waist of the tube in response to a field along the tube axis. In this interpretation the diamagnetism of the tubes would be greater than that of graphite because of the different current pathways provided by the two materials. In graphite, ring currents are confined to the planes and only flow when the field has a component normal to this direction.

It has been shown in band structure calculations that the electronic structure of nanotubes is highly sensitive to the degree of helicity in the carbon atom network (31). Three different categories of helicity are identified, each with its particular band structure. In general, however, the band gap scales with helicity, except for highsymmetry configurations. Because the interband processes that give graphite its large diamagnetism will be absent for large band gaps, it is apparent from the present data that the majority of tubes have a narrow gap band structure similar to that of graphite. Hence, the present data strongly suggest that the bulk of the nanotubes correspond to highly symmetric wrapping of graphite sheets, most likely the result of negligible helicity. However, the small spin susceptibility observed in our previous study (32) provides no evidence for metallic character in the nanotubes. Clearly, further work, both experimental and theoretical, is needed to resolve these issues.

Note added in proof: After submission of this work, we learned of similar studies (33).

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Water on Mars: Clues from Deuterium/Hydrogen and Water Contents of Hydrous Phases in SNC Meteorites

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Ion microprobe studies of hydrous amphibole, biotite, and apatite in shergottite-nakhlitechassignite (SNC) meteorites, probable igneous rocks from Mars, indicate high deuterium/ hydrogen (D/H) ratios relative to terrestrial values. The amphiboles contain roughly onetenth as much water as expected, suggesting that SNC magmas were less hydrous than previously proposed. The high but variable D/H values of these minerals are best explained by postcrystallization D enrichment of initially D-poor phases by martian crustal fluids with near atmospheric D/H (about five times the terrestrial value). These igneous phases do not directly reflect the D/H ratios of martian "magmatic" water but provide evidence for a D-enriched martian crustal water reservoir.

The water in the present martian atmosphere is strongly enriched in deuterium relative to water on Earth, with a D/H ratio approximately five times the terrestrial value (1), corresponding to a δD value of +4000 (2). It is generally assumed that Mars and Earth originally had similar values of the D/H ratio (-1.5×10^{-4}) but that escape of hydrogen (relative to heavier deuterium) from the martian upper atmosphere throughout the planet's history has led to the observed D enrichment (3, 4). It may be possible to test this presumption because the D/H ratio of the martian interior has likely retained its original value. Unlike Earth with its subduction zones, on Mars recycling of near-surface and atmosphere-derived (meteoric) waters into the mantle is generally considered to be an unimportant process [(5) but see (6) for an alternative view]. Thus, a direct measurement or even an indirect inference of the D/H value of martian magmatic (interior) water could provide a fundamental constraint on the extent

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of hydrogen loss on Mars. Moreover, neither the abundance nor the hydrogen isotopic composition of water in the martian crust (present either as a meteoric component or in hydrogen-bearing minerals) is well characterized (4). However, a significant component of the martian water budget could be present in this crustal reservoir, and the determination of its D/H ratio would constrain the nature of its interaction with the atmosphere.

The 10 SNC meteorites are igneous rocks widely believed to be samples from Mars that were ejected from that planet by one or more impact events. The hypothesis of a martian origin for the meteorites is based on their young crystallization ages ($\leq 1.3 \times 10^9$ years), the close correspondence between the composition of the martian atmosphere and that of volatile components trapped in shock-derived glasses, and many other geochemical arguments (7). Because the SNCs are fine- to medium-grained igneous rocks that show evidence for crystal accumulation, they were probably emplaced as shallow intrusions into the martian crust or as crystal-rich surface flows (7). Postcrystallization alteration products that include clay minerals (8) show conclusively that the nakhlites (3 of the 10 SNCs) interacted with fluids in the martian crust at low temperatures after the magmas solidified. The alteration products in the nakhlites have been shown to contain water that

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is significantly enriched in deuterium (9), suggesting that martian crustal water has become D-enriched through interaction with the atmosphere. However, comparable mineralogical evidence of pervasive postcrystallization hydrous alteration of the shergottites and chassignites is not present (10).

