



The Rise of Plants and Their Effect on Weathering and Atmospheric CO₂

Author(s): Robert A. Berner

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the size and number of solvent molecules included in the crystal lattice. Thus, by starting with two-dimensional sheets, the crystal engineering problem is reduced to controlling a single dimension.

As noted above, the caveat in all crystal engineering efforts is that seemingly reliable motifs may fail to form when packing densities are low. Several features of the alkyl sulfonate-guanidinium sheet structure make it particularly robust and less prone to this problem (6, 18). Most importantly, many hydrogen bonds are formed, which are strong and ionic yet pliable enough to allow for small adjustments to accommodate the particular alkyl substituent. These adjustments primarily take the form of a hinge bending by the hydrogen bonds between the quasi-one-dimensional sulfonate anion-guanidinium cation ribbons (the "joists") that make up the sheet. This hinge bending allows the sheets to show varying degrees of corrugation, and thus, the sulfonate stud can adapt to the steric demands of the particular guest molecule. In all, three alkyl disulfonate anions and three aromatic disulfonates were crystallized with the guanidinium cation, and all produced the expected clathrates. When different-sized guests were present with a 4,4'-biphenyldisulfonate stud, clathrates with different floor-to-floor distances were obtained, again pointing to the generality of this approach.

Weber has pointed out that the application of clathrate chemistry is in its infancy (19). Promising applications include the purification and resolution of drugs, trapping and storage of toxic materials, off-peak energy storage, and matrices for slow drug release. Additionally, new synthetic reactions with altered chemical selectivities may take place within the confines of the crystal lattice. One of the oldest practical uses of clathration is in petroleum refining, where products ranging from gasoline to light lubricating oil exhibit enhanced performance when linear paraffins are removed in processing. Extractive crystallization with urea is particularly attractive because straight-chain alkanes from C₇ to C₇₀ are selectively bound in urea clathrate channels. In fact, there have been processing plants successfully operating on a scale of 320 barrels per day with this technology.

Clathrate lattices generally decompose upon loss of the imprisoned guest. Although clathrates formed from metal ion coordination networks might better allow reversible

release and adsorption of guests (20), it seems unlikely that these nanoporous solids will ever compete with zeolites. Nonetheless, the ability of clathrate hosts to shape or enantioselectively surround a guest and then release it upon mild dissolution conditions suggests a bright future in the resolution and purification of specialty chemicals such as pharmaceuticals. Whatever may be the future applications of this class of inclusion complexes, it is clear that the study of clathrates has already contributed substantially to our understanding of the crystal engineering problem and will inspire continuing attempts to create nanoporous solids.

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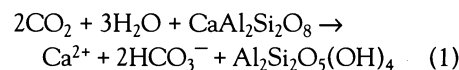
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PALEOCLIMATE

The Rise of Plants and Their Effect on Weathering and Atmospheric CO₂

Robert A. Berner

The spread of rooted vascular plants to upland areas during the Devonian Period (400 to 360 million years ago) most likely had an important effect on many Earth processes (1, 2). As reported on page 583 of this issue by Retallack (1), the first well-differentiated forest soils appeared in the Devonian. Along with this, there is additional evidence of a progressive increase in the size and depth of roots from the Silurian to the late Devonian (1, 3), with relatively deep rooting appearing as early as the late Early Devonian (390 million years ago) (4). Chemical differentiation, combined with deep rooting, suggests that the dissolution of bed rocks by weathering at this time was accelerated by the growth of plants. This enhanced chemical weathering would have resulted in enhanced removal of CO₂ from the atmosphere, because the net effect of silicate mineral weathering is to convert soil carbon, derived ultimately from photosynthesis, into dissolved HCO₃⁻. A representative reaction is



After formation by weathering, the dissolved HCO₃⁻ is carried to the ocean by rivers and, if accompanied by dissolved Ca²⁺ or Mg²⁺, the carbon is removed from the oceans as Ca-Mg carbonate minerals. In this way, if Ca and Mg silicates are involved in weathering, the overall process results in the removal of CO₂ from the atmosphere.

