

structures is a single 6.5-Å axial repeat, with bilayers of molecules—related by glide symmetry and thus of opposite chirality—being found in both phases. Indeed it seems reasonable to suggest that bilayers (Fig. 3) in γ -iPP are a consequence of the coexistence of helices of opposite chirality. Again, 'up-down' statistical disorder is an essential feature of both the α - and γ -structures. Furthermore, the 80° tilt between adjacent layers of isochiral helices in γ -iPP cannot be considered to be totally unexpected—similar arrangements have been postulated^{10,11} to explain, at a molecular level, the tilt angle of ~80° observed in α -iPP branching crystals. In the latter, tilting occurs only at (disordered) branching sites, whereas it is a feature of the regular crystallographic structure in γ -iPP. It breaks the sequence of alternating layers of all left- and right-handed helices, placing isochiral helices in contiguous layers. An analogy may be drawn with helix-to-helix packing in globular proteins, where an interaxial angle of ~50° is most often observed¹³, indicating that favourable ridge-to-groove juxtaposition of isochiral helices is in general expected to induce a strong angular deviation in the interacting chain axes. In globular proteins this feature is local but in γ -iPP the tilt angle of 80° involves entire crystalline bilayers. The reason for this may be the near equality of the helix repeat length and the distance between adjacent parallel isochiral chains in a layer (~6.5 Å).

The driving force leading to the γ -iPP structure is not clear. It is unlikely to be kinetic because of the complex architecture of this phase, the fact that γ -iPP is obtained by slow cooling

and at high pressure, and the reduced importance of chain folding^{17,19}. Thus crystallization of γ -iPP appears to be related to its stability¹⁹, that is, to the favourable packing energy that results from registry of the inclined chains; the melting of the γ -phase at a lower temperature than the α -phase could simply be due to smaller crystallite size¹⁷. □

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Biotic enhancement of weathering and the habitability of Earth

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AN important question in the Earth sciences is the role of the biota in the chemical weathering of silicate rocks, which affects atmospheric CO₂ and therefore climate^{1–10}. No comprehensive study of biotic influences, however, has quantitatively examined the climatic consequences were weathering to take place under completely abiotic conditions. Here we calculate that if today's weathering is 10, 100 or 1,000 times the abiotic weathering rate, then an abiotic Earth would be, respectively, ~15, 30 or 45 °C warmer than today. The upper two temperatures are preferred estimates because of the probable almost complete absence of soil under abiotic conditions, suggesting that without a biota that significantly enhances weathering rates, the Earth today would be uninhabitable for nearly all but the most primitive microbes. Life may have been crucial in cooling early Earth and maintaining relatively cool conditions.

As well as having a role in elevating the partial pressure of CO₂, p_{CO_2} , in the soil⁸, the biota (from microbes to vascular plants) accelerates chemical weathering by stabilizing soil, a reservoir of high surface area, which acts as a sponge for water and thus as a medium for acid attack^{10–13}. Other important roles of biota in accelerating weathering include producing humic and other organic acids, inorganic acids and chelating agents, acting as a sink for the nutrients freed by weathering, and contributing to physical weathering through microfracturing of mineral grains¹⁴.

Polynov¹⁵, as long ago as 1953, emphasized the importance of biotic amplification of weathering. Indeed, organic acids may be essential to give the observed weathering rates because of the slow kinetics of proton production in the CO₂–H₂O system¹⁶.

Whereas the emergence of vascular plants in the Silurian almost certainly accelerated chemical weathering¹⁰, microbial and possibly lichen colonization of the continents in the Precambrian^{12,17} probably resulted in a considerable increase in chemical weathering relative to abiotic conditions at the same atmospheric p_{CO_2} .

