NON-ISOTHERMAL, IN SITU XRD ANALYSIS OF DOLOMITE DECOMPOSITION

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ABSTRACT

In situ X-ray diffraction (XRD) was used to elucidate the thermal decomposition of dolomite. As opposed to previous efforts that required samples be heated to a specific temperature and held for the duration of an X-ray scan, data was collected at $4°C$ intervals while continuously heating the sample at $3°C$ min^{-1}. Under CO_2, dolomite decomposed directly to $CaCO_3$, accompanied by the formation of MgO between 550 and $765°C$. No evidence was offered for the formation of either CaO or $MgCO_3$ during this first stage. Calcite decomposed to CaO between 900 and $960°C$. Under air, simultaneous formation of $CaCO_3$, CaO and MgO accompanied dolomite decomposition between 700 and $740–750°C$. At the latter temperature, the calcite began to decompose even though a significant amount of dolomite was still present. Simultaneous decomposition of the two carbonates terminated at $780°C$. Also, changes in decomposition rates of the various phases correlated with changes in the rate of weight loss determined by derivative thermogravimetric analysis.

INTRODUCTION

As recently summarized by Otsuka [1] in a comprehensive review, considerable controversy still exists with respect to the decomposition mechanism of dolomite in both air and carbon dioxide. Investigators agree that under a sufficiently high CO_2 partial pressure, formation of $CaCO_3$ corresponds to the first stage observed during thermal analysis and that decomposition of this material to CaO constitutes the second stage. While the investigators concur that the equation

$$CaCO_3 \rightarrow CaO + CO_2 \tag{1}$$

represents the second stage reaction, they disagree over the actual reaction(s) responsible for the first stage. Two proposed reactions include direct formation of $CaCO_3$ accompanied by the formation of either MgO or $MgCO_3$. In the latter case, the $MgCO_3$ would further decompose to MgO. Alternatively, the first reaction has been attributed to primary dissociation of dolomite

into oxides followed by recarbonization to $CaCO_3$. With respect to dolomite decomposition under air or low partial pressures of CO_2, the prevailing belief is that dolomite decomposes according to the reaction

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \tag{2}$$
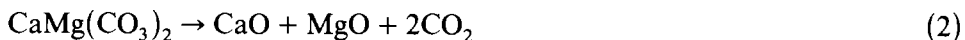
The source of the controversy is that many investigators derive their conclusions solely from conventional thermal analysis techniques, e.g. differential thermal analysis [2] and thermogravimetric analysis [3]. Unfortunately, when used alone, these techniques cannot identify the reaction products that result from each thermal event, and thus cannot fully characterize the reaction. Identification of these products requires analytical techniques such as X-ray diffraction (XRD), infrared and Raman spectroscopy, mass spectrometry and gas chromatography. Of these techniques, XRD is often the most appropriate for characterizing reactions when crystalline materials are involved in the reaction. But even where X-ray diffraction has been used, investigators [4,5] have not been able to agree on the mechanism. A source of the disagreement is that these researchers used a procedure that can prevent the detection of metastable high temperature phases: they heated the samples to progressive stages of thermal treatment, quenched the samples and then transferred the product to the diffractometer.

In contrast to this procedure, we investigated the decomposition of dolomite using in situ, high temperature XRD. This technique allows observation of intermediate, high temperature phases that might otherwise be lost upon cooling. Also, by eliminating the need for multiple samples, in situ analysis allows events to be sampled more frequently. For example, Lange and Roesky [6] and Iyengar et al. [7] used in situ X-ray diffraction to investigate dolomite decomposition at 100 °C and 50 °C intervals, respectively. These studies required that samples be heated to a specific temperature and held for the duration of the X-ray scan.

Recently, we demonstrated that by using a rotating anode X-ray source, data acquisition time could be reduced sufficiently to allow data to be collected while continuously heating a sample [8]. The results reported in this paper were obtained with this technique. We collected data at 4°C intervals while continuously heating the sample.

