Isotope measurements help pin down the ancient rise of oxygen

An extraordinarily well-preserved deposit of water-soluble minerals sheds light on the history of Earth's atmosphere and ocean.

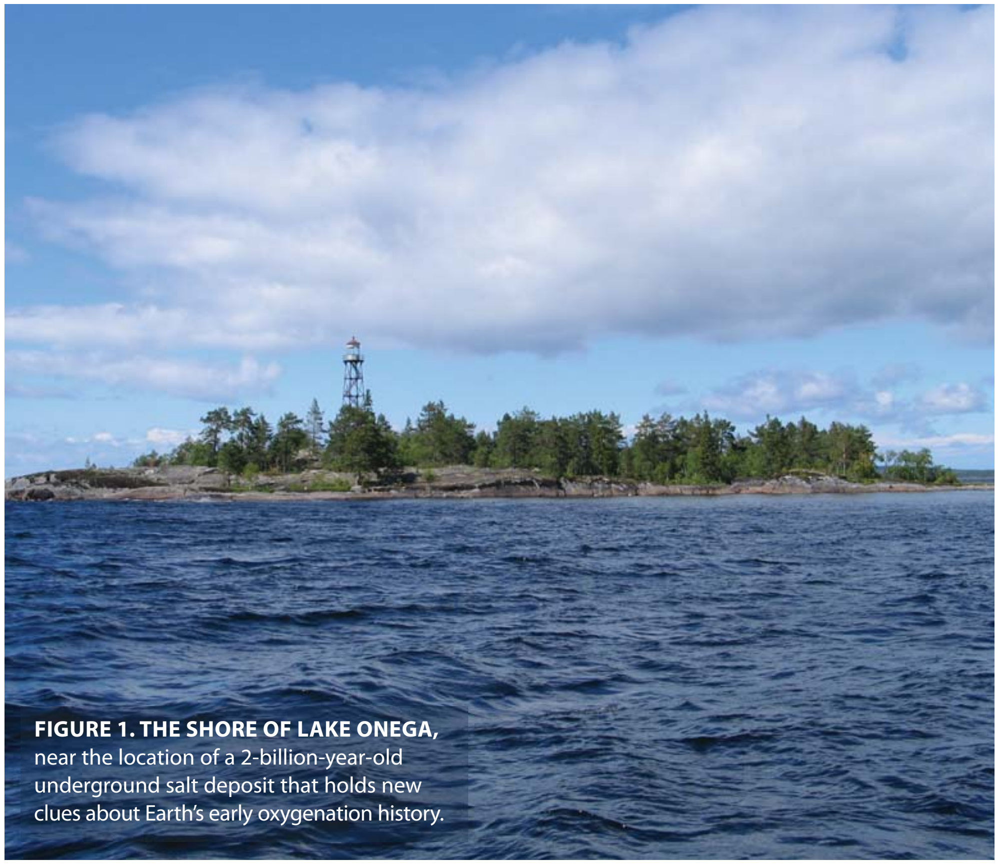

FIGURE 1. THE SHORE OF LAKE ONEGA, near the location of a 2-billion-year-old underground salt deposit that holds new clues about Earth's early oxygenation history.

Oxygen is essential to life on Earth today, but that wasn't always the case. When cyanobacteria first started churning out O_2 as a byproduct of photosynthesis more than 2 billion years ago, the molecule was actually poisonous to most other species of microorganisms alive at the time, and a mass extinction followed. The evolution of atmospheric oxygenation is thus critically entwined with the evolution of life.

The rise of O_2 to its present concentration (21% by volume) was neither a single sudden jump nor a smooth and steady climb. Rather, the concentration grew in fits and starts, stalling or even declining for hundreds of millions of years in between. The exact trajectory is poorly understood, though, because geological records of the ancient atmosphere are rare.

Now Princeton University's Clara Blättler and an international team of collaborators have opened a new window into an important period in atmospheric history.[1] They analyzed a collection of mineral samples extracted from deep under the shore of Lake Onega (shown in figure 1), 300 km northeast of Saint Petersburg, Russia. The minerals were deposited during a sustained period of seawater evaporation two billion years ago, so they constitute a record of the ocean's composition at that time.

The Onega samples are by far the oldest intact marine salts ever found. In most cases, water seeps into a salt deposit and dissolves the minerals. But by the good fortune of some unknown geological mechanism, part of the Onega deposit was protected from water for its entire history. Blättler and colleagues could therefore study not only the salts' chemical composition but also the constituent elements' isotopic ratios. From those measurements, the researchers concluded that the marine concentration of sulfate—produced when atmospheric oxygen reacts with iron pyrite (FeS_2) and a potent oxidizing agent in its own right—was at least 10 millimoles per kilogram, or more than 30% of its present-day level. That's a surprisingly high value for just a few hundred million years after the first appreciable accumulation of O_2 in the atmosphere, and it suggests that Earth's transition to an oxygenated environment may have been more abrupt than previously thought.