The chemical dissolution rates increase with p_{CO_2} as $(p_{\text{CO}_2}/p_{\text{CO}_2}^0)^\alpha$ where $p_{\text{CO}_2}^0$ is the present p_{CO_2} in the atmosphere and α is between 0.3 and 0.4. A value for α of 0.3 used in previous studies^{2,18,19} was derived from experiments on alkali feldspars. From H₂O–CO₂ equilibria, a_{H^+} varies with $(p_{\text{CO}_2})^{0.5}$, assuming continuous reaction of the minerals with fresh water saturated with CO₂. The rate of dissolution of silicates varies with $(a_{\text{H}^+})^n$ where $0 \leq n \leq 1$, and n varies from 0.54 (anorthite) to 1.0 (forsterite) for Ca, Mg silicates¹⁶ corresponding to an α between 0.27 and 0.5, with 0.38 being the mean value for anorthite, forsterite, enstatite and diopside. We suggest that α , for Ca, Mg silicates exposed on the continents of an abiotic Earth, is probably between 0.3 and 0.4. Root respiration and soil biota generate a soil p_{CO_2} that is 10–100 times the level in the atmosphere⁸. Thus, if the p_{CO_2} elevation in soil was the only factor in chemical weathering enhancement, weathering rates in soils should be only 10^{0.3}–100^{0.4} or 2–6 times the rate on bare rock under similar temperature and rainfall conditions; an elevation of this order, by itself, would not have a major effect on planetary habitability²⁰. We will demonstrate, however, that an appreciable additional enhancement in the weathering apparently occurs due to the other biotic factors mentioned above, including of course the soil effect.

Sterile conditions no longer exist naturally on the surface of the Earth so estimates of the rates of abiotic weathering must be made indirectly. Although today's rocks, or rocks dating back as far as the Precambrian, are not models for weathering under abiotic conditions, data from field studies and experiments can be used to set limits on biotic enhancement of weathering. Let us first consider weathering on a two-dimensional surface without the amplification as a result of the small particle size/large surface areas in a soil. Laboratory experiments on Ca, Mg silicates give a maximum dissolution rate of $\leq 5 \times 10^{-5}$ mm yr⁻¹ at 25 °C under the conditions of continuous

contact with undersaturated water, calculated for pH 5.66 (equilibrium with present p_{CO_2})¹⁶. This rate is almost certainly a maximum for natural abiotic weathering of a bare rock surface at the present p_{CO_2} for the following reasons.

First, bare rock in nature, indeed mineral grains in soil, are not in continuous contact with water. This effect reduces the dissolution rate by the fraction of time that there is water contact¹⁶. Second, laboratory preparation of samples, particularly grinding, raises dissolution rates by creating surface deformation and dislocations²¹. Indeed, the natural dissolution rate of silicates without enhancement by organic chelation may be one to three orders of magnitude lower than the rate quoted above²², possibly because bulk dissolution rates may vary little with grain size because of the decrease in the ratio of defect sites to surface area with progressive attack²³.

A study of Hawaiian basalt flows of known age²⁴ indicates that there is an acceleration of chemical weathering on the order of at least 10 to 100 times for lichen covered surfaces relative to bare rock. The chemical weathering enhancement in tropical soils is four to ten times that due to lichen colonization of the Hawaiian lavas, similar to the enhancement found in Iceland,⁹ in a comparison of the bicarbonate levels in rivers traversing 'barren' (that is, lichen colonized land¹¹) and areas of vegetation. For the oldest flow (60-years old at time of collection) under conditions of moderate to heavy rainfall (127–191 cm yr⁻¹) the rate of rind development was $<3 \times 10^{-5}$ mm yr⁻¹ on bare rock. An even lower weathering rate (average of $<5 \times 10^{-6}$ mm yr⁻¹) is derived from a study of rind development on andesitic and basaltic clasts from the western U.S.A. in the last 500,000 years²⁵.