EXPERIMENTAL

The high temperature X-ray diffraction measurements were made with a Rigaku X-ray system that consisted of a 1400 °C attachment mounted on a horizontal, wide angle goniometer interfaced with a 12 kW rotating anode, X-ray generator. The generator was operated at 50 kV and 200 mA. $Cu K\alpha$

TABLE 1

Temperature calibration of high temperature XRD attachment

	Transition temperatures ($^\circ$C)				
	Potassium nitrate			Potassium sulfate	
	XRD run 1	XRD run 2	ICTA standard [a]	XRD	ICTA standard [a]
Start	121–127	128–130		573–577	
Extrapolated onset			128 ± 5		582 ± 7
Peak			135 ± 6		588 ± 6
Finish	127–131	132–142		585–591	

[a] Ref. 10.

radiation was used for all experiments. Monochromatic radiation was obtained through the use of a curved, graphite crystal monochromator between the sample and the scintillation detector.

Approximately 500 mg of dolomite (Wards; determined by ICP emission spectroscopy to be $Ca_{1.00}(Mg_{0.99}Fe_{0.01})(CO_3)_2$ with 0.4% SiO_2), which had been hand ground in an agate mortar and pestle to pass through a 325 mesh ($< 44~\mu$m) screen, were packed in the platinum holder of the high temperature attachment. After closing the attachment, the sample chamber was either purged with air (700–800 ml min^{-1}) or CO_2 (550–650 ml min^{-1}), with the purge being continued for the duration of the experiment. The sample was heated at a nominal rate of 3°C min^{-1}; however, the rate varied between 1.5 and 4.5°C min^{-1} ($\sigma = 0.8^\circ$C min^{-1}). The sample was scanned at 40° 2θ min^{-1} from 25° 2θ to 45° 2θ with approximately 50 s between each scan. These conditions provided a temperature resolution between scans of 2–6°C with each 30 s scan covering 0.75–2.25°C.

Sample thermocouples for the high temperature XRD stage were calibrated by using potassium nitrate (Baker, analyzed reagent grade) and potassium sulfate (Fisher, certified grade), which undergo solid state crystalline phase transformations at 128 and 583°C, respectively [9]. Table 1 shows excellent agreement between transition temperatures obtained from the high temperature stage and the literature [10]. The start temperature range was defined by the temperature for the scan at which the phase transformation could first be detected and the temperature of the previous scan. Similarly, the finish temperature range was defined by the last scan at which the low temperature phase could be detected and the next scan.

Thermogravimetric (TG) and derivative thermogravimetric (DTG) analysis scans were obtained at 3°C min^{-1} under 50 ml min^{-1} of CO_2 using a Du Pont 951 TGA module, which was interfaced to a Du Pont 1090 data analysis system. Sample size was approximately 95 mg.

RESULTS

Dolomite decomposition under CO$_2$

TG and DTG reveal that thermal decomposition of dolomite in a CO$_2$ atmosphere can be defined by four temperature regions as shown in Fig. 1: region I begins at 550°C and ends at approximately 640°C. This region is characterized by a weight loss rate that increases gradually to 0.03% min^{-1} for a total weight loss in this region of 1%. A large (22%) and rapid (as high as 2.1% min^{-1}) weight loss characterizes region II, which ends abruptly at 750°C. A loss of 1% at a fairly constant, slow rate of 0.02% min^{-1} is the main attribute of region III (750–900°C). Finally, in region IV the weight loss rate increases sharply at 900°C to a maximum of 2.7% min^{-1} at 920°C and then decreases. This region, having a weight loss of 14%, ends at 950°C.

Examination of the X-ray data reveals four corresponding regions. Region I of the XRD data begins around 625°C as evidenced by the formation of peaks due to calcite (CaCO$_3$) and periclase (MgO) in the scan obtained at 657°C (Fig. 2a). Both peaks remain relatively small to 705°C, which appears to be the transition temperature between regions I and II of the X-ray data. There is no change in the intensity of the peaks due to dolomite.

