

FIG. 5 Stanol and stenol structures. Compounds designated as in Fig. 2 legend.

A stanol \rightarrow stenol conversion seems to occur in anoxic waters, and it seems to occur primarily in the smaller particles. The lens of anaerobic bacteria occurring at the O_2/H_2S interface of the Cariaco Trench and Black Sea¹⁷⁻²¹ is probably responsible. These small cells would be preferentially collected in the $<53\text{-}\mu\text{m}$ fraction, producing a maximum in the stanol/stenol ratio just below the O_2/H_2S interface. The larger ($>53\text{ }\mu\text{m}$) particles, that is those having greater sinking velocities and contributing more to the vertical flux to the sediments, have lower ratios that are similar to relatively unaltered surface material. Indeed, a sediment-trap sample from 400 m in the Black Sea had a $5\alpha(H)$ -cholestan- 3β -ol/cholest- 5 -en- 3β -ol ratio of 0.21, and ratios of other stanol/stenol pairs were comparably low. At the same time, however, it may be that the slowly sinking 'suspended' particles simply have a longer residence time in the region of the microbially active redox interface. Thus increased apparent conversion of Δ^5 -stenols into $5\alpha(H)$ -stanols may reflect this longer residence time in the 'microbial reactor' rather than strictly higher conversion rates in the small particles.

The conclusion that Δ^5 -stenols are reduced to $5\alpha(H)$ -stanols in anoxic waters contrasts sharply with an earlier report of no such conversion in the Black Sea²⁵. This discrepancy is probably due to the different sampling strategies used. The *in situ* filtering system used in this study collected particles from 1,000–5,000 l of sea water, whereas 20 l collected in standard water bottles were processed previously. It is thus likely that the two techniques sampled different portions of the particle field, thereby yielding different results.

The stanol to stanol conversion as a classical indicator of diagenesis in Recent sediments seems to work in the water column as well. Studies at redox boundaries, or other biogeochemical discontinuities, in aquatic water columns offer a unique opportunity to evaluate the role of microorganisms in organic-matter transformations. □

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Liquid sulphur lakes at Poás volcano

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THE level of the hot, acidic crater lake at Volcán Poás, Costa Rica, dropped progressively over a two-year period up to April 1989, when only scattered boiling mud pools remained¹⁻³. Here we report the observation of large bodies of molten sulphur occupying part of the former lake bottom, which formed after the last of the lake water had disappeared. To our knowledge, this is the first reported occurrence of terrestrial sulphur lakes. We suggest that their formation resulted from removal of the overlying water, which allowed lake sediment temperatures to rise above the liquidus of the elemental sulphur deposits contained within them. The sulphur ponds bubbled vigorously because of the flux of hot gases from below, which kept them molten at a temperature of $\sim 116^\circ\text{C}$. The low viscosity of sulphur at this temperature is likely to have been critical in enabling its migration through the lake sediments to collect at fumarole vents. Some aspects of the origin of the sulphur lakes at Poás may be analogous to the putative formation of sulphur bodies on the jovian moon Io^{4,5}.

Poás is a composite volcano of the Cordillera Central in Costa Rica, rising 1,300 m above its base at 1,400 m. Historically it has been in a state of nearly continuous mild activity. Since an episode of explosive/effusive eruptions in 1953–5 it has been characterized by intense fumarole emissions and intermittent phreatic eruptions, usually through a shallow crater lake. The lake has an important role in the hydrothermal system of the volcano, typically condensing $\sim 100\text{ kg s}^{-1}$ of steam from lake-