We conclude that the chemical weathering rate of a two-dimensional rock surface of the continental crust under abiotic conditions with similar temperature and rainfall conditions as the Hawaiian case is $\leq 5 \times 10^{-5}$ mm yr⁻¹, perhaps even one to three orders of magnitude lower. Of course, weathering in a soil

environment dramatically increases the chemical denudation rate relative to bare rock as a result of much higher surface areas of exposed minerals for a given land area. The typical chemical denudation rate in tropical and saprolitic soils is 0.04–0.05 mm yr⁻¹ (refs 26, 27) or $\geq 10^3$ times the inferred abiotic bare-rock rate. An amplification of this order can probably be accounted for by soil formation with p_{CO_2} elevation and other biotic influences.

But would soils be formed and stabilized under abiotic conditions? Frost wedging, a particularly effective mechanism of mechanical weathering would be unlikely at the high temperatures prevailing on an abiotic Earth (see later calculations). Other mechanisms of mechanical weathering, such as cracking from clay and salt formation²⁸, may well be amplified at present by microbial biota retaining water in cracks, although joint formation and cracking from thermal stresses would still occur under abiotic conditions. We suspect that the amplification of weathering from the latter effects is either small compared to that resulting from the presence of soil itself, or that the two-dimensional abiotic rock surface rate is indeed one to three orders of magnitude lower than 5×10^{-5} mm yr⁻¹—otherwise tropical and saprolitic soil chemical denudation rates would be several orders of magnitude higher, from the combined amplifications, than those observed (the soil effect itself must contribute several orders of magnitude of amplification).

We propose that soil formation on Earth would probably be largely prevented by the rapid erosion due to running water and wind in the absence of a stabilizing crust of algae, lichens or more advanced biota (see refs 11–13 for discussion of this role of biota), as well as the absence of biotic contribution to physical weathering. Soils would probably not form at all in mountainous regions, precisely those sites where the most rapid chemical denudation now occurs because of a combination of mass movement exposing fresh rock and vegetation-anchoring soil²⁹. Some

