fraction of the volcanic gas can supply the S and O in Io's torus and these same species, as energetic heavy ions, may be responsible for the supply by sputtering of high velocity neutral sodium.

We thank our colleagues on the Voyager imaging science team, S. Kumar and J. Pearl of the Voyager IRIS team and R. W. Carlson and D. L. Matson of JPL for stimulating discussions. We also thank F. P. Fanale (JPL) for helpful criticisms. This article presents results of one phase of research carried out at JPL under NASA contract NAS7-100.

Received 16 July; accepted 3 August 1979.

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Sulphur flows on Io

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The colour patterns observed on Io indicate extensive surface flows of quenched molten sulphur

Io has the reddest surface in the Solar System, with the possible exception of Amalthea, which may in fact, be coloured by material lost from Io. Io also displays the largest variation of colour with planetocentric longitude of any other object in the Solar System[1]. Voyager 1 close-encounter photomosaics have clarified both the coloration of Io and its surface variation (see, for example the colour images in Smith *et al.*[2]). Although the Voyager 1 photometric fidelity is not better than 10%, general colour patterns are clear. The surface is mottled with dozens of large, and, probably, thousands of small randomly distributed dark patches, which in most cases are adjacent to red or orange coloured terrain. Equatorial and temperate latitudes are rich in these bright colours. Polar terrain tends to be darker, confirming earlier groundbased impressions. There are also extensive yellow, and white or blue-white, provinces on the satellite's surface. Many of the dark spots are active or recently active shallow volcanic constructs[2–6]; seven of the volcanoes have been observed by Voyager 1 in violent eruption. The pattern of albedo features points strongly to a succession of complex effusive and fluvial events. Some dark localised diffuse features exhibit radiating patterns implying downslope flow, such as in *Plate* 2, p 783. In this image there is a hint of sinuous anastamosing channels, ~300 km long, which are blood-red with some traces of black material down the principal channel. One channel is red proximate to the caldera, fading to yellow distally. In general, dark flows are short and diffuse, red flows longer, and orange and yellow flows tend to be distributed in sheets of considerable area.

A crude similarity between the integrated-disk colour of Io and the spectrum of elemental sulphur led Wamstecker *et al.*[7] to suggest the presence of abundant sulphur on the ionian surface. Sulphur has also been identified in the Io-related circumjovian torus both by Earth-based observations[8] and by Voyager 1 experiments[9,10]; SO_2 has been identified in the gas phase by Voyager 1 IR spectroscopy[11]; and it has been suggested that SO_2 frost may explain some of the broadband IR spectral features in the integrated disk of Io[12,13]. After water and CO_2, sulphur and its compounds are generally the first or second most abundant effluents in terrestrial volcanoes, and fumaroles, in some cases comprising tens of per cent by mass[14]. Where fumarole temperatures are $\lesssim 650$ °C, sulphur gases tend to be the major constituents after steam, and the corresponding volcanic constructs are called solfataras. Sulphur and its compounds have been thought[2,15] to drive the volcanic plumes because of the absence on Io, unlike the other galilean satellites, of surface water frost in groundbased IR spectroscopic observations. Io has been substantially devolatilised. H_2S is rapidly photodissociated and, because of its very low freezing point, hydrogen has an opportunity to escape efficiently from Io by processes such as Jeans evaporation, or magnetospheric sweeping. As Io becomes more and more oxidising, S_n and SO_2 become prime candidates for the principal volcanic effluents. Ionian effusive flows and sulphur volcanoes may be driven by the lithostatic pressure gradient and explosive decompression of volatiles[16], with the energy derived from tidal dissipation dependent on the resonance lock with Europa[17]. However, the following discussion is independent of the mechanics of Io volcanism.

