ratios do not reflect those of a closed system. Because the Pb isotopic ratios remain unaffected by late alteration or laboratory treatment, the Pb-Pb age remains accurate despite any shifts in the U/Pb ratio that may have recently occurred.

It has long been assumed that the solar system inherited a fixed inventory of galactically derived ^{238}U and ^{235}U that was homogeneously distributed in the protosolar molecular cloud and that they were not measurably fractionated in natural systems. All ages reported in the literature today are based on this assumed fixed ^{238}U/^{235}U ratio. The isotopic composition of U is typically not measured in samples owing to the technical challenge of measuring the extreme ^{238}U/^{235}U ratio of small amounts of U sufficiently precisely and the lack of evidence, despite prior attempts (*3*), that this ratio varies measurably in meteorites. But Brennecka *et al*. demonstrate that this assumption of a fixed U ratio is incorrect for some of the solar system's oldest solids, calcium-aluminum–rich inclusions (CAIs), and that the ratio may vary up to 3000 parts per million from the accepted value of 137.88. This translates into a potential age offset of 5 My for a given radiogenic ratio $(^{207}\text{Pb}/^{206}\text{Pb})_R$—or about 50% of the life span of the solar protoplanetary disk. They attribute this heterogeneity to the variable fractionation of short-lived ^{247}Cm that decays to ^{235}U, by using Nd as a geochemical proxy for the now extinct Cm.

Ages from a relative chronometer can be mapped into absolute time in the past when a single object is found to be suitable for both a Pb-Pb age and a relative age. For example, CAIs anchor the ^{26}Al-^{26}Mg system (*4*), whereas the differentiated basaltic angrite LEW 86010 provides the anchor for the ^{53}Mn-^{53}Cr system (*5*, *6*). If the short-lived nuclides were homogeneous and the ^{238}U/^{235}U ratio was consistent, all ages from different chronometers for samples that behaved as a closed system should be concordant. But they are not. For example, age offsets of up to 3 My exist between Pb-Pb ages and the available relative chronometers for some rapidly cooled volcanic meteorites (*7*).

Homogeneity of short-lived nuclides in the disk has commonly been singled out as the least robust assumption in geochronology, from which one can infer that the relative chronometers are most likely in error. But it is now possible that variations in the ^{238}U/^{235}U ratio in meteorites and their components may, at least in part, be to blame for the discordances. However, so far the offsets in the ^{238}U/^{235}U ratio of CAIs reported by Brennecka *et al*. will only make the discordance between Pb-Pb ages and the relative chronometers worse.

With the rapidly growing identifications of planets that orbit distant stars, and the tantalizing perspective of discovering an Earth-like world, understanding the sequence of events leading to the formation of the planetary bodies in our solar system has never been so relevant. Brennecka *et al*. convincingly relate for the first time the important discovery that U is isotopically variable in CAIs, implying that the currently accepted age for the formation of the solar system's first solids (*4*) may be incorrect. At the same time, they have defined a new benchmark for high precision and accurate geochronology: All future Pb-Pb studies must include ^{238}U/^{235}U ratios. Only then can we be certain that we have an internally consistent Pb-Pb chronometric database and a correct temporal framework within which to interpret meteorites and, in turn, understand the origins of our solar system.

References

1. G. Brennecka *et al*., *Science* **327**, 449 (2010); published online 31 December 2009 (10.1126/science.1180871).
2. A. Trinquier *et al*., *Science* **324**, 374 (2009).
3. C. Stirling, A. N. Halliday, D. Porcelli, *Geochim. Cosmochim. Acta* **69**, 1059 (2005).
4. Y. Amelin, A. N. Krot, I. D. Hutcheon, A. A. Ulyanov, *Science* **297**, 1678 (2002).
5. D. P. Glavin, A. Kubny, E. Jagoutz, G. W. Lugmair, *Meteorit. Planet. Sci.* **39**, 693 (2004).
6. Y. Amelin, *Geochim. Cosmochim. Acta* **72**, 221 (2008).
7. J. N. Connelly, M. Bizzarro, K. Thrane, J. A. Baker, *Geochim. Cosmochim. Acta* **72**, 4813 (2008).

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MATERIALS SCIENCE

Epitaxial Growth Writ Large

The technological goal of optimizing the controlled deposition of atomic monolayers is simplified by studying models of deposition of larger colloids.

