# AN IMPROVED CARBON DIOXIDE SNOW SPECTRAL ALBEDO MODEL: APPLICATION TO MARTIAN CONDITIONS

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## 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; Larson 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; Brown et al., 2014]. Significant portions of atmospheric CO<sub>2</sub> (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 CO2 snow albedo and influences of properties such as dust content, ice grain size, and snow thickness, as well as the albedo effects of mixing and layering of CO<sub>2</sub> and H<sub>2</sub>O snow.

Our work determines the albedo of  $CO_2$  snow by extending the Earth-based Snow, Ice, and Aerosol Radiation (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 deltahemispheric 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  $CO_2$  snow albedo across the UV, visible and near-IR spectrum [*Warren* et al., 1990; *Hansen*, 1999]. 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  $CO_2$  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; Clancy 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 cry-osphere 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].

#### **Data and Methodology:**

Hansen [1997, 2005] made extensive laboratory measurements of the complex refractive indices of solid  $CO_2$  ice in the spectral range from 0.174 µm to 333 µm. We apply these data along with 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 area-weighted 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 hematite" 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) were 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 µm) 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  $r_{eff}=1.5\mu$ m and effective variance ( $v_{eff}$ )=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).



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



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.

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 asymmetry 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 framework of SNICAR to first simulate the albedo of pure CO<sub>2</sub> snow across the visible and near-IR spec-

trum. We then explore and compare the impacts of Earth dust, Mars dust and palagonite on  $CO_2$  and  $H_2O$  snow albedo. Finally, we adopt a two layer model (with the bottom layer being semi-infinite) to calculate the impacts of  $H_2O$  snow presence on top of  $CO_2$  snow and vice-versa. In all other cases we assume only a single snow layer, either with semiinfinite 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.

### **Results:**

We have simulated the spectral albedo of CO<sub>2</sub> snow using an enhanced 480-band version of SNICAR, which was previously developed for terrestrial snow. We explored CO<sub>2</sub> 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 8 times more absorptive than CO<sub>2</sub> snow in the near-IR region, and 7 times more absorptive averaged over the entire solar spectrum. Figure 3 shows the spectral hemispheric albedo of pure, semiinfinite CO<sub>2</sub> and H<sub>2</sub>O snow with spherical grain effective radius of 100 µm and solar zenith angle of  $60^{\circ}$ . It is evident that the CO<sub>2</sub> is more reflective than H<sub>2</sub>O snow, especially in the near-IR 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 broadband 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<sub>2</sub> snow and H<sub>2</sub>O snow range from approximately 6.5 - 100 cm and 5 - 83 cm, respectively, for effective grain sizes ranging from 50 to 1500 µm, though we caution again that these thicknesses may be smaller with non-spherical ice particles. Nonspherical grains scatter less strongly in the forward direction, thereby decreasing the penetration depth of solar radiation. Thicker CO2 snow is required to negate the impact of underlying surface because CO<sub>2</sub> ice grains scatter more strongly than H<sub>2</sub>O ice grains, especially in the near-IR spectrum. The presence of 0.01% dust reduces the broadband albedo of CO<sub>2</sub> snow by about 50%, with Martian dust being the darkest type of dust explored here, followed by typical Earth dust and palagonite (Figure 4). The spectral shape of albedo changes caused by palagonite, which is often used as a Martian dust analog, closely follow those of Mars dust, but palagonite is not as absorptive as Mars dust. The impact of dust on CO2 snow albedo saturates after its mass mixing ratio exceeds roughly 0.1%.



