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# Low Water outgassing from (24) Themis and (65) Cybele – 3.1 $\mu\text{m}$ NIR spectra implications

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## Abstract

Asteroids (24) Themis and (65) Cybele have an absorption feature at 3.1  $\mu\text{m}$  reported to be directly linked to surface water ice. We searched for water vapour escaping from these asteroids with the Herschel Space Observatory Heterodyne Instrument for the Far Infrared (HIFI). While no  $\text{H}_2\text{O}$  line emission was detected, we obtain sensitive  $3\sigma$  water production rate upper limits of  $Q(\text{H}_2\text{O}) < 4.1 \times 10^{26} \text{ mol. s}^{-1}$  for Themis and  $Q(\text{H}_2\text{O}) < 7.6 \times 10^{26} \text{ mol. s}^{-1}$  for Cybele. Using a Thermophysical Model (TPM), we merge data from Subaru/Comics and Herschel/SPIRE with the contents of a multi-observatory database to derive new radiometric properties for these two asteroids. For Themis, we find a thermal inertia  $\Gamma = 20^{+25}_{-10} \text{ J m}^{-2} \text{ s}^{-1/2} \text{ K}^{-1}$ , a diameter  $192^{+10.7}_{-7} \text{ km}$  and a geometric V-band albedo  $p_V = 0.07 \pm 0.01$ . For Cybele we obtain a thermal inertia  $\Gamma = 25^{+28}_{-19} \text{ J m}^{-2} \text{ s}^{-1/2} \text{ K}^{-1}$ , a diameter  $282 \pm 9 \text{ km}$ , and an albedo  $p_V = 0.042 \pm 0.005$ . Using all inputs, we estimate that water ice intimately mixed with the asteroids' dark surface material would cover  $< 0.0017\%$  for Themis and  $< 0.0033\%$  for Cybele of their surfaces, while an areal mixture with very clean ice (bond albedo 0.8 for Themis and 0.7 for Cybele) would cover  $< 2.2\%$  for Themis and  $< 1.5\%$  for Cybele, of their surfaces. While surface (& sub-surface) water ice may exist in small localized amounts on both asteroids, it is not the reason for the observed 3.1  $\mu\text{m}$  absorption feature.

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## 1. INTRODUCTION

Observational and theoretical data suggest that solar system objects located in the main asteroid belt hold more water ice than originally thought. Indeed the detection of water vapour on (1) Ceres (Küppers et al. 2014; Combe et al. 2016), asteroids that present cometary behaviour (active asteroids - Hsieh & Jewitt 2006), and  $3.1\ \mu\text{m}$  absorption features in asteroid reflectance spectra (Campins et al. 2010; Licandro et al. 2011) have reinforced this line of thinking. Hydrated minerals (any mineral containing  $\text{H}_2\text{O}$  or  $\text{OH}$ ) and water ice are known to have strong spectral absorptions in the  $\sim 2.5\text{--}3.5\ \mu\text{m}$  wavelength range (Rivkin et al. 2002). Features at  $0.7\ \mu\text{m}$  and  $2.7\ \mu\text{m}$  are attributed to the presence of hydrated minerals and those at  $\sim 3.05\ \mu\text{m}$  to water ice.

Takir & Emery 2012 examined the distribution and abundance of hydrated minerals on 28 outer main-belt asteroids and proposed four  $3\ \mu\text{m}$  spectral groups based on the absorption shapes observed: Ceres-like, Europa-like, rounded and sharp. Of the four absorption shapes, only the rounded  $3\ \mu\text{m}$  band shape has been linked to the presence of water ice on the surface. Besides being observed on both Themis (Fornasier et al. 1999; Rivkin & Emery 2010; Campins et al. 2010) and 65 Cybele (Licandro et al. 2011), it has been found on numerous other asteroids e.g. (76) Freia (Hargrove et al. 2012), (361) Bononia (Usui et al. 2019), correlating well with laboratory experiments suggesting (Rivkin & Emery 2010) that a fine coating of ice on pyroxene grains mixed with amorphous carbon was covering the entire surface of these asteroids.

(24) Themis is the parent body of the Themis family of asteroids located at the edge of the Main Belt consisting of about 5000 members (Nesvorný et al. 2012), mostly belonging to primordial C and B-type (Fornasier et al. 2016a). In addition, to the  $3.1\ \mu\text{m}$  feature, the asteroid also has an absorption feature at approximately  $2.76\ \mu\text{m}$  associated with hydrated minerals (Usui et al. 2019), with no feature at  $0.7\ \mu\text{m}$ . (65) Cybele, a P-type asteroid, is the most prominent member of a primitive outer edge main-belt asteroid population, known as the Cybele asteroids. Although it has the  $3.1\ \mu\text{m}$  feature, the asteroid has no hydrated features at  $0.7\ \mu\text{m}$  nor at  $2.76\ \mu\text{m}$  (Usui et al. 2019).

Besides the search therefore for hydration in asteroids with spectral features from hydroxyl-bearing minerals (Takir & Emery 2012; Usui et al. 2019) or oxidized iron in phyllosilicates (Fornasier et al. 2014), the detection of gaseous water vapour or its disassociation products provide a more direct way to identify the presence of water. Up to now water vapour has not been detected on Themis or Cybele although upper limits have been derived for each.

Optical spectra was obtained (Jewitt & Guilbert-Lepoutre 2012) of the two asteroids from the Keck I  $10\ \text{m}$  telescope to search for outgassed CN, a photodissociation product of HCN. An average  $\text{CN}/\text{H}_2\text{O}$  ratio of 0.3% was applied (as done for comets) to these asteroids, and upper limits for the water production rate of  $Q(\text{H}_2\text{O}) < 1.3 \times 10^{28}\ \text{mol. s}^{-1}$  for Themis and  $Q(\text{H}_2\text{O}) < 1.2 \times 10^{28}\ \text{mol. s}^{-1}$  were derived. A global coverage of water ice was discarded by the authors with these upper limits constraining the ice coverage on the Earth-facing asteroids surface to be less than 10% based upon the presence of “relatively clean” (non-mixed) ice with a bond Albedo  $> 0.3$ .

