

ATMOSPHERIC CHEMISTRY

Quick cycling of quicksilver

Models predict that mercury undergoes rapid oxidation in the upper atmosphere. Aircraft measurements support this prediction and provide evidence for a previously unrecognized sink for stratospheric mercury.

Christopher D. Holmes

Unlike other metals, mercury exists as a gas in Earth's atmosphere. In its elemental form, gaseous mercury can remain in the atmosphere for months, enabling its transport around the globe¹. However, oxidized mercury — which can be found in both gaseous and particulate form — is water-soluble and semi-volatile. As such, oxidized mercury is readily absorbed by aerosols, or removed from the atmosphere through deposition. Atmospheric chemistry thus controls the spread of mercury contamination from industrial and natural sources to distant ecosystems (Fig. 1). Writing in *Nature Geoscience*, Lyman and Jaffe² report simultaneous measurements of elemental and oxidized mercury in stratospheric-influenced air, providing the most complete picture yet of the chemistry of this toxic metal in the upper atmosphere.

Elemental mercury accounts for more than 90% of total (elemental and oxidized) mercury in the lower troposphere¹ — the portion of the atmosphere stretching from the Earth's surface to an altitude of around 15 km. The oxidants of elemental mercury are uncertain^{3–5}. However, the abundance of all candidates (bromine, chlorine, ozone and hydroxyl radicals) increases high in the troposphere and into the stratosphere — the layer of the atmosphere that lies just above the troposphere. In addition, the known sinks for mercury — deposition and aqueous photoreduction — are absent in the stratosphere. Therefore, model simulations suggest that a large or dominant fraction of the mercury in the upper troposphere and in the stratosphere is oxidized⁶. Most of that oxidized mercury should condense onto available aerosols at the cold temperatures found near the tropopause. Indeed, previous aircraft campaigns in the stratosphere found low levels of gaseous elemental mercury^{7,8} and high levels of oxidized mercury in aerosols⁹. Until now, however, no measurements of oxidized mercury in both gaseous and aerosol form have been made in stratospheric air, limiting the ability to quantitatively test models⁵.

Lyman and Jaffe² developed an instrument capable of measuring total,

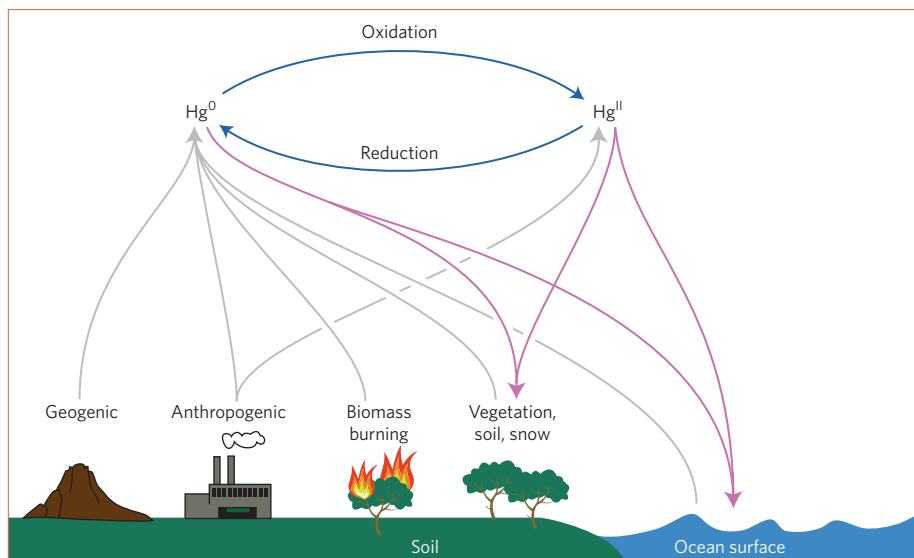


Figure 1 | Atmospheric chemistry of mercury. The majority of mercury that enters the atmosphere is in elemental form (Hg⁰), whereas most of the mercury that is deposited on the land and oceans is oxidized (Hg^{II}). According to model simulations, the oxidation process is fastest in the stratosphere. Now Lyman and Jaffe² provide observational evidence for the stratospheric oxidation of mercury, and tentative evidence for the gravitational sedimentation of oxidized mercury out of the stratosphere.

elemental and oxidized mercury simultaneously from an aircraft. Using observations made while flying through a stratospheric intrusion in the upper troposphere, they confirm that elemental mercury is rapidly oxidized in stratospheric air. They also detect a strong correlation between the concentrations of oxidized mercury and ozone levels. The correlation does not necessarily imply that ozone is responsible for the oxidation of elemental mercury, as ozone is also a tracer of stratospheric air, and mixing between stratospheric and tropospheric air could also cause some correlation. Nevertheless, matching the correlations of elemental and oxidized mercury with ozone will be a stringent test for models of mercury chemistry and transport.