We report D/H and water contents of kaersutitic (Ti-rich) amphiboles (10 to 80 μ m in size) in the Chassigny, Shergotty, and Zagami (a shergottite) meteorites, one 15-µm biotite in Chassigny (the only biotite thus far reported in the SNCs) (11), and one \sim 1-mm-long apatite in Zagami. The kaersutites and biotite are found only inside partially crystallized magmatic inclusions enclosed within olivine and pyroxene crystals (Fig. 1A). The kaersutites and biotite in these meteorites have been described (11-14), and the inclusion compositions have been used to constrain the nature of SNC parental liquids because the meteorites are at least partial cumulates (7) and thus are not directly representative of the liquids from which they crystallized. Although the bulk SNCs are



Fig. 1. Scanning electron microscope backscattered electron images. (A) A kaersutite and biotite-bearing magmatic inclusion in Chassigny. The inclusion is olivine-hosted (ol), and the kaersutite (k) and biotite (b) crystals are marked. Other magmatic inclusion phases present include high-calcium (p1) and low-calcium (p2) pyroxene, chromite (c), and two high-silica glasses (g1 and g2) (11). Scale bar, 100 μ m. (B) The apatite grain (a) in Zagami DN. The grain is not contained in a magmatic inclusion. Surrounding phases include pigeonite (p), maskelynite (m), and a fayalite-rich intergrowth (f) (16). Scale bar, 300 μ m.

poor in water, it has been suggested that the magmatic inclusions have concentrated magmatic water through crystallization of anhydrous phases until hydrous kaersutites (and biotite) were stabilized (11, 13, 15). Although the water contents of the kaersutites and biotite have not been measured directly, on the basis of the crystal chemistry of the amphibole group and electron microprobe and qualitative ion microprobe analyses (11-13) it has been suggested that the kaersutite crystals contain hydroxyl (OH) as a major constituent; for example, Johnson et al. (11) estimated that the Chassigny kaersutites contain 1.5% (by weight) water as OH (a fully hydroxylated amphibole would contain $\sim 2\%$ water). The apatite crystal in Zagami (Fig. 1B) is not contained within a magmatic inclusion; rather, it occurs in a lithology referred to as Zagami DN (16), interpreted to represent a late-crystallizing melt.

The D/H ratios of the SNC kaersutites, biotite, and apatite cannot be determined by conventional isotopic heating-extraction techniques because the crystals are too small and few in number. Consequently, we measured the D/H ratios of individual crystals in situ, in the thin sections listed in Table 1, using the ion microprobe. We made the measurements with a modified Cameca IMS-3f instrument using a mass resolving power of ~1200, sufficient to resolve D⁺ and H₂⁺, and an ${}^{16}O^{-}$ primary beam of ~1.5 to 3.1 nA focused to a diameter of 3 to 8 µm. Water-bearing glass standards with the same major element composition as the Chassigny kaersutites (11) were used to correct the measured D/H values of the kaersutites and biotite for composition-dependent instrumental mass fractionation (17, 18). We calculated the total water contents of the kaersutites and biotite from the measured ${}^{1}H^{+}/{}^{30}Si^{+}$ secondary ion ratios using a calibration between measured ${}^1\mathrm{H}^+/{}^{30}\mathrm{Si}^+$ secondary ion ratios and true OH and Si contents determined from analyses of the glass standards and terrestrial amphibole and biotite standards. A terrestrial apatite from Pacoima Canyon, California, was used as a standard for the apatite analyses of D/H and water contents (19).

The kaersutites were found to contain ~ 0.1 to 0.2% water (20), an order of magnitude less than the amount previously assumed (11–13, 15), and the biotite contained $\sim 0.5\%$ water. The Zagami DN apatite grain contained ~ 0.3 to 0.4% water. The low OH content of the SNC kaersutitic amphiboles combined with their low F and Cl contents (11–13) suggests the presence of a significant oxy-amphibole component (O²⁻ substitutes for OH⁻ in the amphibole O3 site) (21). Some terrestrial oxy-amphi-

boles may form by posteruptive oxidation or mantle metasomatism involving the oxidation of Fe²⁺ and corresponding loss of H (21, 22). However, terrestrial kaersutites display a negative correlation between Ti content and the sum of OH + F + Cl (21), consistent with the primary incorporation of the oxy-amphibole component at the time of crystallization, with the OH concentration strongly influenced by crystal chemical factors. Thus, the low H contents of the SNC amphiboles are consistent with their high Ti contents [7% TiO₂ for Chassigny kaersutites (11) and $\sim 9\%$ TiO₂ for shergottite (13) kaersutites]. In the absence of phase equilibrium data appropriate for amphiboles of these compositions, it is difficult to make inferences about the water content of the parent magmas of these meteorites. Furthermore, published esti-

