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Search for signs of ancient life on Mars: expectations from hydromagnesite microbialites, Salda Lake, Turkey

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Abstract: The ‘White Rock’, constituting a portion of what may be a lacustrine sedimentary sequence near the margin of a crater *c.* 90 km across in Sabaea Terra, Mars, measures 18 × 15 km × 180–540 m high. It is re-interpreted as a lens of magnesium carbonate precipitated where ground waters seeped into an ancient evaporating crater lake. Were life to have emerged on Mars, as seems feasible, then the ‘White Rock’ might be expected to comprise a complex of stromatolitic mounds. Salda Gölü (Lake) in Turkey, is taken as an analogue. This enclosed lake is nearly surrounded and underlain by partially serpentinized harzburgite. Hydromagnesite stromatolites (microbialites) up to 7 m high coalesce to form a group of small islands 200 m across. The microbialites are seen to be growing near the mouth of the usually dry Salda River in the southwestern sector. Smaller developments of hydromagnesite encircle the lake and image processing of satellite data reveals a second extensive zone beneath the lake surface over a delta in the southeast. Individual columns a few centimetres high constitute bulbous mounds which are about 2 m in diameter. These columns terminate in domes a centimetre or so across. The domes are often annulated and are covered with a green biofilm a few millimetres thick comprised of cyanobactrial filaments. The columns consist of alternating fine and coarse hydromagnesite layers differentiated on a millimetric scale. The coarser layers near the surface still contain traces of the biofilm.

Fossil microbialites were also discovered in the friable hydromagnesite cliffs shoreward of the main developments, though the structures of the individual microbes have not survived. Instead the vestiges of microbialites are easily recognized and delineated by their coarse grain size and high porosity. Annular structures on their upper surfaces can be seen in places. The intervening and overlying material, also comprised of hydromagnesite, is a semi-lithified mud.

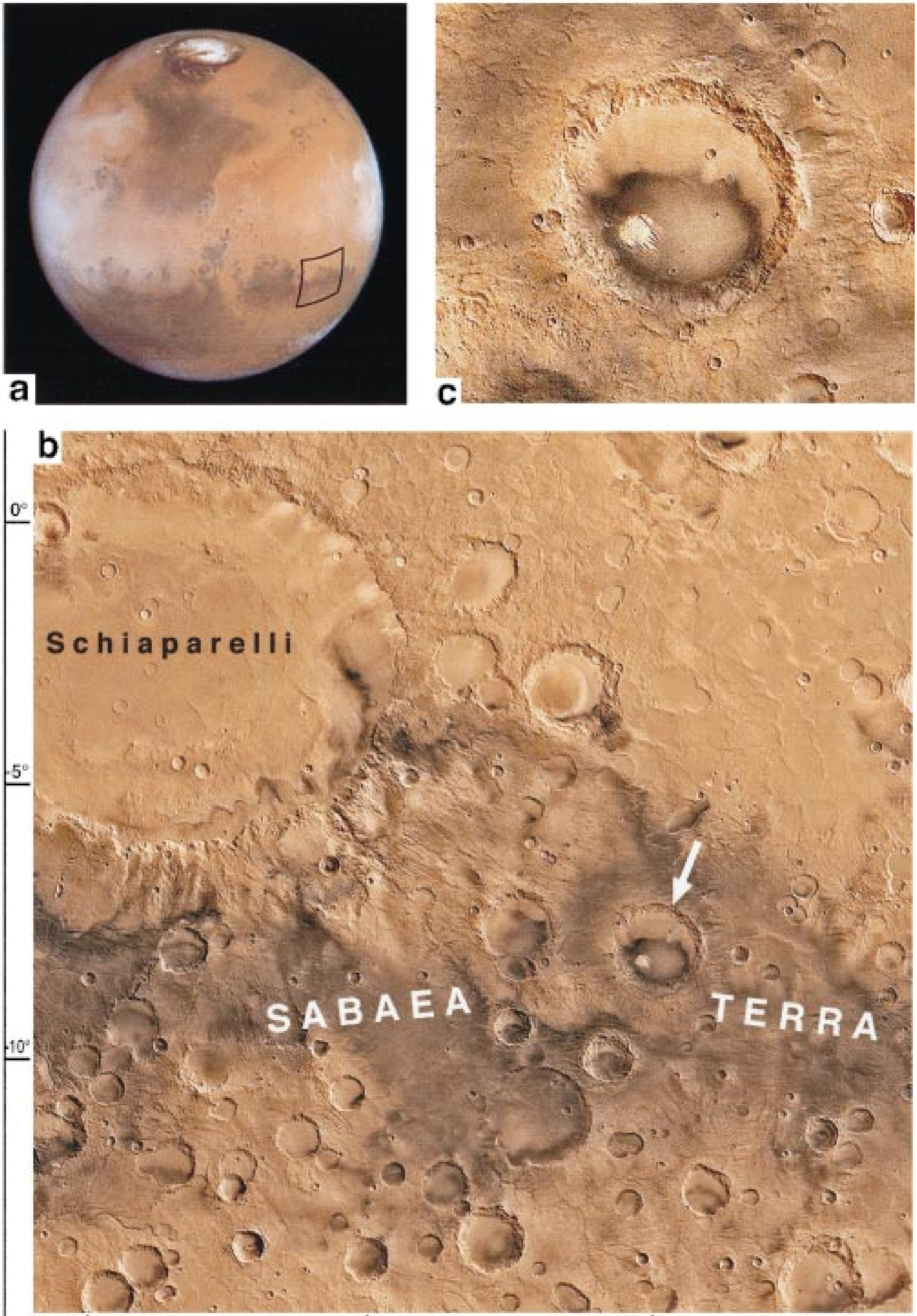
Bulbous megascopic structures, separated by finer grained magnesium carbonate mudstone, within strata in the ‘White Rock’, would be strong evidence of a photosynthetic microbial genesis. Another deposit of white rock on the western margin of Juventae Chasma could have a similar origin.

Keywords: Mars, White Rock, crater lake, hydromagnesite, microbialite, stromatolite.

‘*Consult the genius of the place in all*’.
Alexander Pope, Epistle to Lord Burlington 1731

Two recent extraordinary events are reminding geologists of their credentials as planetologists. The first of these was the discovery of ‘hot jupiters’ orbiting neighbouring stars (Mayor & Queloz 1995; Marcy & Butler 1996; Butler & Marcy 1996). Arising from this are plans for the building of infrared space interferometry telescopes to detect, within 15 years, Earth-sized planets, and to analyse spectroscopically their atmospheres (Mariotti *et al.* 1997; Penny *et al.* 1998). The second event is the controversial claim for evidence of possible microbial life in Martian meteorite ALH84001 (McKay *et al.* 1996; Gibson & McKay 1997, and see Bradley *et al.* 1996, 1997; Nealson 1997; Leshin *et al.* 1998; Thomas-Keprta *et al.* 1998, for critiques and comparisons and Tan & VanLandingham 1967 for an earlier description of the (contaminated) Orgueil meteorite). Yet the equilibrated nature of the atmosphere and lack of a hydrosphere on Mars today, would seem to preclude the presence of life, at least on the surface (Biemann *et al.* 1977; Klein 1978; Thomas & Schimel 1991; Krasnopolsky *et al.* 1998). Nevertheless, given the evidence for surface water on Mars for at least the first 800 million years, the smaller size of that planet, its distance from the Sun, its more rapid cooling history (Melosh & Vickery 1989), then life might be conjectured to have emerged there even before it did here on Earth.

It has been argued that all wet rocky volcanic planets will have given rise to life (Russell *et al.* 1994; Shock 1996). This is because in these circumstances life is the fastest way to process chemical energy (notionally $2nH_2+nCO_2 \rightarrow [CH_2O]_n+nH_2O$) and information (de Duve 1995). Life will have emerged where ground waters, already equilibrated with Martian crust and charged with hydrogen, met the hydrosphere, specifically at medium enthalpy alkaline hot springs (Russell & Hall 1997, 1999). Electrochemical energy would have been provided by protons in the early, acidic Northern Ocean and lakes (Schaefer 1990, 1992; Macleod *et al.* 1994; Russell *et al.* 1994). Photoxidized iron would have been the electron acceptor (cf. Cairns-Smith *et al.* 1992; Russell & Hall 1999). The transition


a
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elements required to constitute active catalytic centres for a protometabolism appear to be well represented on the planet (Wänke & Dreibus 1988; Newsom & Hagerty 1997), though Jakosky & Shock (1998) caution that the overall amount of life produced through *chemical* reactions on Mars, at least laterly, would have been small.

Surviving fossil edifices built by the first replicating chemosynthetic organisms on the *surface* of wet, rocky planets such as Mars might be expected to have the appearance of pyrite stromatolites (Russell 1996). But these may be hard to find given the surface oxidation state. Moreover the most likely site for their development would be in the northern lowland plains where they would be covered by a substantial pile of turbidites and later flood deposits (Parker *et al.* 1993; Sleep 1994).

So, with a mind on the generative potential or *genius loci* of Mars and knowing what we do of procaryotic life on Earth, where might we look for evidence of the former presence of simple though sophisticated cells? Ancient seepage sites, indicated by carbonates, are likely to offer the best prospects. This is because, with time, inorganically produced fuel for primary metabolism (Shock 1997) was probably supplemented by the exploitation of solar photons for microbes exposed to sunlight, especially in the equatorial zone. In fact, as lakes rapidly became neutral or alkaline (Schaefer 1992; cf. Kempe & Kazmierczak 1994, 1997), a result of groundwater additions of alkaline elements produced during the hydrolysis of silicates, and of the partial draw-down of carbon dioxide in the Martian crust (Griffith & Shock 1995), organisms would have been obliged to turn to photosynthesis as a means of generating their own protonmotive force (Russell & Hall 1998). A by-product of photosynthesis is familiar to us as carbonate stromatolites (Walter 1976, 1983, 1996) which often grow over seepages (Kempe *et al.* 1991). Carbonate rather than pyrite is likely to offer a more salient target to exopalaeobiological exploration (McKay & Nedell 1988; Burns & Fisher 1990; Kempe & Kazmierczak 1997), and in this paper we consider exploration targets for such putative fossil edifices on Mars.

As Mars, unlike Earth, did not have an all-enveloping hydrosphere but only restricted bodies of water subject to evaporation, the carbonate there would have precipitated directly as hydromagnesite from magnesium bicarbonate waters emanating from the 'dark' (olivine/pyroxene-rich) rocks. This is because evaporation would drive the magnesium concentration, already at saturation point, well above its solubility product. On Earth, microbially generated small scale structures in hydromagnesite are lost during lithification. Evidence of such microbial origin is restricted to a differentiation of fabric, stromatolitic material tending to retain porosity while interstitial mud becomes porcelaneous. Dehydration to magnesite completes the process. At the low temperatures obtaining on the surface of Mars it appears that hydrous magnesium carbonates have remained stable (Calvin *et al.* 1994; and see Raade 1970; Blaney & McCord 1989), though they are likely to have dehydrated to magnesite at depth (Zedef *et al.* 1999).

Conditions on Mars at *c.* 3.1–4.6 Ga

There is now abundant evidence that during the Noachian and early Hesperian eras, free-standing and free-flowing water was widespread on Mars (Carr 1996; Forget & Pierrehumbert 1997; Smith *et al.* 1997). (The Noachian and Hesperian eras are defined, somewhat inexactly, on globally mapped rock sequences, channels as well as crater sizes and densities and their extrapolation to the impact history of the moon (e.g., Tanaka 1986; Scott & Tanaka 1986; Greeley & Guest 1987; Tanaka *et al.* 1992; but see Neukum & Wise 1976). The Noachian extends from about 4.6 to *c.* 3.5 Ga and the Hesperian from *c.* 3.5 to *c.* 1.8 Ga). A Northern Ocean probably occupied the northern lowlands, a feature possibly generated by plate tectonics in the Late Noachian (3.85 to *c.* 3.5 Ga) and Early Hesperian (3.5 to *c.* 3.1 Ga) (Sleep 1994). Life is likely to have emerged in this, or an ealier ocean (Russell & Hall 1999).