Sulphur coloration

There are perhaps dozens of sulphur allotropes with differing physical, chemical and optical properties derived from differences in both the packing and the bonding of polyatomic sulphur; their melting points vary from 110 to 119 °C. Because the melting point of sulphur is ~1,000 °C less than that of

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silicate, a stochastic distribution of thermal events in the interior of Io should melt sulphur—already known to be abundant near the surface—more often than it should melt silicates. At its melting point liquid sulphur is yellow, intensifying to orange at about 150 °C, red at about 180 °C, and black at about 250 °C (see ref. 18). At the normal boiling point, 444 °C, the composition is mostly cyclic S_8 with some S_6 and S_2; at 1,000 °C, sulphur is largely S_2. Therefore, the species of sulphur in the ionian atmosphere depends strongly on the temperature in the volcanic vent and the rate of cooling. The chemistry of liquid S_n, with $2 \leq n \leq 22$ at least, is complex and incompletely understood[19,20].

At 25 °C, solid sulphur shows a steep absorption edge[18] at about 2,850 Å which moves at lower temperatures to shorter wavelengths at about 2.3 Å K^{-1} and at higher temperatures (until the melting point) to longer wavelengths at about 2.0 Å K^{-1}. Thus, at the mean ionian surface temperature, the absorption edge is near 2,500 Å and at the melting point, near 3,000 Å. This absorption edge is partly responsible for the yellow coloration of solid sulphur at room temperature; at liquid nitrogen temperatures orthorhombic sulphur is snow-white because the wings of the absorption edge are sufficiently far into the UV.

Remarkably, if liquid sulphur is rapidly quenched or freeze-dried to low temperatures, its colour is preserved. The faster the freezing, the better the preservation; the higher the initial temperature of the melt, the deeper the hue. These colours have three sources[18]: (1) the S_n absorption edge in the violet or near UV; (2) an absorption peak near 4,000 Å due to S_3; and (3) an absorption peak at 5,500 Å due to S_4. S_3 and S_4 are typically present in abundances of ~1% in the frozen melt; they are trapped metastable species and their influence declines markedly at post-quenching temperatures $T \gtrsim 180$ K. Therefore, away from calderas and other localised heating, these metastable species are preserved on Io and should affect the coloration of the surface. The colour of quenched liquid sulphur depends on its thermal history and associated metastable allotropes, as well as on impurities.

Terrestrial flows of molten sulphur—such as at the Japanese volcano Siretoko-Iosan[21]—are chocolate brown. However, this is unlikely to be due to a sulphur allotrope; a minimal abundance of organic matter of 1 part in 10^5 can colour sulphur brown[18]. The absence of brown coloration on Io would suggest that virtually no organics are present, a conclusion consistent with substantial devolatilisation and escape of hydrogen during Io's history.

The dominant absorption edge of sulphur continues to move to longer wavelengths, through the entire visible spectrum, between the melting point and the normal boiling point, at a rate of approximately 6 Å K^{-1}, or more than twice the rate for the solid [18]. Nelson and Hapke[22], in a prescient paper, suggested that the integrated-disk coloration of Io is due to quenched liquid sulphur and even proposed, before Voyager, "volcanic fumaroles" as one possible means of melting the sulphur. They suggest that the observed 3300 Å absorption feature on Io is due to quenched liquid sulphur. The above temperature-dependence of the sulphur absorption edge means that a 3,300 Å absorption feature requires liquid sulphur which had been raised to about 155 °C before quenching, that is, temperatures high enough to produce vivid orange-red coloration.

Viscosity, colour and flow time

Figure 1 shows the temperature-dependence of the dynamic viscosity, ν, of liquid sulphur and a rough indication of its colour-dependence. In this model the black patches in and around the volcanic calderas are quenched liquid sulphur originally at $T \gtrsim 250$ °C. The connection of such temperatures with volcanic mechanics is discussed in ref. 16. As in terrestrial volcanoes, the incidence of melt in the caldera should be intermittent; there is no Voyager IR evidence for extensive regions with temperatures above the melting point in any one of the few calderas examined to date[23]. Because of its comparatively high viscosity (comparable to olivine basalts), black and red-black