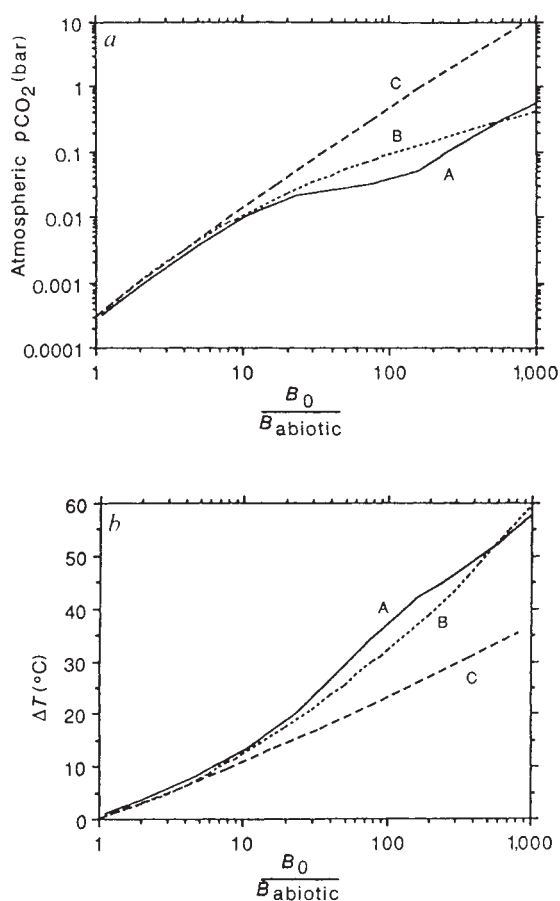


FIG. 1 *a*, Atmospheric CO_2 (p_{CO_2}) and *b*, average global surface temperature (T , expressed as deviation (ΔT) from today's T) as a function of B_0/B_{abiotic} (see equation (1)) the enhancement of present biotic weathering relative to an abiotic weathering rate, under the same conditions of p_{CO_2} and T . The plots indicate what today's Earth might have been like without the colonization of the continents by biota. Results were calculated from equation (1) with the following conditions: $V/V_0=1$ and $A/A_0=1$ (present Earth conditions), $\alpha=0.4$ to minimize the ΔT and p_{CO_2} values for the abiotic world (also see text), $\beta=0.056$ from ref. 2, and $\gamma=0.017$ from ref. 2. Estimates of β range from 0.046 (ref. 19) to 0.056 (ref. 2). The lower value is inferred from the observed temperature dependence of K^+ or silica in river water, while the higher is from laboratory experiments on albite. We believe the higher estimate of β is preferable for an abiotic model as it corresponds, for a temperature range of 100 °C, to an activation energy of ~ 50 kJ/mole, a reasonable estimate for a mean activation energy for Ca, Mg silicates of the continental crust (which ranges from 35 kJ mol⁻¹ for anorthite to 79 kJ mol⁻¹ for augite; see ref. 16). Using the higher estimate of β results in a lower computed ΔT for an abiotic model. Higher values for γ have been used¹⁸, but since we set $e^{\gamma(\Delta T)} \leq 2$ because of energy constraints¹⁸, the results for highest values of B_0/B_{abiotic} do not depend on γ . Curves A, B, and C, use the greenhouse relations for T as a function of p_{CO_2} from, respectively, refs 32, 2, and 19. Kasting and Ackerman³² presented results for $T(p_{\text{CO}_2})$ using a full radiative-convective model with p_{CO_2} as high as 100 bar. Walker, Hays, and Kasting² derived a greenhouse equation by parameterizing effects of CO_2 and water vapour, and although this cannot be preferred to results from a radiative-convective model, we present it here because, interestingly, it gives results so close to the model of ref. 32. The third greenhouse model from Marshall *et al.*¹⁹ is from a parameterization of radiative-convective model results from Kuhn up to 0.1 bar CO_2 . Results in the plots above 0.1 bar for C should be treated, therefore, with caution and we present them only as an alternative formulation and a possible lower bound to the calculation. Significant differences in the details of the treatment of water vapour exist in the radiative-convective models (curves 'A' and 'C'). To date, the model from ref. 32 is apparently the only one to calculate temperature with the high values of p_{CO_2} shown. The behaviour of atmospheric water vapour is crucial and is an important unknown (J. Kasting, personal communication; W. Kuhn, personal communication), but we believe that our results represent the best available calculations.

soils might form in lowlands, but the complete absence of any vegetative cover would allow easy erosion even on small slopes. Even today, changes of land use from forest to cultivation result in an orders-of-magnitude increase in sediment yield³⁰. Moreover, because of the lack of water storage under abiotic conditions, compared to that of areas of vegetation, the lowlands could be virtual deserts with most rainfall concentrated in mountain ranges. The enhancement factor of today's Earth relative to that of an abiotic Earth with some abiotically-stabilized soil would be less than the enhancement of $\geq 10^3$ relative to an abiotic Earth of bare rock. The degree of soil stabilization in an abiotic Earth is of course uncertain; we believe that the available evidence supports a low estimate. If under abiotic conditions, say $\leq 10\%$ of the land area was covered by soil with a weathering enhancement factor of ≤ 100 (from surface area increase alone, without any biotic factors) then the chemical denudation rate would be ≤ 0.01 times the present biotically enhanced rate.

We propose, therefore, that chemical weathering under biotic conditions is significantly enhanced relative to abiotic continental crust exposed to similar rainfall, temperature and p_{CO_2} conditions. The enhancement factor is uncertain; the key role of soil stabilization combined with other biotic effects suggests factors on the order of at least 100 to perhaps $> 1,000$.