Several examples of ancient lake sites have also been described (Forsythe & Zimbelman 1995). Most lakes occupied crater basins in Noachian highland regions. Lacustrine and associated fluviatile geomorphologies are clearly recognizable. Terraces, layered sedimentary rocks and some inflow and outflow channels may also be discerned. McKay & Stoker (1989), Walter & Des Marais (1993) and Rothschild (1995) have suggested that such sedimentary rocks might host stromatolites. In this contribution one particular structure, the 'White Rock' of Williams & Zimbelman (1994), is interpreted to be a giant stromatolitic mound lying near the margin of a crater up to 95 km across rim to rim, filled with Hesperian sediments, some of which are dark (Fig. 1).

A good proportion of the rocks underlying the Martian regolith are ultramafic, probably komatiitic, and at least some presumably date from the Noachian (McGetchin & Smyth 1978; Treiman 1986; Pinet & Chevrel 1990; Burns & Fisher 1990; Mustard & Sunshine 1995; Mittlefehldt 1994; Christensen 1998). Dark Hesperian sediments are possibly directly derived from these ultramafic rocks. The supposed andesitic rocks discovered by Sojourner (Reider *et al.* 1997) might have been generated by the partial remelting of parental mafic and ultramafic rocks.

Although it is widely acknowledged that running, as well as standing, bodies of water were present on Mars (Squyres & Kasting 1994; Donahue 1995; Carr 1996; Smith *et al.* 1997) there is still controversy regarding the concentrations of carbon dioxide early in the planet's history (Anders & Owen 1977; Dreibus & Wänke 1987; Pepin 1994). Here it is assumed that surface waters were present and that the partial pressure of atmospheric CO_2 was significantly higher than it is today, perhaps between 1 and 10 bar (Pollack *et al.* 1987; Melosh & Vickery 1989; McKay & Stoker 1989; Schaefer 1993; Griffith & Shock 1995; Owen 1997; Forget & Pierrehumbert 1997; Brain & Jakosky 1998). In such conditions CO_2-bearing shallow ground waters might have reacted with Mg,Fe^{2+}-orthosilicates to have dissolved quantities of magnesium as the carbonate or

Fig. 1. The eroded, mound-like 'White Rock' deposit lies within a currently unnamed, ancient (Noachian), 95 km diameter crater in Sabaea Terra (formerly Sabaeus Sinus) at 335.20°W and 8.30°S. The crater is some 320 km SE of the large crater basin Schiaparelli (rim to rim): (**a**) Hubble Space Telescope image of Mars (March 1997 opposition), processed by P. James (University of Toledo), T. Clancy (Space Science Institute), S. Lee (University of Colorado) and NASA, showing location of image in Fig. 1b; (**b**) Schiaparelli and part of Sabaea Terra, showing location of 'White Rock' crater. Adapted from highest resolution monochrome digital photomosaic, processed by United States Geological Survey, Flagstaff, Arizona, from Viking Orbiter data, which has been merged with lower resolution digital colour data using Adobe Photoshop software. Mercator projection. Image is some 950 km across in centre; (**c**) Detail of 'White Rock' crater which averages 90 km across rim to rim.

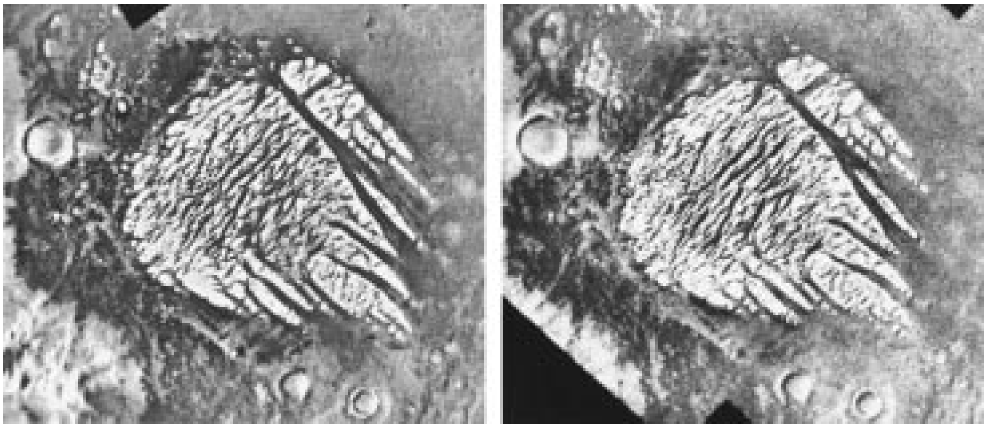

Fig. 2. Stereoscopic view of part of 'White Rock' crater showing extent of the originally mound-like deposit some 18 km by 15 km on crater floor near its SW wall. Yarding topography is evident. Adapted from photographs kindly supplied by J. R. Zimbelman (Center for Earth and Planetary Studies, National Air and Space Museum, Smithsonian Institution, Washington D.C.) originally published by Williams & Zimbelman 1994 (with permission from the Geological Society of America). Viking Orbiter high resolution mosaics processed by Brian Fessler (Lunar and Planetary Institute, Houston, Texas) and J. R. Zimbelman.

bicarbonate, and in the process become somewhat alkaline (Russell & Hall 1999). The iron remains insoluble in alkaline solutions (Crerar *et al.* 1978; Macleod *et al.* 1994) though it could have been transported to the surface, along with sulphide and other metals required by metabolists, in high temperature hydrothermal solutions (Crerar *et al.* 1978). These other metals could also have been introduced from degassing melts (Cu, Zn, Mo, and W), or distributed from impacts of CI chondrites (Ni and Cu) (Newsom & Hagerty 1997).

Were life to have emerged on Mars *c.* 4.3 billion years ago (Shock 1996, 1997; Russell & Hall 1999) then, given the shallowness of that planet's first lakes and ocean (Carr 1996: but see Baker *et al.* 1991 and Schaefer 1992 for different views), it probably evolved quickly with energy contributions gained from photosynthetic metabolic processes (cf. Walter 1983; McFadden & Shively 1991; Blankenship 1992; Hauska *et al.* 1995). Cool to warm springs and seepages would have continued to provide chemical energy to metabolists in the form of hydrogen and other reduced entities (Neal & Stanger 1983; Coveney *et al.* 1987; Hovland 1990). Any such CO_2-metabolists could have built stromatolite-like mounds similar to those in Lake Salda described below. Carbonate mounds could be sampled by future Martian landers such as *beagle* for their possible micro and molecular fossil content (McKay & Stoker 1989; Rothschild 1995; Forsythe & Zimbelman 1995).

In this paper we are concerned with low-temperature waters. Magnesite and hydromagnesite veins, stockworks, tufas, travertines, sediments and crusts could have been generated on Mars just as they are in ultramafic terrains on Earth (e.g., O'Neil & Barnes 1971; Fallick *et al.* 1991). Magnesite and hydromagnesite would have been precipitated from these solutions during decarbonation or, more likely, evaporation of ground and lake waters (Warren 1998). Below we review descriptions of what we take to be a deposit of magnesite or hydromagnesite in lacustrine sediments, i.e., the 'White Rock' of Williams & Zimbelman (1994). Given this interpretation, we develop the hypothesis that were life to have emerged on Mars, then this site may afford the metric scale biogenic morphologies consistent with it having been a giant microbialite. We do not expect the detail afforded in calcite stromatolites to survive in magnesite or hydromagnesite bodies. Nevertheless we will show that a delineation of gross lithological contrasts has the potential to afford the necessary evidence for, or against, a biotic origin. As hydromagnesite is unstable, its dehydration to magnesite has the effect of obliterating all signs of life at the micro level. If this transformation were to have taken place, which is not at all certain (Calvin *et al.* 1994), it should still be possible to recognize macroscopic signs of former microbialites.

'White Rock'

The 'White Rock' is a lenticular structure lying within and near the margin of an unnamed crater of some 6000 km^2 in central Sabaea Terra at an elevation of *c.* 4000 m (US Geological Survey Topographic Map of the eastern region of Mars 1991). The host crater lies *c.* 320 km southeast of the large crater basin, Schiaparelli, at 335.5°W–8.3°S (Williams & Zimbelman 1994; Forsythe & Zimbelman 1995; and see Greeley & Guest 1987 for context) (Figs 1 & 2). These authors also identify a discontinuous line of light coloured material high on the southern wall of the same crater which they compare with shore-line gypsum deposits found in playa lakes on Earth, and go on to assume an evaporitic origin for 'White Rock'. By analogy with comparable structures and settings on Earth, Forsythe & Zimbelman (1995) assume that the 'White Rock' comprises chlorides and/or sulphates, sculpted by the wind into a giant yardang (or yardangs) (cf. Ward 1979, fig. 12). While this interpretation seems reasonable it does not address the rarity of this type of deposit. Nor does it pay attention to the possible source constituents of the body.

Calvin *et al.* (1994) interpret absorption features identified in Mariner 6/7 infrared spectra of the regoliths as hydrous magnesium carbonates such as hydromagnesite $[Mg_5(CO_3)_4(OH)_2.4H_2O]$ and artinite $[Mg_2CO_3(OH)_2.3H_2O]$. They could not identify magnesite itself. The clearest indications of hydromagnesite are found in the Meridiani Sinus at 0°–4°S (see Scott & Tanaka 1986 for context). If we assume much of the earliest surface of Mars to have comprised high magnesium basalts and komatiites (Mustard & Sunshine 1995) then, given a hydrosphere and a carbon dioxide-rich atmosphere, hydrated magnesium carbonates are just the kind of secondary minerals to be expected on the surface, both as weathering products and as the constituents of evaporites. This is in contrast to expectations for the early Earth which had an almost all-enveloping ocean at the end of the Hadean (Taylor & McLennan 1995). Thus there was little opportunity for evaporite development at, and no potential for evaporite survival on, our planet from that time.

We suggest that the interpretation of Calvin and her co-workers (1994) could be applied to encompass 'White Rock' composition as well as the white deposits marking the strand line. Recall that these workers found the clearest indications of hydromagnesite in Meridiani Sinus at 0°–4°S, about 1500 km to the west of the 'White Rock'.

As yet there is no high spatial resolution spectroscopy data for this area of Mars, so the composition of the 'White Rock' itself is left to speculation. The mound-like shape and what resemble large scale grykes and clints (enlarged orthogonal joints in karst terrain) are indicative either of dissolution of carbonate by acid rain percolating through joints, or of long term wind erosion, producing yardangs (Williams & Zimbelman 1994). Another possibility is that the structures represent a combination of the two processes yielding a 'yarding' topography (Stone 1967) (see Fig. 2).

Reinterpreting the supposed calcium sulphate as magnesite or hydromagnesite, we can still follow the logic of Forsythe & Zimbelman (1995) and assume deposition from an open hydrologic system, subject to evaporation. The erosional patterns in this large, dome-like body are also suggestive of a carbonate mound nucleated about a concealed crater some 3 km across (Fig. 2). A carbonate mound would be significant in that it is more likely to develop over a seepage even if precipitation were from waters driven to supersaturation by evaporation. We are inclined to favour a magnesite composition for 'White Rock' given the probable high partial pressure of CO_2 early in the history of Mars (e.g., Owen 1997). Furthermore, were there to have been photosynthetic microbes on Mars then we know that Mg/Ca carbonate is especially prone to nucleation in periplasmic mucilage (Miller & Colman 1980; Thompson & Ferris 1990).

As magnesite is less soluble than anhydrite, it is more likely to have survived later dissolution in cold rain water. Given these expectations we now turn to a present day environment on Earth broadly comparable to that envisaged to have occurred on Mars around 3.5 billion years ago.

