



HAL
open science

Dry powders reflectance model based on enhanced backscattering: case of hematite α -Fe₂O₃

Morgane Gerardin, Pauline Martinetto, Nicolas Holzschuch

► **To cite this version:**

Morgane Gerardin, Pauline Martinetto, Nicolas Holzschuch. Dry powders reflectance model based on enhanced backscattering: case of hematite α -Fe₂O₃. Journal of the Optical Society of America. A Optics, Image Science, and Vision, 2023, 40 (9), pp.1817-1830. 10.1364/JOSAA.487498. hal-04316639v2

HAL Id: hal-04316639

<https://inria.hal.science/hal-04316639v2>

Submitted on 1 Dec 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

1 Dry powders reflectance model based on 2 enhanced back-scattering: case of hematite 3 $\alpha - \text{Fe}_2\text{O}_3$

4 MORGANE GERARDIN,^{1,2,*} PAULINE MARTINETTO,² AND NICOLAS
5 HOLZSCHUCH¹

6 ¹Univ. Grenoble Alpes, CNRS, Inria, Grenoble INP, LJK, 38000 Grenoble, France

7 ²Univ. Grenoble Alpes, CNRS, Institut Néel, 38000 Grenoble, France

8 *gerardin.morgane@gmail.com

9 **Abstract:** By performing Bidirectionnal Reflectance Distribution Function (BRDF) measure-
10 ments, we have identified back-scattering as the main phenomena involved in the appearance of
11 dry nano-crystallized powders. We introduce an analytical and physically-based BRDF model
12 that relies on the enhanced back-scattering theory to accurately reproduce BRDF measurements.
13 These experimental data were performed on optically thick layers of dry powders with various
14 grains' morphologies. Our results are significantly better than the ones obtained with previous
15 models. Our model has been validated against the BRDF measurements of multiple synthesized
16 nano-crystallized and mono-disperse $\alpha - \text{Fe}_2\text{O}_3$ hematite powders. Finally, we discuss the ability
17 of our model to be extended to other materials or more complex powder morphologies.

18 © 2023 Optica Publishing Group

19 1. Introduction

20 Accurate reproduction of powdered material appearance is an important issue in many domains,
21 such as environmental sciences, teledetection, digital prototyping, entertainment and art preser-
22 vation. Powder materials are ubiquitous in real life. They can be used with a binder like pigments
23 in most painting techniques and in some cosmetics e.g. lipstick. But they are also used without
24 any binder. Dry powders are found as spices, dry soils, dust, and dry pigments for example.

25 The latter are particularly important as they are involved in parietal paintings from paleolithic to
26 neolithic era. In some cases, the pigments were used pure and dry on the wall. Other application
27 techniques required the pigments to be dispersed in an organic binder [1, 2]. However, only few
28 traces of these binders are left nowadays, and they are not the main component responsible for
29 the painting color. The parietal paintings that are visible nowadays can therefore be described
30 as a dry pigment layer on top of a rock substrate. These cultural heritage artefacts have been
31 degraded over the years by both environmental and anthropogenic causes, so that some of them
32 are nowadays almost illegible [1]. Images of such heavily deteriorated artefacts are recorded
33 using image enhancement techniques [3, 4]. Time, weathering and human activity are responsible
34 for the peeling off, the erasure and possible color changing of the original paintings.

35 Computer Graphics is a real asset for the preservation of parietal paintings. Photo-realistic
36 image renderings using accurate appearance models would allow the reproduction of such
37 artefacts and the reconstruction of the most erased ones. It will also promote their broadcasting
38 to a large audience.

39 The colour of a powder material depends on both its chemical composition and on its
40 morphometry, which refers to the size and the shape of its grains. This hypothesis is well known
41 and particularly well justified in the case of pure $\alpha - \text{Fe}_2\text{O}_3$ hematite powders that can show
42 various shades from light red to purple [5, 6]. The chemical composition of the material is
43 involved in the absorption phenomena, while the morphology of the grains influences the way
44 light is scattered by the material. Such light/matter interactions at the nanometric scale result in

45 the macroscopic material appearance an observer perceives.

46 At the macroscopic scale, light scattering by a material is modeled using a *Bidirectional*
47 *Scattering Distribution Function* (BSDF) model. When there is no light transmission and
48 only light scattered in reflection is at stake, the BSDF is reduced to *Bidirectional Reflectance*
49 *Distribution Function* (BRDF). Most models assume that the light is mainly scattered at the
50 surface of an object, around the specular direction ie. in the direction opposite to the incident
51 direction. Depending on the roughness of the surface, a diffuse look is obtained. According
52 to these surface models, the color of the rendered materials only depends on their chemical
53 composition through the optical constants. These models are not suitable in the case of dry
54 powders for two reasons. First, powders are a medium composed of a collection of randomly
55 oriented scatterers, so light is scattered multiple times in the volume of the medium. To account
56 for volume scattering, one may use the Mie scattering theory [7, 8]. This is relevant for powders
57 diluted into a binder, and takes into account volume scattering depending on the size and shape
58 of the grains. However, in the absence of a binder, the grains composing the powder are too close
59 to each other, making the Mie scattering model unsuitable as shown by [6]. The second issue is
60 that only few of surface scattering models account for scattering in the backward direction [9].

61
62 In this paper, we show that contrary to the prediction of most BRDF models, the major
63 contribution to a dry powder BRDF is not the specular peak, but the back-scattering peak. We
64 propose an analytical and physically-based BRDF model involving six parameters able to simulate
65 the appearance of optically thick layers of dried pigments. We separate the model into two
66 independent contributions: volume scattering and surface scattering. The former decomposes
67 into single and multiple scattering that are responsible for the sharp back-scattering lobe, while
68 the latter accounts for the specular scattering. This model has been developed and experimentally
69 validated for seven hematite $\alpha - \text{Fe}_2\text{O}_3$ powders of different morphologies. Although our model
70 still tends to slightly underestimate the back-scattering contribution to the BRDF, it gives a good
71 intuition on the color variations of the studied samples. It is ready-to-use to reproduce the color
72 of multiple studied hematite powders through renderings.

73 In Section 2 we will review previous works on BRDF models suitable for the description of dry
74 powder materials, and more particularly on models that take into account the back-scattering
75 contribution. The theoretical background necessary for the modeling of light scattering in a
76 particle medium is introduced in Section 3. The $\alpha - \text{Fe}_2\text{O}_3$ samples and their measurements are
77 described in Section 4. The description of our appearance model and its optimization procedure
78 is done on Section 5 whereas in Section 6 we present its results, showing that it fits well the
79 experimental BRDF of the studied samples. We conclude and give some future work directions
80 in Section 7.

81 2. Previous work

82 Dry powders and pigments are complex materials composed of a dense collection of particles
83 with nanometric to micrometric grains size. In the absence of a binder, the dry grains are too
84 close to each other to be modeled using Mie scattering theory [6]. Their appearance is the result
85 of absorption and scattering phenomena, so its description suggests the full understanding of the
86 interactions of light with the material, at both its surface and in its volume.

87 We have identified two models that could be used for dry powders' BRDF simulations: the
88 spectralon model and the RTLSR model. Firstly, they both take into account the *back-scattering*,
89 a phenomena which has already been observed on dry powders such as meteorite soils [10].
90 Then, although these models have not been used for reproducing the appearance of dry powders
91 or pigments, they have been introduced for describing particulate media without binder. These
92 two reasons make them worthy to study in the case of dry powders.

93 2.1. Spectralon

94 An empirical model has been developed by [11] to reproduce the BRDF of the Spectralon®, a
95 material that resembles a powder since it is made out of a collection of compressed polymer
96 particles. This model proposes a decomposition into four independent scattering phenomena.
97 These contributions are by order of importance: **Deep scattering D**, which accounts for volume
98 scattering at small incidence and observation angles, **Back-scattering B** and **Specular scattering S**,
99 to account for the backward and forward surface scattering, and **Subsurface scattering SS**,
100 which accounts for volume scattering at more grazing incidence/observation geometries. Each of
101 these contributions is modeled using very simple analytical expression.

$$BRDF(\theta_i, \theta_o) = D(\theta_i, \theta_o) + B(\theta_i, \theta_o) + S(\theta_i, \theta_o) + SS(\theta_i, \theta_o) \quad (1)$$

102 One should note that this model has been developed in the incident plane. To model the
103 complete BRDF of a material some extension is necessary to account for the different azimuth
104 angles. We propose such an adaptation in Supplementary work.

105 **Volume scattering contributions:** For small incident angles θ_i , there is a higher probability
106 for the light to penetrate deeply into the medium before it exits with a direction close to the
107 surface normal, with a small observation angle θ_o . In this case, the entry and the exit points of
108 the light are quite close. Such a phenomenon is called **Deep scattering D** and is identified as the
109 main contribution to the BRDF. Its modeling in the incident plane is inspired from an empirical
110 expression from [12] and involves five material dependent fitting parameters d_j :

$$D(\theta_i, \theta_o) = d_0 + d_1(\theta_i^2 + \theta_o^2) + d_3(\theta_i^4 + \theta_o^4) + d_3\theta_i^2\theta_o^2 + d_4\theta_i^4\theta_o^4 \quad (2)$$

111 Deep scattering results in a large scattering lobe that describes the general shape of the measured
112 BRDF.

113 For larger incident angles, light penetrates much less deeply and propagates right underneath
114 the medium surface to an exit further away from the entry point which is modeled by the
115 **Subsurface scattering SS**. Two models were proposed by [11] involving an exponential term so
116 that the more grazing the angle, the more important this contribution is. For simplicity, we only
117 give here the expression of the simplest, which involves two empirical parameters s_{s0} and s_{s1} :

$$SS(\theta_i, \theta_o) = s_{s0} \exp(s_{s1}|\theta_i + \theta_o|) \quad (3)$$

118 **Surface scattering contributions:** The surface scattering phenomena are responsible for the
119 finer details of the measured BRDF. The **Back scattering** is modeled using a Lorentzian function
120 with amplitude b_0 and width b_1 , whereas the **Specular scattering** is described as a Gaussian
121 function with width s_1 and whose amplitude depends on two other parameters s_0 and s_2 .