Although their measurements are limited to altitudes of less than 8 km, Lyman and Jaffe extend their observations to around 20 km altitude, using correlations of mercury species with

ozone and a typical ozone profile. The modelled vertical profile suggests that oxidized mercury concentrations peak near the tropopause at around 15 km, where high mercury concentrations in aerosols have been observed⁹. At higher altitudes, corresponding to ozone levels above 400 ppb, the findings suggest that all stratospheric mercury is oxidized.

Perhaps most significantly, Lyman and Jaffe find that total mercury concentrations decline with increasing height in the stratosphere. According to their model profile, little mercury (in any form) reaches altitudes much higher than 15 km. To explain this gradient, Lyman and Jaffe suggest that gravitational sedimentation of aerosols containing oxidized mercury is an important and unrecognized sink for stratospheric mercury. According to this interpretation, mercury behaves much like sulphur, entering the stratosphere mainly as a reduced gas and returning to the troposphere as an oxidized aerosol product.

The proposed vertical gradients in stratospheric mercury could be used to test the accuracy of chemistry and transport models of atmospheric mercury. However, the linear relationships between mercury species and ozone that Lyman and Jaffe use to predict the vertical profiles may change across the extrapolated altitudes. More observations near and above the tropopause are needed to determine if rapid formation of particle-bound oxidized mercury in the lower stratosphere does indeed provide a short circuit back to the troposphere, preventing

mercury from entering further into the stratosphere.

The suggestion by Lyman and Jaffe² that sedimentation is an important sink for stratospheric mercury was based on their ability to measure elemental and oxidized mercury simultaneously. Research on other unresolved problems in the mercury cycle is also likely to benefit from their airborne survey technique, including the improvement of mercury emission inventories and understanding the mechanisms of mercury ageing in plumes from industrial sources and urban areas. □

Christopher D. Holmes is in the Department of Earth System Science, 2101 Croul Hall, University of California, Irvine, California 92697, USA.
e-mail: cdholmes@post.harvard.edu

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ECONOMIC GEOLOGY

Uranium-ore giants

Toxic heavy metals can accumulate in Earth's near surface to form ore deposits. Experimental and direct measurements of ore fluids reveal the efficient mobilization and deposition of uranium, implying potentially rapid formation of economic-grade ore.

Enikő Bali

Uranium is a radioactive heavy metal that is soluble in water under certain conditions. However, a small change in any physicochemical conditions can decrease its solubility, leading to the deposition of uranium ore. The ease with which this metal can be dissolved, transported and precipitated means that smaller enrichments of uranium within Earth's crust are widespread and occur on every continent. These are generally economically insignificant, but can be hazardous to health. Large, economically important uranium deposits are found rarely, which suggests that their formation needs very special geological conditions. Notably, large deposits occur in Kazakhstan, Australia and Canada. Writing in *Nature Geoscience*, Richard *et al.*¹ show that one of the richest world-class uranium ore deposits found in the Athabasca Basin, Canada, formed in the shallow crust by deposition from acidic and exceptionally uranium-rich ore fluids.

Hydrothermal ore deposits form when metals precipitate from hot fluids flowing through Earth's crust. Ore deposits that are sufficiently concentrated and extensive to make mining economically viable are thought to form either from fluids with relatively low metal concentrations over a protracted period of time², or from discrete pulses of metal-rich fluids^{3,4}. The latter mechanism is important during deposition of world-class gold and lead-zinc



Figure 1 | Uranium mine at McClean Lake, Athabasca Basin, Canada. Richard *et al.*¹ show that the giant high-grade uranium ore found in the Athabasca Basin could have formed in the Earth's near surface by deposition from acidic and extremely uranium-rich ore fluids, potentially over a short period of time.

hydrothermal deposits^{3,4}, but it has not yet been observed in other types of ore deposit.

The composition of the aqueous fluids that produce hydrothermal ore deposits can be studied in different ways. Experimental determination of mineral solubilities can expose the form and quantity of ore metals dissolved in water.

Experiments can also identify the main physicochemical parameters — such as pressure, temperature, oxygen fugacity and pH — which may control whether the metals are deposited to form ore, or remain in the fluids to be transported elsewhere^{5,6}. In another approach, the composition of real ore-forming fluids can be measured