Figure 2b (which displays every third XRD scan from 709 to 773°C) shows that region II is characterized by rapid growth of peaks due to CaCO$_3$ and MgO and rapid shrinkage of peaks due to dolomite. The XRD scan at
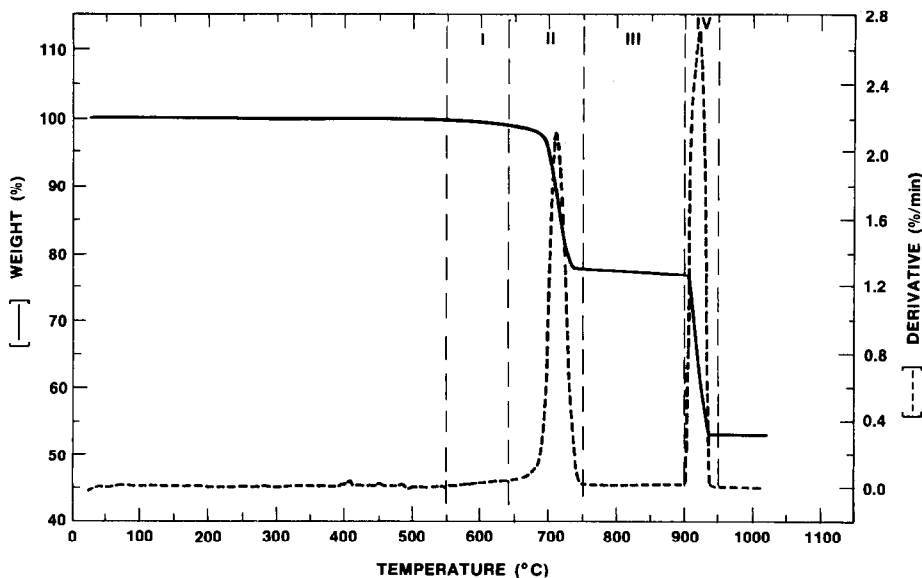

Fig. 1. TG and DTG analysis of dolomite heated at 3°C min^{-1} under CO$_2$.

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TABLE 2

Thermal decomposition of dolomite CO_2 atmosphere

Region	TG				XRD			
	Temperature range (°C)	Weight loss (%)	Rate of weight loss (% min^{-1})	Temperature range (°C)	Dolomite	Calcite	MgO	CaO
I	550–640	1	0 → 0.03	625–705	No activity	Appears at 625°C, little growth	Appears at 650°C little growth	–
II	640–750	22	As high as 2.1	705–765	Decreases rapidly	Increases rapidly	Increases rapidly	–
III	750–900	1	0.02	765–910	Small amount persists to 900°C and disappears	No activity	Slight increase	–
IV	900–950	14	As high as 2.7	910–960	–	Decreases rapidly and disappears	Slight increase	Appears at 915°C and increases rapidly

773°C in Fig. 2c (which displays region III scans between 773 and 906°C) reveals that even after the rapid weight loss that describes region II, some dolomite still remains. As shown in Fig. 2c, a small dolomite peak persists to approximately 900°C. Although the calcite peaks remain constant in region III, a small growth in MgO occurs between 870 and 890°C.

Finally, the rapid decrease of peaks due to $CaCO_3$, beginning at 910°C, and rapid increase of peaks due to CaO, beginning at 915°C, occur in region IV (Fig. 2d). The MgO peak also continues to grow slightly at these temperatures. This reaction appears to be complete by 960°C.

