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Probing the Evolutionary History of Comets: An Investigation of the Hypervolatiles CO, CH_4, and C_2H_6 in the Jupiter-family Comet 21P/Giacobini–Zinner

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Abstract

Understanding the cosmogonic record encoded in the parent volatiles stored in cometary nuclei requires investigating whether evolution (thermal or otherwise) has modified the composition of short-period comets during successive perihelion passages. As the most volatile molecules systematically observed in comets, the abundances of CO, CH_4, and C_2H_6 in short-period comets may serve to elucidate the interplay between natal conditions and post-formative evolution in setting present-day composition, yet secure measurements of CO and CH_4 in Jupiter-family comets (JFCs) are especially sparse. The highly favorable 2018 apparition of JFC 21P/Giacobini–Zinner enabled a sensitive search for these "hypervolatiles" in a prototypical carbon-chain depleted comet. We observed 21P/Giacobini–Zinner with the iSHELL spectrograph at the NASA Infrared Telescope Facility on four pre-perihelion dates, two dates near-perihelion, and one post-perihelion date. We obtained detections of CO, CH_4, and C_2H_6 simultaneously with H_2O on multiple dates. We present rotational temperatures, production rates, and mixing ratios. Combined with previous work, our results may indicate that the hypervolatile coma composition of 21P/Giacobini–Zinner was variable across apparitions as well as within a particular perihelion passage, yet the spread in these measurements is a relatively small fraction of the variation in each molecule from comet to comet. We discuss the implications of our measured hypervolatile content of 21P/Giacobini–Zinner for the evolution of JFCs, and place our results in the context of findings from the *Rosetta* mission and ground-based studies of comets.

Unified Astronomy Thesaurus concepts: Molecular spectroscopy (2095); High resolution spectroscopy (2096); Near infrared astronomy (1093)

1. Introduction

Comets are among the most primitive remnants of the solar system's formation. They accreted in the early stages of the protosolar nebula and have been stored for the last ~4.5 Gyr in the cold outer solar system in the scattered Kuiper disk or in the Oort cloud dynamical reservoirs. Because comets lack a known mechanism for efficient internal self-heating owing to their small sizes, the present-day volatile composition of their nuclei likely reflects to a large degree the composition and conditions where (and when) they formed. Thus, measuring the volatile composition of comets offers an opportunity to place observational constraints on the history of the early solar system by measuring the abundances of trace species in their nuclei (Bockelée-Morvan et al. 2004; Mumma & Charnley 2011).

The volatile inventory of comets can be inferred by studying their coma composition during passages into the inner solar system (heliocentric distance $R_h \leqslant 3$ au). Such studies at multiple wavelengths have revealed extensive chemical diversity among the comet population (e.g., A'Hearn et al. 1995, 2012; Crovisier et al. 2009; Cochran et al. 2012; Ootsubo et al. 2012; Dello Russo et al. 2016). In particular, high-resolution near-infrared spectroscopy provides a valuable tool for sampling the composition of primary volatiles (i.e., ices subliming directly from the nucleus) of comets via analysis of fluorescent emission in cometary comae. To date, over 30 comets have been characterized in this manner, with the hypothesis that the primary volatile composition of the coma can be used to infer the composition of the nucleus, and can therefore be tied to nascent solar system conditions.

However, the results of recent rendezvous missions to comets, such as the *Rosetta* mission to comet 67P/Churyumov–Gerasimenko, have raised significant questions regarding the nature of comets. These include questions such as: how did comets form? How are comet ices put together? How do comets change with time? To what degree do comets retain cosmogonic signatures in their nuclei? How does coma composition vary throughout a perihelion passage? (see A'Hearn 2017 for a discussion of these questions). Whereas

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Table 1
Observing Log for 21P/Giacobini–Zinner

UT Date (2018)	iSHELL Setting	UT	R_h(au)	dR_h/dt (km s^{-1})	Δ (au)	$d\Delta/dt$ (km s^{-1})	T_{int}(minutes)	Slit PA/Length
Jul 25	M2	12:02–13:58	1.20	−12.72	0.64	−13.67	85	220°(15″)
Jul 28	Lp1	10:58–12:41	1.18	−12.25	0.61	−13.53	92	222°(15″)
	M2	13:32–15:44	1.18	−12.23	0.61	−13.39	96	222°(15″)
Jul 29	Lcustom	11:17–13:08	1.17	−12.07	0.61	−13.43	100	223°(15″)
	M2	13:25–15:23	1.17	−12.06	0.61	−13.32	86	223°(15″)
Jul 31	Lp1	10:42–12:56	1.16	−11.72	0.59	−13.30	120	225°(15″)
	M2	13:50–15:24	1.16	−11.70	0.59	−13.16	74	225°(15″)
Sep 7	Lp1	14:01–16:14	1.01	−0.94	0.39	−1.89	54	270°(5″)
	Lcustom	16:56–18:16	1.01	−0.90	0.39	−1.61	34	270°(5″)
Sep 11	Lp1	13:27–15:53	1.01	0.47	0.39	0.36	66	271°(5″)
Oct 10	M2	13:21–14:23	1.10	9.49	0.51	11.16	50	276°(15″)
	Lp1	14:35–16:58	1.10	9.51	0.51	11.32	108	276°(15″)

Note. R_h, dR_h/dt, Δ, and $d\Delta/dt$ are heliocentric distance, heliocentric velocity, geocentric distance, and geocentric velocity, respectively, of 21P/Giacobini–Zinner, and T_{int} is total integration time on source. The slit position angle (PA) was oriented along the projected Sun–comet line on all dates. The slit length for each date is given in parentheses. The slit width was 0.″75 on all dates.

Oort cloud comets (OCCs) can generally be observed only during a single apparition, short-period (or ecliptic) comets, observable primarily as Jupiter-family comets (JFCs), offer the opportunity to investigate potential evolutionary effects on volatile composition resulting from frequent and repeated perihelion passages, as well as a search for variability in coma composition on a variety of timescales (e.g., Knight & Schleicher 2013; Combi et al. 2019) depending on observational opportunities. Most processes that may alter the properties of the nucleus are expected to affect a thin (at most a few meters deep) layer near the surface, which is likely lost over the course of a typical perihelion passage (see Stern 2003). Nonetheless, an ecliptic comet that experiences many perihelion passages, particularly at small R_h, may (potentially) experience considerable processing compared to an OCC. Indeed, measured JFCs are on average depleted in certain primary volatiles, such as C_2H_2 and C_2H_6, relative to OCCs (Dello Russo et al. 2016). Understanding these potential evolutionary (or, natally inherent) effects, including observed differences between JFCs and OCCs, is essential for placing the results of coma composition studies into a meaningful context in the framework of solar system formation.

As the most volatile molecules systematically observed in comets, the "hypervolatiles" CO, CH_4, and C_2H_6 may be the most sensitive to both primordial conditions as well as thermal processing in comets (Dello Russo et al. 2016), and characterizing each molecule in an individual ecliptic comet may provide unique insights into its evolutionary history. Being symmetric hydrocarbons, CH_4 and C_2H_6 can only be sampled in the near-infrared due to their lack of a dipole moment and thus lack of allowed rotational modes. Of these molecules, detection of C_2H_6 has been reported in 10 ecliptic comets to date. Whereas CO is readily detectable at radio wavelengths and has been measured in several ecliptic comets (Crovisier et al. 2009), near-infrared measurements of CO and CH_4 in such comets are more elusive. The reason for this is that measuring near-infrared transitions of CO and CH_4 requires sufficiently large geocentric velocities (Δ_{dot}) to Doppler shift cometary emission lines away from their corresponding highly opaque telluric counterparts and into regions of adequate atmospheric transmittance. However, the overall lower gas production rates and hence fainter nature of JFCs (compared with OCCs) means that most observations traditionally take place near closest approach to Earth, coinciding with insufficient Δ_{dot} to measure their emission lines from CO and (especially) CH_4. This results in a paucity of complete hypervolatile inventories for JFCs (e.g., see Dello Russo et al. 2016).

Fortunately, the increased sensitivity and long on-source integration times afforded by the high-resolution iSHELL spectrograph, which became available for use at the NASA Infrared Telescope Facility (IRTF) in late 2016, together with unusually favorable apparitions for several short-period comets have to date enabled sensitive searches for these molecules in short-period comets 2P/Encke (Roth et al. 2018) and JFC 45P/Honda–Mrkos–Pajdušáková (DiSanti et al. 2017). The highly favorable 2018 perihelion passage of JFC 21P/Giacobini–Zinner (hereafter G-Z) featured sufficiently high geocentric velocity simultaneously with small geocentric distance, and thereby afforded the opportunity to characterize its hypervolatile content. G-Z is the prototype for the eponymous "GZ-type" of carbon-chain depleted comets, depleted in both C_2 and NH_2 with respect to H_2O and accounting for ~6% of comets measured (A'Hearn et al. 1995; Fink 2009). Coupled with published near-infrared observations of G-Z during the 1998 and 2005 apparitions (Weaver et al. 1999; Mumma et al. 2000; DiSanti et al. 2013), our measurements also enabled searches for coma compositional variability of hypervolatiles on timescales of days, both pre- versus post-perihelion, and across multiple perihelion passages. In Section 2, we discuss our observations and data analysis. In Sections 3 and 4, we present our results. In Section 5, we compare our results to those from previous perihelion passages. In Section 6, we examine G-Z's place in the context of other comets characterized to date.