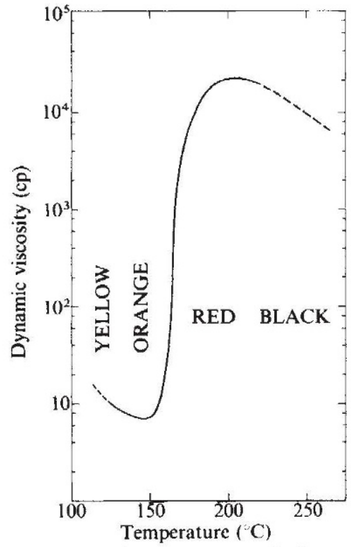

Fig. 1 Viscosity (after the *International Critical Tables*) and colour of molten sulphur as a function of temperature.

liquid sulphur will flow sluggishly and therefore be confined to the vicinity of the caldera. The liquid will cool by radiation and evaporation, the colour will change to red and orange, and the viscosity will drop dramatically, permitting substantial downslope flow and suggesting that the red sinuous deposits are frozen sulphur rivers. When the sulphur melt cools to the orange-yellow and yellow range, just above the melting point, the viscosity is less than 10 times that of liquid water (1 cp at 20 °C), and the melt which is not contained by topographic relief has the opportunity to spread laterally and to form extensive yellow and orange-yellow sheets by flooding the lowland plains. Because of the Stefan–Boltzmann temperature dependence, cooling is about an order of magnitude more rapid in the black and red than in the orange and yellow, and the deposits of the latter coloration should cover more ionian surface area than the former, as is observed. The increase in area covered by the low-viscosity low-temperature melt leads to still faster radiative cooling. Fan-shaped flows, running from red-black interiors to orange-yellow exteriors, are also consistent with the model.

The increase of viscosity with temperature above 157 °C, atypical of most liquids, is produced by the rupturing of the cyclic octatomic form of sulphur to produce long and complex sulphur chains and polymers, with fragmented octagonal forms prominent. At $T > 187$ °C this long-chain structure begins to dissociate thermally. Thus the most interesting and complex sulphur chemistry on Io should occur in the red provinces.

Flow of a sulphur melt in a cylindrical channel on Io will be laminar when the Reynolds number $(V\rho d/\nu) < 2{,}000$, where V is the velocity of flow, ρ the density of liquid sulphur (1.8 g cm^{-3}) and d the channel width. For $d \sim 100$ m, and red liquid sulphur, the condition reduces to $V < 10$ cm s^{-1}, which may be plausible for high-viscosity flow. Narrower channels are more likely to be laminar. For laminar flow, Poiseuille's equation indicates that the discharge $Q \propto \nu^{-1}$, for a fixed channel diameter and a fixed pressure drop per unit length. The shallow slopes on Io and the lower acceleration due to gravity make both V and Q correspondingly lower than on Earth. A red flow at $V \sim 10$ cm s^{-1} will traverse 100 km in a period of weeks. But for orange and yellow liquid sulphur, ν is so small that the laminar flow condition is unlikely to be met. Thus, black and red liquid sulphur on Io should mobilise slowly and may exhibit laminar flow; while orange and yellow sulphur melts should be correspondingly much faster and fully turbulent. The surface of Io attests to a very complex sequence of overlapping flows. Both the ubiquity of sulphur flows and the likely volcanic mechanisms[16] point to the tapping of an underlying ocean of liquid sulphur, for which the name 'thiosphere' is here proposed.