Table 1. Values of **bD** of kaersutites, biotite, and apatite in the SNC meteorites. The uncertainty is reported as twice the standard deviation of the mean and includes the uncertainty in α (the instrumental fractionation correction) from the standard analyses (18). The first two δD values in USNM 624-1 represent single analyses of kaersutites in two different inclusions. The next three kaersutite analyses are on two separate crystals within a third inclusion (Fig. 1A), with the latter two representing replicate analyses of the same crystal during different measurement runs. This third inclusion also contains the biotite grain. The three SD values for UH 106 represent three areas of one ~70-µm kaersutite. The two kaersutite measurements in Zagami are single grains in two separate inclusions. The seven analyses from Zagami DN are on a single ~1-mm-long apatite (Fig. 1B). Abbreviations: k, kaersutite; b, biotite; a, apatite.

Thin section no.	Phase analyzed	δD (per mil)
	Chassigny	
USNM 624-1	k	+897 ± 81
USNM 624-1	k	+1425 ± 71
USNM 624-1	k	+823 ± 81
USNM 624-1	k	+1043 ± 72
USNM 624-1	k	+1014 ± 101
USNM 624-1	b	+987 ± 40
UH 106	k	+1338 ± 42
UH 106	k	+1253 ± 42
UH 106	k	+1879 ± 48
	Sheraotty	
USNM 321-1	ĸ	+512 ± 89
	Zaoami	
UNM 991	ĸ	+1672 ± 57
UNM 991	k	+1498 ± 62
	Zagami DN	
UH 234	ĭa	+4053 ± 174
UH 234	a	$+4358 \pm 185$
UH 234	a	+3146 ± 144
UH 234	а	+3749 ± 164
UH 234	а	+2962 ± 139
UH 234	а	+3609 ± 160
UH 234	а	+2963 ± 141

mates of magmatic water content, which are based on phase equilibria of nonkaersutitic amphiboles (23) and on the assumption that the water contents of the SNC amphiboles are about an order of magnitude higher than they actually are (11, 15), are probably invalid. The water contents of the SNC parent magmas at the time of inclusion entrapment were most plausibly lower than reported estimates of 1.4 to 1.5% (11, 15, 24).

The samples and phases studied and the hydrogen isotopic results are summarized in Table 1 and Fig. 2. Eleven kaersutite analyses on eight individual crystals gave δD values ranging from $+512 \pm 89$ to +1879 \pm 48, the biotite had $\delta D = +987 \pm 40$, and seven analyses of the Zagami DN apatite yielded δD values between +2962 ± 139 and +4358 ± 185. The D/H values measured in the SNC hydrous minerals exhibit two striking features: first, large enrichments in D relative to terrestrial materials, with δD values up to ${\sim}+4400,$ and second, large variability in the D/H ratio both among different amphiboles and within individual crystals.

Although some of the variability in the measured D/H values may be attributable to contamination by terrestrial water adsorbed on the sample surfaces ($\delta D \approx -200$), on the basis of the evidence presented below we believe that the samples are intrinsically heterogeneous in their D/H values. As discussed by Deloule *et al.* (17), the value of H_2^+/H^+ can be used as a tracer of contamination by adsorbed water. By reporting data only for analyses with $H_2^+/H^+ < 7 \times 10^{-4}$, we have tried to minimize the effects of contamination on our results.

