

Figure 1 The dimeric capsule **1** encapsulates molecules of the proper size and shape and inhibits their reactivity. Reagent **4** and products **5a** and **6** are good guests, but the slightly larger product anilide **5b** is not. DCC, dicyclohexylcarbodiimide; DCU, dicyclohexylurea.

guest species between these environments is thus a means of controlling reactivity.

Consider the reaction of *p*-toluic acid (molecule **2a** in Fig. 1) or *p*-ethylbenzoic acid, (**2b**) with *p*-ethylaniline (**3**) and dicyclohexylcarbodiimide (DCC; **4**). When 5 mmol each of **2a** or **2b**, 10 mmol of **3** and 1 mmol of **4** are mixed at 295 K in mesitylene, the almost identical anilides **5a** and **5b** are formed at almost identical rates, together with dicyclohexylurea (**6**) and *N*-acylurea byproducts.

These initial rates are much lower in the presence of stoichiometric amounts of **1**, which encapsulates **4** and ablates its reactivity. The initial, equilibrium concentration of free **4** is too low to be seen by nuclear magnetic resonance spectroscopy, and the reaction of **2a** or **2b** with the aniline proceeds only through these trace amounts of **4** in solution. In contrast to the kinetics in the absence of **1**, the reaction of the shorter acid **2a** is now much faster than that of the longer **2b** (Fig. 2). Moreover, addition of the shorter product **5a** accelerates the initial rate of the reaction involving **2a**, but addition of the only slightly longer product anilide **5b** has no effect.

This behaviour results from feedback loops in a self-regulating reaction cycle (Fig. 2a). The urea molecule **6** and toluic anilide (**5a**) — the products of the reaction — are both good guests for the host **1** (relative binding affinities: **5a**~**6**>**4**). Once formed, the products displace DCC from the capsule into the bulk solvent, where it can react with the acid. A single molecule of DCC reacts to yield one molecule each of urea and anilide, which each displace further DCC molecules, leading to the production of more urea and anilide in a chain

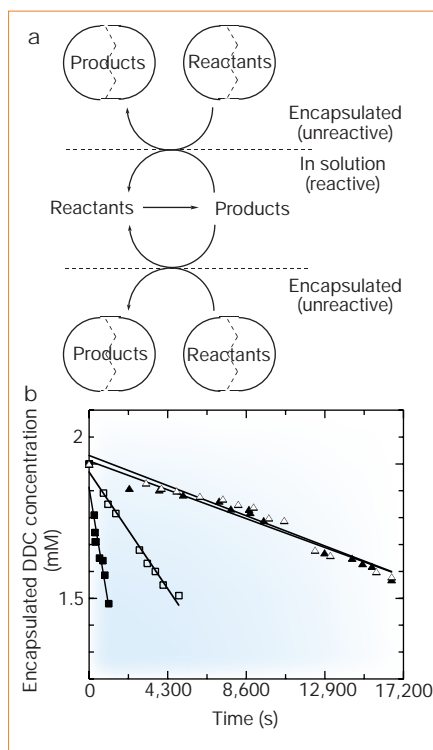


Figure 2 Reaction of compartmentalized reagents. **a**, For the reaction shown in Fig. 1, products **5a** and **6** displace reagent **4** from the capsule interior, creating a feed-forward reaction cycle. When acid **2b** is used, the slightly larger product anilide **5b** is a poor guest, and half of the reaction cycle is not operative. **b**, Dicyclohexylcarbodiimide (DCC) released from the capsule interior as a function of time for the reactions shown in Fig. 1. Initial concentrations: **4**, 2 mM; **1**, 2 mM; **3**, 10mM; **2a**, 2 mM (open squares) or 2 mM with 0.25 mM equivalents of amide **5a** (filled squares); **2b**, 2 mM (open triangles) or 2 mM with 0.25 mM equivalents of amide **5b** (filled triangles). Errors in integrations and concentrations are within 5%; straight lines are shown for guidance.

reaction. The capsule does not influence the reaction between acid and DCC — it merely limits the rate at which reagents encounter each other, giving rise to kinetics that accelerate with the increased concentration of free 'reactive' DCC.

The reaction of **4** with the very similar **2b** occurs with different kinetics because the product molecule *p,p'*-diethylbenz-anilide (**5b**) cannot fit into the capsule³. Only one good guest — the urea molecule **6** — is generated in this instance, and no further reagents are released; the kinetics are not accelerated.