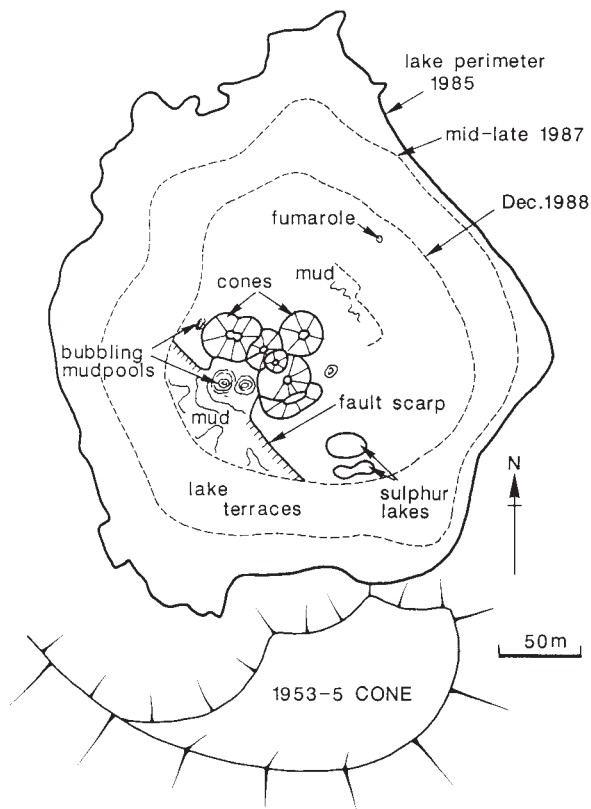


FIG. 1 Sketch map of the Poás intracater on 23 April 1989, with former lake levels shown for comparison.

floor fumaroles and transferring heat by evaporation, radiation and conduction at the water surface (ref. 6; D.S., G. C. Brown and H. Rymer, manuscript in preparation). A shallow injection of magma beneath the lake between 1987-1988, inferred from microgravity increases³, may be responsible for its recent desiccation (Figs 1, 2).

Between early 1987 and March 1989 the water level dropped by ~32 m (ref. 1), falling the last 6 m in less than 2 months, revealing a muddy floor scattered with boiling mud pools. Two of these pools located towards the south-east part of the crater subsequently dried up and became the site of several 1-3 m high yellow cones composed of fragmental sulphur and lithic particles (Fig. 3a). Occasionally, 1-m-high chimneys developed at their apices. The cones collapsed repeatedly, forming pits that continued to emit gases. When we observed the volcano on 16 March 1989, one of these pits, ~2 m in diameter, contained a bubbling pool of brown liquid (Fig. 3b). A sample of this material quenched rapidly to vesiculated pale-green sulphur with minor admixed lake sediment. Qualitative X-ray fluorescence analysis has since confirmed the purity of the sulphur, although significant traces of selenium and arsenic were detected.

By 19 April 1989, following a period of continual modification of the cones (Fig. 3c-e), two larger sulphur lakes were established side by side within steep-sided collapse pits. One had a dumbbell-shaped perimeter with maximum dimensions ~24 × 11 m; the other was roughly elliptical with axes ~28 × 15 m (Figs 2, 3e). When the crater was next visited on 23 April 1989, the sulphur-pond surface had dropped about 0.5 m and was >1 m below the rim of each pit. Blocks of sediment from the pit walls seemed to float on the liquid, which was dark brown in colour, visibly translucent and remarkably fluid, bubbling vigorously over most of its surface. The temperature of the molten sulphur, measured by thermocouple, was 116 °C (J. Barquero, personal

