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ABSTRACT

Robust marine carbon sensors with small size, low power consumption, and high sensitivity provide greater insight into the carbon cycle studies and resolve environmental variability. We report here the development of a diminutively integrated tunable diode laser absorption spectroscopy (TDLAS) system with a specially designed multipass gas cell for small amounts of dissolved gas extractions and measurements. It was used to detect and monitor carbon dioxide (CO₂) dissolved in water and seawater. Systematic experiments have been carried out for system evaluation in the lab. Extracted CO₂ was determined via its 4989.9 cm⁻¹ optical absorption line. The achieved TDLAS measurement precision was 4.18 ppm for CO₂, measured by averaging up to 88 s. The integrated absorbance was found to be linear to gas concentrations over a wide range. Comparison measurements of the atmospheric CO₂ values with a commercial instrument confirmed a good accuracy of our TDLAS-based system. The first test campaign was also accomplished with a hollow fiber membrane contactor, and concentrations of CO₂ were quantitatively detected with partial degasification operations. The results clearly show the ability to continuously measure dissolved gases and highlight the potential of the system to help us better understand physical and geochemical processes in a marine environment.

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I. INTRODUCTION

In the coastal ecosystem, elemental fluxes to or from other ecosystems are controlled by intricate biogeographical drivers. In such heterogeneous environments, rapid carbon cycling involves carbon burial as the mineralization of organic matter to carbon dioxide (CO_2) and aquatic carbon turnover, such as being lost to the atmosphere and dissolved as inorganic forms. Recent studies highlight the transfer of CO_2 from land to ocean and supersaturated CO_2 concentrations in oxygenated marine surface waters. The studies suggest that marrying large-scale geophysical studies with site-scale biogeochemical and microbial studies will be key to this. $^{\rm 1-3}$

Numerous cases indirectly calculated CO_2 in the seawater by measuring pH, total alkalinity, etc., of the carbonate system.^{4–9} Because of the potential uncertainties associated with indirect estimations, the method used for direct quantification of collecting discrete isobaric (pressure-retaining) water samples (i.e., headspace technique and equilibrator technique) is preferable for the aqueous system.¹⁰ However, discrete sampling generally suffers outgassing due to depressurization and temperature change during recovery. Therefore, there is a need for reliable systems that are capable of

Brand	Measurement method	Maximum range	Accuracy	Response time	Dimension/ weight
Vaisala CARBOCAP, (GMP252)	Membrane, NDIR	0%-1%	±40 ppm-±2%	$\tau_{90}^{b} < 3 \min$	ϕ 25 × 130 mm 58 g
Sunburst, (SAMI-CO ₂)	Membrane, colorimetric reagent	150–700 μatm	$\pm 3 \mu \text{atm}$	5 min	ϕ 152 × 550 mm 7.6 kg
PMEL/Batelle, (MAPCO ₂)	Equilibrator/air block, NDIR	100–600 ppm (surface only)	5 ppm	30 min (pumped)	~80 kg
Contros, (Hydro-C/CO ₂)	Membrane, NDIR	200–1000 µatm	5 μ atm at surface	6 min–15 min	ϕ 90 × 530 mm 5.5 kg
Pro-Oceanus, (CO ₂ -Pro)	Membrane, NDIR	0–2000 ppm	±0.5%	τ ₆₃ =2.5 min (20 °C, pumped)	ϕ 190 × 330 mm 5.5 kg
Picarro, (G2401)	Membrane, CRDS	300–500 ppm (surface only)	0.5 ppm	5 min (pumped)	430 × 178 × 448 mm 27 kg

TABLE I. Brands and some parameters of several commercially available dissolved CO₂ instruments.^a

^aThese data are from their manufacturer's website.

 ${}^{b}\tau_{90}$ is the time for a 90% response and so forth.

sensitive real-time *in situ* measurements and analysis in remote deep-sea environments.