It should be emphasized that the contribution of the background hydrogen signal is most important for the SNC kaersutites, because the crystals are so water-poor (25). The strongest argument that contamination



Fig. 2. Histogram of the δD values reported in this work. The bin size is 200 per mil. Uncertainties for each measurement are given in Table 1 and average ± 68 per mil for the kaersutites and ± 158 per mil for the apatite. The uncertainty on the biotite measurement is ± 40 per mil. The range of δD values of terrestrial hydrogen and the most recent measurement of the δD value of the current martian atmosphere (1) are shown in black.

is unimportant in the reported data is provided by analyses of kaersutite and biotite in the same inclusion. The biotite contains roughly three times as much water as the kaersutite, so if background or terrestrial contamination were overwhelming the true D/H signal of the water-poor kaersutite, then the water-rich biotite, having a much smaller fractional contribution from this contaminant, should have a significantly higher measured D/H value. However, within error, both phases contained in this inclusion have identical D/H values: $\delta D =$ $+1014 \pm 101$ for the kaersutite and $\delta D =$ $+987 \pm 40$ for the biotite. Thus, we conclude that, for analyses with $H_2^+/H^+ <$ 7×10^{-4} , contribution from the background is not an overwhelming problem and, furthermore, a significant fraction of the measured variability between +500 and +1900 in SNC kaersutites reflects intrinsic grain-to-grain variations in δD . Likewise, the δD variation observed in the single apatite grain is much larger than the uncertainty of the measurements. Like the biotite analysis, the apatite analyses are relatively unaffected by the background, because the apatite contains significantly more water than the kaersutites. We believe that the variation observed in the apatite also reflects real heterogeneity in the D/H ratio within this crystal. Given the challenging nature of the ion microprobe measurements of D/H, more detailed interpretation of individual measurements is not warranted.

The results presented here clearly show that the D/H ratio of individual amphiboles, biotite, and apatite in the SNC meteorites are significantly higher than terrestrial values and, especially in the case of the apatite, are consistent with values as high as the current martian atmosphere (δD \approx +4000). Moreover, the variability of the δD values of the kaersutites within a single meteorite, their differences from the apatite values, the isotopic heterogeneity of the apatite grain, and the similarity of the high end of the apatite δD values to the current martian atmosphere (all illustrated in Fig. 2) suggest that the observed δD values are the result of events involving the postcrystallization interaction of the samples with martian crustal fluids carrying a D-enriched signature derived from the martian atmosphere. Hence, we conclude that the measured D/H values do not directly reflect the D/H value of "magmatic" water from the martian mantle.

We believe that the simplest scenario that satisfactorily explains both the high and variable δD values of these minerals involves substantial but incomplete post-crystallization exchange of hydrogen in the kaersutites, biotite, and apatite with D-enriched hydrous (meteoric?) fluids, perhaps in an environment analogous to terrestrial

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magmatic hydrothermal systems. The nakhlites show extensive evidence of such interaction (8) in the form of clay-bearing alteration products that contain D-enriched water (9), but no secondary water-bearing silicates have been reported in the shergottites and Chassigny. However, small grains of carbonate and sulfate have been described (10) and used as evidence of mild preterrestrial alteration of Chassigny and shergottite EETA 79001 (10).

Although it is likely that the exchange of hydrogen in a groundmass phase such as the Zagami DN apatite would be relatively easy, the mechanism of exchange of hydrogen in the magmatic inclusion phases is more enigmatic. On the one hand, it may seem difficult to envision how the kaersutites and biotite could be altered within their anhydrous pyroxene and olivine containers. Moreover, if the samples had been altered in the way we are proposing, the glass present in the magmatic inclusions might be expected to be hydrated or devitrified. However, as reported by Johnson et al. (11) and on the basis of ion microprobe measurements by us, this glass is essentially anhydrous. On the other hand, if fluids could exchange with the enclosed phases [for example, by diffusion of hydrogen through the anhydrous containers or through microcracks (26)], then the interaction would be slower than for unenclosed phases such as the Zagami apatite, thus possibly explaining the systematically lower D/H value of the enclosed kaersutites relative to the apatite in Zagami. The interaction of D-enriched crustal fluids with the SNC meteorites after crystallization, resulting in the incomplete exchange of their magmatic water, best explains both the lower δD values of the kaersutites and biotite relative to the apatite and their large variability, as well as the δD variation in the apatite grain.

