

# Evidence of vanished evaporites in Neoarchaeon carbonates of South Africa

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**Abstract:** A detailed sedimentological and petrographic analysis of the Neoarchaeon Campbellrand and Malmani carbonates of South Africa provides evidence that collectively indicates the former existence of evaporites and the early replacement of primary sulphate deposits by calcite. Diagenetic disruption of sedimentary structures, solution collapse breccias, cross-cutting relationships, corrosion surfaces, pseudomorphs of displacive nucleation cones, flowage and nodular structures are all characteristic of evaporites and their ductile behaviour. In thin section, rosettes of length-slow chalcedony around the heads of the silicified stromatolites also testify to the former presence of sulphates. Calcite, in the unusual form of herringbone/flamboyant spar in 'cusped' and nodular facies, may preserve the fold shapes of enterolithic gypsum, picked out by deformed trails of degraded organic matter and dolomitized clusters of filaments. Subvertical columns of compressed organic material in a matrix of herringbone/flamboyant calcite appear to be the result of squeezing and compression between adjacent sulphate nodules. Carbonate replacement of evaporites was largely driven by bacterial sulphate reduction in sapropels and microbialites during early diagenesis. The petrographic evidence indicates that the replacive herringbone/flamboyant calcite precipitated after enterolithic and nodular structures formed, the sulphate having been used up before the enclosed organic material was totally consumed.

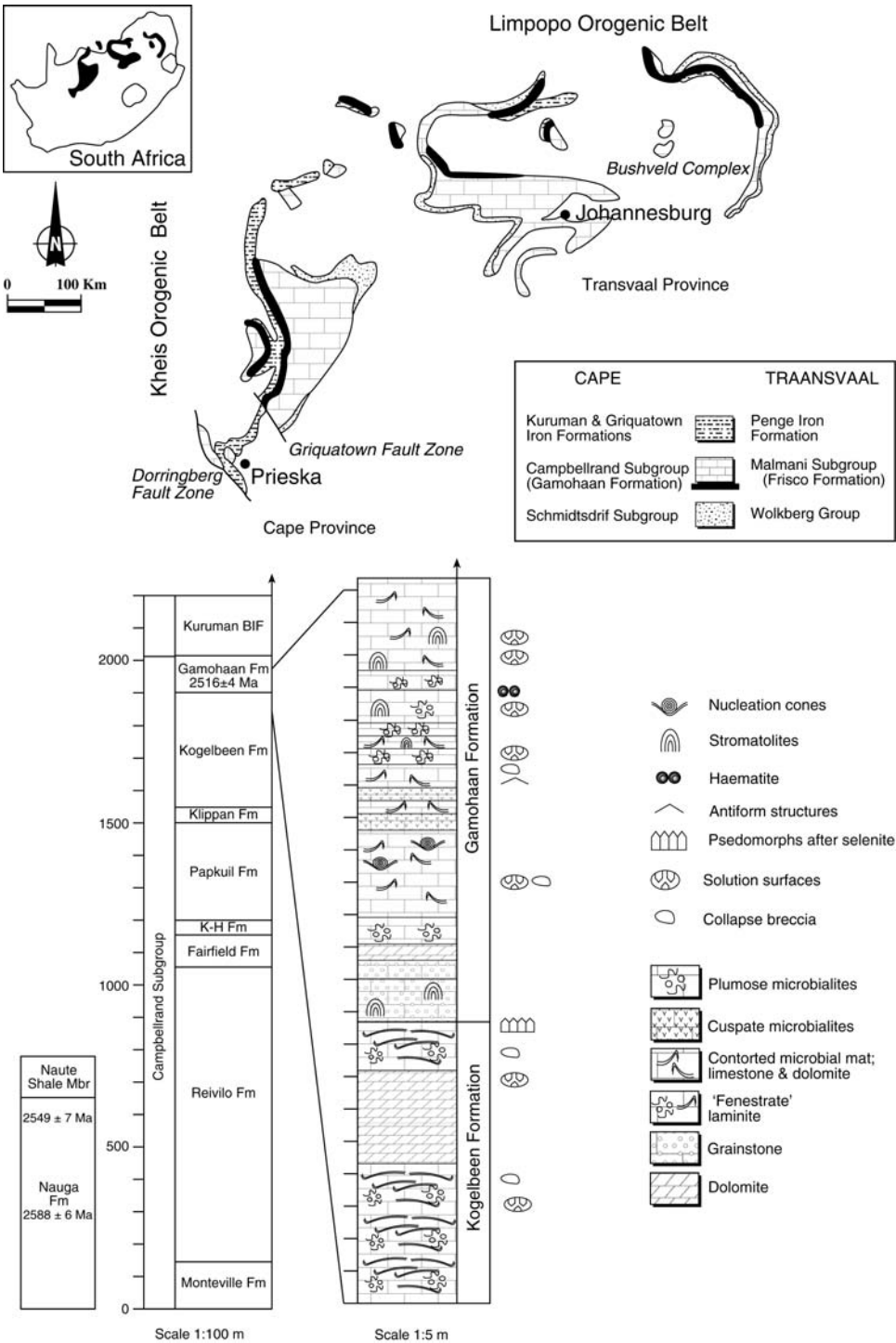
Sedimentary structures in carbonates observed by the authors in the first extensive cratonic platform that appeared in the history of the Earth, the Neoarchaeon Kaapvaal carbonate platform, are exposed in two sections (Fig. 1) at Kuruman Kop (Kogelbeen and Gamohaon Formations, Campbellrand Subgroup) and at the R36 road-cut near Echo Caves (Frisco Formation, Malmani Subgroup). These structures, as well as those illustrated from other intermediate localities and interpreted as fenestrate microbialites (Sumner 1997, 2000), show macro- and microfacies that have never been reported from the sediments of the carbonate platforms of the Phanerozoic. They are characterized by deformed and contorted fabrics that can best be explained by the presence during early diagenesis of plastic materials that suggest an evaporitic origin of the sediments. Petrographic analysis and comparison with recent, mainly Messinian, analogues, strongly support this interpretation.

Although calcite or barite pseudomorphs after sulphates have been reported from Neoarchaeon deposits of Australia and Canada (Walker *et al.* 1977; Buick & Dunlop 1990; Simonson *et al.* 1993; Aspler & Chiarenzelli 2002), researchers working in Archaeon carbonates have argued that, under an anoxic atmosphere, the  $\text{SO}_4^{2-}$  content of the oceans would be low (e.g. Walker &

Brimblecombe 1985; Canfield & Teske 1996; Habicht *et al.* 2002), and therefore large-scale precipitation of sulphates on the first carbonate platforms of the Earth history would be unlikely. However, cyanobacterial biomarkers have been recorded from Neoarchaeon sediments (e.g. Brocks *et al.* 1999), and the vast regional extent and variety of microbialites comprising the bulk of the Campbellrand carbonates represent huge populations of photosynthesising cyanobacteria, which would have pumped significant volumes of oxygen directly into the shallow epeiric seas. Under restricted conditions, sulphates could easily have precipitated. Interestingly, Melezhik *et al.* (2005) report widespread syn-depositional, marine, anhydrite-containing pseudomorphs after solid calcium sulphates from the 2100 Ma Tulomozero Formation in the SE Fennoscandian Shield, implying that Palaeoproterozoic surface waters already contained significant aqueous sulphate.

## Features suggestive of former evaporitic deposits

Many of the depositional and early diagenetic features observed in the Neoarchaeon Campbellrand/Malmani carbonate beds show fabrics that can be



**Fig. 1.** Location map of the Neoproterozoic Campbellrand and Malmani Subgroups of South Africa, together with a simplified stratigraphy of the Gamohaam and Kogelbeen Formations of the Campbellrand Subgroup at Kuruman Kop (after Sumner 1997 and the authors' fieldwork). This is the lateral equivalent of the section exposed on the R36 road-cut near Echo Caves (Frisco Formation; Malmani Subgroup).

better explained as generated by mechanical processes derived by early diagenetic deformation of original evaporitic deposits encasing or interbedded with stromatolites and organic material (Gandin *et al.* 2005) rather than related to unusual microbialites and associated supposed carbonate sea-floor cements (Sumner 1997, 2000, 2001; Sumner & Grotzinger 2000, 2004). These include solution/collapse breccias, calcite pseudomorphs after halite and probable selenite, and a variety of contorted and nodular structures which can be compared with possible analogues found in well-preserved Triassic and Messinian evaporites of the Mediterranean area. Calcite pseudomorphs after halite have been reported from Neoproterozoic carbonate or silicified deposits of Canada, Australia and South Africa (Badham & Stanworth 1977; Boulter & Glover 1986; Sumner & Grotzinger 2000).

Direct evidence of the existence of sulphate deposits is subject to interpretation, though according to Usiglio's order of precipitation of evaporitic salts, gypsum should be deposited before halite (Usiglio 1849). However, precipitation of solid sulphate is dependent on  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations, and it should also be noted that any aqueous sulphate present may have been removed by sulphate-reducing bacteria (SRB), as for example in the dolomitic lakes of the Coorong, South Australia (Wright 1999; Wright & Wacey 2005). Nevertheless observed macro and micro features can be interpreted as primary evaporitic sediments that in an early stage of diagenesis were replaced by calcite.

### Depositional components

The Kogelbeen Formation in outcrop comprises over 300 m of limestone, dolomite and chert lithologies, with abundant microbialites, oolites and laminites, and a number of doleritic intrusions (Altermann & Siegfried 1997). It is interpreted as shallow-subtidal to intertidal, with organic-rich and apparently fenestral sediments dominant in the upper part, suggesting a lagoonal facies. Coccoid and filamentous microfossils have been preserved in silicified stromatolites of the Lime Acres Member (Altermann & Schopf 1995).

The c. 2516 Ma (Altermann & Nelson 1998), 110m-thick Gamohaan Formation and its eastern equivalent (Frisco Formation, Malmani Subgroup) exposed on the R36 road-cut near Echo Caves are dominantly sapropelic, with abundant contorted microbial laminae, common dolomitic intercalations and apparently fenestral limestones (including the 'cusate' and 'plumose' microbialites of Sumner 2000). Ripple cross-laminated dolarenites occur in the lower part of the Gamohaan Formation,

with cycles of grainstones and stromatolites clearly indicating energetic shallow-water conditions. Abundant pyrite nodules occur in the middle and upper parts of the formation.

The dominant depositional facies in the surveyed sections are microbialitic plane parallel laminites and stromatolites (Figs 2a & 5a, b); granular dolomite and small stromatolites are characteristic of the lower part of the Gamohaan Formation. The early diagenetic, contorted laminites and fenestrate facies are commonly associated with grey herringbone calcite and white drusy calcite nodules (Figs 2a, 6a, e, 8e, 9a, 10a, f & 13b).

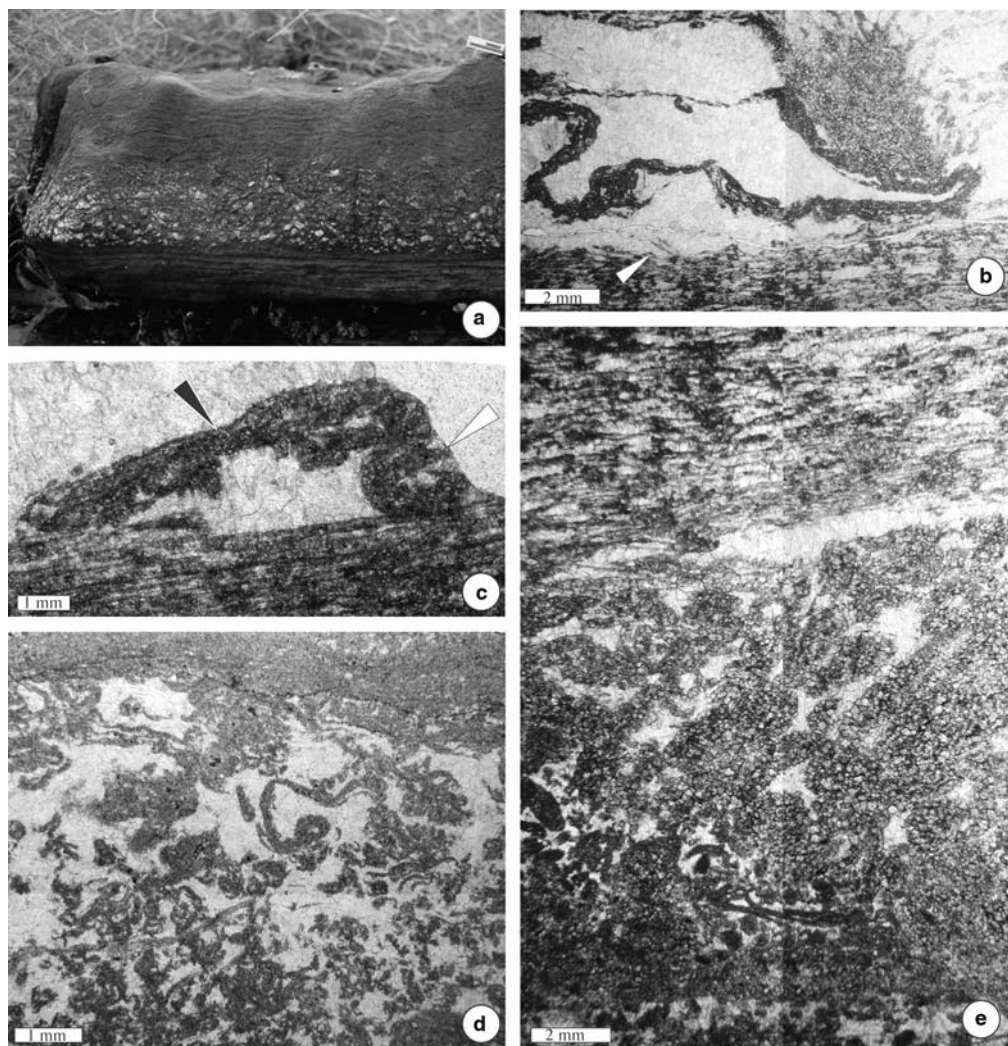
### Laminites

**Description** Laminites consist of thin, regular layers or bundles of partially degraded organic filaments forming a microbial mat, with less frequent dolomicrosparitic and granular laminae. Preserved micrite is lacking or rarely found as a thin lining of organic filaments. Centimetric, wavy or plane layers (Figs 2a–d, 6a & 14a, b) are commonly found associated with the deformed beds consisting of lenticular or contorted laminar shreds (Figs 2b–d, 3b, c, 7d, e, 11d & 12e, 14a–c) and/or rolled up ribbons (Figs 3a & 9c) enclosed in calcite spar. The contortions generally range from the micro-scale up to a few centimetres length.

