# An improved carbon dioxide snow spectral albedo model: Application to Martian conditions

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Key Points

- We extend an Earth-based H<sub>2</sub>O snow model to simulate CO<sub>2</sub> snow albedo
- Improved CO<sub>2</sub> ice refractive indices produce very high (~0.96) CO<sub>2</sub> snow albedo
- we explore a range of conditions applicable to Mars and evaluate the model against measurements

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#### Abstract

Carbon dioxide ice is abundant on the Martian surface, and plays an important role in the planet' energy budget due to its high reflectivity and seasonal variation. Here, we adapt the terrestrial Snow, Ice, and Aerosol Radiation (SNICAR) model to simulate CO2 snow albedo across the ultraviolet, visible, and near-IR spectrum (0.2-5.0 µm). We apply recent laboratory derived refrictive indices of CO2 ice, which produce higher broadband CO2 snow albedo (0.93–0.92) than previously estimated. Compared with H<sub>2</sub>O snow, we find that CO<sub>2</sub> snow albedo is much higher in the near-IR spectrum, less dependent on ice grain size, less dependent on solar zenith angle, and more susceptible to darkening from dust. A mass concentration of 0.01% Martian dust reduces visible and near-IR CO<sub>2</sub> snow albedos by about 60% and 25%, respectively. The presence of small amounts of  $H_2O$  snow on top of  $CO_2$  snow can substantially decrease the surface albedo. Whereas 2.5 cm of H<sub>2</sub>O snow can completely mask the impact of underlying CO<sub>2</sub> ice or the surface, roughly twice as much overlying CO<sub>2</sub> snow is required to mask underlying H<sub>2</sub>O snow. Similarly, a 10% mixing ratio of H<sub>2</sub>O ice embedded in CO<sub>2</sub> snow decreases broadband albedo by 0.18, while 10% CO<sub>2</sub> ice elevates H<sub>2</sub>O snow broadband albedo by 0.10. We also present comparisons between hemispherical albedo produced by SNICAR and observations of directional reflectance of Martian polar ice caps. While imperfect, this best-fit analysis provides general ranges of physical parameters in different Martian environments that produce reasonable model-observation agreement.

#### 1 Introduction

The Martian atmosphere consists primarily of carbon dioxide, and Martian polar caps are covered primarily with carbon dioxide ice [*Leighton and Murray*, 1966; *Herr and Pimentel*, 1969, *Lasson and Fink*, 1972; *Forget*, 1998; *Bibring* et al., 2005]. H<sub>2</sub>O ice is also present at the surface of the perennial ice caps, with small amounts of seasonal deposition in other parts

of the planet [e.g., *Kieffer* et al., 2000; *Bibring* et al., 2004; *Brown* et al., 2014]. Significant portions of atmospheric  $CO_2$  (25-30%) deposit seasonally in each hemisphere, as indicated by model simulations and surface pressure measurements [*Tillman* et al., 1993; *Forget* et al., 1998; *Kieffer and Titus*, 2001]. To understand the impact of these ices on the planet's cryosphere albedo, it is important to accurately determine the spectral dependence of  $CO_2$  snow dibedo and influences of properties such as dust content, ice grain size, and snow thickness, a well as the albedo effects of mixing and layering of  $CO_2$  and  $H_2O$  snow.

Our work determines the albedo of  $CO_2$  snow by extending the Earth-based Snow, Ice, and Aeroso Padiation (SNICAR) model [*Flanner* et al., 2007; *Flanner* et al., 2009], originally designed for H<sub>2</sub>O snow. SNICAR utilizes the multiple scattering, multi-layer two-stream radiative approximation described by *Toon* et al. [1989], with the delta-hemispheric mean approximation. We extend the current version of SNICAR from 470 bands (over the wavelength range 0.3-5.0 µm) to 480 bands spanning 0.2-5.0 µm at 10 nm spectral resolution. We include these extra 10 bands in the ultraviolet (UV) spectrum because of the lack of ozone in the Martian atmosphere compared to Earth [*Montmessin and Lefèvre*, 2013], meaning more UV radiation reaches the Martian surface and interacts with snow. A single-layer implementation of SNICAR can be operated interactively on the web at: *http://snow.engin.umich.edu*.

Very few studies have focused on modeling of Martian CO<sub>2</sub> snow albedo across the UV, visible and near-IR spectrum [*Warren* et al., 1990; *Hansen*, 1999; *Bonev* et al., 2008]. *Langevin et al.*, [2007] and *Appéré et al.*, [2011] present modeled near-IR albedo of Martian cryospheric surfaces, as discussed in Section 4. With the availability of more accurate and spectrally resolved laboratory measurements of CO<sub>2</sub> ice complex refractive indices across the solar spectrum [*Hansen*, 1997; *Hansen* 2005], we provide improved and updated spectral albedos of carbon dioxide snow with applicability to Martian conditions. The presence of light-absorbing impurities generally lowers snow albedo. We simulate the impact of Martian dust [*Wolff* et al., 2006; *Wolff* et al., 2009; *Wolff* et al., 2010] and palagonite [*Clark* et al., 1990; *Clarcy* et al., 1995] on surface cryosphere albedo. Palagonite is a volcanic rock and serves as a terrestrial analog for Martian dust [*Banin* et al., 1997]. We perform multiple

analyses to determine the sensitivity of cryosphere spectral albedo to the amount and type of dust, presence of both ices, ice grain size, snow layer thickness, and solar zenith angle. We also compare our simulations with observed Mars surface albedo derived from Compact Reconnaissance Imaging Spectrometer (CRISM) measurements, and the OMEGA instrument [*Appéré et al.*, 2011] (section 4). Apparent albedo, derived by *Brown* et al [2014] using CRISM measurements, were provided by Adrian Brown (SETI Institute, personal communication), and observations and modeled albedo from the OMEGA instrument were provided by Thomas Appéré (IPAG, Grenoble, personal communication).

# 2 Data and methodology

Hansen [1907, 2005] made extensive laboratory measurements of the complex refractive indices of solid CO<sub>2</sub> ice in the spectral range from 0.174  $\mu$ m to 333  $\mu$ m. We apply these data along hith Mie calculations to derive optical properties of different lognormal size distributions of CO<sub>2</sub> ice particles, reported with effective radius ( $r_{eff}$ ), or the surface areaweighted mean radius of the size distribution. Our simulations of H<sub>2</sub>O snow albedo utilize refractive indices of H<sub>2</sub>O ice provided by Warren and Brandt [2008]. We use "central hemalite" dust mineral fractions from *Balkanski* et al. [2007] as a proxy of typical Earth dust. These mineral abundances are representative of aeolian dust from the Saharan desert. Refractive indices for this dust mixture are derived using the Maxwell-Garnett mixing approximation, following e.g., Sokolik and Toon [1999], along with measurements of mineral refractive indices from various sources. Refractive indices of Martian dust (hereafter Mars dust) upre-provided by Mike Wolff (Space Science Institute, personal communication), and were derived using data from instruments onboard the Mars Reconnaissance Orbiter (MRO), as described by Wolff et al. [2009], and Wolff et al. [2010]. We combine refractive indices of palagonite from Clark et al. [1990] over the 0.2 µm to 0.6 µm spectral range and measurements from 0.6 µm to 5 µm made by Clancy et al. [1995] to derive data over the

solar spectrum. In this study, we divide our broadband (0.2-5.0  $\mu$ m) into two sub-regions: Visible (0.2-0.7  $\mu$ m) and near-IR (0.7-5.0  $\mu$ m).