An alternative explanation for the D-rich crystals is that the D/H ratio of the water dissolved in the SNC melts was enhanced relative to the primitive values inherited from their mantle source regions, perhaps by the assimilation of crustal material enriched in deuterium through interaction with meteoric fluids. On the basis of trace element and isotopic data, it has been suggested that the process of assimilation plays an important role in shergottite petrogenesis, although it has not been invoked in the history of the nakhlites or Chassigny (27). It would be difficult, however, to explain the systematic difference between the D/H of the apatite and amphibole by this hypothesis. Moreover, the range of amphibole δD values from a single meteorite and within the single Zagami apatite (Fig. 2) would require that any incorporation of crustal hydrogen into the

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magma took place almost immediately before entrapment of the magmatic inclusions and crystallization of the apatite; otherwise diffusion would have homogenized the D/H value of the magma, resulting in uniform D/H values of the hydrous phases (28).

Our interpretation that the δD signature of the hydrous phases reflects incomplete exchange with crustal fluids or rocks with near-atmospheric D/H values implies that the D/H ratio of magmatic water on Mars (that is, that reflects the D/H ratio of mantle source regions) cannot be directly measured with the available samples. However, our interpretation also implies that the δD values of the water in the parent magmas must have been lower than +500to +1000, the lowest values observed in the amphiboles, and significantly lower than that of the current martian atmosphere. With the available data it is impossible to rule out the prospect that water in the source regions of the SNC magmas could have a D/H ratio up to 50% higher (that is, a δD value of ~+500) than that of Earth's mantle.

If the high D/H values of hydrous magmatic minerals in SNC meteorites are ultimately due to interaction of hydrogen in the martian crust with that in the atmosphere, our results also provide some indirect insights into atmospheric processes on Mars. For example, this interpretation of our results implies that perhaps as early as $\sim 1.3 \times 10^9$ years ago, the earliest possible time of crystallization for the SNC meteorites (29) (the youngest reasonable crystallization age of some SNC meteorites is $180 \times$ 10^6 years) (30), the D/H value of the martian atmosphere was already high relative to the terrestrial value (and perhaps even as elevated as that of the modern atmosphere) because hydrothermal alteration is not likely to have significantly postdated primary crystallization of the magmas. Moreover, the data support the hypothesis that, at the time of igneous activity, a fluid phase was present in the martian crust and its high D/H value suggests that the hydrogen in this fluid once resided in the atmosphere or was part of an exchangeable reservoir in isotopic communication with it.

This result is consistent with measurements of the oxygen isotopic composition of water in bulk SNC samples (31), which can be explained by the equilibration of the oxygen in crustal water with atmospheric oxygen that has been affected by loss processes (32). Consequently, models of the evolution of the martian atmosphere should take into account this possibly large and exchangeable crustal reservoir of water (that is, to change the D/H value of a large reservoir of water, a very large amount of hydrogen must have escaped the planet). In addition, our measurements support the assertion that, for Mars to have lost the amount of water implied by geological arguments, the escape rate of hydrogen must have been higher in the past (3) because 10^8 to 10^9 years ago the D/H ratio was already close to the value of the current martian atmosphere.

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- 18. Previous ion microprobe studies of terrestrial silicates have shown that, because of instrumental mass fractionation favoring H+, measured values of D+/H+ differ substantially from the true D/H value of the sample being studied (17). The magnitude of the fractionation is strongly dependent on major element composition, requiring the use of standards similar in chemical composition to the samples. Because the SNC kaersutites and biotite are outside of the typical compositional range of these phases on Earth (11, 13), we synthesized three standard glasses with the same bulk composition as the Chassigny kaersutite [from (11)], containing dissolved water spanning a large range of D/H (+48 < δ D < +1130), in a