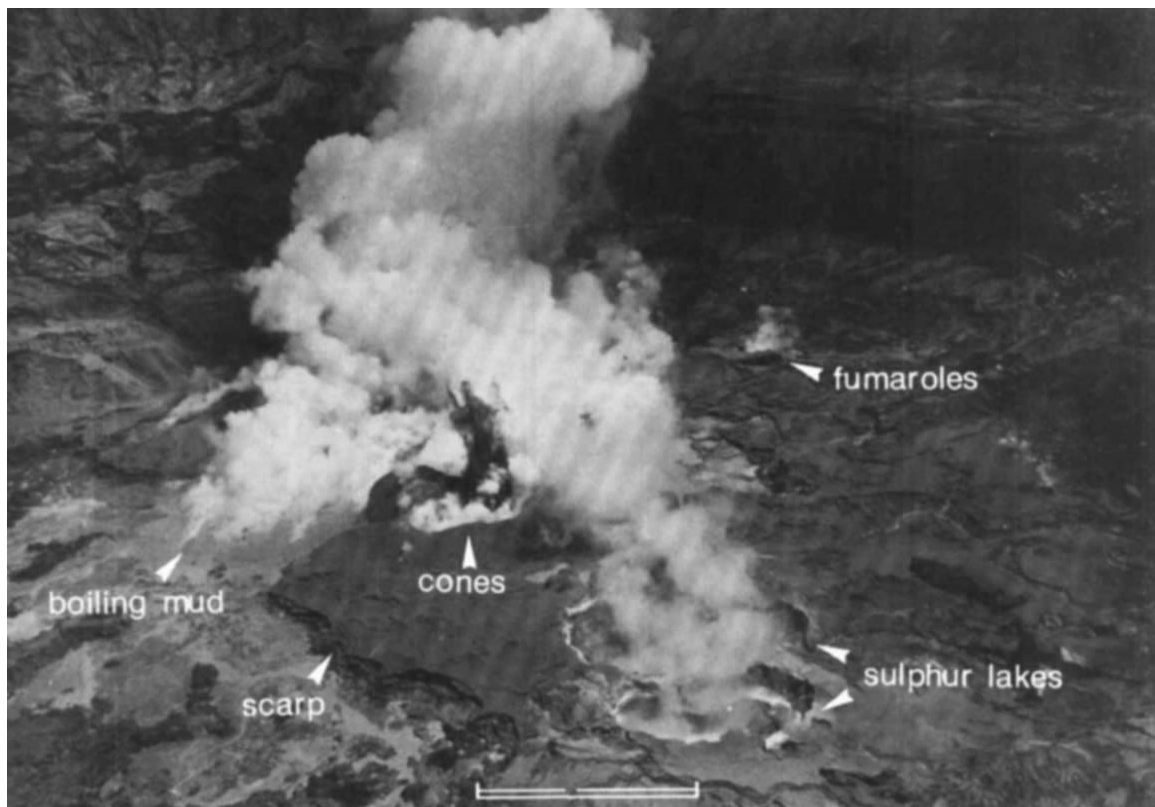


FIG. 2 Photograph of desiccated lake floor (on 23 April 1989) taken from eastern end of the 1953-5 cone, looking approximately north-west. Scale

bar is ~25 m.

communication), well below the boiling point of sulphur ($\sim 444^\circ\text{C}$). There was no crust on the surface although a terrace of pale-yellow solid sulphur had formed around the edge, and pit walls and rims were coated in bright-yellow sulphur sublimates. Clouds of condensed steam rose above the liquid surface and the smell of sulphur dioxide was strong. These observations are important as they indicate that the sulphur was kept molten and uncrusted by the passage of hot gases (presumably at a temperature close to 116°C). Meanwhile, 50–100 m away, spectacular phreatic emissions of non-juvenile ash and blocks were building a cluster of at least six cones, about 10 m high (ref. 2) (Figs 1 and 2). Some of the plumes were dark and cypressoid; others were yellow, presumably because they contained elemental sulphur.

To our knowledge, terrestrial sulphur lakes have not been documented before. 'Steaming pits' and 'niches' containing liquid sulphur were reported⁷ at Ebeko volcano (Kuriles, USSR) in 1952 but, unfortunately, their dimensions were not recorded. These features may have been nothing more unusual than the dribbles of molten sulphur commonly found at fumarole fields and solfataras. However, Ebeko did produce a sulphur flow in 1934⁸ and similar flows have also been recorded at Siretoko-Iôsan (Japan)⁹, Volcan Azufre (Galapagos Islands)¹⁰, Mauna Loa (Hawaii)^{11,12} and Lastarria (Chile)¹³. These rare occurrences of flows of molten sulphur have been attributed^{13,14} to melting and mobilization of sulphur deposits of fumarolic origin.