We determine the spectrally-varying single scatter albedo ( $\omega_0$ ), scattering asymmetry parameter (g), and mass extinction cross-section for all three dust types using Mie Theory with an assumed gamma size distribution [*Hansen and Travis*, 1974] with  $r_{eff}$ =1.5µm and effective variance ( $\upsilon_{eff}$ )=0.3 [*Wolff* et al., 2006]. Figure 1 shows the optical properties for these dust types. Mass absorption cross-section (Fig. 1d) is the product of single scatter co-albedo (Fig. 1a) and mass extinction cross-section (Fig 1b). We assume the same dust density of 2000 kg/m<sup>3</sup> for both palagonite and Mars dust [*Stroncik and Schmincke*, 2002], and a dust density of 2570 kg/m<sup>3</sup> for Earth dust, based on the volume fraction-weighted densities of the constituent minerals [*Balkanski* et al., 2007].

The bulk optical properties (extinction optical depth ( $\tau$ ),  $\omega_0$ , and g) for each snow layer are calculated from the abundances of each constituent [e.g., *Flanner* et al, 2007], with  $\tau$  calculated as the sum of that associated with each constituent,  $\omega_0$  as a  $\tau$ -weighted average of each constituent, and g as a scattering optical depth (product of  $\tau$  and  $\omega_0$ ) weighted average of the asymptetry parameter of each constituent. These bulk layer properties are then applied in the two stream multiple scattering approximation adopted by SNICAR. We utilize this extended barnework of SNICAR to first simulate the albedo of pure CO<sub>2</sub> snow across the visible and near-IR spectrum. We then explore and compare the impacts of Earth dust, Mars dust and palagonite on CO<sub>2</sub> and H<sub>2</sub>O snow albedo. Finally, we adopt a two layer model (with the bottom layer being semi-infinite) to calculate the impacts of H<sub>2</sub>O snow presence on top of CO<sub>2</sub> snow and vice-versa. In all other cases we assume only a single snow layer, either with semi-infinite thickness or varying shallow thicknesses. Here, a layer with thickness of 100 m is referred to as semi-infinite. Figure 2 shows simplified diagrams of the various model configurations applied in this paper.

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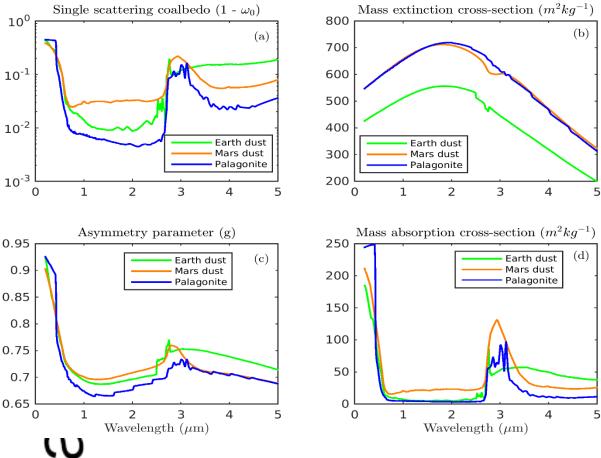


Figure 1: Spectral optical properties of the Earth dust, Martian dust, and palagonite applied in this study.

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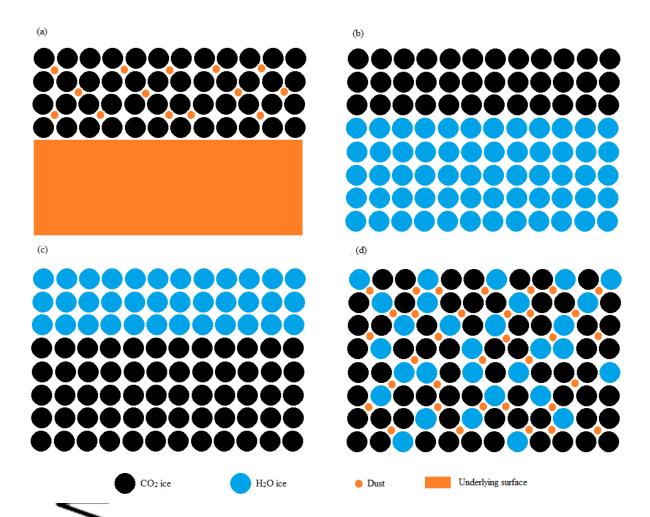


Figure 2. Schematic of the various model configurations applied in this paper: (a) a single  $CO_2$  or  $H_2O$  snow layer (with dust) on top of solid underlying surface; (b)  $CO_2$  snow with variable thickness on top of a semi-infinite  $H_2O$  snow layer; (c)  $H_2O$  snow with variable thickness on top of a semi-infinite  $CO_2$  snow layer; (d) mixed snow layers with dust.

#### 3 Results

Figure 3 shows the spectral hemispheric albedo of pure, semi-infinite  $CO_2$  and  $H_2O$  snow with spherical grain effective radius of 100 µm and solar zenith angle of 60°. It is evident that the  $CO_2$  is more reflective than  $H_2O$  snow, especially in the near-IR spectrum. Table 1 compares colar broadband, visible and near-IR albedo for both types of snow, where bandaveraged values are weighted with solar spectral irradiance measurements from *Labs and Neckel* [1968].  $H_2O$  snow albedo is only about two-thirds of the  $CO_2$  snow albedo in the nearIR spectrum, although this ratio is grain size dependent (section 3.2). With the presence of both  $CO_2$  and  $H_2O$  ices on Martian polar caps, the contrasting reflectivity of these types of snow could significantly impact planetary shortwave energy fluxes, both at the surface and top of atmosphere.

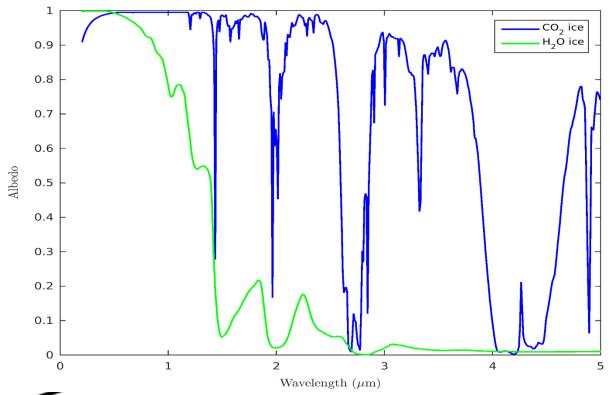


Figure 9. Comparison of CO<sub>2</sub> and H<sub>2</sub>O snow spectral albedo simulated with the SNICAR model (Grain size =  $100 \,\mu\text{m}$  and solar zenith angle =  $60^{\circ}$ )

Table 1: Albedo values for pure, semi-infinite  $CO_2$  and  $H_2O$  snow in different spectral bands (Grain ize 100 µm and solar zenith angle = 60°)

	pure CO <sub>2</sub>	pure H <sub>2</sub> O
Visible (0.2.0.7 μm)	0.991	0.988
Near-IR (0.7-5.0 μm)	0.952	0.609
Broadband (0.2-5.0 µm)	0.970	0.787

Snow albedo depends on many physical quantities, including grain size, solar zenith angle, layer thickness, and type and amount of impurities. We performed a sensitivity analysis to

understand the effect of these parameters on carbon dioxide snow albedo, and describe this analysis below. We assume an effective grain size of 100  $\mu$ m and solar zenith angle of 60° for all analyses, unless stated otherwise. For comparing CO<sub>2</sub> and H<sub>2</sub>O albedo, we also assume identical pore volume fractions for each type of ice. A typical bulk density of settled snow on Earth is 200 kg/m<sup>3</sup> (e.g., *EN 1991-1-3*). Because the bulk densities of H<sub>2</sub>O and CO<sub>2</sub> ice are assumed to be 917 kg/m<sup>3</sup> and 1500 kg/m<sup>3</sup>, respectively, we therefore assume H<sub>2</sub>O and CO<sub>2</sub> snow densities of 200 kg/m<sup>3</sup> and 327.15 (= 200×1500/917) kg/m<sup>3</sup>, respectively.