The activities of vascular plants should result in enhanced weathering and, thus, enhanced removal of atmospheric CO₂. There are several reasons for this enhancement: (i) Rootlets (plus symbiotic microflora) with high surface area secrete organic acids and chelates, which attack minerals in order to gain nutrients; (ii) organic litter decomposes to H₂CO₃ and organic acids, providing additional acid for weathering; (iii) on a regional scale, plants circulate water by means of transpiration followed by rainfall and thereby increase water-mineral contact time; and (iv) plants anchor clay-rich soil, retarding erosion and allowing the retention of water and

The author is in the Department of Geology and Geophysics, Yale University, New Haven, CT 06520-8109, USA.

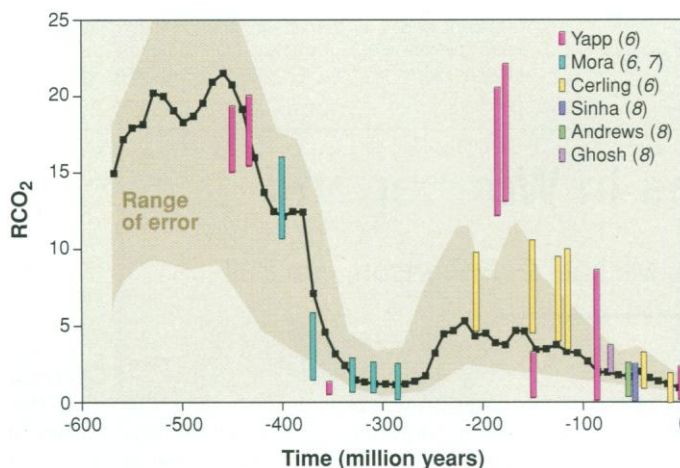
continued weathering of primary minerals between rainfall events.

It should be kept in mind that enhanced weathering by plants did not simply mean an increase in the global weathering rate. As is often misunderstood, the actual rate of CO₂ removal from the atmosphere by weathering, on a multimillion-year time scale, is not an independent parameter and must be essentially equal to the supply of CO₂ from degassing (5). Thus, an acceleration of weathering by the rise of vascular land plants in this case must have been matched by some decelerating process because there is no evidence of any equivalently large changes in the rate of degassing at this time. The decelerating process, I believe, was a drop in atmospheric CO₂. Lower CO₂, by means of the atmospheric greenhouse effect, brought about lower global temperatures and less river runoff, which had a decelerating effect on global weathering rates and helped balance the accelerating effect of the plants.

Estimates of Phanerozoic paleo-CO₂ (see figure) are a quantitative demonstration of the importance of the rise of vascular plants on the continents. An outstanding feature is the large drop in CO₂ during the Devonian (400 to 360 million years ago). Much of this drop likely was due to the spread of vascular plants to upland areas, where deep roots could bring about enhanced weathering and the development of differentiated forest soils (1). The figure summarizes all published data to date on CO₂ derived from the study of the carbon isotopic composition of paleosols. The paleosol isotopic technique has been used by a number of independent investigators (6–8), and results are in rough semiquantitative agreement, as can be seen from the figure. The paleosol method is based on (i) the determination of the ¹³C/¹²C ratio of CaCO₃ or the carbonate ion in goethite and (ii) a model for the mixing of soil CO₂, derived from organic matter decomposition, with atmospheric CO₂. It has been further tested by the analysis of the ¹³C/¹²C of soil organic matter included with calcium carbonate (7).

Also shown in the figure are the results of GEOCARB modeling (9, 10) for Phanerozoic carbon dioxide. The GEOCARB model is based on estimates of relative rates of removal of CO₂ from the atmosphere over time by means of the burial of organic matter in sediments and the weathering of Ca and Mg silicate rocks followed by the deposition of the Ca and Mg as carbonates in marine sediments. This removal is essentially balanced by the release of CO₂ back to the atmosphere

by means of the weathering of ancient organic matter in rocks plus degassing resulting from the thermal decomposition of deeply buried sedimentary carbonates and organic matter. There is semiquantitative agreement between the GEOCARB modeling and paleosol results in the general trend of CO₂ versus time. Besides the large drop during the



Atmospheric CO₂ versus time for the Phanerozoic (past 550 million years). The parameter RCO₂ is defined as the ratio of the mass of CO₂ in the atmosphere at some time in the past to that at present (with a pre-industrial value of 300 parts per million). The heavier line joining small squares represents the best estimate from GEOCARB II modeling (10), updated to have the effect of land plants on weathering introduced 380 to 350 million years ago. The shaded area encloses the approximate range of error of the modeling based on sensitivity analysis (10). Vertical bars represent independent estimates of CO₂ level based on the study of paleosols.