Although sulphur lakes were hitherto unknown, their existence beneath aqueous crater lakes has been inferred from observations of floating sulphur 'spherules' found at the volcanoes Kusatsu-Shirane (Japan)¹⁵ and Ruapehu (New Zealand)¹⁶. Ohashi proposed¹⁵ that the hollow spherules were formed by the upwards passage of gas bubbles through liquid sulphur, and manufactured similar morphologies in a laboratory experiment. Sulphur 'bubbles' have commonly been observed¹⁷ floating on the lake water at Poás but, here, subaqueous sulphur

lakes were postulated on different grounds—the recovery¹⁸ of greenish sulphur pyroclasts ejected by phreatic emissions through the crater lake during the 1970s¹⁹. The morphology of the sulphur ejecta^{18,19}, as in the case of the spherules, indicated formation in the liquid phase. Francis *et al.* suggested¹⁹ that melting of sulphur sublimates in large volumes of rock surrounding fumaroles had taken place at Poás. The liquid then accumulated in fissures and pore spaces before being sprayed into the air by explosive eruptions, such as those in September 1978 (when, perhaps significantly, the lake floor was partially exposed¹⁹).

We suppose that the liquid sulphur ponds at Poás were also supplied by remobilized fumarolic deposits (although a primary melt separated from silicate magma at depth is feasible^{20,21}) on the grounds that secondary sulphur deposits are abundant at Poás. They occur within the lake sediments^{22,23}, as disseminated sulphur particles and as sulphur-filled fumarole pipes and tubes. An eruption in January 1988 ejected lake mud with ~ 5 –10 vol% sulphur particles (G. Brown, personal communication). The oxidation of H_2S by SO_2 in the acidic aqueous conditions of the crater lake¹⁶ may be responsible for their formation. The reaction rapidly precipitates elemental sulphur which would settle on the lake bed. Both H_2S and SO_2 have been identified at Poás: gas analyses⁸ of fumaroles on the near-dry crater floor in February 1989 showed 5.0 mol% H_2S , and the SO_2 flux, measured²⁰ by correlation spectroscopy in February 1982, was $\sim 700 \text{ t d}^{-1}$.

The presence or absence of water must have an important role in the change of state of sulphur. Although there may be localized pockets of molten sulphur where gas temperatures exceed the sulphur liquidus, widespread melting will be inhibited when the aqueous lake is present because the temperature of the water-saturated sediments remains below the local boiling point of water. The loss of the water removes this temperature buffering system so that temperatures of sediment