Earthly comparisons

Some of the largest ultramafic terrains on Earth, constituents of ophiolites, occur in Turkey. As they comprise 'primitive' ocean crust, the ultramafic part of ophiolites will be similar in composition to the earliest Martian crust. The ultramafic complex we are concerned with here, Eslerdagi in the southwest of the country, is unusual in that it is partly occupied by a lake, Salda Gölü (Fig. 3). Hydromagnesite microbialites, discovered by the senior author and presumed then to have been growing over warm seepages in Salda Gölü (Russell 1996), have been described in detail by Braithwaite & Zedef (1994, 1996*a*, *b*). The realization that these uniquely large hydromagnesite edifices (Fig. 4) were microbialites (cf., Burne & Moore 1987) was made in the context of our studies of ophiolite-hosted Miocene magnesite ($MgCO_3$) deposits (Fallick *et al.* 1991) including Bela Stena in Yugoslavia, of Carboniferous bacteriogenic sulphide deposits (Boyce *et al.* 1983) and our model for the origin of life on Earth which conjectures that it emerged *c.* 4.2 billion years ago at medium temperature seepages into standing water (Russell *et al.* 1998).

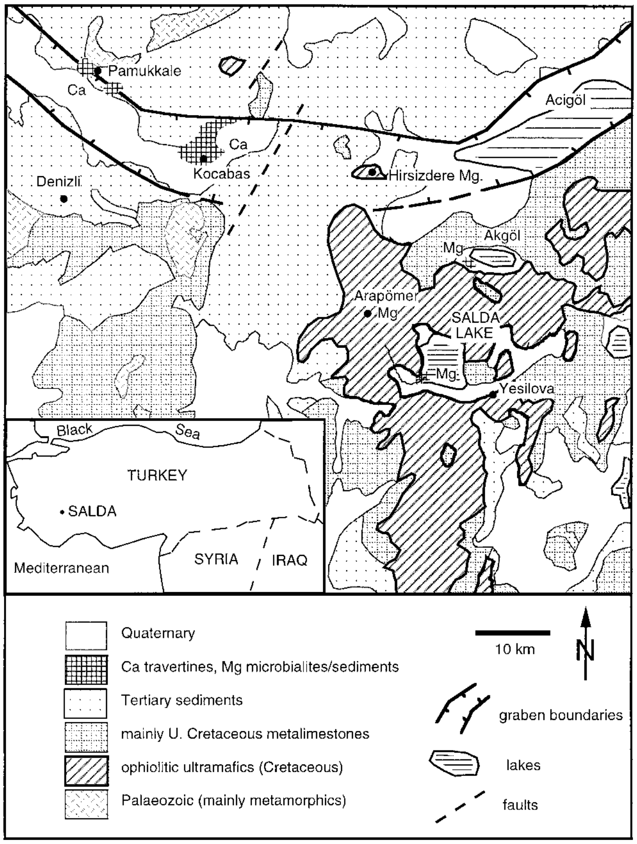

Fig. 3. Geological environment of Salda Gölü in the Eslerdagi ophiolite complex and its relationship to other carbonate deposits in the Menderes Graben to the north and west (from Pamir 1964; Sarp 1976; Altunel & Hancock 1993). Note that Akgöl and Acigöl are evaporated lakes, the former now dried out, the latter still with some surface water.

Appreciation of the role of mafic rocks in the genesis of magnesite deposits (Milan Ilich 1952; Milo Ilich 1968, 1970, 1974; Fallick *et al.* 1991) and the emergence of life on Earth (Russell & Hall 1997) has led us to consider magnesite/hydromagnesite deposits on Mars to be appropriate targets for the exploration for evidence of early life on that planet. Below we examine the process of development of this and comparable bodies as an orientation survey for the exploration of 'White Rocks' by landers such as *beagle,* hopefully early next century. In doing so we also processed satellite digital image data to assess the full extent of hydromagnesite developments in Lake Salda that they might be compared to the digital photomosaics of 'White Rock' and its environs.

Salda Gölü microbialites

Salda Gölü is an evaporitic alkaline magnesian lake covering an area of about 45 km^2 within a partially serpentinized ophiolitic terrain in southwestern Turkey (Fig. 3). Harzburgite is the dominant country rock, though it has been completely metamorphosed to lizardite in places (Sarp 1976). There are subsidiary dunite outcrops. A tract of Upper Cretaceous limestone is faulted down to form a small portion of the

Fig. 4. Hydromagnesite microbialites and emergent stromatolites in Salda Gölü: (**a**) southeasterly prospect across the estuary to the Salda River (Karakova Dere) with living hydromagnesite stromatolites comprising islands just beyond the emergent fossil structures mainly developed to the west of the current river trace, (**b**) view of the same islands looking east from the hydromagnesite cliffs (Upper Cretaceous limestone forms the hill beyond the farther shore; a hydromagnesite terrace can also be seen abutting this limestone), (**c**) photograph of a portion of the island to the right in (b), (**d**) small lagoon between the emergent stromatolite islands, (**e**) older stromatolites developed over and around a mound of harzburgite, (**f**) paddle thrust into the soft hydromagnesite mud lying in pockets between the microbialites pictured in (d).

eastern shore (Figs 3 & 4b). Sarp (1976) was first to report the extensive developments of hydromagnesite in Lake Salda and recognized the main features of the deposits reported by Braithwaite & Zedef (1996*b*) apart from their microbialitic nature.

A biofilm up to a centimetre thick, comprised essentially of green filaments of cyanobacteria, completely covers the submerged portions of the microbial mounds (see underwater photographs in Beköz *et al.* 1997). The direction of growth does not seem to be markedly related to sunlight incidence, though the northerly facing portion of the outer islands are steepest, but this is also the direction of shelve. Some of the mound growth appears to be engendered by diatoms such as *Navicula* and *Cymbella* (Braithwaite & Zedef 1996*b*, and see

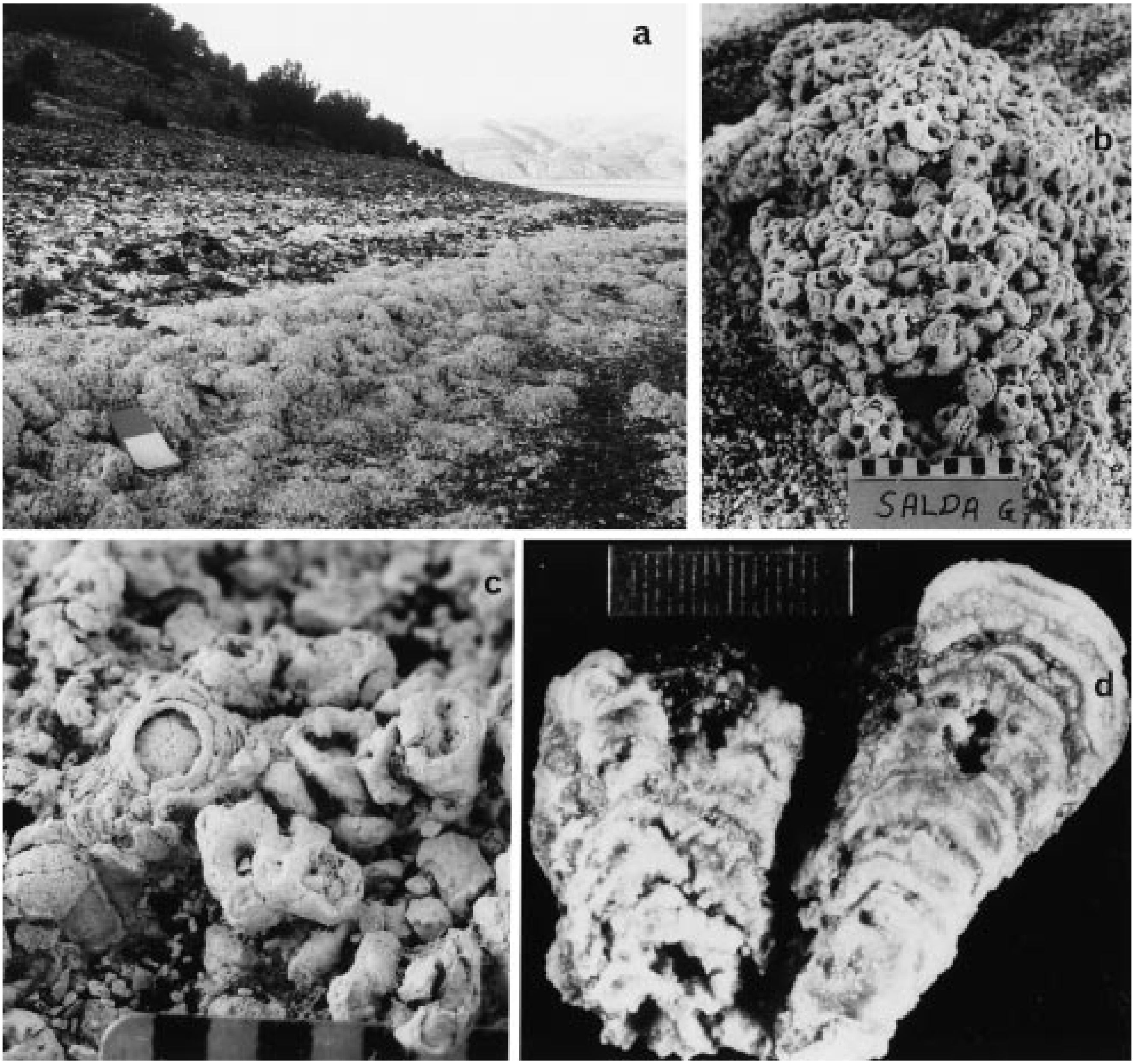

Fig. 5. Photographs of hydromagnesite stromatolites around Salda Gölü: (**a**) typical beach comprising recently exposed stromatolites; notebook in foreground measures 12 cm across, (**b**) close-up looking down on the clumps of columns with central orifices (scale in centimetres), (**c**) mixed morphologies of the stromatolites (scale in centimetres), (**d**) cross-section through two columns (scale 20 mm)

Winsborough & Golubic 1987). Their stalks provide nucleation sites for the initial precipitation of hydromagnesite (Braithwaite & Zedef 1996*b*). Cyanobacteria that also play a part in nucleation and precipitation are *Lyngba* and *Gloeocapsa* (Braithwaite & Zedef 1996*b*).

Once the biofilm decays then the hydromagnesite microbialites are revealed to be columnar with a central orifice (Fig. 5) and partly botryoidal (Fig. 5b,c,d) as described by Braithwaite & Zedef (1996*b*). The columns consist of alternating fine and coarse hydromagnesite layers differentiated on a millimetric scale. The coarser layers near the surface still contain decayed remnants of the biofilm. The reason for the periodicity was not determined, though judging from the overall thickness of the microbialites the individual laminae are likely to represent annual growth.

Consideration of the photograph of Kocaadalar Burnu peninsula pictured in Sarp (1976, plate 1), shows that the main focus of mound development then, as now, was at the very tip of, or just beyond, the promontary (Fig. 4a). Yet the locus of growth appears to have migrated over time at least 2.5 km from the WSW, perhaps tracking the prograding delta front, judging from the extensive Holocene beach deposits of hydromagnesite about 30 m above the present surface of the lake, briefly exposed in 1997 by the road entering Salda Village (Fig. 6). The area of stromatolite growth generated when lake levels were substantially higher than today, amounts to about 2 km^2 (Fig. 3 and see Schmid 1987; Braithwaite & Zedef 1994, 1996*b*; Çoban *et al.* 1995).

Terraces comprised of hydromagnesite are also well developed on the eastern shore. Some of these include

Fig. 6. Photograph taken in October 1997 of recently exposed Holocene beach deposits of hydromagnesite containing pebbles of lizardite beside the road into Salda village (background looking northwest) about 30 m above the present lake level. The original exposure measured 200 m SE–NW, *c.* 100 m across and was about one metre thick. The exposure has now been filled in though the overlying deltaic sequence is still visible to the northeast.

boulders of redistributed hydromagnesite up to 50 cm across (Braithwaite & Zedef 1996*b* fig. 4D). In fact hydromagnesite stromatolites occur all around the lake (e.g., Fig. 5a) and with their debris they render the entire shoreline white (Fig. 8). The larger developments are at the dry estuaries of streams, the ones near the estuary of the Salda River (Karakova Dere) being the largest. Nevertheless the Landsat imagery also reveals a subsurface development of hydromagnesite of comparable extent over the Yesilova delta in the ESE (Fig. 9).

