes and the GOE that builds on Kump and Barley's model. On the basis of studies of lava from modern Hawaii, the authors propose that submarine lavas need not be more reduced than those above the sea. They also performed thermodynamic calculations suggesting that the properties of volcanic gases — specifically, the relative concentrations of SO_2 and H_2S — are little affected by the redox state of lava.

The authors go on to provide a new spin on the volcano theory based on a model of the gas–melt equilibrium of Hawaiian tholeiitic basalt (which is assumed to be a good analogue for the early Earth). Specifically, they attribute increases in the overall amount of sulphur-containing gases released by volcanoes just before the GOE, and the accompanying major shift from reduced H_2S towards oxidized SO_2, simply to decreases in the average pressure of volcanic degassing. The emergence of continents jutting well above the seas would have produced the ubiquitous subaerial volcanoes that lowered the pressure of eruptions. The argument for continental emergence rests with another model[11] asserting that long-term cooling of the mantle allowed for thicker, stronger continental crust, which rose above the oceans about 2.5 billion years ago.

Gaillard and colleagues' theory[1] is built largely on theoretical thermal and chemical models that have ample degrees of uncertainty. But another key part of their proposition relies on data: the structure of sulphur's MIF record. The disappearance of MIF signals for sulphur in sedimentary minerals mirrors the rise of atmospheric oxygen at the GOE (Fig. 1), but equally impressive is the large magnitude of MIF signals that occur in the mineral record just before the disappearance. A recent model[12] ties these large MIF signals to high ratios of SO_2 to H_2S roughly 2.7 billion to 2.5 billion years ago, but does not focus on the mechanisms behind the changing gas composition.

Gaillard *et al.* posit that the mechanistic key to atmospheric oxygenation might have been increased delivery of sulphate to the ocean through the same atmospheric, light-dependent reactions that yielded the high-magnitude MIF signals (Fig. 1). Simply put, increased inputs of sulphate (and indeed increased inputs of sulphur-containing gases overall) could have ramped up the production of H_2S from sulphate reduction occurring at high-temperature volcanic vents on the sea floor. This H_2S might then have reacted with reduced, dissolved iron released from the vents that would otherwise have served as an oxygen buffer. The greater flux of sulphur could even have allowed H_2S to accumulate in parts of the ocean[13].

Questions certainly remain about the buffering systems and the timing of events in Gaillard and colleagues' model. For example, a peak in the abundance of huge sedimentary iron formations occurs 2.7 billion to 2.5 billion years ago — the same time as MIF signals reached their apex. This relationship indicates that large amounts of reduced iron emerged from hydrothermal vents at that time, despite the putative increase of sulphate in the ocean. What's more, the timing of events in thermal (tectonic) models[11] fits only loosely with that of the relevant chemical models and with the timing of the transitional atmospheric oxygenation that occurred before the GOE proper[6–8]. The specific relationships between sulphate availability in the ocean and the processes that buffer iron release from deep-sea vents are open to other interpretations[14] that may challenge the authors' emphasis on thermochemical sulphate reduction and attendant H_2S production. Also, there is much uncertainty about when continental growth and emergence from the ocean occurred.

Gaillard and colleagues' model falls among a growing number of oxygen-buffering scenarios, including one based on molybdenum[13] that is linked to nitrogen bioavailability in the ocean and another that involves nickel[15] and its role in methane production (methane can be an important oxygen sink). It may well be that many diverse processes controlled the oxygenation of the atmosphere to varying extents, and that the ties they share to the emergence of continents on a cooling Earth are anything but coincidental. ■

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QUANTUM ENGINEERING

Spins coupled to a persistent current

Quantum computing architectures based on hybrid systems require strong coupling and information exchange between their constituent elements. These two features have been achieved in one such hybrid setting. See Letter p.221

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The development of electronic technologies based on the principles of quantum mechanics, such as quantum computing, requires coupling and integration of quantum objects of various kinds on the same electronic chip. For such integration to succeed, each object needs to be among the best in its class. On page 221 of this issue, Zhu *et al.*[1] make progress in this direction by successfully demonstrating coupling between two quantum systems: a superconducting flux quantum bit (qubit) and an ensemble of identical, highly 'coherent' quantum spins. The authors show that the two systems exchange quanta of radiation, allowing quantum information encoded in the quanta to be reliably transferred between them. The result is relevant for quantum computing based on hybrid settings, in which the superconducting qubits would process quantum information and the spins would be used to preserve or transfer the information[2].

Superconducting flux (or persistent current) qubits are loops of superconducting material interrupted by insulating barriers known as Josephson junctions. They are an excellent choice among superconducting qubits. This is because their magnetic flux, which is produced by the current circulating in the loop, couples directly to quantum magnets (atomic spins) that either exist in crystals or are artificially induced in them. In Zhu and colleagues' case, the quantum magnets are associated with the electronic spin states of atomic defects created in diamond. The two qubit states, the ground and excited states, are defined respectively by the clockwise and anticlockwise direction of a persistent current of hundreds of nanoamperes. Being a quantum, as opposed to a classical, bit, the qubit can also be in a quantum superposition of the two states — that is, it can be in the ground and excited states simultaneously. In their experiment, Zhu *et al.* used a qubit that has four Josephson junctions[3] (Fig. 1), which allow adjustment of the energy difference between the two qubit states to match the energetic fingerprint of the diamond spins, as well as optimal operation of the qubit.