2. Observations and Data Reduction

During its 2018 apparition, G-Z both reached perihelion (1.01 au) and was closest to Earth (0.39 au) on September 10. On UT 2018 July 25, 28, 29, and 31, September 7 and 11, and October 10, we observed G-Z with the facility high-resolution ($\lambda/\Delta\lambda \sim$ 40,000), near-infrared, immersion-grating echelle spectrograph iSHELL (Rayner et al. 2012, 2016) at the 3 m NASA IRTF to characterize its hypervolatile composition. We utilized three iSHELL settings (Lcustom, Lp1, and M2) so as to fully sample a suite of molecular abundances. We oriented the

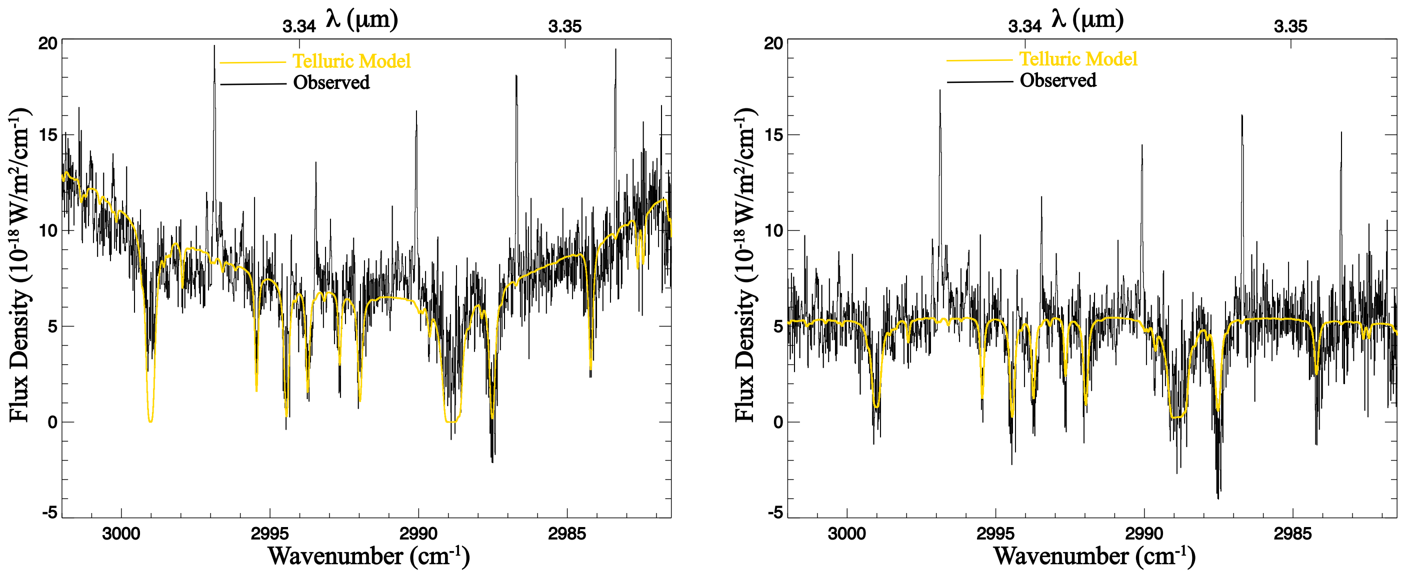

Figure 1. Extracted spectra of comet G-Z showing order 155 of the iSHELL Lp filter taken with the 5″ long slit on UT 2018 September 11 before (left panel) and after (right panel) baseline correction. The gold trace is the telluric absorption model (convolved to the instrumental resolution).

slit along the projected Sun–comet line on all dates (see Table 1).

On our July and October dates, observations were performed with a 6 pixel (0.″75) wide slit, using our standard ABBA nod pattern, with A and B beams symmetrically placed about the midpoint along the 15″ long slit and separated by half its length. A malfunction of the iSHELL dekker precluded the use of the 15″ long slit in September and necessitated off-chip nodding using the 0.″75 wide by 5″ long slit. We placed G-Z in the center of the slit for A frames and nodded 20″ perpendicular to the slit for B (sky) frames. For all dates combining spectra of the nodded beams as A–B–B+A canceled emissions from thermal background, instrumental biases, and sky emission (lines and continuum) to the second order in air mass. Flux calibration was performed using appropriately placed bright infrared flux standard stars on each date using a wide (4.″0) slit. On October 10, observing time was lost owing to a telescope pointing error that precluded the acquisition of flux calibration sets; therefore, we adopted a flux calibration factor (Γ, W/m^2/cm^{-1}/(counts/s)) based on that measured on other dates. Although this could affect absolute production rates, derived mixing ratios should be unaffected, as our targeted molecules were observed simultaneously or contemporaneously with water or OH prompt emission (OH*, a proxy for water production; see Bonev et al. 2006). The observing log is shown in Table 1.

Our data reduction procedures have been rigorously tested and are described extensively in the refereed literature (Bonev 2005; DiSanti et al. 2006, 2014; Villanueva et al. 2009; Radeva et al. 2010), and their application to unique aspects of iSHELL spectra is detailed in Section 3.2 of DiSanti et al. (2017). Here we will only discuss aspects of the reduction of G-Z frames which differed from those previously reported.

Each echelle order within an iSHELL setting was processed individually as previously described, such that each row corresponded to a unique position along the slit, and each column to a unique wavelength. We found that spatially resampling using a third-order polynomial more completely removed the curvature in the spatial dimension from iSHELL frames, and so employed this in place of previously used second-order polynomial resampling (DiSanti et al. 2017). Spectra were extracted from the processed frames by summing the signal over 15 rows (approximately 2.″5), seven rows to each side of the nucleus, defined as the peak of dust emission in a given spectral order.

For our September observations (using the shorter 5″ slit), we found that the iSHELL flat lamp provided illumination of the chip that was not consistent with that of the sky. This introduced a curvature effect into our spectra, which we corrected by fitting and then dividing by a polynomial baseline (Figure 1). This may have affected flux calibration and therefore the calculated absolute molecular production rates (Q's) reported for our September dates. However, emissions from all molecules within each individual iSHELL setting are sampled simultaneously, and therefore our derived mixing ratios should be unaffected. The general consistency of production rates and derived mixing ratios on both September dates suggests that any uncertainties introduced by this illumination offset were likely minimal.

We determined contributions from continuum and gaseous emissions in our comet spectra as previously described (e.g., DiSanti et al. 2016, 2017) and illustrate the procedure in Figure 2. We convolved the fully resolved transmittance function to the resolving power of the data ($\sim 4.0 \times 10^4$) and scaled it to the level of the comet continuum. We then subtracted the modeled continuum to isolate cometary emission lines and compared synthetic models of fluorescent emission for each targeted species to the observed line intensities.

Nucleocentric (or nucleus-centered) production rates ($Q_{\rm NC}$) were determined using our well-documented formalism (Dello Russo et al. 1998; DiSanti et al. 2001; Bonev 2005; Villanueva et al. 2011a); see Section 3.2.2 of DiSanti et al. (2016) for further details. The $Q_{\rm NC}$ were multiplied by an appropriate growth factor (GF), determined using our Q-curve methodology (e.g., Dello Russo et al. 1998; DiSanti et al. 2001; Bonev 2005; Gibb et al. 2012), to establish total (or global) production rates (Q). This GF corrects for atmospheric seeing, which suppresses signal along lines of sight passing close to the nucleus due to the use of a narrow slit, as well as potential perpendicular drift of the comet during an exposure sequence. Global production rates for all detected molecules are listed in

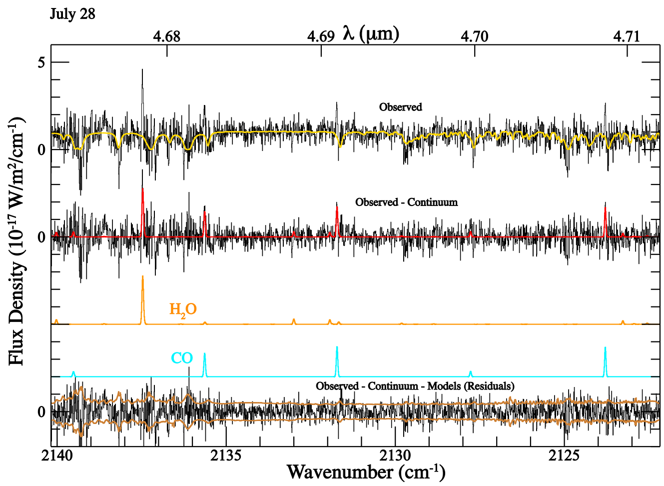

Figure 2. Extracted spectra showing clear detections of CO and H_2O in comet G-Z superimposed on the cometary continuum on UT 2018 July 28. The gold trace overplotted on the uppermost cometary spectrum is the telluric absorption model (convolved to the instrumental resolution and scaled to the observed continuum level). Directly below is the residual emission spectrum (after subtracting the telluric absorption model), with the total modeled fluorescent emission overplotted in red. Individual fluorescence models (color coded by species) are plotted below, offset vertically for clarity. At the bottom of the panel is the residual spectrum (after subtracting the telluric absorption model and all relevant molecular fluorescence models), with the 1σ uncertainty envelope overplotted in bronze.

Table 2. GFs were determined for both gas and dust when the signal-to-noise ratio (S/N) was sufficiently high (i.e., only for H_2O, CO, and C_2H_6). For September dates, the short $5''$ slit precluded the use of *Q*-curves to calculate GFs. Therefore, we assumed a GF of 1.8, a value consistent with that obtained from our other dates (Table 2).

3. Results

3.1. Spatial Profiles

For July dates, we were able to extract spatial profiles for H_2O, CO, and C_2H_6 emissions in G-Z (Figure 3). Within uncertainty, this suggests that emission for all three species closely tracked that of the co-measured dust; therefore, on dates for which molecular GFs could not be well constrained, we adopted that of dust co-measured within each setting when calculating production rates (Table 2).

