INORGANIC SELF-ORGANISATION IN PRECAMBRIAN CHERTS

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Abstract. Silica biomorphs are inorganic self-organized precipitates resulting from a crystal aggregation process controlled by a metal silicate membrane. They display morphological and symmetric properties of living organisms and form under physico-chemical conditions similar to some geochemical conditions suggested for the chemical precipitation of Precambrian chert precursors. In consequence, these inorganic precipitates are proposed as an alternative interpretation to be considered when trying to decipher the biogenicity of putative Precambrian microbiotas.

Introduction

The diffusion of a metal ionic solution into a mildly alkaline silica gel containing carbonate ions (Figure 1), produces highly atypical inorganic precipitates characterised by their singular mosphology. The precipitate is a self-assembled nanocomposite material consisting of two clearly distinct phases: an amorphous or roentgenographically ill-defined metal silicate membrane and a crystalline metal carbonate phase. The two phases can be distinguished by X-ray diffraction, infrared spectra, electron microscopy and chemical dissolution (García-Ruiz & Amorós, 1982). The arrangement of the carbonate crystallites is controlled by the silicate membrane. Because of this property they were called induced morphology crystal aggregates and proposed as a laboratory analogue for shell biomineralization and as a means of emulating them in the production of ceramic-like materials (García-Ruiz, 1985) (Figure 2). These precipitates show very specific morphologies with non-crystallographic symmetry, such as target patterns, scrolls, twisted ribbons, spirals and fingers, ranging in size from microns to milimetres. The morphology varies with gel pH, metal and carbonate concentrations, gel viscosity and ionic strength of the fluid phase (García-Ruiz, 1985; Baird *et al.*, 1992; Dominguez-Bella and García-Ruiz, 1987). In many cases the morphologies are reminiscent of biogenic structures, and show symmetry elements forbidden in crystals and usually considered to be diagnostic for living systems. The emulation of biological forms is so striking that experiments of this type were carried out in the early years of this century by several scientists to emulate life in the laboratory (Herrera, 1911; Leduc, 1914). The existence of these kinds of inorganic precipitates clearly shows that the distinction between "inorganic and organic symmetry" cannot be considered to have a sound basis. The main corollary in Natural History is that morphological similarity, even in those cases in which highly complicated are considered, should not be used as an unambiguous criterion for biogenicity.

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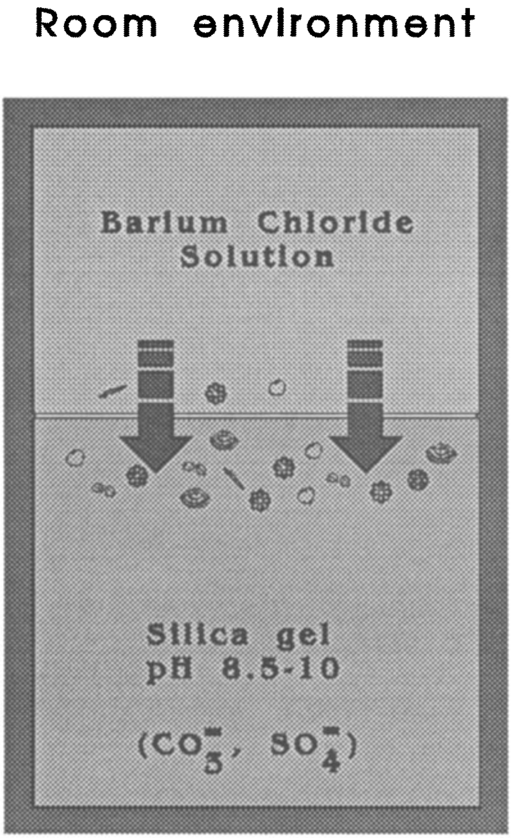


Fig. 1. Experimental set-up to produce silica biomorphs. Alkaline silica sols with pH ranging from 8.5 to 10.5 are obtained by mixing, under continuous stirring, acidic solution (for instance HCl) with a sodium silicate solution of an initial pH about 11. Once the gel forms, it is covered with a water solution of a metal chloride (for instance, $BaCl_2$). The experiment is carried out at room temperature and atmospheric CO_2 pressure. The precipitation is triggered by the reaction between the metal ions with the polimerizable ionic species of silicic acid forming at these pH values. The morphology of the precipitates varies with gel pH, solution concentration and by adding carbonate or sulphate groups into the silica gel. This experimental set-up emulates the formation of chert precursors prior to the appearance of silica secreting organism.

Silica Biomorphs and Precambrian cherts

Merek (1973) pointed out, this morphological similarity is particularly relevant when searching for the fossil remnants of very simple organisms where the absence of hard parts and functional division reduces in practise their identification to a morphological characterisation. For instance, in the last thirty years microbiological remnants found in ancient rock formations ranging in age from 0.9 to 3.8×10^9 years have been described. These are thought to be a record of primordial life on our planet (Schopf, 1983; Schopf & Klein, 1992). Some of these presumed fossils have been considered dubious, or even abiotic in origin (Schopf, 1976; Cloud and

