The parameter of the Cordillera is more robust than that of the wavelength approximately equal to the crustal mantle interface are limited in resolution to a 3 and fig. S8B). Inverse models of the crustal structure also reveals offsets at the crust-mantle interface that do not correlate with rings or excavation cavity (Fig. 3). Our modeling shows that ring location and fault offsets are highly dependent on impactor size and the pre-impact thermal gradient (figs. S9 and S10). In our best-fitting model, the region where crust is thinned from the pre-impact value extends to $R_{\text{thin}} = 200$ km. The parameter $R_{\text{thin}}$ also provides an estimate for the radius of the zone of ejecta provenance or excavation cavity (36). In our best-fitting model of Orientale, these two metrics agree to within 5%. We favor the model with pre-impact crustal thickness of 52 km because it produces a thicker cap of cool crustal material at the center of the basin (Fig. 3), consistent with gravity observations.

Inverse models of GRAIL gravity data suggest that the Outer Rook and Cordillera are associated with localized crustal thinning and offsets at the crust-mantle interface (2). The crustal structure also reveals offsets at the crust-mantle interface that do not correlate with rings and may indicate additional subsurface faults. The faults with small offsets forming on either side of the Cordillera in our simulations may be consistent with these additional faults (Fig. 2). The amount of crustal thinning and magnitude of crust-mantle relief, however, depend on the assumptions of these inverse models (2). Our models exhibit local minima in the crustal thickness (Fig. 3) and offsets at the crust-mantle interface (Fig. 2) associated with the Outer Rook and Cordillera. These results are consistent with normal faults with offsets of a few kilometers cutting through the crust-mantle interface. The simple geometry of a normal fault with a dip angle of 50° and offset of 4 km cutting through 50-km-thick crust will create a ~40-km-wide region where the crust is thinned by ~3 km. This idealized fault geometry is similar to the modeled Outer Rook ring (Fig. 3, red curve) 200 to 340 km from basin center. When extension occurs close to a fault (within ~40 km), the zone of crustal thinning is broader (Figs. 2 and 3 and fig. S8B). Inverse models of the crust-mantle interface are limited in resolution to a wavelength approximately equal to the crustal thickness. Thus, the predicted broader zone of extension may explain in part why the signature of the Cordillera is more robust than that of the Outer Rook (2). Similar local minima in crustal thickness as observed by GRAIL may reveal ring faults in highly degraded or mare-filled basins.

REFERENCES AND NOTES
17. See supplementary materials on Science Online.

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SUPPLEMENTARY MATERIALS
www.sciencemag.org/content/354/6311/441/suppl/DC1 Materials and Methods
Figs. S1 to S10 Tables S1 and S2
Movie S1
References (35–55)

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CHEMICAL KINETICS

Direct frequency comb measurement of OD + CO → DOCO kinetics

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The kinetics of the hydroxyl radical (OH) + carbon monoxide (CO) reaction, which is fundamental to both atmospheric and combustion chemistry, are complex because of the formation of the hydroxycarbonyl radical (HOCO) intermediate. Despite extensive studies of this reaction, HOCO has not been observed under thermal reaction conditions. Exploiting the sensitive, broadband, and high-resolution capabilities of time-resolved cavity-enhanced direct frequency comb spectroscopy, we observed deuterolysis radical (OD) + CO reaction kinetics and detected stabilized trans-DOCO, the deuterated analog of trans-HOCO. By simultaneously measuring the time-dependent concentrations of the trans-DOCO and OD species, we observed unambiguous low-pressure temperature dependence of the reaction rate coefficients for N2 and CO bath gases. These results confirm the HOCO formation mechanism and quantify its yield.

