Incorporation of mineralogical composition into models of the radiative properties of mineral aerosol from UV to IR wavelengths

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Abstract. We describe a technique to model the radiative properties of mineral aerosols which accounts for their composition. We compile a data set of refractive indices of major minerals and employ it, along with data on mineralogical composition of dust from various locations, to calculate spectral optical and radiative properties of mineral aerosol mixtures. Such radiative properties are needed for climate modeling and remote sensing applications. We consider external mixtures of individual minerals, as well as mixtures of aggregates. We demonstrate that an external mixture of individual minerals must contain unrealistically high amounts of hematite to have a single scattering albedo lower than 0.9 at 500 nm wavelength. In contrast, aggregation of hematite with quartz or clays can strongly enhance absorption by dust at solar wavelengths. We also simulate the daily mean net (solar + infrared) forcing by dust of varying compositions. We found that, for a given composition and under similar atmospheric conditions, a mixture of aggregates can cause the positive radiative forcing while a mixture of individual minerals gives the negative forcing.

1. Introduction
Proper treatment of optical properties from the ultraviolet to infrared wavelengths is a major concern in modeling the net (solar-infrared) radiative forcing by dust [Sokolik and Toon, 1996]. The optical properties of dust are also necessary for remote sensing retrievals by channels operating at wavelengths from UV to IR [Kaufman et al., 1997]. Therefore dust optical properties must be quantified over a range of wavelengths from about 0.2 to 30 μm.

The mineral aerosol is a complicated mixture of various minerals whose optical constants vary widely from mineral to mineral. Thus the optical properties of the aerosol are determined by the relative abundance of various minerals and the details of how the minerals are mixed together. Furthermore, the abundance of each mineral, and how it is mixed with others, depends on dust origin, dust mobilization processes, and on dust chemical and physical transformation during transport in the atmosphere.

A common approach used in modeling dust radiative effects relies on refractive indices measured for bulk dust samples (of unknown mineralogical composition) collected at a few geographical locations. Previous studies demonstrated that this approach has serious limitations [Bohren and Huffman, 1983; Sokolik et al., 1993, 1998; Sokolik and Toon, 1996]. The major drawbacks as follows.

1. The available data are rather poor in quality (since the measurement techniques used to obtain the refractive indices are poorly justified; since the dust samples are not related to mineralogical composition; and since the data are limited in terms of representativeness of various dust sources).

2. The data were measured for dust samples which experienced specific atmospheric conditions and specific transformations during their transport from the dust source to the place where they were collected. Therefore, these optical constants are not adequate for the purpose of modeling the time and space varying aerosol optical properties.

3. The data were obtained for mineral mixtures. Due to nonlinear dependencies of aerosol optical properties on the refractive indices, it remains a question if refractive indices measured as an average for a mixture are appropriate to use for modeling the mineral aerosol optical characteristics. Moreover, particles of different sizes may have different chemical compositions. Therefore, it is incorrect to attribute a single set of values for real and imaginary parts of the refractive index to a mixture of various particles.

In this paper we discuss an alternative approach to model the dust radiative properties. This approach employs dust mineralogical composition and the refractive indices of individual mineral constituents. In this manner we are able to relate light absorption by dust to its mineralogy and source region.

In section 2 we examine available data on mineralogical composition of dust from various geographical locations. Then, we select the major minerals which should be taken into account to correctly represent spectral optical properties of dust from UV wavelengths to far infrared wavelengths (see section 3). Next, in section 4 we discuss optical properties calculated for an external mixture of individual minerals as opposed to those computed for a mixture of aggregates. Finally, in section 5 we employ our dust spectral optical models to estimate the potential direct net (solar plus IR) forcing by mineral aerosols of various compositions.

2. Mineralogical Composition of Dust at Various Locations
Minerals are generally defined as naturally occurring elements or compounds formed by inorganic processes. The majority of
dust particles are lofted into the atmosphere by eolian (wind) erosion of arid and semi-arid lands. Human activities (agriculture, industry, construction, deforestation, etc.) can extend the geographical area of dust sources and increase dust loading into the atmosphere. This portion of dust is called anthropogenic dust, and it is of special interest in climate change studies. Because of the diversity of dust sources, the properties of dust originating from various types of land surfaces needs to be studied.

