## Silicate weathering thermostat

Over millions of years, atmospheric carbon dioxide (CO_2) is supplied by volcanic eruptions, as well as during sedimentary rock weathering. If CO_2 increases (red arrow), parts of Earth with high erosion and rainfall can increase CO_2 removal by silicate weathering. This provides a stabilizing feedback on climate over millions of years. However, silicate weathering fixes less CO_2 in the lithosphere if temperatures are cooler, mineral supply is limited, and rainfall is low.
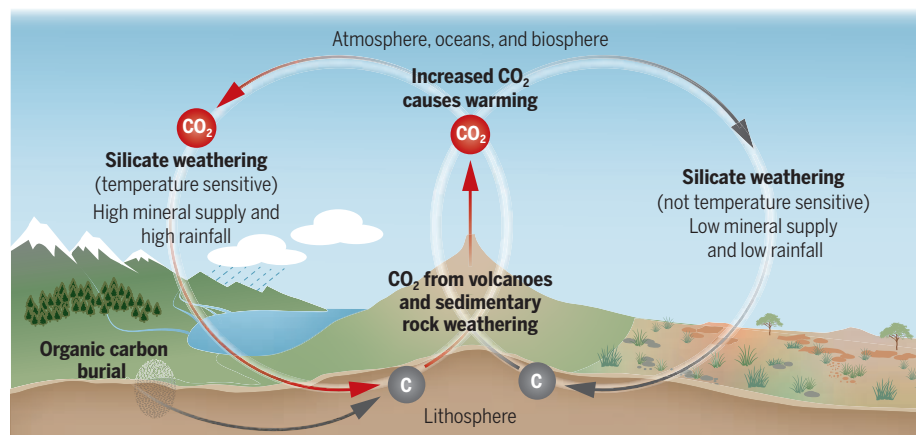
provide support for these conclusions (*10*). For example, recent work has suggested that global erosion could have doubled over the past 10 million to 15 million years and made Earth's surface a more sensitive thermostat by supplying minerals and making reactions more sensitive to temperature and water supply (*10*), which affects climate and atmospheric CO_2.

The important role for erosion in the silicate weathering thermostat means that other factors complicate how it may steer Earth's climate. This is because erosion can supply other phases to the weathering zone (*11*) that release CO_2 when they break down. These phases include ancient organic matter in rocks and sulfide minerals that can be oxidized during weathering (*12*, *13*). These erosion and weathering-induced CO_2 emissions are globally important because they release as much CO_2 as volcanoes. In addition, recent work shows that the CO_2 release may increase with temperature (*13*). This seems to oppose CO_2 removal by silicate weathering. Furthermore, any holistic consideration of the long-term carbon cycle must also account for fluxes and drivers of CO_2 removal by organic matter burial, as has been suggested for the Himalayan erosional system (*14*). More research is needed to assess how the organic carbon cycle affects the thermostat settings.

Unfortunately, the natural silicate weathering process is too slow to help mop up the very large excesses of CO_2 that are released each year from human activities (~9.6 PgC year^{-1}). However, deliberately increasing silicate weathering by grinding up silicate minerals and applying them at a large scale to agricultural areas may provide a way to help reach net zero (*15*). It remains unclear whether the logistical challenges can be met for this enhanced weathering to contribute to CO_2 drawdown, but research into the fundamentals of mineral weathering reactions will be essential to make decisions and assess the water demands of sustaining the reactions (*1*).

The temperature dependence of silicate mineral weathering provides a persistent thermostat to guide Earth's long-term climate. However, changes in patterns of erosion, water supply, and organic carbon cycling have likely changed the thermostat's settings as the continents have drifted and collided over millions of years. Geochemical approaches in the laboratory, in the field, and in silico are crucial to further untangling the dynamics of the carbon cycle on Earth and other rocky planets. ∎

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Decoding complex order in reticular frameworks

Periodicity and aperiodicity coexist in a nonchaotic, information-rich crystal structure

By **Omar M. Yaghi**[1,2] and **Zichao Rong**[1,2]

T he synthesis of chemical structures has largely focused on achieving them as crystalline solids because of the relative ease with which crystals can be characterized at the atomic level using x-ray or electron diffraction techniques. Constituent atoms are arranged in a definite pattern of order that confers homogeneous (uniform) properties, which makes them attractive to industries ranging from energy to pharmaceuticals. What about amorphous solids, in which the atoms are arranged in an aperiodic fashion? Clearly, structures of this type are more complex and far more difficult to design and study because of their disorganized atomic arrangements. On page 357 of this issue, Meekel et al. (*1*) report an example of a crystalline material that combines periodicity with aperiodicity to create what they refer to as "complex order." This duality in structure can be leveraged to hold information that can be decoded, much like QR codes and barcodes.

Typically, a metal-organic framework (MOF) is an extended crystalline material composed of metallic ions or clusters that are building units linked by organic molecules. Meekel et al. generated an MOF with a metal unit that was rotationally disordered throughout the structure. The complex order that was generated is reminiscent of that created using Truchet tiles. Truchet tiles are not rotationally symmetric, and when placed squarely in a grid, they generate interconnecting patterns.