Devonian (which continued into the Carboniferous), there are high values in the early Paleozoic (550 to 425 million years ago), moderately high values in the Mesozoic (240 to 100 million years ago), and a general decrease from the late Cretaceous up to the present (80 to 0 million years ago). GEOCARB sensitivity analysis (10) supports Retallack's contention (1) that most of the Devonian-Carboniferous drop in CO₂ was the result of enhanced weathering and only in the later stages was it augmented by the enhanced burial of organic matter in swamps.

A recently developed independent method of paleo-CO₂ estimation, involving the determination of plant stomatal index (11), is also in good agreement with the results shown in the figure. The stomatal index data are expressed in terms of the ratio of the stomatal index of nearest living equivalents divided by that for the fossil material. Results show a high index ratio to nearest living equivalents (high CO₂) for the Early Devonian (400 to 390 million years ago), a much lower ratio (low CO₂, close to that at present) for the late Carboniferous and early Permian (310 to 285 million years ago), and intermediate ratios (intermediate CO₂) for the mid-Jurassic (≈150 million years ago).

The results shown in the figure support, on a long geologic time scale, the general correlation between climate and the level of atmospheric CO₂, as manifested by the atmospheric greenhouse effect. The large Devonian drop in CO₂ was followed by the Permo-Carboniferous glaciation, the most extensive and longest lived glaciation of the entire Phanerozoic. Also, glaciation during the late Cenozoic correlates with a lowering of atmospheric CO₂, and the high Mesozoic and early Paleozoic CO₂ levels are matched by climates that were distinctly warmer than that at present (12). [A short period of glaciation at the end of the Ordovician represents an exception, but this event has been explained by rather unique paleogeographic circumstances at this time (13).]

In the GEOCARB modeling, the calculated magnitude of the Devonian drop in CO₂ is highly sensitive to what is assumed to have been the quantitative effect of vascular plants in the acceleration of silicate weathering. The theoretical curve in the figure is a best estimate based on studies (14–16) of the role of plants in present-day weathering, where an approximately sevenfold acceleration has been determined (range 3- to 10-fold). This large measured effect by plants on weathering and CO₂ level helps to explain the agreement between theory and the results of the paleosol and stomatal index methods for Siluro-Devonian time. However, much more quantitative data on the role of plants in weathering, as well as further study of paleosols and paleobotany, is needed to better understand how the rise of upland rooted plants and their subsequent evolution (such as the angiosperms) may have affected the evolution of Earth's surface as well as the CO₂ content of the atmosphere.

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trees (in a nature preserve), and bare, partly moss-covered ground show an enhancement of weathering (by means of the release of Ca and Mg in drainage and storage in biomass) of factors varying from 5 to 10 for trees versus bare ground.

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IN VITRO EVOLUTION

Ribozymes in Wonderland

Andrew D. Ellington, Michael P. Robertson, Jim Bull

When Alice followed the White Rabbit down into Lewis Carroll's world of changing perspectives, she was confronted with edibles that made her bigger or smaller. At first, she could not generally predict whether a cake would make her shrink or a mushroom would make her as big as a house, but once she got the hang of things, she was able to change her size at will. A similar adventure comes to a happy conclusion on page 614 of this issue: Several years ago Breaker and Joyce tried to feed ribozymes and make them larger, but the diet did not take, and they grew smaller (1). Now Wright and Joyce have cleverly developed a different menu of substrates for different ribozyme diners, and this time the ribozymes grew larger (2).

