

markedly through stages 26 and 27, even though tourmaline was growing and extracting B from the fluid. Similarly, Cu decreased by only a factor of 40 between stages 22 and 28, even though the nonprecipitating elements show a dilution factor as high as 1300. This observation of apparent Cu and B excess is readily explained by condensation of magmatic vapor into the mixing liquids. The vapor phase of coexisting vapor and brine inclusions was found to be selectively enriched in these two elements compared with the brine. Distribution coefficients, $D = M_{\text{vapor}}/M_{\text{liquid}}$, were calculated for two sets of fluid pairs (Fig. 3). Both show a similar fractionation pattern: strongly chloride-complexed elements partition in favor of the saline liquid, whereas B and Cu partition preferentially into the vapor phase. Copper is enriched in the vapor phase by a factor up to 10, and concentration ratios of Cu to other first-row transition metals exceed the corresponding ratios in the brine by a factor of 100 to 500. High concentrations of Cu have been known from volcanic gas inclusions (24), but earlier evidence for strong metal partitioning between coexisting brine and vapor had been ambiguous (8, 25). We suggest that some copper(I) bisulfide complexes may stabilize Cu in the S-enriched vapor phase (8), in contrast to most other metals which are held in the brine by stable chloro complexes (3). The same chemical behavior would be expected for Au(I), which could be a key factor in the selective enrichment of this element with Cu and As in high sulfidation epithermal deposits.

The fluid inclusion microanalyses also constrain the physical processes of hydrothermal ore formation. Two pulses of magmatic fluid, each associated with an increase in fluid temperature and pressure, passed through the vein system before meteoric groundwater reached the site of the growing quartz crystals and caused Sn precipitation. For the observed metal concentration of up to 20 wt % Sn in the Yankee Lode to be produced, $\sim 500 \text{ m}^3$ of magmatic brine (containing $\sim 400 \text{ ppm}$ Sn) must have flowed through 1 m^3 of vein, precipitating all its dissolved Sn within this volume by mixing with $\sim 10^6 \text{ m}^3$ of meteoric water. For the two fluids to always mix at the same place for an extended period of time, a stable plumbing system is required. This may either be attained at the interface between two overlying convection cells or by mixing of magmatic fluid ascending in one vein with meteoric water penetrating from a cross-cutting vein. The latter case is consistent with the evidence that many deposits in the Mole Granite intrusion and elsewhere contain exceptionally rich ore shoots at the intersection of two fluid channelways (26).