Figure 3: Comparison of CO<sub>2</sub> and H<sub>2</sub>O snow spectral albedo simulated with the SNICAR model (Grain size =  $100 \ \mu m$  and solar zenith angle =  $60^{\circ}$ )

Because of the contrasting properties of H<sub>2</sub>O and CO<sub>2</sub> ice in the near-IR spectrum, different layering and mixing 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<sub>2</sub>O snow is needed to mask the influence of underlying CO<sub>2</sub> snow on net surface albedo (Table 5), while more than double this amount of CO<sub>2</sub> snow is needed to mask the influence of H<sub>2</sub>O snow (Table 6). Such effects are relevant for the perennial H<sub>2</sub>O ice caps of Mars, and where water vapor from the atmosphere condenses on top of CO<sub>2</sub> ice in other areas of the planet. When both snow types are present as a mixture rather than separate layers, 0.01% of H<sub>2</sub>O snow reduces the broadband albedo of CO<sub>2</sub> snow by 0.03, while 1% of  $CO_2$  snow is required to increase the broadband albedo of H<sub>2</sub>O snow by the same amount.



Figure 4: Impact of different types of dust on  $CO_2$  snow albedo, with dust mass mixing ratio of 0.01%. The assumed snow grain size is 100 µm.

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 (Figure 5). SNICAR also provides realistic best-fit parameters for matching OMEGA near-IR observations (Figure 6), 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<sub>2</sub> snow presented here have potentially wide applicability to any planet or system with CO<sub>2</sub> ice, especially Mars.



Figure 5: Observed reflectance for location N (dotted curves) along with modeled albedo using best-fit parameters (solid blue curve). The black vertical line at 2.7  $\mu$ m indicates the outlier.



Figure 6: Comparison of best fit albedo using SNICAR and the model applied by *Appéré et al.*, [2011] against data from OMEGA observation 2621\_1.

#### **References:**

Appéré, T., et al. (2011), Winter and spring evolution of northern seasonal deposits on Mars from OMEGA on Mars Express, J. Geophys. Res., 116, E05001, doi:10.1029/2010JE003762.

Balkanski, Y., M. Schulz, T. Claquin, and S. Guibert (2007), Reevaluation of Mineral aerosol radiative forcings suggests a better agreement with satellite and AERONET data. Atmospheric Chemistry and Physics, 7(1), 81-95.

Banin, A., et al. (1997), Acidic volatiles and the Mars soil, J. Geophys. Res., 102(E6), 13341–13356, doi:10.1029/97JE01160.

Bibring, J. P., et al. (2005), Mars surface diversity as revealed by the OMEGA/Mars Express observations. Science, 307(5715), 1576-1581.

Brown, A. J., S. Piqueux, and T. N. Titus, (2014), Interannual observations and quantification of summertime  $H_2O$  ice deposition on the Martian  $CO_2$  ice south polar cap. Earth and Planetary Science Letters, 406, 102-109.

Clancy, R. T., S. W. Lee, G. R. Gladstone, W. W. McMillan, and T. Roush (1995), A new model for Mars atmospheric dust based upon analysis of ultraviolet through infrared observations from Mariner 9, Viking, and Phobos, J. Geophys. Res., 100, 5251–5264.

Clark, R. N., T. V. King, M. Klejwa, G. A. Swayze, and N. Vergo (1990), High spectral resolution reflectance spectroscopy of minerals. J. Geophys. Res., 95(B8), 12653–12680, doi:10.1029/JB095iB08p12653.

Flanner, M. G., C. S. Zender, J. T. Randerson, and P. J. Rasch (2007), Present day climate forcing and response from black carbon in snow, J. Geophys. Res., 112, D11202, doi:10.1029/2006JD008003.

Flanner, M. G., et al. (2009), Springtime warming and reduced snow cover from carbonaceous particles, Atmos. Chem. Phys., 9, 2481-2497.

Forget, F. (1998), Mars CO<sub>2</sub> ice polar caps. In Solar System Ices, Springer Netherlands, 477-507.

Forget, F., F. Hourdin, and O. Talagrand (1998), CO<sub>2</sub> snowfall on Mars: Simulation with a general circulation model. Icarus, 131(2), 302-316.

Hansen, G. B. (1997), The infrared absorption spectrum of carbon dioxide ice from 1.8 to 333  $\mu$ m, J. Geophys. Res., 102(E9), 21569–21587, doi:10.1029/97JE01875.