There is a large body of data on mineralogical and elemental (or chemical) composition of the Earth's soils. These data demonstrate the complex spatial variability of soil composition. The observed variability is the result of the history of soil formation and weathering processes.

It is common to compare elemental composition of soils from different parts of the world with the average composition of Earth’s crust or of sedimentary rocks [Pye, 1987]. For instance, average sedimentary rocks have a Si/Al ratio of 4.04. It turn, the Si/Al ratio for dust from Sahelian region is 3.18-3.6, while for dust from northern Morocco is about 2.67-2.87 [Bergametti et al., 1989]. In contrast, dust in Arizona has the Si/Al ratio of 4.02, and dust from Tadzhikistan (central Asia) has a ratio of about 3.06 [Gomes and Gillette, 1993]. Petrov [1976] showed that the Gobi desert contains 0.74-1.36% less Fe, but 5-12% more Al and 8.4% more Ca that the average earth crust composition. These data are in agreement with measurements by Parungo et al. [1995] conducted at several locations in China.

Variable elemental ratios reflect variable mineralogical composition of parent soils. For instance, dust in the Sahelian region is characterized by a high Fe/Al ratio due to the abundance of ferrallitic soils in the Sahelian region. In contrast soils in the semi-arid regions of central Asia contain lesser Fe. The variable composition of soils produces their variable color which is often used as a criteria in soil classification. Soil color can be controlled by organic material (the carbon content gives it a dark color) or by the inorganic compounds. The most important inorganic coloring agent is iron. Iron oxides occur, at least in small amounts, in nearly all soils (51 g/kg Fe in Earth’s crust at average). However, large variations are observed. For instance, the soil of the Gobi is chiefly grayish brown, while dust collected in the Negev desert is typically light brown or tan, and Sahelian dust is bright red.

Despite the wealth of dispersed data on soil chemical and mineralogical composition there is no readily available data set on the composition of parent soils on a global scale. Existing global data sets of soil properties currently include soil texture (three size classes: “clay”, “silt” and “sand”) and soil types with a resolution 1°x1° but they do not provide information on size-resolved mineralogical composition of the parent soil [Webb et al., 1991]. There are several systems of soil classification based on different criteria (type, composition, texture, etc.). For instance, the Food and Agriculture Organization (FAO)/UNESCO system and U.S. Soil Taxonomy are two often used classifications of soil types. The Soil Taxonomy system recognizes 11 orders and five categories below the order [Soil Survey Staff, 1996]. They are: suborder, great group, subgroup, family and series. Eleven orders, 47 suborders, about 195 groups, about 1200 subgroups, about 5000 families, and about 12,000 series are presently in the Soil Taxonomy system of the USA. It is at the family level that mineralogy enters into the classification for soils, although it is used as a criterion in a higher category for some soils. However, quantitative information on mineralogical composition of surface soils can not be extracted from these classification systems. There is a clear need for a new data set to provide information on mineralogical composition needed for dust modeling on global and regional scales.

The main constituents found in dust derived from surface soils are quartz, feldspars, calcite, dolomite, gypsum, mica, kaolinite, illite, montmorillonite, palgyorskite, chlorite and organic matter (such as bacteria, fungal spores, pollen grains, seeds, stem tissue, and ash) [Pye, 1987]. Although the chemical and mineralogical composition of airborne dust mimics the composition of the parent surface, it also depends on dust mobilization processes and compositional separation during dust transport. Changes in composition during dust transport have been reported by the numerous investigators. For instance, Rahn et al. [1979] demonstrated that the Si/Al ratio changes during the long-range transport of mineral particles. A study by Prospero et al. [1981] showed the changes in mineralogy of Saharan dust samples collected at various distances off the coast of Africa along the dust plume transported over the Atlantic Ocean. Chester et al. [1972] reported the variations of clay minerals with latitude in dust samples collected off the west coast of Africa.

