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1 **Title: Seasonal exposure of carbon dioxide ice on the nucleus of comet**
 2 **67P/Churyumov-Gerasimenko**

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48 **Abstract:**

49 Carbon dioxide is one of the most abundant species in cometary nuclei, but due to its high
50 volatility CO₂ ice is generally only found beneath the surface. We report the infrared
51 spectroscopic identification of a CO₂ ice-rich surface area, located in the Anhur region of comet
52 67P/Churyumov-Gerasimenko. Spectral modeling shows that about 0.1% of the 80×60 m area is
53 CO₂ ice. This exposed ice was observed a short time after exiting from local winter; following
54 the increased illumination, the CO₂ ice completely disappeared over about three weeks. We
55 estimate the mass of the sublimated CO₂ ice and the depth of the surface eroded layer. The
56 presence of CO₂ ice is interpreted as the result of the extreme seasonal changes induced by the
57 rotation and orbit of the comet.

58

59 **One Sentence Summary:** Quantitative characterization of CO₂ ice sublimating on the surface of
60 67P/CG's nucleus due to seasonal effect.

61

62 **Main Text:**

63 On comets, sublimation due to solar illumination is the major mechanism creating the
64 differentiation of volatile species over their long dynamical lifetimes. The penetration of the heat
65 into the nucleus causes chemical stratification with more volatile molecules, such as CO and
66 CO₂, receding into the interior ices, while less volatile molecules, such as water, remain close to
67 the surface and enrich the near surface ices (**1**). The seasonal variability associated with the
68 relatively large orbital eccentricities of comets is further complicated by the irregular shape of
69 the nuclei and by the inclination of their rotation axis, which amplifies the seasonal effects.
70 Thermal evolution models so far did not provide evidence of recondensation neither of fast
71 sublimation of volatile species following an extreme seasonal cycle. 67P/Churyumov-
72 Gerasimenko (67P/CG) confirmed the general volatiles stratification scheme, during the pre-
73 perihelion period, when the spatial distribution of water vapor and carbon dioxide in the gaseous
74 coma was interpreted as due to CO₂ ice sublimating from inner layers, with H₂O ice sublimating
75 closer to the surface (**2,3,4,5,6**). On the other hand, a diurnal cycle of water ice has been found
76 where an ephemeral frost layer is formed following sudden shadowing conditions and day/night
77 variation (**7**).

78 In early 2015 the southern hemisphere of 67P/CG was emerging from shadows and
79 leaving its cold season, when sub-surface temperatures were maintained as low as 25-50 K (**8**).
80 In particular, an area located in the Anhur region (at lon=66.06°, lat= -54.56° in Cheops
81 coordinate frame (**9**)), experienced a four-year-long winter season before being illuminated by
82 the Sun in mid-January 2015.

83 We used the VIRTIS-M (Visible, InfraRed and Thermal Imaging Spectrometer, Mapping
84 Channel) onboard the Rosetta spacecraft (**10**) to detected a carbon dioxide ice-rich area in Anhur
85 region on March 21-22 2015 when the comet was at 2.05 AU from the Sun. This region is 80 by

86 60 m (resolved at 20 m/pixel on VIRTIS-M images), shown in the general context of the
87 nucleus' digital shape model in **Fig. 1**. The deposit is located in a smooth area of the Anhur
88 region, placed on the large lobe of the nucleus (**11**). The same spectral dataset, for which we give
89 additional details in (**12**), has been used to derive quantitative information on CO₂ abundance.
90 The irradiance/solar flux (I/F) spectrum of the pixel showing the more intense absorption
91 features is shown in **Fig. 2**. The I/F is characterized by a steep red spectral slope shortward of 1.5
92 μm , an absorption triplet at 1.97, 2.01, 2.07 μm , and two further absorptions at 2.7 and 2.78 μm .
93 These features correspond to known absorption features of CO₂ so identify the presence of CO₂
94 ice on the surface of 67P/CG. The CO₂ ice fundamental band at 4.26 μm is not visible on I/F
95 spectra due to the thermal emission from the nucleus. A detailed description of the spectral
96 variability across the CO₂ ice rich area, the removal of thermal emission and spectral modeling
97 are given in (**12**).