3.2. Mixing Ratios of Volatile Species

3.2.1. Molecular Fluorescence Analysis

Synthetic models of fluorescent emission for each targeted species were compared to observed line intensities, after correcting each modeled line intensity (*g*-factor) for the monochromatic atmospheric transmittance at its Doppler-shifted wavelength (according to the geocentric velocity of the comet at the time of the observations). The *g*-factors used in synthetic fluorescent emission models in this study were generated with quantum mechanical models developed for CO (Paganini et al. 2013), CH_4 (Gibb et al. 2003), C_2H_6 (Villanueva et al. 2011b), and H_2O (Villanueva et al. 2012). A Levenberg–Marquardt nonlinear minimization technique (Villanueva et al. 2008) was used to fit fluorescent emission from all species simultaneously in each echelle order, allowing for high-precision results, even in spectrally crowded regions containing many spectral lines within a single instrumental resolution element. Production rates for each sampled species were determined from the appropriate fluorescence model at the rotational temperature of each molecule (Section 3.2.2).

3.2.2. Determination of Rotational Temperature

Rotational temperatures (T_{rot}) were determined using correlation and excitation analyses as described in Bonev (2005), Bonev et al. (2008), DiSanti et al. (2006), and Villanueva et al. (2008). In general, well-constrained rotational temperatures can be determined for individual species having intrinsically bright lines and for which a sufficiently broad range of excitation energies is sampled. Utilizing the large spectral grasp of iSHELL, in the case of H_2O we were able to sample dozens of strong lines simultaneously.

We found consistent rotational temperatures for multiple molecules on all dates (including H_2O). The T_{rot} for H_2O was well constrained on September 7 (being 75 ± 3 K) and was consistent (within 1σ uncertainty) with that for C_2H_6 on September 11 (66^{+12}_{-9} K). Rotational temperatures for our July dates were also in formal agreement, being 64^{+15}_{-11} K for CO on July 28 and 48^{+19}_{-13} K for H_2O on July 29. We were unable to measure well-constrained rotational temperatures for any molecules on October 10. We calculated production rates and mixing ratios at $T_{rot} = 48$ and 64 K for the July dates and varied T_{rot} as a parameter for the October date, calculating production rates and mixing ratios for each molecule at representative values $T_{rot} = 50$, 60, and 70 K. In general, mixing ratios for a given species derived at each temperature are consistent with one another within 1σ uncertainty (Table 2).

3.2.3. Secure Detections of Hypervolatiles

Our detections of CO, CH_4, and C_2H_6 in G-Z are particularly notable for two reasons: (1) they address the paucity of measurements of CO and CH_4 in ecliptic comets in general, and (2) they address the measurement of these hypervolatiles in an individual ecliptic comet across multiple perihelion passages and on multiple dates during its 2018 apparition. Of all primary volatiles systematically measured in comets, these three molecules are most sensitive to thermal processing, but as noted earlier, CO and CH_4 are also among the most difficult to sample from the ground due to the lack of sensitivity and/or adequate geocentric velocity. G-Z's excellent geocentric velocity ($|\Delta_{dot}| > 13\ \mathrm{km\ s^{-1}}$ pre-perihelion, $|\Delta_{dot}| > 11\ \mathrm{km\ s^{-1}}$ post-perihelion) allowed robust detections of all three species. CO and CH_4 have been measured in fewer than 10 ecliptic comets (with most detections being below the 5σ level), making our measurements in G-Z a critical component in establishing statistics for these species in ecliptic comets, and in determining the importance of natal versus evolutionary effects on present cometary volatile composition. Figures 4(A)–(E) show clear CO, H_2O, CH_4, C_2H_6, and OH^* emissions in G-Z superimposed on the cometary continuum during various portions of its 2018 perihelion passage.

4. Coma Hypervolatile Composition throughout the 2018 Perihelion Passage of G-Z

The 2018 apparition of G-Z provided an opportunity to conduct the first comprehensive comparison of hypervolatile abundances for a comet through three perihelion passages and also on multiple dates within a given perihelion passage,

Table 2
Hypervolatile Composition of Comet 21P/Giacobini–Zinner

iSHELL Setting	Molecule	T_{rot}[a] (K)	GF[b]	Q[c] (10^{25} mol s^{-1})	Q_x/Q_{H2O}[d] (%)
		2018 Jul 25, $R_h = 1.20$ au, $\Delta = 0.64$ au, $d\Delta/dt = -13.7$ km s^{-1}			
M2	H_2O	(48)	1.82 ± 0.17[e]	2692 ± 292	100
	CO	(48)	(1.82)	40.5 ± 5.1	1.51 ± 0.25
	H_2O	(64)	(1.82)	3028 ± 306	100
	CO	(64)	(1.82)	47.4 ± 5.9	1.56 ± 0.25
		2018 Jul 28, $R_h = 1.18$ au, $\Delta = 0.61$ au, $d\Delta/dt = -13.5$ km s^{-1}			
Lp1	C_2H_6	(48)	(1.91)	6.26 ± 1.28	0.23 ± 0.05
	CH_4	(48)	(1.91)	17.5 ± 4.2	0.63 ± 0.17
	C_2H_6	(64)	(1.91)	7.02 ± 1.33	0.24 ± 0.05
	CH_4	(64)	(1.91)	26.1 ± 6.2	0.88 ± 0.24
M2	H_2O	(48)	1.91 ± 0.14[e]	2771 ± 251	100
	CO	(48)	(1.91)	45.1 ± 3.6	1.63 ± 0.20
	H_2O	(64)	(1.91)	2961 ± 297	100
	CO	64^{+15}_{-11}	(1.91)	50.4 ± 4.0	1.70 ± 0.22
		2018 Jul 29, $R_h = 1.17$ au, $\Delta = 0.61$ au, $d\Delta/dt = -13.3$ km s^{-1}			
Lcustom	H_2O	48^{+19}_{-13}	(1.97)	2643 ± 229	100
M2	H_2O	(48)	(1.97)	2527 ± 345	100
	CO	(48)	1.97 ± 0.21	34.8 ± 4.7	1.38 ± 0.26
	H_2O	(64)	(1.97)	2726 ± 369	100
	CO	(64)	(1.97)	41.2 ± 4.4	1.51 ± 0.26
		2018 Jul 31, $R_h = 1.16$ au, $\Delta = 0.59$ au, $d\Delta/dt = -13.2$ km s^{-1}			
Lp1	C_2H_6	(48)	(1.66)	6.05 ± 0.77	0.24 ± 0.05
	CH_4	(48)	(1.66)	28.1 ± 4.1	1.12 ± 0.26
	C_2H_6	(64)	(1.66)	6.64 ± 0.94	0.24 ± 0.05
	CH_4	(64)	(1.66)	41.4 ± 6.0	1.52 ± 0.31
M2	H_2O	(48)	(1.66)	2503 ± 385	100
	CO	(48)	1.66 ± 0.22	50.1 ± 4.9	2.00 ± 0.36
	H_2O	(64)	(1.66)	2716 ± 262	100
	CO	(64)	(1.66)	58.6 ± 4.8	2.15 ± 0.27
		2018 Sep 7, $R_h = 1.01$ au, $\Delta = 0.39$ au, $d\Delta/dt = -1.7$ km s^{-1}			
Lp1	C_2H_6	(75)	(1.8)[f]	10.6 ± 1.1	0.35 ± 0.06
	OH^*	(75)	(1.8)[f]	3036 ± 357	100
Lcustom	H_2O	75 ± 3	(1.8)[f]	3206 ± 112	100
		2018 Sep 11, $R_h = 1.01$ au, $\Delta = 0.47$ au, $d\Delta/dt = 0.3$ km s^{-1}			
Lp1	C_2H_6	66^{+12}_{-9}	(1.8)[f]	7.15 ± 0.39	0.26 ± 0.02
		(75)		7.49 ± 0.43	0.28 ± 0.02
	OH^*	(75)	(1.8)[f]	2713 ± 168	100
		2018 Oct 10, $R_h = 1.10$ au, $\Delta = 0.51$ au, $d\Delta/dt = 11.1$ km s^{-1}			
M2	H_2O	(50)	1.93 ± 0.28[e]	2054 ± 257	100
	CO	(50)	(1.93)	22.9 ± 2.9	1.11 ± 0.20
	H_2O	(60)	(1.93)	2029 ± 253	100
	CO	(60)	(1.93)	25.5 ± 3.3	1.26 ± 0.23
	H_2O	(70)	(1.93)	2028 ± 252	100
	CO	(70)	(1.93)	28.1 ± 3.2	1.39 ± 0.25
Lp1	C_2H_6	(50)	(1.93)	2.65 ± 0.42	0.13 ± 0.03
	CH_4	(50)	(1.93)	<10 (3σ)	<0.55 (3σ)
	C_2H_6	(60)	(1.93)	2.92 ± 0.39	0.14 ± 0.03
	CH_4	(60)	(1.93)	<13 (3σ)	<0.72 (3σ)
	C_2H_6	(70)	(1.93)	3.20 ± 0.41	0.16 ± 0.03
	CH_4	(70)	(1.93)	<16 (3σ)	<0.89 (3σ)

Notes.
[a] Rotational temperature. Values in parentheses are assumed.
[b] Growth factor. Values in parentheses are assumed.
[c] Global production rate. Uncertainties in production rate include line-by-line deviation between modeled and observed intensities and photon noise (see Bonev 2005; Dello Russo et al. 2004; Bonev et al. 2007).
[d] Molecular abundance with respect to H_2O.
[e] Continuum (dust) growth factor.
[f] A growth factor for September dates could not be derived owing to use of the 5″ short slit; therefore, a GF of 1.8, consistent with growth factors derived for species pre- and post-perihelion, was assumed.