In turn, dust mobilization processes partly determine the initial particle size distribution of airborne minerals as well as the degree of particle aggregation, and, therefore, influence airborne dust composition. At the same time, surface characteristics (such as composition, particle aggregation, particle size distribution, etc.) are crucial for dust mobilization processes. In fact, fine mineral particles are often present in the form of aggregates in surface soils, rather than in the form of loose grains. This phenomenon is explained by strong interparticle cohesive forces, which decrease with increasing particle size. Aggregates have sizes from about 80 μm to several hundreds micrometers. They can be made of particles of the same mineral or of particles of various mineralogical compositions (clay, quartz, hematite, salts, etc.) [Chatenet et al., 1996, Alfaro et al., 1997]. Aggregation can also depend on mineralogical composition of parent soils. For instance, dust in Australia is more aggregated that Saharan dust [Kiefert et al., 1996].

Dust mobilization mechanisms can cause the complete or partial breakdown of aggregates to particles of size of about 20-50 μm and smaller, which can then be transported by winds. Therefore airborne dust may exist as an external mixture of individual minerals or/and as a mixture of aggregated particles. We are not aware of any parameterization of the size-dependent dust flux with resolved mineralogical composition. However there are several parameterizations of size-dependent dust flux accounting for various surface soil features [Gillette 1979, Marticorena and Bergametti, 1995, Marticorena et al., 1997]. In particular, more recent studies incorporated surface mineralogy and surface roughness into dust emission scheme to simulate the size-resolved dust vertical flux. Such schemes can be extended to simulate size- and composition-resolved dust fluxes.

Summarizing the above discussion, there are several processes leading to the variability of dust composition: (1) variable composition of bed surfaces (supported by measurements of elemental and mineralogical composition; by various soil colors; by various soil types); (2) spatially and temporally varying dust production mechanisms (selective lifting of the minerals from the bed surface); and (3) space and time varying compositional separation due to physical and chemical processes during dust transport.

Since mineralogical data on dust composition are not currently available on the global scale, to perform our modeling we use some representative measurements of dust composition at various locations. Mineralogical composition is often reported for a total (bulk) dust sample or for a clay-size fraction (mass radii < 1μm). Table 1 presents the average composition of the clay-size fraction of dust which originated in Chad, Egypt, Saudi Arabia [Ganor and Foner, 1996], Australia and Mali [Kiefert et al., 1996], and the Sahara [Delany et al., 1967]. Samples analyzed by Ganor and
Plate 1. Same as Figure 1, except at the infrared wavelengths.
Plate 2. Same as Figure 2, except at IR wavelengths.
Table 1. Mineralogical Composition of Clay-Size Mode Particles Which Originated From Various Geographical Sources

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chad</th>
<th>Egypt</th>
<th>Saudi Arabia</th>
<th>Mali</th>
<th>Barbados (Saharan Dust)</th>
<th>Australia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illite</td>
<td>87</td>
<td>15</td>
<td>5</td>
<td>26.4</td>
<td>41</td>
<td>38.2</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>11</td>
<td>30</td>
<td>55*</td>
<td>67.8</td>
<td>32</td>
<td>61.8</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>2</td>
<td>55</td>
<td>40</td>
<td>2.7</td>
<td>16</td>
<td>0</td>
</tr>
</tbody>
</table>

* Kaolinite and palygorskite. Values are in units % by weight.

Foner were collected over Israel, but they showed different clay minerals according to their geographical sources, namely, Ahaggar Massif (Chad and Libya), Tibesti Mountains (Egyptian, Libyan, and Negev deserts), and Saudi Arabia (Jordan and Dead Sea deserts) (see first three columns in Table 1). Saharan dust was collected at Barbados [Delany et al., 1967]. Dust which originated from the Ahaggar Massif is characterized by a high abundance of illite, while dust from the Tibesti Mountains has moderate concentrations of illite, kaolinite and montmorillonite. In contrast, dust from Australia has high concentrations of kaolinite.

Table 2 presents the average composition of total dust samples collected at Sal Island, Barbados and Miami [Glaccum, 1978], southern New Mexico [Hoidale and Blanco, 1969], Sudan [Sharif, 1995], and Nigeria [Adedokun et al., 1989]. Table 2 shows large variations of mineral composition with location. For instance, the amount of quartz can vary from 6% (southern New Mexico) to about 83% (Nigeria, sample 4). Another feature which can be seen in Table 2 is that different studies reported different sets of dust mineral constituents extremely entangling modeling and comparison the dust radiative properties. Also, only a few studies reported hematite (a major source of light absorption) along with other minerals. To some extent this variation in minerals reported is explained by problems with identification and quantification of individual minerals.