### 3.1 Solar zenith angle

We see intil effect of solar zenith angle on  $CO_2$  snow albedo (Fig. 4). The broadband albedo only charges from 0.98 to 0.96 over the 80° change in zenith angle. This compares with H<sub>2</sub>O snow abeed, which varies from 0.75 to 0.82 for the same set of parameters. Variability in albedo with solar zenith angle is greater in more absorptive parts of the spectrum (i.e., the near-IF), but for  $CO_2$  snow the variability is small in the parts of the spectrum containing most of the solar energy.

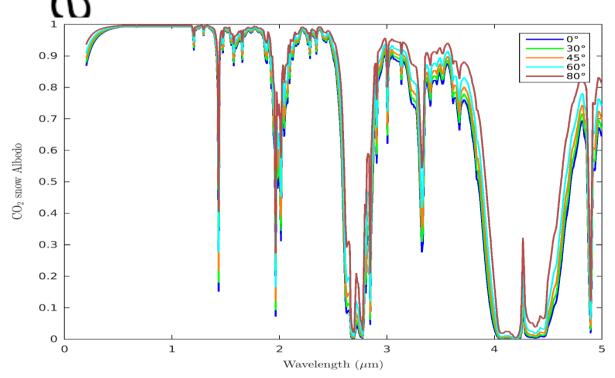


Figure 4: Variation of CO<sub>2</sub> snow albedo with solar zenith angle

#### 3.2 Grain Size

We simulate a monotonic decrease in snow albedo with increasing effective grain size (Fig. 5). With larger grain size, ice volume per surface area increases, resulting in greater absorption of light, as also occurs with H<sub>2</sub>O snow [e.g., *Wiscombe and Warren*, 1980]. The broadband (near-IR) albedo of CO<sub>2</sub> snow drops from 0.98 to 0.93 (0.96 to 0.89) for grain size increasing from 50  $\mu$ m to 1500  $\mu$ m. This is also smaller variability than exhibited by H<sub>2</sub>O snow, whose broadband (near-IR) albedo changes from 0.82 to 0.65 (0.66 to 0.37) over the same range in effective grain size. CO<sub>2</sub> snow albedo varies less with grain size because CO<sub>2</sub> ice is inherently less absorptive in the near-IR than H<sub>2</sub>O ice. Consequently the incremental increase in absorption associated with increasing photon path length within larger ice grains is smaller for CO<sub>2</sub> snow than H<sub>2</sub>O snow.

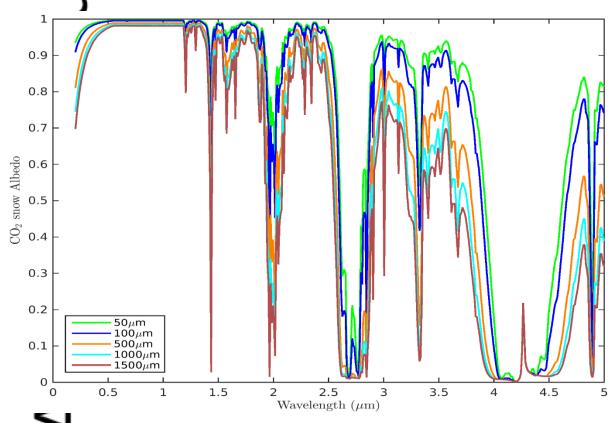


Figure 5: Voriation of CO<sub>2</sub> snow albedo with effective grain radius

#### 3.3 Snow thickness

Figure 6 shows the combined impacts of snow thickness and grain size on  $CO_2$  and  $H_2O$  broadband snow albedo, for snow overlying a surface with spectrally constant albedo of 0.2 (model configuration shown in Fig. 2a). For a given grain size,  $CO_2$  snow albedo has a larger variation over the entire thickness range compared to  $H_2O$  snow albedo.  $CO_2$  snow albedo is almost independent of grain size when the snow layer is thick, and consequently all curves saturate at a similarly high albedo ranging from 0.93-0.98. However,  $H_2O$  snow albedo has a larger 0.65-0.22.

"saturation thickness" as the snow thickness needed for the broadband albedo to We def differ by less than 0.01 from its semi-infinite value. Once the snow layer thickness exceeds the saturation thickness, the impact of the underlying surface becomes negligible as an insignificand amount of light penetrates through the snow to interact with the underlying surface we note, however, that the penetration depth of radiation in snow depends strongly on wavelength, with multiple scattering leading to much deeper penetration and influence of underlying substrate at wavelengths where the ice absorbs weakly [e.g., Wiscombe and Warren 1980]. The saturation thickness also depends on snow density, with higher density producing lower saturation thickness. Table 2 presents the saturation thickness required for different grain sizes for both types of snow. The saturation thickness is grain size-dependent, increasing from about 6 to 100 cm, and from about 5 to 83 cm as grain size increases from 50 to 1500  $\mu$ m for CO<sub>2</sub> and H<sub>2</sub>O snow, respectively. With other factors equal, CO<sub>2</sub> snow has higher vaturation thickness than H<sub>2</sub>O snow because CO<sub>2</sub> ice is less absorptive than H<sub>2</sub>O ice, especially in the near-IR region, enabling multiple-scattered photons to penetrate deeper in the snow. Also the difference in saturation thicknesses increases with larger grain size because of less dependency of CO<sub>2</sub> snow albedo on grain size compared to H<sub>2</sub>O snow (section 3.2). Finally, we note that studies on optical properties of ice particles have found that the southering asymmetry parameter is generally smaller for non-spherical ice particles volume/area ice spheres [e.g., Fu, 2007; Libois et al., 2013; Räisänen et al., 2015]. than equ An implication of this is that saturation thickness will be smaller for non-spherical ice

particles than values reported here, as photons are scattered less preferentially into the forward direction.

Table 2: Saturation snow layer thickness with various grain sizes for each type of snow.  $CO_2$  and  $H_2O$  snow densities are 327.15 and 200 kg/m<sup>3</sup>, respectively.