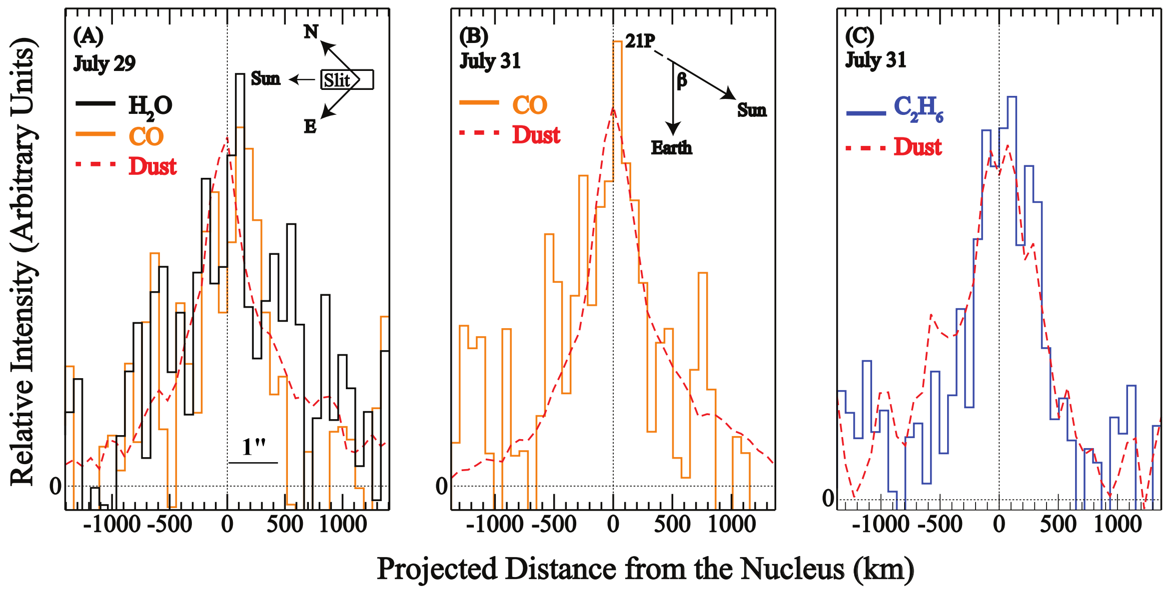

Figure 3. (A) Spatial profiles of co-measured emissions in G-Z for H_2O (black), CO (orange), and dust (red) on UT 2018 July 29. The slit was oriented along the projected Sun–comet line (position angle 223°), with the Sun-facing direction to the left as indicated. Also shown is the Sun–comet–Earth angle (phase angle, β) of 59°. The horizontal bar indicating 1″ corresponds to a projected distance of approximately 449 km at the geocentric distance of G-Z. (B) Spatial profiles of co-measured emissions for CO (orange) and dust (red) on UT 2018 July 31. (C) Spatial profiles of co-measured emissions for C_2H_6 (blue) and dust (red) on UT 2018 July 31. The observing geometry on July 31 was similar to that of July 29, with a position angle of 225° and a phase angle of 60°.

thereby allowing us to address pressing questions in cometary science. These include testing possible evolutionary effects on coma volatile composition, as well as searching for coma compositional variability on multiple timescales, including day-to-day, pre- versus post-perihelion, and across perihelion passages. We discuss each of these topics in turn, and place G-Z in the context of other comets observed to date. Unless otherwise noted, all dates refer to the 2018 apparition.

4.1. CO

We found clear, simultaneously measured detections of CO and H_2O on multiple dates in G-Z (Figures 2, 4(A), 4(D)) pre- as well as post-perihelion. The mixing ratio CO/H_2O was consistent on all pre-perihelion July dates within 1σ uncertainty (Table 2; see also Figure 5) with a weighted average abundance of $1.72 \pm 0.12\%$ for $T_{\rm rot} = 64$ K. This was somewhat lower post-perihelion in October, $1.26 \pm 0.23\%$ for $T_{\rm rot} = 60$ K, suggesting that CO/H_2O in G-Z may display pre- versus post-perihelion asymmetry. However, given the uncertainty in $T_{\rm rot}$ in October, it is important to note that the range of possible October CO mixing ratios is in formal agreement with those from July (Table 2). These mixing ratios are depleted with respect to the mean for all comets measured to date at near-infrared wavelengths ($5.2 \pm 1.3\%$), but are consistent with the few measurements in ecliptic comets (Dello Russo et al. 2016, 2020; DiSanti et al. 2017; Roth et al. 2018).

4.2. CH_4

CH_4 bears the distinction of being the most severely undersampled hypervolatile in ecliptic comets, having been firmly measured in only six to date (Dello Russo et al. 2016 and references therein; DiSanti et al. 2017; Roth et al. 2018; Dello Russo et al. 2020). Utilizing the large spectral grasp of iSHELL, we combined the signal from multiple lines and detected CH_4 in G-Z at the 4σ level on July 28, at $>6\sigma$ on July 31, and derived a meaningful constraint on its mixing ratio on October 10 (see Figure 4(B) and Table 3). Our results suggest that CH_4 may have been variable from day to day in G-Z. However, there are important caveats for our CH_4 study.

We were unable to derive a well-constrained rotational temperature for CH_4 owing to the small spread in excitation energies in the sampled lines (see Section 3.2.2, Figure 4(B)). However, we found that calculated CH_4 production rates and mixing ratios showed a sensitive dependence on assumed $T_{\rm rot}$ (Table 2). Assuming $T_{\rm rot} = 48$ K (from H_2O on July 29), pre-perihelion CH_4 mixing ratios in G-Z ($0.63 \pm 0.17\%$ for July 28, $1.12 \pm 0.26\%$ for July 31) are consistent with mean values in measured OCCs ($0.88 \pm 0.10\%$), yet are enriched compared to the few measurements in JFCs. Adopting a higher $T_{\rm rot}$ (e.g., 64 K from CO on July 28) increases the degree of CH_4 enrichment. Regardless of which $T_{\rm rot}$ we adopt, G-Z is not the first instance of a CH_4-enriched JFC, with similar mixing ratios reported in 45P/Honda–Mrkos–Pajdušáková (DiSanti et al. 2017; Dello Russo et al. 2020). Our (3σ) upper limit for October 10 is similarly sensitive to assumed $T_{\rm rot}$ (Table 2), but is consistent with our July measurements assuming $T_{\rm rot} \geqslant 60$ K, a reasonable assumption given the rotational temperatures measured in July and September for other molecules at similar $R_{\rm h}$.

Additionally, we were unable to extract spatial profiles for CH_4 emission due to low S/N along the slit; therefore, we assumed GFs measured from other species (or co-measured dust) within a given date for CH_4 in order to calculate global production rates. It is possible that CH_4 outgassing differed day to day from that for H_2O, CO, or co-measured dust and that the suggested variability may be due to our assumed GFs for CH_4. That being said, we did not find any unusual outgassing patterns among the other molecules or dust relative to one another in G-Z, so we expect our assumed GF for CH_4 to be reasonable.

Finally, OH^* was weak in G-Z for our July and October dates and was only firmly detected near-perihelion in September. We therefore calculated mixing ratios for CH_4