3. Refractive Indices of Major Minerals

We compiled a data set of published refractive indices for major minerals from UV to IR wavelengths. Table 3 provides references for some available data along with the range of wavelengths where optical constants were measured. Some data from Table 3 are illustrated in Figure 1 and Plate 1, which present the spectral real and imaginary parts of the refractive indices, respectively. Figure 1b and Plate 1b show those minerals from Table 1 which have an imaginary part of their refractive indices larger than 1x10^-5 in solar and infrared wavelengths, respectively.

The minerals with the imaginary part smaller that 1x10^-5 cause negligible light absorption.

For some minerals there are independent measurements of optical constants at visible and infrared wavelengths (Figure 1 and Plate 1). Therefore data sets must be interpolated around 2.5 μm (for instance, montmorillonite, illite, kaolinite). Also, data on spectral optical constants in the visible are missing for some minerals (for instance, chlorite, calcite, gypsum). For these species we use the real part of refractive indices as the average in the visible from Ivlev and Popova [1973], ignoring possible spectral dependencies. Moreover, some minerals (such as, hematite, quartz, calcite, gypsum) can have amorphous and crystalline forms. Further, some crystals are anithotropic, showing different optical constants in the directions of their principal optical axes [Egan and Hilgeman, 1979].

It would be a difficult task to incorporate all the numerous minerals occurring in nature into models of the dust radiative properties relevant for climate and remote sensing applications. Instead, one can try to define the major mineral components of aerosols which should be taken into consideration to correctly represent the spectral dust optical properties over a range of wavelengths from 0.2 to 30 μm. We select minerals with the following two characteristics to be used further in our modeling: minerals which are a minor mass fraction but have specific absorbing bands with a relatively high imaginary part of the refractive index, or minerals with a large mass fraction of the aerosol. From analyses of data on mineralogical composition and on spectral refractive indices (see Figure 1 and Plate 1), we limit ourselves to seven minerals when exploring the spectral dust radiative properties: quartz, hematite, montmorillonite, illite, kaolinite, calcite, and gypsum.

Quartz is often dominant in terms of mass and has strong absorption bands in the IR atmospheric window, although it does not have noticeable absorption at UV and visible wavelengths. Clays (montmorillonite, illite, kaolinite) are abundant in terms of mass and have strong absorption in the IR. Multiple types of

Table 2. Mineralogical Composition of Bulk Dust Samples Collected at Various Locations

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Sal Island</th>
<th>Barbados</th>
<th>Miami</th>
<th>Southern New Mexico</th>
<th>Sudan Sample 2/KH/83</th>
<th>Nigeria Sample 4</th>
<th>Nigeria Sample 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illite</td>
<td>53.8</td>
<td>64.3</td>
<td>62.9</td>
<td>19.0</td>
<td>3.8</td>
<td>1.17</td>
<td>5.6</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>6.6</td>
<td>8.3</td>
<td>6.3</td>
<td>20.0</td>
<td>N/R</td>
<td>N/R</td>
<td>12.0</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>N/R</td>
<td>N/R</td>
<td>N/R</td>
<td>35.0</td>
<td>N/R</td>
<td>N/R</td>
<td>N/R</td>
</tr>
<tr>
<td>Quartz</td>
<td>19.6</td>
<td>13.8</td>
<td>14.2</td>
<td>6.0</td>
<td>56.3</td>
<td>83.3</td>
<td>67.4</td>
</tr>
<tr>
<td>Chlorite</td>
<td>4.3</td>
<td>4.1</td>
<td>4.2</td>
<td>N/R</td>
<td>N/R</td>
<td>N/R</td>
<td>N/R</td>
</tr>
<tr>
<td>Gypsum</td>
<td>N/R</td>
<td>N/R</td>
<td>N/R</td>
<td>5.0</td>
<td>N/R</td>
<td>N/R</td>
<td>N/R</td>
</tr>
<tr>
<td>Calcite</td>
<td>8.2</td>
<td>3.9</td>
<td>6.9</td>
<td>16.0</td>
<td>7.3</td>
<td>N/R</td>
<td>N/R</td>
</tr>
<tr>
<td>Hematite</td>
<td>N/R</td>
<td>N/R</td>
<td>N/R</td>
<td>6.23</td>
<td>N/R</td>
<td>N/R</td>
<td>N/R</td>
</tr>
<tr>
<td>Others</td>
<td>7.5</td>
<td>5.4</td>
<td>5.5</td>
<td>4.0</td>
<td>21.4</td>
<td>3.5</td>
<td>4.4</td>
</tr>
</tbody>
</table>

N/R, data were not reported. Values are in units % by weight.