122
123 As the Spectralon model involves a large number of empirical but material-dependent
124 parameters optimized in the specific case of the Spectralon material, it can be adapted to
125 reproduce with a high fidelity a large range of materials. Nevertheless, these parameters have no
126 explicit relationship with the chemical composition nor the physical parameters of the considered
127 material so they cannot be predicted, but only numerically optimized from measurement fittings.

128 2.2. RTLSR

129 The RTLSR (Ross-Thick Li-Sparse Reflectance) model [13, 14], is a semi-empirical model
130 used in teledetection for simulating the BRDF of forest canopies. It decomposes the BRDF
131 into two contributions: volume scattering contribution R_{vol} deduced from an approximation of
132 the radiative transfer theory (RTT) [15] and accounting for both *single* and *multiple* scattering
133 between the leaves, and surface scattering R_{geo} which is inferred according to geometrical

134 considerations [16] and accounts for shadowing and occlusions of leaves on each others. An
 135 optimization factor α allows to control the proportion of each of the contributions.

$$BRDF(\theta_i, \theta_o, \varphi_i, \varphi_o) = \alpha R_{vol}(\theta_i, \theta_o, \varphi_i, \varphi_o) + (1 - \alpha) R_{geo}(\theta_i, \theta_o, \varphi_i, \varphi_o) \quad (4)$$

136 Initially developed for thick and sparse canopies, extensions of this model have been proposed
 137 for thin and dense media [17]. [18] brought modifications to the model for the study of snow, and
 138 multiple works [16, 19, 20] agree that it can be used for bare soils although they do not explicitly
 139 introduce the changes that should be done in such a case. We propose an adaptation of this model
 140 for dry powders in Supplementary work. Its unique optimization factor makes this model too
 141 rigid and remains unable to reproduce fine appearance variations.

142 3. Background

143 As a dry powder layer involves a large number of scatterers with relatively high density, it is
 144 complex to describe the scattering of light in such a medium. When there is no interference
 145 phenomena at stake, it can be done using the RTT [21, 22]. As it relies on the assumption that the
 146 scattered fields are uncorrelated, RTT by itself is unable to predict the appearance of materials
 147 which exhibits a strong back-scattering contribution.

148 A deeper analysis of the back-scattering phenomena (see Section 3.5) occurring in a scattering
 149 medium refers to *Enhanced Back-Scattering (EBS)*, which describes it as the result of constructive
 150 interferences [23, 24]. Contrary to the RTT, the scattered fields are supposed to be correlated. The
 151 EBS is therefore the sum of the two terms from RTT (*single* and *multiple scattering*) and a third
 152 one accounting for the constructive interferences in the backward direction. As the analytical
 153 results are deduced within the diffusion approximation, only isotropic particles are considered.
 154 Nevertheless, Tsang & Kong [23] extended the model to account for anisotropic scattering in the
 155 case of incident field at normal incidence.

156 This section gives an overview of the theoretical aspects and hypotheses used in the EBS theory.

157 3.1. Medium description

158 Let's consider a region 0 free of scatterers with wavenumber $k_0 = 2\pi/\lambda$, and a medium 1
 159 characterized by an effective complex wavenumber $K = K' + iK''$ containing scattering spherical
 160 inclusions with a density \mathcal{D} . All scatterers have the same radius b and scattering properties
 161 (cf. Figure 1). Note that for clearer reading, we adopt bold notations for vectors representation
 162 ($\vec{v} = \mathbf{v}$) in the following.

163 The medium is illuminated in the incoming direction \mathbf{K}_i with an angle θ_i to the surface normal
 164 and azimuthal angle φ_i by light coming from a point source at the position \mathbf{r}_i in the region 0.
 165 The light scattered by the slab is observed at a point in region 0 in the direction \mathbf{K}_o , described by
 166 the angle θ_o to the normal, and $\varphi = |\varphi_i - \varphi_o|$ in the azimuthal plane at the position \mathbf{r}_o which is
 167 far enough from the interface ($\|\mathbf{r}_o\| \gg 1$). To ease the description of the scattering inside the
 168 layer, a point scatterer approximation is made: the scattering events occur at the center point of
 169 the spherical scatterers.

170 3.2. Foldy's approximation

171 For a sufficiently small density \mathcal{D} of scatterers, the effective wavenumber K can be expressed
 172 using the Foldy's approximation [25]:

$$K \approx \frac{2\pi}{\lambda} + j\lambda\mathcal{D}F \quad (5)$$

173 where $j^2 = -1$, F is the complex scattering amplitude describing the scattering properties of the
 174 particles, and λ is the wavelength at which the light propagates.

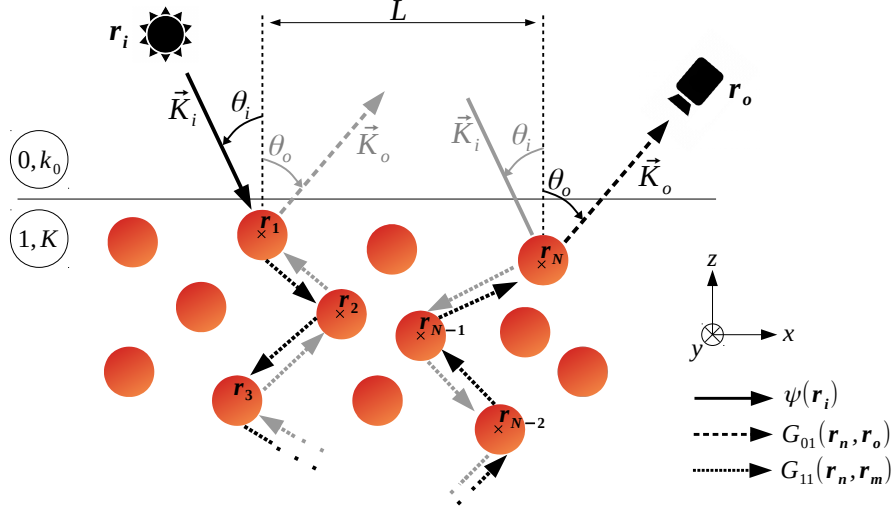


Fig. 1. N -th order multiple scattering in a medium composed of particles. The incident light follows a path going from the particle at \mathbf{r}_1 to the one at \mathbf{r}_N (black path). Interferences occur with a second path that goes from \mathbf{r}_N to \mathbf{r}_1 (gray path). The incoherent part of the resulting field (denoted as \mathcal{L}_N in Section 5.1) contributes to the ladder term whereas its coherent part (denoted as C_N in Section 5.1) accounts for the cyclical term.

175 3.3. Light propagation

176 The propagation of light inside a medium containing scattering particles is illustrated by the
 177 Figure 1. The light wave coming from region 0 without being scattered is described by the
 178 incident field :

$$\psi(\mathbf{r}_i) = \exp(j\mathbf{K}_i \cdot \mathbf{r}_i) \quad (6)$$

179 where \mathbf{K}_i is of magnitude K given by the Foldy's approximation, and oriented in the incident
 180 direction.

181 After it has been scattered by a particle, light travels in the region 1 towards another scatterer,
 182 as if it was in a space free of scatterers. Under this hypothesis, the propagation of light from
 183 a position \mathbf{r}' towards \mathbf{r} is given by the Green's function $G(\mathbf{r}, \mathbf{r}')$, that satisfies the Helmholtz
 184 equation :

$$(\Delta + k^2)G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (7)$$

185 By averaging over the particles, the mean Green's function referring to the propagation of light
 186 from an inclusion to another is given as follows:

$$G_{11}(\mathbf{r}_n, \mathbf{r}_m) = \frac{\exp(j\mathbf{K} \cdot |\mathbf{r}_n - \mathbf{r}_m|)}{4\pi|\mathbf{r}_n - \mathbf{r}_m|} \quad (8)$$

187 where \mathbf{r}_m and \mathbf{r}_n are the positions of two distinct scatterers in the medium 1. In the same way,

$$G_{01}(\mathbf{r}_n, \mathbf{r}_o) = \frac{\exp(jk_0 r_o)}{4\pi r_o} \exp(-j\mathbf{K}_o \cdot \mathbf{r}_n) \quad (9)$$

188 describes the propagation from a scatterer at position \mathbf{r}_n in region 1 towards the camera at \mathbf{r}_o in
 189 region 0. The vector \mathbf{K}_o is of magnitude K and oriented towards the camera.

190 **3.4. Light scattering by one particle**

191 The scattering events caused by the encountering of light with the n -th scatterer is described
 192 using the transition operator T_n that we introduced as :

$$T_n(\mathbf{r}_n) = 4\pi F(\Theta_n)\delta(r_{in} - r_{on}) = 4\pi F(\Theta_n) \quad (10)$$

193 where $\Theta_n = \theta_{on} - \theta_{in}$ is the scattering angle between the incident direction on the n -th scatterer
 194 θ_{in} and the outgoing direction θ_{on} .

195 The complex scattering amplitude $F(\Theta_n)$ is linked to the scattering phase function $p(\Theta_n)$ using
 196 the relationship:

$$\rho p(\Theta_n) = \frac{4\pi N}{\kappa} |F(\Theta_n)|^2 \quad (11)$$

197 where ρ is the single scattering albedo and κ the extinction rate.

198 Although any phase function can be used, a common one would be the Henyey-Greenstein
 199 phase function [26] (Eq. 12). It involves one parameter g known as the *anisotropy* and whose
 200 value lies between -1 and 1 describing either backward or forward scattering. Isotropic scattering
 201 would then be described with $g = 0$.

$$p(\Theta) = \frac{1}{4\pi} \frac{1 - g^2}{(1 + g^2 - 2g\cos\Theta)^{3/2}} \quad (12)$$

202 **3.5. Enhanced back-scattering**

203 The EBS theory offers a physical description of the back scattering phenomenon observed in
 204 dense media. It is an extension of RTT [21, 22]: the so called *ladder terms* accounting for both
 205 single scattering $BRDF_{ebs, \mathcal{L}_1}$ and some multiple scattering $BRDF_{ebs, \mathcal{L}_{2+}}$ take into account the
 206 contribution of uncorrelated scattered fields already described by the RTT. This model also
 207 accounts for coherent scattered fields that induce interference effects as light undergoes multiple
 208 scattering events in the medium. It is described by a *cyclical term* $BRDF_{ebs, \mathcal{C}}$ and results in a
 209 sharp peak in the back-scattering direction.