98 The spectra of the CO₂ ice rich area have been fitted with a radiative transfer model
99 (**13,14**) allowing us to derive quantitative information on endmember abundances, mixing
100 modalities and grain sizes. The I/F spectrum is simulated by using areal and intimate mixtures of
101 two components: the Dark Terrain (DT) unit, corresponding to the measured average organic-
102 rich spectrum of the comet's surface (**15**) after the application of photometric correction (**16**) and
103 carbon dioxide ice derived from optical constants (**17,18**). The composition of the Dark Terrain
104 unit, characterized by low albedo, red slope and a broad absorption feature in the 3.2 μm range,
105 is still uncertain (**19**). In order to check the quality of the spectral retrieval, an additional fit has
106 been performed by replacing carbon dioxide ice with crystalline water ice (**20,21,22**). The
107 VIRTIS spectral mixing and data processing methods are described at length in previous works
108 (**23,24**). The modeling of each individual pixel on which CO₂ ice is detected is discussed in (**12**).

109 The results of the spectral modeling are shown in the left panel of **Fig. 2**. The best fitting
110 model including a water ice component requires 99.7% DT with a slope (necessary to correct for
111 photometric response) of $-3.8\% \mu\text{m}^{-1}$ plus 32 μm water ice grains in areal mixing for the
112 remaining 0.3%. The quality of this fit is very poor however ($\chi^2=3.85$), in particular in the 2.0
113 μm and 2.7-2.8 μm ranges where water ice is not able to reproduce the observed absorption
114 features, indicating its absence in this area. Better fits are achieved by replacing H₂O with CO₂
115 ice, as also shown in **Fig. 2**. We show two possible models. The first corresponds to an intimate
116 mixing (**12**) of 99.2% DT with a $-5.12\% \mu\text{m}^{-1}$ slope plus 0.8% of CO₂ ice grains of 800 μm size.
117 The second case corresponds to an areal mixing of 99.9% DT with a slope of $-4.76\% \mu\text{m}^{-1}$ plus
118 0.1% of 50 μm size CO₂ ice grains. With a residual of $\chi^2=2.05$, the areal solution appears
119 marginally better than the intimate which has $\chi^2=2.45$. The addition of water ice to the
120 components of the mixture does not improve the fit quality. In both models less than 1% of CO₂
121 ice is sufficient to account for the observed spectral absorption features.

122 The CO₂ ice features have been detected on two consecutive days (21 and 22 March
123 2015). This means that the CO₂ ice area was stable against day-night variations in the
124 temperature. However, after the March detection, VIRTIS-M did not observe the Anhur area
125 again until April 12-13 2015, when the heliocentric distance was reduced to 1.87 AU and the
126 pixel scale is reduced from 20 to 39 m/pixel. At this time the spectra acquired did not show any
127 of the previously observed CO₂ absorption features (**Fig. 3**), indicating that the CO₂ ice patch
128 had retreated to a level below the detection limit of the VIRTIS-M instrument (band depth less
129 than 1% relative to the local continuum, corresponding to $<0.1\%$ CO₂ ice abundance), if not
130 disappeared altogether. The reduction of the spatial resolution by a factor about 2 and the
131 increase of the solar phase angle from 54° to 79° occurring between the two sets of observations

132 must be considered in interpreting the disappearance of the CO₂ ice spectral features: apart the
133 change in spatial resolution, the last images are more affected by long shadows caused by local
134 topography, making the detection of the CO₂ ice more difficult. Conversely, assuming a uniform
135 distribution of CO₂ ice in areal mixing with the DT within the initial 80 by 60 m area, one should
136 expect to detect it also on the less resolved images because the instrumental resolution is still
137 within the size of the area of interest.