REFERENCES AND NOTES

1. S. E. Kesler, *Mineral Resources, Economics and the Environment* (Macmillan, New York, 1994).
2. J. W. Hedenquist and J. B. Lowenstein, *Nature* **370**, 519 (1994).
3. T. M. Seward and H. L. Barnes, in *Geochemistry of Hydrothermal Ore Deposits*, H. L. Barnes, Ed. (Wiley, New York, ed. 3, 1997), pp. 435–477.
4. P. A. Candela and P. M. Piccoli, in *Magma, Fluids, and Ore Deposits*, J. F. H. Thompson, Ed. (*Short Course Series 23*, Mineral Association of Canada, Victoria, British Columbia, 1995), pp. 101–127.
5. E. Roedder and R. J. Bodnar, in (3), pp. 657–698.
6. J. Dubessy, B. Poty, C. Ramboz, *Eur. J. Mineral.* **1**, 517 (1989).
7. C. G. Ryan et al., *Nucl. Instrum. Methods Phys. Res. B* **54**, 292 (1991).
8. C. A. Heinrich, C. G. Ryan, T. P. Mernagh, P. J. Eadington, *Econ. Geol.* **87**, 1566 (1992).
9. J. A. Mavrogenes et al., *Geochim. Cosmochim. Acta* **59**, 3987 (1995).
10. T. J. Shepherd and S. R. Chenery, *ibid.*, p. 3997.
11. R. R. Loucks, J. A. Mavrogenes, W. Hibberson, *Geol. Soc. Aust. Abstr. Ser.* **41**, 258 (1996).
12. M. C. Boiron et al., *Geochim. Cosmochim. Acta* **55**, 917 (1991).
13. D. Günther, A. Audétat, R. Frischknecht, C. A. Heinrich, *J. Anal. Atom. Spectrom.*, in press.
14. P. J. Eadington, *Econ. Geol.* **78**, 1204 (1983).
15. C. A. Heinrich and C. G. Ryan, in *Water-Rock Interaction*, Y. K. Kharaka and A. S. Maest, Eds. (Balkema, Rotterdam, 1992), pp. 1583–1587.
16. R. J. Bodnar and M. O. Vityk, in *Fluid Inclusions in Minerals: Methods and Applications*, B. De Vivo and M. L. Frezzotti, Eds. (Virginia Polytechnic Institute and State Univ. Press, Blacksburg, VA, 1994), pp. 117–130.
17. R. J. Bodnar, C. W. Burnham, S. M. Sterner, *Geochim. Cosmochim. Acta* **49**, 1861 (1985).
18. J. L. Bischoff and K. S. Pitzer, *Am. J. Sci.* **289**, 217 (1989).
19. D. Günther, R. Frischknecht, C. A. Heinrich, H. J. Kahlert, *J. Anal. Atom. Spectrom.* **12**, 939 (1997).
20. J. S. Cline and R. J. Bodnar, *J. Geophys. Res.* **96**, 8113 (1991).
21. J. D. Kleeman, in *New England Geology*, P. G. Flood and B. Runnegar, Eds. (University of New England, Armidale, Australia, 1982), pp. 327–334.
22. S. S. Sun and P. J. Eadington, *Econ. Geol.* **82**, 43 (1987).
23. C. A. Heinrich, *ibid.* **85**, 457 (1990).
24. J. B. Lowenstein, G. A. Mahood, M. L. Rivers, S. R. Sutton, *Science* **252**, 1405 (1991).
25. A. H. Damman et al., *Eur. J. Mineral.* **8**, 1081 (1996).
26. C. S. J. Mulholland, in *Geology of Australian Ore Deposits*, A. B. Edwards, Ed. (Australian Institute of Mining and Metallurgy, Melbourne, 1953), vol. 1, pp. 944–949.
27. We thank U. Menet for help with the engineering and construction of the laser ablation system and the modification of the ICP-MS, R. Frischknecht who assisted us during its operation, P. Ashley, J. Stroud, and H. Henley for field support, and J. Ridley and T. Seward for reading through the manuscript and giving critical comments.

16 December 1997; accepted 13 February 1998

Siliceous Tablets in the Larval Shells of Apatitic Discinid Brachiopods

Alwyn Williams,* Maggie Cusack, James O. Buckman, Thomas Stachel

The marine bivalved Brachiopoda are abundant throughout the geological record and have apatitic (CaPO_4 -rich) or calcitic (CaCO_3 -rich) shells. Vesicles covering the larval valves of living apatitic-shelled discinids contain tablets of silica. The tablets are cemented into close-packed mosaics by spherular apatite in glycosaminoglycans. They are usually lost as vesicles degrade but leave imprints on the underlying apatitic shell. Similar imprints ornament larval surfaces of some of the earliest Paleozoic apatitic-shelled brachiopods and may also be indicators of siliceous biomineralization.

The composition of shells of living and extinct marine bivalved Brachiopoda has been regarded as apatitic (CaPO_4) or calcitic (CaCO_3) (1). The shell of the subconical mature discinid brachiopods consists of an outer chitino-proteinaceous coat (periostacum), several micrometers thick, underlain by laminar layers composed of the carbonate fluorapatite, francolite [$\text{Ca}_{10}(\text{PO}_4)_5\text{CO}_3\text{F}_{1.5}(\text{OH})_{0.5}$], and organic compounds (2). The apatite occurs as protein-coated granules, 4 to 8 nm in diameter, aggregated into spherules, 30 to 150 nm in

size, that are either compacted into laminae or further aggregated into mosaics or rods immersed in glycosaminoglycans (GAGs) (3) and supported by proteinaceous strands or mats of β -chitin (2).