210
 211 The BRDF is then composed of three contributions. Since the angular and spectral dependency
 212 of these three components is the same than the overall BRDF $(\theta_i, \theta_o, \varphi_i, \varphi_o, \lambda)$, it is not reminded
 213 in the following equations for readability purposes.

$$BRDF_{ebs}(\theta_i, \theta_o, \varphi_i, \varphi_o, \lambda) = BRDF_{ebs, \mathcal{L}_1}(\kappa, g) + BRDF_{ebs, \mathcal{L}_{2+}}(\kappa) + BRDF_{ebs, \mathcal{C}}(\kappa) \quad (13)$$

214 This model has been developed for thick layers of a medium composed of spherical scatterers
 215 of radius b embedded in a host medium [23, 24, 27, 28].

216 Analytical expressions of the multiple scattering terms are obtained by considering that for
 217 optically thick media with high albedo the resulting overall scattering statistically tends to be
 218 isotropic. So the phase function used in multiple scattering is supposed to be constant $p(\Theta) = \frac{1}{4\pi}$.
 219 This is known as the *diffusion approximation* and leads to results in Eqs. 14.

$$\left\{ \begin{array}{l} BRDF_{ebs, \mathcal{L}_1}(\kappa, g) = \frac{\rho p(\Theta)}{\mu_o + \mu_i} \left[1 - \exp\left(-\kappa d \left(\frac{1}{\mu_o} + \frac{1}{\mu_i}\right)\right) \right] \\ BRDF_{ebs, \mathcal{L}_{2+}}(\kappa) = \frac{3\rho^2}{1 - \mu_i^2 c^2} \left[\frac{2Q}{1 - \mu_o c} - \frac{\mu_i^2}{\mu_i + \mu_o} \right] \\ BRDF_{ebs, \mathcal{C}}(\kappa) = \frac{3\rho^2 [c + v(1 - \exp(-2c\tau_o))]}{2\mu_i \mu_o c v [(c + v)^2 + u^2]} \end{array} \right. \quad (14a)$$

$$\left. \begin{array}{l} \end{array} \right\} \quad (14b)$$

$$\left. \begin{array}{l} \end{array} \right\} \quad (14c)$$

220 with $\mu_i = \cos\theta_i$, $\mu_o = \cos\theta_o$, d the thickness of the powder layer, and τ_o the extinction ratio
 221 whose expression is given in Eq. 16.

222 Multiple parameters involved in Eqs 14 are introduced to make the equation more legible and
 223 depend on the geometry under which the medium is illuminated and observed. These parameters
 224 have been introduced by [24] for isotropic scatterers such as:

$$\left\{ \begin{array}{l} u = \frac{k_0}{\kappa}(\mu_i - \mu_o) \end{array} \right. \quad (15a)$$

$$\left\{ \begin{array}{l} v = \frac{1}{2} \left(\frac{1}{\mu_i} + \frac{1}{\mu_o} \right) \end{array} \right. \quad (15b)$$

$$\left\{ \begin{array}{l} \alpha = \frac{k_0}{\kappa} f \end{array} \right. \quad (15c)$$

$$\left\{ \begin{array}{l} c = \sqrt{3(1 - \rho) + \alpha^2} \end{array} \right. \quad (15d)$$

$$\left\{ \begin{array}{l} Q = \frac{[1 + \mu_i c - (1 - \mu_i c) \exp(-2c\tau_o(\lambda))]}{4c} \end{array} \right. \quad (15e)$$

225 where f is the norm of the vector \mathbf{f} defined as difference between the projections of the normalized
 226 incoming and outgoing direction vectors (Figure 2) which allows the BRDF modelization in any
 227 azimuthal plane.

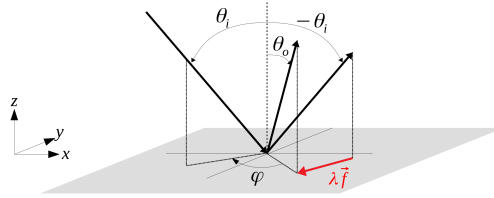


Fig. 2. Definition of the vector \mathbf{f} .

228

229 Only the single scattering term involves the phase function in such a case, and therefore the
 230 anisotropy parameter g if the Henyey-Greenstein phase function is at use (see Eq. 12). Tsang &
 231 Kong [23] introduced the consideration of anisotropic scatterers but only with normal incidence.
 232 We will discuss the extension of the model for anisotropic scattering in the Section 5. The last
 233 parameter involved in the BRDF expressions (Eqs. 14) is the extinction ratio τ_o that is defined as
 234 intrinsic to the scatterers' material. It accounts for internal reflections that may occur between
 235 the interface of the medium. A definition is given by [29]:

$$\tau_o(\lambda) = \frac{2}{3} \frac{1 - \bar{R}(\lambda)}{1 + \bar{R}(\lambda)} \quad (16)$$

$$\text{with } \bar{R}(\lambda) = \frac{3C_2 + 2C_1}{3C_2 - 2C_1 + 2} \quad \text{and} \quad C_i = \int_0^{\frac{\pi}{2}} R(\theta, \lambda) \cos^i \theta \sin \theta d\theta$$

236 In the previous equations, $R(\theta)$ is the Fresnel's angular reflection coefficient [30]. The
 237 parameter τ_o thereby depends on the optical constants of the material the particles are made of
 238 and on the wavelength.

239 4. Sample description and BRDF measurements

240 The macroscopic physical phenomena at stake in the appearance of a material can be inferred
 241 through BRDF measurements.

242 **4.1. Sample description**

243 For the study of dry powder appearance, we focused on synthetic nano-crystallized hematite
244 $\alpha - \text{Fe}_2\text{O}_3$ powders with various colors, that we obtained using different routes allowing to control
245 the nucleation and growth of $\alpha - \text{Fe}_2\text{O}_3$ crystallites in solution. These samples are presented in
246 Figure 3.

247 The samples denoted from 1 to 5 have been prepared following methods described by
248 Schwertmann & Cornell [31]. 1, 2 and 5 have been obtained by forced hydrolysis of Fe^{III} salts
249 solutions in acidic conditions, while 3 and 4 are the results of the transformation of a ferrihydrite
250 precipitate in aqueous suspension under basic conditions. We generated peanut-like hematite
251 particles 6 following the routes proposed by Sugimoto et al. [32], NaH_2PO_4 salts. Sample 7 is a
252 commercial Iron(III) oxide powder sample purchased from Puratronic®.

253 The color and the morphometry of each sample are respectively deduced from naked eye
254 observations completed with optical microscopy using a Nikon Eclipse LV100ND microscope,
255 and by scanning electron microscopy observations performed with a Zeiss Ultra+ microscope.
256 Various grain shapes and sizes ranging from 10 nm to 10 μm are obtained. The small grains
257 are characterized by a lighter red color (samples 1 to 5) whereas a darker purple hue is observed for
258 the pigments with larger grains (samples 6 and 7). We may also note that samples 5, 6 and 7 can
259 be described by two grain sizes: either two different size populations (sample 5), or large grains
260 that are agglomerates of smaller ones (samples 6 and 7).

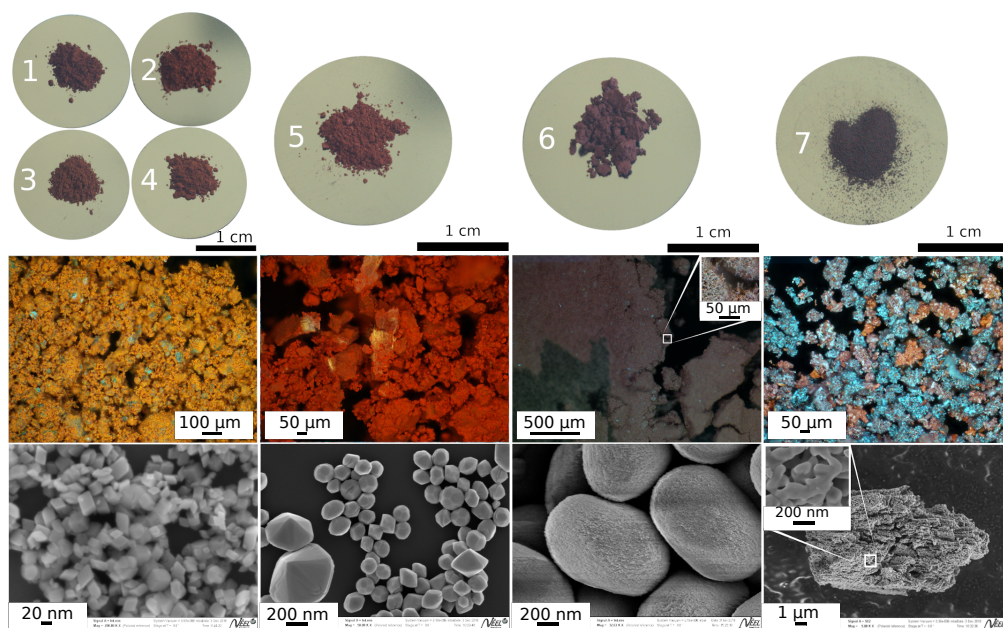


Fig. 3. $\alpha - \text{Fe}_2\text{O}_3$ hematite samples under study, showing various colors and grains morphology. Upper row: The photographs are calibrated using an X-rite 24 patches Classic Colorchecker. Middle row: Observations using optical microscopy. Lower row: Samples morphology observations using Scanning Electron Microscopy. The samples 1 to 4 show similar grain shape, with slightly different sizes from 10 to 50 nm in diameter, and light red hue. Sample 5 presents two size populations and shows a red-pinkish hue. Samples 6 and 7 have a more complex morphology with grains that seem to be agglomerations of smaller ones. The grains are larger and a darker purple hue is observed. According to optical microscopy, 7 is even composed of different types of grains, with different colors.