Radio and UV observational searches for OH emission around Themis were performed (Lovell et al. 2010) using the National Radio Astronomy Observatory (NRAO) 100-m Green Bank Telescope (GBT) and the Lowell Observatory 1.1-m Hall Telescope. A  $3\sigma$  upper-limit for  $Q(\text{H}_2\text{O})$  of  $1 \times 10^{28} \text{ mol. s}^{-1}$  was obtained.

A more recent study (McKay et al. 2017) presented the result of a non-detection following a search for gaseous  $\text{H}_2\text{O}$  at optical wavelengths using the forbidden oxygen line at  $6300.3 \text{ \AA}$  in line with similar observations performed on comets (McKay et al. 2014, 2015). While no detection was made, an upper limit of  $Q(\text{H}_2\text{O}) < 4.5 \times 10^{27} \text{ mol. s}^{-1}$  was provided for Themis and conclusions equivalent to Jewitt & Guilbert-Lepoutre (2012) were reached as regards the localized nature and purity of the ice needed to match the upper limit obtained.

The Heterodyne Instrument for the Far Infrared (HIFI; de Graauw et al. 2010) on board the ESA *Herschel Space Observatory* (Pilbratt et al. 2010) has proven to be the most sensitive instrument ever built for directly observing water vapour on comets (Bockelée-Morvan et al. 2010) as well as in the asteroid belt. Indeed, it was through use of the HIFI instrument that  $\text{H}_2\text{O}$  gas was successfully detected around (1) Ceres (Küppers et al. 2014).

In section 2 the observations obtained by the HIFI instrument of Cybele and Themis as well as those from Subaru/COMIC (Cooled Mid-Infrared Camera and Spectrometer) and the Herschel/SPIRE (Spectral and Photometric Imaging Receiver) instrument are presented and the data analysed. In section 3 we present new radiometric properties derived from our Thermophysical Model (TPM). In section 4 we feed in our radiometric properties to derive upper limits for the water production rate of both asteroids. In section 5, we calculate the fraction of ice coverage required to achieve this upper limit, discuss our results and present our conclusions.

## 2. OBSERVATIONS & DATA ANALYSIS

### 2.1 Herschel HIFI observations

Themis was observed with the HIFI instrument on Herschel on 2012 January 30 (see Table 1). The asteroid was travelling in-bound (2.92 au) and close to perihelion (2.75 au) when the observation was carried out. Cybele was observed with the HIFI instrument on Herschel on 2012 December 21 (see Table 1) when the asteroid was 3.52 au from the sun and was outbound having already passed aphelion (3.8 au). It's important to highlight that with the low escape velocity from these asteroids, any escaping water vapour would have been visible to Herschel independent of its source location as the footprint of the telescope was much larger than the asteroids themselves.

The line emission from the fundamental *ortho*- $\text{H}_2\text{O}$   $1_{10}-1_{01}$  line at 556.936 GHz was searched for in the lower sideband of the HIFI band 1b mixer. The observations were performed in the frequency-switching observing mode, using both the wide-band spectrometer (WBS) and the high-resolution spectrometer (HRS). The spectral resolution of the WBS is 1 MHz ( $0.54 \text{ km s}^{-1}$  at the frequency of the observed line),

while the HRS was used in its high-resolution mode with a resolution of 120 kHz ( $0.065 \text{ km s}^{-1}$ ). Initial processing of the HIFI data set was carried out using the standard HIFI processing pipeline of HIPE v15.0.1 (Herschel interactive processing environment; Ott 2010), followed by processing with the GILDAS CLASS Software.

In CLASS, vertical and horizontal polarizations were folded and averaged. The frequency switching observing mode introduces quite a strong baseline ripple, which was removed through a polynomial baseline correction performed on the final spectra. The averaged and baseline corrected HRS spectra of the two asteroids are shown in Fig. 1(a) and (b). The pointing offset of both the vertical and the horizontal polarization spectra is  $3.5''$  in band 1b with respect to the target position. The Half Power Beam Width (HPBW) is  $38.1''$  at 557 GHz. The main beam brightness temperature scale was computed using a forward efficiency of 0.96 and a beam efficiency of 0.62. The output line area r.m.s. values are provided in Table 2.

Although the  $\text{H}_2\text{O}$  line is not detected in the resultant spectra for either of the two asteroids, sensitive upper limits could be derived. Table 2 provides a summary of the  $1\sigma$   $\text{J TmBdv}$  line area upper limits calculated for both asteroids. The  $1\sigma$  upper limits were computed on a  $[-1, 1 \text{ km s}^{-1}]$  window. The mean of the HRS and WBS derived values have been used to derive the  $3\sigma$  upper limits of  $8.7 \text{ mK km s}^{-1} \text{ J TmBdv}$  for Themis and  $8.5 \text{ mK km s}^{-1} \text{ J TmBdv}$  for Cybele.

## 2.2 Observations used for the radiometric analysis

### 2.2.1 Database of existing observations

For the radiometric analysis of these two asteroids we used a wide range of thermal IR and submm/mm measurements. Contrary to Cybele, Themis has not been well observed at thermal IR wavelengths. Besides using a Spitzer-IRS spectrum (Landsman et al. 2016), our study was limited to AKARI and WISE measurements. We used two different AKARI datasets; the first was taken from the SBNAP public database<sup>10</sup> (Szakáts et al. 2020) and originated from the IRC instrument using the MIR-S ( $5.8\text{--}14.1 \mu\text{m}$ ) and the MIR-L ( $12.4\text{--}26.6 \mu\text{m}$ ) cameras. For the second, produced by the IRC-NIR camera, we used the spectral data in the range  $4.5$  to  $5.0 \mu\text{m}$  only (Usui et al. 2019) where the fluxes are pure thermal emission. We note that in the case of the WISE data, the W3 data ( $11.10 \mu\text{m}$ ) was strongly saturated and the saturation-corrected fluxes problematic while the W4 ( $22.64 \mu\text{m}$ ) data was only partly saturated and the saturation-corrected fluxes of good quality. We added to these observational datasets the Subaru/COMICS dataset as presented in section 2.2.2.