Table 2 summarizes the corresponding behavior measured by XRD and thermal analysis. The discrepancy in temperature measured by the two techniques can be attributed to two reasons: first, the thermocouple control
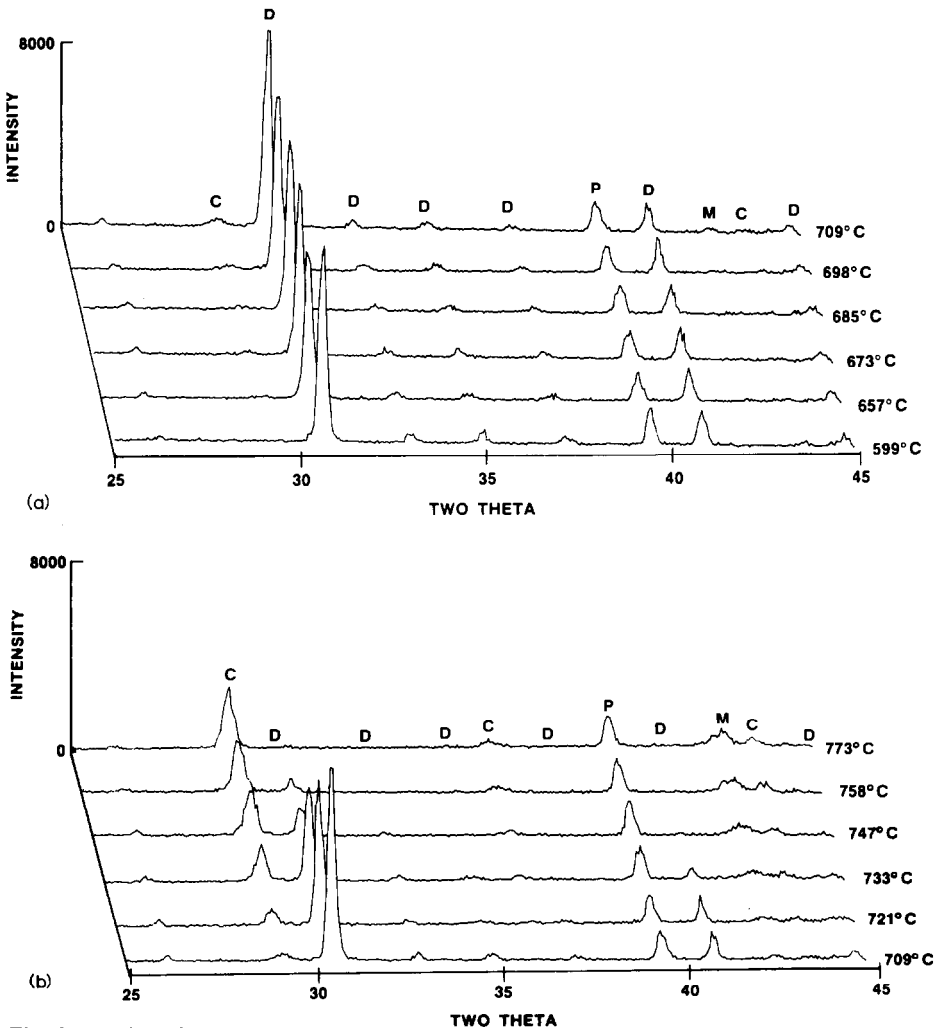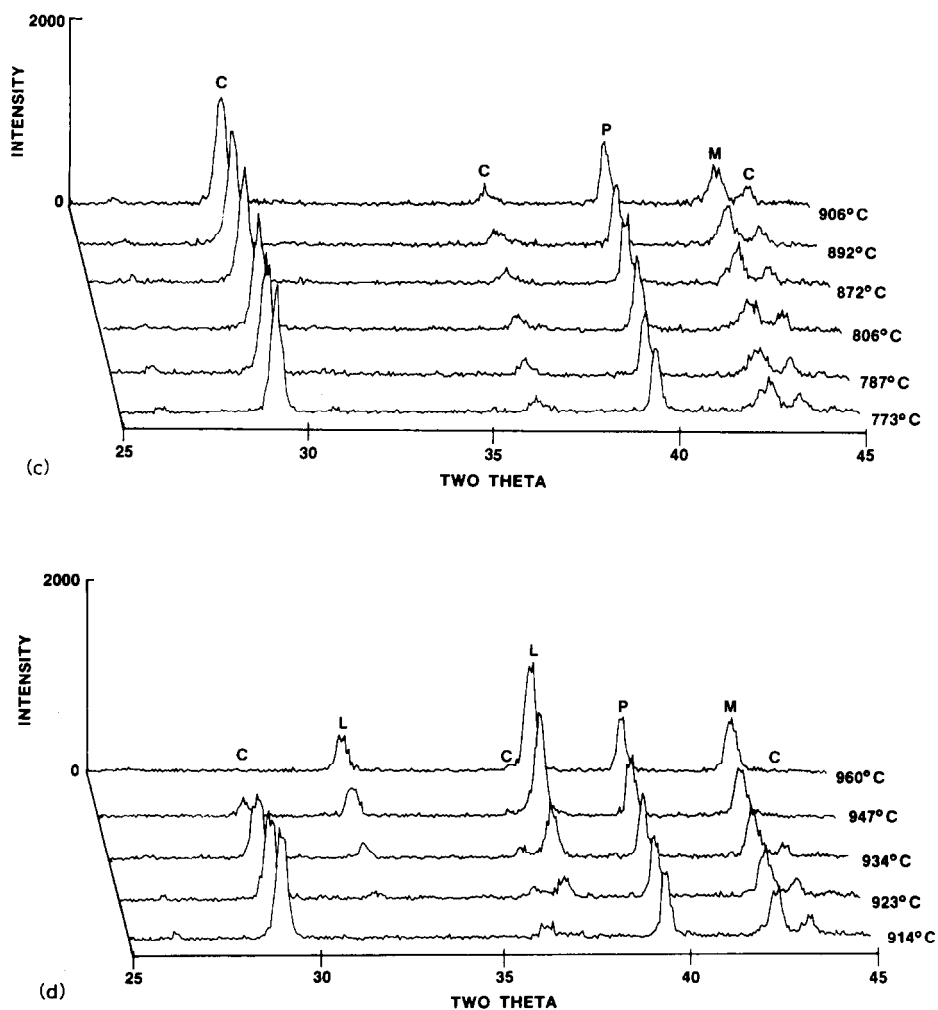