Consider the cooling of a single eruption of liquid sulphur, sufficient to fill a channel 100 km long, 100 m wide and 10 m

Table 1 Minimum thicknesses d, and rough turnover times t_t, of films of quenched liquid sulphur for $\tau \sim 1$ at $\lambda \simeq 5{,}000$ Å

Colour	Original T	d	t_t
Yellow	$\simeq 120$ C	tens of centimetres	centuries
Orange	$\simeq 140$ C	centimetres	decades
Red	$\simeq 170$ C	millimetres	years
Black	$\gtrsim 250$ C	tens of micrometres	days

deep. The sulphur mass is $M \sim 2\times10^{14}$g and the radiating surface area is $A \sim 10^{11}$ cm^2. The cooling time will then be $t_c \gg [(c_p\Delta T + L)M]/[\sigma \bar{T}^4 A]$, where c_p is the specific heat at constant pressure of liquid sulphur $\sim 9.5\times10^6$ erg g^{-1}, $L \simeq 3.8\times10^8$ erg g^{-1} is the latent heat of fusion of sulphur, σ is the Stefan–Boltzmann constant, ΔT is taken as $\simeq 500$ °C, and the average radiative temperature during the flow $\bar{T}$ is taken as 400 K. The result of this crude calculation is $t_c \gg 2$ months.

Considerably thinner films of liquid sulphur from much more modest eruptions can significantly colour the surface. Table 1 gives rough estimates (data from refs 18 and 24) of the thickness of quenched liquid sulphur necessary to provide significant optical depth in visible light. Because of the high viscosity of hot liquid sulphur, very large deposits should accumulate near the calderas; however, extremely thin quenched films initially at such high temperature would be enough to provide the observed coloration. In contrast, the yellow intercrater plains must be covered by at least tens of centimetres of quenched liquid sulphur.

Table 1 also shows the turnover time t_t, for variously coloured deposits to be laid down, assuming a mean planetary deposition rate of volcanic effluvia (other than surface flows) of 10^{-1} cm yr^{-1} as estimated by Johnson *et al.*[15]. Because the deposition rates are not well known[15], and in any case should be much larger than the planetary average near the calderas and somewhat less than the planetary average in the intercrater plains, these figures are very rough. The gross silicate productivity ratio[25] of fragmentary ejecta to lava for all volcanic systems on Earth is ~5. If a similar ratio is applied to sulphur on Io, then the mean liquid sulphur flooding rate would be $\gtrsim 10^{-2}$ cm yr^{-1}, implying (Table 1) that albedo changes in dark circumcaldera regions can take place in periods less than 2 weeks, and changes in red flows in periods less than years. Volcanoes are concentrated at equatorial latitudes[5], as are the deposits here hypothesised to be recently frozen sulphur melts. Synoptic observations of the surface of Io may uncover large-scale surface albedo and colour changes—particularly in the deeply coloured regions. There are several other possible sources of variable features not involving liquid flows, including the direct deposition of solid volcanic effluvia in the immediate vicinity of calderas and the surface condensation of gas phase effluvia, including SO_2 and S_n. The white deposits on Io might be S_n, rapidly cooled from just above the melting point, but frozen SO_2 is a very promising candidate. The white deposits, like the volcanoes, are also concentrated towards equatorial latitudes.

Decay of sulphur chromophores

A related question concerns the timescale for decay of the sulphur chromophores, particularly the metastable allotropes, at ionian ambient conditions. The colour of quenched liquid sulphur at room temperature persists 'indefinitely' (M. Gouterman, personal communication). Conservatively, we interpret 'indefinitely' as $\gg 1$ month $\sim 3\times10^6$ s. We adopt exponential colour decay statistics of the form $t = t_0(\exp(E/kT) - 1)$, where E is the bond energy of the chromophore, and where the equation satisfies the boundary conditions that $t=\infty$ at $T=0$ and $t=0$ at $T=\infty$. We then readily find that the characteristic time for chromophore decay at $T = 135$ K greatly exceeds the lifetime of Io for $E > 1$ eV. Thus, provided the ionian chromophores are caused by chemical bonds stronger than van der Waals forces or hydrogen bonds (roughly ~0.1 eV), the coloured deposits on the surface of Io should persist for geologically significant periods of time, from a reaction kinetics standpoint. Charged particle impact and UV radiation damage might, however, change the coloration in shorter times.