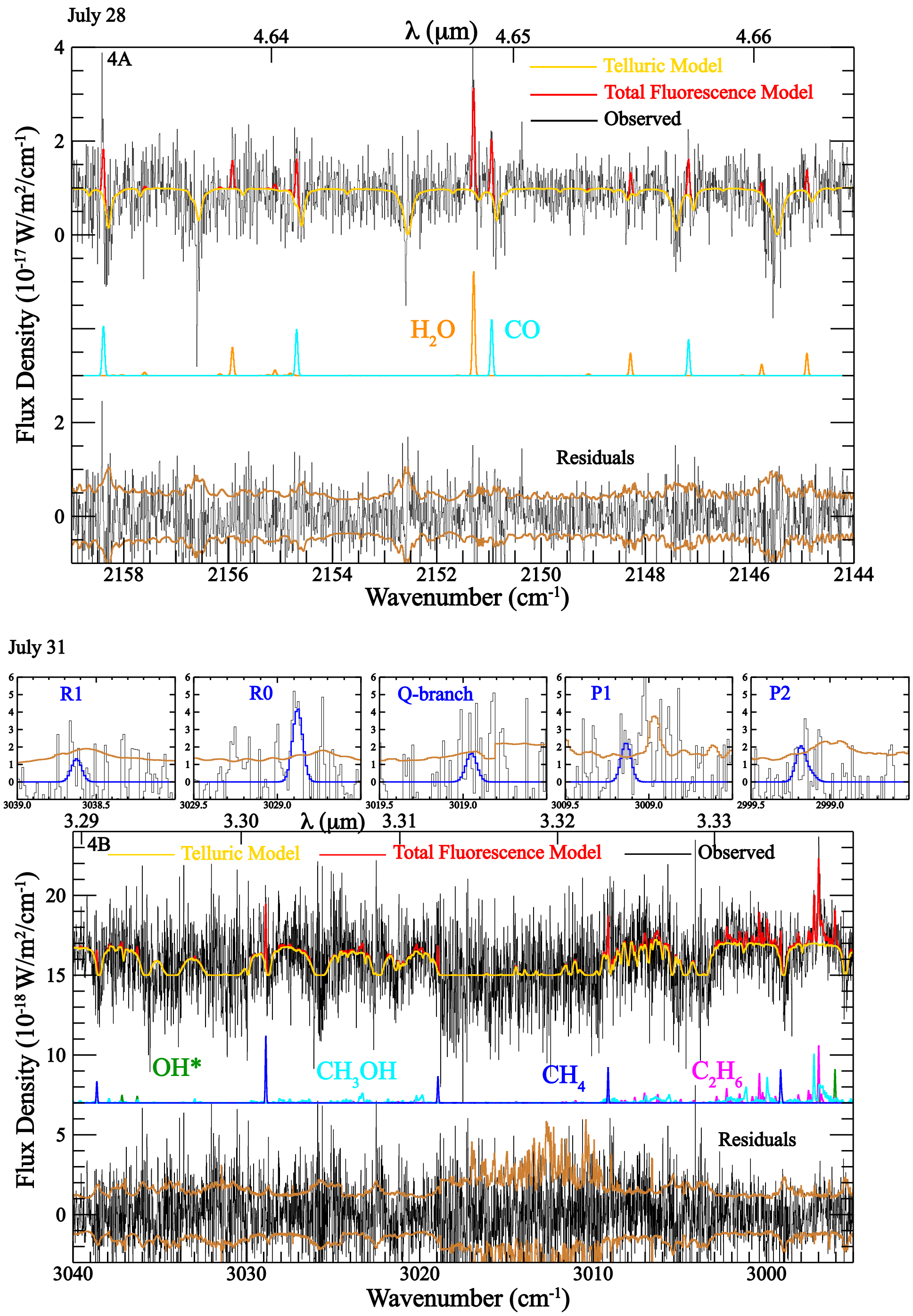

Figure 4. (A) Extracted spectra showing detections of CO and H_2O in comet G-Z on UT 2018 July 28, with traces and labels as described in Figure 2. (B) Detections of CH_4, C_2H_6, CH_3OH, and OH^* (prompt emission) on UT 2018 July 31. The zoomed subplots highlight the locations of individual (observed and modeled) CH_4 emissions, and each subplot has the same units as the larger plot. (C) Detections of C_2H_6, CH_3OH, and OH^* on UT 2018 September 11. Analysis of CH_3OH in G-Z is the subject of a future paper. (D) Detections of CO and H_2O on UT 2018 October 10. (E) Detections of H_2O and OH^* on UT 2018 September 7.

using $Q(H_2O)$ obtained from the M2 setting on the same date. We estimate the inter-setting calibration uncertainty to be ∼10%, and have incorporated this into the reported uncertainty in our mixing ratios. Use of contemporaneously (but not simultaneously) measured $Q(H_2O)$ for CH_4 abundances in July and October may account for some of the spread in abundances from date to date. However, the formal agreement between $Q(H_2O)$ obtained from OH^* (in Lp1) and H_2O (in Lcustom) on September 7 (Table 2) argues against both a systematic difference in retrieving water production rates in these two ways, and also against short-term variations in $Q(H_2O)$ in G-Z. Clearly, further measurements of G-Z are necessary to clarify the possible variability of its coma CH_4 content.

4.3. C_2H_6

Of all the hypervolatiles, C_2H_6 is the most routinely sampled in comets owing to its intrinsically strong near-infrared transitions and the availability of multiple emissions in regions of favorable telluric transmittance independent of Δ_{dot}. This enabled us to measure C_2H_6 mixing ratios on multiple dates

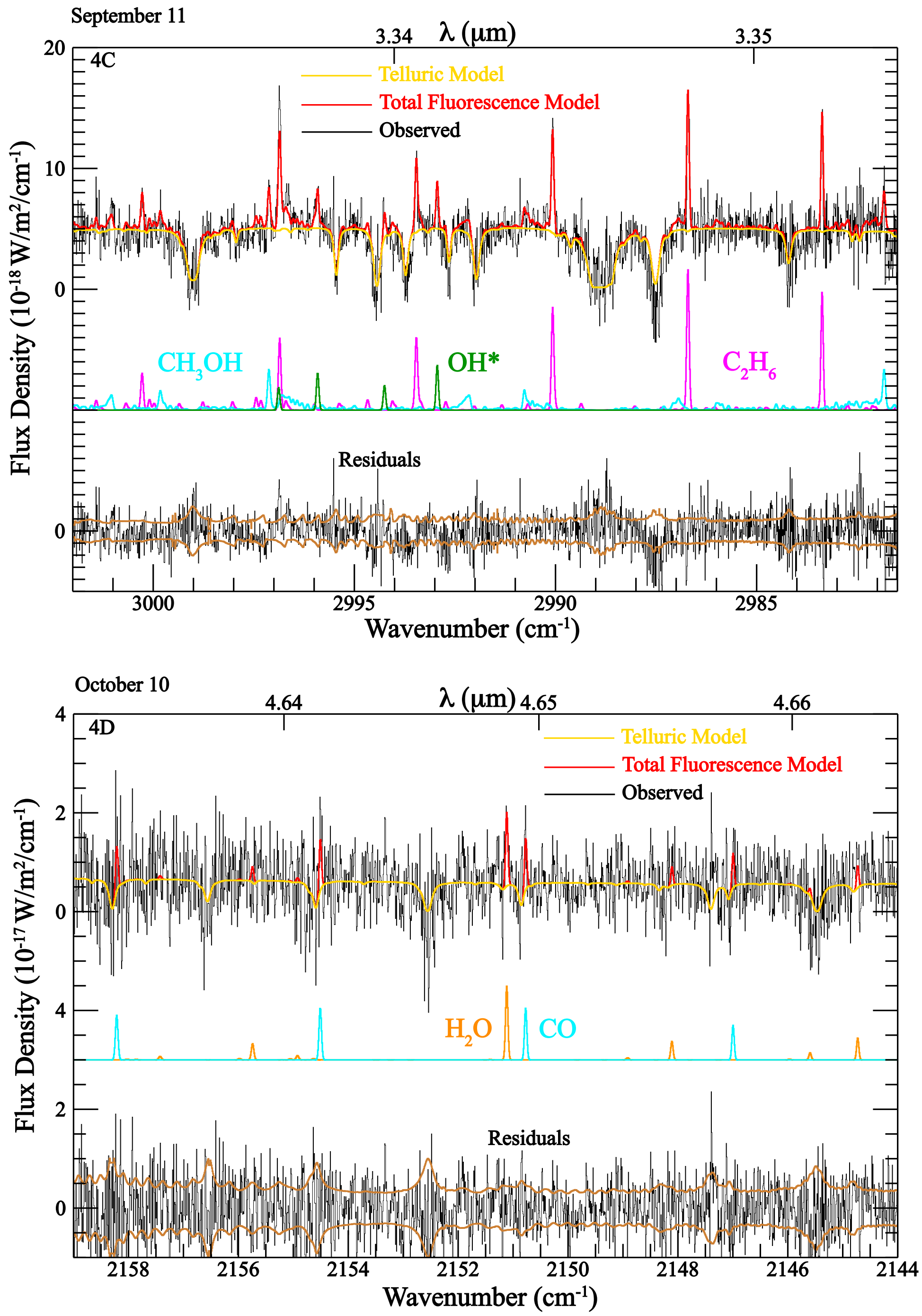

Figure 4. (Continued.)

during G-Z's 2018 apparition, including pre-perihelion, near-perihelion, and post-perihelion. Similar to CO, we found that C_2H_6 mixing ratios were consistent (within uncertainties) pre-perihelion (weighted average $0.24 \pm 0.03\%$ for $T_{\rm rot} = 64$ K) and additionally near-perihelion (weighted average $0.29 \pm 0.02\%$). However, C_2H_6 was lower post-perihelion with a mixing ratio of $0.14 \pm 0.03\%$ (assuming $T_{\rm rot} = 60$ K). Compared to ecliptic comets measured to date, pre-perihelion and near-perihelion G-Z was consistent with the mean mixing ratio measured for C_2H_6 ($0.34 \pm 0.07\%$), but was depleted post-perihelion (and was severely depleted compared to the mean for all comets measured ($0.55 \pm 0.08\%$), including ecliptic comets). In the same manner as CH_4, the use of $Q(H_2O)$ from H_2O in the M2 setting rather than from OH^* in the Lp1 setting to calculate C_2H_6 mixing ratios in July and October may have contributed to its suggested variability. Similarly, the use of assumed GFs for C_2H_6 on some of our dates may have introduced additional uncertainty into the mixing ratio C_2H_6/H_2O. However, we note that $Q(H_2O)$ was dramatically lower in October compared with both July and September, being closer to 2×10^{28} than to 3×10^{28} molecules s^{-1} (see Table 2), consistent with the asymmetry in water production with respect to perihelion found by A'Hearn et al. (1995). This in turn could indicate distinct regions of the nucleus dominating the activity in G-Z pre- vs. post-perihelion, and that its chemical composition

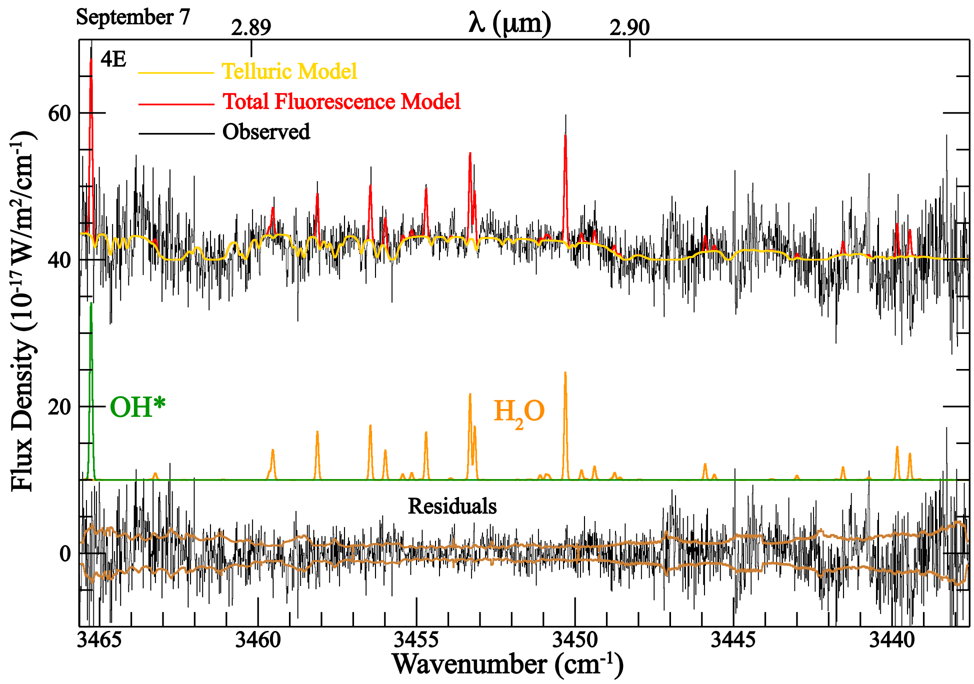

Figure 4. (Continued.)