In the case of Cybele, there exists a significant set of observational data available for our radiometric study. In particular, we used Herschel-PACS data (Alí-Lagoa et al. 2020), IRAS (Tedesco et al. 2002) and AKARI measurements (Usui et al. 2011) both extracted from the SBNAP public database (Szakáts et al. 2020); UKIRT-MAX and ISO-ISOPHOT data (Müller & Lagerros 1998, 2002); AKARI data

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<sup>10</sup> <https://ird.konkoly.hu/>

(Usui et al. 2019); multiple ground-based data from literature and archives, as well as additional spectroscopic and photometric data from ISO-ISOPHOT and ISO-ISOCAM (Müller & Blommaert 2004b) and finally Spitzer-IRS data (Licandro et al. 2011). We added to this the Herschel SPIRE as explained in section 2.2.3

### **2.2.2 Subaru/COMICS datasets for Themis**

The Mid-infrared photometric observations for Themis were conducted using the Cooled Mid-Infrared Camera and Spectrometer (COMICS; Kataza et al. 2000) installed at the f/12 Cassegrain focus of the 8.2 m Subaru Telescope. The 320 x 240 pixel Si:As BIB detector for COMICS has 50  $\mu\text{m}$  square pixels, giving a 42" x 32" field of view with a pixel scale of 0.135". The N-band filters were centered on 8.8  $\mu\text{m}$  and 11.7  $\mu\text{m}$ , and 12.4  $\mu\text{m}$  with effective bandwidths of 0.8 and 1.0  $\mu\text{m}$  were utilized. See Table 1.

To reduce the atmospheric and telescopic background radiation, a standard chopping and nodding method was used. HD108985 was selected as an absolute calibration star (Cohen et al. 1999) as it was positioned near to Themis in the sky. The fluxes of Themis and HD108985 as provided in Table 2 were measured through circular apertures with a diameter of more than four times that of the full-width at half maximum size, using the APPHOT function in the IRAF software. Since the colour difference between the spectral energy distributions of Themis and that of HD108985 in the N88 and 11.7 filter were found to be about a few percent, colour corrections for observations with COMICS were not performed.

### **2.2.3 SPIRE datasets for Cybele**

The Herschel SPIRE instrument covering 3 far-infrared bands – 250  $\mu\text{m}$ , 350  $\mu\text{m}$  and 500  $\mu\text{m}$  - observed Cybele nine times during the period 2009-2012. See Table 1. The observations were taken directly from the Herschel Science Archive<sup>11</sup>. Photometry was carried out using the Timeline Fitter method available in HIPE. The derived total monochromatic flux densities were colour corrected to account for the assumed spectral index of  $\alpha=2$ . A flux calibration uncertainty of 5.5% was added in quadrature for the total error budget. The output fluxes corresponding to the three SPIRE wavelength bands and associated errors are provided in Table 2.

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<sup>11</sup> The Herschel Science Archive web page : [https://herchel.esac.esa.int/Science\\_Archive.shtml](https://herchel.esac.esa.int/Science_Archive.shtml)

Target	Observatory & Instrument	OBSID	Date/Time (UT)	rh (au)	$\Delta$ (au)	$\alpha$ (°)
Themis	Herschel HIFI (556.936 GHz)	1342262585	2013.01.30 17:30:38	2.92	2.37	18.1
	Subaru COMICS (N-band 8.8 $\mu\text{m}$ )	n/a	2003.06.20 06:46:30	2.87	2.64	20.7
	Subaru COMICS (N-band 11.7 $\mu\text{m}$ )	n/a	2003.06.20 06:43:30	2.87	2.64	20.7
Cybele	Herschel HIFI (556.936 GHz)	134225765	2012.12.21 16:53:19	3.52	3.11	15.5
	Herschel SPIRE (Large Map)	134187509	2009.12.01 13:14:28	3.45	3.27	16.6
	(250/350/500 $\mu\text{m}$ )	134187511	2009.12.01 13:44:47	3.45	3.27	16.6
		134228344	2011.09.08 16:48:43	3.80	4.09	14.1
		134230779	2011.10.10 22:51:21	3.79	3.61	15.2
	Herschel SPIRE (Small Map)	134244177	2012.04.12 19:47:23	3.72	3.86	15.1
	(250/350/500 $\mu\text{m}$ )	134244840	2012.04.22 18:30:51	3.72	3.99	14.4
		134254082	2012.10.28 19:50:08	3.57	3.93	14.2
		134255059	2012.11.15 00:37:22	3.56	3.68	15.6
		134257368	2012.12.17 23:39:25	3.53	3.16	15.7

**Table 1 : Observations & Observing conditions for the previously unpublished measurements used in this paper.** Columns : Target (the 2 asteroids), Observatory & Instruments used, OBSID (Observation ID reference number), Date and time in UT, rh (heliocentric distance),  $\Delta$  (Earth to asteroid distance),  $\alpha$  (Phase angle).

Target	Herschel/HIFI		Subaru/COMICS			Herschel/SPIRE					
	Line area	Line area	Air	Flux	Err	PSW	PSW	PMW	PMW	PLW	PLW
	$1\sigma$ mK km s <sup>-1</sup> (HRS)	$1\sigma$ mK km s <sup>-1</sup> (WBS)	mass	(Jy)	(Jy)	Flux (Jy)	Err (Jy)	Flux (Jy)	Err (Jy)	Flux (Jy)	Err (Jy)
Themis	2.98	2.82	1.27	3.81	0.22						
			1.26	11.50	0.66			n/a			
						1.680	0.092	0.896	0.049	0.450	0.025
Cybele	2.96	2.68	n/a			1.181	0.065	0.630	0.035	0.307	0.017
						0.993	0.055	0.528	0.029	0.260	0.015
						0.857	0.047	0.459	0.025	0.229	0.013
						0.937	0.052	0.493	0.027	0.246	0.014
						1.040	0.057	0.546	0.030	0.271	0.015
						0.795	0.044	0.411	0.023	0.201	0.012
						1.673	0.092	0.883	0.049	0.431	0.024
						1.669	0.092	0.874	0.048	0.431	0.024

**Table 2 : Output results following processing of the data in Table 1.** Columns : Target (the two asteroids), Herschel/HIFI Instrument (the calculated line areas for the HRS and WBS spectra for both asteroids), Subaru/COMICS instrument (the airmass, flux & error obtained for Themis), Herschel/SPIRE Instrument (the fluxes and errors derived from the SPIRE 250/350/500  $\mu$ m observations of Cybele).