Hansen, G. B. (1999), Control of the radiative behavior of the Martian polar caps by surface  $CO_2$  ice: Evidence from Mars Global Surveyor measurements, J. Geophys. Res., 104(E7), 16471–16486, doi:10.1029/1998JE000626.

Hansen, G. B. (2005), Ultraviolet to near-infrared absorption spectrum of carbon dioxide ice from 0.174 to 1.8 µm. J. Geophys. Res., 110, E11003, doi:10.1029/2005JE002531.

Hansen, J. E., and L. D. Travis (1974), Light scattering in planetary atmospheres. Space Science Reviews, 16(4), 527-610.

Herr, K. C., and G. C. Pimentel (1969), Infrared absorptions near three microns recorded over the polar cap of Mars. Science, 166(3904), 496-499.

Kieffer, H. H., and T. N. Titus, (2001), TES mapping of Mars' north seasonal cap. Icarus, 154(1), 162-180.

Kieffer, H. H., et al. (2000), Mars south polar spring and summer behavior observed by TES: Seasonal cap evolution controlled by frost grain size, J. Geophys. Res., 105(E4), 9653–9699, doi:10.1029/1999JE001136.

Langevin, Y., J.-P. Bibring, F. Montmessin, F.

Forget, M. Vincendon, S. Douté, F. Poulet, and B. Gondet (2007), Observations of the south seasonal cap of Mars during recession in 2004–2006 by the OMEGA visible/near-infrared imaging spectrometer on board Mars Express, J. Geophys. Res., 112, E08S12, doi:10.1029/2006JE002841.

Larson, H. P., and U. Fink (1972), Identification of carbon dioxide frost on the Martian polar caps. The Astrophysical Journal, 171, L91.

Leighton, R. B., and B. C. Murray (1966), Behavior of carbon dioxide and other volatiles on Mars. Science, 153(3732), 136-144.

Montmessin, F., and F. Lefèvre (2013), Transport-driven formation of a polar ozone layer on Mars. Nature geoscience, 6(11), 930-933, doi:10.1038/ngeo1957.

Sokolik, I. N., and O. B. Toon (1999), Incorporation of mineralogical composition into models of the radiative properties of mineral aerosol from UV to IR wavelengths, J. Geophys. Res., 104(D8), 9423– 9444, doi:10.1029/1998JD200048.

Tillman, J. E., N. C. Johnson, P. Guttorp, and D. B. Percival (1993), The martian annual atmospheric pressure cycle: Years without great dust storms. Journal of Geophysical Research: Planets (1991–2012), 98(E6), 10963-10971.

Toon, O. B., C. P. McKay, T. P. Ackerman, and K. Santhanam (1989), Rapid calculation of radiative heating rates and photodissociation rates in inhomogeneous multiple scattering atmospheres, J. Geophys. Res., 94 (D13), 16287-16301, doi:10.1029/JD094iD13p16287.

Warren, S. G., W. J. Wiscombe, and J. F. Firestone (1990), Spectral albedo and emissivity of CO<sub>2</sub> in Martian polar caps: Model results, J. Geophys. Res., 95(B9), 14717–14741, doi:10.1029/JB095iB09p14717.

Warren, S. G., and R. E. Brandt (2008), Optical constants of ice from the ultraviolet to the micro-wave: A revised compilation, J. Geophys. Res., 113, D14220, doi:10.1029/2007JD009744.

Wolff, M. J., R. T. Clancy, J. D. Goguen, and M. C. Malin, and B. A. Cantor (2010), Ultraviolet dust aerosol properties as observed by MARCI. Icarus, 208(1), 143-155.

Wolff, M. J., et al. (2009), Wavelength dependence of dust aerosol single scattering albedo as observed by the Compact Reconnaissance Imaging Spectrometer, J. Geophys. Res., 114, E00D04, doi:10.1029/2009JE003350.

Wolff, M.J. et al. (2006), Constraints on dust aerosols from the Mars Exploration Rovers using MGS overflights and Mini-TES. J. Geophys. Res., 111, E12S17, doi:10.1029/2006JE002786.