In *Discinisca tenuis*, the coat secreted by the larval epidermis is preserved as a pair of circular patches, about 500 μm in diameter, at the apices of mature valves. The larval valves are delineated by a raised margin (Fig. 1A) and are covered with close-packed vesicles (4) containing biomineralized tablets (2), about 70 nm thick, which are hexagonal, rhombic, or ditetragonal in outline and virtually of constant size with major axes averaging 1.3 μm (Fig. 1, B and C). The tablets were separated from the larval shell surfaces (5) and their composition estimated by energy-dispersive x-ray (EDX) spectra on a scanning electron mi-

A. Williams and J. O. Buckman, Palaeobiology Unit, University of Glasgow, Glasgow G12 8QQ, UK.

M. Cusack, Department of Geology and Applied Geology, University of Glasgow, Glasgow G12 8QQ, UK.

T. Stachel, Institute of Mineralogy, Johann Wolfgang Goethe-University, Frankfurt D-60054, Germany.

*To whom correspondence should be addressed.

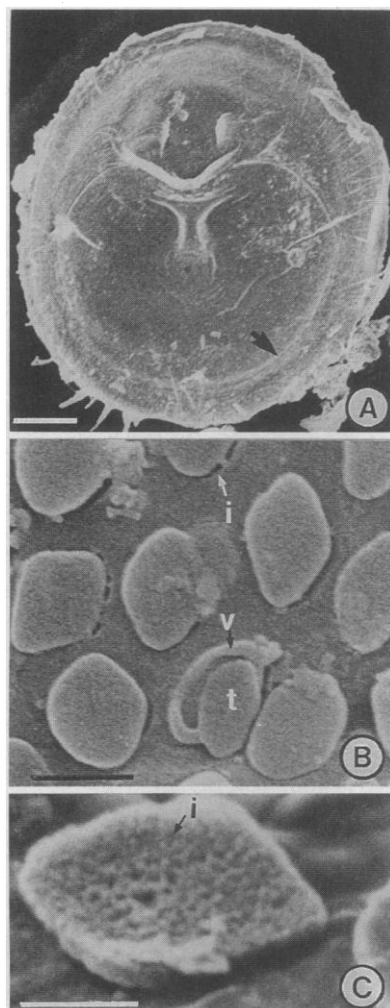


Fig. 1. (A) Ventral view of a dried young *Discinisca tenuis* Jackson. Arrow indicates the margin of the larval ventral valve. (B) Enlargement of the larval shell surface showing a ruptured vesicle (v) with a dislodged tablet (t) and the edge of an imprint (i). (C) A tablet degraded in bleach (8) showing siliceous granules and their imprints (i). Bar, 100 μm (A), 1 μm (B), and 0.5 μm (C).

croscopically (SEM) (6). The tablets showed carbon, silicon, and oxygen peaks in the EDX spectra (Fig. 2). Wavelength-dispersive mapping on an electron microprobe (7) also indicated that the tablets were enriched in silicon (Fig. 3B). From these semi-quantitative measurements, we infer that the tablets are composed of silica (SiO_2).

Vesicular covers of tablets degrade in subtilisin, chitinase, and bleach (8), all of which also expose apatitic spherules in the substrate. Thus, vesicular membranes and substrate are apparently composed of the same chitino-proteinaceous components as the periostracum and primary layer (3) of the postlarval shell. Exposed tablets were not digested by chitinase but were degraded into close-packed granules of silica in a proteinaceous matrix by subtilisin and bleach (Fig. 1C). The regular form and

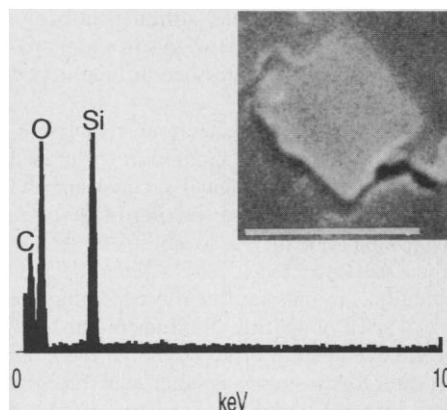


Fig. 2. EDX spectrum (full scale 300 counts) of a carbon-coated tablet in cellulose acetate (5, 6) (inset). Bar, 1 μm .

spacing of the siliceous tablets suggest that they are assembled intracellularly within vesicles (9) and exocytosed onto a bounding, chitino-proteinaceous pellicle (including vesicular coats) simultaneously with spherules of protein-coated apatite dispersed in GAGs of the primary layer (3). Membranous vesicles are fundamental to the structural organization of biogenic silica, acting as spatial restraints by imparting scalar and vectorial control on siliceous structures (9).