138 The maximum surface temperature T , derived by modeling the 4.5-5.0 μm thermal
139 emission using a Bayesian method (25), in this area increased from $T=218.8$ K on 21 March
140 2015 to $T=225.9$ K on 13 April 2015. However, as the surface is not isothermal at the sub-pixel
141 scale due to local roughness and shadows, these should be considered as an upper limit,
142 representative only of the warmest fractions of the pixel, corresponding to the more illuminated
143 sub-pixel areas. The measured temperatures are well above the sublimation temperature of CO₂
144 ice, which is about 80 K (26), therefore the CO₂ ice-rich region cannot be in thermal equilibrium
145 with the DT and continuous sublimation must occur. For this reason the intimate mixing between
146 CO₂ ice and DT is much less favorable than the areal. As a result of the sublimation of the
147 volatile species on the surface an increase of the local roughness on the more illuminated areas is
148 very likely to occur.

149 The illumination history of the Anhur CO₂ ice-rich area has been investigated by tracing
150 the variation of the incident solar flux during the time when VIRTIS-M observations were
151 available. Throughout the period January 2011 - January 2015 the Anhur region was in
152 permanent shadow while from January 14 2015 the combined effect of decreasing heliocentric
153 distance and longer insolation caused a net increase of solar flux on the area (Fig. 4). After
154 scaling the instantaneous solar flux with the cosine of the incidence angle calculated using the
155 nucleus digital shape model (27,28), we found that at the time of the carbon dioxide ice detection
156 (March 21-22 2015) the maximum solar flux at local noon was about 80 W/m² (Fig. 4). At the
157 time of the second series of VIRTIS-M observations the maximum solar flux at local noon had
158 increased to about 135 W/m².

159 The integrated solar flux accumulated by an area of 0.4 m², corresponding to the CO₂
160 areal occupancy within the 400 m² VIRTIS-M pixel, is equal to 2.026×10^7 J over 45 rotations of
161 the comet occurring between the VIRTIS-M available observations. Assuming a CO₂ ice latent
162 heat of sublimation of 552 kJ/kg (26) and neglecting the thermal conduction in view of the very
163 low thermal inertia reported for 67P/CG (8,29), we derive (further details are given in (12)) a
164 value for the total amount of sublimated ice of 35 kg, equivalent to the erosion of a 5.6 cm thick
165 layer. This value is an upper limit, assuming a complete sublimation of the ice during 45
166 rotations. A similar estimate, performed from the beginning of the illumination conditions in
167 early January 2015 until the time of the carbon dioxide ice detection, gives an additional
168 sublimated ice mass of 22 kg. Hence, the area within a VIRTIS-M pixel has experienced a
169 maximum sublimation of 57 kg of CO₂ ice, corresponding to an erosion of a 9 cm layer, in about
170 three months. The temporal trend of the cumulative CO₂ ice sublimation mass is shown in Fig. 4.

171 This amount of sublimated CO₂ ice is too small to contribute significantly to the gaseous
172 coma emissions. Above the south hemisphere VIRTIS has detected a CO₂/H₂O ratio of about 4%
173 (4) but no evidence has been found of increased H₂O or CO₂ gaseous activity in the surrounding
174 of the Anhur region from VIRTIS-M spectra. In fact, even assuming a sublimation rate of 1 kg of
175 CO₂ ice per day from a 20 by 20 m area, the resulting column density of 10¹⁷ m⁻² in the ambient
176 coma is about two orders of magnitude lower than the average value of 10¹⁹ m⁻² measured by
177 VIRTIS-M (4).

178 The observation of the CO₂ ice-rich spot was unexpected at these heliocentric distances
179 due to the high volatility of carbon dioxide; water ice, a less volatile species, was not observed in
180 the same region at the same time, as sustained by spectral fit shown in *Fig. S5* in ref. (12).
181 67P/CG falls in the ensemble of the CO₂ rich comets as demonstrated by the high activity level
182 of CO₂ above the southern hemisphere where the ratio CO₂/H₂O is considerably larger than in
183 the northern hemisphere (4,30).

