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Hydrothermal Metastability

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Structures emerge as energy flows through complex systems. Reactions of water, gases, minerals, organic compounds, and microbes in hydrothermal systems are poised to generate structure or dissipate it through far-from-equilibrium, metastable, and stable states. Manifestations of stable equilibrium include crystallizing minerals whose presence lowers the energy state of the system. Sluggish rates engender persistent departures from stable equilibrium allowing hydrothermal fluids to carry historical records of their travels, including the familiar example of geothermometry using inorganic solutes. If kinetic barriers are high enough, subsets of chemical systems are walled off from stable equilibrium states and can participate in metastable equilibria. Experimental evidence shows that many small organic solutes react reversibly in hydrothermal systems, which is a requirement for attaining metastable equilibrium states. Hydration-dehydration reactions among alcohols and alkenes; alcohols, ammonia, and amines; acids, ammonia, and amides; and amino acids and peptides are all reversible in hydrothermal fluids, as are amination reactions involving primary, secondary, and tertiary amines, and ammonia. Similarly, hydrothermal hydrogenation-dehydrogenation reactions among alkenes and alkanes, alkenes and dienes, and ketones and alcohols, can all be reversible. These experimental demonstrations allow models of metastable states involving networks of reversible reactions perched at higher energy states than stable equilibrium. As an example, the system ethane-ethene-ethanol-ethylamine-ammonia-hydrogen-water can record temperature, pressure, ammonia abundance, pH, and hydrogen activity set by fluid-rock reactions. Given sufficient analytical and thermodynamic data, metastable equilibria can be seen to expand to include larger organic compounds including biomolecules. In hydrothermal ecosystems, membrane lipid molecules from the interface between microbial cells and their external environment show structural and compositional changes reflecting temperature, pH, and redox states that are consistent with their thermodynamic properties. Similarly, changes in homologous proteins coded in hot spring metagenomes track fluctuations in temperature, redox states and composition. Evidently biomolecules have to work as cheaply as possible. This principle can extend to changes in microbial assemblages defined by relative abundances of lineages that differ in bulk chemical composition and reflect local minima in metastable states. As a result, shifts in microbial communities have parallels to changes in hydrothermal mineral paragenesis.