The larvae of living discinids are evidently encased in a shell composed of discrete tablets of silica in protein, no more than 100 nm thick (Fig. 1C) and cemented together into valvular mosaics by the outermost films of apatite and GAGs of the primary layers. Growth of such larval valves ceases with the secretion of a periostracum, which serves as a substrate for postlarval apatitic successions. The association of silica and apatite in discinid larval shells is noteworthy because silica is critical to bone formation (10) and apatite precipitates on silica gel at ambient conditions in vitro (11). Studies of biocompatible material have also revealed that bioactive glasses bind to living bone by an apatite layer formed on the surface of the glass in a tissue milieu (12). In such systems, the silanol (SiOH) groups of the silica gel have a catalytic effect on the precipitation of apatite. Hydrated silica gel, which has a high concentration of silanol groups, induces apatite formation under conditions in which pure silica glass and quartz, with low silanol contents, do not (12). The siliceous tablets may likewise induce secretion of the apatitic shell of discinid larvae before the formation of the periostracum on which the mature apatitic shell is seeded.

On dried shells, exposed tablets are normally concave externally and variably dislodged, through ruptured vesicular coats,

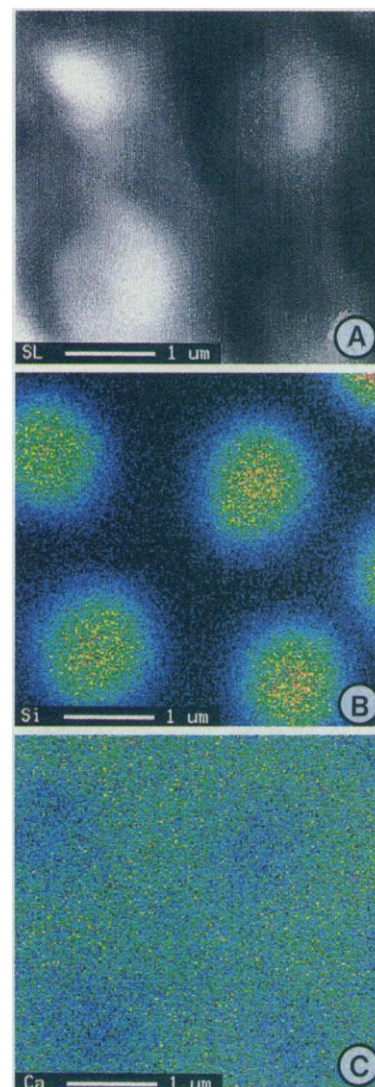


Fig. 3. (A) Secondary electron image of siliceous tablets on the gold-coated surface of the chitino-phosphatic primary layer of a larval shell of *D. tenuis*. Wavelength-dispersive maps of the same area for silicon (B) and calcium (C) with a JEOL superprobe (JXA 8900RL) on gold-coated *D. tenuis*. The concentration of elements increases from blue through green to yellow and finally red. Bar, 1 μm (A to C).

from their original sites recorded as imprints on the primary layer (Fig. 1B). Tablets are rarely preserved on the larval surfaces of adult shells because they are dissolved or drift free of their substrates as their vesicular covers degrade but leave behind their imprints. Imprints identical to those described for *D. tenuis* occur on the larval shell of *Discina striata*, whereas those of *Pelagodiscus atlanticus* are close-packed rhombohedral moulds separated by strips of apatitic substrate, about 100 nm wide (Fig. 4A).