261 4.2. BRDF measurements

262 The whole BRDF of each sample is measured by combining two distinct measurements, performed
263 with two different setups depending on which scattering geometry is at stake. The first one does
264 not account for the back-scattering, while the second one is specifically performed to account for
265 this contribution. All the measurements are done on $d = 1$ mm thick powder layers.

266 4.2.1. Measurement out of the back-scattering direction

267 The main part of the BRDF is measured using the spectro-goniophotometer SHADOWS [33],
268 for over 180 geometries: the scattered light is observed for $\theta_o \in [-70^\circ, 70^\circ]$ with a step of 10° ,
269 for incidences $\theta_i \in \llbracket 0^\circ, 20^\circ, 40^\circ, 60^\circ \rrbracket$ and azimuthal angles $\varphi \in \llbracket 0^\circ, 30^\circ, 60^\circ, 90^\circ, 135^\circ \rrbracket$.
270 The spectral range has been limited to 360 nm - 860 nm with a step of 20 nm. The reflectance
271 measurements are calibrated with a Spectralon. Every point is measured with an integration time
272 of 300 ms and averaged over 10 spectra. Such measurement takes about 18 hours.

273 When it comes to a geometry where incident and observation directions are identical, the
274 instrument design causes the sensor to be obstructed by the light source. A specific device needs
275 to be designed to evaluate the amount of light scattered in these directions.

276 4.2.2. Measurement in the back-scattering direction

277 Our design for measuring the back-scattering contribution to the BRDF is inspired from the
278 work of [9] and [11]. As these only deal with vertically held samples, they cannot be used for
279 studying dry powders. We propose a new design to allow the measurement of any horizontally
280 held sample.

281 We chose a halogen light source to illuminate at normal incidence the sample after being
282 reflected by a beam splitter at 45° . The size of the illumination spot is minimized by focusing
283 the light with a 50 mm focal lens. An additional diaphragm is added to clean the focused beam.
284 The direction of the incident light θ_i is adjusted by positioning the beam splitter at an angle of
285 $45^\circ + \theta_i/2$. As the light interacts with the powder, it is scattered in every direction and preferably
286 back into the incident direction. It is then partially transmitted through the beam splitter and
287 collected by a Thorlabs F950FC-A collimator. The latter is fixed on a vertical rotating plate
288 so that we can scan different observation directions around the exact back-scattering one in the
289 incident plane. Although the incident light may be partially polarized after reflecting on the beam
290 splitter, for small enough incident angles the diffuse interaction with the sample has the property
291 of depolarizing the light. For large incidence angles, the reflection on the surface becomes more
292 important and so are the polarization effects. To neglect these polarization effects, we will only
293 consider incident angles smaller than 40° . We use a fiber spectrometer OceanOptics USB650
294 along with the SpectraSuite software in order to detect and visualize the measured signal.

295 In the incident plane ($\varphi = 0^\circ$), we scan the observation angles in the range $[\theta_i - 10^\circ, \theta_i + 10^\circ]$
296 with a step of 2° , for incidences $0^\circ, 20^\circ$ and 40° . For each incidence angle of interest, the
297 observation angles the furthest from the exact back scattering direction that are scanned are
298 redundant with geometries reached by the SHADOWS instrument. This allows for verification
299 that the two distinct measurements are consistent with one another. The reflectance measurements
300 are calibrated with a Spectralon. The integration time is chosen to maximize the detected signal
301 and an averaging over 5 spectra is performed to minimize the noise. Less than 20 seconds is
302 necessary to measure one spectrum.

303 5. Powder BRDF Model

304 As shown by the measurements on Figure 6, powders' BRDFs mainly involve back-scattering
305 and almost no specular scattering which makes the usual specular BRDF models ineffective to
306 reproduce their appearance.

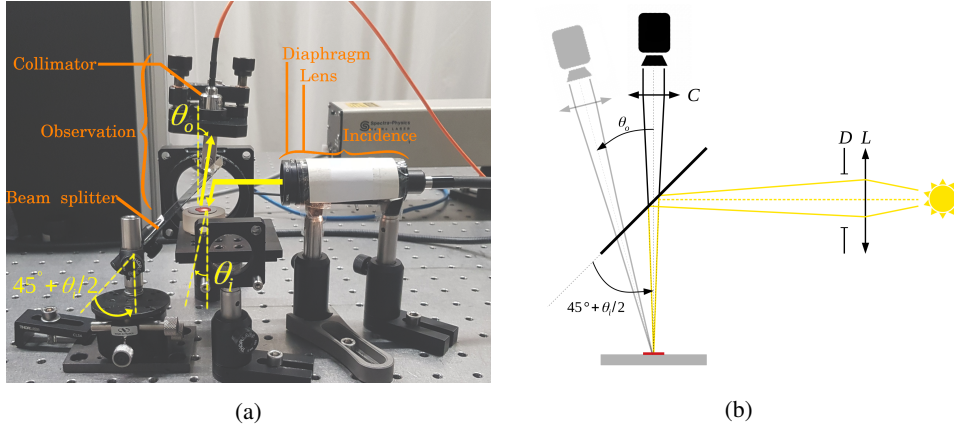


Fig. 4. Back-scattering measurement device. The beam of a white source is focused on the sample surface at an incidence θ_i using a 50 mm focal lens L and a beam splitter. The reflected light is collected through a collimator C in different observation directions θ_o .

307 Although our model is derived from a study on pure nano-crystallized hematite powders, we
 308 chose a physically-based approach so that it can be applied to any other pigment. It involves
 309 both chemical composition and morphological parameters to accurately account for the color
 310 variations observed on such pigments. Moreover it allows to consider either isotropic or
 311 anisotropic scatterers. Inspired by both RTLSR and Spectralon's models, our model is divided
 312 into two contributions, accounting for volume and surface scattering respectively.

$$BRDF(\theta_i, \theta_o, \varphi_i, \varphi_o, \lambda) = A_v BRDF_v(\theta_i, \theta_o, \varphi_i, \varphi_o, \lambda) + A_s BRDF_s(\theta_i, \theta_o, \varphi_i, \varphi_o, \lambda) \quad (17)$$

313 These two contributions are weighted with the scalar amplitude parameters A_v and A_s . Because
 314 the angular and spectral dependency of the two contributions $BRDF_v$ and $BRDF_s$ is the same as
 315 the complete BRDF, it will not be reminded in the following equations for readability purposes.
 316 The main difference with the previous models is that, based on the EBS theory the back scattering
 317 is considered as part of the volume contribution. The surface contribution is then reduced to
 318 specular scattering caused by surface roughness.

319 5.1. Volume scattering

320 As EBS theory is established within the diffusion approximation, the average scattering is assumed
 321 to be isotropic. This greatly simplifies the multiple scattering contribution by considering the
 322 scattering phase function as constant over the whole scattering hemisphere. The anisotropic
 323 scattering of each particle is accounted for by choosing the phase function parameter g involved
 324 in the single scattering contribution. The extension of the model for taking into account this
 325 anisotropy in multiple scattering has only been done for a normal incidence by Tsang et al. [23].

326 In the following we expose the calculations we made in order to consider anisotropic scattering
 327 in both single and multiple scattering terms for any $\theta_i/(\theta_o, \varphi_o)$ geometry. The final model only
 328 involves two variable parameters (phase function anisotropy parameter g , extinction rate κ) that
 329 rely on the physical and chemical properties of the material that is under study.

330 **First order ladder term \mathcal{L}_1 :** This contribution accounts for light that is only scattered once
 331 before being observed and is similar to the one introduced in Section 3.5. The anisotropy is taken
 332 care of by the scattering phase function involved in the analytical expression of $BRDF_{EBS, \mathcal{L}_1}$ in
 333 Eq. 14.

334 **Multiple ladder term \mathcal{L}_{2+} :** The phase function is involved at every scattering event that
 335 light encounters as it travels the particulate medium. We denote P_1 and P_n respectively the first
 336 and the last particles that are responsible for light scattering along a light path.

337 At the second scattering order, the light is first incoming on P_1 , scattered with an angle Θ_1
 338 towards the particle P_n , and finally scattered towards the observer with an angle Θ_n as illustrated
 339 by the Figure 5.

340 For the n -th scattering order, light undergoes n scattering events. As for the second order, it
 341 undergoes a first one described by the angle Θ_1 while encountering the particle P_1 and last one
 342 with the particle P_n and the angle Θ_n . But it also interacts with $n - 2$ other particles in between,
 343 resulting in $n - 2$ scattering events respectively described by the scattering angles $\Theta_k = \theta_{ik} - \theta_{ok}$,
 344 difference between the incoming direction θ_{ik} and outgoing direction θ_{ok} on the k -th particle,
 345 with $k = \llbracket 2 ; n - 1 \rrbracket$ as it is shown on the Figure 5.

346

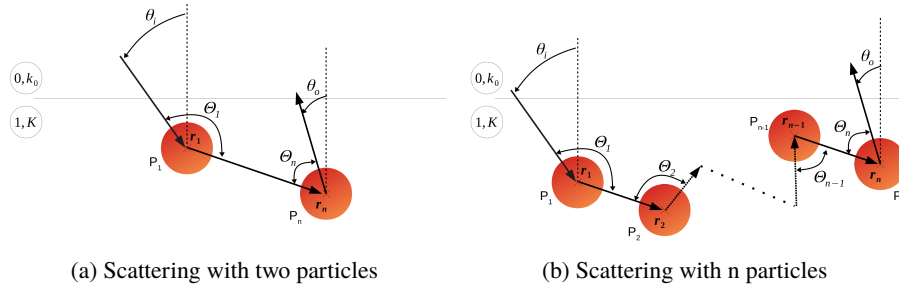


Fig. 5. Multiple scattering with two and n particles. The first scatterer that light encounters as it travels inside the medium is denoted as P_1 and involves a scattering event described by the angle Θ_1 . The last scattering event before light goes out of the medium is caused by the scatterer P_n with an angle Θ_n . In between these two scatterers, light is scattered with an angle Θ_k at each interaction with a particle k .