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piston-cylinder apparatus at 10 kbar and 1550°C. At the beginning of each of the four occasions when data were collected for this work, analyses of the standard glasses were used to calculate an instrumental fractionation factor, α , equal to (D⁺/ $(D/H)_{measured} = (D/H)_{true}$. The value of α was used to correct the measured D⁺/H⁺ values for all kagrsutites and the biotite, and only the corrected values are reported. The value of $\boldsymbol{\alpha}$ ranged from 0.592 ± 0.006 to 0.631 ± 0.006 , depending slightly on the instrument tuning in each analysis session. The uncertainty in the δD values is reported as twice the standard deviation of the mean and includes the uncertainty in α from the standard analyses. Because the meteoritic kaersutites and biotite do not all have the same bulk composition, an additional uncertainty in the δD values for the shergottite kaersutites and the Chassigny biotite may be anticipated. However on the basis of D/H measurements of a variety of common terrestrial materials with a much larger range in major element composition than that of the meteorite samples, we place an upper limit of 20% (relative) on the magnitude of the uncertainty in α for the shergottite kaersutites and Chassigny biotite. This uncertainty has no effect on our conclusions

- 19. We corrected the Zagami DN apatite δD values for instrumental mass fractionation using an α value of 0.706 ± 0.024, determined from analyses of the Pacoima Canyon, CA, apatite. We determined the water content of the Zagami DN apatite from the ¹H+/⁴⁴Ca⁺ secondary ion ratios, using a sensitivity factor determined from the Pacoima Canyon apatite analyses.
- 20. Although the ideal experiment would involve measurement of both the D/H and the water contents of every grain studied, because of the nature of the instrument tuning required for precise D/H measurement it proved impossible to measure the ¹H⁺/³⁰Si⁺ secondary ion ratio (used to calculate the water content) in conjunction with each D+/H+ measurement. Thus, only a few selected water contents were measured. These include one for a Chassigny kaersutite (in section UH 106), one for a Zagami kaersutite (in section UNM 991), and one for the Chassigny biotite (in section USNM 624-1). Although the interpretation of the water content data remains unchanged, we have reported slightly higher water contents of the kaersutites in abstract form. The first reported value of <0.3% [L. L. Watson, I. D. Hutcheon, S. Epstein, E. M. Stolper, Lunar Planet. Sci. 24, 1493 (1993)] was based solely on the H⁺ count rates (rather than on the 1H+/30Si+ secondary ion ratios) of Chassigny kaersutites relative to the glass standards and was intended as only a rough estimate. The second estimate of ~0.5% [L. L. Watson, I. D. Hutcheon, S. Epstein, E. M. Stolper, Meteoritics 28, 456 (1993)] was an upper limit based on one Shergotty and one Chassigny measurement. On the basis of the measured H_2^+/H^+ , both of these analyses were subsequently found to have been affected by terrestrial contamination, and these data have been superseded by the data in the text
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- 24. The water content of the biotite, although higher than that of the kaersutites, is still lower than that of typical terrestrial biotites [A. L. Boettcher and J. R. O'Neil, Arn. J. Sci. 280-A, 594 (1980); (22)]. However, the Chassigny biotite contains ~9% TiO₂ (11) and thus, like the kaersutites, may be expected to have a low water content based on its bulk composition and the presence of an oxy component.
- 25. Although evidence for a significant contribution of an adsorbed water component is not observed (only those analyses for which $H_2^+/H^+ < 7 \times 10^{-4}$ are included), the δD values of all of the samples

could still be affected by some contribution from the machine background. The kaersutites are most susceptible because they contain the least intrinsic hydrogen. It is difficult to correct quantitatively for this background contribution other than to apply a constant correction, an unquestionably inaccurate approach. Because adsorbed water is characterized by a low D/H ($\delta D \approx -200$) value, any background correction will increase the reported δD values. To take a conservative approach, no background correction was made. If a correction were made, however, we estimate it would raise the δD values of the Chassigny kaersutites by no more than ~500 per mil, taking an average background contribution of ~1/5 the total H+ count rate. In addition, the small size of the kaersutites can also contribute to lower H⁺ count rates as a result of overlap of the primary beam onto neighboring anhydrous phases. This problem was observed (by microscopic examination of the samples after measurement) to be most pronounced in the shergottite kaersutites [they are the smallest measured (~10 µm)]. Thus, the shergottite kaersutites had lower H⁺ count rates than the Chassigny samples and could need a maximum correction of ~+1500 per mil, taking an average background contribution of ~2/5 of the total H+ count rate. Again we emphasize that these corrections represent the maximum that could be needed, and the similarity in measured D/H of coexisting biotite and kaersutites described in the text suggests that the actual effects are much smaller. Moreover, any correction will not eliminate the variable nature of the δD values observed in the kaersutite and would not significantly change the interpretations presented.