The apparent simplicity of the gas-phase bimolecular reaction kinetics of free radicals often belies the complexity of the underlying dynamics. Reactions occur on multi-dimensional potential energy surfaces that can host multiple prerequisite and bound intermediate complexes, as well as multiple transition states. As a result, effective bimolecular rate coefficients often exhibit complex temperature and pressure dependences. The importance of free radical reactions in processes such as combustion and air pollution chemistry has motivated efforts to determine these rate constants both experimentally and theoretically. Quantitative ab initio modeling of kinetics remains a major contemporary challenge (1), requiring accurate quantum chemical calculations of energies, frequencies, and anharmonicities; master equation...
The reaction of hydroxyl radical with CO through a prereactive weakly bound OH–CO complex to form a highly energized HOCO* (where the asterisk denotes vibrational excitation) in one of two isomers, trans-HOCO or the less stable cis-HOCO (2). In the low-pressure limit at room temperature, HOCO* primarily back-reacts to OH + CO, but there is a small probability of overcoming the low barrier (8.36 kJ mol⁻¹) and reacting to form H + CO₂. In the presence of buffer gas, energy transfer by collisions with third bodies M (molecular process) can deactivate or further activate the HOCO*. Deactivation can lead to the formation of stable, thermalized HOCO products (reaction 1a in Fig. 1A, inset), which diminishes the formation of H + CO₂ (reaction 1b in Fig. 1A, inset). Approaching the high-pressure limit, HOCO formation becomes the dominant channel, and H + CO₂ product formation decreases. The overall reaction rate is characterized by an effective bimolecular rate constant $k_1([M],T) = k_{1a}([M],T) + k_{1b}([M],T)$, where $T$ is temperature (8–12).

There have been numerous experimental studies of the temperature and pressure dependence of the overall rate coefficient $k_1([M],T)$; these all have measured OH loss in the presence of CO (9, 11–17). In principle, master equation calculations with accurate potential energy surfaces within a statistical rate theory can compute $k_1([M],T)$, but a priori kinetics are rarely possible because the energy transfer dynamics are generally not known. A number of studies have thus fit the theoretical models to the observed overall rate constants, using a small number of parameters to describe collisional energy relaxation and activation (9, 11, 15, 16, 18, 19). Although these previous studies have had success in describing $k_1([M],T)$, they do not capture the dynamics that would be revealed from the pressure-dependent branching between stabilization of HOCO and barrier crossing to form H + CO₂ products. Detection of the stabilized HOCO intermediate and measurement of its pressure-dependent yield would confirm the reaction mechanism and quantitatively test theoretical models. The spectroscopy of HOCO is well established, and recently HOCO has been observed in the OH + CO reaction generated in a discharge (20–22); however, measurements under thermal conditions are necessary to derive rate constants.

To directly and simultaneously measure the time-dependent concentrations of reactive radical intermediates such as HOCO and OH, we applied the recently developed technique of time-resolved direct frequency comb spectroscopy (TRFCS) (23). The massively parallel nature of frequency comb spectroscopy allows time-resolved, simultaneous detection of a number of key species, including intermediates and primary products, with high spectral and temporal resolution. The light source is a mid-infrared (IR) (wavelength $\lambda = 3$ to 5 μm) frequency comb, generated from an optical parametric oscillator (OPO) synchronously pumped with a high-repetition-rate ($f_{\text{rep}} = 136$ MHz) mode-locked femtosecond fiber laser (24). The OPO spectrum is composed of spectrally narrow comb teeth evenly spaced by $f_{\text{rep}}$ and shifted by an offset frequency, $f_o$. By matching and locking the free spectral range of the enhancement cavity to $2 \times f_{\text{rep}}$, we keep the full comb spectrum resonant with the cavity during the data acquisition. The broadband transmitted light (~65 cm⁻¹ bandwidth, ~700 comb teeth) is spatially dispersed in two dimensions by a virtually imaged phased array etalon and a grating combination and is then imaged onto an InSb camera (fig. S1). Absorption spectra are constructed from these images as a function of time (with a resolution of ±10 μs determined by the camera integration time), which are compared with known molecular line intensities to obtain absolute concentrations. The absorption detection sensitivity is greatly enhanced with our high-finesse ($F = 4100$) optical cavity that employs mid-IR mirrors with low-loss crystalline coatings. These mirrors, with a center wavelength of 3.72 μm and a spectral bandwidth of about 100 nm, have substantially lower optical losses and hence yield enhanced cavity contrast compared with traditional amorphous coatings (as covered in detail in (25)), enabling an improved sensitivity by a factor of 10 for the direct detection of trans-DOCO.