347 By averaging over all the possible paths that light can follow inside the medium while
 348 encountering n scatterers, we can write the n -th order ladder term as follows:

$$\mathcal{L}_n = \frac{(4\pi)^{n-2} (\rho\kappa)^n}{r^2} \times \int |p(\Theta_n)|^2 |G_{11}(\mathbf{r}_n, \mathbf{r}_{n-1})|^2 \dots |p(\Theta_1)|^2 \exp\left(\kappa \left(\frac{z_1}{\mu_o} + \frac{z_n}{\mu_i}\right)\right) d\mathbf{r}_1 d\dots d\mathbf{r}_n \quad (18)$$

349 with r the distance from the sample to the observation point.

350 The total ladder term accounting for multiple scattering $k = \llbracket 2 ; \infty \rrbracket$ can be written in a
 351 recursive way, giving:

$$\mathcal{L}_{2+} = \iint \exp\left(\kappa \left(\frac{z_i}{\mu_o} + \frac{z_o}{\mu_i}\right)\right) A(\mathbf{r}_i, \mathbf{r}_o) d\mathbf{r}_i d\mathbf{r}_o \quad (19)$$

352 with $A(\mathbf{r}_i, \mathbf{r}_o)$ defined such as:

$$A(\mathbf{r}_i, \mathbf{r}_o) = \left(\frac{\rho\kappa}{4\pi}\right)^2 p(\Theta_1) p(\Theta_n) \frac{\exp(\kappa |\mathbf{r}_i - \mathbf{r}_o|)}{|\mathbf{r}_i - \mathbf{r}_o|^2} + \int \left(\frac{\rho\kappa}{4\pi}\right) p(\Theta_k) \frac{\exp(\kappa |\mathbf{r}_i - \mathbf{r}_k|)}{|\mathbf{r}_i - \mathbf{r}_k|^2} A(\mathbf{r}_k, \mathbf{r}_o) d\mathbf{r}_k \quad (20)$$

353 Under the assumption of the diffusion approximation, this term can be simplified to average
 354 the contributions of all scatterers by extending the work from [23]. The resulting BRDF of the
 355 ladder contribution is therefore reduced to the following analytical expression:

$$BRDF_{\mathcal{L}_{2+}}(\kappa, g) = \frac{3\rho^2}{1 - \mu_i^2 c^2} \left[\frac{2Q}{1 - \mu_o c} - \frac{\mu_i^2}{\mu_i + \mu_o} \right] \quad (21)$$

356 with

$$c = \sqrt{3(1 - \rho)(1 - \rho g) + \alpha^2} \quad (22)$$

357 and parameters α and Q defined as in Eqs 15.

358 One should note that the ladder term expression is similar to the one defined by the Eq. 14,
 359 except that it accounts for possible anisotropic average scattering in the medium through a
 360 varying phase function of parameter g (Eq. 22). If one wants to describe isotropic scattering, a
 361 constant phase function such as $p(\Theta) = p$ (similarly $g = 0$) should be used which leads back to
 362 the expression originally introduced in Section 3.5.

363

364 **Multiple cyclical scattering C :** As for the ladder term, we are aiming to take into account
 365 the anisotropic scattering of particles in the cyclical term. We will use the same assumptions
 366 as illustrated by the Figure 5. We consider a beam of light that is scattered by n particles as it
 367 follows a path inside the medium. By accounting for the correlation between this path and its
 368 reversal and averaging over all the possible paths, the n -th order cyclical term can be written:

$$C_n = \frac{(4\pi)^{n-2} (\rho\kappa)^n}{r^2} \int |p(\Theta_n)|^2 |G_{11}(\mathbf{r}_n, \mathbf{r}_{n-1})|^2 \dots |G_{11}(\mathbf{r}_2, \mathbf{r}_1)|^2 |p(\Theta_1)|^2 \\ \times \cos\left(k(\mu_i - \mu_o)(z_1 - z_n)\right) \exp\left(\frac{\kappa}{2}\left(\frac{1}{\mu_o} + \frac{1}{\mu_i}\right)(z_1 + z_n)\right) d\mathbf{r}_1 \dots d\mathbf{r}_n \quad (23)$$

369 The complete cyclical contribution is obtained by summing over the n -th orders and can be
 370 simplified replacing G_{11} by its definition (Eq. 8). By using the new expression of $A(\mathbf{r}_i, \mathbf{r}_o)$ given
 371 by Eq. 20:

$$C = \iint \cos(2k(\mu_i - \mu_o)(z_o - z_i)) \exp\left(\frac{\kappa}{2}\left(\frac{z_i}{\mu_o} + \frac{z_o}{\mu_i}\right)\right) A(\mathbf{r}_i, \mathbf{r}_o) d\mathbf{r}_i d\mathbf{r}_o \quad (24)$$

372 Finally, by using the diffusion approximation, the cyclical term contributes to the complete
 373 appearance of the dry powder through the partial BRDF:

$$BRDF_C(\kappa, g) = \frac{3\rho^2 [c + v(1 - \exp(-2c\tau_o))]}{2\mu_i \mu_o c v [(c + v)^2 + u^2]} \quad (25)$$

374 where c is defined as in Eq. 22, and u, v as in Eqs. 15.

375 Once again, this expression is similar to the one obtained assuming isotropic averaged scattering
 376 in the medium (Eq. 14). However it involves the phase function parameter g to account for
 377 anisotropic scattering. The use of a constant phase function $p(\Theta) = p$ (similarly $g = 0$) brings
 378 back to the isotropic case already discussed in Section 3.5.

379

380 Our model's complete EBS contribution accounting for anisotropic scattering in the powder
 381 medium is the sum of the two ladder components given by first equation of Eq. 14 and Eq. 21,
 382 and the cyclical component given by Eq. 25.

383 5.2. Surface scattering

384 In our model, surface scattering is reduced to the specular contribution. The light that is incoming
 385 on a rough surface such as the interface between air and a dry powder is scattered in a lobe
 386 around the specular direction.

387 Two options have been considered to include such a phenomenon in our model. The former is
 388 to model the specular peak by a gaussian function. According to the measurements performed
 389 in Section 4 the specular scattering is very weak so this simple method is reliable enough to
 390 reproduce the specular contribution of dry powders, although it is empirical. By assuming a
 391 uniform distribution of the surface normals, it requires only one parameter which is the gaussian
 392 standard deviation σ . With this modeling the surface scattering BRDF is written as:

$$BRDF_s(\sigma) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(\frac{-\theta^2}{2\sigma^2}\right) \quad (26)$$

393 The second option, which is the one we chose to use, relies on the physical approach from
 394 Harvey-Shack [34] that accounts for diffraction effects caused by the surface asperities. Using
 395 this theory, the incoming light on a rough surface is then scattered around the specular direction
 396 according to the following BRDF:

$$BRDF_s(l_c) = \frac{4\pi^2}{\lambda^4} (\cos \theta_i + \cos \theta_o)^2 PSD(\mathbf{f}) \quad (27)$$

397 where the power spread function (PSD) models a rough surface topography. We chose a gaussian
 398 power spread function, involving a roughness parameter σ_s and a correlation length l_c that
 399 quantifies the mean distance for which the surface roughness of two points on the surface are
 400 completely independent.

$$PSD(\mathbf{f}) = \pi\sigma_s^2 l_c^2 \exp(-\pi^2 l_c^2 (f_x^2 + f_y^2)) \quad (28)$$

401 5.3. Complete model

402 Our complete model is the weighted sum of volume and surface contributions according to
 403 Eq. 17 respectively given by the adapted enhanced back scattering model and a specular model.
 404 Note that the roughness parameter involved in the surface contribution has been included in the
 405 amplitude parameter $A'_s = A_s \sigma_s^2$ in order to reduce the number of optimization parameters.

$$BRDF(\theta_i, \theta_o, \varphi_i, \varphi_o, \lambda) = A_v [BRDF_{\mathcal{L}_1}(\kappa, g) + BRDF_{\mathcal{L}_{2+}}(\kappa, g) + BRDF_C(\kappa, g)] \\ + A'_s BRDF_s(l_c) \quad (29)$$

406 The model depends on a total of 2 empirical (A_v and A_s) and 3 physical (g, κ, l_c) parameters to
 407 accurately simulate the BRDF of dry powder. As it is shown in the Section 6, our model works
 408 even better while including another physical parameter to refine which is the *effective radius*
 409 of the grains, defined as the mean size of the grains actually seen by the incoming light and
 410 therefore responsible for the scattering. The influence of such parameter is shown on Figure 7.
 411 The parameters involved in our model are summarized in Table 1.

412 5.4. Optimization procedure

413 In order to reproduce the BRDF of a powder sample, the model is fitted to measurements by
 414 optimizing the variable parameters of Table 1. We used the least squares minimization of scipy
 415 along with the sequential least square programming method (SLSQP) to fit our BRDF model
 416 to the measurement data y_m (Eq. 30). A first option is to optimize while using a fixed radius.

Volume scattering	
A_v	Intensity of volume scattering
g	Scattering anisotropy
κ	Extinction rate
b	effective radius (optional)
Surface scattering	
A'_s	Intensity of surface scattering
l_c	Correlation length

Table 1. Parameters involved in our BRDF model. The model can be optimized by refining only 5 parameters while the grain radius b is fixed, or by refining 6 parameters including the same 5 previous ones and an effective radius.