We now consider the implications of a present biotic enhancement of weathering ranging up to 1,000 times over the abiotic rate. Using a standard technique for quantitatively estimating effects on the carbonate-silicate geochemical cycle², we balance metamorphic and magmatic outgassing of CO_2 relative to the present, (V/V_0) , with the CO_2 sink of global silicate weathering. This weathering is a product of terms, relative to the present values, for the temperature dependence of global runoff, $e^{\gamma(\Delta T)}$, and of mineral dissolution, $e^{\beta(\Delta T)}$. The ΔT is the global average temperature deviation from the present value ($\Delta T = T - T_0$). We also include the weathering dependence on atmospheric CO_2 into a unitless term to account for the biological enhancement. The actual values for the p_{CO_2} terms are most correctly taken as soil p_{CO_2} (ref. 5), but because in the abiotic case $p_{\text{CO}_2} = p_{\text{CO}_2}^{\text{soil}}$ and $p_{\text{CO}_2}^{\text{soil},0}$ can be written as $n(p_{\text{CO}_2}^0)$ where $10 < n < 100$ (ref. 8), we can write $(p_{\text{CO}_2}^{\text{soil}}/p_{\text{CO}_2}^{\text{soil},0})^\alpha = (p_{\text{CO}_2}/p_{\text{CO}_2}^0)^\alpha (1/n)^\alpha$ and then include the constant term $(1/n)^\alpha$ in a term that accounts for the biological enhancement. Expressed as a ratio of the abiotic weathering rate, B_{abiotic} , and the rate for the present Earth, B_0 , this term is taken here as a concatenation of all the specific biota-linked processes described above. We include a land area term (A/A_0) on the weathering side of the equation³, and write:

$$\frac{V}{V_0} = \frac{B_{\text{abiotic}}}{B_0} \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}_2}^0} \right)^\alpha e^{\beta(\Delta T)} e^{\gamma(\Delta T)} \frac{A}{A_0} \quad (1)$$

The biotic enhancement, B_0/B_{abiotic} , is varied between 1 and 1,000. We taken $\alpha = 0.4$ (discussed above), $\beta = 0.056$ (ref 2) and $\gamma = 0.017$ (ref. 2). We present results using three different greenhouse calculations (see Fig. 1 caption for further details). The results in Fig. 1 show that if the present, biotic enhancement ratio, B_0/B_{abiotic} , is 10, then an abiotic Earth would be 10–15 °C warmer. If the biotic enhancement is 100, the abiotic Earth would be warmer by 20–40 °C, and if 1,000, warmer by 35–60 °C. If the present enhancement $\geq 1,000$, then all greenhouse functions result in a surface temperature of greater than 50 °C ($T = T_0 + \Delta T$; $T_0 = 15$ °C). The temperature 50 °C is the estimate of the habitability limit for all but thermophile microbes, because of the thermolability of proteins and cellular membranes of the non-thermophiles³¹. Even with a biotic enhancement ratio as low as 80, greenhouse functions of refs 2 and 32 give a surface T of 50 °C. A pioneering quantitative approach to estimating temperatures on a present abiotic Earth was made by Lovelock and Watson¹, assuming the diffusion of atmospheric CO_2 into soil. They calculated a temperature increase of ~ 20 °C corresponding to atmospheric $p_{\text{CO}_2} = 0.01$ bar (ref. 31 gives a ΔT of

13 °C for this p_{CO_2}) or roughly the present soil p_{CO_2} , to equal volcanic emissions. Although they recognized that the p_{CO_2} and temperature would be somewhat higher because of a concentration gradient in the soil, the model did not include the temperature dependence of weathering which would lower the required p_{CO_2} and surface temperature. In any case, as we have argued, simply subtracting biotic enhancement of soil p_{CO_2} only goes part of the way to abiotic conditions.

Life appeared at least 3.6 if not 3.8 Gyr ago, with the oldest fossils occurring at 3.6 Gyr and indications from carbon isotope fractionation in metasediments that a biota (photosynthetic bacteria) existed at 3.8 Gyr (ref. 33). The most primitive extant life forms are, apparently, thermophile archaeobacteria³⁴, some enjoying optimal growth at 105 °C. If the transition from abiotic to biotic conditions occurred 3.8 Gyr ago with a transition temperature of the order of 100 °C, this required $p_{\text{CO}_2} = 15$ bars in the atmosphere (ref. 32, greenhouse function), agreeing with other estimates³⁵. Outgassing rates were possibly higher in the Archaean as a result of a greater juvenile contribution, as well as lack of subduction loss of carbon to the mantle³⁶. Kump (personal communication) suggests, however, that the Archaean outgassing rates were lower than the present rates because of the relative absence of carbonate sediments available for metamorphism. Higher chemical-weathering intensities would probably be required to balance outgassing, in any case, because of significantly smaller Archaean land areas, necessitating much higher p_{CO_2} in the atmosphere and surface temperature for abiotic models then, than for the present abiotic case.