This behaviour, although easily understood, is difficult to classify. The kinetics have a sigmoidal character that depends on product formation, but the reaction is not autocatalytic as it has no true catalyst. Moreover, unlike templated autocatalysis, no direct contact is required between reagents and products — an advantage in that catalyst inhibition due to self-complementary products is not an obstacle. The nonlinear kinetics are viewed more correctly as an emergent property of the system as a whole, rather than of specific

molecules within the system.

The combination of compartmentalization and molecular recognition does, however, result in chemical amplification, which is useful for increased sensitivity and self-replication. Other compartmentalized chemistry has similar potential, and product formation influences subsequent reactivity in zeolites⁴. The inherent benefits of compartmentalization are thought to be an important, if not essential, characteristic of living systems (for example, see ref. 5). As long as the relative timescales of guest exchange and reaction are appropriate, our approach can be generalized to a range of reactions and even to complex but well-defined chemical systems.

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COMMUNICATIONS ARISING

Palaeoclimatology

CO₂ and the end-Triassic mass extinction

The end of the Triassic period was marked by one of the largest and most enigmatic mass-extinction events in Earth's history¹ and, with few reliable marine geochemical records, terrestrial sediments offer an important means of deciphering environmental changes at this time. Tanner *et al.*² describe an isotopic study of Mesozoic fossil soils which suggests that the atmospheric concentration of carbon dioxide (*p*CO₂) across the Triassic–Jurassic boundary was relatively constant (within 250 p.p.m.v.), but this is inconsistent with high-resolution evidence from the stomatal characters of fossil leaves³. Here I show that the temporal resolution of the fossil-soil samples may have been inadequate for detecting a transient rise in *p*CO₂. I also show that the fossil-soil data are consistent with a large increase in *p*CO₂ across the Triassic–Jurassic boundary

when variations in the stable carbon isotope (denoted as $\delta^{13}\text{C}$) in terrestrial plant leaves are taken into account. These factors suggest that the linkage between $p\text{CO}_2$, global warming and the end-Triassic mass extinction remains intact.

The stability of the atmospheric carbon reservoir across the Triassic–Jurassic boundary is inferred from $p\text{CO}_2$ estimates derived using measurements of the $\delta^{13}\text{C}$ composition of pedogenic carbonates, ranging over 20 million years (between the Late Triassic and Early Jurassic), and a palaeosol $p\text{CO}_2$ barometer⁴. A temporal resolution of 20 million years is, however, lower than in the study of fossil leaves³ and so is unlikely to be compatible with detecting the same transient carbon-cycle event. Moreover, a well-characterized feature of the palaeosol $p\text{CO}_2$ barometer is its sensitivity, not only to the concentration of CO_2 in the soil, as acknowledged by Tanner *et al.*², but also to the isotope composition of terrestrial organic matter ($\delta^{13}\text{C}_{\text{OM}}$)^{4,5}. It is therefore necessary to measure $\delta^{13}\text{C}_{\text{OM}}$ coexisting with soil carbonates^{4,5}, but unfortunately, under the very conditions in which palaeosol carbonates form (well-drained soils from arid and semi-arid regions), soil organic matter is rarely preserved, so this feature of the method is often poorly constrained.

Tanner *et al.* calculate $p\text{CO}_2$ by applying a single $\delta^{13}\text{C}_{\text{OM}}$ value because they lacked organic materials with a stratigraphic resolution that corresponds to all of their soil samples. For the interval across the Triassic–Jurassic boundary, however, at least one land-plant stable-carbon-isotope record is available³, providing a means to account for natural variations in $\delta^{13}\text{C}_{\text{OM}}$ at this time. This negative isotopic excursion has subsequently been recorded in organic matter from the Queen Charlotte Islands in British Columbia⁶ and from St Audries Bay, UK⁷, as

well as in marine carbonates and organic matter from Hungary⁸, indicating that it could be a general geochemical fingerprint of the carbon-cycle perturbation across the Triassic–Jurassic boundary.

Calculation of palaeo- $p\text{CO}_2$ levels using the mean isotopic ratios of Triassic and Jurassic palaeosol carbonates determined by Tanner *et al.*, but constrained using stratigraphically detailed terrestrial-plant $\delta^{13}\text{C}_{\text{OM}}$ records from Jameson Land, east Greenland³, indicates a substantial increase across the Triassic–Jurassic boundary (Fig. 1a). Within the margins of uncertainty of the palaeosol approach, this increase in $p\text{CO}_2$ is consistent with the original $p\text{CO}_2$ reconstruction based on fossil stomata of *Ginkgo* cuticles³ (Fig. 1b) and equates to a rise of around 1,000 p.p.m.v. The rise is more strongly expressed if CO_2 -related global warming is allowed to influence the fractionation of soil CO_2 in the reaction-diffusion model in a manner that is consistent with theory (Fig. 1a). Both the stomatal and palaeosol reconstructions (Fig. 1) show a marked $p\text{CO}_2$ increase that is broadly coincident with the emplacement of the Central Atlantic Magmatic Province (CAMP) flood basalts⁹.