The secretion of siliceous tablets by larvae belonging to a phylum with apatitic or calcitic mature shells could have implications for brachiopod ancestry. Such larval

valves presently appear to be a synapomorphy of post-Paleozoic discinids because tablet imprints have been found on fossil discinids but not on supposedly ancestral, Paleozoic orbiculoids (2). The larval shell of fossil discinoids, however, merits reinvestigation because imprints, which are seldom more than 50 nm deep, are commonly affected by degradation in living species and could be further obscured during fossilization. Moreover, larval shells of other early Paleozoic brachiopods with organophosphatic shells, the acrotretides (13–15) and the lingulides *Paterula* (15) and bostfordioids (16), bear imprints, ranging in size from 0.2 to over 2 μm in close-packed hexagonal arrays. These imprints have been interpreted as impressions of thickly coated vesicles (13) forming an organic cover analogous to the vesicular periostracum of terebratulids (17). There are, however, two kinds of imprints. Some, like those on bostfordioid larval shells (16), are hemispherical and could have been moulds of vesicles accumulating beneath an external pellicle. Many acrotretide imprints, however, are shallow and flat-bottomed (Fig. 4B) (4, 18, 19) and could also have been made, like those ornamenting living discinid larvae, by biomineralized, possibly siliceous, tablets. There is presently no evidence of direct descent of living discinids from this ancient

stock, and it is possible, although unlikely, that the association between silica and apatite evolved more than once in brachiopod phylogeny.

The only siliceous metazoan remains recorded from the Early Cambrian (or indeed throughout the geological record) are the intracellularly secreted spicules of sponges, suggesting that metazoan ability to secrete silica was restricted (20). However, degradable siliceous mosaics like those forming the larval shell of apatitic discinids might have been developed in other phyla but recorded on their fossils simply as superficial imprints and hitherto overlooked as indicators of biomineralization.

REFERENCES AND NOTES

1. A. Williams *et al.*, in *Introduction*, vol. 1 of *Treatise on Invertebrate Paleontology: Part H, Brachiopoda*, R. Kaesler, Ed. (Geological Society of America and Univ. of Kansas Press, New York, and Lawrence, KS, 1997).
2. A. Williams, M. Cusack, J. O. Buckman, *Philos. Trans. R. Soc. London Ser. B.*, in press.
3. Glycosaminoglycans (GAGs), formerly known as mucopolysaccharides, are the principal component of the outer primary layer of the post-larval organophosphatic brachiopod shell.
4. L. E. Holmer, *Fossils Strata* **26**, 1 (1989).
5. The larval surfaces of atmospherically dried immature dorsal valves of *D. tenuis* were irrigated with acetone. Strips of cellulose acetate film (10 μm thick) were placed on top and then peeled off, removing some biomineralized tablets.
6. The strips were carbon-coated and examined in a Cambridge 360 SEM (operating voltage = 20 kV, probe current = 132 pA).
7. Wavelength-dispersive maps for silicon and calcium were obtained by a JEOL superprobe (JXA 8900RL) on a gold-coated surface of the larval shell of *D. tenuis* (accelerating voltage = 8 kV, beam current = 6 nA, dwell time per pixel = 30 ms).
8. Dorsal valves of *D. tenuis* were incubated with the serine proteinase, subtilisin (E.C. 3.4.21.4) (2 μM) in sodium phosphate buffer (50 mM, pH 7.2), chitinase (E.C. 3.2.1.14) (1 μM) in sodium phosphate buffer (50 mM, pH 7.2), or an aqueous solution of sodium hypochlorite (bleach) (0.2% v/v) for 24 hours at 22°C. Solutions were removed and the specimens dried in a laminar-flow cabinet before gold coating for SEM study.
9. S. Mann and C. C. Perry, in *Silicon Biochemistry*, D. Evered and M. O'Connor, Eds. (Wiley, Chichester, UK, 1986), pp. 40–58.
10. W. J. Landis, D. D. Lee, J. T. Brenna, S. Chandra, G. H. Morrison, *Calcif. Tissue Int.* **38**, 52 (1986).
11. P. Li, C. Ohtsuki, T. Kokubo, K. Nakanishi, N. Soga, *J. Am. Ceram. Soc.* **75**, 2094 (1992).
12. K. Ohira *et al.*, *J. Biomed. Mater. Res.* **25**, 357 (1991).
13. G. Biernat and A. Williams, *Palaeontology* **13**, 98 (1970).
14. A. Williams and L. E. Holmer, *ibid.* **35**, 657 (1992).
15. L. Popov, J. Nölvak, L. E. Holmer, *ibid.* **37**, 627 (1994).
16. L. E. Holmer, L. E. Popov, R. Wrona, *Palaeontol. Pol.* **55**, 37 (1996).
17. A. Williams and S. MacKay, *Proc. R. Soc. London Ser. B* **202**, 191 (1978).
18. R. Ludvigsen, *Neues Jahrb. Geol. Palaeontol. Monh.* **3**, 133 (1974).
19. A. Williams and G. B. Curry, in *Brachiopods Through Time*, D. I. MacKinnon, D. E. Lee, J. D. Campbell, Eds. (Balkema, Rotterdam, 1991), pp. 133–140.
20. H. A. Lowenstam and S. Weiner, *On Biomineralization* (Oxford Univ. Press, New York, 1989), p. 324.
21. Financial support from The Royal Society of London and the Natural Environment Research Council is greatly appreciated.