The maximum allowable intensity of chemical weathering would be limited by global-uplift rates³⁷. If mean uplift rates in the early Archaean were significantly higher than today's rate (E. Nisbet, personal communication) then higher chemical denudation rates would be possible. Alternatively, a steady state CO_2 level in the atmosphere-ocean system was not achieved until later in the Precambrian, as volcanic emissions declined and land areas increased.

We offer the following scenario: origin of life near 100 °C, colonization of land by ancestral archaeobacteria and photosynthetic bacteria (note that water is of course liquid at 100 °C at external pressures > 1.0 bars, well below the p_{CO_2} inferred for an abiotic Earth in the early Archaean); natural selection would favour mutants with greater nutrient-extraction ability and growth forms with habits promoting water retention, all which would drive up weathering rates leading to soil development and drive down p_{CO_2} and surface temperatures to allow the evolution of lower-temperature forms, the microbial biota of the Archaean. The history of surface temperatures on early Earth³⁵ is consistent with a major increase in biotic influence with the appearance of land biota in the Archaean; subsequent developments, such as emergence of vascular land plants¹⁰, and then angiosperms⁶, produced further increases. We believe this is a plausible scenario for the emergence of a geophysiological³⁸ influence on global temperature with life playing an essential part along with inorganic geological processes. The Earth's earliest biota in this scenario did not optimize conditions for its existence, but was a critical factor in creating conditions for low-temperature life to emerge and thrive. □

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⁴⁰Ar/³⁹Ar laser-probe dating of diamond inclusions from the Premier kimberlite

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INCLUSIONS encapsulated by diamonds at the time of their formation provide a means for determining diamond crystallization ages and the chemistry of the surrounding upper mantle at that time. Sm–Nd studies of peridotitic inclusions, from Cretaceous-age kimberlites in southern Africa, suggest that the diamonds formed 3.3 Gyr ago¹. By contrast, eclogite-suite inclusions generally yield younger ages, sometimes approaching the time of kimberlite eruption^{2–4}. Here we report the results of ⁴⁰Ar/³⁹Ar laser-probe analyses of individual eclogitic clinopyroxene inclusions from Premier diamonds, which yield a mean age of 1,198 ± 14 Myr. This age agrees well with Sm–Nd (ref. 2) and ⁴⁰Ar/³⁹Ar (ref. 3) analyses on similar Premier inclusions, and is indistinguishable from the inferred time of emplacement of the host kimberlite (1,150–1,230 Myr)², which implies that diamond formation was essentially synchronous with kimberlite generation. The extrapolated non-radiogenic ⁴⁰Ar/³⁶Ar ratio of 334 ± 102 is similar to the present-day atmospheric composition. This value is inconsistent with Sr and Nd isotopic signatures from Premier eclogite inclusions², which suggest a depleted mantle source (⁴⁰Ar/³⁶Ar > 20,000). Pre-entrapment equilibration of the inclusions with an ³⁶Ar-rich fluid is the most probable explanation for the low non-radiogenic (⁴⁰Ar/³⁶Ar) composition.