### 3. THERMOPHYSICAL MODELLING OF THE TWO ASTEROIDS

A thermophysical model (Lagerros 1996,1998; Müller & Lagerros 1998, 2002) was used to derive the radiometric properties of the two asteroids. This model has been successfully used in the study of near-Earth asteroids (Müller et al. 2004a, 2011, 2012), of main-belt asteroids (Müller & Blommaert 2004b; O'Rourke et al. 2012), and also of more distant objects (Lim et al. 2010, Müller et al. 2019).

For both asteroids, we performed a radiometric analysis combining all available mid-to-far-IR measurements with the Subaru/COMICS and Herschel/SPIRE values as described in section 2.2 of this paper and presented in Tables 1 and 2.

For our work we followed a similar strategy as in Alí-Lagoa et al. (2020) and references therein. In the case of Themis, non-convex spin-shape solutions (Viikinkoski et al. 2017; based on two spin solutions from Hanuš et al. 2016) as well as two simpler convex solutions (DAMIT database) were tested against the available thermal measurements presented in section 2.2 in our model. Since the data coverage in rotational phase, phase angles, aspect angles or wavelength was very limited, it was not possible to identify the object's true spin and shape properties via our  $\chi^2$  approach.

We obtained a best fit however using the second convex spin-shape solution with  $(\lambda_{\text{ecl}}, \beta_{\text{ecl}}) = (137^\circ, 59^\circ)$  and  $P_{\text{sid}} = 8.374187$  h. This model has 2040 surface elements and 1022 vertices<sup>12</sup> (model ID1006; Hanuš et al. 2016). Our resulting derived radiometric properties are: thermal inertia  $\Gamma = 20^{+25}_{-10}$  J m<sup>-2</sup> s<sup>-1/2</sup> K<sup>-1</sup>, effective diameter  $D_{\text{eff}} = \text{diameter } 192^{+10}_{-7}$  km and a geometric V-band albedo  $p_v = 0.07 \pm 0.01$ , (connected to an absolute V-band magnitude of  $H=7.11$  mag from Oszkiewicz et al. (2011)) for an intermediate to low level of surface roughness ( $0.1 < r.m.s < 0.5$ ) (Table 4). See Figure 1c (left-image) and 1d (left plot) for the Themis TPM output. While this multi-observatory dataset output provides a diameter consistent with previously published values it is lower than the NEATM derived measurements based on Spitzer of  $218 \pm 1$  km (Hargrove et al. 2015)..

For Cybele, Viikinkoski et al. (2017) were able to eliminate the pole ambiguity via multiple AO images using a non-convex shape model with a spin pole at  $(\lambda_{\text{ecl}}, \beta_{\text{ecl}}) = (208 \pm 1^\circ, -3 \pm 3^\circ)$  and  $P_{\text{sid}} = 6.081435$  h. They estimated a diameter of  $296 \pm 25$  km, which is within  $1\sigma$  of the earlier published radiometric diameter of  $273 \pm 11$  km (Müller & Blommaert 2004b) and also that published by Alí-Lagoa et al. (2020).

Alí-Lagoa et al. (2020) analysed IRAS, AKARI and Herschel-PACS measurements using the latest spin-shape solution (ADAM model by Viikinkoski et al. (2017)) with a spin-pole at  $(\lambda_{\text{ecl}}, \beta_{\text{ecl}}) = 208^\circ \pm 1^\circ, -3^\circ \pm 3^\circ$  and a rotation period of 6.08 h. They found that a best-fitting radiometric diameter of  $277^{+4}_{-2}$  km and a thermal inertia value of  $30^{+10}_{-15}$  J m<sup>-2</sup> s<sup>-1/2</sup> K<sup>-1</sup> could explain these thermal fluxes very well based on a reduced  $\chi^2$  minimum  $< 1$ . Therefore, we used, as in the case of Themis, the shape model with the size as a free parameter.