Efforts to provide oceanic biogeochemical sensors and the in situ dissolved CO₂ analytical instruments in the inland aquatic, estuary, and coastal ecosystem have been reported by several research groups.¹¹⁻¹⁵ Recently, a few studies presented the temporal and spatial resolution of mechanisms controlling dissolved CO₂ distribution in the aquatic systems.^{12,16-19} One direct optical sensing technique is the well-known infrared spectroscopic approach, routinely used for atmospheric measurements and monitoring. The methods include nondispersive infrared (NDIR)^{20,21} or laser absorption spectroscopy techniques, such as tunable diode laser absorption spectroscopy (TDLAS),²² cavity ring-down spectroscopy (CRDS),^{14,17,18,23} and off-axis integrated cavity output spectroscopy (ICOS).²⁴ Most of them are coupled with a water/gas equilibration, optionally employing a membrane to extract dissolved sample gases through the inlet as these techniques are merely ideal for measurements in the gas phase. Others like Raman spectroscopy²⁵⁻²⁷ and laser calorimetry spectroscopy²⁸ detect gases dissolved in liquids. However, Raman- and calorimetry-based instruments are deemed insufficient due to their lower accuracy and need to frequently recalibrate with reference gas samples. The classification of some commercially available dissolved CO2 sensors according to the brand and sensor type is listed in Table I.

Dissolved gas measurement based on TDLAS has many advantages, such as simple structure, fast response, high accuracy, and nonintrusiveness; also, they can be calibration-free and easily miniaturized.²⁹ As the infrared signatures of many gases are within the operation wavelength ranges of TDLs, TDLAS is highly suitable for real-time measurements and engineering applications in various environments.

The objective of this project was to develop an *in situ* system, which was compact in size and consumed less power, for spectroscopic measurements of CO₂ (at 2.0040 μ m or 4989.9 cm⁻¹) dissolved in water or seawater by using the TDLAS technique and

fast dissolved gas extraction. A series of experiments were conducted to evaluate the feasibility of detecting dissolved gas in seawater. Details of this sensor system and the experimental results will be described in this paper.

II. MATERIALS AND METHODS

A. Field gas extraction device and compact system design

The field gas extraction work has been developed to expose the sampled seawater to a pressure below the gas solubility equilibrium pressure by using a hollow-fiber membrane contactor (Liqui-Cel



FIG. 1. The assembled compact module based on TDLAS for the monitoring of dissolved CO₂. It includes an internal multipass gas cell with an optical path length of 2.86 m. This total system (including a module for dissolved gas extraction, not shown here) is portable (5 kg weight), with a power consumption of <5 W.



FIG. 2. Fiber-coupled diode laser and control electronics developed for the compact laser-based spectroscopic real-time trace-gas sensing system.

EXF-2.5 × 8 with a recommended flow rate of 1.9–11.3 l/min, 3M Industrial Group, USA). Due to its large surface area of 1.4 m², large surface to volume ratio, and membrane porosity (50%), the Liqui-Cel membrane expedites the gas transfer and achieves equilibration efficiently. The CO₂ gas that was permitted through the hollow-fiber membrane was gathered in a gas cell with a volume of 0.4 l for TDLAS measurements. This module and some other system components will be shown later in Fig. 9.

The mechanic design of the newly developed compact TDLAS sensor head for monitoring of dissolved CO_2 is shown in Fig. 1. It comprises a compact multipass Herriott cell, a reference gas cell, two laser sources, and optical and electronic modules/components. The multipass cell was enclosed within an aluminum cylinder. The overall dimensions of the sensor head were $\phi 80 \times 430$ mm. The system can operate both with equilibrators for measuring surface seawater and a flat plate membrane setup on "pressure housing" for deep sea purpose. Figure 2 shows the electronic module of laser sources and data acquisition and analyzing.

The schematic of the TDLAS subsystem for the spectroscopic data acquisition of dissolved CO₂ concentration is presented in Fig. 3. One DFB (distributed-feedback) InGaAsP diode laser (Nanoplus Laser, Germany) emitting single-mode radiation around 4989.9 cm⁻¹ was employed in this study. For a further extension of other dissolved gases measurements (i.e., CH₄, H₂S), a second DFB laser diode was also implemented in the setup for time-division operation between multiple laser sources. Their output beams were combined to a hybrid light beam and then split into two beam paths. The main beam (80%) was coupled through a home-made compact Herriott multipass gas cell formed by two concave mirrors (diameter: 20 mm, curvature of radius: 2030 mm). The incident beam spot alignment was optimized with the help of three length-adjustable screws mounted on the back of each of the two mirrors. The exit beam was focused onto detector 2 for spectroscopy absorption measurements. The multipass cell offers 11 optical passes and yielded an effective optical path length of 2.86 m for a physical cell length of 26 cm. The other part (20%) was directed through a reference gas cell (CO2 10% and N2 90%) for laser wavelength locking. The reference cell together with collimator 1 and detector 1 was enclosed in a small volume of 0.1 l.