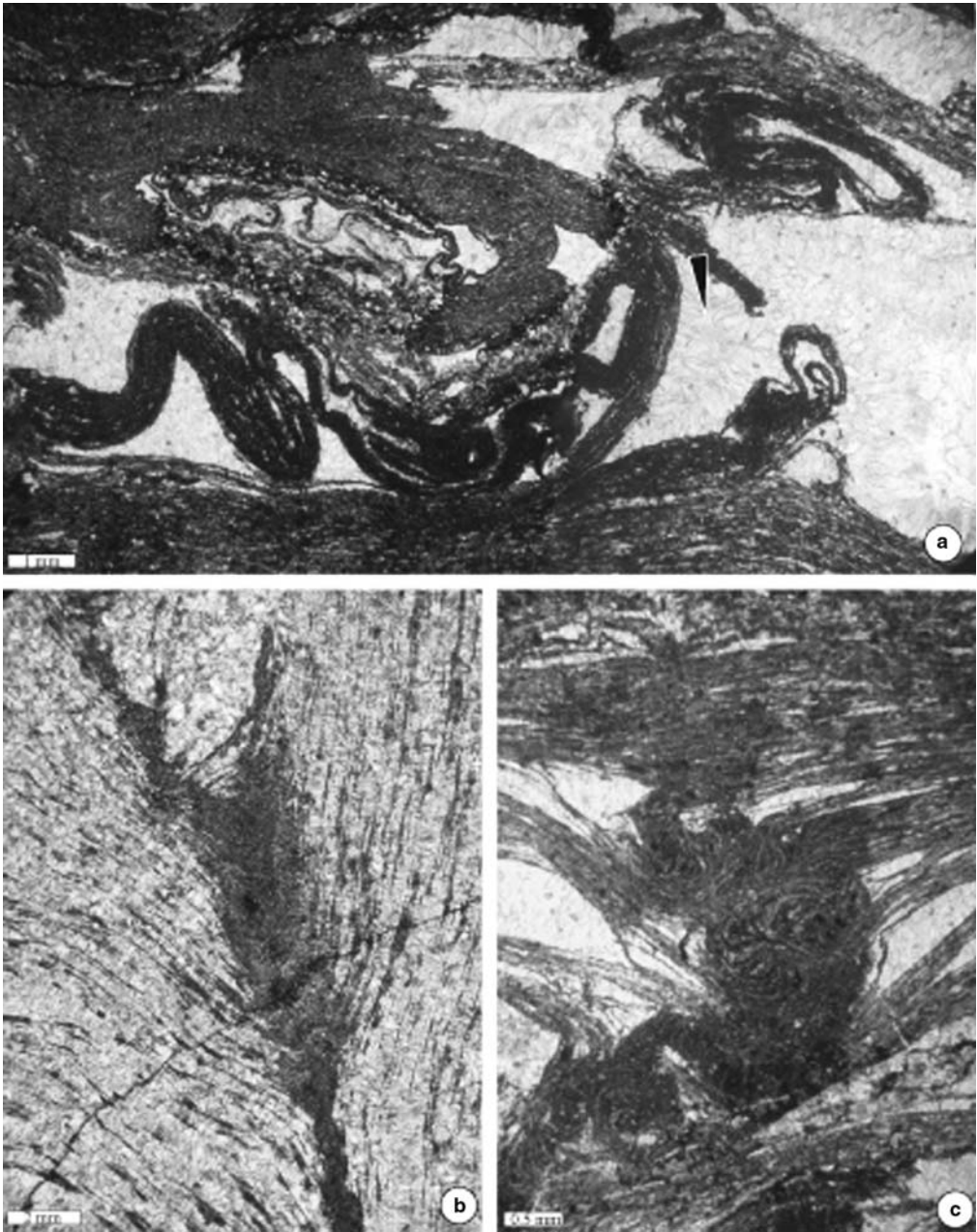
Filamentous laminites consist of microbial filament bundles 10–20  $\mu\text{m}$  thick, embedded in microcrystalline (20–60  $\mu\text{m}$ ) brick-like or lenticular hyaline calcite with undulose extinction (Figs 2b–d, & 3b). The filaments, originally tightly disposed, are locally intruded by lenses of undulose calcite that appears to push the filaments upwards (Figs 2b, c & 7d) and displaces and stretches filament bundles (Fig. 12e) in zones of strain. In contrast, bundles appear curled and crushed (Fig. 3a & c) in the zones of compression. The resulting folded, cable-like (Figs 3b & 4e) or contorted structures (Fig. 3b, c) floating in herringbone calcite (Fig. 14a, b), are commonly pervaded by selective dolomitization.

**Interpretation** The laminated filamentous fabrics, which can be compared to the laminar calcium sulphate facies in the Mediterranean Messinian basins, indicate a subtidal, organic-rich sediment, formed by bacterial films covering the basin floor. Anoxic bottom conditions in density-stratified water, associated with mineralization through organic diagenesis, would favour the preservation of the organic matter.

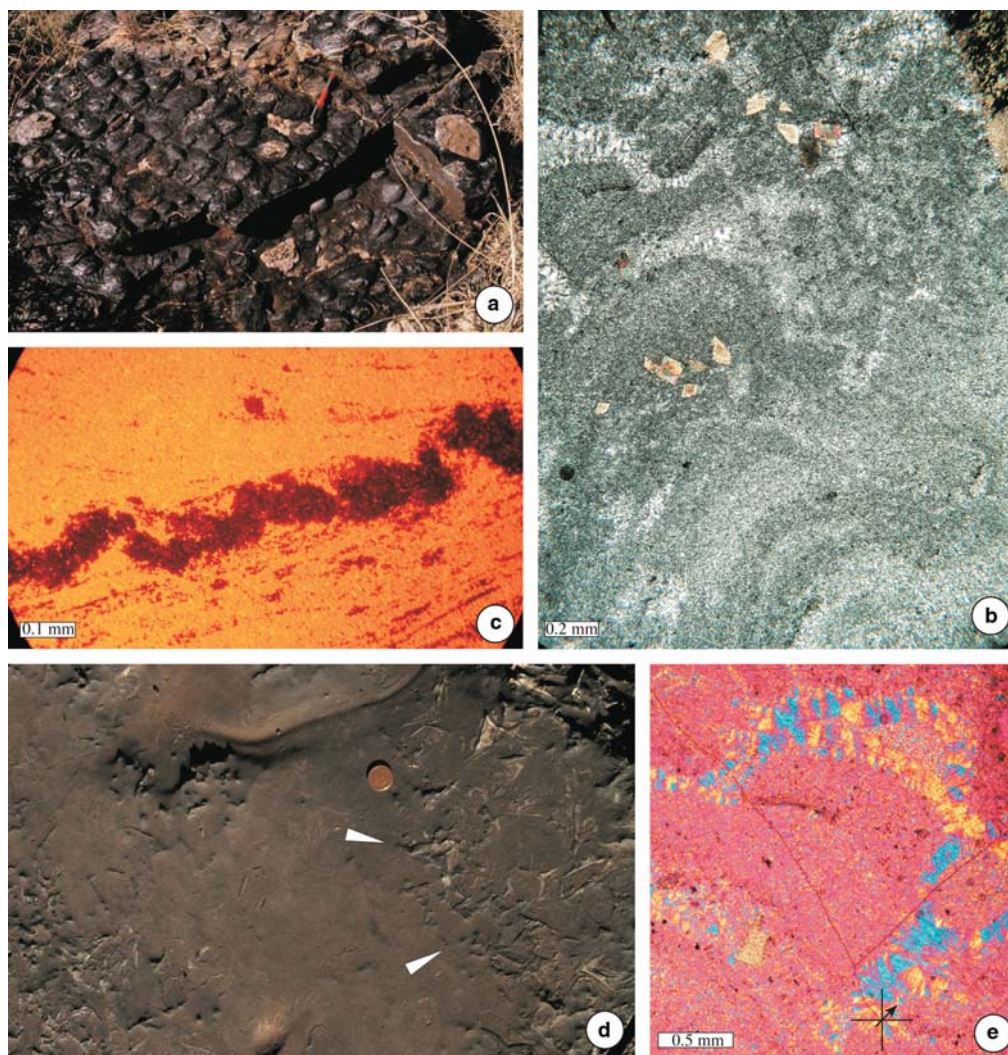
Dolomitization of the filaments appears to have been an early diagenetic process that occurred before the formation of the enclosing herringbone calcite. The scale and morphology of the contorted



**Fig. 2.** Depositional and early diagenetic features: (a) Outcrop showing calcite nodules growing within a wavy-laminated bed which overlies a planar laminite layer. The growth of the nodules tends to bend the orderly depositional arrangement of the mat (the same relationships can be observed in thin section, see (b) (sample R36; Echo Caves section). (b–e) Thin section views (photomicrographs) of the transition from a well bedded sediment to a diagenetic nodular fabric. (b) The nodular fabric consists of stacked, half moon domains of herringbone calcite bounded by more or less stretched microbial filaments which laterally converge in deformed bundles. Uplifted single filaments (with arrow) and contorted cable-like dark bundles at the transition with the filamentous mat, suggest that each filament has been pushed upwards by the growth of a ductile precursor to herringbone calcite. Growth of the nodules pushes the filaments upwards and displaces bundles of them that are folded and crushed in the zones of compression and stretched in the zones of strain. The laminite consists of layers of filamentous microbial mat overlying granular facies (b, e). The organic filaments and the poorly sorted, selectively dolomitized ooids/peloids in the lower part of the thin section, are embedded in brick-like, flamboyant calcite that fills the irregular intergranular porosity. The laminated filamentous fabrics are interpreted as representing bacterial films covering the sea floor (sample Rau 5.4; Kuruman Kop section). (c) An arched bundle of filaments partially separated from well-preserved, filamentous microbial mat. The bundle appears to have been detached and pushed upward from the planar mat, representing an early stage in the deformational process that led to the development of the nodular fabric of (a). Volume increase of the expanding material, now replaced by herringbone calcite, caused the filaments to curl/fold (white arrow) and locally to break up/be eroded (black arrow) (sample Rau 5.1.a.II; Kuruman Kop section). (d) Stromatoclasts floating in flamboyant calcite, partly replaced by a mosaic of neomorphic equant calcite. The uneven distribution of stromatoclasts ‘floating’ in calcite, and the lack of a fabric characteristic of the grainstone cements (isopachous acicular fringes and later drusy mosaic), suggest that the clasts, rather than forming a sand with grains in contact with each other, were supported in a precursor soft matrix, later replaced by herringbone calcite (sample 1A.VM; Kuruman Kop section). (e) Filamentous microbial mat overlying a granular facies (lower part of slide).



**Fig. 3.** Unusual structures embedded in herringbone calcite (all seen in thin section; plane light). **(a)** Rolled-up ribbons of filamentous laminites and partially dolomitized bundles. Discrete sets of laminae are in places pushed apart, while elsewhere they are compressed and folded together. The voids formed in the detachment zone and in the loops of the folds are filled by late stage prismatic cement (arrow). The cement grows from the herringbone/flamboyant calcite lining of the filament ribbons. This structure is interpreted as the first stage of plastic deformation driven by the volume increase of the inferred former sulphate mass interbedded in a planar filamentous laminite (sample Rau 5.1C; Kuruman Kop section). **(b)** Flower-like structure encased within the herringbone/flamboyant calcite. The structure is formed by the compression of sets of filaments which are amalgamated in a crinkled 'stem' and dolomitized at their core. The brick-like calcite interspersed with the outer, relict filaments of this peculiar structure does not show any of the features of (and has no affinity with) a marine cement precipitate (sample Rau 5.1; Kuruman Kop section). **(c)** Bundled cyanobacterial mats amalgamate to form a flower-like structure which display an evident plastic behaviour of the filaments, suggesting that the deformation process occurred when the curled bundles were still soft and supported in some way by a 'plastic matrix' probably originally represented by sulphate (sample Rau 5.1C; Kuruman Kop section).



**Fig. 4.** Silicified and dolomitized microbial sediments. (a) Small, silicified stromatolites with a flat, shallow-domed profile. (Kuruman Kop section: outcrop view). (b) Thin section photomicrographs of a silicified stromatolite replacing micrite or microcrystalline gypsum mush (cross-polarized light–XPL) (sample Rau 5.2; Kuruman Kop section). (c) Dolomitized, cable-like, crinkled ‘stem’ of a flower-like structure (see Fig. 3b) resulting from amalgamated and folded filaments. Seen under cathodoluminescence is evident that dolomitization is strictly associated with the partially degraded organic filaments (sample Rau 5.1; Kuruman Kop section). (d) Moulds with partially hollow interiors (arrows) characteristic of hopper halite crystals form a mesh with other pseudomorphs probably related to gypsum and/or celestite crystals (Kuruman Kop section). The coin in the figure is 25 mm in diameter. (e) Thin section photomicrograph showing a detail of (b): the intermound spaces are now filled with spherulitic, length-slow chalcidony. The arrow marks the direction of the *c* axis parallel to the fibres, indicative of the presence of sulphates in the silicifying fluids: XPL with  $\lambda$  (gypsum) plate.

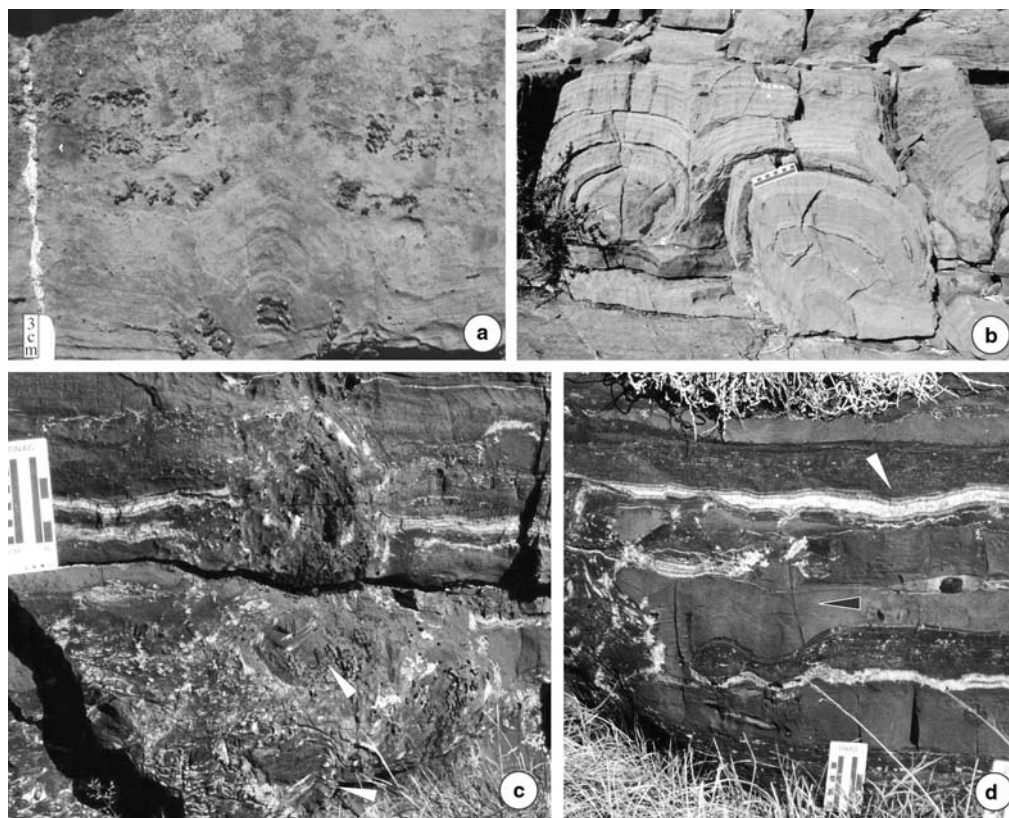
laminae, from the microscale up to a few centimetres in length, argue for *in situ* deformation caused by expansion and contraction of a ductile material, later replaced by the more brittle crystalline calcite mosaic.