Reading pseudomorphs

Preserved ancient salt deposits are rare, but even when a deposit is not well preserved, all is not lost. As water gradually dissolves the soluble minerals, it often replaces them with others that have the same crystal shapes. From those so-called pseudomorphic replacements, one can learn a lot about the salts' original composition. For example, cubic crystals are a telltale sign that halite, or sodium chloride, had been there in the past.

Although NaCl is the principal salt in seawater, with a concentration of 3.5% by weight, its high solubility means it's not necessarily the first to precipitate. A kilogram of water can hold more than 350 g of NaCl in solution, so halite crystals don't begin to form until seawater is concentrated by about a factor of 10.

Calcium sulfate is present in lower concentrations than NaCl but is also much less soluble. Typical modern seawater need only be concentrated by a factor of 3 or 4 to precipitate $CaSO_4$ in the form of gypsum. In the past, when sulfate levels were lower than they are now, a larger concentration factor would have been necessary.

Geological salt deposits are produced from evaporated seawater, but not necessarily from a single volume of water

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FIGURE 2. ANCIENT SALT SAMPLES with different compositions. The deeper specimen **(a)**, produced from highly concentrated seawater, contains sodium chloride, calcium sulfate, magnesium sulfate, and other minerals. The shallower specimen **(b)**, produced when the seawater was less concentrated, is mostly $CaSO_4$ and magnesium carbonate. The absence of NaCl in the second sample means that the seawater's Ca^{2+} and SO_4^{2-} concentrations were high enough that $CaSO_4$ precipitated before NaCl.

completely drying up. Rather, a common case is a shallow inlet where water is warmed and concentrated and where new seawater can continually flow in. Those conditions can persist for many years, with the steady-state concentration slowly varying as the local landscape changes. The result is an enormous amount of salt—the Onega deposit is almost a kilometer thick—whose composition varies with depth.

If some layers of a deposit contain gypsum but no halite, the seawater sulfate concentration must have been high enough that gypsum precipitated first. On the other hand, if halite is present without gypsum, it means the sulfate concentration was relatively low. Which of those conditions held can be deduced from the shapes of pseudomorphic replacement crystals. But it's only a weak indicator of past marine chemistry.

Isotope clues

The Onega samples were discovered a decade ago. Aivo Lepland, of the Geological Survey of Norway and a coauthor on the new work, was leading a collaboration with scientists of the Karelian Research Centre of the Russian Academy of Sciences in Petrozavodsk, Russia, to search for evidence of Earth's early oxygenation history. Beginning in 2007 they drilled 15 cores in locations around northwest Russia; among them was the 3.5-km-deep hole on the shore of Lake Onega, where they found the ancient salt formation.[2]

Based on the ages of the rocks above and below, and from isotopic dating of the salts themselves, the deposit must be between about 1.95 billion and 2.09 billion years old. And it's made up of layers with distinct compositions. The bottommost layer contains a variety of salts that were produced when the overlying water was most concentrated. The topmost layer contains only the most easily precipitated salts produced when conditions were close to that of the open ocean.

Gypsum is unambiguously precipitated before halite. The specimen in figure 2a, from near the bottom of the deposit, contains both NaCl (made dark translucent pink by impurities) and $CaSO_4$ (the white embedded nodules). The specimen in figure 2b, extracted from one of the middle layers, contains

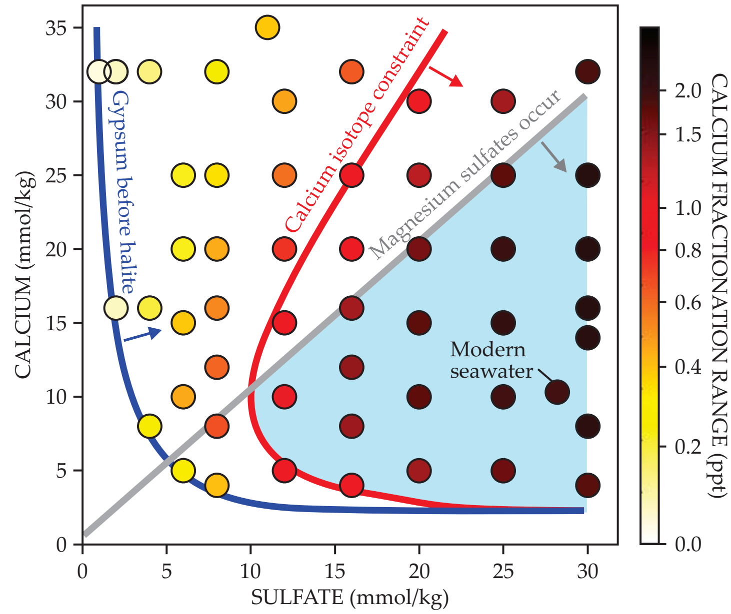

FIGURE 3. SEAWATER CHEMISTRY 2.0 billion years ago, as revealed by the salt samples from Lake Onega. Colored circles indicate the range of calcium isotope fractionations that could result from each calcium and sulfate concentration. The measured range, 0.9 parts per thousand (bright red), is a lower bound on the actual range. The isotope constraint and presence of magnesium sulfates imply that the ancient seawater composition must lie somewhere in the blue shaded region. Modern seawater is shown for comparison. (Adapted from ref. 1.)