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photocrosslinking to determine directly-

RNAP that is in proximity to the activating

region of CAP in the ternary complex of

the *lac* promoter, RNAP, and CAP. Our approach had five steps: (i) We covalently

attached a photoactivatible crosslinking

agent at a single, defined amino acid within

the activating region of CAP. (ii) We

verified that the resulting CAP derivative

retained the ability to activate transcrip-

tion. (iii) We formed the ternary complex.

(iv) We irradiated the ternary complex

with ultraviolet (UV) light. (v) We deter-

mined the site at which crosslinking oc-

curred (Fig. 1). To facilitate identification

of the site at which crosslinking occurred,

we used a photoactivatible crosslinking

agent that contained a radiolabel and that

was attached to CAP through a disulfide

linkage (Fig. 1A). This permitted, after

UV irradiation, cleavage of the crosslink

and transfer of the radiolabel to the site at

which crosslinking occurred (Fig. 1, B and

site

on

without preconceptions—the

Identification of the Target of a Transcription Activator Protein by Protein-Protein Photocrosslinking

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ere it is shown, with the use of protein-protein photocrosslinking, that the carboxylrminal region of the α subunit of RNA polymerase (RNAP) is in direct physical proximity the activating region of the catabolite gene activator protein (CAP) in the ternary complex of the *lac* promoter, RNAP, and CAP. These results strongly support the proposal that transcription activation by CAP involves protein-protein contact between the carboxylterminal region of the α subunit and the activating region of CAP.

C).

Escherichia coli CAP is a structurally characterized transcription activator protein (1, 2). Genetic studies have indicated that amino acids 156 to 164 of CAP constitute an "activating region" that is essential for transcription activation at the lac promoter but not essential for DNA binding by CAP or DNA bending by CAP (3). Further genetic studies have indicated that the 100 COOH-terminal amino acids of the α subunit of RNAP are essential for transcription activation by CAP at the lac promoter but are not essential for CAP-independent transcription (4). The simplest interpretation of the genetic results with CAP and RNAP is that transcription activation at the lac promoter involves protein-protein contact between the activating region of CAP and the COOH-terminal region of the α subunit of RNAP.

In this study, we used protein-protein

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We constructed and analyzed a CAP derivative with a photoactivatible crosslinking agent incorporated at amino acid. 161: [125I]-{[S-[N-(3-iodo-4-azidosalicyl)cysteaminyl]-Cys¹⁶¹; Ser¹⁷⁸]CAP} (IAC¹⁶¹CAP) (Fig. 2). Amino acid 161 is located within the activating region of CAP (3) but is not essential for transcription activation (5, 6). Saturation-mutagenesis studies have indicated that position 161 tolerates a wide range of amino acid substitution without loss of ability to activate transcription (6). We reasoned that position 161 might likewise tolerate incorporation of a photoactivatible crosslinking agent without loss of ability to activate transcription.

To construct IAC¹⁶¹CAP, we used a two-step procedure consisting of (i) introduction of a unique surface cysteine residue at position 161 of CAP and (ii) cysteinespecific chemical modification. In step (i), we used site-directed mutagenesis to replace the preexisting surface cysteine residue at position 178 with serine and to replace the aspartic acid residue at position 161 with cysteine (7). In step (ii), we reacted the resulting CAP derivative with [125I]-{S-[N-(3-iodo-4-azidosalicyl)cysteaminyl]-2-thiopyridine} (10) (Fig. 3, A and B) under conditions that resulted in highly efficient, highly selective, derivatization of surface cysteine (12, 13) (Fig. 3C).

To assess the ability of IAC¹⁶¹CAP to activate transcription, we did abortive initiation in vitro transcription experiments with a derivative of the *lac* promoter having a consensus DNA site for CAP: *lacP(ICAP)* (14). The results establish that IAC¹⁶¹CAP retains nearly full ability to activate transcription (\approx 70% of the level of transcription activation shown by

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