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The complex order in the Truchet MOF of Meekel *et al.*, which they call TRUMOF-1, is realized by having a rotationally disordered metal zinc and organic linker (1,3-benzenedicarboxylate) that propagates across the crystal in an aperiodic fashion while still being affixed to an otherwise ordered lattice of oxygen (see the figure). What makes TRUMOF-1 distinctive is that the disordered and ordered constituents are covalently linked in a three-dimensional structure that is also porous. This MOF is a major addition to a larger family in which such complex order provides for anisotropy and directionality in crystals (*2*). In considering the amount of chemical information that periodic and aperiodic atomic arrangements contain, aperiodic structures are far richer and arguably more interesting because they exhibit more diversity, variation, and complexity. However, the lack of a means to characterize aperiodic materials has prevented the full exploitation of their potential as chemical information storage systems. The establishment of reticular chemistry—the linking of molecular building blocks with strong bonds to create extended crystalline structures—offers an entry point to addressing the characterization problem by making structures such as MOFs in which periodic and aperiodic atomic arrangements are combined, giving rise to emergent properties (*3*).

Given the flexibility with which reticular frameworks such as MOFs can be designed, variability of constituents, and ability to chemically modify their pores, complex order appears to be a natural outcome of this ultrahigh variability, especially when applied to a single framework. Thus, an MOF structure can be investigated at the atomic scale in detail to immediately articulate forms of complex order. This is a typical computational approach for characterizing a complex system when no physical techniques exist otherwise. There are several examples of structures in which periodicity and aperiodicity coexist to embody the desirable qualities of both. DNA is a perfect example of complex order in one dimension. The polyphosphate sugar chain serves as the repetitive and periodic backbone onto which aperiodic spatially arranged nucleotides are covalently bound. The complex order in DNA is based on variation in the composition of the

rungs of the double helix as represented by nucleotide pairs, whereas in a Truchet MOF, it is based on the relative configurations of the constituent units.

There are other forms of complex order. In multivariable MOFs, up to 10 different metal ions are incorporated into their metallic units to generate a heterogeneous spatial arrangement of metals in the form of, for example, metal sequences that contain short or long metal repeats (*4*–*6*). When eight different organic moieties are covalently attached to a three-dimensional MOF, a "guest" molecule that passes through the pores of the MOF can sample a specific sequence of functional groups across the entire crystal (*7*). This can impart gas selectivity properties onto the MOF, which allows the whole to be greater than the sum of its parts—that is, the way that the constituents of the MOF combine adds a different

quality to the final complex structure. The importance of complex order in catalysis is also revealed in a reticular structure that incorporates a heterogeneous arrangement of short peptides. Notably, these crystals carry out selective amide bond cleavage akin to an enzyme (*8*).

Although the complex order in the Truchet MOF of Meekel *et al.* was elegantly decoded by analyzing the diffuse x-ray scattering of the crystals, it is not always possible to apply this method to other MOFs because of their openness and large unit cells. Attempts to use atom probe tomography (*4*) and solid-state nuclear magnetic resonance (*9*) techniques have only facilitated decoding the sequence (that is, the spatial order) of constituent metal units and organic linkers down to the nanometer level, which leaves many questions unanswered about the design of properties in reticular structures that bear complex order. Decoding such complex order on a routine basis requires moving away from the traditional practice of making, characterizing, and measuring properties of a structure according to methods in which inputs into what is made are related to outputs. Rather, materials chemistry must decode the correlation between the inputs and outputs. This understanding should reveal the rich information that is held by structures of complex order. The execution of this vision can be achieved by blending the chemistry and synthesis of materials with computing and data science fields. This approach will most certainly require machine-learning tools (*10*). The Truchet MOF demonstrated by Meekel *et al.* highlights the power of using creative thinking to decode complex order. ∎

Duality in structure

The building units of a metal-organic framework can be linked to form aperiodic, rotationally variable configurations. These organic linkers (which bear variability in functional groups) and metallic units can be superimposed on (and strongly bonded to) a periodic lattice.

Organic linker

Metallic unit

Oxygen atom

Periodic lattice
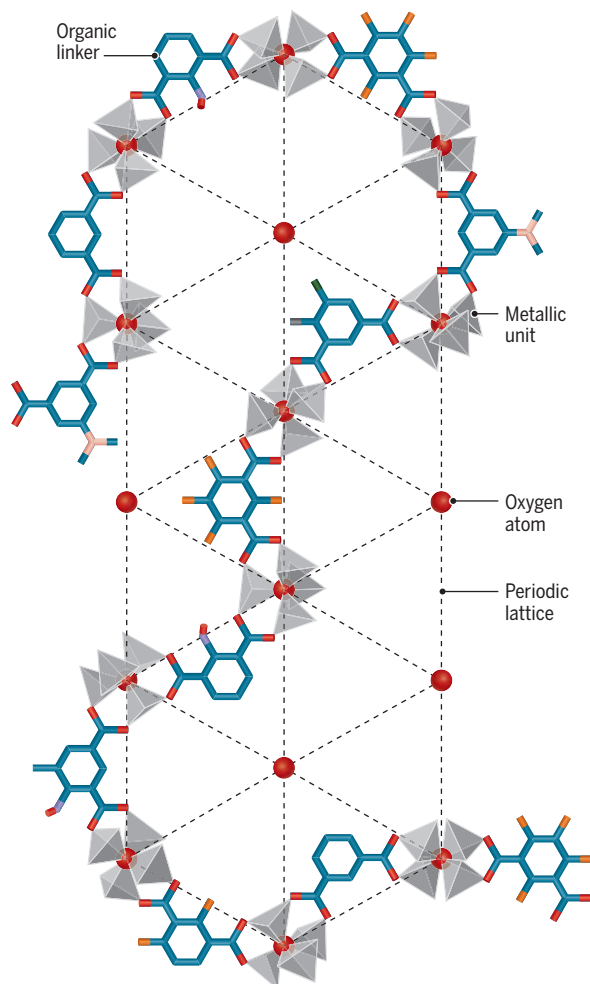
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