# A precision instrument (?)

despite the planar defects, was the Kamhi structure; the minor but clearly distinct structure is unknown. We did not observe an ordered array of these two structures, but rather an apparently random distribution.

The possibility that the observed phenomenon was induced by the focused ion beam can be ruled out. All samples prepared from the same "single crystal" showed what appeared to be a perfect single crystal along the c axis; in addition, the multiple-structure phenomenon was observed only along the specific zone axis perpendicular to the c axis. This was further verified when we prepared TEM samples with the same zone axis by means of bombardment with argon ions and observed the same structures (fig. S3).

Because the two distinct structures were observed only when imaging a sample tilted to a zone axis perpendicular to the main long axis of a single thorn (the c axis in the Kamhi model), we tried to image the structure by tilting to a zone axis parallel to the long axis of a single thorn, [001]. Although hardly any beam damage was observed at other orientations, samples tilted to the [001] zone axis were always sensitive to the electron beam, and we therefore had to work with the much lower acceleration voltage of 80 keV. We are not sure why this zone axis was the most vulnerable to the electron beam, but it seemed that intracrystalline organic macromolecules were situated mainly on planes perpendicular to the c axis (fig. S3). When the image obtained at low acceleration voltage was stable, it could be seen that although the structure diffracted as a single crystal, it was actually made up of smaller domains.

When two coexisting domains were observed, such as those seen in Fig. 4, it was evident that not only were they rotated by 30° from one another, but they also had distinct d-spacings,
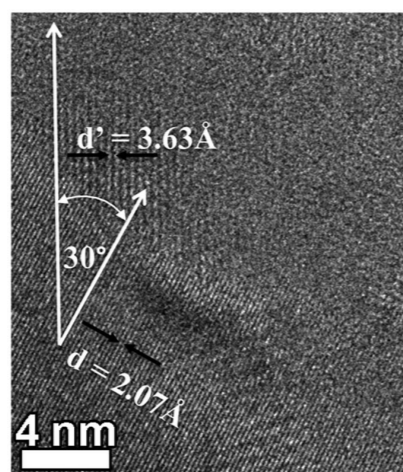
intercorrelated by exactly $\sqrt{3}$. The d-spacing of the first domain showed a good fit to that of the Kamhi {110} d-spacing (2.07 ± 0.05 Å), whereas the d-spacing of the minor structure was 3.63 ± 0.05 Å. In his original paper on vaterite Kamhi observed, by means of single-crystal diffraction, eight weak diffraction points that he was not able to index, but he was able to report that the observed image resembled a supercell with a lattice rotated by 30° around the c axis and with lattice parameters of $a' = \sqrt{3}a$ and $c' = 2c$. Here, we instead observed two distinct crystalline structures that were not parts of a supercell but were completely different structures coexisting within a "single crystal" of vaterite. Clearly, the predominant structure was the Kamhi structure.

It is intriguing that both electron diffraction and phase contrast revealed what appeared to be perfect single crystals, and that the coexisting two structures were revealed only when the samples were tilted to the two zone axes ([210] and [001]). We stress that although all the various models suggested for vaterite have different unit cells, they all share common features: The carbonate ions are parallel to the c axis, and the calcium ions are organized in a hexagonal structure with similar inter-ion distances. Because TEM is much more sensitive to heavier atoms (calcium in vaterite) than to lighter atoms (oxygen and carbon), most of the contrast under standard conditions is derived from the calcium ions. If the calcium ions in the main and minor distinct structures we observed had matching organizations, it is unlikely that these two structures would be distinguishable in most crystallographic directions. It is therefore likely that the local calcium ion arrangement is conserved across the main and the minor structures, and that only the carbonates differ. This would produce a pseudo-epitaxial effect.

The finding that two distinct atomic structures coexist in a "single crystal" of vaterite may well explain the discrepancies and disputes generated by the experimental results and theoretical calculations published over the past 60 years (for data regarding the d-spacings derived from the FFT in Fig. 3F, and for comparisons with calcite and aragonite, see table S2). Inconsistencies among the published results are found not only in diffraction data but also in spectroscopic data such as Raman spectra and even solid-state nuclear magnetic resonance (27). In Raman spectra, for example, symmetric stretching vibration (v1) of the carbonates reveals a triplet in some studies and a doublet in others. The Kamhi structure predicts a doublet for this peak (21). In the seminal Raman study of vaterite by Wehrmeister et al. (21), it was concluded that the vaterite, owing to stacking of the carbonate groups, might possess a lower symmetry than that proposed by Kamhi or Meyer. Lower symmetry was also recently proposed by Mugnaioli et al. (25) who, in an elegant study based on ADT and other techniques, proposed two low-symmetry struc-

tures, one of which has triclinic symmetry (space group $P\bar{1}$), which is almost the lowest symmetry possible. The electron beam diameter in that study was 50 nm. In our study we saw domains on a much smaller scale, only a few nanometers in diameter, in two different structures. We believe these two structures were not found by other researchers because they did not have the resolution we were able to achieve with the aberration-corrected HRTEM, and so they reported an average over the two structures. Even in the work of Mugnaioli et al. (25), where a 50-nm electron beam was used, what the authors observed was a superposition of the two structures.