The calcite occurring among the filaments displays a very compact fabric comprising brick shaped crystals with the typical undulose extinction of herring

bone calcite. It may represent the replacement of a muddy sediment or of a cement. However no evidence of an earlier cement fabric can be recognized.

### *Stromatolites*

**Description** Stromatolites varies in size from centimetric (Fig. 4a) to larger (up to 50 cm)



**Fig. 5.** Stromatolites and autoclastic breccias (outcrop photographs). (a) Stromatolites with concentrations of iron oxides, probably resulting from the alteration of early diagenetic, organic-derived pyrite (Kuruman Kop section). (b) Finely laminated stromatolites with a very smooth profile. (Kuruman Kop section). (c) Autoclastic breccia associated with a diapir-like, domal structure. Contorted and disrupted mat facies appear to have intruded, pierced and displaced overlying sediment, thinning and breaking dolomitized layers which now appear as broken, corroded rafts (Kuruman Kop section). (d) Prograding of the brecciation front from left to right: chaotic, contorted sediment encroaches on the rusty red dolomitized sediment and associated grey herringbone calcite (black arrow). Associated, planar and vertical fractures in the undeformed rock have been filled by multiple rims of white diagenetic cement (white arrow) (Kuruman Kop section).

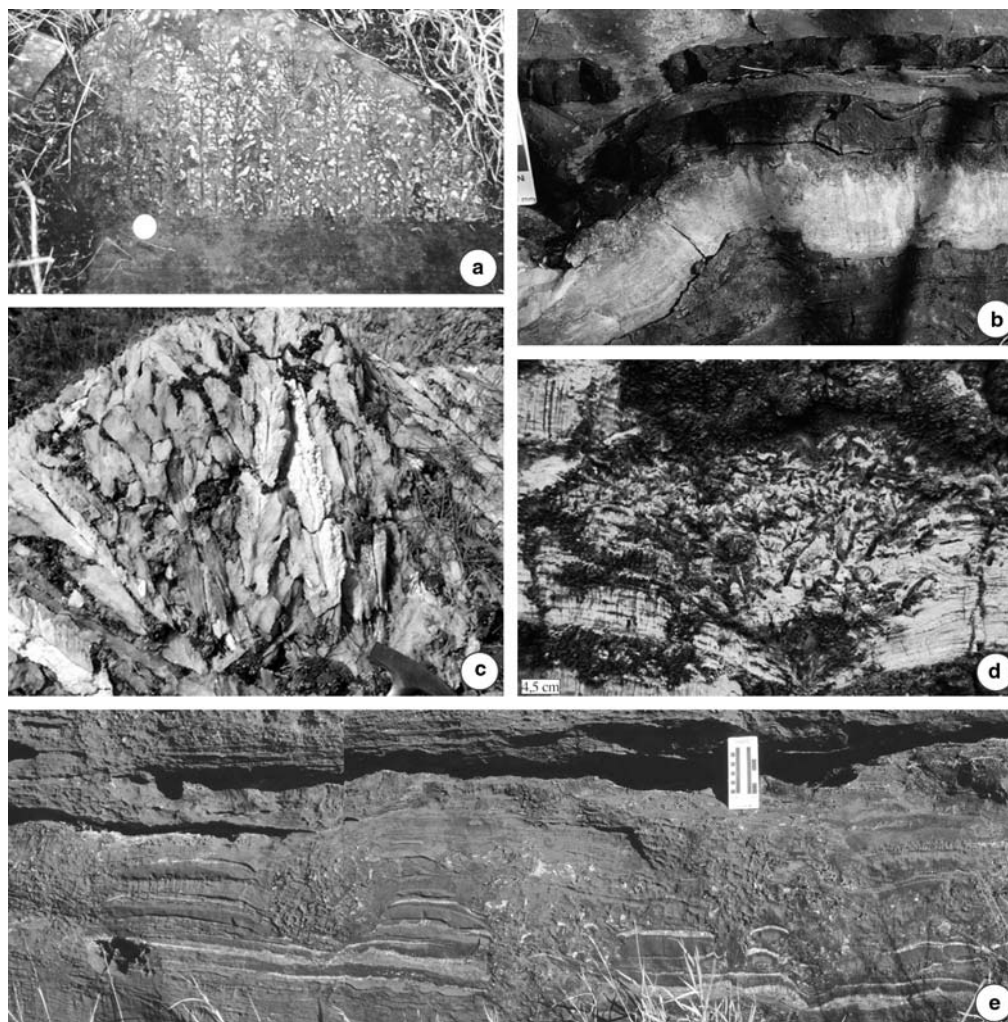
forms (Fig. 5a, b). Some are preserved by silicification (Fig. 4a) with superposed, irregular laminae (Fig. 4b) of dense, microcrystalline former primary sediment (micrite or gypsum mud). Spherulitic length-slow chalcedony is locally associated in the intermound voids (Fig. 4e).

The larger and more developed stromatolites are made from a very regular lamination similar to that of the planar laminites, and commonly exhibit a very smooth profile (Fig. 5a, b). They may be embedded in herringbone calcite and show frequent concentrations of iron oxides, often with yellowish haloes (probably hematite and sulphur after early-diagenetic pyrite) distributed along the laminae (Fig. 5a).

Smaller forms that may be interpreted either as stromatolites or incipient antiform/tepee structures

(Fig. 7e) are low-relief domes composed of thin and irregular, often broken laminae of dense microsparite alternated with thicker ones made of stromatoclasts and pyrite crystals enclosed in a fine, irregular mosaic of herringbone calcite.

**Interpretation** On the whole the stromatolite shapes and sizes suggest a very quiet, shallow-water, low-energy depositional environment, in which the dominant marine chemical precipitate was probably sulphate mush rather than carbonate micritic mud, as suggested by the presence of length-slow chalcedony in the silicified stromatolites, indicating that silicification occurred before the dissolution/disappearance of the primary sulphate.

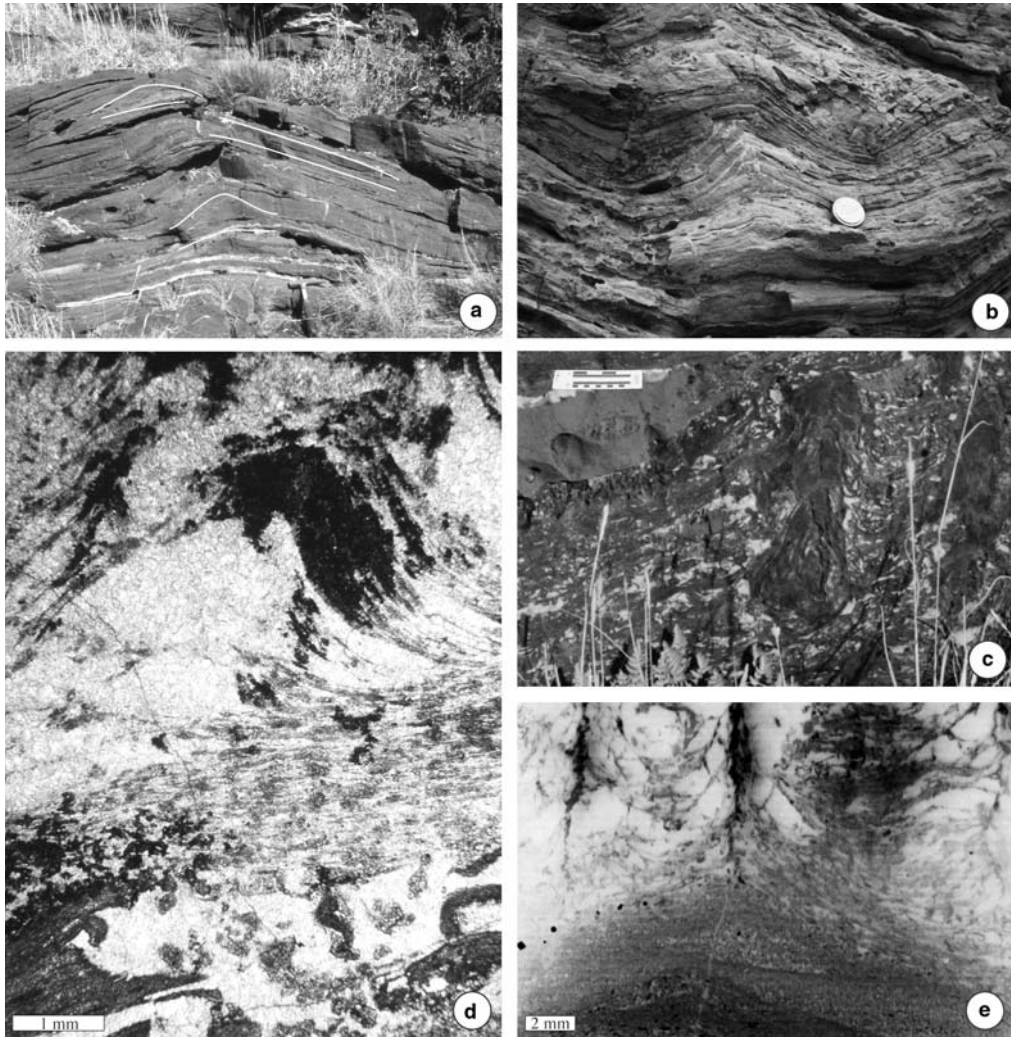


**Fig. 6.** Macroscopic structures suggesting the former presence of solid sulphate deposits. (a) Calcite nodules growing above a planar laminated layer, are disposed in a pattern reminiscent of tickets of 'grass-like', swallow-tail selenite crystals. The white calcite domains (comprising a cortex of herringbone calcite) may be interpreted as replacive after solid sulphate. They resemble nodules grown at the expenses of selenite crystal twins (see for comparison fig. 8.53 in Schreiber 1986) rather than a marine calcite cement (sample R36; Echo Caves section). The coin is 25 mm in diameter. (b) A band of white calcite formed by vertically oriented chevron-like crystals interbedded in laminated sediments, interpreted as pseudomorphs after swallow-tail selenite (Kuruman Kop section). (c) Vertically oriented swallow-tail crystals of selenite; for comparison with (a) (Montalcinello, Messinian Basin of Radicondoli, Tuscany). (d) Gypsum nucleation cone in deflected, gypsum laminites, for comparison with (e) (Messinian, Cyprus). (e) Cauliflower (cavoli) structures, comparable with the Messinian nucleation cones at Cyprus (d), have displaced laminated, soft-sediments, which are deflected downwards. (Kuruman Kop section).

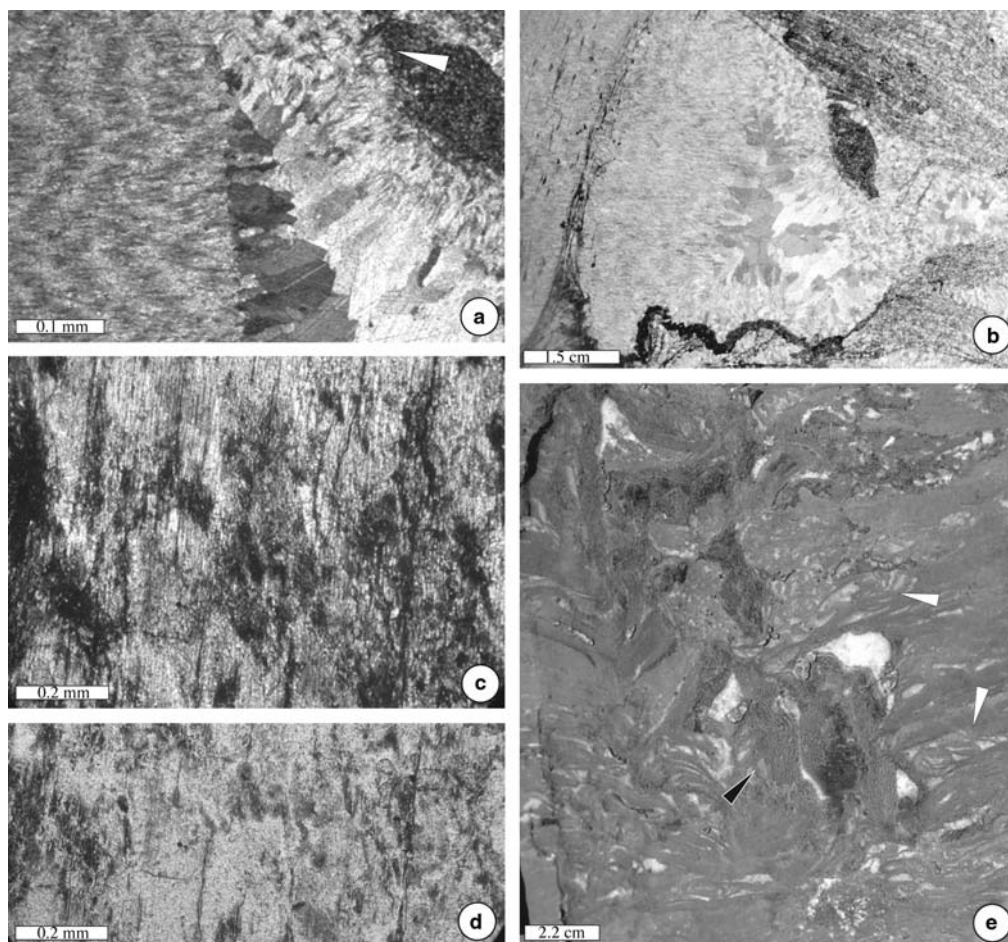
### *Granular facies*

**Description** Granular facies locally occur at the base of contorted beds as a grain supported, massive or planar laminated sediment (Fig. 2e), or associated with nodular/contorted structures. The grains are represented by rare allochems: ooids,

peloids (Fig. 2e) and more frequent stromatoclasts (Sami & James 1994) comprising microsparitic or dolomicrosparitic thin fragments and shreds derived from the fragmentation of stromatolitic material (Figs 2d, 7d & 14a, c). Most of them are selectively pervaded by dolomicrite rhombs (Fig. 2e), and the coated grains still retain



