Ancient air caught by shooting stars

Ashes of ancient meteors recovered from a 2.7-billion-year-old lake-bed imply that the upper atmosphere was rich in oxygen at a time when all other evidence implies that the atmosphere was oxygen-free. See Letter p235

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It is a truth almost universally acknowledged that Earth’s atmosphere before about 2.5 billion years ago had little or no free oxygen. The classic argument for anoxia on ancient Earth is that a distinct change occurred in the oxidation state of many surface rocks and minerals around the end of the Archaean eon (which lasted from 4 billion to 2.5 billion years ago). A more recent argument is that a sudden, permanent change in the relative abundances of rare sulfur isotopes preserved in sediments also occurred at that time — a change that can be linked to differences in sulfur’s atmospheric chemistry in the presence or absence of oxygen. These arguments are strong. It therefore comes as a surprise that melted meteor fragments recovered from Archaean limestone indicate that the contemporaneous atmosphere above 75 kilometres was highly oxidized, as reported by Tomkins et al. on page 235.

The authors recovered 60 micrometeorites...
from 2.7-billion-year-old limestone in the Pilbara region of Western Australia. Micrometeorites are the surviving bits of meteors that were too small to burn up as shooting stars in the atmosphere, and are typically tens of micrometres in diameter. All but one of the Pilbara micrometeorites were originally sand-sized grains of iron and nickel alloy. Of the 11 studied in detail, 9 are composed of an oxidized mineral called magnetite (Fe₃O₄) and retain a distinctive morphology that indicates fast cooling. The other two retain some of the original metal and wüstite (FeO), an iron oxide that occurs in meteorite fusion crusts. Nearly as remarkable as their existence is that there is nothing otherwise remarkable about them — they look like, and are as oxidized as, the iron micrometeorites that fall to Earth today.

Tomkins et al. argue that the micrometeorites look modern because the air above 75 km was roughly as oxidized during the Archaean as it is today, and back this up using a model of meteor physics and chemistry tuned for modern Earth. The model shows that the air in that region needed to be oxygen-rich for it to oxidize all the iron to magnetite as it slowed the meteor's flight. If, however, the chemical reaction continued for a little longer than was modelled, it might have sufficed for the air to be less oxic. Carbon dioxide could have acted as an alternative oxidant (see Extended Data Fig. 5 of the paper), although the kinetics for oxidation with CO₂ are less favourable than with oxygen.

The idea that an oxygen-rich upper atmosphere sat on top of an anoxic lower atmosphere poses a serious challenge to atmospheric modellers. Models predict that oxygen can be abundant at extremely high altitudes in otherwise anoxic atmospheres, but because the oxygen comes from CO₂ that was split by sunlight (photolysis), it is balanced by a stoichiometric complement of carbon monoxide (Fig. 1). Overall, the resulting gas mixture would be no more oxidizing than CO₂ itself.

To create a local superabundance of oxygen from CO₂, the CO must be preferentially removed. There is no obvious way to do this. Some other molecule is therefore required that can be split into oxygen and a chemically reduced species that can be easily removed. One possible candidate is sulfur dioxide (SO₂) from volcanoes. This gas can be split by sunlight into oxygen and elemental sulfur, which can condense to form particles that fall to Earth, leaving oxygen behind. Isotopes in sedimentary rock indicate that elemental sulfur did fall from the skies during the Archaean, which makes SO₂ an attractive candidate.

The other obvious candidate is water vapour, which can be split by sunlight to free hydrogen atoms that escape to space, leaving oxygen behind. Water can do double duty here: the hydroxyl (OH) radicals generated by water photolysis react with CO to regenerate CO₂. The hydrogen would have escaped to space, leaving oxygen behind. Alternatively, if sulfur dioxide from volcanoes was split by solar UV to form oxygen and sulfur, then the particles could have fallen to Earth's surface, leaving oxygen behind.

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