A time-division sawtooth signal generator was based on a Field Programmable Gate Array (FPGA) with an integrated dual-channel 14-bit DAC (DAC5672, Texas Instruments), which swept the laser currents at a repetition rate of 200 Hz. The waveform consisted of three parts: a below-laser-threshold level for detecting the detector's output offset at no light, a linear ramp for providing a laser frequency sweep of ~1.8 cm⁻¹ for CO₂ absorption detection, and then back to a below-laser-threshold level, allowing the system to start the next scan cycle. The laser output temporal profiles were highly stable.

The dependence of laser wavelength/frequency changes upon any preset laser current sweep configuration was precharacterized by using a 5-cm Fabry–Pérot etalon. We improved the wavelength stability by actively locking the laser wavelength scan with the help of a reference gas cell. The single-pass reference gas cell was of a length of 100 mm and filled with an appropriate concentration of CO_2 in



FIG. 3. Simplified block diagram of major system components for *in situ* monitoring of dissolved CO₂, which consists of a sample gas cell and a reference cell for detecting laser wavelength drift. A Fabry–Pérot etalon (not shown) was used for precharacterizations of laser wavelength/frequency changes upon any preset laser current sweep configurations. N_2 at a total pressure of 1 atm for providing an absolute laser wavelength reference. We devised closed-loop feedback electronics to monitor the reference absorption feature position during the 200-Hz laser wavelength scan process and then compensate the laser dc current to keep the laser wavelength drift within a range of 1 pm.

The analog photodetector's signals were amplified and had a high signal-to-noise ratio (SNR). We employed a low-noise, 18-bit, wide dynamic analog-to-digital converter (ADC) (ADC7982, Analog Devices) to accurately transmit the photodetector signal to a Microprogrammed Control Unit (MCU) for subsequent spectral data analysis, with results saved onto an SD memory card. The hardware synchronization was applied between DAC wavelength scanning and ADC signal sampling at a sample rate of 1 MHz. The minimum voltage values that can be reliably differentiated by the ADC reached a 16-bits noise-free resolution (NFR), with the background signal noise of 40 μ V. With the accuracy given above, the minimum detectable absorption was of 10^{-4} optical density (OD). In addition, MCU handled the data streaming over an Inter-Integrated Circuit (I²C) connection from an MS8607 digital PTH sensor, which measured absolute pressure (accuracy of ± 2 mbar, full-scale 2 bars), temperature (resolution of 0.01 $^{\circ}$ C), and humidity (accuracy of ±3% RH) of the absorption cell. This highly integrated system is advantageous for the long-term monitoring in a marine environment due to its low power consumption, high reliability, and onboard storage of measurement data.

B. Dissolved CO₂ spectrum data acquisition

Optical gas detection using absorption spectroscopy relies on the Beer-Lambert law. The spectral absorbance α_{ν} can be expressed as

$$\alpha_{\nu} = -\ln(I/I_0)_{\nu} = k_{\nu}L = Px_{abs}S_i(T)\Phi_i(\nu, T)L,$$
(1)

where k_{ν} (cm⁻¹) is the spectral absorption coefficient, P is the total pressure, x_{abs} is the gas concentration, and $S_i(T)$ (cm⁻² · atm⁻¹) and $\Phi_i(\nu, T)$ (cm) are the line-strength from database HITRAN³⁰ of the transition i and normalized line-shape function, respectively. The integrated absorbance (cm⁻¹) can be inferred from Eq. (1) as

$$A_i = \int_{-\infty}^{\infty} \alpha_{\nu} d\nu = P x_{abs} S_i(T) L, \qquad (2)$$

whereby the concentration x_{abs} of the gas molecules could be determined once the gas temperature, pressure, and optical path length are known.