Fossil microbialites were also discovered in the friable hydromagnesite cliffs shoreward of the main developments, though the structures of the individual microbes have not survived. Instead the vestiges of microbialites are easily recognized and delineated by their coarse grain size and high porosity. These stromatolitic morphologies do not survive long-term exposure and lithification. Generally the stromatolites degenerate to a porous, coarse-grained, poorly lithified rock as seen in the cliffs opposite the islands (Fig. 7). Only the fact that the intervening muds, pictured in Fig. 4f, retain their relationship with the former microbialites betrays their origin (Fig. 7b,d). Although occasionally the upper, annulated botryoidal surface survives immediately beneath the lithifying muds, all trace of the laminations have been obliterated (Fig. 7c). (Paradoxically microfossils are only found in sparry magnesites, and then preservation is restricted to that of blastospores, irrelevant in this context (Brunel *et al.* 1985; Chaye d'Albissin & Guillou 1986).)

Just how Salda Gölü itself formed is not known though it is in a region of tectonic extension (Seyitoglu & Scott 1991; Westaway 1990, 1993). This is a suitable environment for the development of intermontaine basins (Sarp 1976) and topographically-driven hydrologic flow. Grand *et al.* (1993) have argued that, since the late Neogene, tectonic activity in the eastern Mediterranean has been mainly extensional with the exception of compressional events of short duration in the Cyprus ophiolitic massif. Salda Gölü occurs in a zone of low heat flow and no warm springs are known from the immediate area (Tezcan 1979; Braithwaite & Zedef 1996*b*). Nor did we discover any in Salda Gölü itself. Sarp (1976, p. 3) noted that all the rivers draining into Salda Gölü traverse peridotites and that all these rivers follow faults. There are no surface outlets (Sarp 1976). Although the lake shelves relatively gently for the first few hundred metres from the southern shore it attains a depth of 184 m (Saracoglu 1990).

The dimensions of the hydromagnesite developments suggest a mass of the mineral totalling well over one million tonnes. The magnesium concentrations in wells and cold springs (generally 12–15°C, pH 8–10) in the ultramafic surrounds of the lake average 60 ppm (Braithwaite & Zedef 1996*b*). Sodium, by contrast, has an average concentration of *c.* 5 ppm (Table 1). Ions of both these metals are concentrated in the lake, but to different degrees. Water samples collected from the lake surface and down to a depth of 80 m invariably contain *c.* 300 ppm Mg and *c.* 200 ppm Na at a pH of 9.1. Evaporation and loss through sublacustrine fractures partly balances influx. While Mg in the lake has only been concentrated by a factor of six or so over the contributaries, Na has been enriched some forty-fold. Evaporation can thus account for the known mass, and more, of hydromagnesite in and around the lake. Mass balance calculations suggest that the hydromagnesite developments took in the order of 5000 years to generate. Such an age happens to correspond with the end of the 'warm and wet' period (Gagan *et al.* 1998; Malville *et al.* 1998). We assume the lake itself must be younger than the last very dry period dated at 15 ka BP (Landmann *et al.* 1996).

In spite of the fact that magnesite ($MgCO_3$) appears to be the thermodynamically stable magnesian carbonate phase in the low temperature aqueous environment, hydromagnesite is widespread, kinetically favoured (Christ & Hostetler 1970) and easy to synthesize (Zachmann 1989) (Fig. 10). It is evident from the components of its formula [$Mg_5(CO_3)_4(OH)_2.4H_2O$] (Akao & Iwai 1977) that, relative to magnesite, it is generated at higher pH, lower pCO_2 and lower water activity, that is, its growth is encouraged by evaporation. Magnesite seems to require relatively high pCO_2 and pressure (Zachmann 1989).

The precipitation of hydromagnesite on increase in pH resulting from CO_2-depletion (more specifically HCO_3^- depletion) can be accounted for as illustrated in Figs 10 & 11a. This model is also supported by the carbon and oxygen isotope data (analytical methods are detailed in Fallick *et al.* 1991; Zedef 1994; Table 2). The $\delta^{13}C_{(PDB)}$ values of the Lake Salda hydromagnesites are generally around +4‰. This represents an 11‰ fractionation from atmospheric carbon dioxide which has a value around −7‰. The $\delta^{18}O_{(SMOW)}$ values have a broader range extending from +31 to +38‰, though most fall around the mean at +36‰. The water from Salda Lake had a value of about +3‰ (in October 1992) whereas local rainwater approximates −5‰ (Zedef 1994).

The enrichment in ^{13}C producing isotopically heavy carbon in the hydromagnesite is considered to have resulted from selective removal of ^{12}C by cyanobacteria and diatoms. The isotopically heavy nature of the carbonate carbon also means that it is unlikely that the hydromagnesite is precipitated as a result of direct carbonation of alkaline (magnesium hydroxide rich) lake water (cf. Evans & St. Clair 1949). This view is grounded in the research of Macleod *et al.* (1991) on the carbonation of concrete in alkaline waters. They demonstrated that a marked kinetic, rather than equilibrium fractionation, produces carbonate with carbon isotope values of −17‰ or less, i.e., at least 10‰ lower than that of atmospheric carbon dioxide. Such a process would therefore produce a carbon

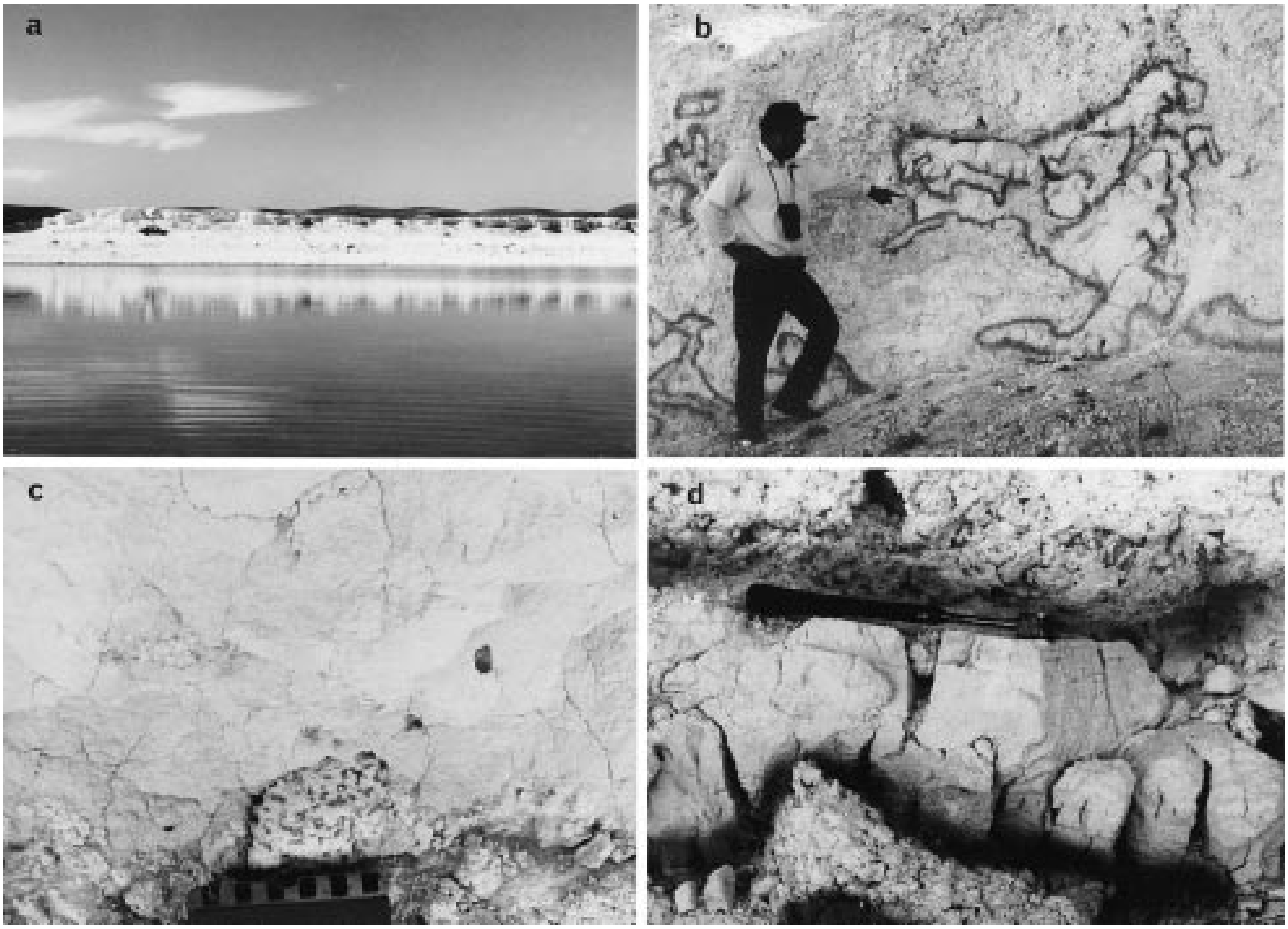

Fig. 7. Photographs of cliff taken from the islands featured in Fig. 4: (**a**) looking southwest, (**b**) close-up of outcrop to the extreme right in (a) demonstrating the (painted) contact between the coarse porous hydromagnesite comprising much of the picture, i.e., the remnants of stromatolitic structures figured in Figs 4d and 5 and the consolidating intervening hydromagnesite mud pictured in Fig. 4f, (**c**) close-up of a remnant of stromatolite with a morphology comparable to that pictured in Fig. 5b, overlain by partially lithified hydromagnesite mud, (**d**) a close up of (b) showing a layer of lithifying mud between to developments of stromatolite: the consolidated mud exhibits conchoidal fracture.

isotope fractionation in the opposite sense to that observed at Lake Salda.

The oxygen isotope exchange fractionation factor for hydromagnesite deposition from water has been measured experimentally by O'Neil & Barnes (1971). These authors report per mil fractionations of 37.6 at 0°C and 31.7 at 25°C. Recall that lake water in Salda Gölü has a present-day $\delta^{18}O$ value of +3‰ (Zedef 1994). The average $\delta^{18}O_{(SMOW)}$ of 22 hydromagnesite samples is +36‰ ± 1‰ (Zedef 1994), similar to the $\delta^{18}O$ value of *living* stromatolite growing in Lake Salda reported here (Table 2). Thus the per mil fractionation is 33, giving a temperature of stromatolite deposition of *c.* 19°C, in agreement with summer lake temperature (Table 1). But what of the more extreme $\delta^{18}O$ values recorded in Table 2? Influx of isotopically lighter meteoric water can contribute to the production of isotopically lighter hydromagnesite (e.g. Rosen *et al.* 1988) at a given temperature and similarly, periods of drought and high evaporation could lead to hydromagnesite having a low value of $\delta^{18}O$. The $\delta^{18}O_{(SMOW)}$ values of hydromagnesite from the dried-out lake bed of Akgöl (MV19, another enclosed lake 10 km NNE of Salda Gölü occupying limestone as well as an ultramafic terrain) at 28‰, are particularly low, though if ground water were to be derived directly from meteoric water at −5‰, the temperature of deposition would have again been about 19°C (Table 2). On the other hand, if the $\delta^{18}O$ of the ground water were high then elevated temperatures for precipitation would be implied, as to be expected if precipitation was from fluids brought to the surface by capillary action to the dry lake floor in the summer.

The low $\delta^{18}O$ value of the mudstone MV 12 in Salda Gölü may be explained by precipitation from water at *c.* 35°C, a temperature commonly reached in the summer in the shallows between the microbialites. The cobble of hydromagnesite mudstone (MV 42) collected from a stream running into the bay just to the west of Kocaadalar Burnu may have been originally generated in the same way. Alternatively it may have re-equilibrated with rain water. A fuller exposition is given in Zedef *et al.* (in press).