Grain Size	CO <sub>2</sub> snow saturation thickness	H <sub>2</sub> O snow saturation thickness
50 µm	6.5 cm	5.0 cm
100 µm	10.9 cm	8.9 cm
250 µm	24.0 cm	18.8 cm
500 µm	43.1 cm	33.7 cm
1000 µ.m.	73.8 cm	59.4 cm
1500 in	100.2 cm	83.2 cm

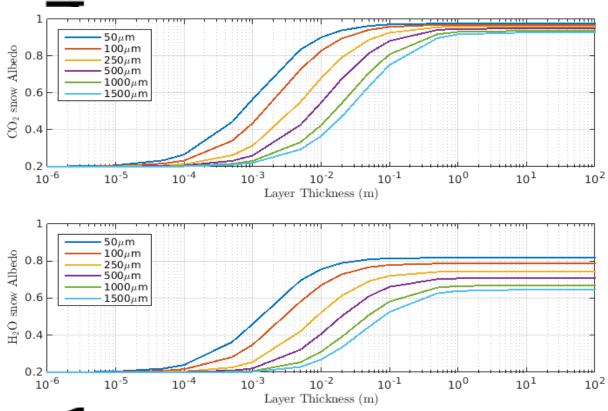


Figure 6 Broadband  $CO_2$  (top) and  $H_2O$  (bottom) snow albedo dependence on snow layer thickness for various effective grain sizes. The underlying surface is assumed to have a

constant albedo of 0.2. The snow density is 327.15 kg/m<sup>3</sup> and 200 kg/m<sup>3</sup> for CO<sub>2</sub> and H<sub>2</sub>O snow, respectively.

#### 3.4 Dust type

The snow albedo impacts of different types of dust depend on their optical properties, and in particular or their mass absorption cross-section. Here we compare the impacts of Earth dust, Mars dase and palagonite on semi-infinite snow albedo (Fig. 7). Again, identical size distributions are assumed for each type of dust, and only the refractive indices are varied as input to Mie calculations. Mars dust has the greatest albedo impact of the three between wavelengths of 0.5 and 2.5  $\mu$ m, which contains most of the incident solar energy, while palagonite has the least. Mars dust is relatively dark due to the presence of higher amount of iron oxides [Bell III et al., 1990; Bell III, 1996; Christensen et al., 2000; Christensen et al., 2001a; Christensen et al., 2001b], combined with its large mass extinction cross-section. Although average Earth dust has a lower near-IR single-scatter albedo than the Mars dust, it also has a lower absorption per unit mass of dust, expressed via the mass absorption cross-section (Fig. 1d).

We consider "mass mixing ratio" as the mass of impurity divided by the mass of ice in which the impurity is mixed. Table 3 presents the effective  $CO_2$  snow albedo in the presence of 0.01% mass mixing ratio of dust (kg of dust / kg of ice). Dust causes a larger albedo drop in the visible region (~0.6) compared to the near-IR region (~0.3) because all three types of dust have very two single scatter albedo in the blue and green spectra while ice grains scatter very efficiently at these wavelengths (Fig. 1). Furthermore, the drop in albedo in the blue spectrum (~0.8) (s much higher than the drop in the red spectrum (~0.3), helping explain the planet's red appearance even in its cryospheric regions. Although palagonite is less absorptive than Mars dust, the spectral variations in albedo impacts of the two species are similar.

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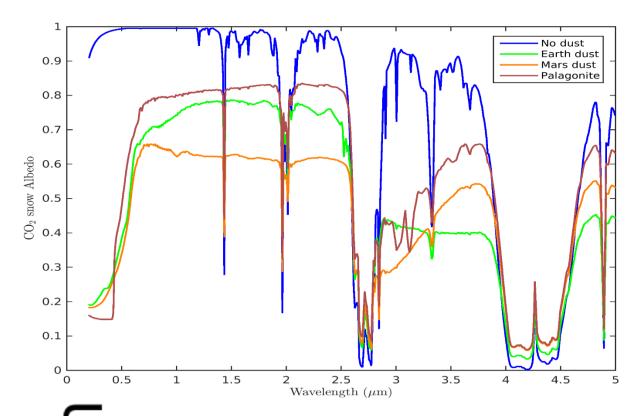


Figure 2: Impact of different types of dust on  $CO_2$  snow albedo, with dust mass mixing ratio of 0.01  $\infty$  The assumed snow grain size is 100  $\mu$ m.

Table 3: Impact of different types of dust on  $CO_2$  broadband snow albedo (grain size of 100  $\mu$ m), with dust mass mixing ratio of 0.01%.

	pure CO <sub>2</sub>	Earth dust	Mars Dust	Palagonite
Visi <b>ble (0.</b> 2-0.7 μm)	0.991	0.429	0.395	0.477
Near IR (0.7-5.0 μm)	0.952	0.718	0.616	0.779
Broadband (0.2-5.0 µm)	0.970	0.583	0.513	0.637

Table 4: Impact of different types of dust on  $H_2O$  broadband snow albedo (grain size of 100  $\mu$ m), with dust mass mixing ratio of 0.01%

	pure H <sub>2</sub> O	Earth dust	Mars Dust	Palagonite
Vi tole (0.2-0.7 µm)	0.988	0.450	0.415	0.494
Near-IR (0.7-5.0 μm)	0.609	0.551	0.503	0.599

Broadband (0.2-5.0 µm)	0.787	0.504	0.461	0.550

Table 4 presents the effective  $H_2O$  snow albedo in the presence of 0.01% mass mixing ratio of dust. Pure  $H_2O$  snow is relatively absorptive in the near-IR spectral region (Table 1, Table 4), so dust has little impact on near-IR albedo, or in the most absorptive portions of the spectrum, it even increases albedo (Fig. 8). Fundamentally, this occurs because the singlescatter albedo of dust exceeds that of  $H_2O$  ice grains at wavelengths longer than about 1.5 µm. Similar to  $CO_2$  snow, the drop in albedo is large in the visible region for  $H_2O$  snow. However in the near-IR region the change is less than 0.1, leading to smaller broadband albedo impacts of dust on  $H_2O$  snow albedo than on  $CO_2$  snow albedo. These differences indicate that dust can have greater impact on Martian cryosphere albedo than Earth cryosphere-albedo due to the higher abundance of  $CO_2$  ice compared to  $H_2O$  ice.

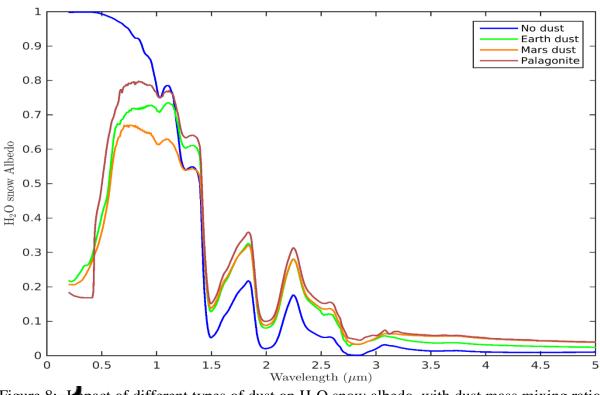


Figure 2: Inpact of different types of dust on H<sub>2</sub>O snow albedo, with dust mass mixing ratio of 0.01% The assumed snow grain size is 100 μm.
3.5 Dust Concentration

Figure 9 shows the effect of varying amounts of Mars dust on  $CO_2$  snow albedo (Fig. 2a). It is obvious that albedo decreases with increasing amount of dust, except in the strong absorption bands of  $CO_2$  ice (e.g., near 1.4 µm, 1.9 µm, and 2.7 µm). Again we see maximum impact in the visible part of the spectrum. Saturation of the albedo from this type of dust is evident with dust mixing ratios exceeding 0.01%, with almost no difference in albedo between secharios with 0.1% and 1% dust. Also, the strong absorption features of  $CO_2$  snow at various wavelengths disappear with high dust concentrations.