As carbon dioxide (CO₂) abundance in an aquatic environment is commonly measured as a partial pressure (p_{CO_2}) in microatmospheres (μ atm), a determination of dissolved CO₂ can be achieved by accounting for local pressure and humidity with the dry-air mixing ratio conversions,³¹

$$p_{\rm CO_2} = x_{\rm CO_2} (P_{eq} - p_{\rm [H_2O]}), \tag{3}$$



FIG. 4. Flow chart of the measurement and analysis processes on the embedded platform.

where P_{eq} is the pressure at the equilibrators or membrane contactors in atmosphere; $p_{[H_2O]}$ is the vapor pressure of water at the salinity S and temperature of equilibration, described by Weiss and Price,³²

$$p_{[\rm H_2O]} = \exp(24.4543 - 67.4509 \frac{100}{T} - 4.8489 \ln \frac{T}{100} - 0.000544S). \tag{4}$$

The amount of CO_2 gas dissolved in water, $[CO_{2,aq}]$, is proportional to the pressure of the gas in contact with the water as stated by Henry's law,

$$p_{\rm CO_2} = K_{\rm H} [{\rm CO}_{2,aq}]. \tag{5}$$

Here, K_H (μ atm · kg · μ mol⁻¹) is represented as the thermodynamic solubility constant for the actual water temperature and salinity. It is available at http://www.henrys-law.org. For this study, Henry's solubility coefficient at 298.15 K was 3.4 ×10⁻⁴ for CO₂ as given by Sander.³³

The inverse algorithm of the dissolved CO₂ measurement system was completed with the embedded platform on the control circuit board. A flow chart of the process is presented in Fig. 4. The absorption feature of CO_2 near 4989.9 cm^{-1} and three nearby weak spectral lines of water vapor absorption were modeled to a Voigt profiles by a Levenberg-Marquardt least-square fitting method.³⁴ The modified Hui's rational approximations from Schreier³⁵ were used for a Voigt profile. The center frequency, the Lorentzian FWHM, and the normalized integral area were fitted as parameters, while the Gaussian FWHM was kept fixed and calculated as a function of temperature and molecular parameters. Obviously, the stability of the laser emission frequency and frequency/wavelength scan characteristics became essential so that the corresponding reference signal was acquired to calculate the parameters of absorbance at known concentrations during which the analog switch circuit was enabled. Figure 5 shows an



FIG. 5. Comparison between a model profile (blue line) and an air measurement absorption spectrum (red line) of the CO_2 in air inside a multipath gas cell (T = 296 K, 1 atm, path length = 2.86 m). (a) The model profile is calculated as a Voigt profile. (b) Difference between the experimental spectrum and its simulation.

example of such modeling, with the maximum absorbance deviation of 1.10×10^{-4} between the measurement spectrum and the model. Weak residual existed, corresponding to the standard deviation (1σ) of 2.32×10^{-5} . Such small deviations existed commonly in multipath cell applications due to the scattering of multiple beams.

In the end, the dissolved CO_2 gas concentrations in water were calculated by Eqs. (2)–(5) and were then stored on an SD card, along with the related environmental parameters (i.e., T, P, S). In addition, portions of the original spectrum data, including the signals coming from the two detectors and of the fitting results, were saved in scheduled time intervals to another time-stamped file for later verification/diagnosis of the system operation.

III. EXPERIMENTS AND RESULTS

The efficiency of dissolved gas extractions depends on properties of the membrane, gas solubility, and operating conditions such as the flow rate of liquid or gas and the amount of fouling on permeable surface.^{19,36,37} To assess measurement accuracy and quantify the efficiency, the hollow-fiber Liqui-Cel gas separation system was compared against an independent system that had a showerhead equilibrator coupled to the same seawater supply. During the laboratory equilibration tests, we observed that extraction efficiency was about 25%–50% higher at lower-flow rates. At a liquid flow rate of 3 l/min, the equilibration time was less than 90 s, which was more than two times faster than the previously published method from Webb *et al.*,¹⁸ and this response time was short enough to suit field measurement uses. The results reported below were all carried out at a fix liquid flow rate of 3 l/min.

