synthesis. It is also interesting to note that they did not observe much in the way of broader mixtures of compounds that might be regarded as irrelevant — such as the non-proteinogenic amino acids observed by Miller.

It is noted that the network cannot yet function in one pot without external interference. For instance, the system relies on the sequential delivery of reagents such as hydrogen cyanide and hydrogen sulfide instead of addition of all of the components at the start. To address this limitation, the authors describe a model scenario in which rains hitting mineral deposits on early Earth may have sequestered reagents that are incompatible early in the synthesis in separate streams that merged later. Of course, the limitations of this scenario render it vulnerable to some of the same scrutiny levelled at models that invoke multiple disparate reaction systems, such as the formose chemistry and Oró nucleoside synthesis. The key advantage of the Sutherland system is that all of the soups for these families are prepared from the same broth, even if they must be minded by a cook or kept in separate pots.

The most anticipated advances in origin-of-life chemistry are those systems that develop complexity from reasonable prebiotic conditions with as little contrivance and intervention from the cooks as possible. This new report represents a fantastically interesting approach, but origin-of-life chemists still have plenty of work to do in the kitchen. Our hunt for the primordial soup that cooks itself continues.

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References

1. Patel, B. H., Percivalle, C., Ritson, D. J., Duffy, C. D. & Sutherland, J. D. *Nature Chem.* **7,** 301–307 (2015).
2. Orgel, L. E. *Crit. Rev. Biochem. Mol. Biol.* **39,** 99–123 (2004).
3. Miller, S. L. *Science* **117,** 528–529 (1953).
4. Butlerow, A. *Justus Liebigs Ann. Chem.* **120,** 295–298 (1861).
5. Oró, J. *Biochem. Biophys. Res. Commun.* **2,** 407–412 (1960).
6. Powner, M. W., Gerland, B. & Sutherland, J. D. *Nature* **459,** 239–242 (2009).
7. Ritson, D. & Sutherland, J. D. *Nature Chem.* **4,** 895–899 (2012).
8. Ritson, D. & Sutherland, J. D. *Angew. Chem. Int. Ed.* **52,** 5845–5847 (2013).

INORGANIC MATERIALS

The quest for new functionality

Building on our understanding of the chemical bond, advances in synthetic chemistry, and large-scale computation, materials design has now become a reality. From a pool of 400 unknown compositions, 15 new compounds have been realized that adopt the predicted structures and properties.

Aron Walsh

Materials chemists are spoiled for choice. The 98 naturally occurring elements of the periodic table give rise to 4,753 potential binary compounds (that is, C_2^{98}), 152,096 ternary compounds and 3,612,280 quaternary compounds, assuming equal amounts of each element in a single phase. The combinations exceed 65 million for a five-component system. This is an underestimate of the number of accessible materials owing to variations in stoichiometry (for example Pb and O can form Pb_2O, PbO, PbO_2 and Pb_3O_4) and atomic arrangement (for example TiO_2 is naturally found in the anatase, rutile and brookite polymorphs, with several other phases accessible synthetically). More realistic estimates place the total number of possible materials as a googol (10^{100}), which is more than the number of atoms in the known universe (see discussions at http://hackingmaterials.com).

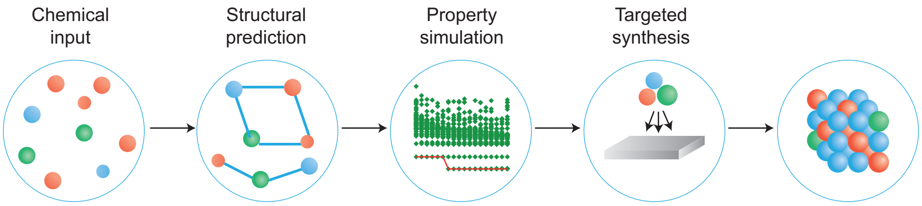

Figure 1 | A modular materials design procedure, where an initial selection of chemical elements is subject to a series of optimization and screening steps. Each step may involve prediction of the crystal structure, assessment of the chemical stability or properties of the candidate materials, before being followed by experimental synthesis and characterization. A material may be targeted based on any combination of properties, for example a large Seebeck coefficient and low lattice thermal conductivity for application to heat-to-electricity conversion in a thermoelectric device.

The search for new materials thus requires navigating a multidimensional landscape of bewildering complexity. The motivation, however, is strong. Every advance in technology, including those for energy generation, storage and conversion, requires or would benefit from new components. The objective is to reduce cost, increase performance or replace rare elements with more sustainable earth-abundant alternatives. Given the vast quantity of potential materials, even the most extensive high-throughput experimental or computational set-up will not succeed in screening all possibilities given realistic time and funding constraints. A key question is how to identify the specific arrangement of elements that produce the properties of interest as efficiently as possible? As they report in *Nature Chemistry*, Kenneth Poeppelmeier, Alex Zunger and co-workers have now tackled this issue using first-principles thermodynamics, and followed up their predictions with experimental validation[1].