**Fig. 7.** Deformational antiform structures. (a) Antiform structure similar to a tepee (outcrop photograph): apparently originated in shallow burial conditions, as attested by the characteristic accumulation in the hinge zones (marked by white outline) of rusty-coloured, dolomitized material which evidently was deposited in between the grey beds and migrated towards the top during the deformation, and before lithification (Kuruman Kop section). (b) Diagenetic, tepee-like fold observed in carbonate beds (outcrop photograph): associated with spectacular intrastratal collapse breccias and calcite pseudomorphs after gypsum and anhydrite (not in the picture), suggests the upward-running flow, in very shallow burial conditions, of interbedded, now vanished, sulphates; for comparison with (a) (Middle Triassic, Campumari section, southern Sardinia). (c) Diapir-like, cusate structure interspersed within contorted and disrupted mat facies, appears to have expanded and displaced the overlying sediment, causing the flexible filamentous laminae to form columns while the more brittle, dolomitized layers are left floating as broken, corroded rafts (Kuruman Kop section; outcrop photograph). (d, e) Small-scale antiform structures, seen in thin section, apparently caused by the upward-running flow of plastic material, resulting in a nodular structure now of herringbone calcite. In the zones of strain, the swelling up of the nodules stretched and destroyed filaments, locally leaving relict stromatoclasts while in the zones of compression, filaments and laminae were crushed, and now appear as dark dolomitic material (d). Pyrite crystals (e) probably of early diagenetic origin, are aligned along the inclined shoulder of the antiform structure (samples Rau 24B and R36; Echo Caves).



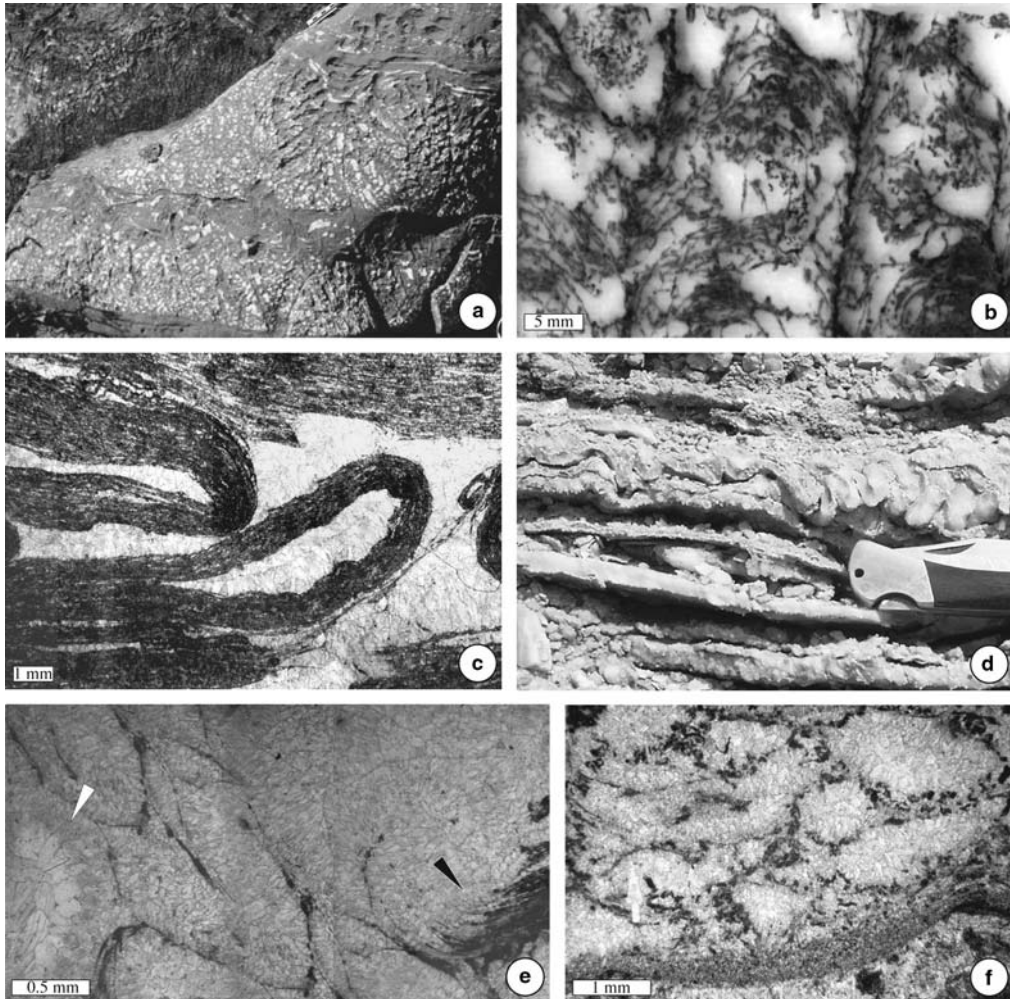
**Fig. 8.** Neoproterozoic herringbone calcite compared with the fabric of Messinian selenite crystals. (a, b) Photomicrographs showing well ordered zebra-like mosaic of herringbone calcite, associated with randomly disposed rosettes of flamboyant calcite (arrow), form the cortex of a nodule with a central cavity filled by a true geodic cement. The prismatic and equant spar, which evidently fills a primary structural cavity, is in sharp contact with herringbone calcite (a, XPL; b, PL) (sample Rau 5.1; Kuruman Kop section). (c, d) Photomicrographs of crystal aggregate texture characterized by sweeping extinction of Messinian selenite crystals (c, XPL; d, PL) (La Spicchiaiola, Volterra Basin, Tuscany). (e) Cut section showing folded rinds of herringbone calcite (black arrow) connected with partially folded/deformed filament laminites (white arrows) similar to those of Figure 3a and 9c. The hinge cavities of herringbone calcite folds are infilled with geodic cements of prismatic and equant spar (white irregular patches) (Kuruman Kop section).

relicts of calcite, consistent with a calcite origin for the ooids. They form a grain-supported fabric in which the intragranular spaces are filled by inequigranular calcite spar with undulose extinction, which does not show any of the typical features of cement either of marine or phreatic-meteoric derivation (Figs 2d, e & 7d); rather, it is always in optical continuity with the herringbone calcite of the overlying nodular facies.

**Interpretation** The allochems and part of the stromatoclasts may have been formed in a marginal site

by hydraulic erosion of poorly calcified stromatolites, with the transport of the clasts and other grains (e.g. ooids) into subtidal sapropel-mud deposits.

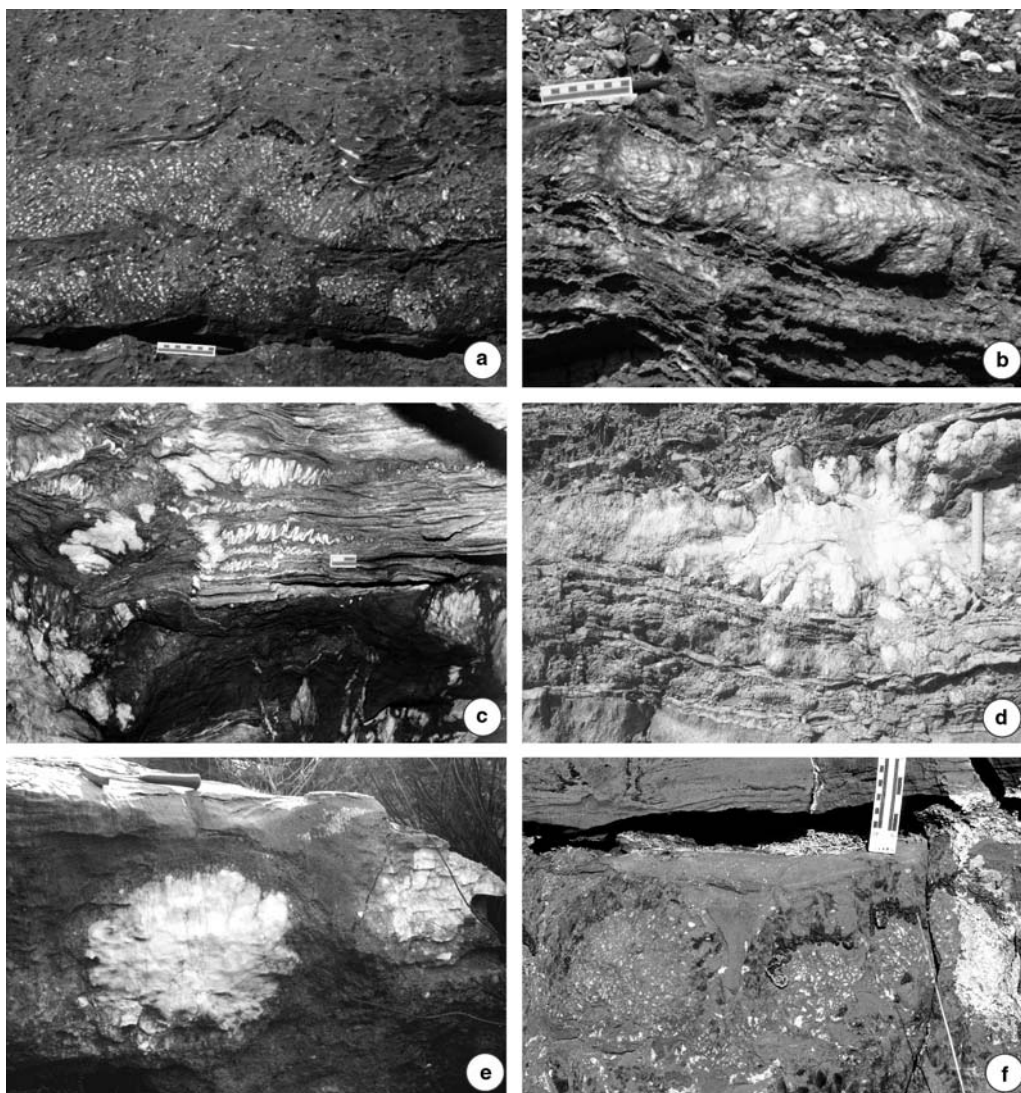
The unsorted deformed stromatoclasts associated with the nodular and contorted structures are always found as unsupported grains floating in a mosaic of herringbone calcite (Figs 2d & 14c), with no trace of isopachous cements. They clearly derive from *in situ* disruption, evidently resulting from deformation strain of the organic laminites. This very unusual wackestone-like



**Fig. 9.** Enterolithic and chicken-wire structures. (a) Outcrop section of large composite ('plumose') nodular structure with radially disposed nodules (compare with Fig. 10d), upward fading in the laminated sediment. Seen in thin section this fabric reveals the presence of assembled enterolithic folds (see Figs 9e & 12d) forming small lobate nodules (Fig. 9b) that in turn tend to coalesce into a chicken-wire fabric (Fig. 9f) (Kuruman Kop section). (b) Cut slab showing lobate nodules formed by enterolithic folds, encased in a web of compressed and contorted, relict filaments. This fabric appears to represent an early stage of deformation, when the dolomitization of the organic matter was still incomplete (samples Rau 24C & R36; Echo Caves). (c) Folded sets of dark filaments outline enterolithic-like structures in herringbone calcite. They attest to the original presence of a microbial mat displaced and destroyed by the growth of a ductile precursor, interpreted as solid sulphate. The hinge loop of the folds has been filled by diagenetic cement (sample Stop 5.1.B.II; Kuruman Kop section). (d) Enterolithic folds in Messinian gypsum. Structural voids at the hinge of the folds are at present empty or filled with residual clayey sediment. (Faltona Quarry, Tuscany). (e) Enterolithic folds made of flamboyant, subhedral sucrosic calcite, merge to form hollow subrounded bodies filled with drusy calcite cement (white arrow). Folds and nodules are bounded by relicts of dolomitized filaments (black arrow) which are also concentrated in the tightly folded hinge zones (samples Rau 24 & R36; Echo Caves). (f) Photomicrograph of chicken-wire fabric composed of nodules, made from a flamboyant, subhedral sucrosic calcite mosaic, bounded by dolomitized relict clusters of filaments (sample Rau 5.1A; Kuruman Kop section).

fabric can be interpreted by assuming that the original supporting matrix, of which no traces are now preserved, was removed and replaced by the herringbone calcite.