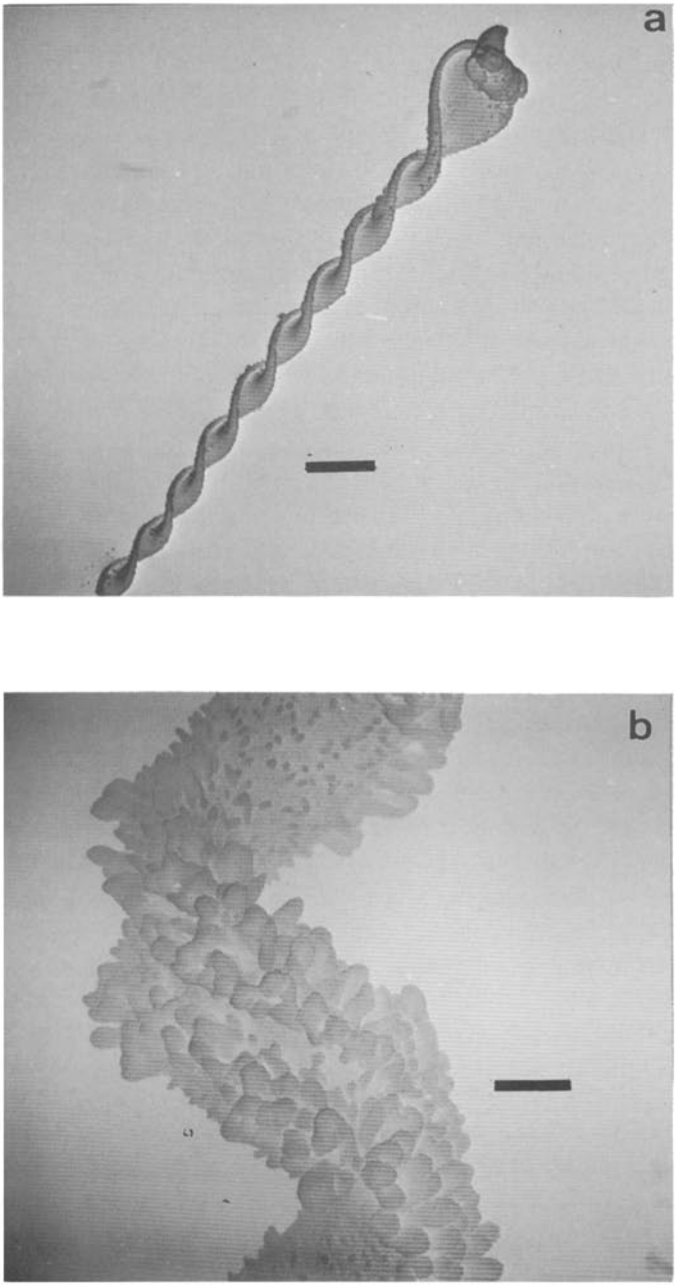


Fig. 2. a) SEM view of a twisted ribbon. Scale bar = 50 microns. b) The nannocomposite structure is revealed after etching of the ribbon with a sodium hydroxide solution. Note that the crystalline phase always orientates in the normal to the twisted silicate membrane. Scale bar = 10 microns.

Morrison, 1979). The Isua Supergroup contains microstructures (Pflug & Jaeschke-Boyer, 1979) that – in spite of their organic content – have been interpreted either as fluid inclusions (Bridgwater *et al.*, 1981) or as crystalline weathering products (Roedder, 1981). Some spheroids from the Precambrian have also been explained as quartz microspheres inorganically formed during crystallisation of colloidal silica (Oehler, 1986), or even as relics of protobiotic assemblages (Fox *et al.*, 1983). However, there is an important group of "real" Precambrian microfossils showing spheroidal shapes made of carbonaceous matter and even more complex morphologies such as septate threads, helixes or thin filaments with bulges, which are clearly similar in size and shape to modern organisms. The biogenicity of these remnants is sometimes supported by their association with stromatolites and organic remnants, but crucial to their interpretation as microfossils is to demonstrate that their biological-like morphologies can not be the result of non vital processes (Cloud, 1965). As shown in Figure 3, the self-organised inorganic structures obtained in silica gels also display a remarkably similar morphological behaviour to known organisms within the range of size from microns to millimetres. This similarity invites to a comparison with the remnants of primordial life but such morphological convergence, by itself, might be the result of a fortuitous coincidence. However, apart from morphology, silica biomorphs are also relevant to these Precambrian structures for the following reasons.

One of the conspicuous characteristics of Precambrian microfossils is that a number of them, from the 3.5 billion-year-old microfossils from the Warrawoona Group (Awramik *et al.*, 1983) to the younger microfossils of the latest Proterozoic (e.g. Knoll and Calder, 1983), are preserved in cherts. Cloud (1965) concluded for the Gunflint Iron Formation the chert was a chemical precipitate and was originally deposited at the same time as microbiota were emplaced. Chert from Precambrian formations is often thought to have formed from gelatinous sodium silicate precursors precipitated from water containing silica by far in excess the saturation value (about 120 ppm at 25 °C) (Iller, 1979) for amorphous silica (Pflug and Jaeschke-Boyer, 1979; Cloud, 1965; Hay, 1968; Govett, 1966). Such an excess of silica, leading eventually to polymerization, requires pH values greater than 8.5, at which point the equilibrium concentration of silica increases drastically due to ionisation of H_4SiO_4 to $H_3SiO_4^-$ and $H_2SiO_4^=$. Silica is relatively soluble in sodium carbonate-bicarbonate solutions, which, when exposed to the atmosphere generally present a basic pH, sometimes as high as eleven (Jones *et al.*, 1967). According to Eugster and co-workers (1965; 1968; 1970), the most probable scenario for the formation of Precambrian cherts is that of shallow lacustrine environment where the main inflow came from alkaline sodium carbonate/bicarbonate springs in volcanic terrains. The silica leached from the volcanic rocks would be concentrated in the alkaline brines and later precipitated as gels by evaporation or local change in pH. Recently, a non-marine lacustrine setting has been proposed for the late Protozoic Bitter Spring Formation (Southgate, 1986). The presence of metals such a barium, strontium or iron in these environments cannot be discarded as, for instance, barite and ankerite have been frequently reported to occur associated with Precambrian cherts although much of the barite might be replacement of gypsum. The formation of silica biomorphs (Figure 1) occurs under essentially the same chemical conditions as suggested above and thus might have been abundant in the gelled precursor of primary Precambrian cherts. It is worth noting that in the experimental set-up described in Figure 1, it is possible to produce silica biomorphs in the metal chloride solution outside the silica gel. Therefore, provided that a moderate alkaline environment exists, silica biomorphs could also form into the supernatant brine and later settle and englobed by the gelatinous chert precursor. To my knowledge, the formation of silica biomorphs in natural environments has never been reported. The appearance of silica secreting organisms, probably in the late Proterozoic (Allison and Hilgert, 1986; but see Kaufman *et al.*, 1992 for revised age), restricts the suitable scenario for inorganic silica precipitation to a limited number of environmental settings and most of the younger cherts clearly originated from accumulated siliceous tests. Fortunately, there are modern alkaline lakes such as those studied by Peterson and Van der Borch (1965) in South Australia and those in the Magadi area in Kenya (Eugster & Jones, 1968). In both cases, the authors reported the formation of inorganic bedded cherts from a sodium silicate gel precursor. Likewise Pleistocene chert Natron in Kenya (Govett, 1966) and cherts in Jurassic and Eocene rocks from Wyoming (USA) (Surdam *et al.*, 1972) are presumed to share the same environmental context. Another possible scenario is represented by particular setting occurring along the mid-ocean ridge system, such as the low temperature alkaline springs exposed in Iceland. We might expect to find silica biomorphs forming nowadays in these kinds of alkaline environments.