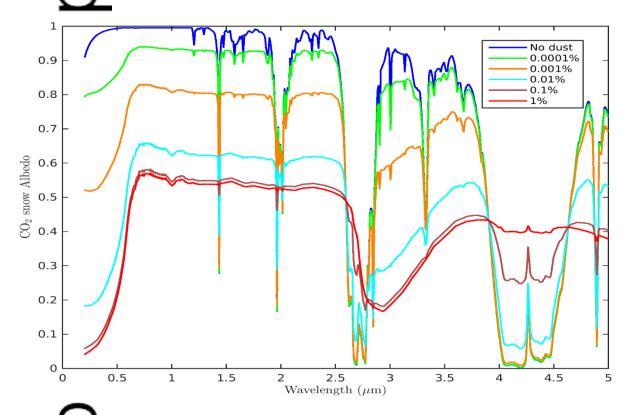


Figure 9: Impact of various amounts of Martian dust on  $CO_2$  snow albedo. Snow effective grain radius is  $100\mu m$ .

#### 3.6 Presence of both H<sub>2</sub>O and CO<sub>2</sub> ice

#### 3.6.1 Separate layers

 $H_2O$  and  $O_2$  ice interact quite differently with radiation in the visible and near-IR portions of the spectrum and also exhibit different sensitivities to different physical parameters. These ice types are also known to co-exist on the surface of Mars [e.g. *Byrne* et al., 2008; *Brown* et

al., 2014]. Here, we explore the albedo effects associated with thin slabs of one type of ice overlying the other, building on sensitivity studies conducted by *Warren* et al., [1990]. Figure 10 shows spectral albedo of surfaces with  $H_2O$  snow on top of  $CO_2$  snow (scenario shown in figure 2c), and figure 11 shows albedo with the reverse situation (scenario shown in figure 2b).

Albedo decreases markedly with the presence of thin slabs of H<sub>2</sub>O snow on top of CO<sub>2</sub> snow. This decrease occurs more rapidly with increasing thickness of H<sub>2</sub>O ice than the rate of albedo increase that occurs with increasing thickness of CO<sub>2</sub> snow overlying H<sub>2</sub>O snow. For a grain sine of 100  $\mu$ m, about 2.5 cm of H<sub>2</sub>O snow is required to completely mask out the albedo effect of CO<sub>2</sub> snow (Table 5), whereas about 5.5 cm of CO<sub>2</sub> snow is required to completely mask out the albedo effect of underlying H<sub>2</sub>O snow (Table 6). Again, differences are more pronounced in the near-IR spectrum (e.g., Fig. 3, Table 1), where the contrast in absorptivity between CO<sub>2</sub> and H<sub>2</sub>O ice is greater (Tables 5 and 6). Rows marked with an asterisk (\*) correspond to saturation thickness. In summary, very little H<sub>2</sub>O snow is needed to mask the presence of underlying CO<sub>2</sub> snow, whereas a larger thickness of CO<sub>2</sub> snow is needed to prevent underlying, more absorptive H<sub>2</sub>O snow from effecting surface albedo.

*Warran* et al., [1990] determined that the presence of  $H_2O$  snow on top of  $CO_2$  snow will increase the net surface albedo, contrary to the analysis presented here. The  $CO_2$  ice refractive indices applied in that study, however, were measured using unpurified commercial dry ice [*Egan and Spagnolo*, 1969], and data in the 1.0-2.5 µm spectral region were extrapolated from the 0.3-1.0 µm spectral region. The higher quality measurements on pure  $CO_2$  ice provided by *Hansen* [1997, 2005], and applied here, indicate that  $CO_2$  ice is much less absorptive than previously assumed, leading to our opposite conclusion.

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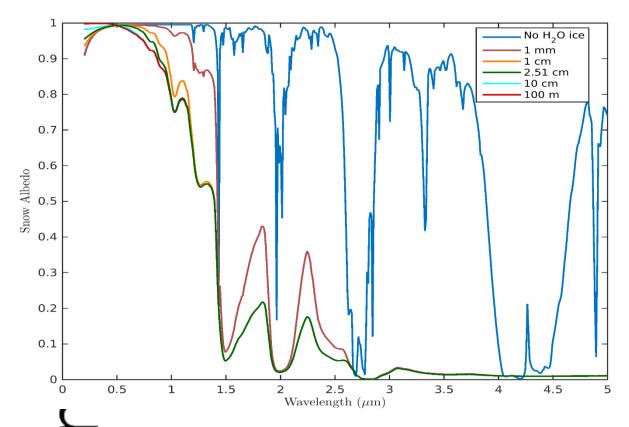


Figure 10: Spectral albedo of surfaces with  $H_2O$  snow layers of varying thickness on top of  $CO_2$  snow the green curve thickness corresponds to saturation thickness.

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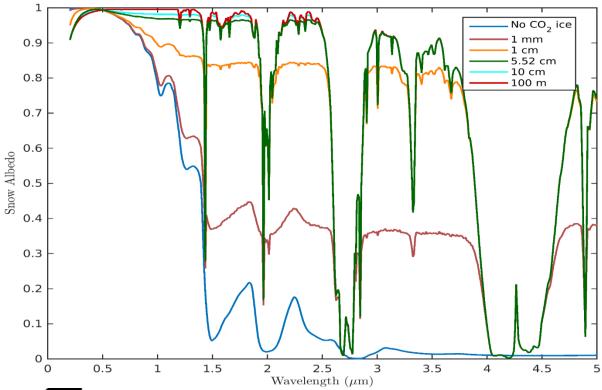


Figure 11: Spectral albedo of surfaces with CO<sub>2</sub> snow layers of varying thickness on top of H<sub>2</sub>O snow. The green curve thickness corresponds to saturation thickness. Table 5: Broadband albedos of surfaces with H<sub>2</sub>O snow layers on top of CO<sub>2</sub> snow

H <sub>2</sub> O laver unickness	Vis	Near-IR	Broadband
	0.991	0.952	0.970
1 mm	0.991	0.739	0.857
1  cm	0.991	0.639	0.804
2.51 cm*	0.987	0.618	0.793
10 c h	0.990	0.610	0.787
<u>100 m</u>	0.988	0.609	0.787

\*Saturation thickness (section 3.3)

Table 4: Breadband albedos of surfaces with CO2 snow layers on top of H2O snow

CO <sub>2</sub> layer thickness	Vis	Near-IR	Broadband
0	0.988	0.609	0.787
<b>A</b> nm	0.988	0.703	0.837
1 cm	0.989	0.869	0.925
5.52 cm*	0.989	0.934	0.960

10 cm	0.990	0.943	0.965
100 m	0.991	0.952	0.970
	1		

\*Saturation thickness (section 3.3)

Figure 12 shows the broadband net surface albedo dependence on layer thickness for different snow types. The black lines indicate the saturation thickness (section 3.3) for the two scenarios discussed above. To further explore the behavior of albedo with layer thickness, we divide each curve into two regions: with thickness lesser and higher than saturation thickness. Table 7 lists the slopes of albedo per layer thickness for these two regions. For top layer thickness less than saturation thickness (first region), higher slope (in absolute values) of data shown in Fig. 12a than 12b substantiates the conclusion that H<sub>2</sub>O snow is narder to mask out compared to CO<sub>2</sub> snow. However, for the second region with thickness higher absolute slope than the reverse situation. This indicates that H<sub>2</sub>O snow is less sensitive to thickness variation (once a minimum threshold is reached), owing to its more absorptive nature in the near-IR spectrum compared to CO<sub>2</sub> snow.