184 The OSIRIS instrument did observe water ice in this same region (31) in April-May
185 2015, about six weeks after the initial detection of the CO₂ ice by VIRTIS-M. At this time, by 4
186 May 2015, the VIRTIS-M IR channel has stopped operating, due to the permanent failure of the
187 active cooler, making impossible to further study the temporal evolution of the Anhur area. Until
188 then, the entire part of the southern hemisphere illuminated by the Sun was observed by VIRTIS-
189 M with a spatial resolution between 20 and 40 m/pixel. So far, the presence of the CO₂ ice has
190 been recognized only in the Anhur area discussed in this study, localized approximately between
191 a slope and a flat terrain showing a regular topography on OSIRIS images (31). The morphology
192 and the illumination conditions above this place are similar to many other neighborhood areas
193 observed by VIRTIS-M.

194 The presence of CO₂ ice at the surface of the nucleus thus appears to be an ephemeral
195 occurrence, which provides clues to the emplacement mechanism. After perihelion passage, the
196 activity of a cometary nucleus starts to decrease, with water sublimation decreasing first.
197 Nucleus thermodynamical modeling (1) shows that a stratigraphy associated to the volatility of
198 the major gaseous species is produced on the outer layers. However, the combination of spin axis
199 inclination and nucleus shape is such that the Anhur CO₂ ice-rich area experiences a fast drop in
200 the illumination going into permanent shadow quickly after equinox and, consequently, quickly
201 reducing the surface temperatures in winter to less than $T=80$ K, while the interior remains
202 warmer for a longer time due to the low thermal inertia (8,29). Sublimation of water ice at depth
203 is prevented but not that of CO₂, which can continue to flow from the interior to the surface
204 where it begins to freeze due to the low surface temperatures. Moving further towards the
205 aphelion, the low surface temperatures are able to preserve the CO₂ ice on the surface and to
206 grow >100 μ m size grains until, on the next orbit, it is exposed again to sunlight and sublimates
207 away. This inverse-temperature profile of cometary surfaces (warmer inside and cooler on the
208 surface) going into winter (in permanently shadowed regions) subsequent to perihelion could
209 potentially freeze other volatiles that are sublimed from the warmer interior as well. Based on the
210 temperature of these surface areas, more volatiles species such as CO and CH₄ could also be
211 frozen until the next exposure to solar photons occurs. The same phenomenon could also explain
212 why no water ice was seen at this site during the initial exposure to the sun, as the H₂O-ice would
213 have been frozen at lower depths than the CO₂ ice.