The moderate alkaline environment required for the formation of silica biomorphs made the pH the main parameter restricting the geological settings to be scanned for their search and in consequence, for its use as a plausible inorganic alternative for microstructures currently interpreted as microbiota. As above discussed, the precursor of a non-marine primary precipitate is the most likely candidate for the formation of silica biomorphs. However, marine or marine-influenced environments could be also considered of the extension of the Eugster's model to Precambrian ocean waters is accepted as proposed in the "soda ocean hypothesis" by Kempe and Degens (1985). Nevertheless, as stated in the petrographic studies accompanying microbiota description in the literature, Precambrian fossil remnants are sometimes embedded in replacement cherts. The modern 'force of crystallisation' model explaining the origin of this type of chert (Maliva and Siever Geology, 1988; Maliva and Siever, 1989; Dewers and Ortoleva, 1990) does not need either low pH values for carbonate dissolution or high pH values for quartz dissolution, but it does not precludes these extreme conditions too. So far, this mechanism has been applied to silicification of limestone with a biogenic source of silica but Precambrian silica sources are restricted to volcanic silica currently associated to volcanoclastic sediments or solica-rich water. My opinion is that the precise mechanism for replacement is not yet completely understood and in consequence we cannot define a close range of values for the physico-chemical variables relevant to this process. Therefore, it should be considered that, at least some replacement cherts could be formed under conditions precluding the formation of silica biomorphs.

Criteria for identification

There are several criteria that can be advanced to evaluate the silica biomorph alternative for presumed Precambrian microfossils: a) the anomalous concentration of metals detected in some of these 'microfossils' have been proposed to support the biogenic viewpoint and why the membrane, apparently the most delicate part of the cell, is preserved (Golubic, 1977). It could alternatively represent a relic of the metal silicate membrane. b) As shown in Figure 4, silica biomorphs appear most of the time as hollow structures. Sometimes they are filled with radially arranged carbonate crytals, but this fabric is unlikely to survive subsequent chertification thus explaining the hollow nature of the putative Precambrian microbiota considered a key criterion for biogenicity (Buick, 1990). c) Another key indicator of biogenicity is the existence of cellular elaboration and complexity. The gallery of shapes displayed by silica biomorphs is consistent with an amphiphilic character for the two-dimensional silica membrane. The elastic properties of this membrane can be maintained because of the absence of physical continuity of the carbonate crytalline phase (see for instance Figure 2b). As demonstrated for other polymeric organic membranes, this character explains the formation of lamellar bilayers, vesicles, budding and inverse budding structures (Lipowsky, 1991), and because the helical arrangement of silica tetrahedra, the formation of tubules and twisted ribbons (Georger *et al.*, 1987). In addition, the existence of layered walls is a current feature in spheroidal and ellipsoidal silica biomorphs and this feature extends to threads and more complex silica biomorphs where the persistence of the synmorphous silicate envelope can be demonstrated by dissolution of the carbonate phase (García-Ruiz & Amorós, 1982). d) proposed Precambrian microfossils are often iron stained or carbonaceous. Iron silicate behaves in a similar way that barium silicate behaves. In relation to organic matter, we know that silica biomorphs form in the presence of HCN, alanine and glycine (García-Ruiz and Moreno, in preparation). Because of the amphiphilic character of the silica bilayer, it would be not surprising that abiotic organic compounds could be chemisorbed on its structure. 2) It is know that biological populations show a rather narrow normal size frequency distribution. The size of silica biomorphs increases as the diffusive front advances but it must be also considered that this is generally accompanied by a global morphological change and in consequence, it is common to observe that a given morphological pattern is restricted to a narrow size range. Finally, the arrangement of silica biomorphs in laminae parallel to the diffusion front is also not rare (Figure 3q).