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The performance of semiconductors in device applications often depends on their crystallinity—the grain boundaries and defects of a polycrystalline material interfere with transport of charge carriers. Single crystalline layers can be grown through epitaxy: Atoms are deposited from the gas phase on top of an existing crystal to form new layers. However, if the growth process is not well controlled or is too rapid, unwanted surface features, such as mounds, may form. Thus, the fabrication process relies heavily on monocrystalline growth of a single element. Models to find optimal conditions for this process have been studied for a long time (*1*, *2*) and have had to become increasingly sophisticated (*3*, *4*). Insights from related processes involving molecules or even larger particles can test our understanding of how epitaxy works and can be easier to observe directly. On page 445 of this issue, Ganapathy *et al*. (*5*) describe epitaxial growth with colloidal spheres some four orders of magnitude larger than atoms. Models developed for atomic epitaxy can describe these processes, despite colloid-colloid attractions arising in a way very different from atomic interactions.

Models of epitaxial growth must account for how adsorbed atoms, called adatoms, interact with each other and the surface template, as well as the effects of different incoming fluxes F of atoms and different growth temperatures. Adatoms are trapped by attractive forces in wells of the corrugated surface potential but move when they have enough energy to "hop" over these barriers (see the figure, panel A). A minimal model describing how adatoms move requires attractions between neighboring atoms (such as chemical bonds) to create the potential wells and energy barriers to describe the hopping process. Analysis of the energy barriers helps in estimating the thermal surface diffusion coefficient D. The model must also account for the greater difficulty of atoms dropping over a step edge, because they must break even more bonds. In the simplest picture, this leads to the so-called "Ehrlich-Schwoebel" (ES) barrier (see the figure, panel B) (*6*, *7*).

For colloidal particles, attractive forces arise from a "depletion interaction." Smaller surrounding polymer "depletants" have a hard time getting between closely spaced colloids,

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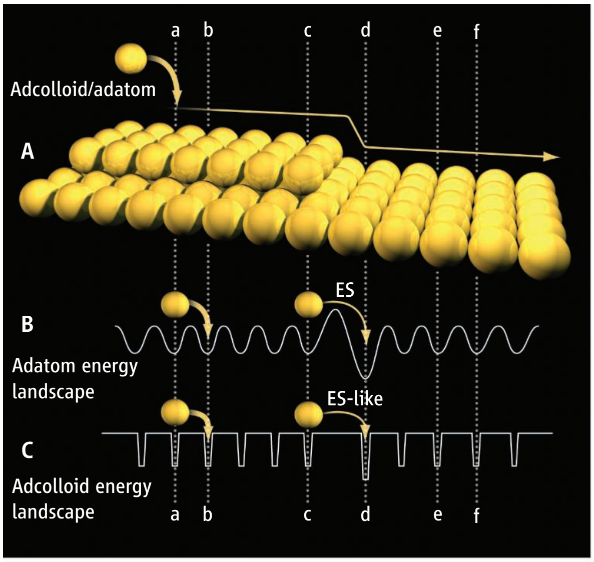
and the depletion layer creates a pressure imbalance that pushes the colloids together (*8*), creating an effective bond. This bond is broken when an adsorbed colloid, or adcolloid, hops between neighboring sites. Unlike adatoms, the bond is very short range (relative to the size of the adcolloid), and the energy landscape is nearly flat for most of the hop (see the figure, panel C). Thus, once the initial detachment is taken into account, the remaining part of the hopping time (inverse rate) is proportional to the path length of the hop alone and does not depend on barrier height. Because this length is greater for hops over steps or around the corners of disconnected regions of the same layer (called "islands"), colloids spend more time at these locations, just as atoms spend more time overcoming an ES barrier.



Colloidal versus atomic epitaxy. **(A)** The physical landscape for epitaxial growth is depicted. The colloids in the system described by Ganapathy *et al.* are 10,000 times as large as atoms, but their epitaxial dynamics are remarkably similar because both types of adsorbed particles—adatoms or adcolloids—encounter a step-edge barrier (ES or ES-like) for downward hops (**c**→**d**). The energy landscape for adatoms (**B**) undulates more robustly than its mesa-like adcoillodal counterpart (**C**) because colloidal bonds are too short to produce similar barriers. Because the segment lengths **cd** are greater than those for **ab** and **ef**, a colloid trying to move from **c** to **d** will have a smaller chance than one diffusing between **a** and **b** or **e** and **f**. Like atoms, colloids tend to settle at site **d** because of its higher coordination.

This ES-like barrier leads to a great simplification compared with atomic systems. The energy or time associated with a mobile colloid crossing over step edges, going around corners or kinks, and other common routes, can be computed in terms of path length alone. For example, there should be simple relations between the barriers for colloidal deposition on square and triangular templates. The motion of atoms on a surface involves subtle relaxations, as well as long-range or multiatom interactions, that would confound similar computations.