214 In summary, the 67P/CG nucleus shows two different temporal activity cycles caused by
215 H₂O and CO₂ ices present in different regions: while water ice has diurnal variability, with
216 surface sublimation and condensation cycle occurring in the most active areas (7), the surface
217 condensation of carbon dioxide ice has a seasonal dependence. Similar processes are probably
218 common among many Jupiter family comets, which share with 67P/CG short revolution periods
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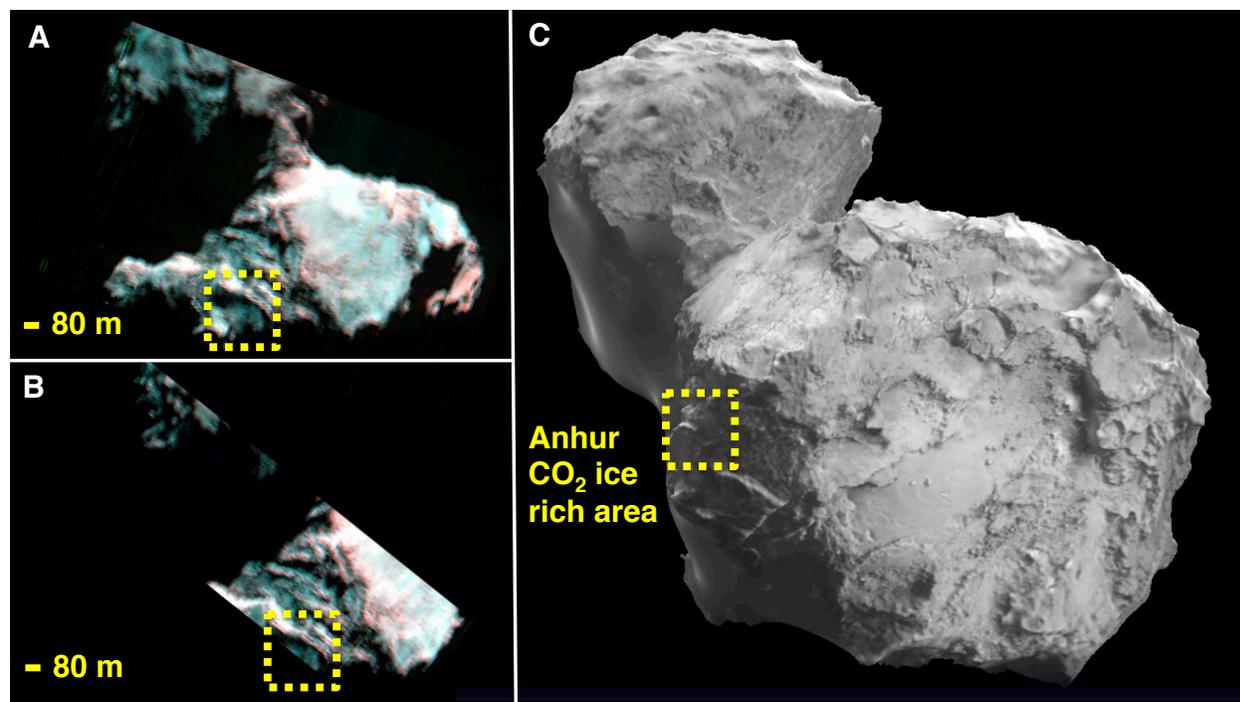
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Figures captions:



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Fig. 1. VIRTIS-M infrared images of the Anhur CO₂ Ice-Rich Area on March 21-22 2015.
The center of the yellow line dashed area indicates the location of the carbon dioxide rich patch

378 on two VIRTIS-M images (I1_00385598211 in panel A and I1_00385688463 in panel B) and on
 379 the nucleus shape model rendering (from <http://sci.esa.int/comet-viewer/?model=esa>, panel C).
 380 VIRTIS-M color images are a RGB combination of IR bands (blue at 1.2 μm , green at 2.0 μm
 381 and red at 4.0 μm). A description of the VIRTIS-M acquisitions is given in (12).