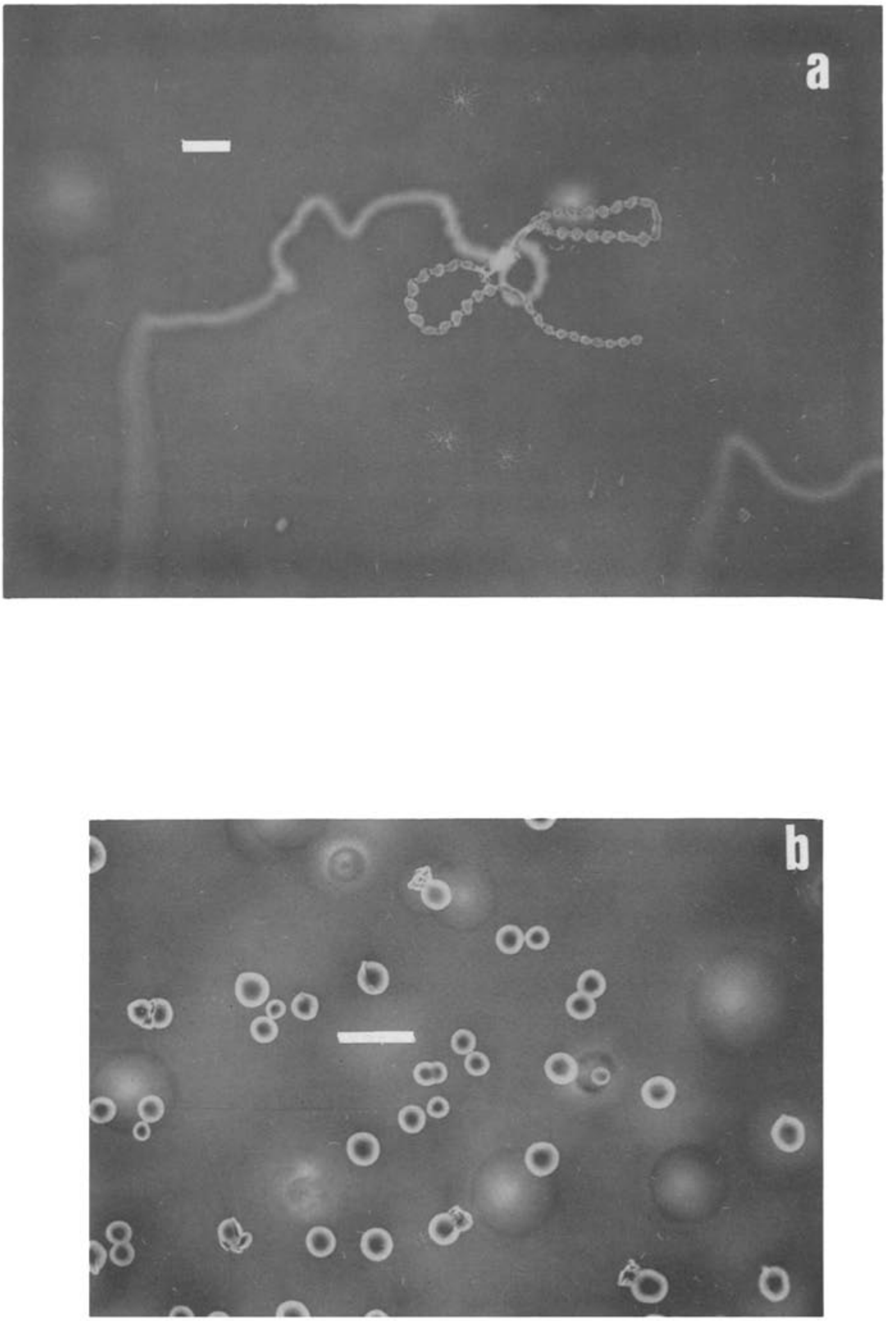


Fig. 3a–b.

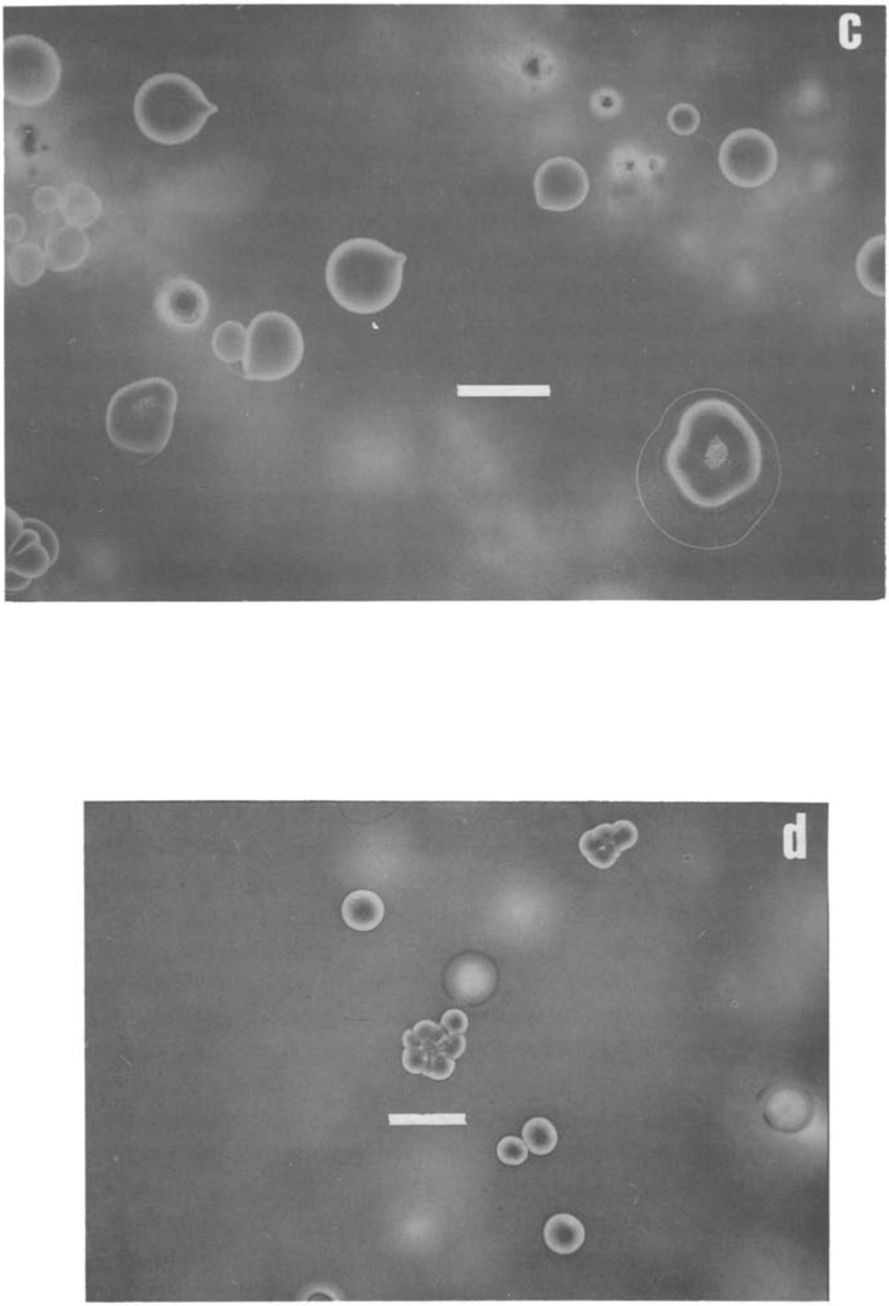


Fig. 3c–d.