417 The average dimensions of the grains of a powder sample is deduced from SEM images and
 418 reduced to only one dimensional parameter by computing the radius of a sphere that is equivalent
 419 to the grain. To better account for the shape anisotropy this radius is computed so that the ratio
 420 of the surface over the volume of the equivalent sphere and of the grain remains constant. The
 421 final mean radius is obtained by averaging on the radii of multiple grains that are in the field
 422 of view of a single SEM image. A second option is to optimize on the grains' effective radius,
 423 which both releases constraints on the optimization process and gets rid of the uncertainty on the
 424 experimental grain size definition.
 425 The optimization is performed for all measurement geometries $\gamma = (\theta_i, \theta_o, \varphi_i, \varphi_o)$ with $\theta_i < 60^\circ$.
 426 For larger incidences, we were not able to measure the back-scattering contribution so we do not
 427 account for these geometries in the optimization process.

$$E = \min_{\gamma, \theta_i \leq 40^\circ} \sum |BRDF_\gamma(A_v, g, \kappa, b, A'_s, l_c) - y_{\gamma,m}|^2 \quad (30)$$

428 We only account for the measurements at the wavelength 700nm. The spectral dependency of the
 429 model will be discussed later on.

430 6. Results

431 6.1. Complete measurement

432 The complete BRDF measurements of dry hematite $\alpha - Fe_2O_3$ powders were performed in
 433 two independent steps described in Sections 4.2. By comparing the results for geometries
 434 reached by both instruments, the measurements happen to be shifted in amplitude from one
 435 another. This may be caused by the underestimation of the back scattering of the spectralon
 436 used for photometric calibration. Since the difference is smaller than 5%, a re-scaling of the
 437 back-scattering measurement is done so it matches the goniometer results.

438 A typical experimental BRDF is shown on Figure 6 after merging the measured data. The
 439 measurements show that the BRDF of dry hematite powders is composed of an overall diffuse
 440 contribution, and two directional scattering phenomena including mainly back-scattering and
 441 some specular scattering (Figure 6). The BRDFs of characterized samples vary in intensity and
 442 width of the specularly and back scattered lobes. We give results for the six other samples under
 443 study in Supplementary Work.

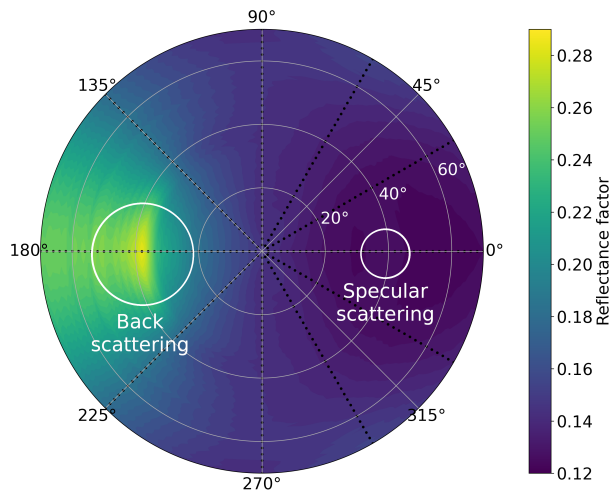


Fig. 6. Complete BRDF measurement of the hematite powder sample 1 at the wavelength 700 nm for an incidence $\theta_i = 40^\circ$. The measured geometries are spotted with black dots, and the intermediate values are interpolated. Light is mostly reflected in the backward direction, and a very weak specular scattering peak may be observed as well. The spreading of the back scattering peak with the azimuth angle is due to the colormap interpolation between the measured points.

444 6.2. Model validation

445 The ability of the model to simulate the BRDF of pigments is validated against the various
 446 hematite powders measurements by following the procedure of Section 5.4. In the following
 447 we chose to define the grains' effective radius as an optimization parameter as it leads to better
 448 results. Indeed, as it is shown in Table 2 it allows a nicer modeling of the back scattering peak
 449 amplitude, while keeping values pretty close to the radius deduced from microscopy observations.
 450 Although the two populations are well distinguishable in samples 5 and 7 (see Figure 3), it is
 451 harder to spot on sample 6. In that case, the smaller grains actually refer to the roughness at the
 452 surface of the observed ellipsoidal grains. For illustration, the results from two optimizations
 453 involving or not the radius performed on sample 1 are shown on Figure 7.

454 The same optimization process is performed using both Spectralon and RTLSR models adapted
 455 to be relevant in the case of dry powders. Such adaptations to the original models are detailed in
 456 Supplementary work. To compare our results to the one obtained through these two other models
 457 allows a better evaluation of our model.

458
 459 Our model is able to reproduce the measured BRDF of hematite powders with an accuracy
 460 comparable to that of the Spectralon model ($< 8\%$ of the measured reflectance factor), but with
 461 a much lower complexity: only 6 parameters related to physical properties of the samples are
 462 required against 12 empirical ones for the Spectralon's model (cf. Figures 9, 10 and 11). Our
 463 model nicely fits the back-scattering peak, and is even more accurate than the other ones for
 464 reproducing the slope of the measured BRDF (cf. Figure 8). The mean squared error (MSE) from
 465 the fitting procedure is also of same magnitude for both Spectralon and our model ($MSE < 0.05$).
 466 In comparison, the RTLSR gives much poorer results ($MSE > 0.1$). Detailed values are
 467 given for each samples in Table 2. Our model is particularly efficient in the case of samples
 468 whose morphology is easily characterized, that is to say for the samples with well-crystallized
 469 single-crystals. Both the back-scattering and the specular contributions are detected and modeled,

470 even though the latter is sometimes too weak for the modeling to be reliable. Errors are mostly
 471 spotted around the back scattering peak because of the insufficient measurement resolution and
 472 interpolation at these geometries.

473 One should note that we have encountered difficulties in the modelization of samples 5 and 7's
 474 BRDFs that we attributed to the more complex morphology of these powders. These powders
 475 are not monodisperse since they show two size populations and agglomerations of grains. An
 476 extension of our model is proposed in Supplementary work to deal with powders presenting two
 477 grain size populations.

Sample	Radius SEM (nm)	Effective radius (nm)			Ours MSE	Spectralon MSE	RTLSR MSE
1	12 ± 1.6	16			0.035	0.043	0.17
2	13 ± 3.0	17			0.052	0.052	0.21
3	22 ± 3.7	16			0.044	0.046	0.25
4	25 ± 4.1	15			0.037	0.039	0.29
Sample	Large radius SEM (nm)	Effective radius (nm)	Small radius SEM (nm)	Effective radius (nm)			
5	83 ± 34	83	47 ± 5.3	46	0.063	0.074	0.71
6	687 ± 64.0	687	10 ± 0.4	43	0.041	0.043	0.49
7	2222 ± 1054	2222	49 ± 13	49	0.019	0.019	0.30

Table 2. Results from optimizations on radii. The radius deduced from SEM observations are compared with the effective radius obtained by the optimization of our model. For samples 5 to 7, the model extension for two size populations presented in Supplementary work is used. As it takes two different radii to optimize, two effective radii are obtained. The resulting MSE of such optimizations are also given and can be compared to MSE of optimizations over the Spectralon model and the RTLSR model.

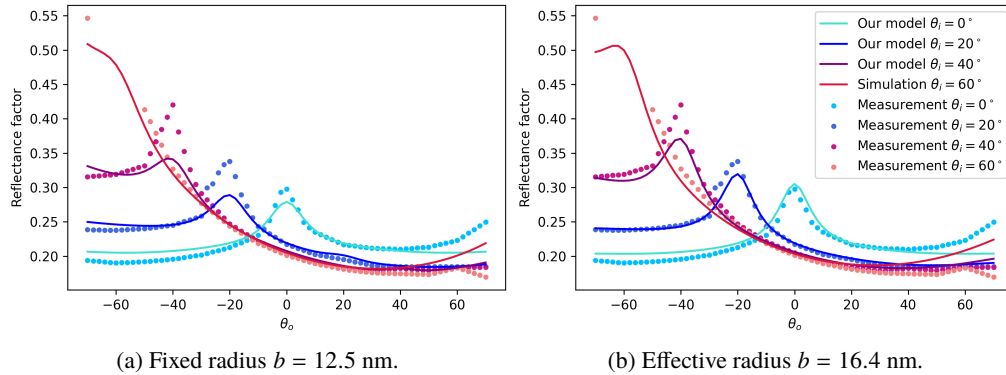


Fig. 7. Influence of the grain radius optimization on the results of sample 2, in the incident plane ($\varphi = 0^\circ$) for incidences $\theta_i = 0^\circ, 20^\circ$ and 40° . The effective radius found by optimization ($b = 17$ nm) is pretty close to the theoretical result deduced from SEM observations ($b = 13 \pm 3.0$ nm).

478 Since the refined parameters permit our model to fit quite precisely with the measurements in
 479 any geometry, it appears that none of them depends on the incoming, outgoing and azimuthal

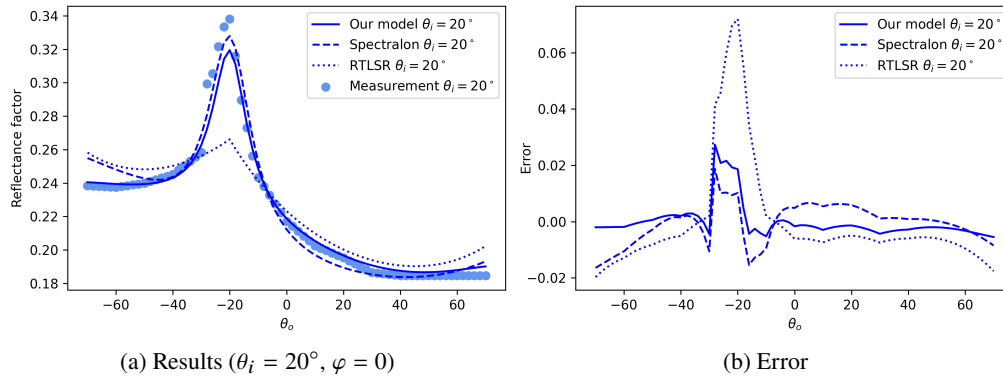


Fig. 8. Comparison of the optimization results of sample 2 from the three BRDF models: Our model, Spectralon model, RTLSR model. (a) Results in the incident plane ($\varphi = 0$) for incidence $\theta_i = 20^\circ$. (b) Residual error between the measurements and the fits. Our model slightly underestimates the back-scattering peak compare to the Spectralon model. However, it fits the slope of the measured BRDF much better. The residual error of these two models are similarly small. In comparison, the RTLSR model is less suitable to fit the measured data.