Because of their chemical inertness and high-pressure/temperature stability at low *f*_{O₂}, diamonds provide a resilient refuge for impurities and inclusions ranging from atomic helium to millimetre-sized silicate grains^{5–8}. Consequently, diamonds and

their inclusions provide a unique opportunity to ascertain the mantle chemistry at the time of diamond formation. Syngenetic silicate inclusions are present in a small proportion of diamonds and can usually be classified into eclogitic or peridotitic associations⁹. The peridotite suite includes olivine, enstatite and pyrope whereas the eclogitic suite is dominated by garnet and omphacitic clinopyroxene^{10,11}. Eclogitic clinopyroxene is of particular interest to K–Ar dating of diamonds, because of their high potassium contents (≤0.9 wt% K₂O (ref. 12)).

So far, the most successful attempts to date diamonds by their inclusions have used the U–Pb and Sm–Nd decay schemes. Kramers¹³ reported U–Pb model ages of >2,000 Myr and ~1,200 Myr from two suites of sulphide inclusions from diamonds, the first derived from the ~90 Myr Finsch- and Kimberley-group kimberlites and the second from the ~1,180 Myr Premier kimberlite. Richardson *et al.*¹ obtained Sm–Nd model ages averaging 3,300 ± 200 Myr (2σ error) from peridotite-suite inclusion composites extracted from Finsch- and Kimberley-group diamonds. In a subsequent study², two-point Sm–Nd isochron ages of 1,150 ± 60 Myr (2σ error) for Premier and of 1,580 ± 60 Myr (2σ error) for the Argyle mine (Australia) eclogitic diamond inclusions were obtained. The wide range of Sm–Nd model ages, from 1,443 ± 188 to 2,408 ± 180 Myr (ref. 4), measured for large single eclogitic inclusions from the Finsch (90 Myr) kimberlite implies multiple episodes of diamond genesis.

K–Ar and ⁴⁰Ar/³⁹Ar analytical techniques have been less successful in constraining diamond formation ages. In many cases, isotope measurements have been made on whole

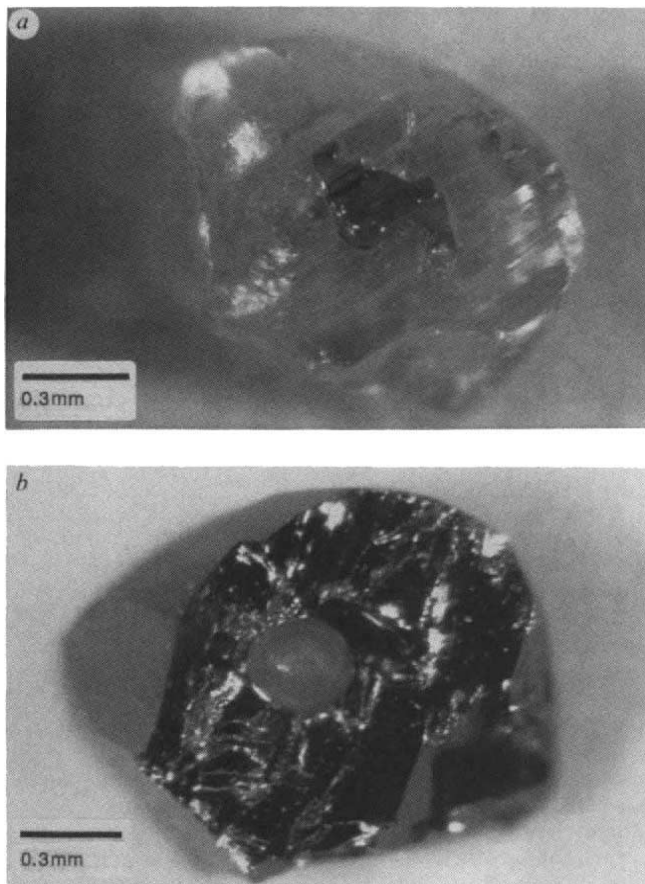


FIG. 1 *a*, Photomicrograph of Premier clinopyroxene inclusion P120, partly exposed in its host diamond. *b*, P120 after irradiation and laser-probe fusion. The diamond turned dark green after irradiation. On laser heating, the clinopyroxene inclusion coalesced to a bead above the cavity in the diamond that it had occupied previously.