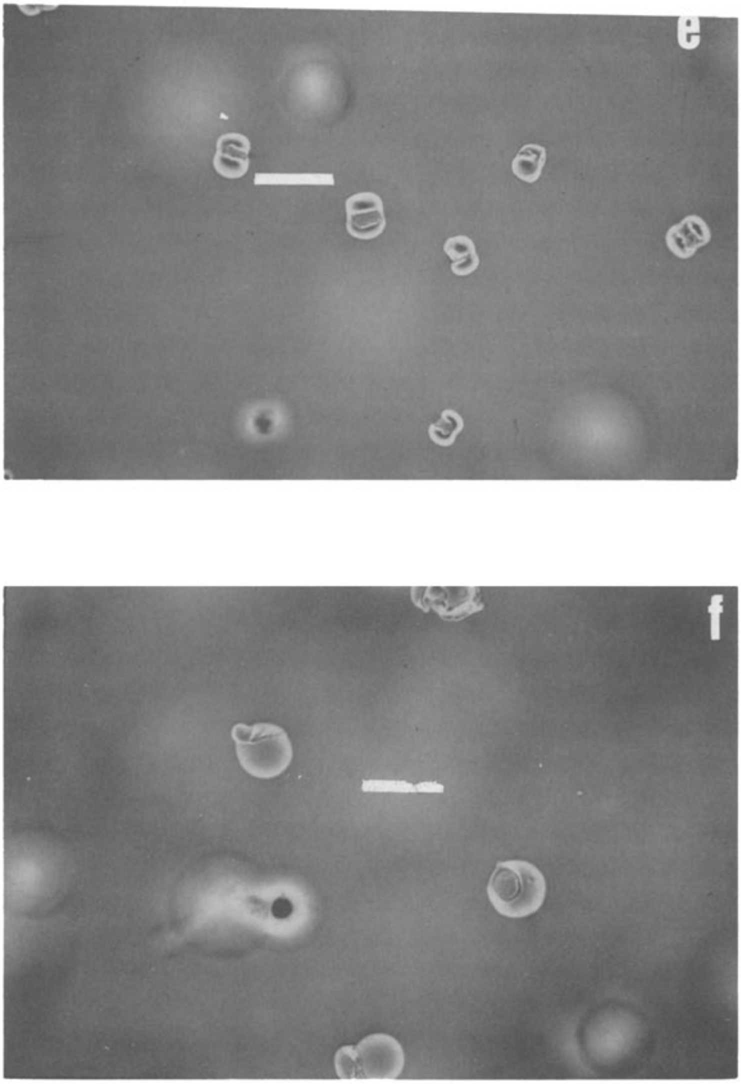


Fig. 3e–f.

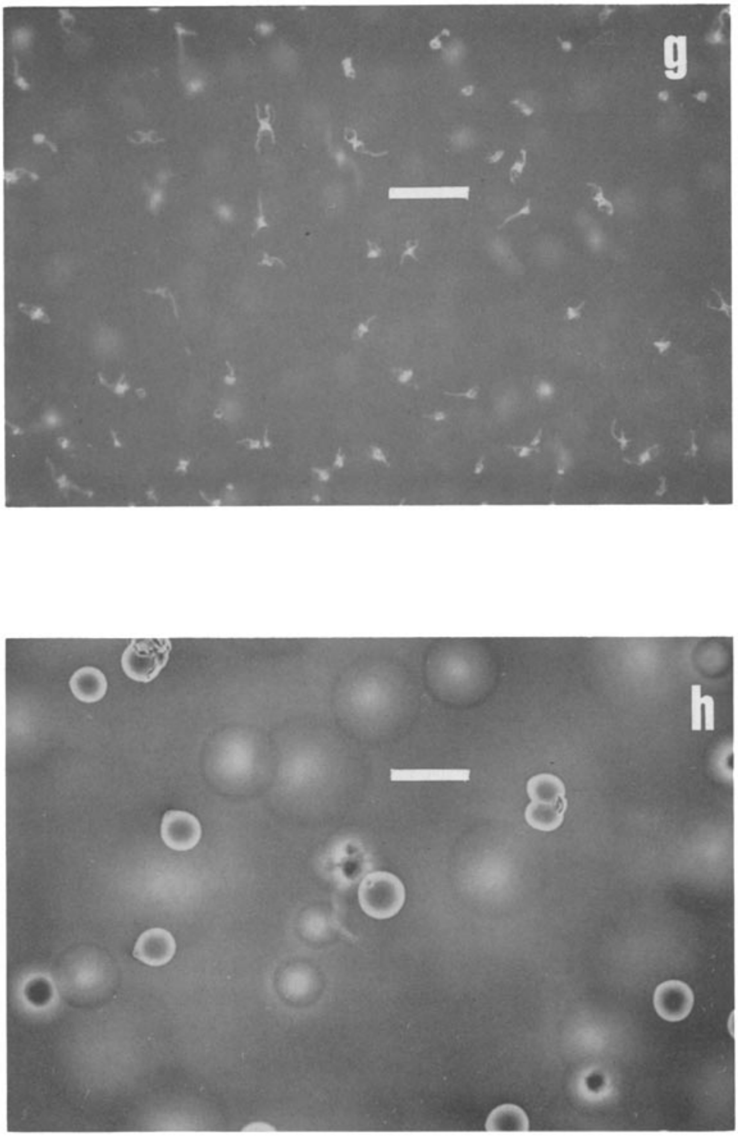


Fig. 3g–h.