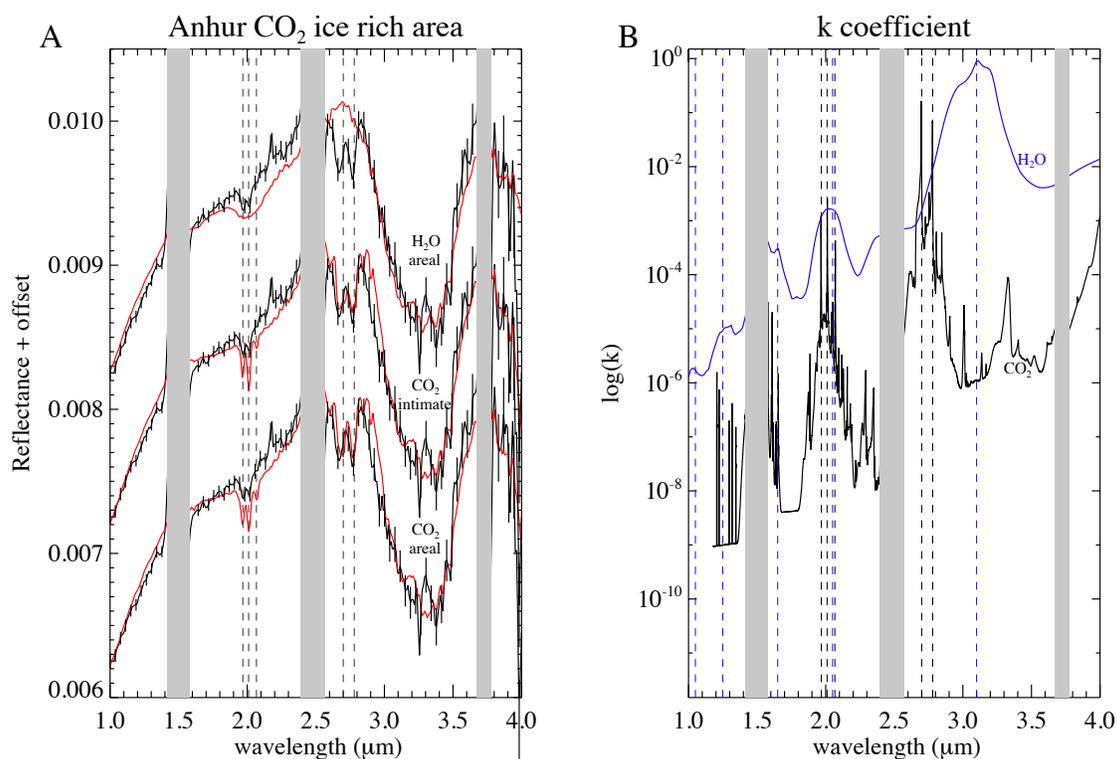
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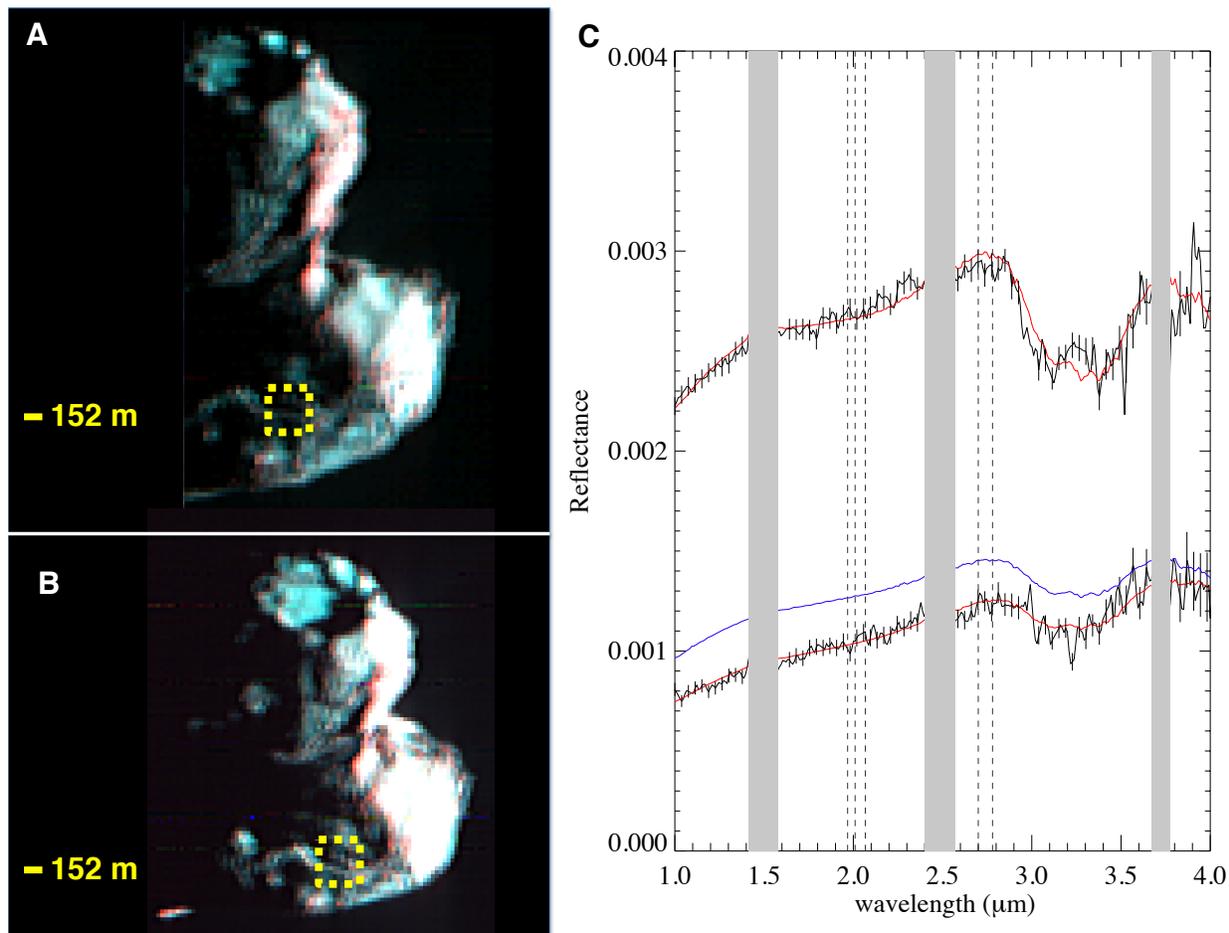
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389 **Fig. 2. Spectral modeling of the CO₂ surface ice on March 21 2015 observation.** Panel A:
 390 VIRTIS-M reflectance (black curve, from observation I1_00385598211, pixel s=126, l=109) and
 391 spectral simulations carried out with Dark Terrain (DT) and H₂O ice in areal mixing (top, plus
 392 0.002 offset), DT and CO₂ ice in intimate mixing (centre, plus 0.001 offset) and areal mixing
 393 (bottom) for the Anhur CO₂ ice-rich area. Spectral intervals marked in gray correspond to
 394 missing data due to instrumental order sorting filters. Error bars, shown every 5 bands to
 395 improve readability, give the instrument noise on the pixel. A description of VIRTIS-M
 396 acquisitions is given in (12). Panel B: imaginary part k of refractive indices for H₂O ice (blue
 397 curve) and CO₂ ice (black curve). Optical constants for CO₂ are from ref. (17,18) and for H₂O
 398 from ref. (20,21,22). Vertical lines mark the k local maxima corresponding to the strongest
 399 absorption bands at 1.05, 1.25, 1.65, 2.05, 3.10 μm for H₂O (in blue color) and at 1.97,
 400 2.01, 2.07, 2.70, 2.78 μm for CO₂ ice (in black color, also shown in panel A).