2 December 1997; accepted 12 February 1998

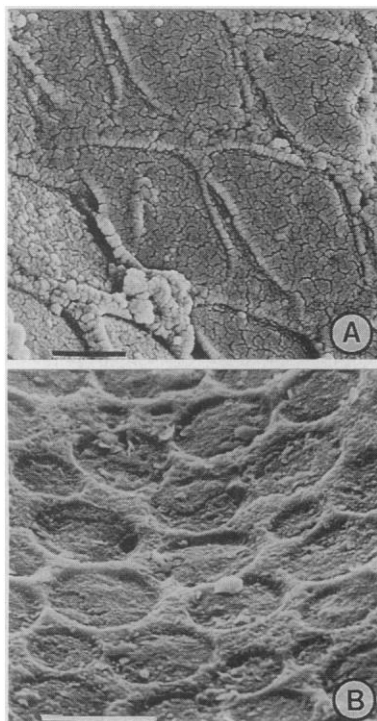


Fig. 4. Comparison of the imprints on larval shell surfaces made by (A) tablets of proteinaceous silica in living *Pelagodiscus atlanticus* (King) and (B) tablets of unknown composition in Late Cambrian *Linnarssonella girtyi* Walcott, Wilberns Formation, Texas. Bar, 0.5 μm (A) and 5 μm (B).

Anomalous Strain Accumulation in the Yucca Mountain Area, Nevada

Brian Wernicke, James L. Davis, Richard A. Bennett, Pedro Elósegui, Mark J. Abolins, Robert J. Brady, Martha A. House, Nathan A. Niemi, J. Kent Snow

Global Positioning System (GPS) surveys from 1991 to 1997 near Yucca Mountain, Nevada, indicate west-northwest crustal elongation at a rate of 1.7 ± 0.3 millimeters per year (1σ) over 34 kilometers, or 50 ± 9 nanostrain per year. Global Positioning System and trilateration surveys from 1983 to 1997 on a 14-kilometer baseline across the proposed repository site for high-level radioactive waste indicate that the crust extended by 0.7 to 0.9 ± 0.2 millimeter per year (50 to 64 ± 14 nanostrain per year), depending on the coseismic effect of the M_s 5.4 1992 Little Skull Mountain earthquake. These strain rates are at least an order of magnitude higher than would be predicted from the Quaternary volcanic and tectonic history of the area.

Strain buildup on major plate boundary fault zones appears to be relatively continuous between major earthquakes, which recur every few centuries. But is this also true of faults in more diffusely deforming intraplate settings, where recurrence intervals are several to tens of millennia? Or does strain accumulate rapidly in brief episodes,

perhaps migrating from region to region? The answer is fundamental to the physics of the earthquake cycle and for hazards assessment, but has remained elusive because of the difficulty of measuring the low strain rates characteristic of intraplate settings. Here we use GPS measurements to examine this issue near Yucca Mountain, Nevada.