A. Calibration experiments

The TDLAS system employed in this study measures absolute absorbance, which is related to the gas concentration and the linestrength of the gas absorption transitions as indicated by Eq. (1). To ensure the repeatability and accuracy of this compact TDLASbased dissolved gas analyzer, a series of laboratory tests were performed. The multipass cell was refilled with the standard samples of CO₂ of various concentrations in N₂ carrier gas. The reference gas samples had a relative concentration uncertainty of 2% and were supplied by Guangming Research and Design Institute of Chemical Industry. Each of the gas samples of different CO₂ concentrations flowed successively through the gas cell, and the absorption spectra were recorded and analyzed for 15-20 min. Pure N2 gas was used to flush the gas cell for creating an absorption-free condition. The experiments were done at room temperature and 1 atm pressure. Results of these calibration measurements of CO2 are plotted in Fig. 6.

The spectral measurements of the integrated absorbance of CO_2 at various reference concentrations in N_2 are displayed in Fig. 6(a). The average integrated absorbance values and corresponding uncertainties at different concentrations of these measurements are also presented in Fig. 6(b). The inset of zoom-expanded data points was the last measurement after the CO_2 concentration was changed from a 1.4% high concentration to a much lower concentration of 698 ppm. The dependence of the measured integrated absorbance on reference gas concentrations follows



FIG. 6. (a) Calibration measurements of the integrated absorbance of the 4989.9 cm⁻¹ absorption feature of CO₂ at various reference concentrations in N₂ and (b) straight-line fit of the measured integrated absorbance as a function of the reference concentrations, where the inset shows a zoom-expanded measurement data point at low concentration.

a linear dependence as confirmed by a straight line fit to the measurement data ($R^2 = 0.9995$). The slope of integrated absorbance was 1.451×10^{-5} cm⁻¹ per 1 ppm CO₂. The uncertainty in the determined slope values was about 2%, which was similar to the nominal 2% concentration uncertainty of the reference gas samples used. Therefore, we conclude that the TDLAS spectral detection implemented in this study provides reliable measurements for detecting CO₂ within wide concentration ranges.

B. Minimum detection limit

The minimum detection limit of the developed compact system, with a miniature multipass gas cell, was evaluated by using low concentration reference gases (CO₂ 76 ppm). The reference gas filled the multipass cell at 1 atm in the experiment. Concentration measurement results of 2000 s were recorded at a rate of 0.5 Hz. During this measurement period, the root means square (rms) noise of the measured CO₂ concentration was 15 ppm. The uncertainty of the mean value of concentration measurements can be reduced by data averaging over a considerable time before the background drift became significant. We used the Allan variance, plotted in Fig. 7, to seek the optimum averaging time and the corresponding minimum detection limit for the system. It shows that a minimum Allan deviation of 4.18 ppm for CO₂ was achieved at an averaging time of 88 s. The drifts of wavelength, temperature, and pressure remained less significant within this time scale. The detection limit is below the respective concentration (~400 ppm CO₂) in the atmosphere and significantly lower than the minimum concentrations previously reported in hydrothermal fluids.





C. Atmospheric CO_2 observations and comparison with the data of Picarro-G2301

The Picarro-G2301 gas concentration analyzer has been reported as a CRDS-based tool for multispecies (CO₂, CH₄, H₂O) measurements in the atmosphere. It has high resolution and ultrahigh measurement precision. Thus, a comparison was completed to assess the stability and performance of our TDLAS-based measurements in the same place. As there is an offset between systems, a correction was applied to the atmospheric CO₂ values after the calibration test (which used different standard reference gases from approximately 100 to 1000 ppm). The observed CO₂ concentrations over nearly 24 h, from 10:13 am to 09:55 am the next day, are compared in Fig. 8(a).

A good concordance was found between the recorded CO₂ concentrations by our compact TDLAS system and the commercial Picarro apparatus. Both sets of data were well aligned with the same trend of CO₂ concentration variations, with changes up to 40 ppm over the course of a day. The slope value 1.005 ± 0.003 of the near-linear relationship between the measured CO2 concentration values by the two instruments provides strong evidence of tight correlation, as shown in Fig. 8(b). However, there were some deviations that occurred when environmental CO₂ concentrations rapidly increased or decreased. The reasons for the minor difference between data sets were considered to be due to the different response times and some nonuniformity in the gas transfer/diffusion process of the two instruments. The well-established commercial CRDS instrument is designed for monitoring applications at atmospheric conditions, and its resolution, precision, and performance are superior to that of our developed compact TDLAS system. The CRDS yields a lower noise level due to a much enhanced interaction length with gas molecules inside a high-finesse optical cavity, and active temperature and pressure stabilizations. However, the TDLAS has its advantages of low price, high concentration measurement range, and compact size. It also meets the requirements for application of dissolved CO₂ concentration measurements, as previously discussed.