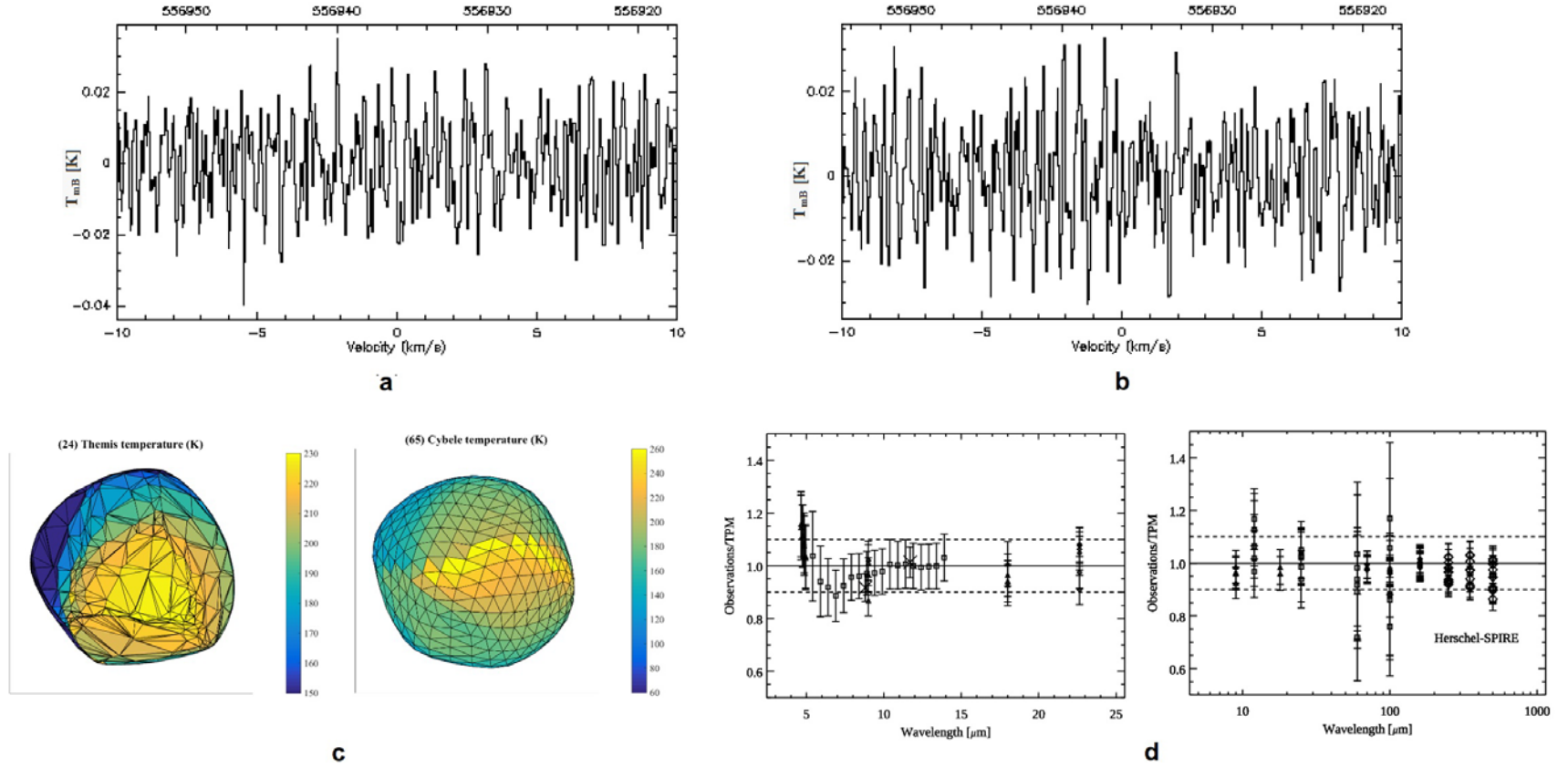
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<sup>12</sup> [https://astro.troja.mff.cuni.cz/projects/damit/asteroid\\_models/view/1006](https://astro.troja.mff.cuni.cz/projects/damit/asteroid_models/view/1006)

In our work we used the same non-convex shape model of Cybele as in Ali-Lagoa et al. (2020) which has 2040 surface elements and 1022 vertices<sup>13</sup> (DAMIT Database ID1843) with a spin pole at  $(\lambda_{\text{ecl}}, \beta_{\text{ecl}}) = (207, -6)$  and  $P_{\text{sid}} = 6.081435$  h. The reduced  $\chi^2$  minimum was at 0.75 for an intermediate surface roughness (rms of surface slopes of 0.4). We find an effective diameter  $D_{\text{eff}} = 282 \pm 9$  km, a best-fit thermal inertia of  $\Gamma = 25^{+28}_{-19}$  J m<sup>-2</sup> s<sup>-1/2</sup> K<sup>-1</sup>, and a geometric V-band albedo of  $p_V = 0.042 \pm 0.005$  (connected to an absolute V-band magnitude of  $H=6.82$  mag from Oszkiewicz et al. (2011)) (Table 4). Our solution was found to match all photometric IR data points as well as the Spitzer-IRS spectrum and the ISO-ISOCAM CVF spectrum (except in the range of the emission feature discussed in Müller & Blommaert (2004b)). See Figure 1c (right image) and 1d (right plot) for the resultant TPM output. The inclusion of the SPIRE data contributed to confirm that Cybele shows a normal sub-mm (spectral) emissivity behaviour similar to many other large regolith-covered main-belt asteroids like Ceres, Pallas and Juno (Müller & Lagerros 1998).

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<sup>13</sup> [https://astro.troja.mff.cuni.cz/projects/damit/asteroid\\_models/view/783](https://astro.troja.mff.cuni.cz/projects/damit/asteroid_models/view/783)



**Figure 1: Averaged HIFI Spectra and Thermophysical modelling output.** HRS averaged spectra for (a) asteroid Themis and (b) asteroid Cybele with TPM outputs (c) for Themis (left) and Cybele (right). These outputs represent the Herschel view with orientation “ecliptic-sky” at the specific HIFI observing start epochs. Plots (d) show for Themis (left) and Cybele (right) the observations divided by the TPM predictions using the best solution described in the text as a function of wavelengths. For Themis, the data shown are the good photometric data points coming from Spitzer-IRS ( $\square$ ), Subaru (X), Akari below 5  $\mu\text{m}$  and above 18  $\mu\text{m}$  ( $\Delta$ ) and WISE-W4 at 22  $\mu\text{m}$  ( $\blacklozenge$ ) while for Cybele: IRAS ( $\square$ ), AKARI ( $\Delta$ ), PACS ( $\blacklozenge$ ), SPIRE ( $\blacklozenge$ ), ISOCAM (X), Spitzer-IRS ( $\blacklozenge$ ), with identification linked to wavelength.

#### 4. OUTGASSING RATE UPPER LIMITS

To derive the upper limits on the water production rate for the two asteroids, we used a molecular excitation model that calculates the population of the rotational levels of water as a function of distance from the asteroid. Our excitation model takes into account collisions of water and electrons, infrared pumping of the vibrational bands, and treats self-absorption using the escape probability formalism (Biver et al. 2015, 2012; O'Rourke et al. 2013; Zakharov et al. 2007). Further to this the model takes into account the thermal background emission from the asteroid and non-constant gas kinetic temperature radial profiles (Biver et al. 2019).