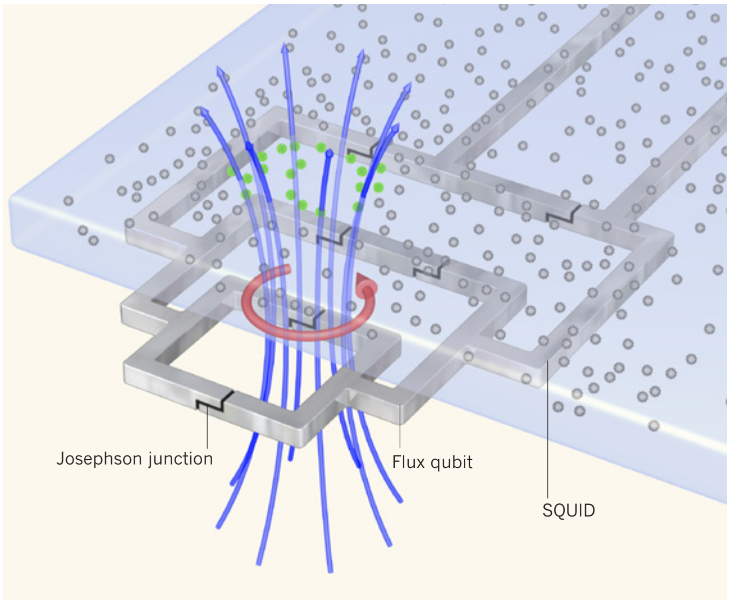

Figure 1 | Quantum hybrid. Zhu and colleagues' hybrid quantum system[1] involves a slab of diamond (blue) placed on top of a superconducting circuit (grey). A persistent current (red), the direction of which can be either clockwise or anticlockwise, characterizes a tunable flux quantum bit featuring four Josephson junctions. A larger structure known as a superconducting quantum interference device (SQUID), which features two additional Josephson junctions, is used to detect the average value of the persistent current. The magnetic flux (blue arrows) generated by the persistent current couples to some of the spins (green dots) in the diamond. The spins (grey and green dots) are in the form of defects located in a plane inside the diamond slab that is separated from the flux qubit by about 1.2 micrometres. This coupling allows quantum information to be transferred from the flux qubit to the spin ensemble.

Coupling between atoms and electromagnetic fields in resonators was first studied in atomic physics because atomic energy levels in diluted gases have a sufficient lifetime for the transfer of quanta to be observed. Proposed by Tavis and Cummings[4] in the 1960s, the coupling between atoms and a standing electromagnetic wave has been observed for an ensemble of atoms[5] and single atoms[6] in cavity quantum electrodynamics experiments, in which the photons and atoms interact in a cavity. More recently, trapping molecules above a superconducting microwave resonator has been proposed[7] as a means to implement cavity quantum electrodynamics on a chip. These studies[5–7] made use of the electric-field component of an electromagnetic field to coherently exchange photons between the field and the system under study.

Although the magnetic-field component of an electromagnetic field offers much less coupling than the electric-field analogue, magnetic two-level systems (such as the 'up' and 'down' spins in an ensemble of atoms) have much longer lifetimes than their electrical counterparts. This aspect is central to cavity quantum electrodynamics experiments in solid-state systems, which are relevant to the implementation of quantum computing on a chip but rapidly lose quantum information to the surrounding environment. Dipolar interactions between spins in such systems are a major cause of information loss because they affect the spin lifetime. But these interactions can be reduced by 'diluting' the spins in the host solid. Strong magnetic coupling between the electromagnetic field in the cavity and a spin ensemble has been demonstrated theoretically[8] and experimentally (see ref. 2 for a discussion), and requires a coupling strength larger than both the cavity's photon decay rate and the rate at which the spin loses its quantum-state information.

In typical cavity quantum electrodynamics experiments, the cavity field is a harmonic oscillator and is coupled to an ensemble of one or more two-level systems. But in their experiment, Zhu *et al.*[1] reversed the roles of these elements: they demonstrated strong coupling between the flux qubit (a two-level system) and the ensemble of spins, which is treated as a single harmonic oscillator. The authors prepared a diamond slab with a number of nitrogen-vacancy (NV) defects located in a plane inside the diamond that is separated from the flux qubit by about 1.2 micrometres (Fig. 1). Each NV defect has three states, with the state of lowest energy being separated from the two higher-energy states owing to an internal magnetic field in the crystal (see Fig. 1c of the paper[1]). It is this energy-level separation that defines the ground and excited states of the ensemble of NV defects and that allows these states to be entangled with the ground and excited states of the flux qubit.

Zhu *et al.* used a flux qubit with an energy gap between its ground and excited states that can be tuned to have the same energy as the energy gap between the ground and excited states of the NV ensemble. In this way, the NV ensemble and qubit can be coupled and placed in an entangled state in which the qubit is in its excited state and the NV ensemble is in its ground state. This state can be reversed into a state in which the qubit is in the ground state and the ensemble is in its first excited state. This allows quantum information encoded in the qubit state to be stored in the collection of long-lived NV spins. Zhu and colleagues estimated that the number of NV defects that take part in this process is as large as 3×10^7, giving a collective qubit–NV-ensemble coupling of 70 megahertz, which is sufficiently large to split the energy of the joint state and its reverse (see Fig. 3b of the paper[1]). They showed that a coherent oscillation between these two states lasted for about 20 nanoseconds, and suggested ways to increase this duration.

Compared with set-ups in which a resonator is used instead of a flux qubit[2], the flux qubit gives a more localized coupling. In addition, the external magnetic fields used to control the two states of the spin system alter a resonator's frequency and so affect the coupling process, which does not happen for a qubit of such small dimensions. What's more, this type of device has a larger qubit–ensemble coupling[9] than devices involving resonators, and operates in a frequency range of a few gigahertz, which is practical for low-temperature experiments. Finally, a four-junction flux qubit such as that of Zhu and colleagues can be used for studies involving materials other than diamond, because it can be tuned to be in resonance with spin states over a broad energy range. ■

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