$CaSO_4$ but no NaCl. The presence of magnesium sulfate in the deeper specimen provides an additional insight into ocean chemistry: Magnesium salts precipitate only when the calcium level is not too high and the sulfate level is not too low.

A more quantitative analysis had to wait until the advent of new geochemical tools. In 2014 Blättler, a Princeton postdoc, was working with her adviser John Higgins to understand how calcium isotope fractionation manifests in seawater salt deposits.[3] It was known that lighter isotopes, such as ^{40}Ca, preferentially precipitate relative to heavier ones, such as ^{44}Ca. Consequently, a precipitate that removes a small fraction of seawater's Ca is isotopically lighter than a precipitate that removes almost all of it. When layers of a deposit are produced by seawater concentrated to different degrees, they'll have different Ca isotopic compositions. But no single measurement can easily be connected to the original seawater composition.

Blättler and Higgins's insight was to use the range of isotopic compositions present in a deposit to derive a constraint on ocean chemical conditions. Qualitatively, seawater with much less sulfate than calcium produces salts with a small range of isotope compositions: All are highly enriched in the lighter isotopes, which remain plentiful even as the sulfate is depleted. Sulfate-rich, calcium-poor seawater, on the other hand, gives rise to a wide range of isotope compositions: As the seawater grows progressively more concentrated and the lighter isotopes are removed from solution, more of the heavier isotopes must make their way into the precipitating salts. The Princeton researchers made that relationship quantitative.

While working on a different project, Blättler met up with Lepland. The two agreed that Lepland's Onega samples were a good match for Blättler's new isotopic method, and he sent her some specimens to work on. She measured $\delta^{44/40}$Ca, the degree to which the salts were depleted in ^{44}Ca with respect to ^{40}Ca, and found that the highest and lowest values observed throughout the core differed by about 0.9 parts per thousand. The measured range could be considerably narrower than the full range of possible values, which might not all be present in the salt deposit.

Figure 3 shows how those measurements relate to the ancient seawater composition. The colored dots show the range of $\delta^{44/40}$Ca values theoretically derived for various concentrations of calcium and sulfate. The isotope measurement establishes a minimum sulfate concentration that's considerably higher than can be obtained from the salts' chemical compositions alone.

Great oxidation

As Blättler explains, the result represents a rare quantitative benchmark on the chemistry of ancient Earth. "It's easier to derive a qualitative understanding of conditions—for example, there was less oxygen, it was warmer or colder than today, there was more iron, and so on," she says. "But quantitative estimates are really hard to come by when dealing with materials this old."

Although marine sulfate concentration isn't a direct measure of how much O_2 was in the atmosphere at the time, it does give a sense of how much O_2 must have passed through the atmosphere at some point. That's because each SO_4^{2-} ion must have been produced from two O_2 molecules. And because sulfate doesn't stay in the ocean forever, the total amount present sets a lower bound on the cumulative amount of O_2 produced before that time.

To get a sense of where Earth was on its path from oxygen free to oxygen rich, Blättler and colleagues considered the atmosphere and ocean as an integrated system and estimated its total oxidizing capacity. To do that, they needed to multiply their sulfate concentration by the volume of the ancient ocean. "That's a big unknown," says Blättler: Large quantities of water could have been taken up by or released from the mantle over time. Assuming a modern-sized ocean, the researchers found that the ancient SO_4^{2-} reservoir would have had more than 20% of the oxidizing capacity of today's atmosphere and ocean.

Most evidence indicates that O_2 first appreciably built up in the atmosphere between 2.4 billion and 2.1 billion years ago in what's known as the Great Oxidation Event (GOE).[4] But exactly when cyanobacteria started producing oxygen is much less well understood; their rise could have coincided with the GOE or preceded it by as much as 1.5 billion years. The first O_2, the thinking goes, was consumed through reaction with iron pyrite and other minerals just as quickly as it was produced, so it didn't stay in the atmosphere for long.

It's not clear what caused the O_2 to stop reacting and start accumulating—whether O_2 simply ran out of minerals to react with or whether the transition was helped along by geological processes like a change in the rate of mixing between Earth's crust and mantle. Blättler and colleagues' results don't answer that question directly, but they create a new hoop for proposed theories to jump through: Any comprehensive model of the GOE must reproduce the high sulfate concentrations the researchers found.

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References

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