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# Unlocking Earth's 4.5-billion-year secret: The case of the missing lead

by Nanyang Technological University

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An NTU Singapore-led team predicted that the lead-sulfur compound  $\text{PbS}_3$  forms under conditions usually found deep in the Earth's mantle. But the compound might occasionally turn into a liquid that rises towards the Earth's surface, which could explain why ancient lead is sometimes found in volcanic rocks today. Credit: Pexels

Geoscientists have long relied on different forms of lead to understand Earth's geological history and how it was created over billions of years. However, there is a mystery that has been puzzling scientists for decades: Earth is missing a massive amount of lead that ought to be in the planet's crust, and no one knows where it has gone to.

Recently, a groundbreaking study from researchers led by Nanyang Technological University, Singapore's (NTU Singapore) Asian School of the Environment (ASE) may have finally provided new insights into this long-standing mystery.

By exploring how lead behaves under the crushing pressures of Earth's interior, they found that the solution to one of our planet's oldest chemical secrets could in fact be hiding beneath our feet in the

planet's mantle layer. Their study was [published](#) in *Nature Communications*.

## The missing lead paradox

Lead and its various forms, collectively called lead isotopes, have been the most useful tools in providing answers to Earth's geological history and formation processes. They help to date the ages of rocks and can also help to track the movement of materials between Earth's crust, mantle, and core.

Lead has four forms, three of which—called lead-206, lead-207 and lead-208—are radiogenic, which means they are produced by the radioactive decay of uranium or thorium. This decay involves the atoms of these elements breaking down and releasing radiation over time to turn into lead atoms.

In contrast, the fourth form of lead, lead-204, is the "original" lead that has existed since Earth's formation and is non-radiogenic since it does not come from radioactive decay.

[Radioactive decay](#) occurs at a fixed rate and can therefore act as a sort of "geological clock," allowing scientists to figure out the ages of rocks by, for example, measuring the ratio of lead from radioactively decayed uranium to lead that originally existed on Earth.

Put simply, if the rock has a lot of lead from uranium, for example, but very little original lead, the rock can be deemed "young." If there is a lot of original lead but very little lead derived from uranium, the rock is ancient.

The missing lead paradox arises when we compare the levels of lead in Earth's surface rocks to samples of ancient meteorites that helped form Earth.

Currently, surface rocks contain too much "young" lead produced from radioactive decay, like lead-206 and lead-207, a lot more than theory predicts. This gives the impression that Earth is much younger than expected compared to these ancient meteorites, which is certainly not the case. The overabundance of "young" lead on the surface also suggests that much of Earth's ancient, original lead appears to be missing.

For many years, a leading theory proposed that this ancient lead had sunk into Earth's iron core during its formation. While this core theory has been a popular model, it is unable to fully explain the mechanisms for how lead got to the core and has been able to remain there for millennia. Might there be another explanation then?

## The hunt for hidden lead reservoirs

In a bid to find this missing lead, the research team, led by Professor Simon Redfern and former Research Fellow Dr. Liu Siyu from NTU's ASE, focused on the behavior of lead sulfide (PbS). Lead sulfide is a likely candidate for how lead is stored in Earth because lead naturally has a high affinity for sulfur and is more likely to be found as a compound formed with sulfur.

Using [computer simulations](#), the researchers showed that lead sulfide becomes extraordinarily stable under extreme pressures, which are conditions that can be found deep in Earth's mantle. In fact, it can remain solid at temperatures as high as 5,000°C, far hotter than the actual conditions in the mantle.

This suggests that hidden reservoirs of ancient lead could have formed early in Earth's history, and then remained tucked away deep in the mantle, sitting solid and hidden from the crust's uranium and thorium. So, this ancient lead is unlikely to contribute to the original lead levels found in rocks on the surface, which results in their lower-than-expected levels.

## **New minerals in the deep**

The team's computer simulations also predicted two entirely new chemical structures of lead-sulfur minerals, called polysulphides ( $\text{PbS}_2$  and  $\text{PbS}_3$ ), that could form in Earth's mantle. These compounds are expected to form under high-pressure conditions in the locally sulfur-enriched regions of the mantle.

One of these minerals ( $\text{PbS}_2$ ) likely remains solid in conditions like that of the upper mantle. But the other lead-sulfur compound ( $\text{PbS}_3$ ) has a lower melting point and can occasionally turn into a liquid. So, as it rises towards Earth's surface, it could carry small amounts of ancient lead that "leaks" into the crust, which might explain why we sometimes find such ancient lead in volcanic rocks today.



Professor Simon Redfern (right) and former Research Fellow Dr Liu Siyu from Nanyang Technological University, Singapore are part of the research team whose study provides new insights into the long-standing mystery of Earth's missing lead. Credit: NTU Singapore

## **Virtual exploration through supercomputing**

Since we cannot travel thousands of kilometers below Earth's surface to study it, the researchers turned to advanced computer simulations. They used a sophisticated software called CALYPSO that can predict the structures of materials given only their chemical composition and external conditions. It allowed the team to predict how lead and sulfur atoms in different ratios would behave at extreme subsurface pressures.

The researchers also ran simulations to evaluate how atoms move within lead-sulfur minerals at high temperatures. Their rigorous computational approaches showed that these theoretical high-pressure sulfides are thermodynamically feasible minerals that can withstand the churning of Earth's interior for billions of years.

## Why this research matters

This discovery is a major moment for geology. It shows that the missing lead could be nestled deep within the mantle. It also helps scientists to understand why they sometimes find very ancient lead signatures in volcanic rocks, a result of ancient lead "leaking" to the surface.

There is also a cosmic side to this story as it changes our understanding of the chemistry of planets. Knowing how sulfur plays a critical role in the distribution of metals like lead throughout Earth's interior, we can apply this knowledge to other rocky planets like Mars and improve our understanding of how other planets evolve chemically.

## What the future holds

The next step in the team's research will now involve recreating the extreme conditions of Earth's mantle in a laboratory to test their computer predictions, while simultaneously refining their computer models to give a clearer picture of when and how Earth's layers separated. They will also search for further evidence of these minerals in rock samples brought up by tectonic or volcanic activity.

Finding clues for Earth's missing lead is a step towards a greater understanding of our planet and opens the possibility for further secrets to be found in Earth's interior.

### Publication details

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### Key concepts

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