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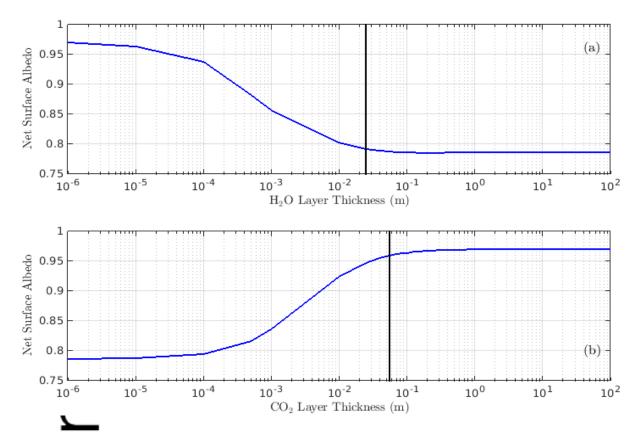


Figure 12: Dependence of net surface broadband snow albedo on layer thickness for (a) an  $H_2O$  snow layer on top of a semi-infinite  $CO_2$  snow layer, and (b) a  $CO_2$  snow layer on top of a semi-infinite  $H_2O$  snow layer. The black line indicates the saturation thickness for each case. Snow grain size is assumed to be 100  $\mu$ m in both cases.

Table **Slop**es of albedo per change in layer thickness for the two scenarios shown in figure

$\frac{12}{2}$		
Thickness regime	H <sub>2</sub> O snow layer on top of	CO <sub>2</sub> snow layer on top of
	CO <sub>2</sub> snow layer (Fig 11a)	H <sub>2</sub> O snow layer (Fig 11b)
Less than saturation thickness	$-7.10 \text{ m}^{-1}$	$+3.14 \text{ m}^{-1}$
Higher than saturation thickness	$-5.54 \times 10^{-5} \text{ m}^{-1}$	$+1.05 \times 10^{-4} \text{ m}^{-1}$

In addition to the possibility of different snow types being present as separate layers, both types of snow can also become mixed together on the surface of Mars [e.g. *Brown* et al.,

Mixed layers

3.6.2

2014]. In this section, we explore the net surface albedo changes caused by one snow type becoming mixed with the other snow type. In practice, this is simulated by treating the less abundant ice type as an externally-mixed "impurity" with specified mass mixing ratio (scenario shown in figure 2d), analogous to the treatment of dust described earlier. Figure 13 shows the net surface albedo when H<sub>2</sub>O snow is present as an impurity within CO<sub>2</sub> snow, and figure 44 shows the net surface albedo for the reverse situation. We assume a semi-infinite snow layer, and effective grain size of 100  $\mu$ m for both snowpacks.

Broadband (near-IR) albedo drops by ~0.18 (~0.34) for an associated increase of H<sub>2</sub>O snow from 0% to 10% within CO<sub>2</sub> snow. However, broadband (near-IR) albedo increases by ~0.10 (~0.18) in the reverse situation. This is consistent with our earlier findings that H<sub>2</sub>O snow is relatively darker (especially in the near-IR region) compared to CO<sub>2</sub> snow, hence causing larger impact on net surface albedo. 0.01% of H<sub>2</sub>O snow is sufficient to reduce the net broadband albedo of the mixture by 0.03, while 1% of CO<sub>2</sub> snow is required to increase the net surface broadband albedo of the mixture by same amount.

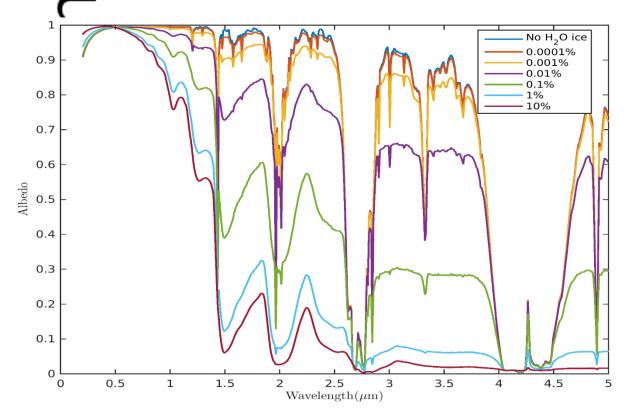


Figure 13: Spectral albedo of surfaces with  $H_2O$  ice present as an impurity within  $CO_2$  snow. Effective grain size for both snow types is 100  $\mu$ m and the layer is semi-infinite.

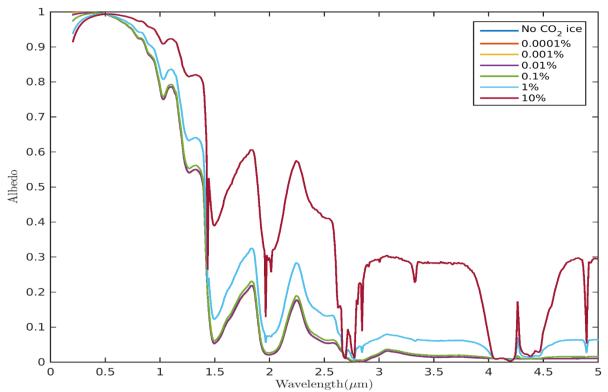


Figure 14: Spectral albedo of surfaces with  $CO_2$  ice present as an impurity within  $H_2O$  snow. Effective grain size for both snow types is 100  $\mu$ m and the layer is semi-infinite.

#### 4 Comparison with observed Martian albedo

In this pection, we compare our simulations with some observations of surface reflectance in the Mattan cryosphere and try to identify parameter combinations that produce reasonable agreement between the modeled and observed data. We first note that SNICAR produces directional-hemispherical albedo, whereas the CRISM and OMEGA observations evaluated here are bidirectional reflectances. This discrepancy renders the model-observation comparison imperfect, but the analysis does have some usefulness in illustrating broad agreement between modeled and observed spectral reflectance features, and in identifying general ranges of physical parameters that produce reasonable modeled spectra in different environments.

#### 4.1 Comparison with CRISM measurements

We obtained spectral reflectance data for one location in the Southern Hemisphere [point A, Fig. 3 of *Brown* et al., 2014] identified to have a majority of  $CO_2$  ice (hereafter location S), and one location from the Northern Hemisphere [point B, Fig 4c of *Brown* et al., 2012] identified to have mostly H<sub>2</sub>O ice (hereafter location N). The observed reflectance were obtained using radiance measurements from CRISM in the 1-4 µm spectral range. Therefore we only compare our simulations in this spectral range.

Since the reflectance data display a time dependency, we choose two of the least noisy endmember (i.e., most different) observed spectra for each location. Then we determine the best fit for each location by minimizing the weighted RMSE between each of the identified spectral reflectance curves and our hemispheric albedo simulations, which span a wide range of the parameter space described earlier. Spectral weighting for the RMSE calculation is done with the some solar spectral irradiance measurements [*Labs and Neckel*, 1968] applied throughout this study. Therefore, reflectance values for longer wavelengths are weighted less strongly and consequently do not fit as well with observations. We also note that reflectance measurements at wavelengths longer than  $2.5 \,\mu$ m are not very reliable (on Earth too) because there is very little incoming solar energy at these wavelengths.