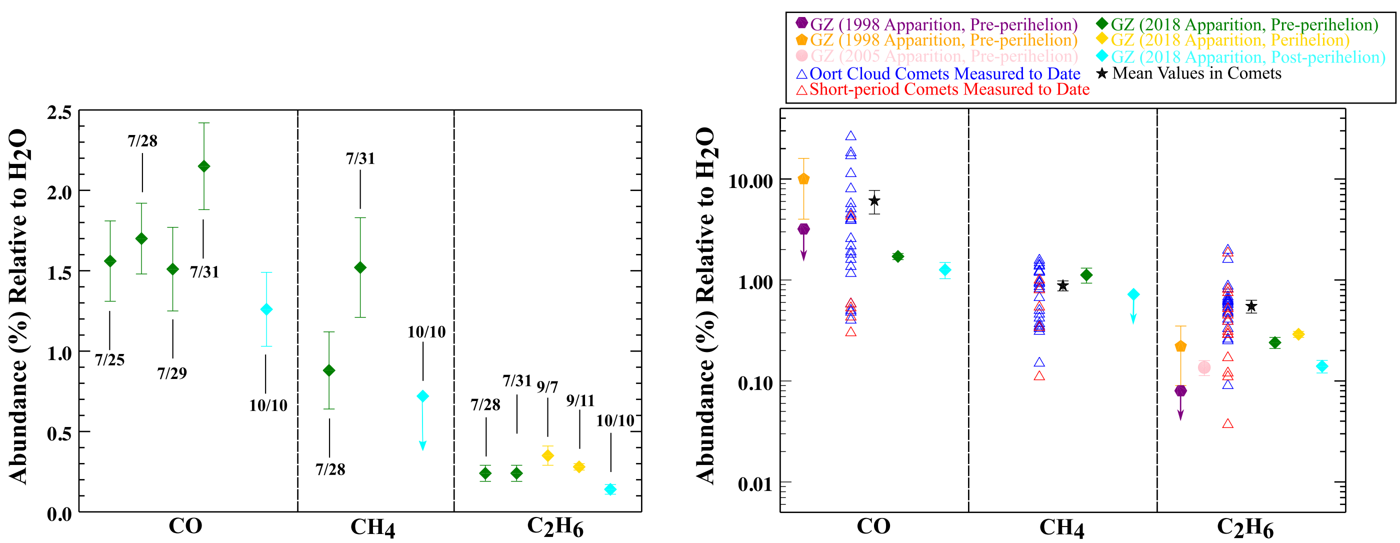

Figure 5. Left: comparison of mixing ratios (abundances relative to H_2O, expressed in percentages) of hypervolatiles in G-Z sampled on each date during the 2018 apparition. Right: comparison of mixing ratios of hypervolatiles sampled in G-Z during the 1998 apparition (purple, Weaver et al. 1999; orange, Mumma et al. 2000), 2005 (pink; DiSanti et al. 2013), and 2018 (green, yellow, cyan; this work), as well as near-infrared measurements of each volatile in OCCs (blue) and ecliptic comets (red) measured to date, and the respective mean values for CO and CH_4 among OCCs and for C_2H_6 among all comets (black; Dello Russo et al. 2016, 2020; DiSanti et al. 2017; Roth et al. 2017, 2018; Faggi et al. 2018). Error bars indicate measurements with $\pm 1\sigma$ uncertainties, whereas downward arrows indicate 3σ upper limits. Measurements shown from 2018 are given as weighted averages for pre-perihelion and perihelion dates, and assume $T_{\rm rot} = 64$ K for July, $T_{\rm rot} = 75$ K for September, and $T_{\rm rot} = 60$ K for October.

(at least in terms of CH_4/H_2O and C_2H_6/H_2O) may also be different on October 10 compared with our pre-/near-perihelion dates.

5. Comparison with Previous Perihelion Passages

5.1. Comparison with Previous Perihelion Passages of G-Z

G-Z is the only comet for which hypervolatiles have been measured at near-infrared wavelengths during three different perihelion passages: 1998 (Weaver et al. 1999; Mumma et al. 2000), 2005 (DiSanti et al. 2013), and 2018 (this work), and is just the second comet to have a comprehensive comparison of hypervolatile abundances across apparitions (the other being 2P/Encke; see Radeva et al. 2013; Roth et al. 2018). The left panel of Figure 5 shows our individual 2018 measurements of hypervolatile abundances in G-Z. The right panel of Figures 5 shows our mean pre-, near-, and post-perihelion hypervolatile abundances together with those for G-Z from 1998 and 2005,

Table 3
Hypervolatile Abundances in 21P/Giacobini–Zinner across Apparitions

Year	1998		2005	2018[a]			Mean among Comets[b]	Range in Comets[c]
	Pre-perihelion		Pre-perihelion	Pre-perihelion	Perihelion	Post-perihelion		
CO	<3.2[d]	10 ± 6[e]	…	1.72 ± 0.12	…	1.26 ± 0.23	$6.1 \pm 1.6(19)$	0.30–26
CH_4	…	…	…	0.63–1.52	…	$<0.55 - <0.89$	$0.88 \pm 0.10(19)$	0.11–1.6
C_2H_6	<0.08[d]	0.22 ± 0.13[e]	0.14 ± 0.02[f]	0.24 ± 0.04	0.29 ± 0.02[a]	0.14 ± 0.03	$0.55 \pm 0.08(27)$	0.037–1.9

Notes. Upper limits for nondetected species are 3σ. In all cases values are expressed as percentages relative to H_2O.
[a] This work. Abundances for CO and C_2H_6 are given as weighted averages for molecules detected on multiple dates, assuming $T_{\rm rot} = 64$ K for pre-perihelion values, $T_{\rm rot} = 75$ K for perihelion values, and $T_{\rm rot} = 60$ K for post-perihelion values. Owing to its sensitive dependence on $T_{\rm rot}$, the mixing ratio for CH_4 is given as a range based on the values in Table 2. Weighted mean values of $Q(H_2O)$ were $(2.86 \pm 0.15) \times 10^{28}$ mol s^{-1} pre-perihelion, $(3.05 \pm 0.09) \times 10^{28}$ mol s^{-1} near-perihelion, and $(2.02 \pm 0.25) \times 10^{28}$ mol s^{-1} post-perihelion.
[b] Mean values and 1σ uncertainties among measured comets taken from Dello Russo et al. (2016). The number of measurements used to calculate the mean is given in parentheses. Mean values for CO and CH_4 are given for OCCs only owing to the extreme paucity of such measurements in JFCs, whereas the mean for C_2H_6 is given for all comets measured (JFCs and OCCs).
[c] Range among comets measured after Dello Russo et al. (2016, 2020), DiSanti et al. (2017), Roth et al. (2017), Roth et al. (2018), and Faggi et al. (2018).
[d] Abundances taken from Weaver et al. (1999).
[e] Abundances taken from Mumma et al. (2000).
[f] Abundances taken from DiSanti et al. (2013).

and (for comparison) those for all measured comets. Table 3 gives a similar comparison numerically. Figure 5 and Table 3 suggest that each hypervolatile may display at least some degree of variability, whether across perihelion passages or during a particular apparition. We discuss each species in turn.

5.1.1. CO

In the case of CO, our pre- and post-perihelion mixing ratios are consistent with (yet lower than) the upper limit from the 1998 apparition (using CSHELL) found by Weaver et al. (1999), but considerably lower than the mixing ratio reported by Mumma et al. (2000) from observations conducted approximately three weeks earlier. However, Mumma et al. did not detect H_2O, even though the strong line near 2151 cm^{-1} (as we show in Figures 4(A) and (D)) was encompassed together with the CO R0 and R1 lines in the same CSHELL setting. Instead, their value for CO/H_2O was inferred from the measured CO abundance relative to C_2H_6 (detected at the $\sim 5\sigma$ confidence level), and an adopted (1.9σ) value for $Q(H_2O)$ based on residual flux at the Doppler-shifted frequency of the 2151 cm^{-1} line. In any case, results obtained to date suggest that the abundance ratio of CO in G-Z may display variability, both during a single apparition (as is also suggested by our 2018 measurements) and across multiple apparitions.

It is important to note that the 1998 measurements of G-Z with CSHELL—the small spectral grasp of which precluded measuring H_2O simultaneously with CH_4 or C_2H_6—introduced uncertainties due to inter-setting calibration in addition to potential temporal variations in production rates. In contrast, the large spectral grasp of iSHELL enabled simultaneous measurements of all three hypervolatiles with either H_2O or OH^* during the 2018 perihelion passage of G-Z.