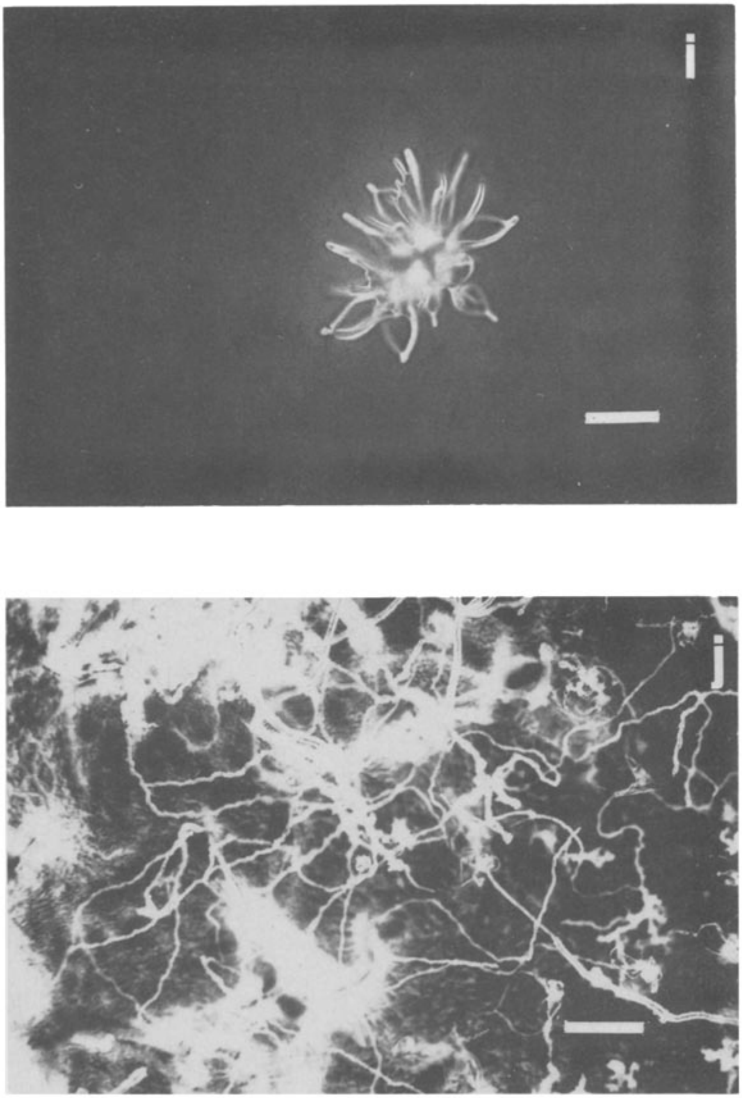


Fig. 3i–j.

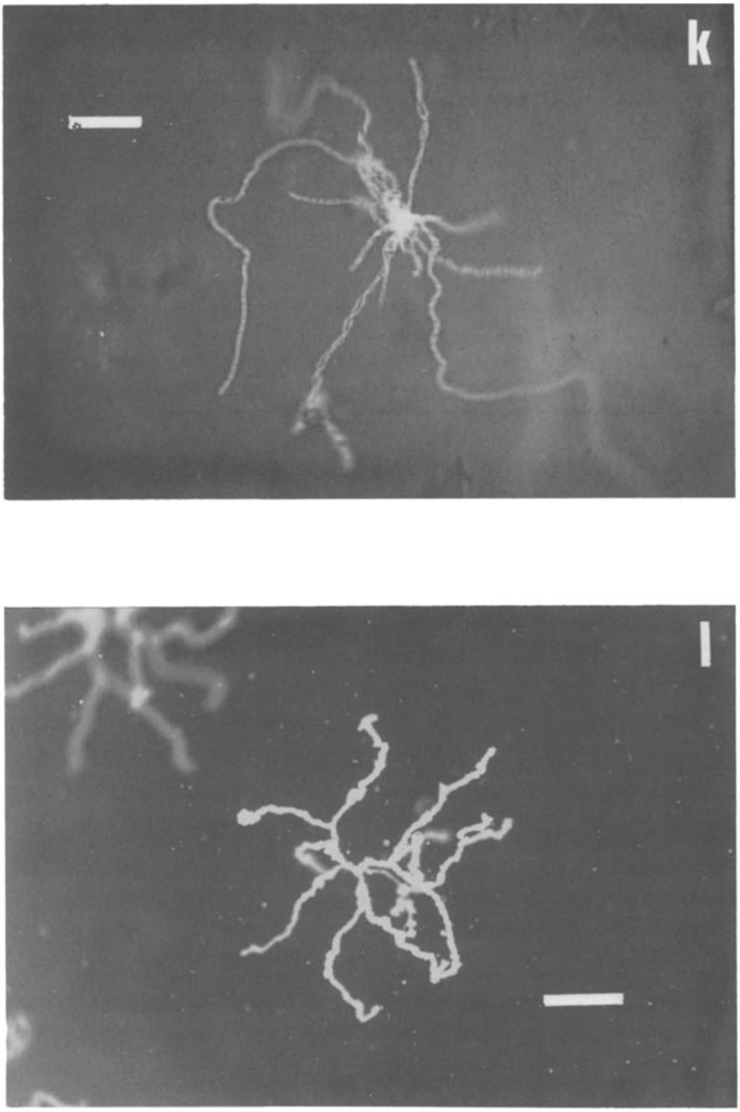


Fig. 3k–l.

