# Geochemists show experimental verification of principle of detailed balance

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Geochemists at Indiana University and Virginia Tech have developed and demonstrated a technique for assessing the validity of a principle that has long been important in thermodynamics and chemical kinetics but has proven resistant to experimental verification.

Called the principle of detailed balance, the concept is widely used in models to ensure the long-term safety of environmental projects such as storage sites for nuclear waste and for carbon dioxide.

"Even though this principle is the cornerstone of a great deal of chemistry and quantum mechanics, it is difficult to demonstrate," said Chen Zhu, professor of geological sciences in the College of Arts and Sciences and an author of the study. "We have assumed that it works in many situations without experimental verification."

The study, "A stable isotope doping method to test the range of applicability of detailed balance," was published in *Geochemical Perspectives Letters*, a publication of the European Association of Geochemists. Co-authors are IU postdoctoral researcher Zhaoyun Liu and doctoral student Yilun Zhang; J. Donald Rimstidt of Virginia Tech; and Honglin Yuan of Northwest University in Xian, China.

The principle of detailed balance says that when a system is in a state of equilibrium, each process or reaction will be balanced by a reverse process or reaction occurring at the same rate. For example, if a solid is in equilibrium with a solution, it will precipitate back to solid form at the same rate that it dissolves.

The principle was introduced in the late 1800s and early 1900s, and it became a foundation for modern chemical kinetics. But demonstrating the rate of reverse processes is difficult, Rimstidt said, and experimental tests of the principle's applicability are rare in the scientific literature.

Zhu and his colleagues take advantage of recent developments in analytical technology called MC-ICP-MS, for multiple collector-inductively coupled plasma-mass spectrometry. They created a novel experiment in which quartz, a mineral composed largely of a common isotope of silicon, was reacted with a solution that contained high concentrations of a stable but rare isotope of silicon.

By measuring the relative concentrations of the two isotopes in the solution over time, they were able to establish rates of dissolution and precipitation. The results showed that these rates were essentially the same at equilibrium, confirming that the principle of detailed balance was applicable.

And the principle matters, Zhu said, for a number of reasons. For example, it is used in models that predict the long-term performance of underground nuclear waste disposal projects and the movement of plumes of carbon dioxide captured from power-generation plants and stored underground or undersea. To meet safety requirements, such models must accurately predict what will happen over more than 10,000 years as geological conditions shift over time.

Verification of the principle of detailed balance in an experiment with quartz is significant, Rimstidt said, because quartz makes up about 20 percent of the Earth's continental crust. He said the method can and should be used for additional investigations to confirm the principle's applicability with other minerals using different isotopes.

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