(a)

(b)

Fig. 2 (continued).

Fig. 2. XRD patterns of dolomite heated in situ at $3°C$ min^{-1} under CO_2. Patterns were obtained at $40°$ 2θ min^{-1} with $CuK\alpha$ radiation. $C = CaCO_3$, $D = dolomite$, $M = MgO$, $L = CaO$, $P = platinum$ (from sample holder). (a) $600–710°C$, (b) $710–775°C$, (c) $775–905°C$, (d) $915–960°C$.

of the X-ray high temperature stage is not nearly as accurate as for the thermal analyzer; second, thermal analysis is inherently more sensitive to phase transformations than X-ray diffraction, which requires crystallites sufficiently large to produce detectable diffraction peaks.

Dolomite decomposition under air

Only one peak appears in the DTG curve for dolomite decomposing in air (Fig. 3). This peak can be divided into two regions: a region having a very
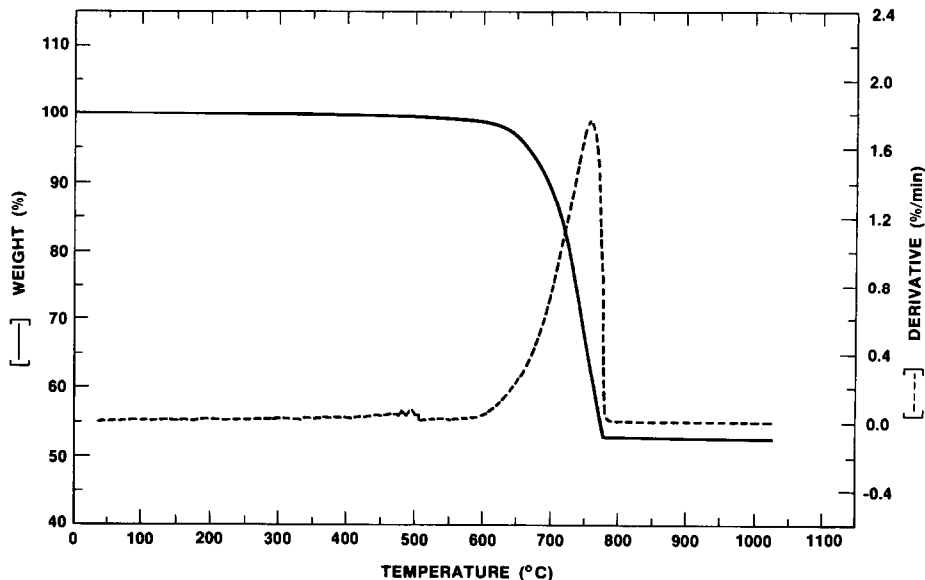
Fig. 3. TG and DTG analysis of dolomite heated at 3°C min⁻¹ under air.

slow and small (1%) weight loss beginning at approximately 500°C and a region of very rapid rate loss beginning at 590°C and ending at 785°C. The loss rate in this higher temperature region peaks at 1.77% min⁻¹ at 760°C and the total weight loss in this region is 46%.