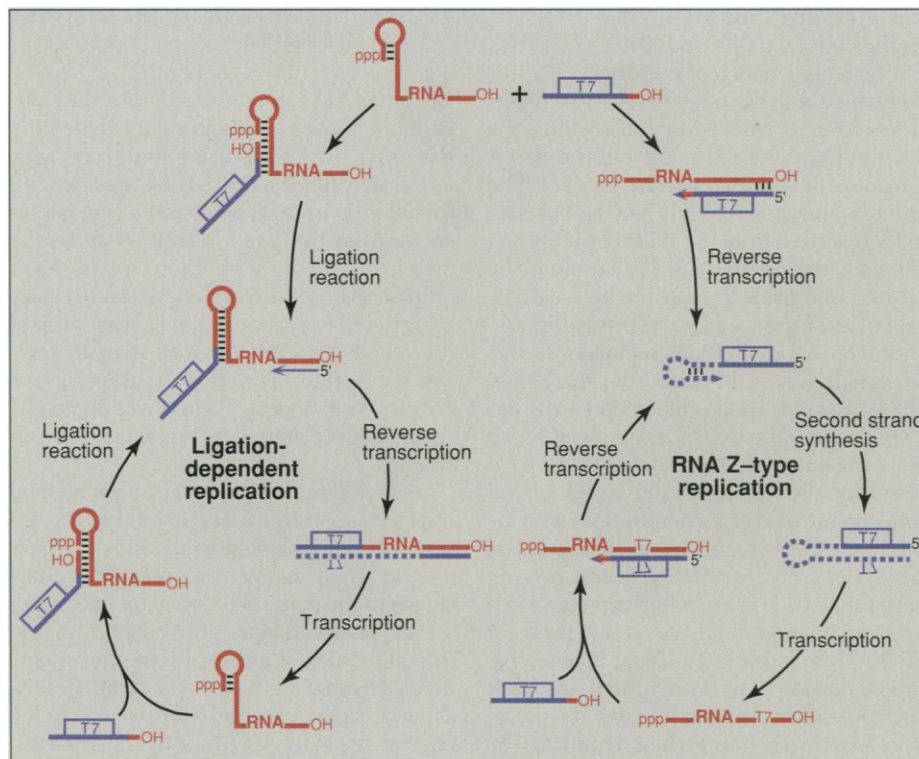
The diverse possible courses of ribozyme evolution were not initially anticipated. Breaker and Joyce (1) attempted to develop a scheme for continuous evolution in which a group II ribozyme would ligate a primer sequence to itself and thus become fodder for a retroviral-like amplification reaction (see figure). Amplification required two steps: cDNA and second-strand synthesis from the RNA ribozyme template, then transcription from this double-stranded molecule to create new, descendant ribozymes (3). The primer sequence to be ligated was chosen to carry the T7 promoter sequence, and T7 RNA polymerase was provided in the reaction mix; hence, only ligated ribozymes could be amplified. The end product of the amplification cascade should have been the original ribozyme without the primer sequence, and any variants that arose during amplification would have competed for

primer sequences in subsequent rounds of ligation and amplification. These reactions thus potentially enabled the continuous evolution of progressively better ligases.

Much to their surprise, this scheme did not evolve ligases. Within hours of starting the reaction, a short, self-replicating entity appeared that self-primed its own cDNA synthesis; a hairpin in the single-stranded DNA con-

stituted the T7 promoter site, and the RNA polymerase generated an RNA complement to the cDNA, completing the cycle. This small molecule (dubbed RNA Z) had bypassed any need for ligation to a primer sequence, and from Breaker and Joyce's perspective, was a parasite of the reaction. Alice had gotten smaller. The rapid ascendance of RNA Z in the reaction mixture thwarted the more deliberate evolution of a better ligase.

In today's report, Wright and Joyce finally got Alice to grow larger—by ligation. Because the group II ribozyme appeared unsuited to continuous evolution, Wright and Joyce chose a faster ribozyme, a ligase selected from a completely random sequence pool by Bartel and Szostak (4) and optimized for function by



An evolutionary decision. The left-hand cycle depicts the ligation-dependent replication of a ribozyme, as described in this issue (2). The right-hand cycle depicts the ligation-independent replication of a parasite, RNA Z (7). The group II intron on the right "devolved" into RNA Z in part because its initial rate of ligation was slower than the formation of RNA Z-like intermediates; the Bartel ligase on the left evolved faster and faster variants in part because its initial rate of ligation was faster than the formation of RNA Z-like intermediates.

A. D. Ellington and M. P. Robertson are in the Department of Chemistry, Indiana University, Bloomington, IN 47405, USA. E-mail: adelling@indiana.edu; J. Bull is in the Department of Zoology and the Institute for Cell and Molecular Biology, University of Texas, Austin, TX 78712-1064, USA. E-mail: bull@bull.zo.utexas.edu