Sulphur coverage

Typical ballistic flight times for solids in the ionian volcanic plumes are ~1,000 s. With the minimum mass ejection rates of Johnson *et al.*[15] we calculate productivities for Io volcanoes of 4×10^6 to 3×10^5 g s^{-1}, which is comparable to the Mt Pelee or (1924) Kilauea eruptions, but less than the Surtsey and much less than the Krakatoa eruptions[14]. What is striking about Io volcanism is not the individual production rates but the number, frequency, altitude (because of the low atmospheric pressure) and sulphur chemistry of the events. It is of interest to calculate what the mean surface area covered by molten sulphur is at a given moment. Microwave occultation measurements made by Pioneer 10 derive[8,26], from the ionisation profile of the nightside ionian atmosphere, a surface pressure of neutral constituents, but for an incorrect composition model. An earlier upper limit, derived from a stellar occultation, of 10^{-6} bar[27] is consistent with the Voyager discovery[11] of 10^{-7} bar of SO_2. We conservatively assume that the atmosphere is composed mainly of S_2, in vapour pressure equilibrium with a sulphur melt and that the gas phase volcanic effluvia are so hot that they produce significant lateral spreading before they chemically react or freeze out. Rough values for the vapour pressure over black liquid sulphur near 250 °C are then ~10 mbar; over red liquid sulphur ~1 mbar, and over yellow ~0.1 mbar. Therefore, in the three cases, for the mean atmospheric pressure to be 10^{-6} bar the fractional coverage of black melts must be $<10^{-4}$; for red, $<10^{-3}$; and for yellow $<10^{-2}$. To reach 10^{-7} bar ($[S_2] \sim [SO_2]$) these values must be lowered by one order of magnitude. Thus only a tiny fraction of the surface of Io can be molten at present, although that fraction may be much larger than the corresponding fraction for Earth. Accordingly, the existence of a major flow may be accompanied by a significant increase, at least locally, of surface pressure. Even if 10^{-3} of the surface is at $T \simeq 300$ °C its relative contribution to the net thermal emission from Io will be small.

Vertical relief of several kilometres, tending to localise around calderas on Io, has been recognised[6]. These may be silicate extrusions through the underlying thiosphere. But it is of interest to examine the possibility that they are constructions largely of elemental sulphur which is otherwise in such abundance on the ionian surface. In the Peale *et al.* model[17] of tidal heating in the interior of Io the melting point of sulphur is reached only several kilometres below the surface. Thus, sulphur relief features on Io could have roots extending subsurface only by an amount equal roughly to their height above surface. The tensile and yield strength of such sulphur constructs could be as low as 10^8 dyn cm^{-2} for the density of sulphur and the low acceleration due to gravity on Io and the constructs would still not be crushed by their own weight. (Typical tensile and yield strengths for silicates at room temperature are in excess of 10^9 dyn cm^{-2}). However, the density of solid sulphur exceeds the density of the liquid; if the solid were porous to account for flotation, the strength of the solid would decline markedly, and melting of such a sulphur iceberg at its base would require a rapid production rate for such constructs to maintain the observed steady state population. On the whole, silicate relief on Io may be more likely than sulphur relief (see ref. 4), although surface flows are very probably liquid sulphur and not silicates.