Our findings indicate that the vaterite crystal structure is not a single entity; rather, vaterite consists predominantly of a hexagonal structure with at least one other coexisting crystallographic structure. The two structures are rotated by 30° with respect to one another and have lattice parameter relationships: $a' = \sqrt{3}a$. The challenge ahead is to fully characterize and solve the crystallographic structure of the minor structure and to understand how these two structures are organized relative to one another in space.
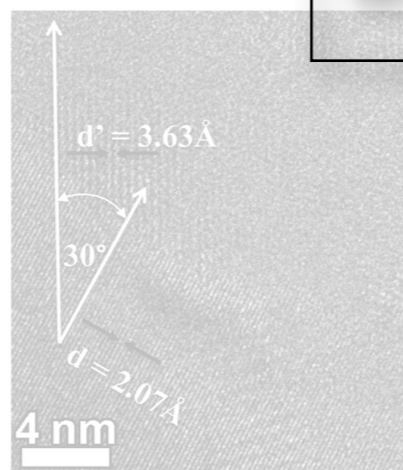
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Fig. 4. HRTEM image (acceleration voltage 80 kV) with two lattices. The lower lattice has d-spacing = 2.07 ± 0.05 Å and the upper d'-spacing = 3.63 ± 0.05 Å, and the two lattices are rotated by 30°.

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Semantics:

combinations of words mean what they mean because of the meanings of the words and the way they are combined

[Principle of Compositionality]
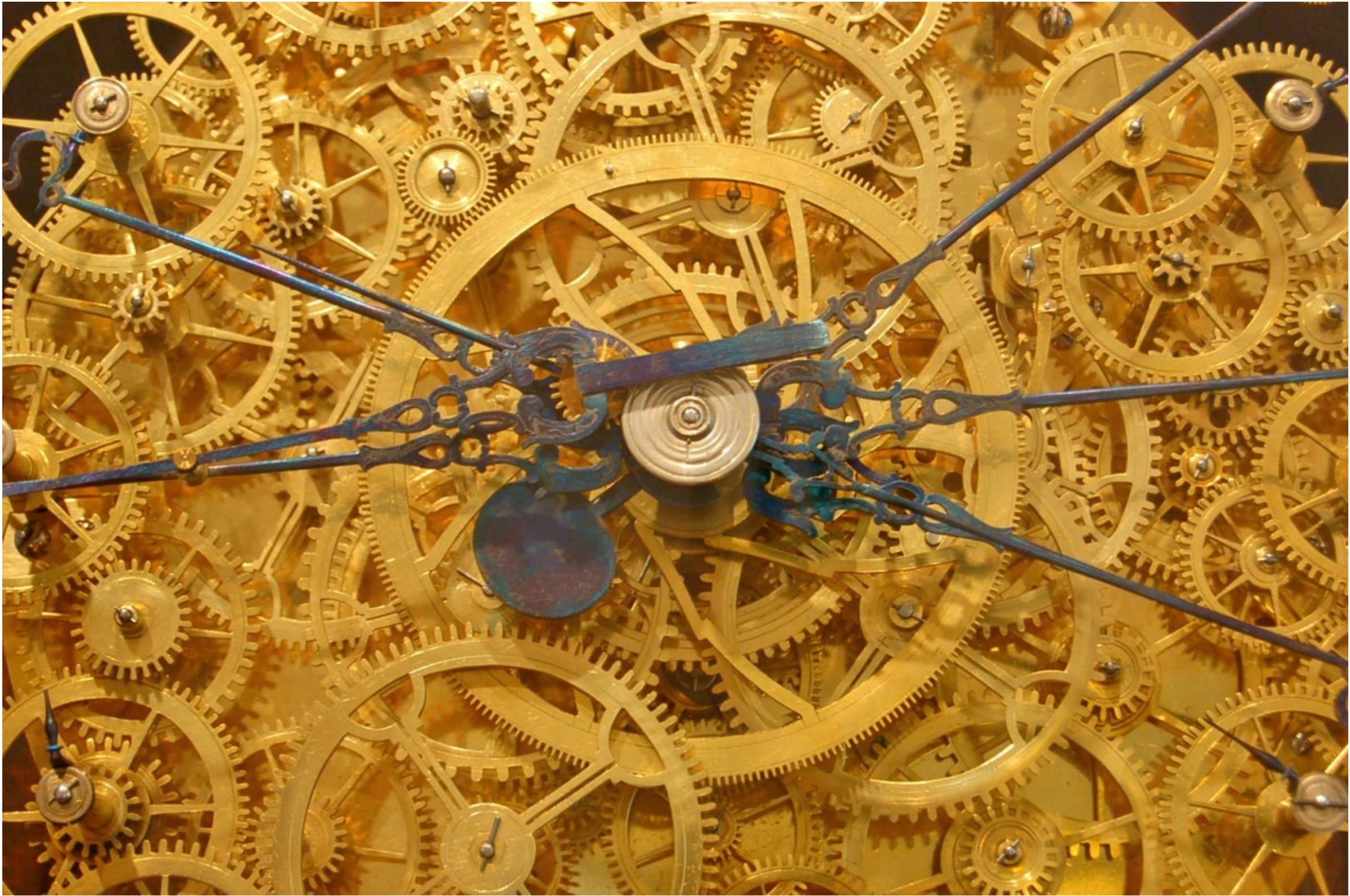
THE
SEARCH FOR
THE PERFECT
LANGUAGE

Umberto
Eco

Sit in the *apple juice seat!*

(the seat in front of which a glass of apple juice had been placed)

Kim's team

– the team she owns
– the team she coaches
– the team she picked in the office pool
– the team she just mentioned as the best example of a team that will never again win the championship

Language is designed
to leave a lot of meaning to context.

Finding the meaning of what someone said requires mind-reading.

Colorless green ideas sleep furiously
– Noam Chomsky

– Mikael Parkvall

Art hyperactivates
our ability to read full meaning
into semantically under-specified structures