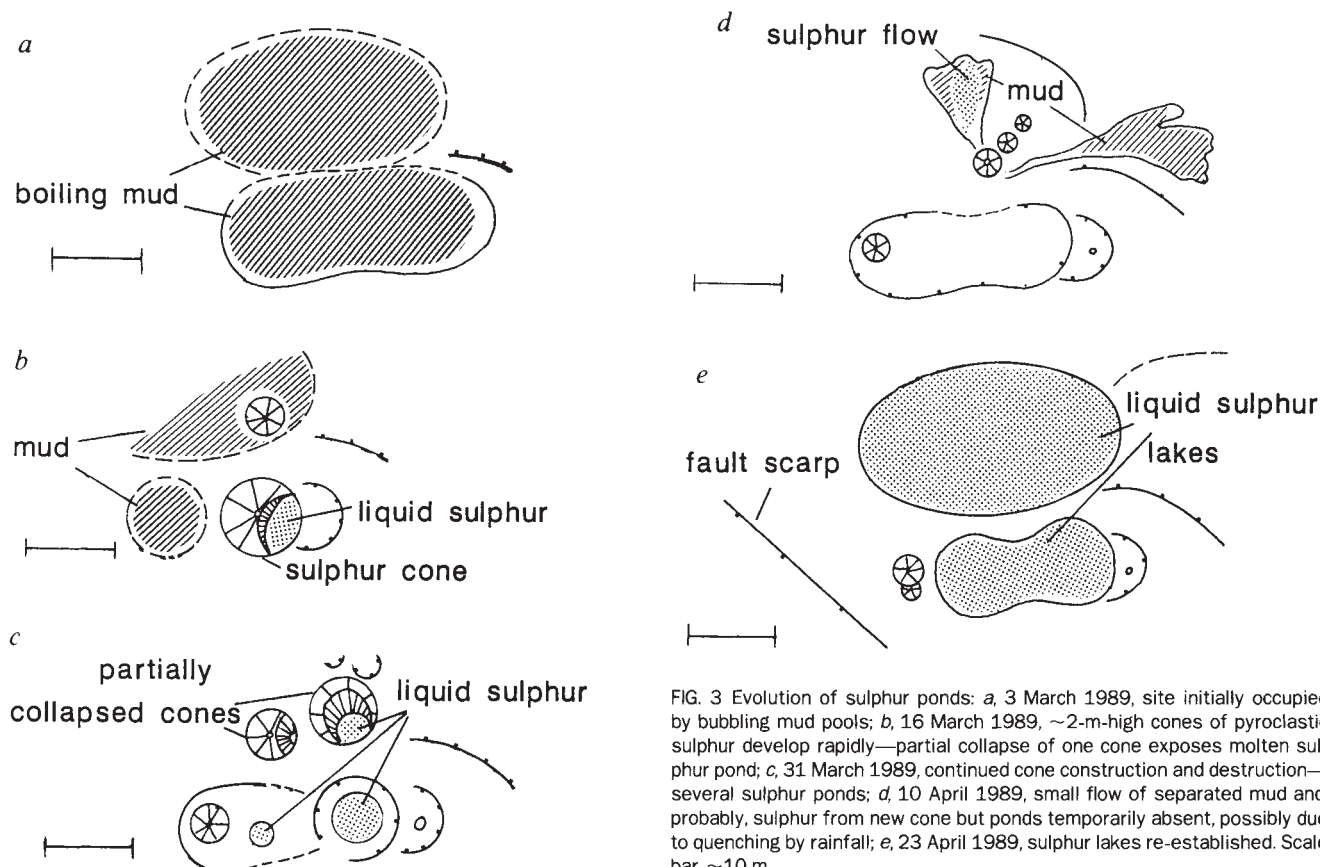


FIG. 3 Evolution of sulphur ponds: a, 3 March 1989, site initially occupied by bubbling mud pools; b, 16 March 1989, ~ 2 -m-high cones of pyroclastic sulphur develop rapidly—partial collapse of one cone exposes molten sulphur pond; c, 31 March 1989, continued cone construction and destruction—several sulphur ponds; d, 10 April 1989, small flow of separated mud and, probably, sulphur from new cone but ponds temporarily absent, possibly due to quenching by rainfall; e, 23 April 1989, sulphur lakes re-established. Scale bar ~ 10 m.

fluxed by hot gases can increase above the sulphur liquidus, generating much greater volumes of melt. The Poás sulphur ponds did not appear until all the water in the vicinity had been driven off, and then following a period of sulphur-cone construction and destruction. The collapse of the cones into molten sulphur pools indicates that chambers of the liquid may have developed at very shallow levels beneath the lake bed.

Concentration of the molten sulphur at these specific sites is more difficult to explain. There is no obvious topographic cause, as seemed to be the case of the Mauna Loa sulphur flow¹². However, in the absence of data on the volume of the sulphur lakes at Poás, or of the proportion of sulphur contained in the sediments, it is not possible to estimate the region over which the sulphur has migrated. Clearly, proximity to fumarolic vents is important as indicated by the gas flux through the sulphur lakes but the pond temperature of 116 °C is also highly significant. Between its melting point, ~113 °C, and ~159 °C, at which cyclic octatomic sulphur begins to polymerize, the viscosity of liquid sulphur is of the order of only 10 cp (refs 13, 14), about ten times that of liquid water at room temperature⁴. Such low viscosity is likely to have been a critical factor enabling the molten sulphur to move towards fumarole sites through fractures in the lake sediments or through pores created by melting of the originally disseminated sulphur.