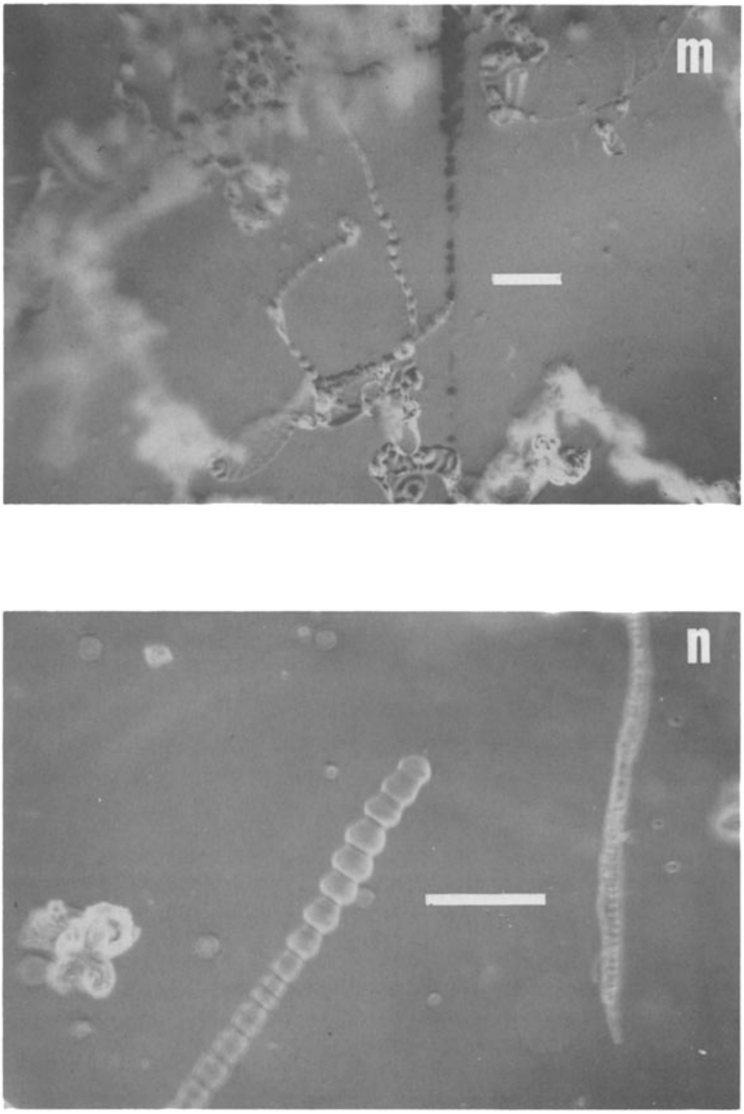
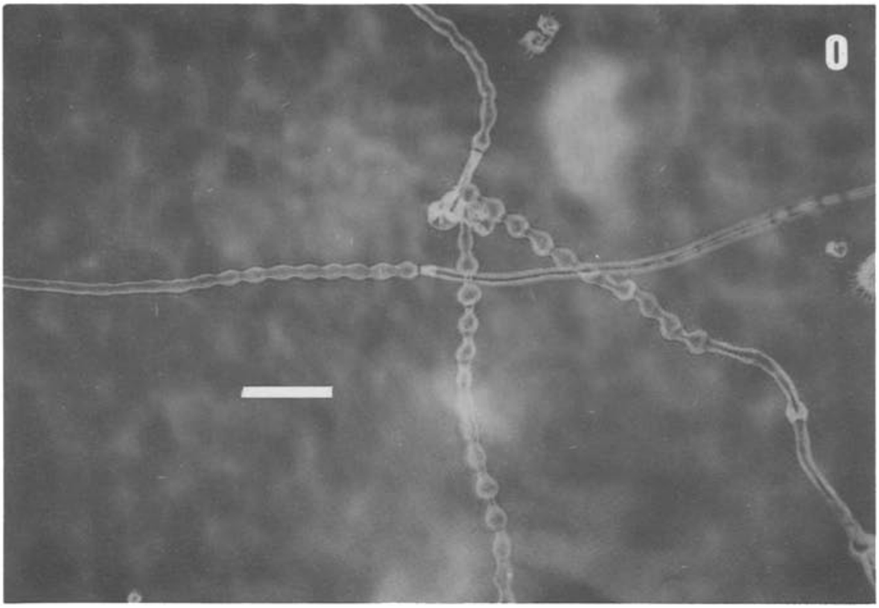


Fig. 3m–n.



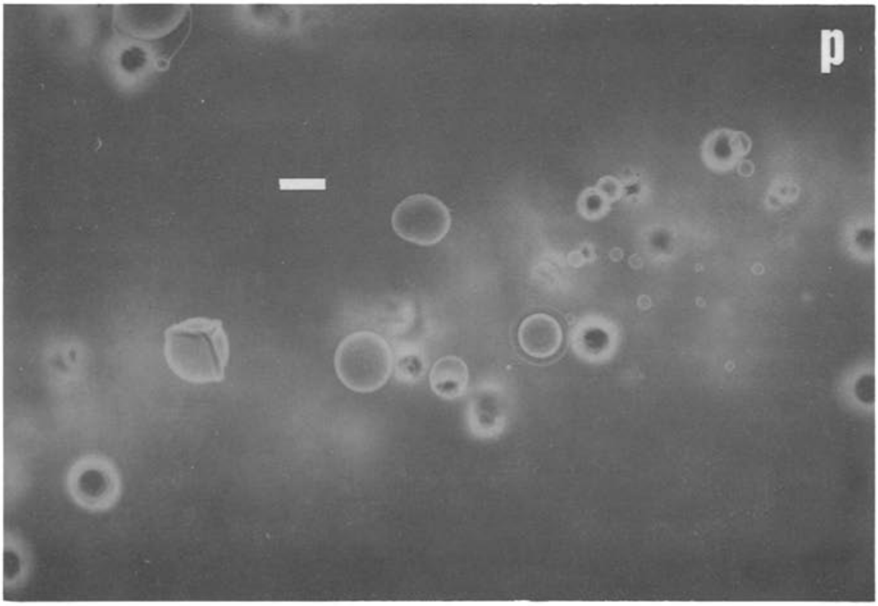


Fig. 3o–p.