Conclusions

The variegated black, red, orange, yellow and (perhaps) white coloration on Io seems explicable in terms of liquid sulphur, produced in ionian volcanoes and solfataras, and quenched at Io ambient temperatures $\simeq 135$ K. A number of liquid sulphur flow fronts and frozen rivers appear in the Voyager images. The darker hues may be regions of past sluggish laminar flow, the lighter hues of fast turbulent flow. Opaque layers are at least tens of micrometres to tens of centimetres thick, depending on colour, and, at present volcanic eruption rates, should have lifetimes against covering by airborne effluvia between days and centuries. The time scale for thermal degradation of chromophores at ambient Io temperatures is significantly longer. Thus coloured liquid flow fronts would have been covered over by solid volcanic effluvia in geologically very short periods of time unless new fluid flows occurred in the same interval. Since the fluvial patterns observed are almost certainly surface rather than atmospheric flows, this suggests that the average renewal time scale of the colour and albedo (but not topographic) features on Io is $\lesssim 10^3$ yr. In this sense it is the youngest solid surface in the Solar System. The white deposits on Io might be orthorhombic sulphur or SO_2 or other atmospheric effluvia deposited from the atmosphere. However, they must be laid down fast enough not to be covered by flows of molten sulphur. The coloured regions of Io may be where liquid sulphur flows dominate the condensation and deposition of volcanic effluvia; while the white regions represent the opposite case. The dark poles of Io may represent a non-uniform distribution of previous volcanic events, concentrated towards high latitudes. Alternatively, the lower polar temperatures may produce more rapid quenching of hot sulphur melts, and the preferential preservation of their deep colour. From the deduced neutral atmospheric surface density of Io and the vapour pressure of gas phase sulphur above a melt we provisionally calculate an upper limit to the present fractional surface area of Io which is molten between 10^{-2} and 10^{-5}. Even with the high value for this fraction, the time interval between the appearance of successive major flows of molten sulphur on Io must be less than a decade for the renewal of the entire surface in colour and albedo in $<10^3$ years to be accounted for. But this is consistent with the turnover times calculated independently in Table 1. Thus arguments from volcanic deposition rates and from the vapour pressure over sulphur melts are both consistent with the notion that the surface of Io changes significantly in geologically very short periods of time. Systematic and synoptic observations of Io over several years, as by the Galileo mission, promises the discovery of major surface changes.

I thank B. Smith, M. Gouterman, E. Shoemaker, M. Carr, D. Morrison, D. Pieri, E. Posner and, especially, S. Squyres, for helpful comments. This research was supported by NASA.

Received 18 July; accepted 3 August 1979.

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Photometric evidence on long-term stability of albedo and colour markings on Io

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Historical measurements of the albedo and colour of Io are examined for evidence of major resurfacing events.

THE Voyager discovery[1,2] of intense volcanic activity on Io raises the possibility that endogenic processes could alter the large-scale distribution of colour and albedo on the surface of this satellite in extremely short times on a geologic scale. Estimates of the resurfacing rates on Io from the observed volcanic eruptions and from the lack of observed impact craters have led Johnson *et al.*[3] to estimate average resurfacing rates of at least 0.1 mm yr^{-1}, probably $\sim$1 mm yr^{-1} or more. In a region where an eruption is taking place, the rate could be two or more orders of magnitude larger. Given the size of the observed eruptions[4], it is not difficult to imagine deposition of an optically thick layer of fresh pyroclastics or recondensed volatiles over tens of thousands of square kilometres on Io in times as short as a few weeks.

Precision measurements of the brightness of Io and the other Galilean satellites have been carried out several times since the pioneering photoelectric work of Stebbins and Jacobsen[5,6] 50 yr ago; similar measurements of colour extend back to the work of Harris[7] in about 1950. This article reexamines the historical measurements of the albedo and colour of Io to determine whether there is evidence of variations, or if not, to set a limit on major resurfacing events resulting in hemispheric brightness changes during the past half century.

Historical data

Extensive broad-band, unfiltered photoelectric measurements of the galilean satellites were first carried out in 1926 and 1927 (refs 5, 6); in the 1950s, less extensive observations on the *UBV* system were undertaken[7]; and by the mid 1970s extensive sets of observations in *UBV* and *uvby* had been obtained by several observers[8–11]. Because the brightness of the satellites varies with both orbital longitude (rotation) and solar phase angle, many observations are required to separate the functional dependence of brightness on these two parameters. (Alternatively, all of the data necessary to define the mean brightness and rotation curve can be obtained over a very small range in phase, say 5–7°, neglecting the phase dependence.) The available observations have been reviewed elsewhere[10–12], and the present results are derived from those discussions.

Table 1 summarises the measurements of brightness. In order to minimise variations due to differences among photometric