In this experiment, we studied the deuterium analog of Eq. 1, OD + CO $\rightarrow$ D + CO₂, exploiting the sensitivity and resolution of TRFCS to detect the reactant OD (in vibrational level, $v = 0$).
and \( v = 1 \) states) and the product trans-DOCO by absorption spectroscopy in a pulsed-laser-photolysis flow cell experiment. We sought to measure the pressure-dependent effective bimolecular rate coefficients and the yield of trans-DOCO at total pressures of 27 to 75 torr (3.3 to 10 kPa). Such measurements would be especially sensitive to the competition between termolecular DOCO stabilization and the reaction to form \( D + CO_2 \). Detection of the deuterated species allowed us to avoid atmospheric water interference in our spectra. We further anticipated that the yield of stable DOCO would be higher, because deuteration substantially reduces the rate of tunneling to form \( D + CO_2 \) products while increasing the lifetime of DOCO* because of the higher density of states.

The OD + CO reaction was initiated in a slow-flow cell by photolyzing O₃ in a mixture of D₂, CO, and N₂ gases with 266-nm (32-mJ, 10-Hz) pulses from a frequency-quadrupled Nd:YAG laser, expanded to a profile of 44 mm × 7 mm and entering the cell perpendicular to the cavity axis. The initial concentration of O₃, \([O_3]_0\), was fixed at a starting concentration of \( 1 \times 10^{16} \) molecules cm\(^{-3} \) and verified by direct ultraviolet (UV) absorption spectroscopy. The initial concentrations of CO, \( N_2 \), and \( D_2 \) were varied over the range 1 to 47 torr (0.13 to 6.3 kPa), whereas the \( O_3 \) concentration was restricted to 3 to 300 mTorr (\( 4 \times 10^{-4} \) to \( 4 \times 10^{-2} \) kPa) to minimize secondary reactions. A complete description and tabulation of the experimental conditions is included in section 1 of the supplementary materials.

Each photolysis pulse dissociated 15% of the ozone (supplementary materials, section 1) to form \( O_2 + O(1D) \) at nearly unity quantum yield (26). The resulting \( O(1D) \) either reacts with \( D_2 \) to form \( OD + D \) or is quenched by background gases to \( O(3P) \) within 1 µs. \( O(1D) + D_2 \) is known to be highly exothermic and produces vibrationally excited \( OD(\nu = 0 \rightarrow 4) \) with an inverted population peaking at \( \nu = 2 \) and 3 (27). Vibrationally excited OD was rapidly quenched or formed D atoms by collisions with CO (28, 29). Formation of vibrational Feshbach resonances of DOCO* from collisions of OD(\( \nu > 0 \)) with CO may be possible, but the lifetimes are on the order of picoseconds, as previously observed for the HOCO* case (30–33). Therefore, only vibrationally and rotationally thermalized OD(\( \nu = 0 \)) is expected to form DOCO by the mechanism described in the inset of Fig. 1A. OD and DOCO reach a steady state after 100 µs through the cycling reactions depicted in Fig. 1B: D atoms produced from OD + CO → D + CO₂ react with \( O_3 \) to regenerate the depleted OD.

Absorption spectra covering a \( \sim 65 \) cm\(^{-1} \) bandwidth were recorded at a sequence of delays from the time \( t = 0 \) photolysis pulse, using a camera integration time of either 10 or 50 µs, depending on the sensitivity to trans-DOCO signals. The broad bandwidth of the comb covers \( 6 OD, \sim 200 D_2O, \) and \( \sim 150 trans-DOCO \) transitions. These spectra were normalized to a spectrum acquired directly preceding the photolysis pulse and were fitted to determine time-dependent concentrations. With this approach, we captured the time-dependent kinetics of trans-DOCO, OD, and \( D_2O \) from OD + CO within a spectral window of 2660 to 2710 cm\(^{-1} \). Representative snapshots at three different delay times are shown in Fig. 2A. The OD and trans-DOCO data were compared to simulated spectra, generated with PGopher (34) by using measured molecular constants (35–37) and known or computed intensities. The simulated spectra are fitted to these experimental data at each delay time to map out the full time trace of the three observed species (Fig. 2, B and C), with error bars derived directly from the fit residual. Section 2 of the supplementary materials includes details of the data analysis.

We determined the effective bimolecular rate coefficient for the trans-DOCO channel, \( k_{3\alpha}(M, T) \), from simultaneous measurements of time-dependent trans-DOCO and OD. In the low-pressure regime studied here, the DOCO formation rate obeys a termolecular rate law, whereas the effective bimolecular coefficient for the \( D + CO_2 \) channel remains close to the zero-pressure value, \( k_{3\alpha}(M) = 0 \). We measured the dependence of the effective bimolecular rate constant on the concentrations of all of the major species present in the experiment (\( N_2, CO, D_2, \) and \( O_3 \)).