Neither the palaeosol nor the stomatal approach to estimating $p\text{CO}_2$ variations in deep time are certain, but both provide self-consistent results for the Palaeozoic⁴ era and the mass-extinction event across the Triassic–Jurassic boundary (Fig. 1). Such self-consistency argues against strongly coordinated ocean–atmosphere buffering of CO_2 from volcanic outgassing during the end of the Triassic, possibly because of the geologically short duration (about 0.5 Myr)¹⁰ and high intensity of CAMP activity. Precise dating of the proposed CO_2 excursion is critical in this context.

Moreover, it is hard to envisage a mechanism other than extreme, CO_2 -forced

global warming that can explain the widespread selective floral extinctions and turnovers that are evident in the fossil record at this time. The proposed transgressive–regressive change in sea level² would be unlikely to provoke such a marked response from the terrestrial biota. The mechanisms that drive mass extinction in the marine and terrestrial realms warrant urgent investigation in the face of the current exponential rise in the Earth's atmospheric CO_2 concentration.

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Triassic–Jurassic atmospheric CO_2 spike

question the claim by Tanner *et al.*¹ that atmospheric CO_2 levels remained constant across the Triassic–Jurassic boundary on the grounds of problems with stratigraphic completeness and contamination with atmospheric methane. Because methanogenic CH_4 has a light isotope composition and oxidizes readily to CO_2 , methane–clathrate dissociation and oxidation events cannot be detected by palaeobarometers that use the carbon-isotope composition of palaeosol carbonate.

The palaeosol isotopic data of Tanner *et al.* are not presented in the context of measured sections, nor is there any other indication of stratigraphic completeness that is suitable for identification of a transient greenhouse effect. It is therefore unsurprising that the few sampled palaeosols missed the brief CO_2 greenhouse effect inferred from the stomatal index of fossil leaves in three beds within two continuous sequences in Sweden and Greenland². The duration of the isotopic excursion that occurred at the same time as this transient CO_2 greenhouse effect was probably no more than 500,000 years³. This slim target is easy to miss when examined from a distance of 200 million years.

A more serious problem with isotopic palaeobarometers of CO_2 is the compromising effect of massive dissociation events

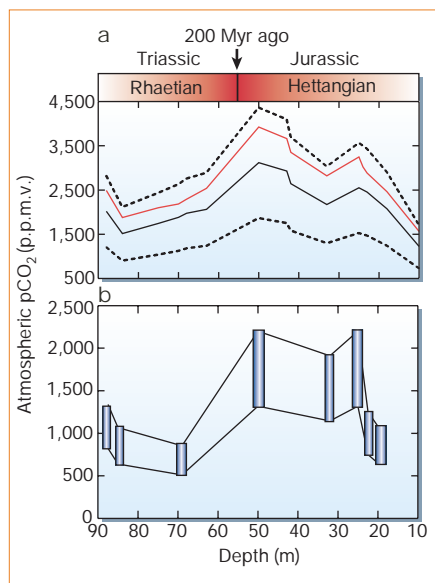


Figure 1 Palaeo-atmospheric $p\text{CO}_2$ changes across the Triassic–Jurassic boundary 208 million years ago. **a**, Atmospheric $p\text{CO}_2$ changes were calculated using the carbon-isotope composition of North American fossil soils² and land-plant organic-matter records from Jameson Land, east Greenland³, using a standard diffusion model⁵, where $S(z)$ (the concentration of CO_2 contributed by biological respiration) is 5,000 p.p.m.v. The horizontal axis represents the depth of successive fossil-plant-bearing beds of the Cape Stewart formation from Jameson Land. $p\text{CO}_2$ values were calculated using a constant Triassic palaeosol carbonate value up to the Triassic–Jurassic boundary and thereafter a constant Jurassic palaeosol value (both from ref. 2). Red line indicates the effects of CO_2 -driven global warming on the temperature dependence of soil CO_2 fractionation^{4,5}, with $S(z) = 5,000$ p.p.m.v. only. Upper and lower broken lines denote the variability in these estimates by varying $S(z)$ between 3,000 and 7,000 p.p.m.v. **b**, Atmospheric $p\text{CO}_2$ changes reconstructed from the stomatal characteristics of fossil leaves from Jameson Land³. Vertical bars denote the upper and lower range for any given depth calculated using this technique.