The rapid increase in computer processing power and the availability of large-scale supercomputers has placed simulation at the forefront of the search for new materials[2]. Using quantum mechanical techniques, quantitative information on the structure and properties of a material can be provided at relatively modest computational and economic cost. Efforts such as the Materials Project have succeeded in tabulating the properties of many known inorganic systems, with more than 33,000 compounds in their current database[3]. For materials discovery, the most pragmatic approach is to introduce simulation constraints. By fixing the chemical composition, novel polytypes can be explored through crystal structure prediction, with many successes for microporous materials[4]. Alternatively, by fixing the crystal structure, the screening of different combinations of elements can be used to identify previously overlooked stable compositions[5,6]. As search algorithms are improving, such constraints are gradually being overcome[7,8].

In the work of Poeppelmeier, Zunger and co-workers[1], a valiant route was taken. They chose to fix the valence state of their target compounds to satisfy the 18-electron rule, and screen both the chemical composition and crystal structure. From 483 chemically plausible ternary compounds with 18 valence electrons, 83 have been previously reported, leaving 400 'missing' compounds. A rigorous multi-step selection process was implemented (Fig. 1 shows one such process), and validated by 'searching' known compounds — the method did correctly predict their stability and structures. A crystal structure search was carried out to ensure a global minimum configuration was identified, and the vibrational spectrum of each candidate material was investigated to confirm its dynamic stability. Finally, thermodynamic calculations were performed to ensure stability with respect to each competing phase. This screening procedure ensures that fanciful predictions of hypothetical compounds with exotic properties are avoided. In the end only 54 candidates survived — that is, were predicted to be stable — and of these, 15 new materials were successfully synthesized.

One of the roles of materials prediction in this study is to reduce the possible phase space and direct synthetic efforts to the most realistic and important targets. The simulations also provide valuable information to expedite the characterization of the novel compounds, ranging from predicted crystal structure parameters to vibrational and electronic spectral signatures. For all 15 materials predicted then synthesized in the study, the simulated and measured X-ray and electron diffraction patterns are in very good agreement. Although in the past materials modelling has been largely responsive to experiment, the predictive power of modern simulation techniques is becoming increasingly apparent.

The 18-electron compounds predicted to be stable are distributed amongst eight structure types. Phenomenologically, compounds with one transition metal (such as MgPdTe) are found to be metallic; those with two transition metals (such as TaIrSn) have a gap between their valence and conduction bands. The potential applications of these new materials with unconventional chemical bonding are wide ranging. For example, HfIrAs is a topological semi-metal of interest in quantum electronics, ZrNiPb is a small-gap semiconductor with a large Seebeck coefficient suitable for thermoelectric applications, and ZrIrSb is a rare example of a transparent p-type conductor with high conductivity of holes.

It is an exciting time for materials chemistry. The ability to synthesize materials of increasing complexity continues to astound. Even fundamental thermodynamic limits can be overcome, as metastable structures and kinetically stable compositions are accessible through non-equilibrium growth techniques. The challenge now is not simply to make new compounds, but to enable new functionality. The combination of theory and simulation has adopted a new role in the field, as a quantitative tool that can direct and inform experimental synthesis and characterization. When used appropriately, it can help to navigate the immense structural and compositional landscape at a fraction of the time and cost of an empirical search. The googol of possible materials may contain a room-temperature superconductor, the next high-voltage battery, or indeed, a viable photocatalyst for splitting H_2O or converting CO_2 into a chemical feedstock. The quest is to find them. ❐

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References

1. Gautier, R. *et al. Nature Chem.* **7,** 308–316 (2015).
2. Curtarolo, S. *et al. Nature Mater.* **12,** 191–201 (2013).
3. Jain, A. *et al. APL Mater.* **1,** 011002 (2013).
4. Woodley, S. M. & Catlow, R. *Nature Mater.* **7,** 937–946 (2008).
5. Castelli, I. E. *et al. Energy Environ. Sci.* **5,** 9034 (2012).
6. Chen, S., Gong, X. G., Walsh, A. & Wei, S.-H. *Phys. Rev. B* **79,** 165211 (2009).
7. Meredig, B. *et al. Phys. Rev. B* **89,** 094104 (2014).
8. Zhang, W. *et al. Science* **342,** 1502–1505 (2013).

SUPRAMOLECULAR SENSING

Enzyme activity with a twist

A supramolecular polymer comprising stacked artificial chromophores to which zinc(II) complexes are appended is able to respond to enzymatic hydrolysis in aqueous solution. The assembly of molecules can twist reversibly and quickly in response to changes in the type of adenosine phosphate present.

David B. Amabilino

Monitoring the activity of chemical processes in biological systems can lead to a greater understanding of how they function and also provides an opportunity find out when they go wrong. Particularly interesting targets are the adenosine phosphates (APs) because of the integral part they play in various processes in living cells. A great number of chemical-sensing approaches relevant to APs have been demonstrated with small-molecule probes[1,2,3], but genetically encoded indicators composed of fluorescent proteins have also been used to measure their levels inside single cells[4].

Now, writing in *Nature Communications*, a team led by Subi George has shown that entirely synthetic supramolecular polymers — a series of monomeric molecular units held together by non-covalent bonds — can also act as useful reporter groups for enzyme activity through their interaction with adenosine triphosphate (ATP)[5]. Up to now, such supramolecular polymers have been primarily of interest for their mimicry of biological self-assembly processes as well as for the preparation of synthetic materials with novel properties[6,7]. This present work show how the non-destructive and dynamic response of supramolecular polymers to the presence of APs can be used to monitor biochemical activity and is a fascinating development with regard to potential new applications.