4. Modeling the Dust Radiative Properties

As we discussed in section 2, depending on the production mechanisms and transformation processes during transport, mineral particles can be in aggregated or in disaggregated forms. First, we consider radiative properties of an external dust mixture assuming that it consists of individual minerals, then we will address modeling the radiative properties of dust particles in aggregated forms (in other words, an internal mixtures). Since the latter problem cannot be solved in a general way, we will explore several approximations to model optical properties of composite particles.

Aggregation of dust particles could be important for their ability to scatter and absorb radiation. The available studies on aggregation of other types of atmospheric aerosols have demonstrated that inclusion of small amount of highly absorbing material (such as soot) in a transparent host (such as sulfates or cloud droplets) can cause an absorption enhancement by aggregates [Ackerman and Toon, 1981; Chylek and Hallet, 1992; Fuller et al., 1999]. In the case of dust, hematite (a strong absorber at solar wavelengths) can be aggregated with clays or quartz (relatively transparent at solar wavelengths), resulting in higher absorption. A correct assessment of solar absorption by dust is a crucial problem in modeling the impact of dust upon climate.

We focus here on modeling the mineral aerosol spectral optical properties which are needed for climate modeling: the extinction coefficient $K_{	ext{ext}}$ (which is the sum of scattering and absorption coefficients), single scattering albedo $\omega_0$, and asymmetry parameter (a cosine weighted integral of the scattering phase function) $g$. This set of parameters allows calculation of radiative forcing in the two-stream approximation, which is often used in climate models.

### 4.1. Optical Properties of a Mixture of Individual Minerals

Individual minerals which compose an external mixture of the airborne mineral particles can have the same particle size

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**Table 3. Refractive Indices of Major Constituents of the Airborne Mineral Aerosols**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Wavelength, μm</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amorphous form</td>
<td>7.14-50.0</td>
<td>Popova et al. [1972]</td>
</tr>
<tr>
<td>Crystalline form</td>
<td>7.14-25.0</td>
<td>Steyer et al. [1974]</td>
</tr>
<tr>
<td></td>
<td>0.736-36.0</td>
<td>Peterson and Weinman [1969]</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>0.185-2.6</td>
<td>Egan and Hilgeman [1979]</td>
</tr>
<tr>
<td></td>
<td>5.0-40.0</td>
<td>Toon et al. [1977]</td>
</tr>
<tr>
<td></td>
<td>2.5-200</td>
<td>Querry [1987]</td>
</tr>
<tr>
<td>Illite</td>
<td>0.185-2.6</td>
<td>Egan and Hilgeman [1979]</td>
</tr>
<tr>
<td></td>
<td>2.5-200</td>
<td>Querry [1987]</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>0.185-2.6</td>
<td>Egan and Hilgeman [1979]</td>
</tr>
<tr>
<td></td>
<td>5-25</td>
<td>Roush et al. [1991]</td>
</tr>
<tr>
<td>Calcite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amorphous form</td>
<td>2-32.8</td>
<td>Querry et al. [1978]</td>
</tr>
<tr>
<td>Crystalline form</td>
<td>2.5-300</td>
<td>Long et al. [1993]</td>
</tr>
<tr>
<td>Gypsum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystalline form</td>
<td>2.5-300</td>
<td>Long et al. [1993]</td>
</tr>
<tr>
<td>Mica</td>
<td>0.185-2.6</td>
<td>Egan and Hilgeman [1979]</td>
</tr>
<tr>
<td>Feldspar</td>
<td>0.185-2.6</td>
<td>Egan and Hilgeman [1979]</td>
</tr>
<tr>
<td>Chlorite</td>
<td>2.5-50</td>
<td>Mooney and Knacke [1985]</td>
</tr>
<tr>
<td>Serpentine</td>
<td>2.5-50</td>
<td>Mooney and Knacke [1985]</td>
</tr>
<tr>
<td></td>
<td>5-25</td>
<td>Roush et al. [1991]</td>
</tr>
<tr>
<td>Hematite</td>
<td>0.2-50</td>
<td>Querry [1978]</td>
</tr>
<tr>
<td></td>
<td>8.3-50.0</td>
<td>Popova et al. [1973]</td>
</tr>
</tbody>
</table>