This interpretation is supported by the uneven distribution of the grains and the lack of pore filling cements characteristic of grainstones (isopachous acicular fringes and later drusy mosaic). The

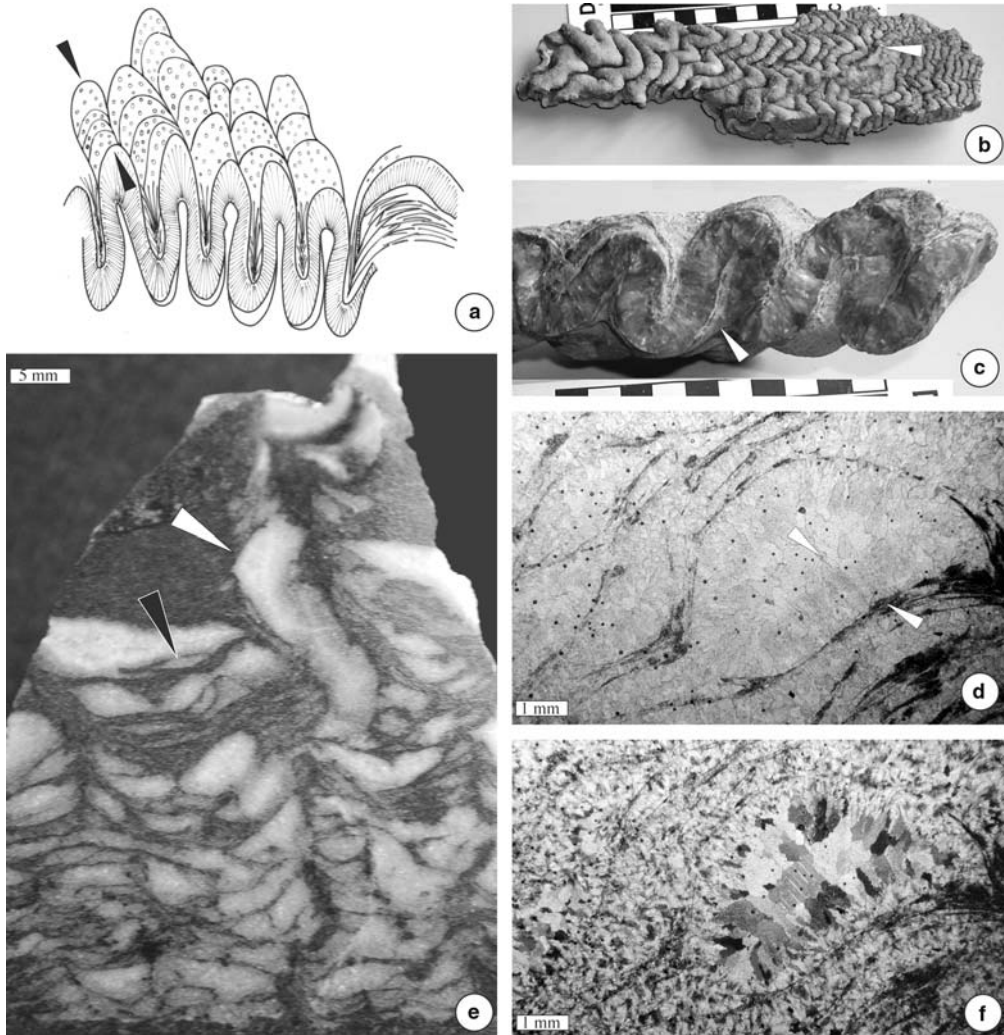


**Fig. 10.** Evolution of the enterolithic structures in nodular, half-moon and ball-like bodies. (a, b) Irregular bands of concentrated calcite nodules interbedded in partially disrupted, contorted laminar sediment (a), (Kuruman Kop section). Similar deformation of the original deposits can be observed in the Messinian gypsum. (b), (Faltona Quarry, Tuscany). (c, d) Gypsum nodules derived from the coalescence of enterolithic folds converging to form increasingly larger nodules such as that of (e). A similar trend as well as the incipient radial arrangement of the enterolithic folds can also be seen in the Neoproterozoic structures of (F) and Fig. 9a (Montalcinello Mine (c) and Faltona Quarry (d), Messinian, Tuscany. The scale bar in 1(c) is 2 cm long). (e) Photomicrograph of composite nodule of sucrosic gypsum, for comparison with (f). (Messinian, Ripaiola Quarry, Tuscany). (f) Large composite nodules rimmed by concentrations of iron oxides, interbedded with undisturbed, laminated layers (Kuruman Kop section).

embedding herringbone calcite does not therefore represent a cement, but appears to replace a matrix which was not a micritic mud, but a soft, ductile sediment; we suggest that the precursor matrix was sulphate mush.

### *Calcite mosaics*

**Description** Calcite mosaics are the dominant constituent of the deformed carbonate facies. Herringbone calcite is locally associated with prismatic and equant spar that forms drusy

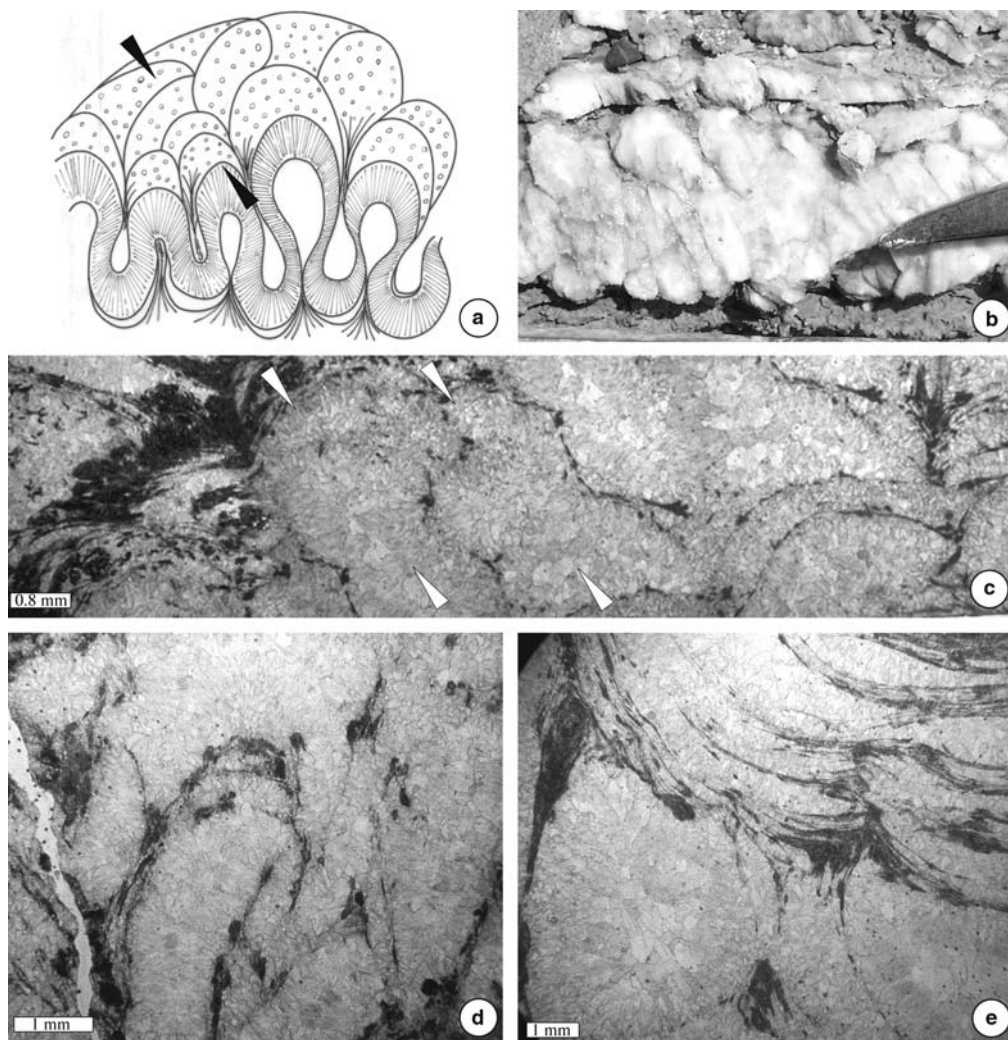


**Fig. 11.** Evolution of enterolithic folds in solid sulphate (based on Messinian gypsum examples), stage 1. (a) This sketch illustrates the first stage of deformation of a sulphate layer: folds develop as a response to volume increase, resulting from diapiric expansion of evaporites. They are made of fine, palisade-like gypsum crystals disposed normal to the edges of the ribbon (b, c). The ridge of each fold is in turn gently folded (arrows in a, and b) so that a tangential/oblique section of a folded system results in a stacked set of half-moon shaped nodules and contorted veins/funnels. These three-dimensional forms are comparable to those shown in the polished slab of an Archaean sample (e). The nodules are composed of a cortex of herringbone calcite (d) disposed normal to their edges (arrows), which outline a core, originally empty, later filled by geodic cement (f). (b, c) Hand samples from the Faltona Quarry and Montalcinello Mine, Messinian of Tuscany. (d, f) Photomicrographs of parts of sample taken at Stop 5.4A (f, XPL). Kuruman Kop section. (e) Cut sample from Rau 5.1.2; Kuruman Kop section.

infillings of large limpid crystals with normal extinction. Herringbone calcite (consisting of spherulitic calcite aggregates, Sumner & Grotzinger 1996) encloses and appears to intrude rolled up ribbons and bundles of filaments (Figs 2b, c, 3a–c & 7d, e) that locally thin out to single threads (Figs 12e & 14b). Three different, commonly

associated, mosaics formed by these spherulitic aggregates of cloudy, inclusion-rich calcite, have been identified, that often merge into each other:

- herringbone calcite *sensu stricto*, made of elongated-lenticular, crenulated crystals arranged in remarkably regular mosaics

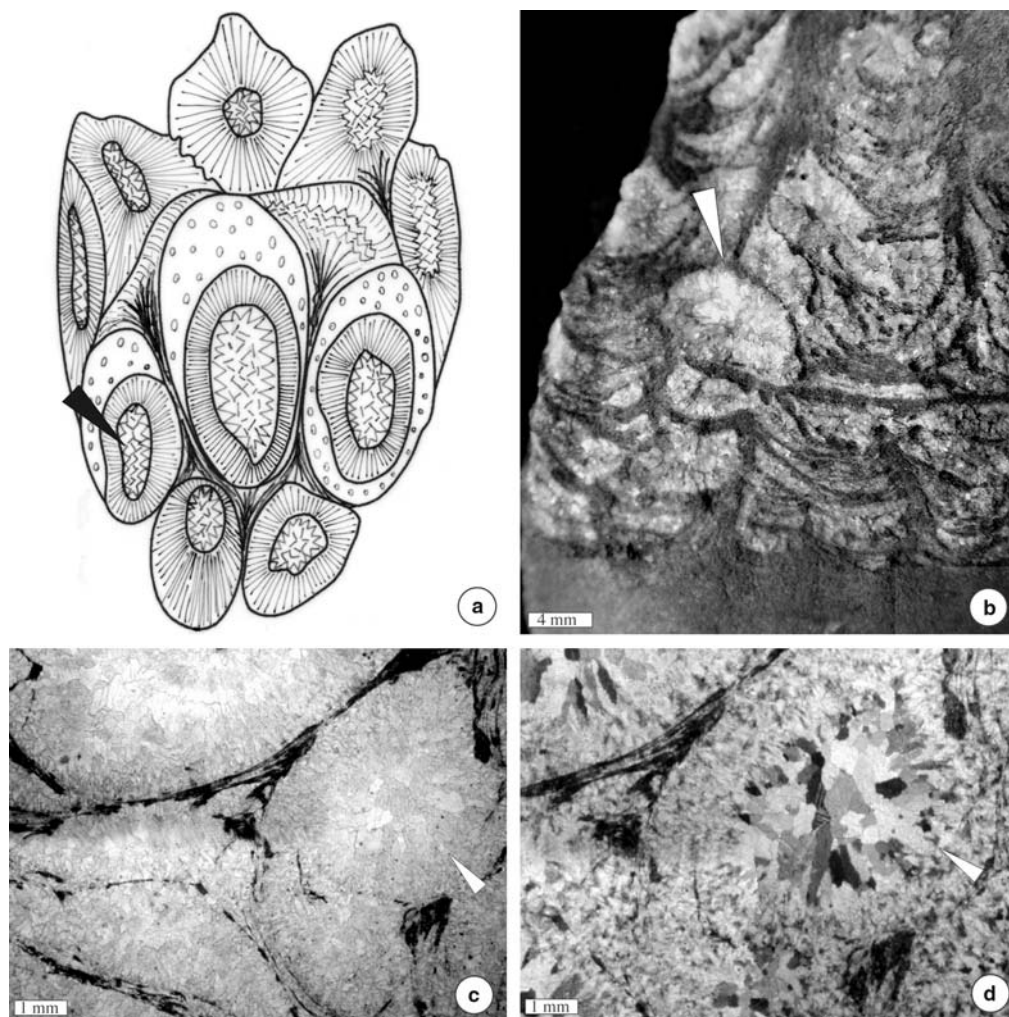


**Fig. 12.** Evolution of enterolithic folds, stage 2. Demand for space increases: as the folds swell (a, b) the microbial filaments are stretched to the point of disappearance (c–e) while every other fold is tightly squeezed (d, e) and their hinges or convergence zones entrap crushed remnants of the microbial filaments (c–e). A tangential/oblique section of the system shows chains of well-rounded nodules (c, arrows) associated with half moon ones (e). (a) Sketch of second stage development showing swelling folds. (b) Outcrop photo of sample similar to (a) from Faltona Quarry, Messinian of Tuscany. Note pick tip for scale (at right). (c) Photomicrograph of sample Rau 5.4; Kuruman Kop section. (d) Photomicrograph of samples Rau 24C; & R36 Echo Caves). (e) Photomicrograph of sample Rau 5.1; Kuruman Kop section.

- (Figs 3b & 8a, b), composed of alternating, light and dark zebra-like bands of lenticular crystals with undulose optical extinction, disposed with the long axes perpendicular to the banding;
- flamboyant calcite forming a felted fabric made of shorter, irregularly lenticular crystals randomly disposed, or rosettes with undulose extinction (Figs 8a, b, 11d, f & 13c, d);

- subhedral, sucrosic calcite with indented crystal boundaries and undulose extinction (Figs 3a, 7d & 9c, e, f). This forms a coarser mosaic, probably related to incipient later recrystallization of herringbone calcite.

The transitions from herringbone-to-flamboyant-to-herringbone fabric may be sharp or gradual,



**Fig. 13.** Evolution of enterolithic folds, stage 3. (a) Sketch of the stage 3 folds: the 'necks' are thinned and then the heads severed and isolated to form subspherical nodules. (b) Features from (a) are evident even on the weathered surface of an Archaean sample. (c, d) Thin sections (photomicrographs) clearly showing the cortex of herringbone calcite with undulose extinction, with a core filled with geodic, prismatic/equant calcite with normal extinction (arrows). Sample from stop Rau 5.4 (d, XPL). Kuruman Kop section.