Assuming deposition of the hydromagnesite to be focused above cold seepages (cf. Russell 1996), we favour a model of hydromagnesite genesis reminiscent of Lur'ye & Gablina's (1972) explanation of Mansfeld-type copper mineralization in the West Ural foreland (and see Calvo *et al.* 1995; Stamatakis 1995). In this kind of model, meteoric water is guided along the deepest portion of the pebble-filled channels of often apparently dry rivers. Lur'ye & Gablina (1972) recall that the beds of many modern rivers are readily traceable into the submarine or

Fig. 8. Rectified natural colour Landsat Thematic Mapper (TM) image of Salda Lake and its southern environs (bands 3/2/1). The peninsula comprising hydromagnesite at Kocaadalar Burnu is seen in the southwestern sector of Lake Salda. The white shoreline may be compared to fig. 3 in Williams & Zimbelman (1994). See Maktav *et al.* (1994) for details of processing. Further interpretations of the spectral data of Lake Salda are to be published elsewhere.

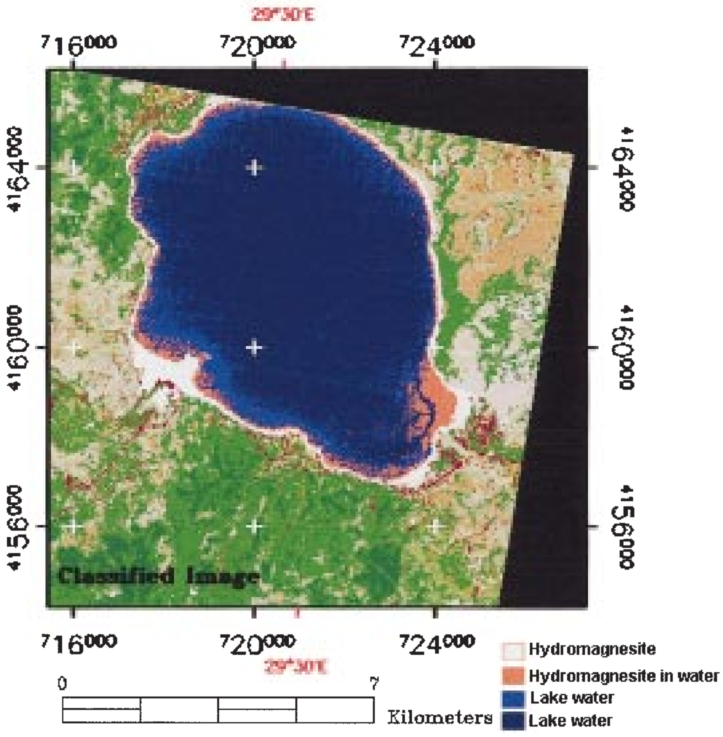

Fig. 9. Rectified and classified Landsat TM (false colour) image of Salda Lake revealing two extensive areas of hydromagnesite: the mostly exposed (white) deposits at Kocaadalar Burnu in the southwest, and the hydromagnesite sediments comprising the mostly submerged (orange) Yesilova delta in the east-southeast. Compare with ‘White Rock’ in Juventae Chasma (Fig. 16b) (all TM bands except band 6).

Table 1. *AAS analyses of waters from Salda Lake and its surrounds*

Sample	Mg	Ca	Na	Si	pH	Description
97-1	306	2	214	<1	9.2	Lake SW surface 17°C
97-3	309	3	204	<1	9.8	SW surface 18°C
97-17	303	3	205	<1	9.1	Mid-lake 0 m 17°C
97-21	305	3	202	<1	9.2	Lake depth 20 m 17°C
97-20	303	2	194	<1	9.2	Lake depth 40 m 9°C
97-16	303	2	193	<1	9.1	Lake depth 40 m 9°C
97-18	303	2	195	<1	9.1	Lake depth 50 m 8°C
97-22	311	2	191	<1	9.2	Lake depth 60 m 7.5°C
97-19	305	2	188	<1	9.1	Lake depth 70 m 7.5°C
97-8	299	2	190	<1	9.0	Lake depth 80 m 7.5°C
93-16	68	2	2	<1	10.0	Spring 13°C
93-14	78	6	6	15	8.7	Stream 22°C
93-18	44	4	2	12	8.6	Stream 17°C
93-1	54	34	20	14	—	Well depth 30 m
93-2	60	21	8	13	—	Well depth 7 m
93-4	49	1	3	<1	9.8	Well 15°C
93-6	83	9	7	13	9.0	Well depth 80 m 12°C
93-7	75	8	6	12	—	Well depth 2 m
93-8	82	7	4	16	7.7	Well 26°C
93-9	93	3	3	8	8.2	Well 24°C
93-13	102	4	5	2	9.5	Well 13°C
93-15	41	2	1	6	—	Well —
93-17	27	2	3	4	9.0	Well 14°C
93-19	22	24	11	11	8.0	Well 14°C
93-20	23	6	5	11	f7.9	Well 15°C

Concentrations in ppm: 97-1 to 97-22 collected October 1997 (*ab intra*); 93-1 to 93-20 (Zedef 1994; Braithwaite & Zedef 1996*b*).

sublacustrine environment still carrying flows of fresh water. In the Eslerdagi ophiolite complex we imagine that magnesium dissolves in such waters bearing atmospheric and soil-derived CO_2. We offer the following idealized reaction to demonstrate the release of magnesium from lizardite, a common bedrock mineral along the Salda River:

$$5Mg_3Si_2O_5(OH)_4 + H_2O + 6CO_2 \rightarrow 3Mg^{++} + 2SiO_2 + 6HCO^-_3. \quad (1)$$

Stream, well and spring waters draining the ultramafic massif carry up to *c.* 100 ppm Mg and their average content is *c.* 60 ppm (Table 1, and see Braithwaite & Zedef 1996*b*). Iron and most of the silica would remain behind as hematite and quartz or chalcedony (cf. Henderson & Fortey 1982) while the magnesium bicarbonate solution presumably seeps into the lake at the base of streams and from the toe of the delta at Kocaadalar Burnu (cf. Lur'ye & Gablina 1972; Kempe & Kazmierczak 1994; Moore 1996) (Fig. 12). The seepages, topographic highs as well as the shore itself, provide foci for the development of microbialites as photosynthetic microbes fix a proportion of the carbon dioxide. Hydromagnesite is precipitated as pH increases (Fig. 10a,b) (and see Langmuir 1965).

The likely mechanism has been described by Miller & Colman (1980) and Thomson & Ferris (1990). These authors show that cyanobacteria are responsible for the alkalization of their immediate micro-environments. In waters of pH of *c.* 8 they fix carbon from HCO^-_3 during photosynthesis and emit hydroxyl ions:

$$nHCO - 3 + nH_2O + h\nu \rightarrow (CH_2O)_n + nOH^- + nO\uparrow_2. \quad (2)$$

We modify their mechanism in order to account for the precipitation of hydromagnesite as follows:

$$5Mg^{++} + 4HCO^-_3 + 6OH^- \rightarrow Mg_5\,(CO_3)_4(OH)_2.4H_2O. \quad (3)$$

In detail initial nucleation of the Mg^{++} will have been on a carboxyl group appended to a periplasmic protein which, as a bridging ion, afforded the possibility of attracting the counter ion, i.e., the bicarbonate:

$$R.COO^- + Mg^{++} + HCO^-_3 \rightarrow R.HCOOMgHCO_3 \quad (4)$$

or

$$HCO^-_3 + OH^- \rightarrow CO{=}3 + H_2O \quad (5)$$

and

$$5Mg^{++} + 4CO^{2-}_3 + 2OH^- + 4H_2O \rightarrow Mg_5(CO_3)_4\,(OH)_2.4H_2). \quad (6)$$

In time dehydration could bring about the crystallization of magnesite with water again being lost but the brucite component retained as shown notionally below:

$$Mg_5(CO_3)_4\,(OH)_2.4H_2O \rightarrow 4MgCO_3 + Mg(OH)_2 + 4H_2O. \quad (7)$$

That such a dehydration might take place is supported by Ilich *et al.* (1991) who record the development of brucite from the Cosovac stockwork magnesite at Razana in western Serbia, Yugoslavia. Here millimetric brucite spheroids are spaced two or three centimetres apart in veins of cryptocrystalline magnesite. Brucite spheroids might be awaiting

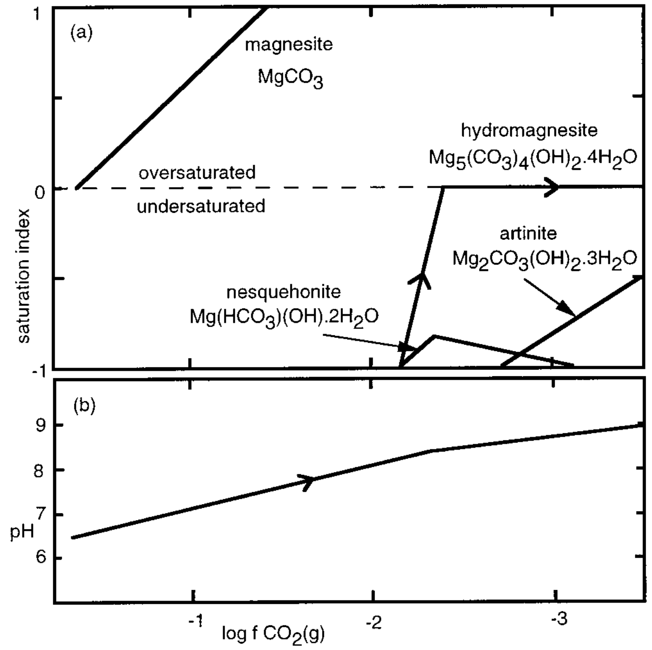

Fig. 10. (**a**) diagram illustrating the saturation in carbonate minerals during a theoretical reaction process. The saturation index is a function of the equilibrium constants for mineral solubility. A magnesite-saturated fluid, as would be formed on equilibration of a CO_2-rich fluid with magnesite at 25°C, is allowed to lose CO_2. Magnesite precipitation has been suppressed (see Christ & Hostetler 1970) and there is no redox aspect. The reaction proceeds from left to right and as CO_2 fugacity falls, the solution becomes increasingly supersaturated in magnesite. Eventually hydromagnesite becomes saturated (arrowed path) when its saturation index reaches zero, so that it precipitates below $\log fCO_2 = -2.3$. Nesquehonite and artinite remain undersaturated as the fCO_2 falls to the atmospheric level on Earth of $10^{-3.5}$ bars. (**b**) The pH increases from 6.5 to 9.0 as the fugacity of CO_2 falls to atmospheric level and beyond. Computed using Geochemists Workbench program REACT (Bethke 1996).

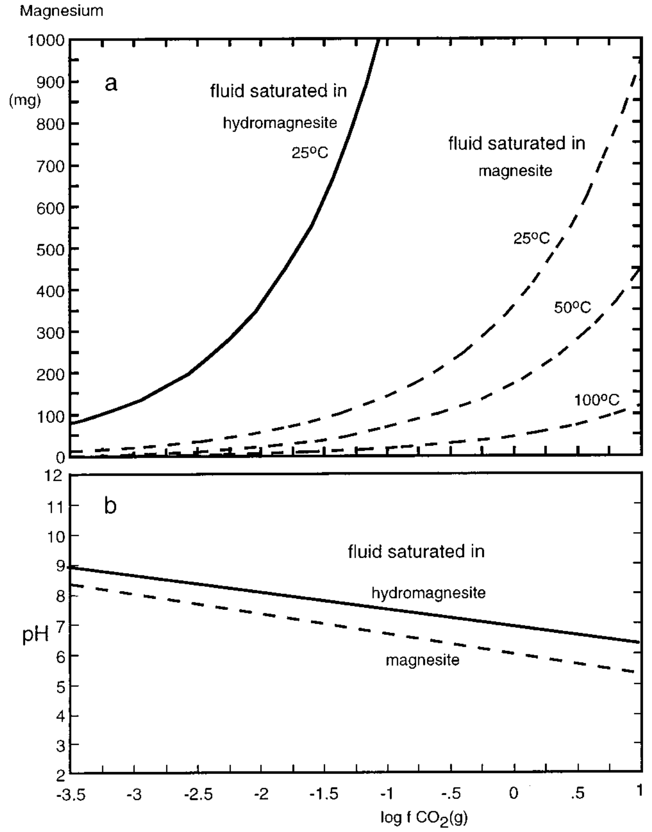

Fig. 11. (**a**) Calculated variation in magnesium solubility with CO_2 pressure for solutions saturated in magnesite for 25, 50 and 100°C and for solution saturated in hydromagnesite at 25°C (with magnesite precipitation suppressed). Total magnesium in fluid in mg/kg. Computed using Geochemist's Workbench, REACT (Bethke 1996). (**b**) Variation in pH with CO_2 pressure for solutions saturated in magnesite (almost identical for 25, 50 and 100°C), and solution saturated in hydromagnesite at 25°C (with magnesite precipitation suppressed). Computed using Geochemist's Workbench, REACT (Bethke 1996).

discovery in many low temperature magnesite deposits as a result of this transition, though if so, they have so far gone unremarked.