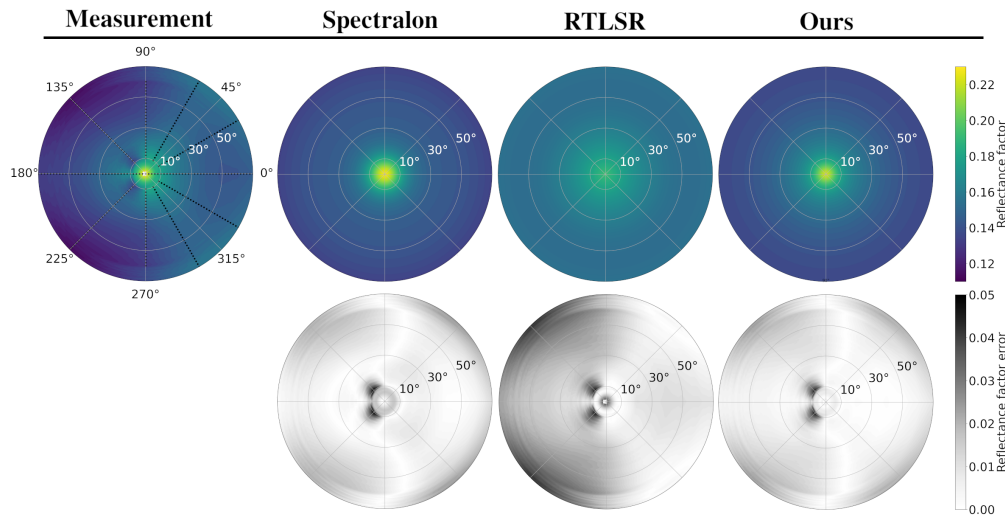


Fig. 9. Upper row: Fitting of the measured BRDF of sample 1 using our model, spectralon and RTLSR models adapted to dry powders, at incidence $\theta_i = 0^\circ$. Lower row: difference between the measurement and the fit. Our physically-based model (6 optimized parameters) gives better results than the two other ones as it is more performant than the RTLSR model (1 optimized parameter) and as performant as the Spectralon model (12 optimized parameters) with far less optimization parameters.

480 directions. The model is then able to predict the appearance of the studied powder in any other
 481 geometry that hasn't been considered during its optimization. The results are convenient even for
 482 more grazing angles such as incidence $\theta_i = 60^\circ$ as shown on Figure 7.

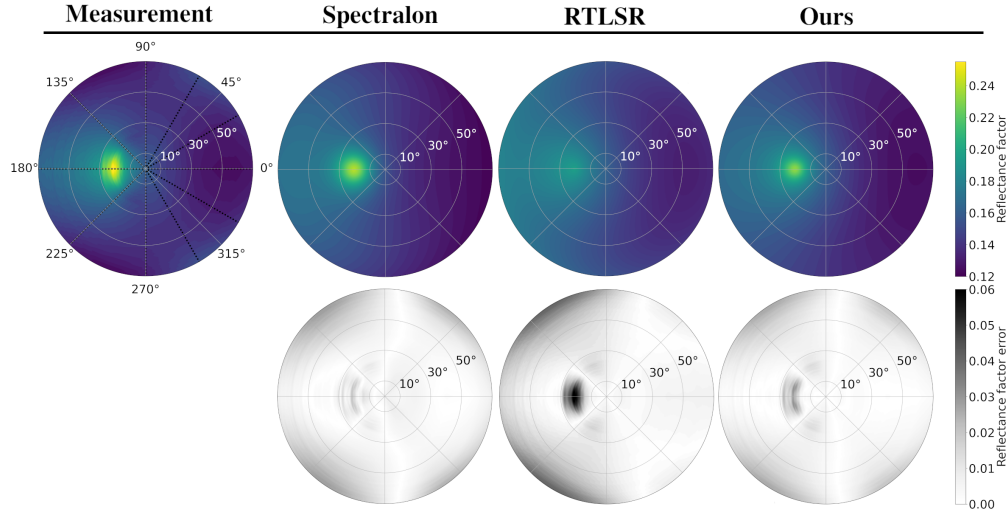


Fig. 10. Upper row: Fitting of the measured BRDF of sample 1 using our model, spectralon and RTLSR models adapted to dry powders, at incidence $\theta_i = 20^\circ$. Lower row: difference between the measurement and the fit. Our physically-based model (6 optimized parameters) gives better results than the two other ones as it is more performant than the RTLSR model (1 optimized parameter) and as performant as the Spectralon model (12 optimized parameters) with far less optimization parameters.

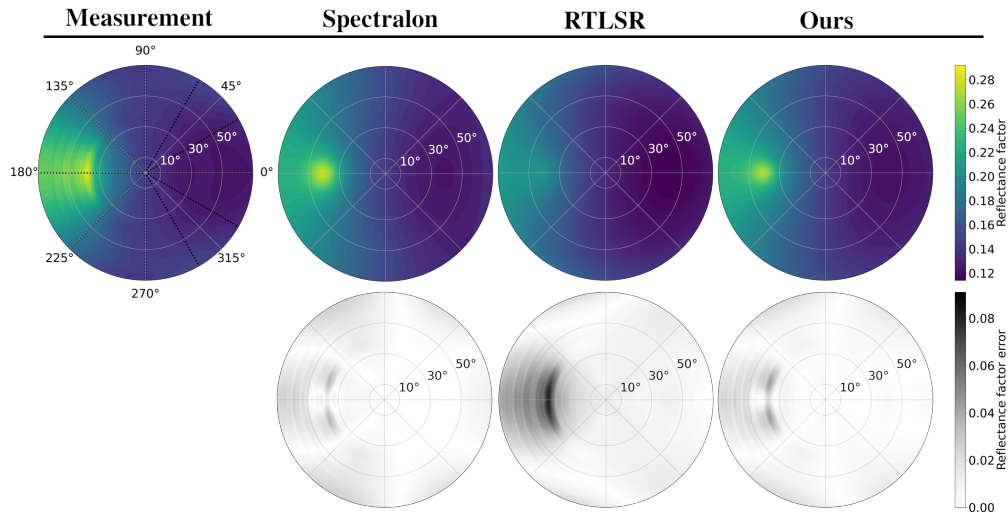


Fig. 11. Upper row: Fitting of the measured BRDF of sample 1 using our model, spectralon and RTLSR models adapted to dry powders, at incidence $\theta_i = 40^\circ$. Lower row: difference between the measurement and the fit. Our physically-based model (6 optimized parameters) gives better results than the two other ones as it is more performant than the RTLSR model (1 optimized parameter) and as performant as the Spectralon model (12 optimized parameters) with far less optimization parameters.

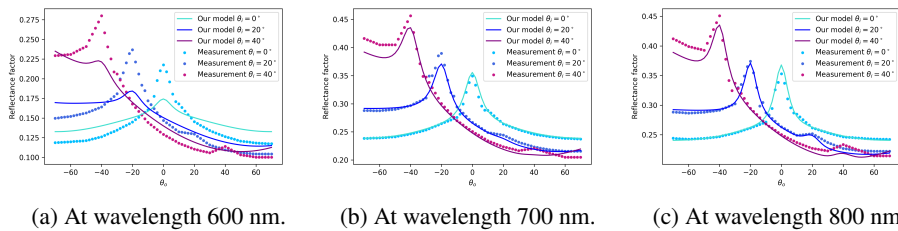


Fig. 12. Optimization of our model on sample 4, at different wavelengths using the optical constants from [35]. For smaller wavelengths, our model is not able to accurately fit the measurements.

483 7. Discussion & Conclusion

484 From BRDF measurements, we highlighted that in the particular case of dry powders, the
 485 light is mainly back scattered. We proposed a new BRDF model accounting for three different
 486 scattering interactions: single scattering, incoherent multiple scattering and coherent multiple
 487 scattering responsible for the sharp peak in the backward direction. It is a semi-empirical and
 488 analytical model based on the propagation of light inside a granular medium that involves the
 489 physico-chemical properties of the powders connected to only six refinement parameters.

490 The model has been validated against the BRDF measurements of seven $\alpha - \text{Fe}_2\text{O}_3$ hematite
 491 powders, and compared to two adapted existing models. Ours is able to reproduce the measured
 492 BRDF with an accuracy comparable to the one of the Spectralon's model, but with a much
 493 lower complexity. It can be used in its original form to reproduce the appearance of a mono
 494 disperse powder with spherical grains, or in its extended form presented in Supplementary work
 495 to account for more complex morphology involving multiple grains size populations.

496
 497 Our model still has some limitations. The results obtained for specular scattering are quite
 498 questionable since the specular contribution is very weak and almost unnoticeable on the BRDF
 499 measurements. A more accurate model should be established by studying powders showing shiny
 500 and sparkling reflections such as eye shadow.

501 For now, our model can only be used as a fitted model. The parameters describing the
 502 appearance of a specific powder are retrieved from the fitting of the model to the measured
 503 BRDF of such powder. In order to predict the BRDF of any other powder of known chemical
 504 composition and morphology that has not been measured, it would be necessary, as a future
 505 work, to establish a relationship between the optimization parameters of the model and the
 506 physico-chemical parameters of the material the powder is composed of. This requires to study
 507 much more samples with more variability in sizes.

508 The validity of the model wavelength dependency is also a main issue that couldn't be solved
 509 throughout this work. At smaller wavelengths, the optimization is not robust enough to lead to
 510 nice fitting results (see Figure 12). This might be caused by a poor knowledge of the optical
 511 constants of the studied material which is the only fixed parameter known as spectrally varying.
 512 Indeed, it is mainly described by the optical constant at stake whose value appears to be quite
 513 doubtful according to the discrepancies between the results in the literature [35, 36]. Such
 514 uncertainties are often ignored in both material science and computer graphics whereas it surely
 515 affects the results.