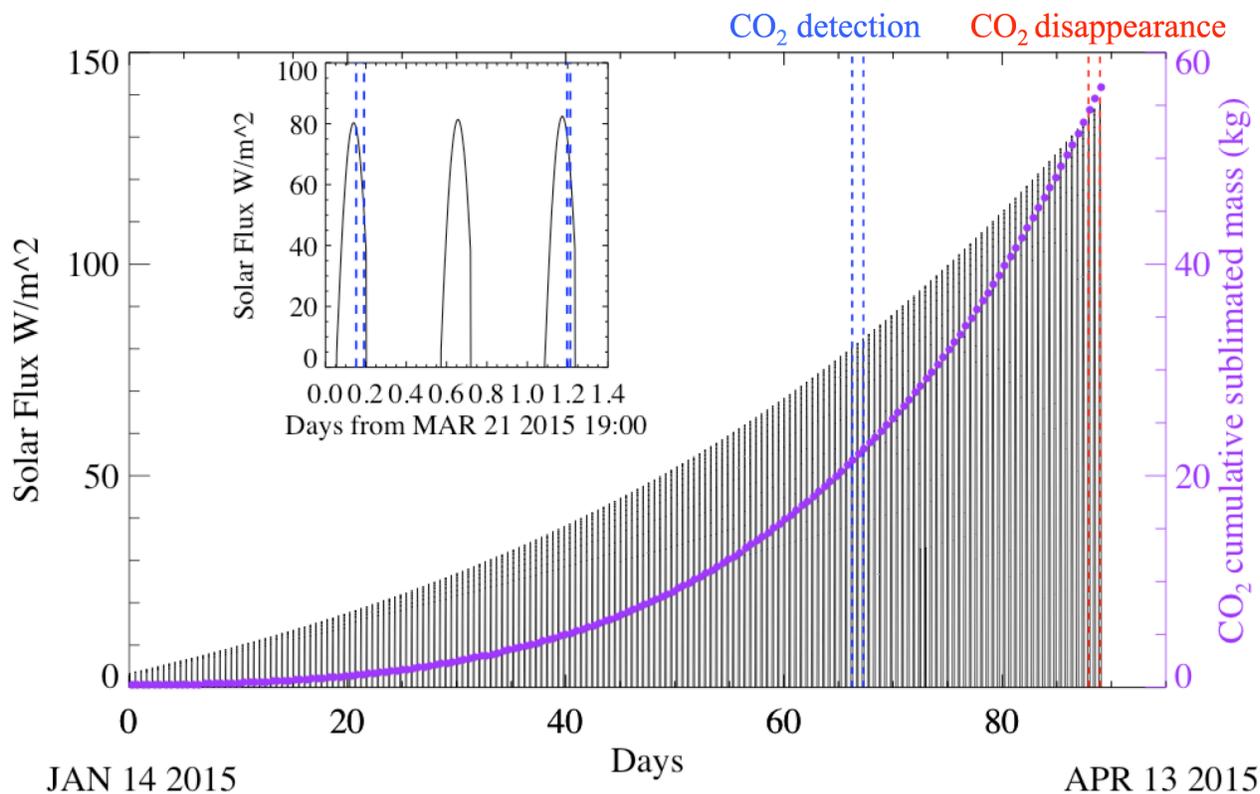
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411 **Fig. 3. The disappearance of the CO₂ surface ice by April 12-13 2015:** VIRTIS-M
412 acquisitions I1_00387470597 (panel A and bottom black plot on panel C) and I1_00387561494
413 (panel B and top black plot on panel C). Spectral modeling results with pure Dark Terrain (DT)
414 are shown in red for the two acquisitions. The position of the Anhur CO₂ ice deposit previously
415 observed is marked by the center of the yellow line dashed area. Panel C: reflectance of the
416 Anhur CO₂ ice-rich area on the two acquisitions do not show the diagnostic triplet absorption at
417 2.0 μm nor the bands at 2.7 and 2.78 μm (dashed vertical lines). The wide feature at 3.2 μm is
418 the DT absorption due to organic material which show a depth correlated with the local
419 reflectance level. For reference, the average DT reflectance as derived from Ref. (16) is shown
420 (blue curve). A description of VIRTIS-M acquisitions and spectral modeling are given in (12).

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 424 **Fig. 4. Variation of the solar flux reaching Anhur CO₂ ice rich area between January 14 -**
 425 **April 13 2015.** The vertical dashed lines indicate the time of the four VIRTIS observations
 426 described in the text: CO₂ ice has been detected during the first two (marked in blue, see zoom in
 427 the inset panel) while it has disappeared in the last two (marked in red). The CO₂ cumulative
 428 sublimated mass during this timeframe is shown by the purple curve. All values are relative to
 429 one VIRTIS pixel area (20 by 20 m) at the time of the CO₂ detection.

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