Braithwaite & Zedef (1996*b*) draw attention to a microbial flora dominated by diatoms with subsidiary low diversity cyanobacteria, and their involvement in the deposition of hydromagnesite. Presumably hydromagnesite precipitates as carbon dioxide is extracted by the bacteria (equations 2 & 3, Figs 10b & Fig. 13a) and the diatoms. The seepages will provide trace elements and, perhaps, a minor amount of H_2 to the microbialite (Coveney *et al.* 1987; Neal & Stanger 1984). Moreover, the methane generated by methanogenic bacteria, which constantly bubbles up from the hydromagnesite-serpentinite-organic ooze comprising the lake floor, is an added nutrient for heterotrophs.

The diatoms appear to take all the available silica. It is represented in the contributaries in a range up to 16 ppm whereas it is below the detection limit of 1 ppm in the lake itself. Diatoms rapidly dissolve out of the consolidating stromatolites (Fig. 13b) and are not found as fossils in the hydromagnesite exposures in the cliffs south of the islands.

Bela Stena magnesite deposit

The Bela Stena magnesite deposit in Serbia, the former Yugoslavia (Ilich 1952; Ilich 1968, 1970), consists of a massive body at least 300 m long and up to 200 m thick. The magnesite body is hosted by Miocene lake sediments strongly deformed in the Alpine orogenic event (Figs 14 & 15). These sediments include irregular ribs of magnesite a metre or so thick with discrete local developments up to 2 m high. 'Bela Stena' is Serbocroation for white rock. There are some striking large-scale morphological similarities between the reworked hydromagnesite comprising some terrace deposits at Salda and outcrops in the open pit at Bela Stena (Fig. 14). In particular boulders of magnesium carbonate a meter or so across, as well as well-bedded fine grained sedimentary carbonate, occur in both (compare Braithwaite & Zedef 1996*b*, fig. 4D with Fig. 14a). The possibility that the discrete smaller bulbous magnesite bodies were individual microbialite mounds is worth further investigation. Vestigal annular and botryoidal shapes on the outer upper surface would be evidence for a similar microbial origin.

Table 2. *Isotopic compositions of hydromagnesite from Salda Lake and its surrounds*

Sample	$\delta^{13}C_{(PDB)}$	$\delta^{18}O_{(SMOW)}$	Description
MV42	4.3	30.6	Stream cobble (SW)
MV49	4.2	36.0	Living microbialite
MV12	4.5	31.1	Mudstone (SW)
MV41	4.4	33.8	Kocaadalar
MV47	4.5	35.1	Bay terrace
MV45	4.1	35.1	Kocaadalar
MV44	4.7	34.8	Bay terrace
MV43	4.5	33.7	On harzburgite (SW)
MV8	4.2	33.8	15 m terrace (SW)
MV48	4.6	33.6	30 m terrace (SW)
92-18	4.5	36.3	Kocaadalar
92-19	4.2	36.1	Burnu
92-20	4.4	36.8	Kocaadalar
92-21	4.7	35.6	Burnu
92-22-A	4.5	36.0	Kocaadalar
92-22-B	3.9	34.5	Burnu
92-24	4.3	36.2	Kocaadalar
93-24-1	3.4	35.8	Burnu
93-24-2	4.3	36.6	Kocaadalar
93-24-3	4.8	38.1	Burnu
93-15	4.4	37.3	Kocaadalar
93-2	3.6	33.0	W lake shore
93-5	3.7	36.2	W lake shore
93-7	4.7	35.3	NW lake shore
93-8	4.3	34.9	E lake shore on
93-9	3.8	36.1	Cretaceous lst
93-10	0.2	35.3	E lake shore on
93-30	4.4	36.0	Cretaceous lst
92-27	4.3	36.5	E lake shore
92-70	4.2	36.2	SE lake shore
93-21	4.1	35.9	SE lake shore
93-22	3.9	35.2	SE lake shore
MV19	0.7	27.9	SW Akgöl surface
MV19	0.1	28.2	Dry lake sediment

Samples MV8 to MV49 collected October 1997 (*ab intra*); 92-18 to 92-70 and 93-2 to 93-30 from Zedef (1994).

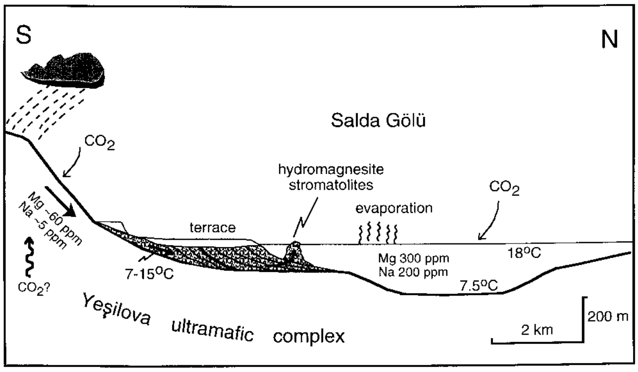

Fig. 12. Model for the generation of hydromagnesite stromatolites in Salda Gölü.

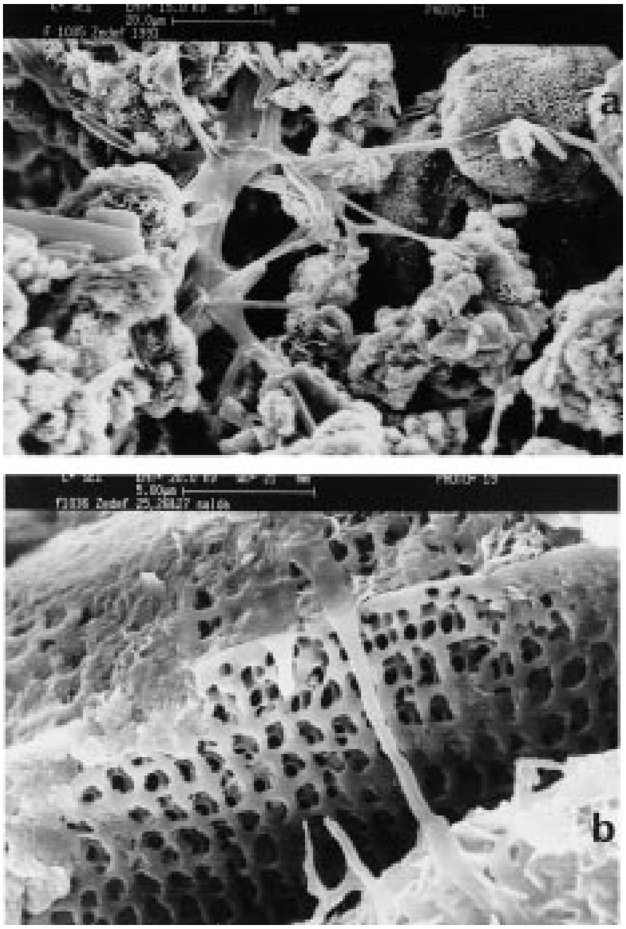

Fig. 13. (**a**) Precipitation of hydromagnesite rosettes on cyanobacterial filaments and mucilage. (**b**) Siliceous test of a diatom in a denaturized microbialite from Salda Gölü in the process of dissolution.

In contrast to the siting of the Salda Lake hydromagnesite developments, the Bela Stena deposit appears to have formed a few hundred metres from the Miocene shoreline (Ilich 1952), immediately to the south of an andesitic inlier (Ilich 1970) (Fig. 15a,b). This andesite is a representative of the broadly coeval volcanic rocks which cover the ultramafic source rocks (Milovanovich & Ciric 1968). A sedimentary borate bed comprising colemanite and haulite has been drilled 1 km north of the magnesite deposit (Fallick *et al.* 1991). Thus a hydrothermal origin for the Bela Stena deposit must still be entertained (Milan Ilich 1952; Miloje Ilich 1974). Even if the hydrodynamic drive was different the depositional process was probably similar to that in Salda Gölü. If so we must assume that hydromagnesite was the precursor to the (diagenetic?) magnesite (cf. Zachman 1989).

Any microscopic evidence of microbialite morphologies appears to have been obliterated, perhaps first by reworking and finally by diagenesis, though the mound-like outcrops at medium and large scales are consistent with such an origin. A smaller though similar magnesite deposit, Rvati, occurs in a separate outcrop of Miocene lacustrine sediments about 8 km to the south (Ilich 1970).

The oxygen and carbon isotopic compositions of magnesite samples collected from Bela Stena overlap with the population from the Salda Gölü hydromagnesites (Fallick *et al.* 1991; Zedef *et al.* in press). Samples from Bela Stena have rather wide ranges of $\delta^{13}C_{(PDP)}$ and $\delta^{18}O_{(SMOW)}$ values of *c.* − 2 to +4‰ and *c.* +31 to 36‰ respectively (Fallick *et al.* 1991), though Zachman (1989) records two $\delta^{18}O_{(SMOW)}$ values around 26.2‰. Having assumed a lake water $\delta^{18}O_{(SMOW)}$ value of − 2‰, Fallick *et al.* (1991) interpreted the oxygen isotope values as recording deposition at 20°C, i.e., around the same temperature as stromatolite growth in Salda Gölü. Neverthe-

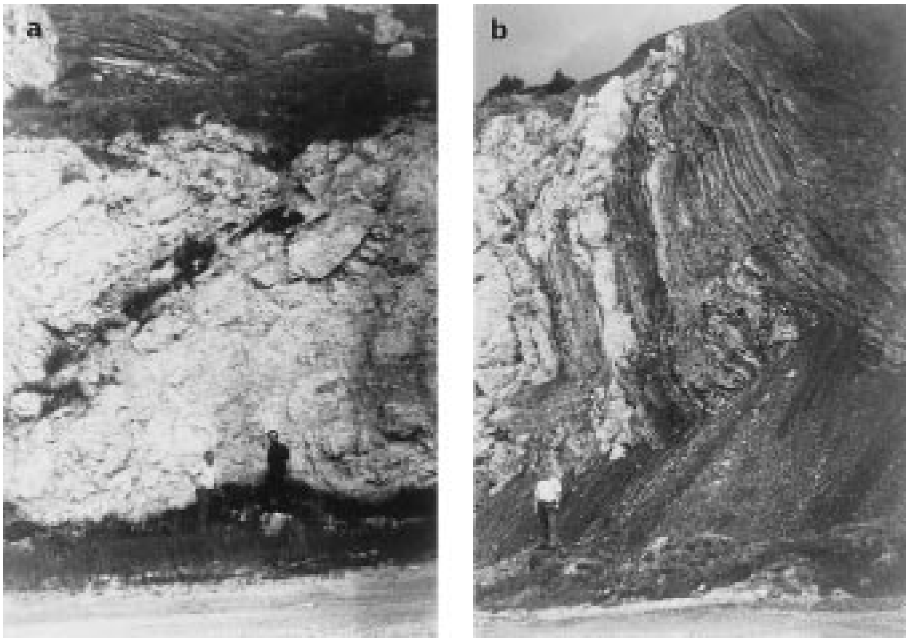

Fig. 14. The Bela Stena magnesite deposit, former Yugoslavia. The Miocene strata have been folded in the Alpine orogeny (Illich 1970): (**a**) boulders of magnesite in massive and finely bedded magnesite host (to be compared with Braithwaite & Zedef 1996*b*, fig. 4d), (**b**) magnesite ribs and lenses developed adjacent to the massive magnesite core at the eastern edge of the deposit. Photographs kindly supplied by Miloje Ilich.