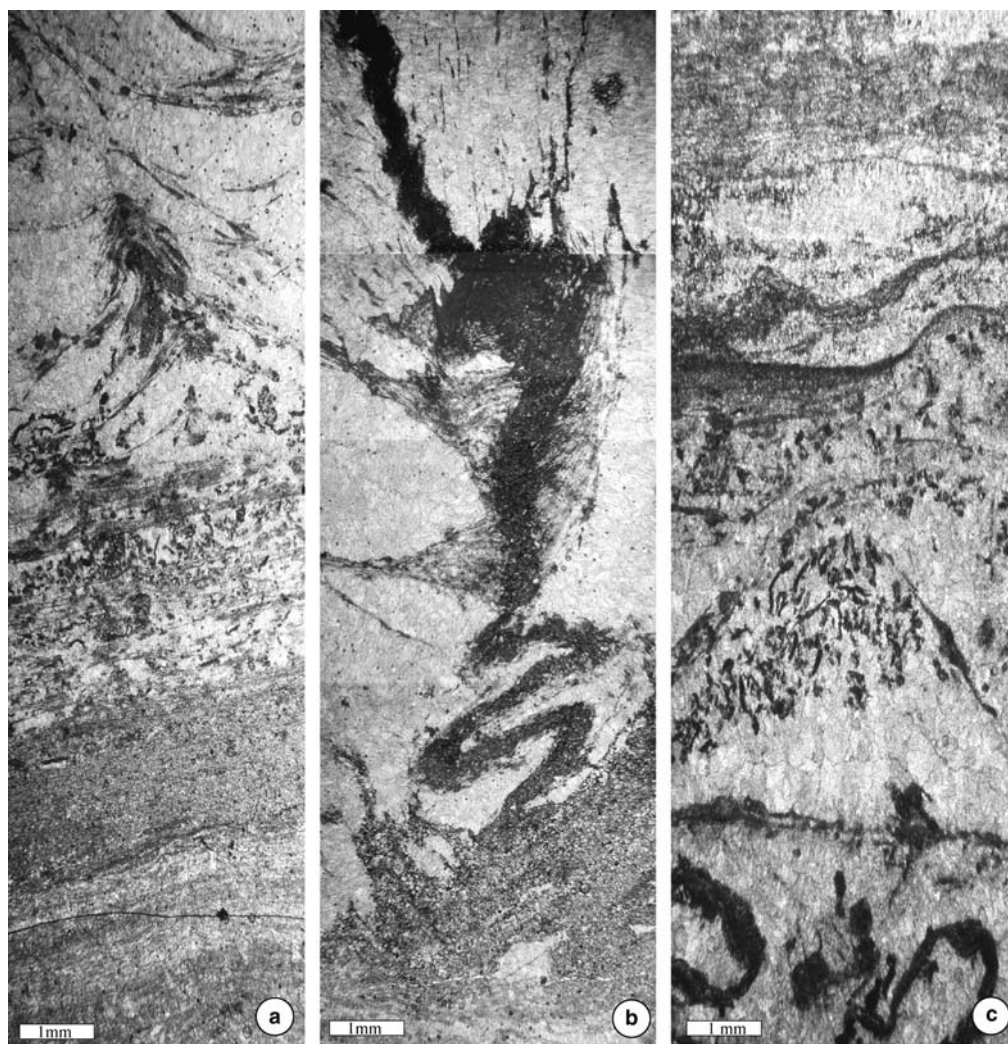
depending on the angle at which the thin section is cut through the spherulitic aggregates. This arrangement suggests that herringbone and flamboyant fabrics can be interpreted as two aspects of the same felted fabric. The tight, well-ordered mosaic (Figs 3b & 8a, b) appears where the section is cut parallel to the main orientation of the spherulitic aggregates while, where obliquely cut, the elongated crystals appear as randomly disposed flamboyant calcite (Fig. 8a, b).

This arrangement of the calcite crystals, implying an original, three-dimensional sub-spheroidal structure, with the crystals of the herringbone

fabric disposed perpendicular to the nodule walls, has been frequently found (Figs 11d–f & 13c, d).

The nodules appear to be made of a cortex of herringbone/flamboyant calcite and an empty core filled with prismatic/equant calcite (Figs 8a, b, 11d, f & 13b, d) that is in sharp contact with the herringbone and flamboyant calcite (Figs 8b, c & 9e).

**Interpretation** Herringbone/flamboyant calcite has formerly been interpreted as a cement precipitated directly on the sea floor (Sumner & Grotzinger 1996). The only true cement found in these sediments, associated with the carbonates of the



**Fig. 14.** The fate of the microbial mats: from well bedded sediment (a) to antiformal/diapiric structures (b), to contorted compressed, elongate bundles, and stromatoclasts floating in herringbone calcite (c). The genesis of such peculiar fabrics can be related to the volume increase of a ductile precursor sediment, leading to enterolithic folds and the formation of nodules which displacively disrupts the well bedded sediment, and pushes apart single or bunched filaments (a). In the zones of compression between enterolithic fold 'limbs', and at the contact of nodules, laminae are folded, crushed and dolomitized (a, b) and in the zones of strain are stretched and fragmented to form stromatoclasts (a, c). This process ends with the total effacement of the depositional signature. (a) Thin section: sample Stop 5.1.A.II; Kuruman Kop section. (b) Thin section: sample rau 5.1.2; Kuruman Kop section. (c) Thin section: sample Stop 5.1.A; Kuruman Kop section.

Gamohaan and Frisco formations, is the prismatic/equant calcite, which is commonly interpreted as a non-marine, late-diagenetic cement that is found in evident sharp contact, associated with herringbone/flamboyant crystalline rinds (Figs 8b & 13b–d). Careful observation of the crystalline mosaics of the herringbone/flamboyant calcite, and their

relationships with unmistakably sedimentary components and with true associated cement, shows that the herringbone/flamboyant calcite represents a sediment rather than a cement. A cement with this kind of crystal fabric has not been described previously, neither should it be mistaken for the distinctive crystal fabric of radial calcite (Sumner &

Grotzinger 1996) formed by large, solid prismatic crystals characterized by distally divergent subcrystals, cross-cut by convergent optic axes (Kendall 1985).

Thus, the herringbone/flamboyant calcite represents a precursor sediment, which acted as a support for the later growth of the cement. The precursor was soft sediment able to migrate within the microbial mat, displacing and deflecting (Figs 2b, c, 3a, c & 7d) the filaments and gradually growing in half-moon shaped (Figs 3c, 11d, 12c, e & 13b, c) and then subspherical bodies/nodules (Figs 8b, 12e & 13b, c).

The fabric of the herringbone/flamboyant mosaics, comprising crystal aggregates with sweeping extinction, displays morphological and mineralogical features that can be compared with the micro-flamboyant quartz described by Milliken (1979) and Arbey (1980) as replacive of sulphate (gypsum) deposits. The shape and arrangement of the nodules are reminiscent of core of originally hollow nodules [equivalent to West's (1979) 'spherical vugs'] that have been later filled by true geodic cement.

Moreover, since marine cements with this kind of undulose extinction, tight, felt fabric and thin lenticular component crystals, have never been described in the Phanerozoic and recent carbonates, and since micrite, representing the lime mud, is commonly missing, the precursor ductile sediment in which the filaments and grains were embedded is likely to have been a gypsum-mush. An alternative is anhydrite which, according to Hardie (1967) and Cody & Hull (1980), can precipitate instead of gypsum directly from more concentrated waters at temperatures lower than 50°C, in a subaqueous environment, rich in organic matter. Subaqueous sulphate associated with organic material in a sediment associated with minor carbonate can also be found in present day marginal marine salinas, sabkha and crystallizer ponds and salterns (e.g. Krumbein *et al.* 1977; Taberner *et al.* 1997; Canfield *et al.* 2004).

### Early diagenetic features

Early diagenetic processes can be recognized from the presence of selective dolomitization, moulds of evaporitic minerals, and a variety of deformational structures (Wright & Altermann 2000; Gandin *et al.* 2005), commonly occurring in planar beds associated with laminated or stromatolitic layers, and comprising antiformal structures, autoclastic solution/collapse breccias, cusped and nodular 'fenestrate' fabrics. Collapse breccias are found associated with many of the other soft-sediment deformational structures.

### Dolomitization

Dolomitization selectively affected grains and microbial filaments. Stromatoclasts, ribbons, laminae and vertical 'stems'/'supports' are commonly the site of concentration of dark/rusty, organic-rich, microdolomite rhombohedra (Figs 4c, 7d & 14a–c). Dolomitization of the grains appears to have been an early diagenetic process that occurred within the precursor matrix, before the formation of the enclosing herringbone calcite, probably linked to bacterial sulphate reduction associated with degradation of cyanobacterial filaments (Wright 1997; Wright & Altermann 2000). This is supported by the frequent occurrence of iron oxides and pyrite (e.g. Fig. 7e) of likely early diagenetic origin.

### *Pseudomorphs after evaporitic minerals and nucleation cones*

**Description** In addition to the already reported moulds of halite cubes (Simonson *et al.* 1993; Sumner & Grotzinger 2000, 2004) occasionally exposed on bed surfaces (Fig. 3d), vertically oriented calcite crystals that resemble selenite crystals (Fig. 6c) may occur either as thickets of 'grass-like' swallow-tail selenite overlying laminated sediments (Fig. 6a) or as bands of white calcite with a chevron-like structure (Fig. 6b).

Cauliform-like (cavoli) structures growing displacively in laminated or thinly bedded sediments (Fig. 6e) are comparable with Messinian nucleation cones (Fig. 6d), also called cauliflower clusters or 'sea-floor fans' (Dronkert 1976, 1985; Schreiber *et al.* 1976), consisting of crystals oriented normal and oblique to the bedding plane, and underneath their base previous existing lamination is bent and deflected while overlying laminae may also curve downwards around the cone top.

**Interpretation** The moulds with partially hollow interiors characteristic of hopper halite crystals, and associated probable gypsum and/or celestite pseudomorphs, found on the surface of a bed intercalated with other layers bearing structures evocative of sulphate deposition, suggest general evaporitic conditions and a normal evolution of the evaporative deposition of salts. In modern evaporitic sediments, chevron or swallow-tail selenite crystals typically form *in situ* on the floor or in the upper part of the bottom sediment of sabkha lagoons or of pre-evaporative salt pans, through crystallization from pore-waters and displacement of the bottom sediments. They are frequently found in the Messinian (Testa & Lugli 2000, and references therein), within finely laminated gypsum.

The cone structure which has punctured and shouldered aside adjacent underlying and overlying layers before they were lithified, and thus postdates their deposition, clearly indicates diagenetic growth and displacement within the original sediment. Brown, thin sandy beds and laminae are clearly disrupted by the growth structure, being deflected downwards and thinned as they approach the cone. The structure thus disrupts the adjacent laminae, and depresses, compresses and truncates those at and near the cone's base – clear evidence that it postdates them. Darker patches can be seen near the base of the cone, indicative of the soft brown sandy sediment being disaggregated and dispersed by the cone, with some of that sediment being incorporated within the base. The possibilities for explaining the behaviour during growth of this structure are limited, but nucleation cones (or cauliflower structures) in evaporites are known to form by expansive and displacive diagenetic growth within soft sediment. It is therefore interpreted as a formerly evaporitic nucleation cone that displaced the surrounding sediment during differential expansion of gypsum/anhydrite during its precipitation in the sediment, and which was later replaced by carbonate.

### *Antiformal structures*

**Description** Antiformal structures are observed in the upper part of the Kuruman Kop section, where they appear as incompletely developed antiform folds, fading upwards into flat undisturbed layers, lacking expansion crests and internal sediment (Fig. 7a). The fold hinge is characterized by the accumulation of yellowish, dolomitized material that evidently was deposited in between the grey beds and migrated towards the top during the deformational event. The antiform folds overlie a bed composed of large composite, plumose nodules interpreted in this paper as pseudomorphs of sulphate nodules. At the microscopic scale, small tepee-like structures are made from microsparitic or granular laminae which show a deformation growing upward and ending with the complete disruption of the upper layers (Figs 2b, c & 7d, e).

**Interpretation** The macro and micro antiform structures are different in shape and origin from true tepees, which are characterized by raised and buckled edges with geopetal infilling of vadose silt and commonly are bounded at the top by an erosional discontinuity. They are typical of the sub-aerial part of arid peritidal environments (Kendall & Warren 1987). The regularity of the Neoproterozoic deformed beds suggests a subtidal depositional setting. However, similar tepee-like features have been described in calcrete soils (Kendall &

Warren 1987) and observed in a Triassic succession of southern Sardinia (Fig. 7b), where abundant calcite pseudomorphs of gypsum and anhydrite in the carbonate beds and spectacular intrastratal collapse breccias, document and confirm the original presence of now vanished, primary evaporite intercalations (Cocozza & Gandin 1976). The process of formation of the Triassic as well as the analogous Neoproterozoic antiform folds can be interpreted as diagenetic structures formed in near surface or very shallow burial conditions, probably induced by the upward-running flow of interbedded sulphates exerting on the carbonate beds pressures sufficient to overcome the lithostatic weight of the overlying sediments (Gammon 2004).

### *Collapse breccias*

**Description** intrastratal collapse and solution breccias are commonly associated with the diapir-like cones and with planar and vertical fractures filled with multiple rims of white diagenetic cement (Fig. 5c, d). They are composed of matrix-supported sub-rounded or angular clasts of dolomite bordered by parallel, folded, stretched and buckled, sparry veins. The fine-grained, contorted and disrupted mat facies, studded with irregularly shaped sublinear calcite blebs, appear to have intruded, pierced and displaced overlying sediment, thinning and breaking dolomitized layers which now appear as broken, corroded rafts (see Alberto *et al.* 2007).

**Interpretation** The genesis of observed collapse breccias can be best explained with the gradual flow of a plastic matrix and the brittle behaviour of the formerly interbedded dolomitic layers. Similar chaotic breccias are considered as the result of diagenetic processes which led to the complete dissolution or liquefaction of the original salt and gypsum matrix and the collapse of the fragments of the brittle, carbonate intercalations (Anadón *et al.* 1992; Gandin *et al.* 2000; Kendall 2001; Rouchy *et al.* 2001). Locally in the Kuruman Kop section, the solution collapse breccias have been cemented, in proximity to a fault, by abundant white blocky spar and saddle dolomite. The occurrence of saddle dolomite (Gregg & Sibley 1984) and of slightly twinned calcite (types I and II of Burkhard 1993) suggests a rather high temperature (about 200 °C) of the localized, fault-related circulating fluids.

### *Columnar structures*

**Description** Columnar structures up to 15 cm high, interspersed within contorted and disrupted mat facies and separated by convex-down laminae (Figs 7c & 8e), appear to have pushed upwards at

various points into overlying flat laminae, so that the flexible, partially degraded organic laminae are now draped between the columns and the more brittle, dolomitized layers are left floating as broken, corroded rafts. Similar structures occur also at the microscopic scale, associated with the nodular fabric (Figs 7d, e & 14a, c).

**Interpretation** This structure provides evidence for the early diagenetic folding of originally ductile, filamentous flat layers with the formation of displacive cones which started to rise, displacing the overlying sediment. The development of these structures, and the folding and subsequent fracturing of the encasing/encased brittle layers, may be related to diapiric migration accompanying volume increase through rehydration of evaporites. Similar diagenetic disruption of the primary arrangement of the depositional layers may also have been caused by inverted density gradients within alternate sulphate, organic and carbonate beds as well as by the growth of clusters of selenite crystals.