In the context of preserving natal solar system signatures in the nucleus ices of JFCs, it is important to note the stark contrast of our CO measurements along with those reported by Weaver et al. compared to those of Mumma et al. The CO/H_2O mixing ratio inferred by Mumma et al. ($10 \pm 6\%$) would place G-Z as the only known CO-enriched JFC to date. If G-Z were indeed so enriched in CO, it would have profound implications for the origins and evolutionary processing history of JFCs. However, as mentioned previously this is based on an extremely tentative "detection" ($<2\sigma$) of H_2O. Nonetheless, our measurements do not support this conclusion, and instead indicate that G-Z has a CO abundance that is more similar to the few measurements in ecliptic comets and is depleted when compared to all comets measured.

5.1.2. CH_4

CH_4 has not been reported previously in G-Z—for both the 1998 and 2005 observations $|\Delta_{\rm dot}| < 10\,{\rm km\,s^{-1}}$, thereby precluding its measure—and our results indicate that it may have been variable on timescales of days to months in 2018. However, as previously noted, there are important caveats regarding its purported variability. In any case, our measurements indicate that G-Z is consistent with to enriched compared to the mean CH_4 abundance for all comets measured.

5.1.3. C_2H_6

Our C_2H_6 mixing ratios obtained pre-perihelion and near-perihelion were consistent with that found by Mumma et al. (2000; $\sim 0.2\%$ relative to H_2O; however, this mixing ratio suffers the same systematic uncertainty noted for CO/H_2O in Section 5.1.1), but were significantly higher than the upper limit ($<0.05\%$–0.08%) reported by Weaver et al. (1999), and also were higher than the measurement from 2005 (0.14%, DiSanti et al. 2013). However, our post-perihelion measurement for C_2H_6 on October 10 was considerably lower (by approximately a factor of 2) than on earlier 2018 dates, yet was consistent with the 2005 pre-perihelion value, suggesting possible short-term (i.e., diurnal, perhaps associated with nucleus rotation, or seasonal effects, such as that seen by *Rosetta* at 67P/Churyumov–Gerasimenko; see Section 5.2) variability in its C_2H_6 abundance ratio when compared with our pre-perihelion results. It is important to note that the possible variability in C_2H_6 implied by our G-Z measurements (as well as those from previous perihelion passages) is small compared to the overall spread of C_2H_6 abundances in all comets measured (Figure 5).

5.2. Discussion of Possible Variability of Coma Hypervolatile Abundances in G-Z

Combined with previous work, our results suggest that coma hypervolatile abundances in G-Z may be variable. At 67P/Churyumov–Gerasimenko, the *Rosetta* mission found that

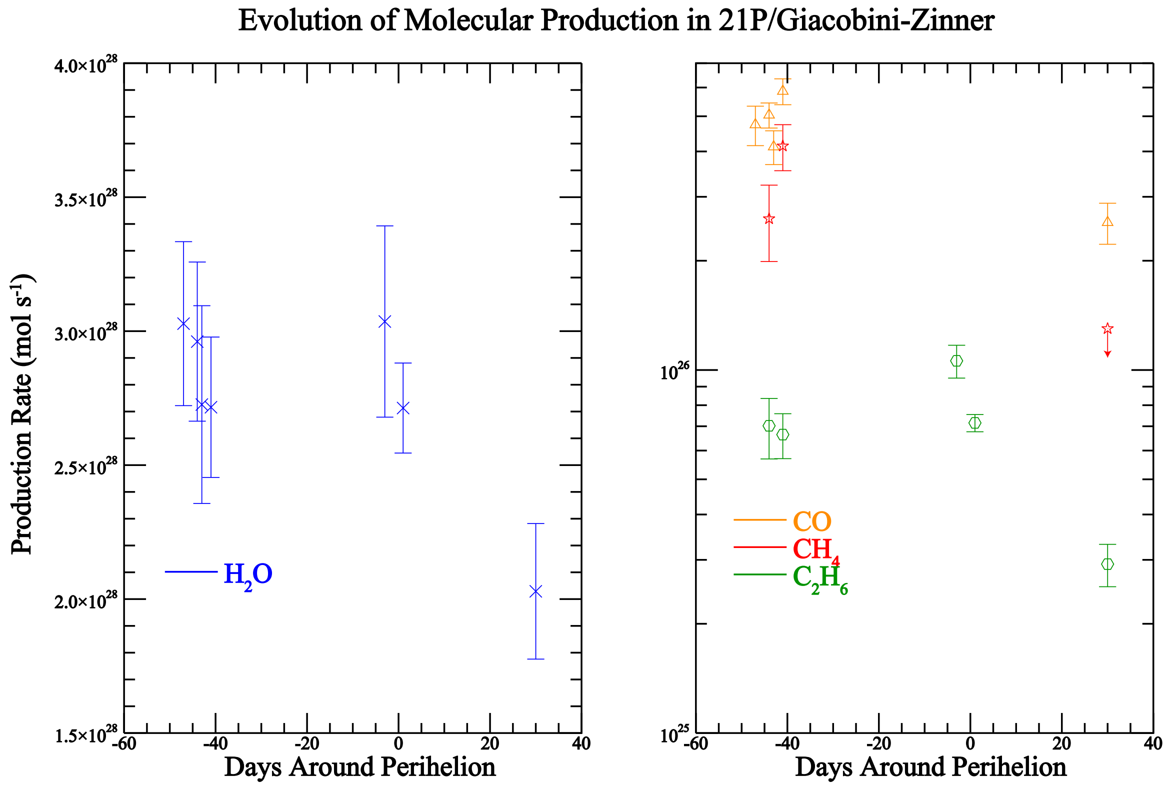

Figure 6. Evolution of molecular production in G-Z throughout the 2018 perihelion passage for H_2O (left panel) and CO, CH_4, and C_2H_6 (right panel) with respect to perihelion (UT 2018 September 10). Error bars indicate measurements, whereas downward arrows indicate 3σ upper limits.

nucleus shape and the location of active areas, combined with seasonal and rotational illumination effects, resulted in coma compositional variability on a variety of timescales. Hässig et al. (2015) found long-term variation in the coma abundances of CO and CO_2 due to seasonal illumination effects; furthermore, other species (such as CH_4) varied on shorter timescales, showing diurnal variations that differed from those of other volatiles, such as CO and C_2H_6 (Luspay-Kuti et al. 2015; Bockelée-Morvan et al. 2016; Fink et al. 2016). Similar effects may have contributed to the suggested coma hypervolatile variability in G-Z. Unfortunately, our ground-based measurements do not have sufficient spatial resolution to test this possibility.

To further examine the nature of the suggested variability in G-Z, we examined the evolution of molecular production for each species reported here during the 2018 apparition. Figure 6 shows the production rate of each species relative to perihelion (on September 10). Our measurements for all four species (H_2O, CO, CH_4, C_2H_6) are consistent with A'Hearn et al. (1995), who found that G-Z was more active pre-perihelion than post-perihelion. However, our results indicate that the relative asymmetry in molecular production is more pronounced for the trace species than for H_2O, which is reflected in their generally lower post-perihelion compared to pre-perihelion mixing ratios (Figure 5, Table 3).

In order to test whether the possible variability indicated by our results is owing to the activity of H_2O versus that of the trace species in G-Z, we compared the ratios CO/C_2H_6 from the 2018 perihelion passage. We found that CO/C_2H_6 was consistent within uncertainty pre- versus post-perihelion, being 7.18 ± 2.14 on July 28, 8.82 ± 1.69 on July 31, and 8.75 ± 1.85 on October 10 (assuming $T_{\rm rot} = 64$ K for July and 60 K for October). Combined with the results shown in Figures 5 and 6, this suggests that although CO and C_2H_6 were consistent relative to one another throughout the 2018 perihelion passage, their contributions to the volatile content of the coma were not, as evidenced by their steeper variation about perihelion compared with the production rate of H_2O.

If the volatile composition of G-Z is indeed variable, it is not the first such comet reported in the literature. As the number of serial measurements (i.e., both within and across perihelion passages) of primary volatiles in comets increases, the number of reports of variability on multiple timescales has similarly increased (e.g., Bodewits et al. 2014; Feaga et al. 2014; McKay et al. 2015; DiSanti et al. 2016; Fink et al. 2016; Roth et al. 2018; Dello Russo et al. 2020), with explanations ranging from diurnal variations in outgassing, to seasonal illumination effects, to chemically heterogeneous nuclei. Understanding whether such variations are common or rare phenomena and how to account for them in our analysis is crucial to placing the results of present-day primary volatile measurements in cometary comae into the framework of solar system formation theories.