Input parameters to the model include; the asteroid radius (from our TPM), electron density, the gas expansion velocity, the derived surface temperature (from our TPM which includes surface roughness effects that enhance the temperatures significantly), and finally the gas temperature. Synthetic spectra are computed taking into account the transfer of line radiation of ortho-water in the asteroidal “atmosphere”. Since the electron density is not well constrained, a scaling factor of  $x_{ne} = 0.2$  with respect to the standard profile derived from observations of comet 1P/Halley has been used (Hartogh et al. 2010). For the radial gas density profile, we adopted the standard Haser law (Haser 1957). We assumed a nominal expansion velocity  $v_{exp}$  of  $0.5 \text{ km s}^{-1}$  (characteristic of weak comets)..

Assuming a rarefied free-expanding exosphere for the asteroids and based on these “nominal”  $x_{ne}$  and  $v_{exp}$  values we calculated the water production rates (see Table 3) based upon gas kinetic temperature values of 10 K, 20 K and 50 K as well as a set of variable temperature profiles. 50K was included as temperatures of approximately 50-60 K are expected for Ceres at 3000 km from its body center (Küppers et al. 2014). We obtained similar results for the two asteroids irrespective of the temperature profile applied. This suggests that we are more likely sensitive to the gas temperature at some distance from the surface where collisions become too weak.

We find that for the low production rates we estimate, water excitation is not affected significantly by electron collisions because of low electron densities. Applying a value of  $x_{ne} = 0.2$  or 0.0 does not change our results. Using  $x_{ne} = 1.0$  decreases the upper limits on the water production rate by 10%, and doubling the collision rate with neutrals decreases the values by 8%.

Taking into account the above findings, we added a column in Table 3 defining highly conservative  $3\sigma$  upper limits for the water production rate of  $Q(\text{H}_2\text{O}) < 4.1 \times 10^{26} \text{ mol. s}^{-1}$  for Themis and  $Q(\text{H}_2\text{O}) < 7.6 \times 10^{26} \text{ mol.s}^{-1}$  for Cybele. These values were obtained by assuming a kinetic temperature of 10 K, a high expansion velocity  $v_{exp}$  of  $0.7 \text{ km s}^{-1}$  and no excitation by photoelectrons i.e.  $x_{ne} = 0.0$ . These upper limits provide more than an order of magnitude improvement on previously published  $Q(\text{H}_2\text{O})$  values which are presented in the final column of Table 3 for comparison purposes. We also have derived sensitive  $3\sigma$  upper limits for the column density of  $N_{col} < 0.58 \times 10^{12} \text{ cm s}^{-1}$  for Themis and  $N_{col} < 0.82 \times 10^{12} \text{ cm s}^{-1}$  for Cybele (Table 3 and Table 4).

		Kinetic Temperature ( $T_{kin}$ )				Variable Temperature $T_{var}$			Previously published data
		Upper Limits	(K)	(K)	(K)	( $T_f = 10$ )	( $T_f = 20$ )	( $T_f = 50$ )	
Themis	$Q(H_2O)$ (mol. s <sup>-1</sup> )	<b>&lt; 4.1 x 10<sup>26</sup></b>	< 3.12 x 10 <sup>26</sup>	< 2.78 x 10 <sup>26</sup>	< 2.5 x 10 <sup>26</sup>	< 2.63 x 10 <sup>26</sup>	< 2.59 x 10 <sup>26</sup>	< 2.55 x 10 <sup>26</sup>	(i) < 1.3 x 10 <sup>28</sup> (ii) < 1.0 x 10 <sup>28</sup> (iii) < 4.5 x 10 <sup>27</sup>
	$N_{col}$ (cm <sup>-2</sup> )	< 0.58 x 10 <sup>12</sup>	< 0.58 x 10 <sup>12</sup>	< 0.52 x 10 <sup>12</sup>	< 0.47 x 10 <sup>12</sup>	< 0.49 x 10 <sup>12</sup>	< 0.49 x 10 <sup>12</sup>	< 0.48 x 10 <sup>12</sup>	
Cybele	$Q(H_2O)$ (mol. s <sup>-1</sup> )	<b>&lt; 7.6 x 10<sup>26</sup></b>	< 5.76 x 10 <sup>26</sup>	< 5.04 x 10 <sup>26</sup>	< 4.46 x 10 <sup>26</sup>	< 4.71 x 10 <sup>26</sup>	< 4.63 x 10 <sup>26</sup>	< 4.53 x 10 <sup>26</sup>	(i) < 1.2 x 10 <sup>28</sup>
	$N_{col}$ (cm <sup>-2</sup> )	< 0.82 x 10 <sup>12</sup>	< 0.84 x 10 <sup>12</sup>	< 0.73 x 10 <sup>12</sup>	< 0.65 x 10 <sup>12</sup>	< 0.69 x 10 <sup>12</sup>	< 0.67 x 10 <sup>12</sup>	< 0.66 x 10 <sup>12</sup>	

**Table 3 : H<sub>2</sub>O Production Rate ( $Q(H_2O)$ ) and Column Density ( $N_{col}$ ) derived for different gas kinetic temperatures**, either constant throughout the coma ( $T_{kin}$ ), or variable ( $T_{var} = (T_0 - T_f) r_N/r + T_f$ , with  $T_0 = 155$  K for Themis and  $T_0 = 138$  K for Cybele corresponding to 86% the surface temperature (Crifo et al. 2002);  $r_N$  is the radius of the asteroid derived from our TPM and  $r$  is the distance to the body centre. The “Upper Limits” column corresponds to the worst case estimate of the upper limit whereby ( $T_{kin}$ ), = 10K,  $v_{exp} = 0.7$  and  $x_{ne} = 0$  (see text). All other estimates are performed with the optimal values  $v_{exp} = 0.5$  and  $x_{ne} = 0.2$ . Previously published data references are as follows : (i) Jewitt & Guilbert-Lepoutre (2012) (ii) Lovell et al. (2010) (iii) Mckay et al. (2017).