Unlike atomic systems, where bond strengths are largely fixed, the colloid-colloid bond can be tuned by varying the depletant concentration. Thus, a key parameter for describing epitaxial growth, the ratio D/F, can be adjusted independently from 10^{-1} to 10^4. This range overlaps substantially with that accessible to atomic systems and should allow for many useful comparisons.

For example, the coalescence of islands is important because unwanted domain walls between islands can form. Ganapathy *et al.* show that for a given D/F, there is a critical concentration n_c of disconnected colloidal islands that marks the end of an initial growth period. The number of islands then decays as further growth causes islands to coalesce, just as in atomic systems (*4*, *9*). The scaling of n_c approaches $(D/F)^{-1/3}$, just as classical nucleation theory would predict. Mound formation during multilayer growth of atoms would also be expected in colloidal systems because of the ES-like barrier at step edges that inhibits the completion of a lower layer. Meandering instabilities—to-and-fro step oscillations—that can prevent the step-flow growth of atoms in device fabrication should also occur on a series of colloidal steps.

Another important concept is the size of the smallest island that is stable to decay—the critical nucleus. This quantity determines the distribution of the sizes of islands (*4*, *9*) and of their capture zones (*4*, *10*)—the areas around an island in which surrounding adatoms will likely attach to the island. The distribution of capture zones was only recently argued to be related to the critical nucleus size (*11*). For colloids, this number is 2 (dimers are stable), so colloidal systems can be used to test this concept directly.

Although it will certainly be instructive to compare colloidal and atomic epitaxy, there are many aspects of growth that will be difficult to realize in colloidal systems. For example, colloidal growth lacks the control over deposition angles available with atomic beams that can cause shadowing effects (*12*) and growth asymmetries when atoms impinge obliquely.

Colloidal epitaxy as described by Ganapathy *et al.* should still prove to be a useful model for many complex systems. For example, colloids of different sizes could model heteroepitaxy, which is used to grow compound semiconductors such as gallium arsenide. In contrast to such covalently bonded systems, where the crystalline structure arises from orbital hybridization, here the ratio of the larger to the smaller radius of the two spheres can be important. In ionic materials, transitions from sodium chloride to cesium chloride to zincblende structures, with 6, 8, and 4 nearest neighbors, respectively, occur as this ratio increases. For colloids, the challenge will be avoiding the formation of amorphous structures, because the ordering in atomic systems stems in part from differences in charge as well as size.

Similarly, colloids of different sizes can be used to explore the role of surfactants and step decoration on the controlled growth of surface structures; for example, the decoration of colloidal islands by colloids of a different size should predictably alter island shape (*13*). Finally, colloids may even prove to be useful models of biological systems, where depletion attractions still play an unappreciated role (*8*). Nonspherical colloids could model the epitaxy of antifreeze proteins (*14*) and kidney stones (*15*). Indeed, a wide range of interesting epitaxial systems should quite literally come into focus when modeled with colloids.

References and Notes

1. A. Pimpinelli, J. Villain, *Physics of Crystal Growth* (Cambridge Univ. Press, Cambridge, 1989).
2. T. Michely, J. Krug, *Islands, Mounds and Atoms* (Springer, Berlin, 2004)
3. A. Voigt, Ed., *Multiscale Modeling in Epitaxial Growth* (Birkhäuser, Basel, 2005).
4. J. W. Evans, P. A. Thiel, M. C. Bartelt, *Surf. Sci. Rep.* **61**, 1 (2006).
5. R. Ganapathy, M. R. Buckley, S. J. Gerbode, I. Cohen, *Science* **327**, 445 (2010).
6. G. Ehrlich, F. G. Hudda, *J. Chem. Phys.* **44**, 1039 (1966).
7. R. L. Schwoebel, E. J. Shipsey, *J. Appl. Phys.* **37**, 3682 (1966).
8. D. Marenduzzo, K. Finan, P. R. Cook, *J. Cell Biol.* **175**, 681 (2006).
9. J. G. Amar, F. Family, P.-M. Lam, *Phys. Rev. B* **50**, 8781 (1994).
10. J. A. Blackman, P. A. Mulheran, *Phys. Rev. B* **54**, 11681 (1996).
11. A. Pimpinelli, T. L. Einstein, *Phys. Rev. Lett.* **99**, 226102 (2007).
12. Y. Shim, J. G. Amar, *Phys. Rev. Lett.* **98**, 046103 (2007).
13. T. J. Stasevich, C. Tao, W. G. Cullen, E. D. Williams, T. L. Einstein, *Phys. Rev. Lett.* **102**, 085501 (2009).
14. J. A. Raymond, P. Wilson, A. L. DeVries, *Proc. Natl. Acad. Sci. U.S.A.* **86**, 881 (1989).
15. S. R. Qiu *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **101**, 1811 (2004).
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