D. Field testing

The compact TDLAS-based system was preliminarily validated in continuous monitoring experiments at a facility of the Institute of





Deep-Sea Science and Engineering in Luhuitou peninsula, located in the southeast of Sanya City, China. Field testing was done by coupling the TDLAS gas sensing system to a dissolved gas extraction system developed by using hollow fiber membranes (Liqui-Cel EXF- 2.5×8). Seawater at 1 m depth below the sea surface was continuously pumped first through a 5- μ m filter and subsequently through the lumen-side of the membrane contactor unit at a stable flow rate of 3 l/min. This was measured by a flow meter and actively controlled by a liquid pump. The gas stream exited the membrane through the shell-side and was dried before entering the system for TDLAS gas analysis, shown in Fig. 9.

A 3-way electromagnetic valve was configured either to exhaust the sample gas container down to the lowest possible pressure (100 mbar) or to form a closed loop for gas circulation with a



FIG. 9. Schematic of our TDLAS-based dissolved gas measurement system. Extraction of dissolved gases was based on hollow-fiber membranes. The bottom section of the figure indicates the path of gas flow for each of the two settings of a 3-way switch value.

small diaphragm pump (KNF UN814KTDC). Flow rate, temperature, and pressure of inlet water were recorded and manipulated to investigate their influence on measurements of dissolved gases. When the pressure of the extracted gases reaches a stable partial equilibrium, the developed TDLAS measuring system detects the infrared spectra of the dissolved CO_2 gas and determine its concentration. In the case of real field measurements, the gas pressure inside the TDLAS sampling cell was increased and kept constant by a flow controller at its exit port. An example of 7-h continuous monitoring results on 3 August 2017 (summer) is shown in Fig. 10.

The partial pressure of CO₂ at surface seawater varied considerably, ranging from 520 to 934 ppm. It was relatively higher than the CO₂ in the atmosphere (~429 ppm). However, the diurnal atmospheric CO₂ concentration change in the same area was relatively small (~30 ppm). In comparison with that of the nearby Luhuitou fringing reef (~579 ppm) previously reported by Yan *et al.*³⁹ in 2011, the mean of seawater dissolved CO₂ collected at our study site (~689 ppm) was higher, which is possibly related to the global environmental changes and human activities. Moreover, the time series dissolved CO₂ concentration fluctuated on an 1 h time scale. This is something not yet observed by previous work due to the limited temporal resolution. Sea surface temperature (SST) variations and hydrodynamic processes might have contributed to these variations. For lack of long term measurement results, diurnal dissolved CO₂



FIG. 10. Experimental results of CO₂ concentration dissolved in seawater as determined by our TDLAS-based system in a continuous 7-h measurement.

variations did not appear to be figured out, but the trend (reaching its maximum at 07:00–08:00) was still observed. The above data indicate that the CO_2 level in this ecosystem was supersaturated with respect to the atmospheric levels in summer. It is consistent with speculation that the gross photosynthesis in the summer was inhibited by high temperatures, and the higher river inflows promoted the respiration.⁴⁰

IV. CONCLUSION AND PERSPECTIVES

A compact dissolved CO2 gas detection system was experimentally demonstrated. It utilized an optical TDLAS technique, employed a compact multipass gas cell of 2.86 m path-length, DFB laser diodes (around central frequencies of 4989.9 cm⁻¹ for CO₂ detection), and InGaAs photodiodes. The electrical components included laser temperature and current controllers, sensitive light detection and high-resolution data acquisition, and reliable spectral processing. By applying wavelength locking to a reference gas cell, good wavelength stability within 1 pm was achieved for long-term monitoring applications. The Allan deviation analysis indicated a minimum detectable concentration of 4.18 ppm for CO2 at an average time of 88 s. The system was designed specifically for compact, low cost, and low power (less than 5 W) operations, while maintaining performance comparable to stand-alone table-size laboratory commercial instruments. The successful preliminary demonstration of the system reported here is a step toward real-time online monitoring of dissolved CO₂ concentration in marine environments for future applications.

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