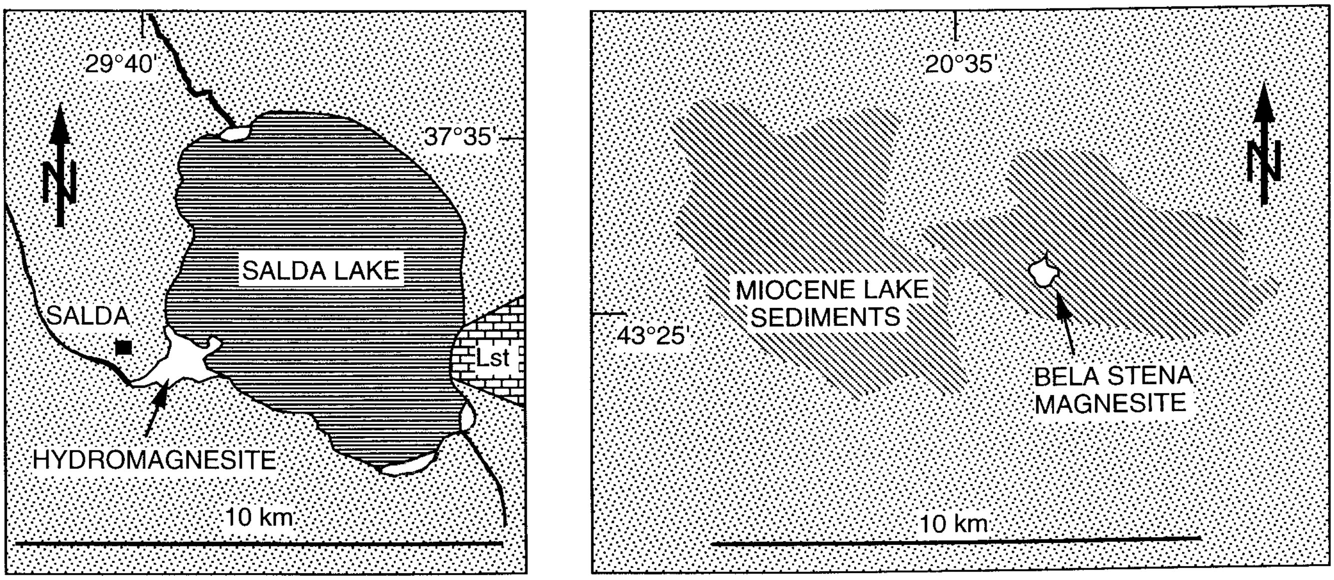

Fig. 15. Comparison between Salda Gölü and Bela Stena: (**a**) disposition of hydromagnesite stromatolites and beach deposits in Salda Gölü, (**b**) Bela Stena magnesite deposit in Miocene lake sediments. Apart from the tract of limestone, the surrounds to Lake Salda comprise partially serpentinized harzburgite (Sarp 1976), whereas those surrounding the Miocene lacustrine sediments hosting Bela Stena consist of serpentinized peridotite overlain by andesitic lavas and pyroclastics (Ilich 1970). Andesite (not shown) outcrops just to the north of the magnesite body (Ilich 1970). Compare both deposits to 'White Rocks' pictured in Figs 1c & 16b.

less, if we assume no diagenetic changes to the values, depositional temperatures approaching 60°C are permitted by the Zachman (1989) data. The carbon isotope values can also be interpreted to be atmospheric as for the Lake Salda deposit, but possibly with the addition of carbonate derived from oxidized plant material in alluvial sediments infiltrated by the groundwaters feeding the Miocene lake (cf. Fallick *et al.* 1991).

Magnesian carbonates in North Greece

Plio-Pleistocene deposits with characteristics intermediate between Lake Salda and Bela Stena occur in the Servian Basin, northern Greece (Wetzenstein 1975; Zachmann 1989). The hydromagnesite in the Servian Basin often exhibits fine botryoidal and reniform morphologies. It is associated with magnesite, huntite, dolomite, aragonite and calcite (Zachmann 1989). The few carbon and oxygen isotope measurements from these deposits (Kralik *et al.* 1989) are comparable with the Lake Salda values. Although no stromatolites have been recorded from these areas, both might be expected to yield such structures on further investigation.

The Martian 'White Rock' and its genesis

The mound-like 'White Rock' on Mars covers an area approaching 200 km^2 and has a maximum dimension of 18 km

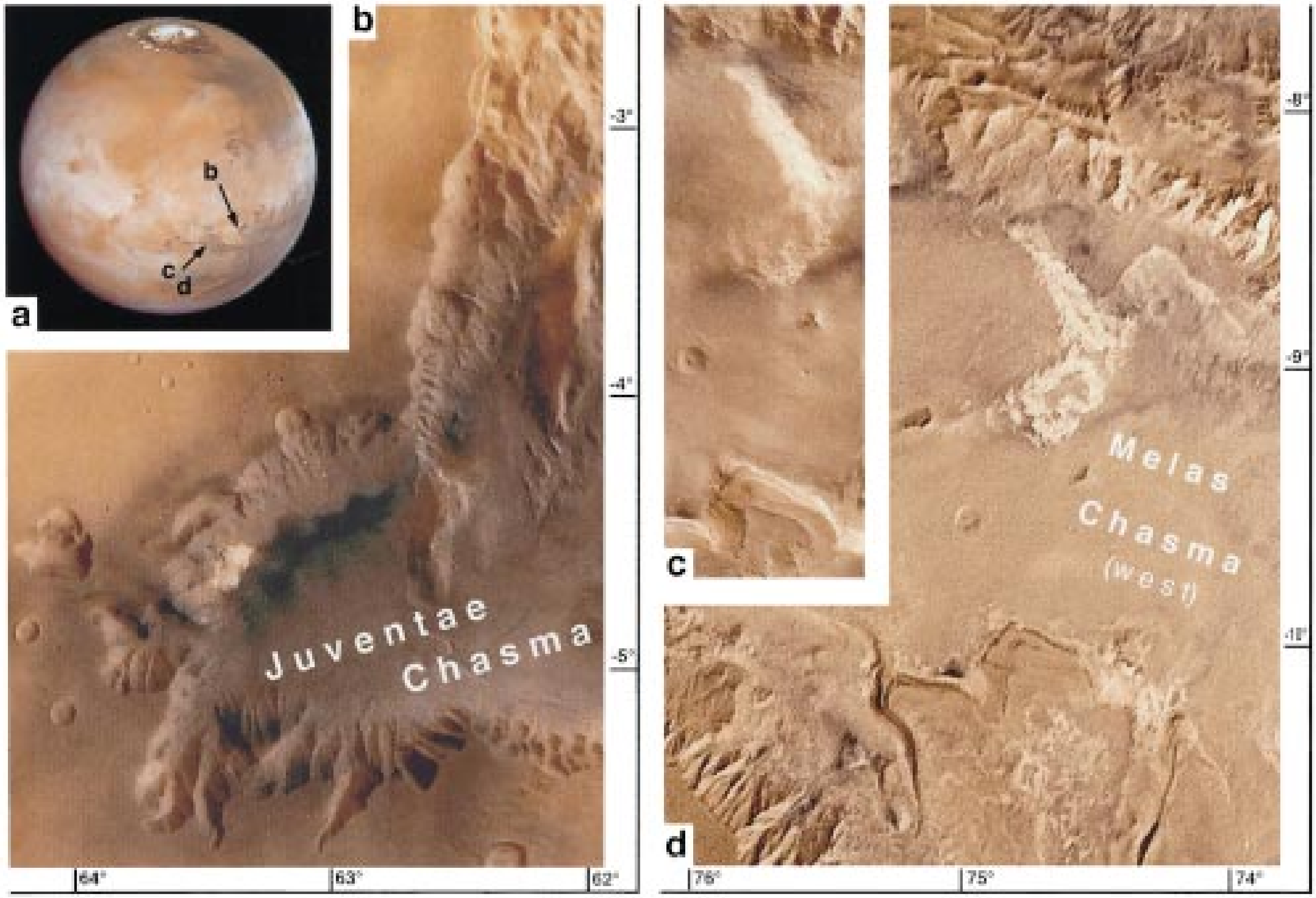

Fig. 16. Martian white rocks in and near Valles Marineris. (**a**) Hubble Space Telescope image of Mars (March 1997 opposition) showing location of images in b–d). Processing information as for Fig. 1a; (**b**) Part of Juventae Chasma (formerly Juventae Fons), showing very dark floor deposits (probably residual heavy mineral sands with pyroxene and olivine: cf. Singer *et al.* 1979; McCord & Cruikshank 1981; Mustard & Sunshine 1995; Lucey 1998; Christensen 1998) and a well-defined light coloured rock outcrop adjacent to the western cliffs of the canyon at 63.40°W, 4.65°S, with a suggestion of yarding topography and the coalescence of two mound-like masses together some 13 km by 8 km ('White Rock'). Note the edge of the depression or *alas c.* 30 km to the west which may have hosted a lake, perhaps one of the sources of the water responsible for the seepages. That a lake once occupied Juventae Chasma is suggested by the interlayering of dark and light layers comprising the north-south trending ridge 50 km to the NNE (Blasius *et al.* 1977, fig. 16). Compare with Fig. 8. Image is some 125 km across. (**c, d**) Part of western Melas Chasma in the central part of the Valles Marineris canyon system, showing a roughly crescentic outcrop of a light-coloured rock mass some 50 km long and close to the northern margin of the canyon. In inset '**c**' lighting is from the NE and in '**d**' it is from the SSE. Differences in illumination, together with outcrop shape, suggest an extensive low scarp facing broadly eastwards, resulting from the erosion of a huge but partly concealed lenticular rock mass within the canyon floor deposits. Some 50 km further south, across the canyon, are seen the much eroded and channelled remnants of younger, stratified canyon floor deposits. McKay & Nedell (1988) interpret the deposit as a dust-covered carbonate precipitated in lake water beneath a protective cover of ice. Images 16b and 16c originate and have been processed as for Fig. 1c. Image 16d is part of a separate Viking 2 Orbiter frame (Cat. No. PIA 00337). Its width is some 140 km.

(Fig. 2). It has a relief, though not necessarily total thickness, of up to 540 m, and is centred on a smaller crater *c.* 3 km in diameter, evidenced by a ghost-like erosional feature SE of the centre of the mass. Williams & Zimbelman (1994) suggest that the 'White Rock' is an erosional remnant of an evaporite originally 700 m or more thick, a formation assumed to have occupied the entire crater. Yet even though the 'White Rock' has been deeply eroded into yarding topography, the original mound-like form is evident. Thus we prefer to interpret the 'White Rock' as reflecting the original structure which is draped over the small crater. This crater may have provided the elevation necessary for nucleation, just as the Salda deposits in Turkey are situated above mafic knolls (Fig. 4e) (Braithwaite & Zedef 1994, 1996*b*). If it is draped around the crater, then the relief may not reflect the true thickness of the deposit. With this uncertainty in mind we estimate the mass of the putative hydromagnesite to be between 10^{10} and 10^{11} tonnes, a giant four orders of magnitude larger than Lake Salda, though commensurate with the epigenetic Kunwarara deposits which have invaded Quaternary alluvium in Queensland, Australia (Wilcock 1998). Assuming a partial pressure of CO_2 of between 1 and 10 bar in the early Martian atmosphere (Pollack *et al.* 1987) and a minimum magnesium concentration in the tributaries of 1000 ppm (Fig. 11), then *c.* 10^{19} grams of water would have been required for transport, reaction with bicarbonate, and deposition. Thus the open hydrologic system, argued to have been necessary to produce the deposit by Williams & Zimbelman (1994), must have operated over a long period in the relatively quiescent tectonic regime obtaining on early Mars. Artesian seepages of ground water into this crater lake (cf. Brandt & Reimold 1995) could have provided nutrients for microbial growth. They would also have replenished the magnesium content of the evaporated lake water. Cauliflower-like megascopic structures, separated by finer grained magnesium carbonate mudstone, within the 'White Rock', would be strong evidence of a photosynthetic microbial origin.