### *Nodular 'fenestrate' fabric*

**Description** Complex structures formed by variably-sized nodules of white calcite associated with grey, herringbone calcite (Fig. 8e), arranged in more or less dense concentrations (Fig. 2a) forming irregular bands (Fig. 10a) or large composite nodular structures ('plumose', Figs 9a & 10f). The microfacies of samples taken from these apparently different structures are characterized by assemblages of white crystalline domains composed of one or more concentric bands of radially disposed spherulitic aggregates or rosette-like bunches of herringbone/flamboyant calcite. Their shapes, illustrated in Figures 3a, 7d, e, 8b, e, 9b, c, e, f, 11d–f, 12c–e & 13b–d, vary from subrounded/nodular to biconvex to half-moon, to loop-shaped (see also fig. 4a in Sumner & Grotzinger 2000). These calcite domains are encased and bounded in a web of compressed and contorted ribbons, bundles, clusters and single threads of more or less dolomitized filaments. They appear to correspond to subrounded nodules made from herringbone/flamboyant (Figs 8b, e, 9b, 11d & 13c, d) or subhedral sucrosic (Figs 3a, 9e, f & 12c–e calcite).

The herringbone/flamboyant calcite forms a cortex of needle-like acicular crystals disposed normal to the edge of the nodule, which outlines a core filled by geodic cement (Figs 3a, 8b, 9e, 11d, f, 12e & 13c, d). The nodules often occur in stacked sets of half-moon shapes (Figs 3c, 11d, e, 12d, e & 13b, c), or chains of irregularly sub-rounded domains (Fig. 12c), or display structures that can be

related to enterolithic folds (Figs 9e & 12d). The hinge zone of these folds can be tightly folded so that only relicts of the included organic filaments are preserved (Figs 9e & 12d). Alternatively, less tight folding would have created structural voids formed by the fold loops, that represent the only cavities that may have formed within such a plastic material, and that were filled by geodic prismatic and equant cements (Figs 3a, 9e, 8b, 11d, f, 12e & 13c, d). This fabric, reminiscent of the chicken-wire fabric (Figs 2a, 7d, e, 9a, b, f, 10f & 12c), is bounded by the remains of organic filaments or by thicker, dark, crinkly, cable-like (Figs 2b, 3b, 4c, 7e, 8b, 9b & 14b) structures (the 'supports' of Sumner 1997; Sumner & Grotzinger 2004) formed by tightly compressed organic filaments which at the end open in flower-like bundles of closely pressed and sometimes curled filaments (Figs 3b, c & 14b). Folded laminae of partially degraded organic material (Figs 2b, c, 3a, c, 7d, e, 9c & 14a–c), and isolated organic filaments and fragments (Figs 2d, 3b, c, 7d & 14a, c) locally appear to float in the calcite mosaic. The laminae forming the contorted mats, mainly represented by preserved remains of bundled cyanobacterial sheaths (Figs 2c & 3c), but also by dolomicrosparitic ribbons (Figs 2b, 3a, c & 9c), show no signs of compaction suggesting that mineralization occurred before any compaction could take place, but after deformation during an early diagenetic stage. The organic filaments display a plastic behaviour (Figs 2b–d, 3a–c, 7d, e, 9c, 11e & 14a–c), which demonstrates that when they were deformed, they were still soft (Klein *et al.* 1987). Uplifted single filaments and contorted cable-like dark bundles at the transition with the filamentous mat, suggest that each filament has been pushed upwards by the growth of a ductile precursor of herringbone calcite. Displacement and digestion of the parent primary sediment results from the growth of gypsum nodules, the growth of the nodules pushes the filaments upwards and displaces bundles of them that are folded and crushed in the zones of compression and stretched in the zones of strain.

**Interpretation** The deformation affecting the organic structures can be explained as derived from the radial pressure exerted by the growth of evaporite nodules, during the coalescence of enterolithic folds, and the consequent compaction of the elastic organic filaments squeezed between them.

The relationships between the laminite shreds and the calcite mosaics are very complex, however, and demonstrate that the volume increase of the calcite precursor resulted in the formation of enterolithic folds (Figs 9c, e & 10a) evolving into nodules (Figs 2a, 9a, b, f & 10a, f) and in the meantime in pushing upwards (Figs 2b, 3b, c, 7d, e, & 9a,

b) and laterally (Figs 3a & 8e) sets of laminites that were folded and crushed.

This behaviour can be related to a plastic sulphate deposit and to the pressure produced by its growth as a consequence of a probable change from anhydrite to gypsum. A concurrent factor to deformation of the laminites and the movement of the sulphate mass, may have also been the gas escaped from the decay processes (Klein *et al.* 1987) of the organic component which grew within it.

The origin of the 'dirty' dolomite may be derived from early diagenetic degradation of the cyanobacteria sheaths involved in the deformational process that caused the planar depositional organic laminae to swell, curl and break. This process was probably driven by volume increase of the sulphate matrix and consequent nodular growth, which pushed aside and compressed insoluble organic matter between adjacent nodules or the limbs of enterolithic folds.

Dolomite probably formed in association with progressive degradation of microbial sheaths located along the pressure/solution seams separating anhydrite nodules (El Tabakh *et al.* 1998; Schreiber & El Tabakh 2000). Cathodoluminescence confirms this (Fig. 4c) as the recalcitrant Mg-rich sheaths were the last element of the cyanobacteria to be degraded, when sulphate was largely exhausted.

## Discussion

The complex structures recognized in the Neoproterozoic Campbellrand and Malmani carbonates in this study, unreported from Phanerozoic calcareous platforms, can be related to deformation processes affecting a soft, ductile material that may be envisaged to have been a sulphate deposit. Contorted cusate and nodular forms have been described as 'fenestrate' fabrics and interpreted as peculiar microbial build-ups produced by organic communities supported only by precipitated carbonate under the form of herringbone calcite (Sumner 1997; Sumner & Grotzinger 2004).

They actually show structural characteristics that suggest soft-sediment deformational processes generated by volume variations, probably induced by crystal growth.

Most of these features appear strikingly similar to the nodular structures resulting from the evolution of enterolithic folds of diagenetic anhydrite growing in the modern sabkhas (Hardie & Eugster 1971) and to the diagenetic and tectonic deformational structures that can be observed in the Mediterranean Messinian evaporites (Schreiber *et al.* 1976; Schreiber 1989; Testa & Lugli 2000), such as nucleation cones/cauliflower clusters (Fig. 6c, d),

tepee-like antiforms (Fig. 7a, b), vertical diapiric flows (Fig. 7c–e) and nodular fabric (Figs 2a, 8b, e, 9a, b, f, 10, 11d–f, 12 & 13).

The sedimentological and petrographic analysis of the Neoproterozoic fabrics suggests that the early diagenetic, deformational behaviour of the precursor sediment of herringbone/flamboyant calcite, is comparable with that resulting in the nodular structures of Messinian gypsum.

Herringbone calcite, described by Sumner & Grotzinger (1996) as a marine cement, is a poorly known crystalline form of calcite so far reported only from Archean and Early/Middle Proterozoic carbonates and probably from Silurian reefal deposits of the Gaspé Basin (Sumner & Grotzinger 1996). However, the herringbone calcite cannot be a true cement, since there is no evidence that it grew from the walls of cavities. It rather appears to be the result of replacement of a primary soft and plastic sediment, with the rheological properties of sulphates. This assumption is also supported by the herringbone crystal aggregate texture, characterized by sweeping extinction (Figs 8a, b, 11f & 13d), which appears very similar to that of the Messinian gypsum selenite crystals (Fig. 8c, d) and to the felted or alabastrine textures of older evaporites (Holliday 1970) recognized also in replacive carbonates (Chafetz 1980) or in silicified evaporites (Arbey 1980).

Field relationships and petrographic analysis clearly show that herringbone calcite was contemporaneously associated with microbialites. Examination of a polished slab of a partially calcified, laminated sapropel permits the observation of herringbone calcite that has progressively replaced organic-rich sediment (Fig. 11e) (W. Altermann, pers. comm. 2004). The calcite occurs as thin stringers or isolated trains of lenses, embedded in the dark laminae and which in other parts of the slab coalesce into thicker bands of herringbone calcite. The polished slab may thus preserve a stage in the progressive replacement of an original sapropel by herringbone calcite as a result of bacterial sulphate reduction of interlayered evaporites. If carried to completion, this process would have formed a bed comprising entirely herringbone calcite, preserving no clue to its former composition, and allowing it to be interpreted (erroneously) as a chemical precipitate directly on the seafloor. Entire beds of herringbone calcite may have sequentially replaced gypsiferous sapropels and/or stratiform microbialites, and were thus not directly precipitated encrustations on the seafloor. Cathodoluminescence of the microbialitic calcite (Fig. 4c) implies an anaerobic, reducing diagenetic environment (Wright & Alterman 2000). The blocky subhedral crystals, which are found in irregular patches and nodules (Figs 3a, 7d, 9c, e, f, 12c, d & 13b) always

associated with the herringbone/flamboyant calcite, resemble the cloudy amoeboid texture of sucrosic gypsum in Messinian nodules (Testa & Lugli 2000). On the contrary the prismatic and equant calcites, which have all the characteristics of a cement, precipitated in the rare structural cavities that are commonly found in the middle of the herringbone/flamboyant mosaic (Figs 3a, 8b, e, 9e, 11d, f, 12e & 13c, d). It grows directly from the herringbone/flamboyant calcite with a rather sharp boundary, forming a geodic structure that suggests the previous existence of a structural cavity corresponding to a void in the loop left open at the fold hinge of enterolithic folds (Figs 3a, 8a, b, 11, 12 & 13) that formed in the sulphate. Volume variations involving anhydrite-to-gypsum-to anhydrite changes are commonly interpreted as driven by hydration/dehydration processes (Holliday 1970; Testa & Lugli 2000).

### Depositional and diagenetic evolution

The restricted shallow-marine basin was dominated by benthic microbial mats and stromatolites that apparently only in rare cases built their domes in a carbonate regime with the production of micrite. The main precipitate in the Campbell/Malmani carbonate beds appears to have been calcium sulphate, whereas calcite was almost absent, since no micrite matrix has been so far been detected in these sediments (Sumner 2001).

During the early phases of diagenesis the following processes can be detected:

- (1) local deformation of the original bedding due to migration of and displacement by sulphates;
- (2) probable contemporaneous formation of calcite and dolomite as a consequence of bacterial sulphate reduction, either below the sulphate reducing zone, or after the sulphate has been locally consumed;
- (3) further migration and volume increase of solid sulphate, with interbedded organic material, led to subsequent stages of deformation, giving rise to structures such as enterolithic folds, nodular gypsum, contorted laminae, nucleation cones, diagenetic tepees, and collapse breccias—all of which were preserved by progressive carbonate mineralization of the sediments.

### Discussion: gypsum to calcite

The absence of preserved evaporites in sediments of Archaean age is not unexpected (e.g. Scholle *et al.* 1992; Taberner *et al.* 1997; Hardie 2003). The major metabolic processes capable of mediating

ambient water chemistry associated with benthic microbial communities today are oxygenic photosynthesis in the living surface colonies and bacterial sulphate reduction in the underlying anoxic decaying mat. The sedimentological and petrographic data above provide credible evidence for a shallow subaqueous environment with evaporite precipitation associated with microbialitic sediments supporting widespread bacterial sulphate reduction in the Kogelbeen and Gamohaana Formations. It is known that sulphate reduction alongside iron reduction will actively drive calcite precipitation (e.g. Coleman 1985; Hendry 1993; Kowalski *et al.* 2001–2002). This is likely to have been the case in the Kogelbeen and Gamohaana depositional environments, where craton-wide cyanobacterial colonies oxidized reduced sulphur species in a largely reducing ocean, providing sulphate and supporting bacterial sulphate reduction on a regional scale. This is supported by results from sulphur isotope analyses of individual pyrite nodules from a sample of the Campbellrand carbonates (Gandin *et al.* 2005) which show a range of  $-6.2$  to  $+8.1$  per million CDT, indicating fractionation by sulphate reducing bacteria.

The petrographic evidence indicates that herringbone calcite has developed by replacing sulphate precipitates, after they began to deform and before they completely destroyed the organic material in which they originally were deposited. The shapes of the laminae between the 'supports' or 'hinges' are the result of evaporite expansion, with compression at the margins of enterolithic folds or nodules related to the diapiric migration of the sulphate, deforming originally planar laminae (Figs 2b, c, e, 3a–c & 7d, e). The lateral and upward growth of the folds and nodules also results in their final coalescence to form the chicken-wire fabric (Figs 2b, 7c & 9b, f).

Although the calcite mosaic enclosing the filaments appears very compact and no primary or dissolution porosity has been found, replacement as a process leading to the calcitization of the primary sediment is probable. Calcified evaporites are frequently cited in the literature even if the mechanism of replacement is not understood, but among other interpretations, it may have acted through bacterial sulphate reduction (Kendall 2001; Gandin *et al.* 2005) or within cyanobacterial sheaths with the production of calcite spherulites (Verrecchia *et al.* 1995).

Recent laboratory experiments suggest that potential depositional rates, biomediated carbonatogenesis, given time and abundance of bacteria (Castanier *et al.* 1999), may explain herringbone calcite production.

## Conclusions

The sedimentation in the Neoarchean Campbellrand/Malmani platform was at times represented by huge quantities of microbial filaments arranged in stromatolites, detrital laminites and sulphates. The granular sediments comprise diagenetically calcitized allochems but do not show marine cements. Diapiric movements in solid sulphates caused the development of deformational structures. Sulphates were calcified by the activity of sulphate-reducing bacteria. It is likely that replacement of evaporites occurred during early diagenesis and through the early stages of burial associated with bacterial sulphate reduction. The remaining sulphates were partly replaced by chert, partly dissolved by late diagenetic hydrothermal waters, causing the formation of collapse breccias. It is likely that the sulphates were composed of both gypsum and anhydrite formed during repeated cycles of de- and rehydration.

The data resulting from the petrographic analysis of the present carbonate Campbellrand/Malmani beds, suggest that the rarity of preserved evaporites in the Archaean/Proterozoic can be explained by the domination of the environment by microbes, especially cyanobacteria and sulphate reducers, which were able to colonize every available environment unchallenged at the time. The anoxic conditions of the degrading organic material just beneath the growing surfaces of microbial mats and stromatolites, together with evaporitic sulphate in the colonized environment, provided the perfect environment and food source for the SRB. Large-scale sulphate reduction led to large-scale carbonate precipitation and replacement.