We analyzed the early-time (\( t < 200 \) µs) rise of trans-DOCO to decouple the measurement of \( k_{3\alpha} \) from secondary loss channels at longer...
The expected time dependence of the DOCO concentration is given by
\[
dt [\text{DOCO}] = k_{1a} [\text{CO}] [\text{OD}] (t) - k_{\text{loss}} [X] [\text{DOCO}] (t)
\]

(2)

\(k_{\text{loss}}\) describes a general DOCO decay through a reaction with species \(X\), and \([\text{OD}](t)\) refers to the time-dependent concentration of OD in the ground vibrational state. The solution to Eq. 2 is a convolution of the DOCO loss term with \([\text{OD}](t)\), given by the integral in Eq. 3 (\(u\) is a dummy variable), \([\text{CO}]\) is in large excess and remains constant throughout the reaction.

\[
[\text{DOCO}] (t) = k_{1a} [\text{CO}] \frac{t}{e} e^{-(\lambda_{\text{tot}})(t-u)} [\text{OD}] (u) du
\]

(3)

The effective bimolecular rate coefficient \(k_{1a}\) can be reduced into two terms dependent on \(N_2\) and CO concentrations

\[
k_{1a} = k_{1a}^{(\text{CO})} [\text{CO}] + k_{1a}^{(N_2)} [N_2]
\]

(4)

where \(k_{1a}^{(\text{CO})}\) and \(k_{1a}^{(N_2)}\) are the termolecular rate coefficients with a third-body dependence on CO and \(N_2\), respectively.

By simultaneously fitting \([\text{DOCO}](t)\) and \([\text{OD}](t)\) as a function of \([\text{CO}\] and \([N_2]\), we uniquely determined all of the \(k_{1a}\) termolecular coefficients. Figure 2B shows an early-time segment of our data at 10-μs camera integration for both \([\text{trans-DOCO}](t)\) and \([\text{OD}](t)\). To fit the non-linear time dependence of \([\text{OD}](t)\), we used derived analytical functions composed of the sum of boxcar-averaged exponential rise and fall functions (supplementary materials, section 3). Equation 3 gives the functional form for fitting \([\text{trans-DOCO}](t)\), which includes the integrated \([\text{OD}](t)\) over the fitted time window of ~25 to 160 μs. The fitted parameters are \(k_{1a}\) and a trans-DOCO loss rate, \(r_{\text{loss,exp}} = k_{\text{loss,exp}} [X]\).

For our first set of data, we varied the CO concentration. For each set of conditions, we acquired data at both 10- and 50-μs camera integration times. By plotting \(k_{1a}\) versus \([\text{CO}]) at 10 and 50 μs, we did not observe any systematic dependence on camera integration time. Moreover, we observed a clear linear dependence (with reduced chi-squared, \(\chi^2_{\text{red}} = 0.86\)), indicating a strong termolecular dependence of \(k_{1a}\) on CO, or \(k_{1a}^{(\text{CO})}\) (Fig. 3A). The offset in the linear fit comes from the \(N_2\) termolecular dependence of \(k_{1a}\), or \(k_{1a}^{(N_2)}\). We then varied \(N_2\) concentration and observed a similar linear dependence of \(k_{1a}\) from Eq. 4. A 50-μs camera integration time was used for this second data set because of the lower trans-DOCO signals at higher \(N_2\) concentrations. The results are shown in Fig. 3B. Because the offset terms from the linear fit to the CO data and the linear fit to the \(N_2\) plot both correspond to \(k_{1a}^{(N_2)}\), we performed a multidimensional linear regression to Eq. 4 to determine \(k_{1a}^{(\text{CO})}\), \(k_{1a}^{(N_2)}\), and \(r_{\text{loss,exp}}\) simultaneously. Because \(r_{\text{loss,exp}}\) describes trans-DOCO loss, it is expected to be invariant to \([\text{CO}]\) and \([N_2]\). Therefore, \(r_{\text{loss,exp}}\) serves as a shared, fitted constant in the global fit across the CO and \(N_2\) data sets. From the fits shown in red in Fig. 3, A and B, we obtained \(k_{1a}^{(\text{CO})} = (9.1 ± 3.6) \times 10^{-18} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\), \(k_{1a}^{(N_2)} = (2.0 ± 0.8) \times 10^{-22} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\), and \(r_{\text{loss,exp}} = (4.0 ± 0.4) \times 10^{-13} \text{ s}^{-1}\). The statistical and systematic errors in these parameters are given in table S4.