Table 3. Best fit parameter combinations for each Mars location. The  $H_2O$  ice at Location S is simulated as a mixture within the  $CO_2$  snow, as opposed to a distinct layer.

Location S		Locati	on N		
$\cap$	Ls=276	Ls=337		Ls=13	Ls=65
CO <sub>2</sub> ice grain size	1000 µm	3000 µm	H <sub>2</sub> O ice grain size	100 µm	500 µm
H <sub>2</sub> Q ice grain size	100 µm	200 µm	CO <sub>2</sub> ice grain size	n/a	n/a
Amount of H <sub>2</sub> O ice	0.024%	0.07%	Amount of CO <sub>2</sub> ice	n/a	n/a
Amound of dust	0.0042%	0.003%	Amount of dust	0.06%	0.01%
RMSE (solar weighted)	0.06	0.07	RMSE	0.055	0.057

Table 8 lists the best fit values of various parameters along with spectrally-weighted RMSE values for both locations. The presence of any  $CO_2$  ice tends to increase the RMSE at location N. This happens because observations from location N occurred during early spring

to mid-summer in that hemisphere, when there is likely no  $CO_2$  ice present on the surface [e.g. *Brown* et al., 2014]. Location S needs about an order of magnitude less dust amount as compared to location N for optimal fitting. One reason for this is that Location S is deemed to have some coincident H<sub>2</sub>O ice, which functions as a competing impurity to dust because H<sub>2</sub>O snow substantially darkens albedo in the near-IR spectral region. For location S, changing  $CO_2$  is grain size does not have any significant impact on RMSE, while the H<sub>2</sub>O ice grain size has significant impact on RMSE for location N. This is consistent with our results described in section 3.2.

Figures 15 and 16 show the observed spectral reflectance curves along with simulated albedol using parameter values shown in Table 8. We observe an outlier point at 2.7  $\mu$ m wavelength in the observed data for both locations and at all times. Reflectance values at this wavelength are uncharacteristically higher than at nearby wavelengths, whereas both CO<sub>2</sub> and H<sub>2</sub>O snows have very high absorptivity at this wavelength (Fig. 3). This leads us to suggest that the high observed reflectance at this wavelength are spurious, and may be due either to an arternet of the measuring spectrometer (CRISM), atmospheric anomalies associated with dust of douds [*Brown et al*, 2010], and/or a calibration issue in the retrieval of surface reflectance at that wavelength. We also emphasize again that the low intensity of sunlight at this wavelength renders the reflectance measurements less certain than at shorter wavelengths.

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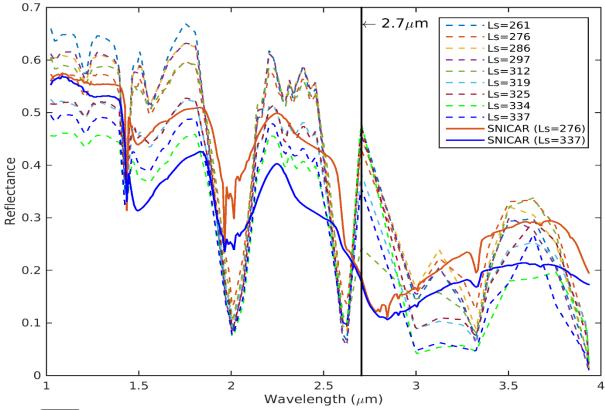


Figure 15: Observed reflectance for location S (dotted curves) along with modeled albedo using bes-fit parameters (solid blue curve). The black vertical line at 2.7  $\mu$ m indicates the outlit described in the text.

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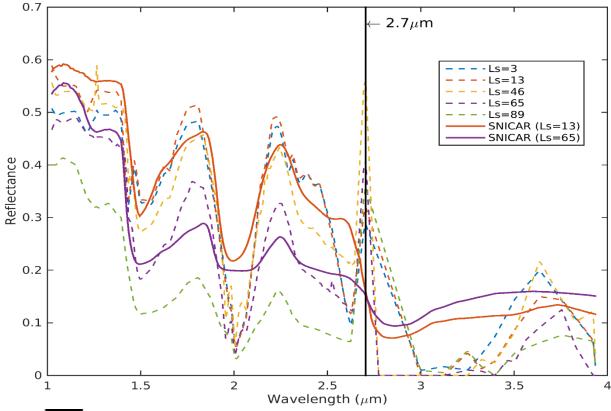


Figure 16: Same as fig. 15 but for location N

# 2 Comparison with OMEGA measurements

We also obtained spectral reflectance for Observation 2621\_1 from the OMEGA instrument [see Fig. 18 from *Appéré et al.*, 2011; shown later here], and modeled spectral reflectance of snow mixture simulated with a different radiative transfer model developed by *Douté and Schmitt* [1988].

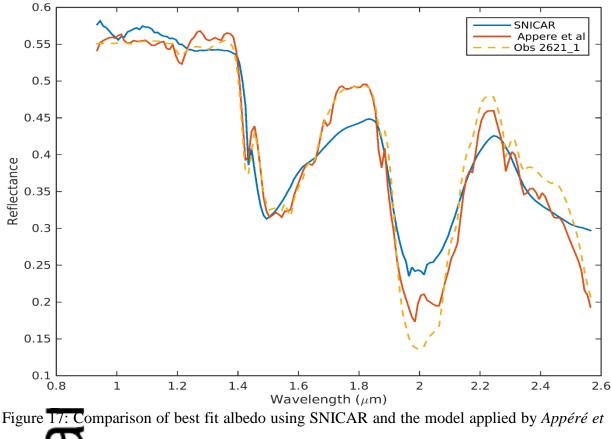
As shown in Table 9 and Fig. 17, *Appéré et al.*, [2011] achieved good agreement between simulated near-IR snow reflectance and OMEGA observations of a  $CO_2$ -rich deposit by assuming a mixed  $CO_2/H_2O$  snow configuration with a  $CO_2$  grain size of 7 cm, which interestingly is much larger than what is deemed to be realistic under most conditions [*Barr and Milkovich*, 2008]. We also achieved a reasonable fit (spectrally-weighted RMSE of 0.021, against the OMEGA observations presented by *Appéré et al.*, [2011] with a mixed  $CO_2$  and  $H_2O$  configuration of SNICAR applying a smaller  $CO_2$  grain radius and slightly

different mass fractions of dust and H<sub>2</sub>O (Table 9; Fig. 17), though admittedly the fit is not quite as good as that obtained by *Appéré et al.* [2011]. It is plausible that the better agreement obtained by *Appéré et al.* [2011] is due to their use of a directional reflectance radiative transfer model [*Douté and Schmitt*, 1988], which provides a more consistent comparison with the measurements. Uncertainties in the observations, however, are described by *Appéré et al.* [2011] **He be** roughly 20%, indicating that both sets of modeled spectra are within the range of uncertainty. Finally, we note that the quality of our fit ceases to change much with larger grain sizes of  $CO_2$  ice.