It is important to note that the variability suggested by the measurements in Table 3 cannot explain the variation in each molecule among comets revealed in measurements to date (Figure 5). If the range of volatile abundances observed among all comets can be reproduced by time-resolved observations of one comet, we could seriously question the extent to which chemical diversity among the population is cosmogonic. Alternatively, a comet such as G-Z, in which measurements over three perihelion passages suggest (with carefully explored caveats) that the abundances of CO/H_2O and C_2H_6/H_2O vary on scales much smaller than the comet-to-comet range, may serve as evidence that we are indeed sampling cosmogonic signatures in our present-day measurements of parent volatiles

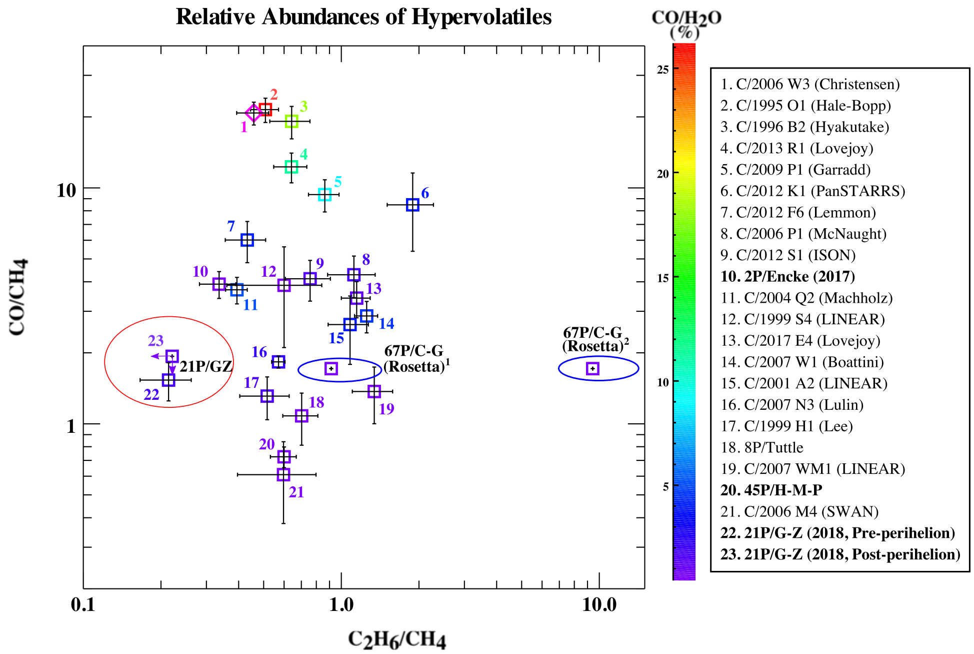

Figure 7. Abundances ratios of hypervolatiles in comets characterized to date, including comets G-Z (this work), 67P/Churyumov–Gerasimenko (Le Roy et al. 2015; Bockelée-Morvan et al. 2016; Biver et al. 2019), 45P/Honda–Mrkos–Pajdušáková (DiSanti et al. 2017), C/2006 W3 (Christensen; Bonev et al. 2017), C/2012 K1 (PanSTARRS; Roth et al. 2017), C/2017 E4 (Lovejoy; Faggi et al. 2018), 2P/Encke (Roth et al. 2018), and 16 OCCs (after Dello Russo et al. 2016). Short-period comets are highlighted with bold text, emphasizing the small number for which complete hypervolatile inventories are available. Values for G-Z were taken from each of the three dates for which all three hypervolatiles were sampled, assuming $T_{\rm rot} = 64$ K for July dates and $T_{\rm rot} = 60$ K for October 10. For the October date, the downward- and leftward-facing arrows indicate the (3σ) upper limits CO/CH_4 and C_2H_6/CH_4. Due to the sensitive dependence of $Q(CH_4)$ on assumed $T_{\rm rot}$, the red oval traces the total possible spread in G-Z's hypervolatile content for the range $T_{\rm rot} = 48$–70 K. Each comet is color coded by its mixing ratio CO/H_2O with the exception of C/2006 W3 (Christensen), shown in pink, for which H_2O was not detected. (1) Values for 67P using C_2H_6/H_2O as reported in Le Roy et al. (2015) for the northern hemisphere. (2) Values for 67P using C_2H_6/H_2O as reported in Le Roy et al. (2015) for the southern hemisphere. In both cases, the blue ovals trace the total possible spread in 67P's hypervolatile content.

in short-period comets. Further unraveling the complex relationship between nascent solar system conditions and evolutionary processes in comets clearly requires increasing the sample size of serial measurements in short-period comets, particularly observations targeting hypervolatiles.

6. Comparison to Comets as Measured at Near-infrared Wavelengths

Comprehensive hypervolatile abundances have been securely measured in 19 OCCs to date, yet in only four ecliptic comets, including G-Z. This highlights that statistics for these species in ecliptic comets (particularly CO and CH_4) are far from being firmly established. Figure 7 shows relative hypervolatile abundances reported in all comets to date, including G-Z and measurements taken by *Rosetta* at 67P/Churyumov–Gerasimenko using *Rosetta* Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) measurements of C_2H_6 (Le Roy et al. 2015), Microwave Instrument for the Rosetta Orbiter (MIRO) measurements of CO (Biver et al. 2019), and Visible and Infrared Thermal Imaging Spectrometer (VIRTIS) measurements of CH_4 (Bockelée-Morvan et al. 2016). The particularly low C_2H_6/CH_4 ratio in G-Z (points 22–23) is supported by observations at other wavelengths. Kiselev et al. (2000) reported a blueish linear polarization spectrum for continuum in G-Z at optical wavelengths, and suggested this was caused by the presence of organic grains (or large-sized complex organics). This implies that G-Z is depleted in simple organics, such as C_2H_6, but is enriched in more complex organics, which may indicate that warmer conditions were present during the formation and subsequent evolution of G-Z's constituent ices. Our low measured C_2H_6/CH_4 supports this hypothesis, and together with the observed blueish polarization, may indicate that simple hydrocarbons were efficiently converted into more complex organics in the ices that were incorporated into the nucleus of G-Z.

It is apparent from Figure 7 that hypervolatile abundances among OCCs span a large range of values. Similarly, as the hypervolatile abundances of more ecliptic comets are completely characterized, it appears that they may span a similar range of CO/CH_4 and C_2H_6/CH_4 as that observed among OCCs, from severely depleted (45P/ Honda–Mrkos–Pajdušáková #20 in Figure 7; DiSanti et al. 2017) to near-mean values (2P/Encke, #10; Roth et al. 2018) to (possibly) enriched values in 67P (Le Roy et al. 2015; Bockelée-Morvan et al. 2016; Biver et al. 2019). It is important to note that comparisons between the in-situ measurements of Le Roy et al. (2015) and bulk coma measurements (e.g., this work; Bockelée-Morvan et al. 2016; Biver et al. 2019) are not straightforward, particularly given the differences in R_h between each set of measurements. Additionally, differences in observational circumstances, techniques, and analysis must be kept in mind when comparing results from studies of different comets.

The relative isolation of G-Z in Figure 7 further highlights the spread in hypervolatile abundances among ecliptic comets, reflecting its unique combination of CH_4 being consistent with the mean among OCCs versus the moderately depleted values for CO and C_2H_6. This underscores that much work remains in firmly characterizing the ranges of hypervolatile abundances in ecliptic comets and understanding their implications for placing such measurements into a meaningful context.

7. Summary of Results

We characterized the hypervolatile composition of the prototypical GZ-type comet 21P/Giacobini–Zinner with the powerful, recently commissioned iSHELL spectrograph at the NASA-IRTF on four pre-perihelion dates, two dates near-perihelion, and one post-perihelion date. Combined with previous work, our results suggest that coma abundances of all three hypervolatiles (CO, CH_4, and C_2H_6) may be variable on several timescales, including day-to-day, pre- vs post-perihelion, and even across perihelion passages. However, as noted in Section 5, there are important caveats to our study, and additional serial measurements of G-Z are needed to confirm possible variability in its coma hypervolatile content. In any case, our results suggest the following.

1. Mixing ratios of CO were consistent (within uncertainty) day to day pre-perihelion, but were slightly lower post-perihelion. Our measurements are consistent with depleted values compared to the mean among measured comets, as well as with an upper limit reported from the 1998 perihelion passage (Weaver et al. 1999).
2. Our measurements of CH_4, the most severely under-represented hypervolatile in studies of ecliptic comets, represent its first reported values in G-Z. CH_4 abundances were consistent with mean values among all comets measured, and may have been variable from day to day. However, there are important caveats to the possible variability of CH_4 in G-Z (Sections 4.2, 5.2).
3. We found that the mixing ratio of C_2H_6 decreased significantly pre- versus post-perihelion, its post-perihelion value being consistent with strongly depleted. Our pre-perihelion C_2H_6 mixing ratios were enriched compared to measurements during the same seasonal phase in 2005 (DiSanti et al. 2013), yet our post-perihelion mixing ratio was consistent with the result from 2005.
4. If G-Z is indeed variable, the spread among our measurements, as well as between those from previous perihelion passages, is significantly smaller than the variation in each molecule among all comets measured (Figure 5). This may be evidence that natal conditions dominate over evolutionary effects due to successive perihelion passages in setting the composition of short-period comet 21P/G-Z.

Understanding the cause(s) of the considerable spread of hypervolatile abundances among comets (both OCCs and short-period comets) seen in Figure 7 is necessary for disentangling primordial from evolutionary effects in setting the present-day (observed) abundances of hypervolatiles (and of primary volatiles in general) in comets. On the one hand, chemical models of protoplanetary disks (e.g., Willacy et al. 2015; Drozdovskaya et al. 2016) predict that comets incorporated a wide range of hypervolatile abundances from their formation region(s) in the protosolar nebula. On the other hand, the nontrivial effects of heterogeneous outgassing and seasonal illumination on coma composition, such as that seen by *Rosetta* at 67P (i.e., Hässig et al. 2015; Luspay-Kuti et al. 2015; Bockelée-Morvan et al. 2016; Fougere et al. 2016a, 2016b; Feldman et al. 2018), cannot be overlooked. This emphasizes the high impact of serial observations of comets, particularly those targeting hypervolatiles in ecliptic comets, which may be most indicative of the role that primordial versus evolutionary effects play in setting the composition of comets. Thankfully the availability of next-generation instruments such as iSHELL, capable of delivering the long on-source integration times and excellent sensitivity required for such measurements, is enabling us to better understand the interplay between nascent solar system conditions, evolutionary processing, and coma compositional variability when interpreting the results of primary volatile studies in comets.

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