To verify the kinetic model, we conducted a rate equation model of the OD + CO chemistry, which included the decay channels from secondary chemistry, to fit the trans-DOCO and OD time traces up to 1 ms (supplementary materials, section 4). We fit one overall scaling factor for both OD and trans-DOCO, which accounts for uncertainties in (i) the optical path length and (ii) photolysis yield and subsequent OD* quenching reactions that establish the initial steady-state concentration of OD. We also fit an additional trans-DOCO loss, \(r_{\text{loss,model}}\), to correctly capture the trans-DOCO concentration at \(t > 100\) μs. The trans-DOCO + O₃ → OD + CO₂ + O₂ rate coefficient (9) \(k_{\text{trans-DOCO}} = 4 \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) and the OD + CO termolecular rate coefficients from our experimentally measured values were fixed in the model. Representative fits for two different conditions based on the same rate equation model are shown in Fig. 4, A and B. We found good fits (\(\chi^2_{\text{red}} = 0.71\)) with a single, consistent set of parameters over a wide range of CO, \(N_2\), and O₃ concentrations, giving \(r_{\text{loss,exp}} = (4.7 ± 0.7) \times 10^{-13} \text{ s}^{-1}\) for all conditions (fig. S13A). The sum of loss contributions from \(k_{\text{trans-DOCO}}[\text{O}_3]\) and an additional loss from \(r_{\text{loss,model}}\) gives a total loss of \(~4.5 \times 10^{-13} \text{ s}^{-1}\), consistent with our measured \(r_{\text{loss,exp}}\). One possibility for \(r_{\text{loss,model}}\) is a second product branching channel of trans-DOCO + O₃ to produce DO₂ + CO₃ + O. The slight discrepancy of the trans-DOCO data with the rate equation model in Fig. 4B is possibly due to the inadequately constrained loss processes at long delay times.

Sources of systematic uncertainty have been carefully evaluated. First, we considered the impact of vibrationally hot OD at early times. We constrained the population of vibrationally excited OD in our system by directly observing several hot band transitions from OD(v = 1) (fig. S7). We observed that CO is an efficient quencher of OD vibration, with a measured OD(v = 1) lifetime (fig. S8) that is consistent with the OD(v = 1) + CO quenching rate reported by Bruning et al. (17) and Kohno et al. (29). These measurements reveal that the lifetime is well below the minimum integration time of 10 μs and that [OD(v = 1)] is less than 10% of [OD(v = 0)] in this time window. Given that OD(v = 1) is expected to produce stabilized trans-DOCO less efficiently than OD(v = 0), the systematic effect caused by the vibrationally hot OD is estimated to be <10%, which has been included in our total error budget (table S4).

Another systematic uncertainty arises from the finite camera integration time, which is large relative to (50 μs) or comparable to (10 μs) the early trans-DOCO rise time. The recovered \(k_{1a}\) values from the two integration times are consistent with each other to within 21%, which we have included as a systematic uncertainty in our measurement (fig. S6).

A third source of systematic uncertainty comes from factors that would cause deviations from Eq. 2; therefore, we investigated the dependence of \(k_{1a}\) on \(D_2\) and \(O_3\) concentrations. Additional experiments were conducted in the same manner as the CO and \(N_2\) experiments, but varying \([\text{O}_3]\) (1 × 10¹⁴ to 4 × 10¹⁵ molecules cm⁻³) and \([D_2]\) (7 × 10¹⁶ to 1 × 10¹⁸ molecules cm⁻³). Under our experimental conditions and using a 50-μs camera integration window, we observed a weak dependence of \(k_{1a}\) on \([\text{O}_3]\) and \([D_2]\).
The termolecular (linear) components of the expected to change only slightly in this range. The OD (blue circles) traces are weighted fits to the model (solid and dashed lines for OD and trans-DOCO, respectively) described in the supplementary materials.

The OD (blue circles) and dashed lines for OD fit the model (solid line).

REFERENCES AND NOTES

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