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## References

- ALBERTO, W., CARRARO, F., GIARDINO, M. & TIRANTI, D. 2007. Genesis and evolution of 'pseudo-carniole': preliminary observations from the Susa Valley (Western Alps). In: SCHREIBER, B. C., LUGLI, S. & BABEL, M. (eds) *Evaporites Through Space and Time*. Geological Society of London, Special Publications, **285**, 129–142.
- ALTERMANN, W. & SCHOPF, J. W. 1995. Microfossils from the Neoarchean Campbell Group, Griqualand West Sequence of the Transvaal Supergroup, and their paleoenvironmental and evolutionary implications. *Precambrian Research*, **75**, 65–90.
- ALTERMANN, W. & NELSON, D. R. 1998. Sedimentation rates, basin analysis and regional correlations of three Neoarchean and Palaeoproterozoic sub-basins of the Kaapvaal craton as inferred from precise U–Pb zircon ages from volcanoclastic sediments. *Sedimentary Geology*, **120**, 225–256.
- ALTERMANN, W. & SIEGFRIED, H. P. 1997. Sedimentology and facies development of an Archean shelf–carbonate platform transition in the Kaapvaal Craton, as deduced from a deep borehole at Kathu, South Africa. *Journal of African Earth Science*, **24**, 391–410.
- ANADÓN, P., ROSELL, L. & TALBOT, M. R. 1992. Carbonate replacement of lacustrine gypsum deposits in two Neogene continental basins, eastern Spain. *Sedimentary Geology*, **78**, 201–216.
- ARBÉY, F. 1980. Les formes de la silice et l'identification des évaporites dans les formations silicifiées. *Bulletin Centre Recherche Exploration–Production Elf-Aquitaine*, **4**, 309–365.
- ASPLER, L. B. & CHIARENZELLI, J. R. 2002. Mixed siliciclastic–carbonate storm dominated ramp in a rejuvenated Palaeoproterozoic intracratonic basin: Upper Hurwitz Group, Nunavut, Canada. *International Association of Sedimentologists*, Special Publications, **33**, 293–321.
- BADHAM, J. P. N. & STANWORTH, C. W. 1977. Evaporites from the Lower Proterozoic of the East Arm, Great Slave Lake. *Nature*, **268**, 516–517.
- BOULTER, C. A. & GLOVER, J. E. 1986. Chert with relict hopper moulds from Rocklea Dome, Pilbara Craton, Western Australia: an Archaean halite-bearing evaporite. *Geology*, **14**, 128–131.
- BROCKS, J. J., LOGAN, G. A., BUICK, R. & SUMMONS, R. E. 1999. Archean molecular fossils and the early rise of eukaryotes. *Science*, **285**, 1033–1036.
- BUICK, R. & DUNLOP, J. S. R. 1990. Evaporitic sediments of early Archaean age from Warrawoona Group, North Pole, Western Australia. *Sedimentology*, **37**, 247–277.
- BURKHARD, M. 1993. Calcite twins, their geometry, appearance and significance as stress-strain markers and indicators of tectonic regime: a review. *Journal of Structural Geology*, **15**, 351–368.
- CANFIELD, D. E. & TESKE, A. 1996. Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulfur isotope studies. *Nature*, **382**, 127–132.
- CANFIELD, D. E., SØRENSEN, K. B. & OREN, A. 2004. Biogeochemistry of a gypsum-encrusted microbial ecosystem. *Geobiology*, **2**, 133–150.
- CASTANIER, S., LE MÉTAYER-LEVREL, G. & PERTHUISOT, J.-P. 1999. Ca-carbonates precipitation and limestone genesis – the microbiogeologist point of view. *Sedimentary Geology*, **126**, 9–23.
- CHAFETZ, H. S. 1980. Evidence for an arid to semi-arid climate during deposition of the Cambrian System in central Texas, U.S.A. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **30**, 83–95.
- COCOZZA, T. & GANDIN, A. 1976. Età e significato ambientale delle facies detritico-carbonatiche dell'Altopiano di Campumari (Sardegna sud-occidentale). *Bollettino della Società Geologica Italiana*, **95**, 1521–1540.

- CODY, R. D. & HULL, A. B. 1980. Experimental growth of primary anhydrite at low temperatures and water salinities. *Geology*, **8**, 505–509.
- COLEMAN, M. L. 1985. Geochemistry of diagenetic non-silicate minerals: kinetic constraints. *Transactions of the Royal Society of London*, **A315**, 39–56.
- DRONKERT, H. 1976. Late Miocene evaporites in the Sorbas basin and adjoining areas. *Memorie della Società Geologica Italiana*, **16**, 341–362.
- DRONKERT, H. 1985. *Evaporite models and sedimentology of Messinian and recent evaporites*. PhD thesis. GUA Papers of Geology, Series 1, **24**, Amsterdam.
- EL TABAKH, M., SCHREIBER, B. C., UTHA-AROON, C., COSHELL, L. & WARREN, J. K. 1998. Diagenetic origin of Basal Anhydrite in the Cretaceous Maha Sarakham salt: Khorat Plateau, NE Thailand. *Sedimentology*, **45**, 579–594.
- GAMMON, P. R. 2004. *Neoproterozoic Cap Carbonate Tepee Structures*. St Catharines 2004 Technical Program; prgammon@yahoo.com.au
- GANDIN, A., GIAMELLO, M., GUASPARRI, G., MUGNAINI, S. & SABATINI, G. 2000. The Calcare Cavernoso of the Montagnola Senese (Siena, Italy): mineralogical–petrographic and petrogenetic features. *Mineralogica et Petrographica Acta*, **43**, 271–289.
- GANDIN, A., WRIGHT, D. T. & MELEZHIK, V. 2005. Vanished evaporites and carbonate formation in the Neoproterozoic Kogelbein and Gamohaan formations of the Campbellrand Subgroup, South Africa. *Journal of African Earth Sciences*, **41**, 1–23.
- GREGG, J. M. & SIBLEY, D. F. 1984. Epigenetic dolomitization and the origin of xenotopic dolomite texture. *Journal of Sedimentary Petrology*, **54**, 908–931.
- HABICHT, K. S., GADE, M., THAMDRUP, B., BERG, P. & CANFIELD, D. E. 2002. Calibration of sulfate levels in the Archean Ocean. *Science*, **298**, 2372–2374.
- HARDIE, L. A. 1967. The gypsum–anhydrite equilibrium at one atmosphere pressure. *American Mineralogist*, **52**, 171–200.
- HARDIE, L. A. 2003. Secular variations in Precambrian seawater chemistry and the timing of Precambrian aragonite seas and calcite seas. *Geology*, **31**, 785–788.
- HARDIE, L. A. & EUGSTER, H. P. 1971. The depositional environment of marine evaporites: a case for shallow, clastic accumulation. *Sedimentology*, **16**, 187–220.
- HENDRY, J. P. 1993. Calcite cementation during bacterial manganese, iron and sulfate reduction in Jurassic shallow marine carbonates. *Sedimentology*, **40**, 87–106.
- HOLLIDAY, D. V. 1970. The petrology of secondary gypsum rocks: a review. *Journal of Sedimentary Petrology*, **40**, 734–744.
- KENDALL, A. C. 1985. Radial fibrous calcite: a reappraisal. In: SCHNEIDERMAN, N. & HARRIS, P. M. (eds) *Carbonate Cements*. SEPM Special Publication, **36**, 59–77.
- KENDALL, A. C. 2001. Late diagenetic calcitization of anhydrite from the Mississippian of Saskatchewan, western Canada. *Sedimentology*, **48**, 29–55.
- KENDALL, C. G. ST. C. & WARREN, J. 1987. A review of the origin and setting of tepees and their associated fabrics. *Sedimentology*, **34**, 1007–1027.
- KLEIN, C., BEUKES, N. J. & SCHOPF, J. W. 1987. Filamentous microfossils in the early Proterozoic Transvaal Supergroup: their morphology, significance and palaeoenvironmental setting. *Precambrian Research*, **36**, 81–94.
- KOWALSKI, W., HOLUB, W., WOLICKA, D., PRZYTOCKA-JUSIAK, M. & BIASZCZYK, M. 2001–2002. Sulphur balance in anaerobic cultures of microorganisms in medium with phosphogypsum and sodium lactate. *Archiwum Mineralogiczne*, **54**, 33–40.
- KRUMBEIN, W. E., COHEN, Y. & SHILO, M. 1977. Solar Lake (Sinai) 4. Stromatolitic cyanobacterial mats. *Limnology and Oceanography*, **22**, 635–656.
- MELEZHIK, V. A., FALLICK, A. E., RYCHANCHIK, D. V. & KUZNETSOV, A. B. 2005. Palaeoproterozoic evaporites in Fennoscandia: implications for seawater sulfate, the rise of atmospheric oxygen and local amplification of the  $\delta^{13}\text{C}$  excursion. *Terra Nova*, **17**, 141–148.
- MILLIKEN, K. L. 1979. The silicified anhydrite syndrome—two aspects of silicification history of former evaporite nodules from southern Kentucky and northern Tennessee. *Journal of Sedimentary Petrology*, **49**, 245–256.
- ROUCHY, J. M., TABERNER, C. & PERYT, T. M. 2001. Sedimentary and diagenetic transitions between carbonates and evaporites. *Sedimentary Geology*, **140**, 1–8.
- SAMI, T. T. & JAMES, N. P. 1994. Peritidal carbonate platform growth and cyclicity in an early Proterozoic foreland basin, Upper Pethei Group, northwestern Canada. *Journal Sedimentary Research*, **64**, 111–131.
- SCHREIBER, B. C. 1986. Arid shorelines and evaporites. In: READING, H. G. (ed.) *Sedimentary Environments and Facies*. Blackwell Scientific, Oxford, 189–228.
- SCHREIBER, B. C. & EL TABAKH, M. 2000. Deposition and early alteration of evaporites. *Sedimentology*, **47** (Supplement), 215–238.
- SCHREIBER, B. C., FRIEDMAN, G. M., DECIMA, A. & SCHREIBER, E. 1976. Depositional environments of Upper Miocene (Messinian) evaporite deposits of the Sicilian Basin. *Sedimentology*, **23**, 729–760.
- SCHOLLE, P. A., ULMER, D. S. & MELIM, L. A. 1992. Late-stage calcites in the Permian Capitan Formation and its equivalents, Delaware Basin margin, west Texas and New Mexico: evidence for replacement of precursor evaporites. *Sedimentology*, **39**, 207–234.
- SIMONSON, B. M., SCHUBEL, K. A. & HASSLER, S. W. 1993. Carbonate sedimentology of the early Precambrian Hamersley Group of Western Australia. *Precambrian Research*, **60**, 287–335.
- SUMNER, D. Y. 1997. Late Archean calcite–microbe interactions: two morphologically distinct microbial communities that affected calcite nucleation differently. *Palaios*, **12**, 302–318.
- SUMNER, D. Y. 2000. Microbial vs environmental influences on the morphology of Late Archean fenestrate microbialites. In: RIDING, R. E. & AWRAMIK, S. M. (eds) *Microbial Sediments*. Springer, Berlin, 307–314.
- SUMNER, D. Y. 2001. Decimeter-thick encrustations of calcite and aragonite on the sea floor and implications for Neoproterozoic ocean chemistry.

- In: ALTERMANN, W. & CORCORAN, P. L. (eds) *Precambrian Sedimentary Environments. A Modern Approach to Ancient Depositional Systems*. International Association of Sedimentologists, Special Publications, **33**, 107–120.
- SUMNER, D. Y. & GROTZINGER, J. P. 1996. Herringbone calcite. Petrography and environmental significance. *Journal of Sedimentary Research*, **66**, 419–429.
- SUMNER, D. Y. & GROTZINGER, J. P. 2000. *Late Archean Aragonite Precipitation: Petrography, Facies Associations, and Environmental Significance in Carbonate Sedimentation and Diagenesis in the Evolving Precambrian World*. SEPM Special Publications, **67**, 123–144.
- SUMNER, D. Y. & GROTZINGER, J. P. 2004. Implications for Neoarchean ocean chemistry from primary carbonate mineralogy of the Campbellrand-Malmani Platform, South Africa. *Sedimentology*, **51**, 1273–1299.
- TABERNER, C., ROUCHY, J. M., RUSSELL, M. & GRIMALT, J. O. 1997. Timing of BSR and carbonate replacement after evaporites in organic-rich deposits. Lorca basin, Messinian, SE Spain. *American Association of Petroleum Geologists*, Annual Meeting, Abstracts, 114.
- TESTA, G. & LUGLI, S. 2000. Gypsum–anhydrite transformations in Messinian evaporites of central Tuscany (Italy). *Sedimentary Geology*, **130**, 249–268.
- USIGLIO, J. 1849. Analyse de l'eau de la Méditerranée sur les côtes de France. *Annales Chimie et Physique*, Série 3, **27**, 92–107, 172–191.
- VERRECCHIA, E. P., FREYTET, P., VERRECCHIA, K. & DUMONT, J.-L. 1995. Spherulites in calcrite laminar crusts: biogenic  $\text{CaCO}_3$  precipitation as a major contributor to crust formation. *Journal of Sedimentary Research*, **65**, 690–700.
- WALKER, J. C. G. & BRIMBLECOMBE, P. 1985. Iron and sulfur in the pre-biologic ocean. *Precambrian Research*, **28**, 205–222.
- WALKER, R. N., MUIR, M. D., DIVER, W. L., WILLIAMS, N. & WILKINS, N. 1977. Evidence of major sulfate evaporitic deposits in the Proterozoic McArthur Group, Northern Territory, Australia. *Nature*, **265**, 526–529.
- WEST, I. 1979. Review of evaporite diagenesis in the Purbeck Formation of southern England. Symposium on West European Jurassic Sedimentation—“Sedimentation Jurassique W. European”, A.S.F. (Association of French Sedimentologists), Special Publication, **1**, 407–416.
- WRIGHT, D. T. 1997. An organogenic origin for widespread dolomite in the Cambrian Eilean Dubh Formation, north western Scotland. *Journal of Sedimentary Research*, **67**, 54–64.
- WRIGHT, D. T. 1999. The role of sulphate-reducing bacteria and cyanobacteria in dolomite formation in distal ephemeral lakes of the Coorong region, South Australia. *Sedimentary Geology*, **126**, 147–157.
- WRIGHT, D. T. & ALTERMANN, W. 2000. Microfacies development in Late Archaean stromatolites and oolites of the Ghaap Group of South Africa. In: INSALACO, E., SKELTON, P. W. & PALMER, T. J. (eds) *Carbonate Platform Systems: Components, Interactions*. Geological Society, London, Special Publications, **179**, 51–70.
- WRIGHT, D. T. & WACEY, D. 2005. Dolomite precipitation in experiments using sulphate reducing bacterial populations in simulated lake and pore waters from distal ephemeral lakes, Coorong region, South Australia. *Sedimentology*, **52**, 987–1008.