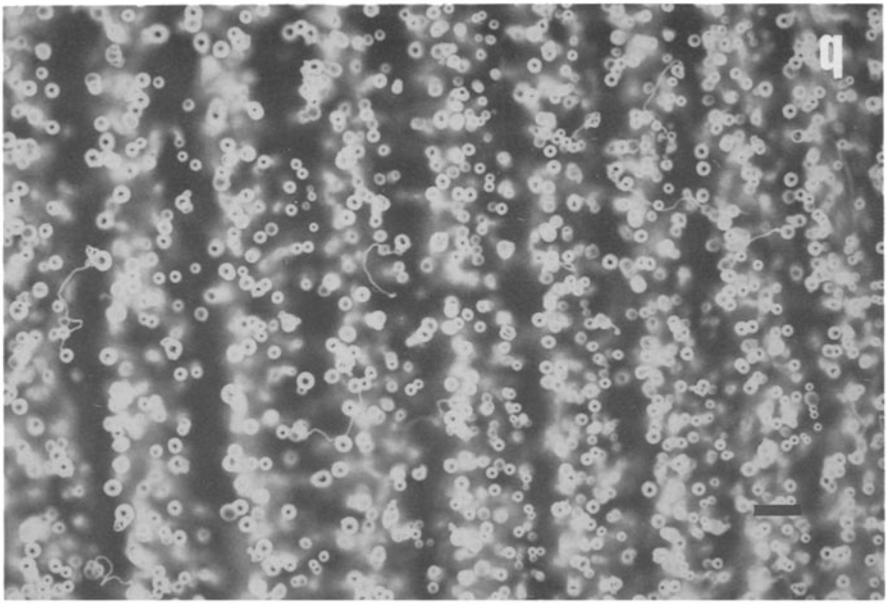


Fig. 3q.

Figs. 3(a)–(q). Some silica biomorphs formed with the experimental arrangement described in Figure 1. Note the existence of sperical, spheroidal and rod-shaped structures as well as paired spheroids, budding structures, ruptured split, outer envelopes and aggregates of spheroids. Radiating filamentous structures with holdfast-like bases and thread-like ribbons are also common as well as septate and globular structures with encapsulation. All they are growth structures with a growth rate in the range of tens of microns per minute. Scale bars represent: a) to h) and l) to p) = 100 microns; i) to k) = 150 microns.

1. Conclusions

I conclude that the precipitation of silica biomorphs into the colloidal precursor of primary Precambrian chert formed from a silica gel at mildly basic pH or into its supernatant brine, was possible. In consequence, because of the morphological and structural resemblance with putative Precambrian microbial relics, I suggest that silica biomorphs be considered as an alternative when deciphering the biogenicity of these Precambrian microstructures. The search for silica biomorphs in chert should be also extended to those objects for which a biological origin has been already discarded but no other explanation exists, because the formation or not of these membrane-controlled inorganic structures in precambrian setting is interesting beyond paleontological considerations.

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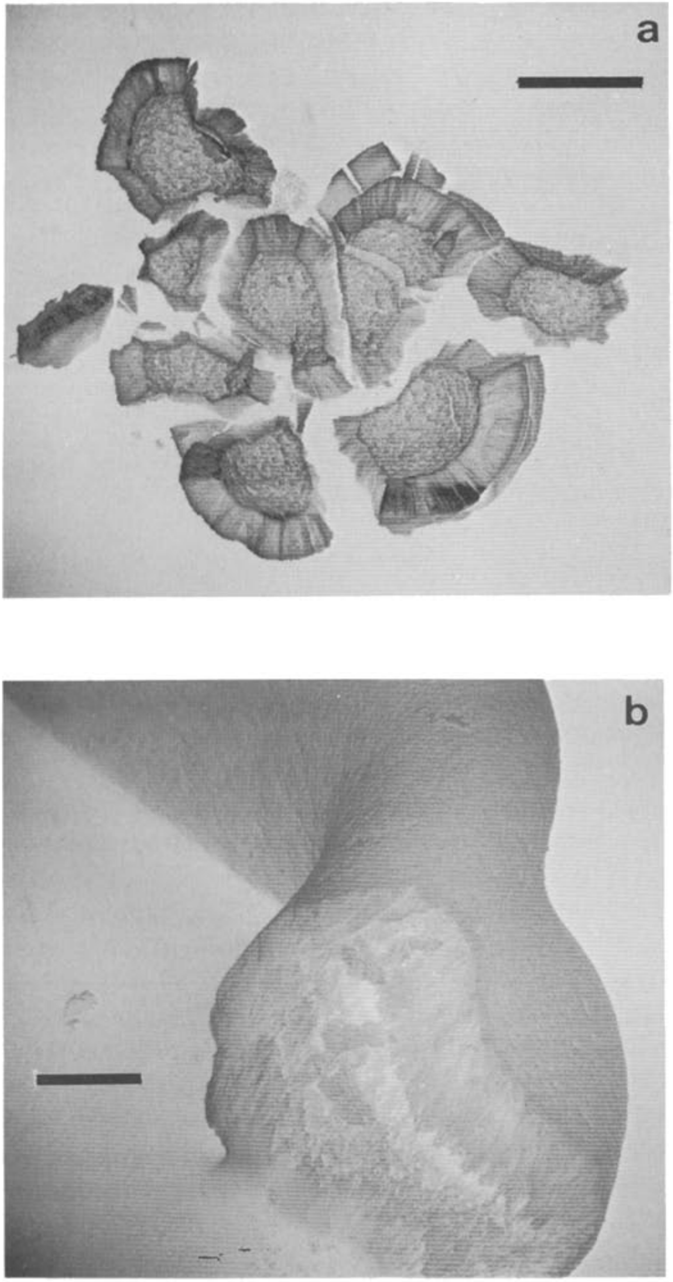

Fig. 4a–b.

Figs. 4(a)–(b). SEM Views of a) a cracked spheroid and b) a cracked filament, showing their hollow inner. Scale bar in a) = 5 microns and in b) = 20 microns.

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