Terrestrial sulphur flows received renewed attention following recognition of the importance of sulphur volcanism on Io, from the images of the Voyager spacecraft. For example, Greeley *et al.*¹² re-examined the Mauna Loa sulphur flow to gain insight on possible processes taking place on Io. Unfortunately, the evidence for liquid sulphur bodies on Io is inconclusive: (1) ground-based and Voyager observations in the infrared identified ~130–430 °C hotspots, temperatures that were argued^{24,25} to be too low for silicate magma. It is well known, however, that lava bodies are typically composed of cool crust as well as glowing cracks and indeed temperatures of terrestrial lava surfaces derived from single-channel satellite data²⁶ fall in the same range. (We measured a peak radiant temperature of 97.0 °C for the surface of the Poás sulphur ponds with an 8–14 µm bandpass radiometer, the low value is probably due to the attenuation of emitted infrared by fumes); (2) the reflectance spectra of volcanic regions of Io have been related to those of elemental sulphur, the colour variations of which with temperature changes are well known^{12,27}. More recently, however, Hapke has argued²⁸ that the only unambiguously identified species is SO₂, and that all the observed spectra can be modelled by a combination of SO₂ condensates and basalt.

Because of this controversy, we make only tentative implications regarding Io from our observations at Poás. The most interesting and instructive parallel concerns the role of water. Unlike the other galilean satellites, Io has lost its water, and so S_n and SO₂ are likely to be the dominant volcanic volatiles⁴—sulphur volcanism on Io takes place in the absence of water. The appearance of sulphur lakes at Poás following desiccation of the aqueous crater lake may therefore mimic to some extent the evolution of sulphur volcanism on Io. The low viscosity, as observed at Poás, is likely to be a significant factor in coalescing large volumes of molten sulphur within a solid matrix. □

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Role of methane and carbon dioxide in gold deposition

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VEIN-HOSTED gold deposits in low- to medium-grade metamorphic terrains are commonly associated with low-salinity hydrothermal fluids rich in CO₂ and/or CH₄^{1–12}. Fluid inclusion studies of gold mineralization indicate that the ore fluid comprised co-existing CO₂/CH₄-rich and H₂O-rich phases, and that phase separation played an integral part in gold deposition^{3,5,6,8–12}. In hydrothermal solution gold is present as the Au(HS)₂⁻ complex¹³. Precipitation of gold caused by decreasing ligand activity involving the formation of iron sulphides from wall-rock iron oxides and silicates¹³ is clearly relevant to gold deposits associated with iron formations and iron-rich igneous rock^{14,15}. It cannot, however, be used to explain the common association of gold deposits with black shales or schists^{3,5,7,8,16}, where wall-rock iron is in the form of sulphides, and therefore generally in equilibrium with the hydrothermal fluid, or with granitoids or felsic volcanics, where the amount of iron is low. This latter association may be explained by the partitioning of H₂S into the non-aqueous phase during fluid immiscibility^{10,12}, but the general applicability of this mechanism is not known. Here we present a new synthesis of experimental data from a variety of sources which puts this mechanism on a semi-quantitative basis, and suggest that it may be applicable to a wide variety of hydrothermal gold environments.

Recent high-pressure (*P*)-high-temperature (*T*) experimental studies of the systems H₂O–CO₂–NaCl (ref. 17), H₂O–CH₄–NaCl (refs 18, 19) and H₂O–H₂S–CH₄–CO₂ (refs 20, 21) enable modelling of fluid unmixing in carbonic/methanoic ore fluids. First, in the system H₂O–H₂S–CH₄–CO₂ at the two-phase boundary, hydrogen sulphide is strongly partitioned into the vapour phase (Fig. 1). For an initial homogeneous ore fluid, the separation of hydrogen sulphide into the non-aqueous, carbon dioxide/methane-rich vapour phase would result in mass transfer of sulphur from the aqueous component of the hydrothermal fluid to the non-aqueous phase with concomitant deposition of gold. Moreover, because the ratio H₂S(v)/H₂S(l) (in terms of orders of magnitude) is largely independent of pressure, temperature and composition, at least up to 200 °C and 200 bar, this mechanism may be valid for a wide range of geological environments. At higher temperatures and pressures, particularly for compositions close to the critical curve, the partition coefficient for hydrogen sulphide between the aqueous and non-aqueous phases will approach unity. In view of the flattened form of the solvus, however, the upper part of the two-phase region corresponds to a restricted *P*–*T* geological domain.

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