## 5. DISCUSSION AND CONCLUSIONS

We use the upper limits for the water loss rate presented in section 4 to produce, using a sublimation model, equivalent upper limits for the percentage of exposed ice that is present on the surface of the two asteroids. In our analysis, we study the implications of mixing both at a fine scale (intimate mixing) and also at a more macroscopic level (areal mixing) the ubiquitous dark dust and the ice present on the asteroid surfaces whereby the level of mixing can affect the contribution of the ice albedo to the area-averaged albedo. For intimate mixing, laboratory experiments show that only a few weight percent of dust is sufficient to reduce the albedo of the ice well below 10% (Pommerol et al. 2015). In the areal mixing case, the cleaner (less mixed) the ice is with the dust, the brighter (higher bond albedo) and colder it will be, resulting in less sublimation as a result. This leads to a higher area percentage coverage deduced from the water production rate for the areal mixing case than for the case of intimately mixed ice (Jewitt & Guilbert-Lepoutre 2012).

We used a sublimation model<sup>14</sup> (Cowan & A'Hearn 1979 – slow rotator version) where the rotational pole is pointed towards the Sun. This is appropriate for bodies with a small thermal inertia, as is the case (from our TPM) for Themis and Cybele. This sublimation model provides the average water sublimation rate per surface unit,  $Z$ , at a given heliocentric distance. The upper limit on the area of exposed ice  $A_{\text{exp}}$  is obtained by dividing the upper limit on  $Q(\text{H}_2\text{O})$  by  $Z$ , and the upper limit on the fraction of the surface occupied by ice ( $f_{\text{ice}}$ ) is obtained by dividing  $A_{\text{exp}}$  by the asteroid surface area ( $4\pi r_N^2$ , where  $r_N$  is the effective radius). In addition to the heliocentric distance, the input parameters of the model include the Bond albedo of the icy material and the infrared emissivity equal to 0.9.

Figure 2 shows derived upper limits for the ice coverage of the two asteroids. We plot our water production upper limits against the Bond albedo and the percentage ice coverage; acceptable solutions must lie on or below the water production curves as otherwise gas production through sublimation would have been large enough for detection by HIFI. In this figure, we study two scenarii for the water ice interaction with the ubiquitous dark dust of the asteroid. In the first scenario, we gradually mix a low geometric albedo (0.02 to 0.04) surface dust with ice of an increasing bond albedo value (brightness) resulting in an “areal” type mixture. In the second scenario, we study the “intimate” mixture case on the basis that the bond albedo of the asteroid represents the combined albedos of the icy dust mixture.

Applying scenario 1 and in line with the approach of Jewitt & Guilbert-Lepoutre (2012), we plot two dotted lines in Figure 2 matching with geometric albedo values for  $p_v(\text{dust}) = 0.02\text{--}0.04$  for Themis and  $0.02\text{--}0.03$  for Cybele corresponding to the least reflective asteroid surfaces known. 0.03 is set as a conservative value for the Cybele upper range due to its already very low albedo (from our TPM) of 0.042. The two constraints (water production rate limit and albedo) are found to be acceptably achieved only if the water ice on the two asteroids is very bright (Bond Albedo of 0.8 for Themis, 0.7 for Cybele) and if the water ice

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<sup>14</sup> <http://pdssbn.astro.umd.edu/tools/ma-evap/>

covers < 2.2% of the surface for Themis and < 1.5% for Cybele. Upper limits of 2.2% and 1.5% ice respectively on the surface of the Themis and Cybele asteroids will lead to similar upper limits in the depth of water ice in the 3.1  $\mu\text{m}$  absorption feature as pure water ice is fully absorbing at this wavelength (e.g. Protopapa et al. 2014). As the 3.1  $\mu\text{m}$  band depth of both asteroids is  $\sim 10\%$  of the local continuum (Rivkin & Emery 2010; Licandro et al. 2011), we conclude that for areal mixing, the 3.1  $\mu\text{m}$  absorption feature cannot be explained by surface water ice on these asteroids.

In scenario 2, we assume that the water ice is intimately mixed with the dark surface material of the asteroids (as observed on other solar system objects including 67P) and as such corresponds to the area-averaged bond albedo of the asteroid. A value for the bolometric bond albedo ( $A$ ) of 0.027 was calculated for Themis and 0.019 for Cybele based on the formula  $A = p \cdot q$  where  $p$  is the bolometric geometric albedo assumed to be equal to the V-band albedo  $p_V$  and  $q = 0.290 + 0.684 \cdot G$ .  $G$  is the slope parameter in the H-G system (Bowell et al. 1989) and it was determined to be 0.16 for Themis and 0.23 for Cybele (Oszkiewicz et al. 2011). From Figure 2 (purple stars) and based on these bond albedo values, we obtain upper limits for the fraction of the surface covered by ice to be 0.0017% for Themis and 0.0033% for Cybele, meaning that only a tiny fraction of intimately mixed ice is present on the surface of these asteroids. These values are an order of magnitude lower than those obtained by Jewitt & Guilbert-Lepoutre (2012) and McKay et al. (2017). Like them, we conclude that such an ice-dust mixture percentage is entirely insufficient to explain the 3.1  $\mu\text{m}$  absorption.