516
 517 As a future work we would like to implement our dry powder BRDF model in a physically
 518 based renderer so that photo-realistic renderings of the powders can be made. This would first
 519 allow the validation of the model by comparing the rendered image with photographs of the actual

520 samples. It would also permit, by letting the user choose the values of the variable parameters to
521 either reproduce the appearance of other powder materials, or to create new ones.

522 Although the model has been tested for only one material, we believe it can be used for any
523 other pure pigment. In the case of parietal paintings, ochers (mixture of one iron-based coloring
524 pigment and colorless powders such as clays) and mixtures of different pigments were more
525 commonly used than pure and almost pure iron oxide. In order to reproduce photo-realistic
526 appearance of such paintings, we would like to extend our model to more complex powders.

527 The assumption of optically thick layer of powder is also too restrictive. An extension of the
528 enhanced back scattering theory for thin films and isotropic scatterers has been proposed by [24]
529 and may be a good starting point for our model adaptation, leading to a better reproduction of the
530 appearance of painting layers.

531

532 **Acknowledgments:** The authors would like to thank Alain Ibanez and Simon Giraud (Institut
533 Néel) for the hematite samples syntheses. We also thank Corinne Félix (Institut Néel) for her help
534 in developing the back-scattering measurement device, as well as Bernard Schmitt and Olivier
535 Brissaud (IPAG) for their help in the reflectance measurements using SHADOWS gonio-spectro-
536 photometer. At last, we thank Romain Pacanowski (INRIA) for the proofreading of this paper.
537 This work was financially supported by the French National Research Agency in the framework of
538 the Investissements d'Avenir program (ANR-15-IDEX-02, Cross Disciplinary Program Patrimalp).

539

540 **Disclosures:** The authors declare no potential conflicts of interest.

541

542 **Data availability:** Data underlying the results presented in this paper are not publicly available
543 at this time but may be obtained from the authors upon reasonable request.

544

545 **Supplemental document:** See Supplement 1 for supporting content.

546

546 References

- 547 1. C. Vignaud, H. Salomon, E. Chalmin, J.-M. Geneste, and M. Menu, "Le groupe des «bisons adossés» de lascaux.
548 étude de la technique de l'artiste par analyse des pigments," *L'anthropologie* **110**, 482–499 (2006).
- 549 2. A. Casoli, "Research on the organic binders in archaeological wall paintings," *Appl. Sci.* **11**, 9179 (2021).
- 550 3. L. M. Brady, "Documenting and analyzing rock, paintings from torres strait, ne australia, with digital photography
551 and computer image enhancement," *J. Field Archaeol.* **31**, 363–379 (2006).
- 552 4. I. Domingo, B. Carrión, S. Blanco, and J. L. Lerma, "Evaluating conventional and advanced visible image
553 enhancement solutions to produce digital tracings at el carche rock art shelter," *Digit. Appl. Archaeol. Cult. Herit.* **2**,
554 79–88 (2015).
- 555 5. E. Chalmin, M. Menu, M.-P. Pomiès, C. Vignaud, N. Aujoulat, and J.-M. Geneste, "Les blasons de lascaux,"
556 *L'anthropologie* **108**, 571–592 (2004).
- 557 6. M. Gerardin, N. Holzschuch, A. Ibanez, B. Schmitt, and P. Martinetto, "Influence of micro-structural features on
558 the colour of nanocrystallised powders of hematite and visible-nir reflectance spectra simulations," *J. international
559 colour association* **26**, 41–48 (2021).
- 560 7. C. F. Bohren and D. R. Huffman, *Absorption and scattering of light by small particles* (John Wiley & Sons, 2008).
- 561 8. J. R. Frisvad, N. J. Christensen, and H. W. Jensen, "Computing the scattering properties of participating media using
562 lorenz-mie theory," in *ACM SIGGRAPH 2007 papers*, (2007), pp. 60–es.
- 563 9. L. Belcour, R. Pacanowski, M. Delahaie, A. Laville-Geay, and L. Eupherte, "Bidirectional reflectance distribution
564 function measurements and analysis of retroreflective materials," *JOSA A* **31**, 2561–2572 (2014).
- 565 10. P. Beck, A. Pommerol, N. Thomas, B. Schmitt, F. Moynier, and J.-A. Barrat, "Photometry of meteorites," *Icarus* **218**,
566 364–377 (2012).
- 567 11. M. Lévesque and M. Dissanka, "Measurement and modeling of the spectralon spectro-polarimetric bidirectional
568 reflectance distribution function (brdf)," Tech. rep., Defence Research and Development Canada (2016).
- 569 12. C. Walthall, J. Norman, J. Welles, G. Campbell, and B. Blad, "Simple equation to approximate the bidirectional
570 reflectance from vegetative canopies and bare soil surfaces," *Appl. Opt.* **24**, 383–387 (1985).
- 571 13. J.-L. Roujean, M. Leroy, and P.-Y. Deschamps, "A bidirectional reflectance model of the earth's surface for the
572 correction of remote sensing data," *J. Geophys. Res. Atmospheres* **97**, 20455–20468 (1992).
- 573 14. W. Lucht, C. B. Schaaf, and A. H. Strahler, "An algorithm for the retrieval of albedo from space using semiempirical
574 brdf models," *IEEE Transactions on Geosci. Remote. sensing* **38**, 977–998 (2000).

- 575 15. J. Ross, "The radiation regime and architecture of plant stands. the hague: Dr. w," Junk Publ. doi **10**, 978–94 (1981).
- 576 16. X. Li and A. H. Strahler, "Geometric-optical bidirectional reflectance modeling of a conifer forest canopy," IEEE
- 577 Transactions on Geosci. Remote. Sens. pp. 906–919 (1986).
- 578 17. W. Wanner, X. Li, and A. Strahler, "On the derivation of kernels for kernel-driven models of bidirectional reflectance,"
- 579 J. Geophys. Res. Atmospheres **100**, 21077–21089 (1995).
- 580 18. Z. Jiao, A. Ding, A. Kokhanovsky, C. Schaaf, F.-M. Bréon, Y. Dong, Z. Wang, Y. Liu, X. Zhang, S. Yin et al.,
- 581 "Development of a snow kernel to better model the anisotropic reflectance of pure snow in a kernel-driven brdf model
- 582 framework," Remote. sensing environment **221**, 198–209 (2019).
- 583 19. T. Nilson and A. Kuusk, "A reflectance model for the homogeneous plant canopy and its inversion," Remote. Sens.
- 584 Environ. **27**, 157–167 (1989).
- 585 20. W. Ni, X. Li, C. E. Woodcock, M. R. Caetano, and A. H. Strahler, "An analytical hybrid gort model for bidirectional
- 586 reflectance over discontinuous plant canopies," IEEE Transactions on Geosci. Remote. Sens. **37**, 987–999 (1999).
- 587 21. S. Chandrasekhar, Radiative transfer (Courier Corporation, 2013).
- 588 22. A. Ishimaru, Wave propagation and scattering in random media, vol. 2 (Academic press New York, 1978).
- 589 23. L. Tsang and J. A. Kong, Scattering of electromagnetic waves: advanced topics, vol. 26 (John Wiley & Sons, 2004).
- 590 24. M. B. Van Der Mark, M. P. van Albada, and A. Lagendijk, "Light scattering in strongly scattering media: multiple
- 591 scattering and weak localization," Phys. Rev. B **37**, 3575 (1988).
- 592 25. L. L. Foldy, "The multiple scattering of waves. i. general theory of isotropic scattering by randomly distributed
- 593 scatterers," Phys. review **67**, 107 (1945).
- 594 26. L. G. Henyey and J. L. Greenstein, "Diffuse radiation in the galaxy," The Astrophys. J. **93**, 70–83 (1941).
- 595 27. B. Bret, "Multiple light scattering in porous gallium phosphide," Ph.D. thesis, Universiteit Twente (2005).
- 596 28. S. Lönn and D. Kroon, "Utilizing enhanced backscattering for determination of scattering properties in turbid media,"
- 597 Lund Reports At. Phys. (2011).
- 598 29. J. Zhu, D. Pine, and D. Weitz, "Internal reflection of diffusive light in random media," Phys. Rev. A **44**, 3948 (1991).
- 599 30. M. Born and E. Wolf, Principles of optics: electromagnetic theory of propagation, interference and diffraction of
- 600 light (Elsevier, 2013).
- 601 31. U. Schwertmann and R. M. Cornell, Iron oxides in the laboratory: preparation and characterization (John Wiley &
- 602 Sons, 2008).
- 603 32. T. Sugimoto, A. Muramatsu, K. Sakata, and D. Shindo, "Characterization of hematite particles of different shapes," J.
- 604 colloid interface science **158**, 420–428 (1993).
- 605 33. S. Potin, O. Brissaud, P. Beck, B. Schmitt, Y. Magnard, J.-J. Correia, P. Rabou, and L. Jocou, "Shadows: a
- 606 spectro-gonio radiometer for bidirectional reflectance studies of dark meteorites and terrestrial analogs: design,
- 607 calibrations, and performances on challenging surfaces," Appl. optics **57**, 8279–8296 (2018).
- 608 34. A. Krywonos, "Predicting surface scatter using a linear systems formulation of non-paraxial scalar diffraction," Ph.D.
- 609 thesis, University of Central Florida (2006).
- 610 35. M. R. Querry, "Optical constants," Tech. rep., Missouri Univ-Kansas City (1985).
- 611 36. A. H. M. J. Triaud, "Refractive indices of hematite," [http://eodg.atm.ox.ac.uk/ARIA/data?](http://eodg.atm.ox.ac.uk/ARIA/data?Minerals/Hematite/(Triaud_2005)/hematite_Triaud_2005.ri)
- 612 [Minerals/Hematite/\(Triaud_2005\)/hematite_Triaud_2005.ri](http://eodg.atm.ox.ac.uk/ARIA/data?Minerals/Hematite/(Triaud_2005)/hematite_Triaud_2005.ri) (2005).