Clays are considered because there are specific features in their spectra (such as band shapes and positions) which distinguish them from quartz and from each other. Moreover, clays absorb at solar wavelengths, showing an increasing imaginary part of the refractive index toward UV wavelengths (see Figure 1). Hematite has the largest absorption at UV and visible wavelengths of the minerals we have considered. Also hematite has strong absorption bands in the IR around 8 μm and 25 μm. In contrast, calcite and gypsum show almost no absorption in the UV and visible, but they do have strong absorption bands in the IR with band positions that are quite different from those of quartz and clays (see Figure 1 and Plate 1).
distribution or different size spectra. The shape of the size spectrum and its variation in time depend on the initial size distribution resulting from particle mobilization, as well as on transformation processes during dust transport.

To model the optical properties of individual minerals we assume that their size distributions may be represented by several lognormal functions as

\[ N(r) = \sum N_j \left( \frac{2\pi}{\sigma_j} \right)^{1/2} r^{-1} \exp \left\{ -\ln(r_0 j)^2 / 2 \ln(\sigma_j)^2 \right\}, \]

where \( N(r) \) is the particle number concentration of a given mineral, \( N_j \) is particle number concentration of the \( j \)-th size mode with its median radius \( r_0j \) and geometric standard deviation \( \sigma_j \). The lognormal function is often used to model aerosol size distributions [e.g., D'Almeida et al., 1991]. We will calculate optical properties of individual minerals using a variety of observed particle size spectra to represent the complex temporal and spatial variation of the size distribution.

First, we calculate optical properties of minerals assuming that they have one size mode but varying median radius. Figure 2 and Plate 2 show calculated normalized extinction coefficients, \( K_{ext}^*(\text{cm}^2/\text{km}) \) (normalized for \( N=1 \text{ cm}^{-3} \)), for individual minerals at the solar and infrared wavelengths (Figure 2 and Plate 2, respectively). The particle size modes have \( r_0 = 0.5 \) (Figure 2a and Plate 2a), and 0.7 \( \mu \text{m} \) (Figure 2b and Plate 2b), and \( \sigma=2 \). The size mode with \( r_0=0.5 \mu\text{m} \) is believed to be representative of the particle size distribution of the long-lived, distant-transport accumulation mode of airborne dust [Patterson and Gillette, 1977, Arimoto et al., 1997]. The larger \( r_0 \) is representative for a particle size mode which occurs near the dust source [Gomes and Gillette, 1993]. In reality, particle size spectra can have one or several modes, characterized by a specific composition.

Figure 2 and Plate 2 demonstrate how the normalized spectral extinction coefficient varies due to the differences in the refractive indices of the minerals. As shown in Figure 2, \( K_{ext}^* \) of hematite has a spectrum which is clearly distinguishable from that of other minerals at solar wavelengths. Some minerals have noticeable differences in \( K_{ext}^* \) for wavelengths larger than a specific wavelength which depends on \( r_0 \). For instance, for \( r_0=0.5 \mu\text{m} \) the minerals considered have differences in their \( K_{ext}^* \) spectra for wavelengths larger than about \( \lambda = 0.6 \mu\text{m} \).

In the IR region, Plate 2 shows various specific features in the \( K_{ext}^* \) spectrum of the individual minerals. For a given mineral, the spectral features in \( K_{ext}^* \) mimic the features in the mineral’s refractive index spectrum, although the magnitude of \( K_{ext}^* \) depends on the parameters of the particle size distribution. Plate
Plate 3 illustrates the single scattering albedo of the minerals which have significant absorption at UV and visible wavelengths for particle size distribution with $r_0=0.25$, 0.5, and 0.7 μm. Quartz, calcite and gypsum single scattering albedos are not shown in Plate 3 because their $\omega_0$ is close to 1 in this wavelength region. For hematite, we show $\omega_0$ for both the E-ray and O-ray to illustrate the differences. In turn, Plate 4 presents calculated single scattering albedos at infrared wavelengths for the same particle size distributions: (a) $r_0=0.25$ μm, (b) $r_0=0.5$ μm, and (c) $r_0=0.7$ μm.