Table 9. Comparison of best-fit parameters between SNICAR	and Appéré et al	[2011]
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0	SNICAR	<i>Appéré et al.</i> , [2011]	
CO <sub>2</sub> ice grain size	3000 µm	7 cm	
Amount of CO2 ice	99.83%	99.75%	
H <sub>2</sub> O ice grain size	100 µm	200 µm	
Amount of H <sub>2</sub> O ice	0.16%	0.19%	
Dust grain size	1.5 μm	13 µm	
Amount of oust	0.0094%	0.06%	
RMS (solar weighted)	0.027	0.016	

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al., [2011] against data from OMEGA observation 2621\_1.



We have simulated the spectral albedo of  $CO_2$  snow using an enhanced 480-band version of SNICAR, which was previously developed for terrestrial snow. We explored  $CO_2$  snow albedo across the entire solar spectrum, including UV, visible and near-IR wavelengths. Our analysis shows significant differences between H<sub>2</sub>O and CO<sub>2</sub> snow albedos. H<sub>2</sub>O snow is about **+** times more absorptive than CO<sub>2</sub> snow in the near-IR region, and 7 times more absorptive overaged over the entire solar spectrum. CO<sub>2</sub> snow albedo shows very little dependence on solar zenith angle and a weaker dependence on grain size than H<sub>2</sub>O snow. The broactional albedo of CO<sub>2</sub> snow decreases by only 0.064 as effective grain size increases from 50 to 1500 µm.

The presence of thin snow layers exposes underlying surfaces to incoming radiation, hence impacting the surface albedo. The saturation thicknesses for  $CO_2$  snow and  $H_2O$  snow range from approximately 6.5 – 100 cm and 5 – 83 cm, respectively, for effective grain sizes ranging from 50 to 1500  $\mu$ m, though we caution again that these thicknesses may be smaller with non-spherical ice particles. Non-spherical grains scatter less strongly in the forward direction, thereby decreasing the penetration depth of solar radiation. Thicker  $CO_2$  snow is required to negate the impact of underlying surface because  $CO_2$  ice grains scatter more strongly than  $H_2O$  ice grains, especially in the near-IR spectrum. The presence of 0.01% dust reduce the broadband albedo of  $CO_2$  snow by about 50%, with Martian dust being the darkest type of dust explored here, followed by typical Earth dust and palagonite. The spectral shape of albedo changes caused by palagonite, which is often used as a Martian dust analog costly follow those of Mars dust, but palagonite is not as absorptive as Mars dust. The impact of dust on  $CO_2$  snow albedo saturates after its mass mixing ratio exceeds roughly 0.1%.

Because of the contrasting properties of  $H_2O$  and  $CO_2$  ice in the near-IR spectrum, different layering maximizing configurations of these types of snow can have substantial impact on net surface albedo. With an effective grain size of 100 µm, only about 2.5 cm of  $H_2O$  snow is needed to mask the influence of underlying  $CO_2$  snow on net surface albedo (Table 5), while more than double this amount of  $CO_2$  snow is needed to mask the influence of  $H_2O$  snow (Table 6). Such effects are relevant for the perennial  $H_2O$  ice caps of Mars, and where water vapor them the atmosphere condenses on top of  $CO_2$  ice in other areas of the planet. When both snow types are present as a mixture rather than separate layers, 0.01% of  $H_2O$  snow reduces the broadband albedo of  $CO_2$  snow by 0.03, while 1% of  $CO_2$  snow is required to increase the broadband albedo of  $H_2O$  snow by the same amount.

With the identification of optimal snow parameter combinations, our results show a decent agreement between modeled spectral albedo and observed reflectance of the Martian polar ice caps in the 1–4  $\mu$ m spectral range. The CRISM data exhibit anomalously high reflectance at 2.7  $\mu$ m, which cannot be explained with presence of either CO<sub>2</sub> or H<sub>2</sub>O ice, as both media are highly absorptive at this wavelength. SNICAR also provides realistic best-fit parameters for

matching OMEGA near-IR observations, though the spectral fit is not as good as that achieved previously with a directional reflectance model [*Appéré et al.*, 2011]. Simulations presented here could potentially be used in combination with observed data to refine the calibration of surface albedo retrieval algorithms. Model results can also be used to interpolate measurements to higher spectral resolution. The new spectrally resolved albedos for CO mode potentially wide applicability to any planet or system with  $CO_2$  ice, especially Mars.

#### Acknowledgements

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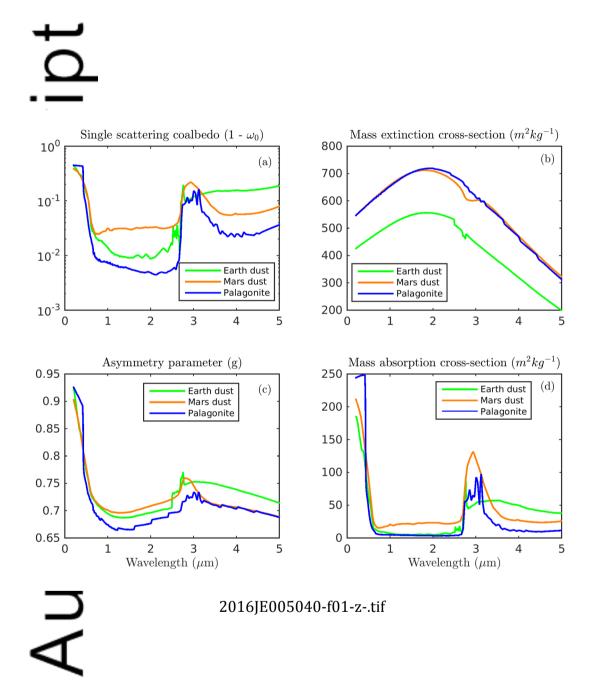
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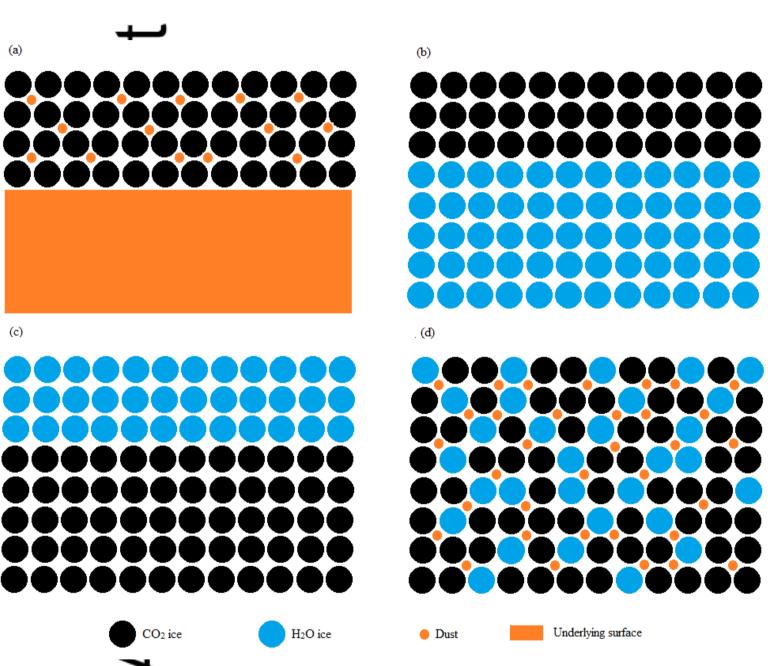
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