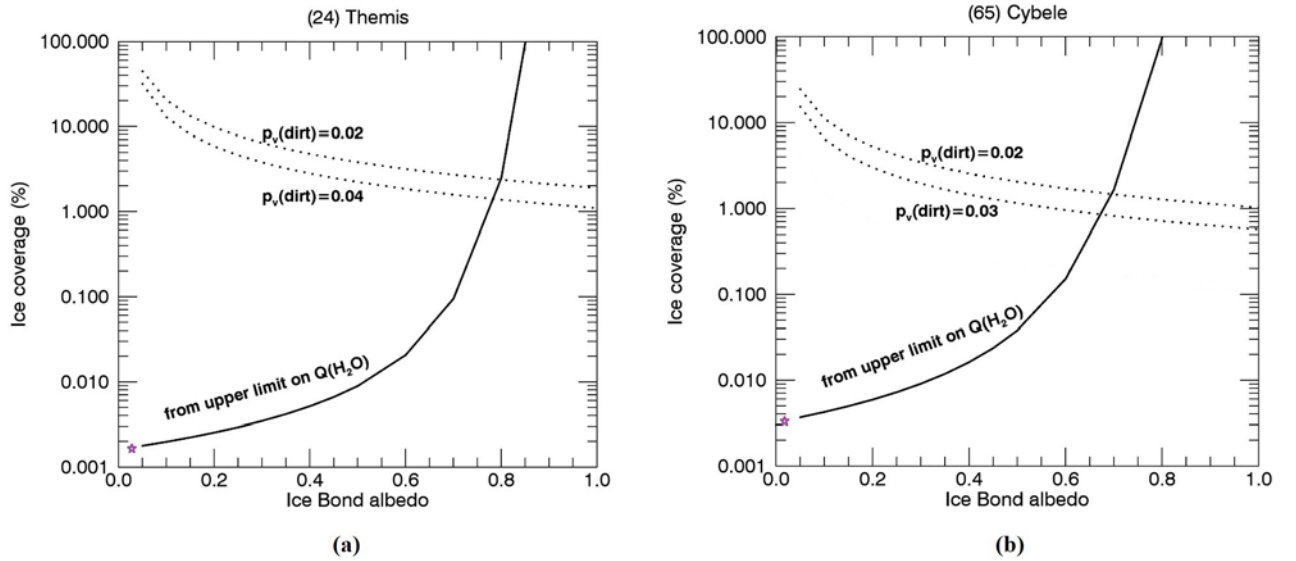
To appreciate the possible percentage of intimately mixed ice below the surface, we compare it with values obtained from 67P/Churyumov-Gerasimenko. On 67P the ice was observed to be intimately mixed with the dust, was visible in localised regions and considered to be just below the surface (Fornasier et al. 2016b). We applied the above model using  $Q(\text{H}_2\text{O})$  measured values of 67P at 3au based on a Bond albedo 0.012 at 3au (Fornasier et al. 2015), and emissivity of 0.97 (Spohn et al. 2015). We find an ice coverage of 0.6% at 3 au pre-perihelion and 0.2% at 3 au post perihelion, percentages more than 2 orders of magnitude higher than those derived for the asteroids. In this comparison, if ice is indeed present just below the asteroid's surface and intimately mixed with dust as in comets, then there is a very low amount present.

While surface water ice may not be the reason for the 3.1  $\mu\text{m}$  absorption feature, the 3- $\mu\text{m}$  region is known to host other volatile species that do show similar absorption curves. The ammonium ( $\text{NH}_4^+$ ) ion has a band centre near 3.1  $\mu\text{m}$  and was interpreted to be present in the (1) Ceres spectrum (King et al. 1992). Poch et al (2020) have recently compared the 3.2  $\mu\text{m}$  spectra of ammonium salts found on comet 67P (Altwegg et al. 2020) with the 3.1  $\mu\text{m}$  feature on Themis and Cybele finding a distinct correlation between the two. Similar features have been observed on the Jupiter Trojan asteroids and the small moon Himalia matching with ammoniated minerals on their surface (Poch et al. 2020; Brown 2016) at this wavelength. Further to the above, minerals such as Brucite (Beck et al. 2011), magnetite (Yang & Jewitt 2010) and adsorbed water molecules in lunar regolith (Clark 2009) all represent other possible alternative explanations to the presence of surface water ice.

In conclusion, we present highly conservative sensitive  $3\sigma$  upper limits for the water production rate on (24) Themis and (65) Cybele. Using these limits to model the maximum surface ice fraction, we find that the  $3.1\ \mu\text{m}$  absorption feature cannot be explained by water ice, be it areal or intimately mixed. Recognising the numerous spacecraft that have visited asteroids and comets where far too little surface ice has been detected to be visible in disk-integrated spectra, our results serve to confirm the continued difficulty in observing ice from the Earth whether via ground or space based observatories.

Target	$Q(\text{H}_2\text{O})$ (mol. s <sup>-1</sup> )	$N_{\text{col}}$ (cm <sup>-2</sup> )	Intimate $f_{\text{ice}}$ (%)	Areal $f_{\text{ice}}$ (%)	$\Gamma$ (J m <sup>-2</sup> s <sup>-1/2</sup> K <sup>-1</sup> )	D (km)	$p_v$ (geometric)	$p_v$ (bond)
Themis	$< 4.1 \times 10^{26}$	$< 0.58 \times 10^{12}$	0.0017	1.4 - 2.2	$20^{+25}_{-10}$	$192^{+10}_{-7}$	$0.07 \pm 0.007$	0.027
Cybele	$< 7.6 \times 10^{26}$	$< 0.82 \times 10^{12}$	0.0033	0.8 - 1.5	$25^{+28}_{-19}$	$282 \pm 9$	$0.042^{+0.03}_{-0.02}$	0.019

**Table 4 : Summary of main results of this paper** where  $Q(\text{H}_2\text{O})$  is the water production rate upper limits,  $N_{\text{col}}$  is the Column density upper limits,  $f_{\text{ice}}$  is the fraction of ice coverage depending if it is an intimate or areal mixture,  $\Gamma$  is the thermal inertia, D is the effective Diameter and  $p_v$  is the V-band Geometric and bond Albedo.



**Figure 2 : Derived allowed values for the ice coverage for (a) Themis and (b) Cybele as a function of the Bond albedo of surface ice.** The solid curve represents the  $Q(\text{H}_2\text{O})$  constraint derived for each asteroid. Acceptable solutions must lie on or below this curve as otherwise gas production through sublimation would have been large enough for detection by HIFI. The dotted curves reflect the albedo constraint (see text) for geometric albedos of non-icy (dust) terrains  $p_v(\text{dust})$  in the range 0.02 to 0.04 for Themis and 0.02 to 0.03 for Cybele. Acceptable solutions for the areal mixing case must lie along or



between these dotted curves to guarantee the area-averaged albedo matches our modelled TPM value. The purple stars represent the positions of the corresponding intimate mixing results.

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