There remains the puzzle as to why such a salient development of a carbonate has only been recognized in one crater, although two other broadly comparable outcrops occurring in equatorial canyons are discussed below. To explain this anomaly we suggest that generally, Martian water courses skirted most of the ancient craters, with access denied by the crater rims. Where they did find a way in, there was also a way out (e.g., in the Vedra Valles, Masursky *et al.* 1977; in the Maumee Vallis system, Baker & Kochel 1979; Theilig & Greeley 1979; Gusev Crater & McKay 1997), so that evaporation did not drive Mg concentrations above the solubility product for hydromagnesite. Another explanation is that microbialite mounds, fed from sub-lacustrine seepages, are buried in later sediment. In support of this possibility we did find a sediment comprising hydromagnesite (*c.* 50%), amorphous clay, lizardite, and minor microcrystalline quartz, calcite and organic matter on the dried out floor of Akgöl ('barren lake') near Mg-rich ($\leq$170 ppm, 14°C) springs 10 km NNE of Salda Gölü. It may be that these sediments hide a stromatolite complex within the pile. Moreover Partridge *et al.* (1993) have intersected carbonates hidden beneath a brine lake, asociated salt flats, muds and granite-derived sands and scree in the Pretoria Saltpan impact structure. This lake is fed from two springs issuing from the crater floor (Brandt & Reimold 1995).

A still further possibility is that magnesite has been transformed to sepiolite (*c.* $Mg_8[Si_4O_{10}]_3(OH)_4.12H_2O$) during flooding by waters of high pH, as in the Miocene lacustrine sediments near Eskisehir, another 240 km to the NNE Salda Gölü (Ece 1998).

Other Martian 'white rocks'

The 'White Rock' appears quite different to the superficial 'whitings' seen in Gusev Crater (Kempe & Kazmierczak 1997) and Schiaparelli (Fig. 1b). Such 'whitings', for example the high albedo feature at 36°W and 23°N following cliffs delineating part of the southern part of Chryse Planitia (Carr & Schaber 1977), may be composed of anhydrite.

The only high albedo rock feature similar in form to the 'White Rock' in Sabaea Terra lies adjacent to the western margin of the 3 km deep Juventae Chasma (Fig. 16b). Although the images currently available are at low resolution, this 8 × 13 km body has a definition somewhat similar to that of the 'White Rock' except that it appears to be composed of *two* coalesced mound-like masses (Fig. 16b). Images also suggest that yarding topography is developed on this composite exposure. It occurs about half way down the canyon wall, above 'Dark Rock' of Noachian or Hesperian age (Scott &Tanaka 1986). The surrounding plateau, which here lies at *c.* 5000 m, consists of Hesperian mafic lavas (Scott & Tanaka 1986). A deep depression or *alas* (Czudek & Demek 1970; Theilig & Greeley 1979) about 30 km to the west of, and up slope from, Juventae Chasma may have provided a ponded source of seepage waters (US Geological Survey Topographic Map of the western region of Mars 1991) (Fig. 16b). The depression looks to have been caused by the kind of foundering which generated the 'chaotic terrains' (Sharp 1973), the ultimate source regions of the outflow channels that fed Chryse Planitia 1500 km to the north-northwest (Carr 1979). Partial melting of the cryosphere beneath the lava plateau probably led to the collapse (a thermokarstic process) and allowed groundwater to pond underneath surface ice (Carr & Schaber 1977). Subterranean migration of the ponded water eastwards to Juventae Chasma would have been through Hesperian lavas, perhaps along a fracture paralleling Valles Marineris to the south (Lucchitta *et al.* 1992). That the permeability of the top kilometre or so of the Martian crust could support such flow has previously been argued by Carr (1979). Thus again this particular 'White Rock' is probably composed of magnesium carbonate. However, the resolution of the image does not allow us to be certain of the form of the supposed carbonate deposit. If a lake occupied Juventae Chasma at the time, as implied by the alternations of light and dark layers comprising the ridge km ENE of the White Rock (Fig. 16b) (Blasius *et al.* 1977, fig. 16), then an origin comparable to that of the two largest hydromagnesite bodies along the southerly shore of Lake Salda is possible (Fig. 8). On the other hand, were the chasma to have been relatively dry at the time, then the carbonate may have formed the kind of terraces found on the northern margin of the Menderes Graben at Pamukkale (Fig. 3), though of hydromagnesite rather than calcite and from cold rather than hot water.

Another much more extensive outcrop of white-coloured rock lies on the floor of Melas Chasma (Fig. 16c & d). This may be a lacustrine evaporitic carbonate deposit (McKay & Nedell 1988). The setting could be considered broadly similar to that in Acigöl, in the Menderes Graben (Fig. 3). However, McKay & Nedell (1988) consider the supposed carbonate deposit, which may have an extent in sub crop of more than 2000 km^2, to have been precipitated in a perenially frozen lake. Nevertheless, it is notable that all the main developments of what appear to be carbonates occur within 10° of the equator. Thus it is at least feasible that precipitation of (hydrous) carbonate was brought about by photosynthetic organisms in enclosed evaporating bodies of water.

Other potential areas for hydromagnesite microbialite developments over cool seepages are where canyons, channels and outwash fans intersect the northern lowland plains, the site of an early ocean (Parker *et al.* 1989, 1993). Cool seepages are sites additional to the warm and hot spring structures expected to be centred over faults, and are further targets for exobiological exploration (Walter & Des Marais 1993; Farmer 1996; Cady & Farmer 1996; cf. McGill *et al.* 1993; Walkden *et al.* 1993).

Discussion

In Salda Gölü individual clumps of microbialite about a metre or so across are often surrounded by a hydromagnesite ooze (Fig. 4d & f). The textural differences are recognizably preserved in the hydromagnesite cliffs of Salda Gölü (Fig. 7). Oxidation and flushing of organic material from the microbialites leaves a porous, somewhat coarse structure, whereas the originally soft intervening mud consolidates to form a cryptocrystalline deposit prone to conchoidal fracture and, on occasion, desiccation cracks. In cases where such deposits remain near the surface long after their formation, we might expect these contrasting textural varieties to survive even on conversion to magnesite. Further investigation of the Bela Stena magnesite body and deposits in the Servian Basin, in Northern Greece, is warranted to test this hypothesis.

One other expectation deriving from our study of Salda Gölü is that the δ^{18}C and δ^{18}O values of the supposed 'White Rock' carbonate may both prove to be fractionated by about +11‰ and +35‰ from their respective atmospheric and hydrospheric reservoirs. As the reservoirs are uncharacterized and their age unkown we can only make speculations based on assumptions regarding isotopic ratios at *c.* 4–2 Ga. The δ^{13}C of Martian CO_2 has been calculated as 36 ± 10‰ (Carr *et al.* 1985). Thus we might expect a low temperature magnesium carbonate precipitate to have a $\delta^{13}C_{(PDB)}$ of around 47 ± 10‰ assuming the atmosphere has not suffered isotopic fractionation over the last 2–4 Ga (Romanek *et al.* 1994) and that volcanic recycling of carbonate maintained a relatively high partial pressure of CO_2 (Schaefer 1993). A preferential loss of the lighter isotopes over time (Jakosky 1991) would permit lower values to be so considered. The same point holds for oxygen isotope ratios. Nevertheless, assuming a $\delta^{18}O_{(SMOW)}$ value of Martian surface waters between 2 and 4 Ga to be around −1‰ (the value for a deglaciated Earth), then magnesite or hydromagnesite samples from the 'White Rock' should also have $\delta^{18}O_{(SMOW)}$ values of +34 to +43‰, the higher values reflecting possible colder conditions on Mars at the time of deposition and the fact that the isotopes of oxygen are more highly fractionated in magnesite (Aharon 1988). These expected ranges of values alone, even if verified, cannot be construed as demonstrating a biotic origin for 'White Rock', merely that the temperatures of formation are as expected for such a precipitate.

Conclusions

The living hydromagnesite microbialites at Salda Lake, and diagenetically modified magnesite deposits at Bela Stena and in North Greece, provide excellent opportunities for study of carbonate morphologies in preparation for an exobiological exploration of Mars. Our research at Salda Gölü has revealed unique composite developments of living hydromagnesite [$Mg_5(CO_3)_4(OH)_2.4H_2O$] microbialites up to 7 m high and approaching 200 m across. Water samples collected from the surface and down to a depth of 80 m invariably contain *c.* 300 ppm Mg and *c.* 200 ppm Na at a pH of 9.1. Judging from well, spring and lake sampling, subterranean streams (≥7°C, pH range 7.8–10) entering the lake are assumed to be charged with *c.* 60 ppm Mg, but only *c.* 5 ppm Na. There are no visible outlets and evaporation and losses through sublacustrine fractures partly balance influx. While Mg in the lake has only been concentrated by a factor of five or so over the contributaries, Na has been enriched some forty-fold. Thus it follows that the precipitation of hydromagnesite, although mediated by photosynthetic microbes, is driven by evaporation. The stable isotopic signatures (δ^{13}C = +4‰: $\delta^{18}O_{(SMOW)}$ = +33 to +38‰) are also taken to imply that the (bi)carbonate is derived from atmospheric CO_2 and is precipitated from lake water at *c.* 20°C prone to evaporation.

Cyanobacteria as well as diatoms play a part in the precipitation of hydromagnesite (Thompson & Ferris 1990; Braithwaite & Zedef 1996*b*). Acidic polysaccharides on their surfaces and stalks respectively, bind Mg^{2+} which in turn acts as the cationic bridge and nucleation site for authigenic carbonate, itself made the more insoluble by a proximal rise in pH. The result is hundreds of cauliflower-like structures rising from the lake floor, separated in places by a hydromagnesite ooze.

We predict that the 'White Rock', constituting a portion of what look to be lacustrine sedimentary rocks near the margin of a crater up to 95 km across in Sabaea Terra, Mars, will prove to be a composite magnesium carbonate mound broadly comparable to that in Salda Gölü. The 'White Rock' is about 18 km long, 15 km wide and up to 540 m thick. Erosional features comprise what look to be clints and grykes. It is apparently centred on, and draped over, a smaller crater *c.* 3 km in diameter. The rim of this small crater may have provided the elevation necessary for nucleation of the mound. Although near-surface hydrodynamic flow regimes would have generally skirted crater rims, ground water seepage into this crater lake, sited at the small crater mentioned above, could have provided nutrients for photosynthetic microbial growth. It would also have replenished the magnesium content of the evaporated lake water.

Another 'White Rock' outcrop on the western margin of Juventae Chasma is also conjectured to be an exposure of magnesian carbonate, but developed over two adjacent seepages from the canyon wall. Were the two major hydromagnesite developments revealed by satellite imagery in Lake Salda to coalesce in time, then they might be expected to generate a similar morphology (Fig. 16b, cf. Fig. 9).

Bulbous megascopic structures, separated by finer grained magnesium carbonate mudstone, within the 'White Rock' strata, would be strong evidence for a photosynthetic microbial origin. The two exposures of 'White Rock' present a large enough target for a Martian exobiological programme. Resolution of the composition of these exposures, as well as the larger body in Melas Chasma, has to await the results from the NASA Mars Global Surveyor which has a thermal emission spectrometer (6–50 μm) with a resolution of *c.* 3 km per pixel. Imaging will give a resolution approaching 1.5 metres per pixel. This probe will be in a circular, near polar orbit around Mars from March/April 1999, and should begin high resolution mapping and other surveying shortly thereafter.

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