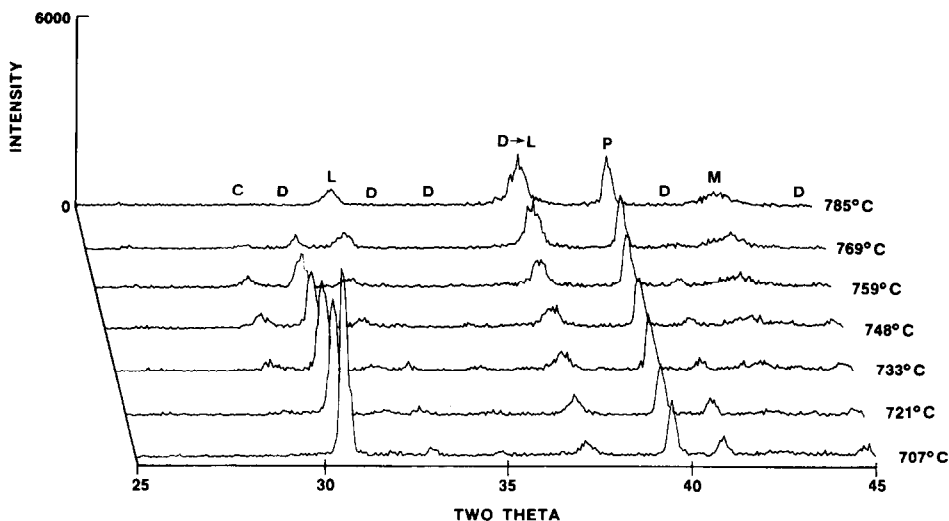Fig. 4. XRD patterns of dolomite heated in situ at 3°C min⁻¹ under air. Patterns were obtained at 40° 2θ min⁻¹ with Cu Kα radiation. C = CaCO₃, D = dolomite, M = MgO, L = CaO, P = platinum (from sample holder).

Figure 4 shows every third X-ray scan between 707 and 785°C. Calcite, CaO and MgO are all first detected between 700 and 705°C, while dolomite begins to disappear at this temperature. Both $CaCO_3$ and CaO grow at similar rates to 740–750°C. Above this temperature, $CaCO_3$ decreases and disappears at 780°C, while CaO increases at a more rapid rate with peak area also reaching a maximum at 780°C. At the same time, dolomite continually decreases from 705°C and disappears at 780°C. Finally, the 2.12 Å MgO and 2.79 Å CaO peaks formed in air were broader than those formed in a CO_2 atmosphere. This indicates that CaO and MgO crystallites do not form as well in air as they do in CO_2.

CONCLUSIONS

Under CO_2, dolomite decomposes directly to $CaCO_3$ accompanied by the formation of MgO between 550 and 765°C. No evidence was offered for the formation of either CaO or $MgCO_3$. This supports the reaction

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \qquad (3)$$
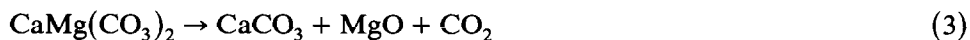
as being responsible for the first stage of dolomite decomposition under a CO_2 atmosphere. Furthermore, the growth of the peak at 29.2° 2θ rather than a gradual shifting of the dolomite peak from 30.6° 2θ suggests the formation of discrete $CaCO_3$ rather than a gradual change in the composition of the solid solution toward the end member. The phases formed by the first reaction are stable to 900–910°C where the second step of the reaction begins. This step, expressed by eqn. (1), is complete by 950–960°C.

Dolomite decomposition becomes a one-step process in an air environment. In situ XRD showed that formation of both $CaCO_3$ and CaO, as well as MgO, accompanies dolomite decomposition between 700°C and 740–750°C as follows

$$2CaMg(CO_3)_2 \rightarrow CaCO_3 + CaO + 2MgO + 3CO_2 \qquad (4)$$

At the latter temperature, the $CaCO_3$ begins to decompose even though dolomite is still present. Thus, two reactions appear to occur simultaneously as follows

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \qquad (5a)$$

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (5b)$$

These reactions end simultaneously at 780–785°C. A comparison of X-ray peak breadths at the completion of the reactions revealed that the MgO formed in the air environment is not as well formed as the MgO formed in the CO_2 environment.

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