The single scattering albedo for hematite is about 0.6 for wavelengths λ < 0.6 μm and varies little with $r_0$ or ray type. In contrast, clays have $\omega_0$ in a range from about 0.8 to 1 for λ < 0.6 μm, showing strong spectral dependence at UV and visible wavelengths. For λ > 0.6 μm, clays have $\omega_0$ of about 0.95 to 1, while hematite has large variations of $\omega_0$ depending on ray type.

In the IR region, $\omega_0$ varies in a wide range from about almost 0 to 1 (Plate 4), and has a complex spectral behavior which varies greatly between the minerals considered.

Plate 5 compares the asymmetry parameter of some minerals at UV and visible wavelengths with size modes having $r_0=0.25$, 0.5, and 0.7 μm. The magnitudes of $g$ are in a range from 0.65 to 0.75 with a few exceptions (Plate 5). Namely, hematite can have $g = 0.35-0.85$, depending on the wavelength. All minerals considered have larger magnitudes of $g$ for shorter wavelengths. In the infrared, $g$ decreases when λ is increasing, although some spectral features in $g$ for the individual minerals can be seen.

Employing calculated optical characteristics of individual minerals (Figure 2 and Plates 2-5) one can model the optical properties of external mixtures of minerals. The large variations in the optical properties of individual minerals illustrated above suggest that the radiative properties of a mixture would strongly depend on the relative abundance of individual minerals. However, the minerals have unequal importance in their contribution to the mixture optical properties at solar and infrared wavelengths. To explore the importance of the abundance of individual minerals for the effective optical properties of their mixture, we use available measurements of the composition of dust samples collected at various geographical locations and...
measured (if available) or assumed lognormal particle size distributions. As we discussed in section 2, mineralogical composition is often reported as a weight fraction of individual minerals in the total sample or as a fraction within some range of particle diameters (see Tables 1 and 2). In particular, we use data from Table 1 to calculate the optical properties of dust with a clay-size particle mode (with mass radius < 1 μm).

Calculations were performed as follows. If $K_{\text{ext mix}}$ (km$^{-1}$) denotes the extinction coefficient of a mixture of individual minerals, it can be written as

$$K_{\text{ext mix}} = \sum (K_{\text{ext*}} \cdot N_i),$$

where $N_i$ is the particle number concentration of the i-th individual mineral and $K_{\text{ext*}}$ is its normalized extinction coefficient calculated above for individual minerals. If $W_i$ is the weight fraction of the i-th mineral in a mixture with a total particle mass concentration $M$, we have

$$N_i = M \cdot W_i / [4/3 \pi (r_0)^3 \exp (9 \ln (\sigma)^2 / 2)],$$

where $\rho_i$ is the density of the i-th mineral. Consequently, $K_{\text{ext mix}}$ is

$$K_{\text{ext mix}} = \sum (K_{\text{ext*}} \cdot M \cdot W_i / \rho_i) / [4/3 \pi (r_0)^3 \exp (9 \ln (\sigma)^2 / 2)].$$

For purposes of illustration we calculate $\Delta K_{\text{ext}}$ as the difference between the extinction coefficient of a given clay mineral mixture from Table 1 and the extinction coefficient of kaolinite. The latter extinction represents a case when composition of clay-size mode is ignored and only one mineral is used to model its optical properties (in this case, kaolinite). Thus we have

$$\Delta K_{\text{ext}} = K_{\text{ext mix}} - K_{\text{ext}}(\text{kaolinite}).$$

Figure 3 shows $\Delta K_{\text{ext}}$ calculated in the solar and infrared wavelengths. We assume $M=10 \, \mu g/m^3$ and a lognormal size distribution with $r_0=0.5$ μm. For various mixtures, the calculated $\Delta K_{\text{ext}}$ (km$^{-1}$) is in a range from $-8 \times 10^{-5}$ to $5 \times 10^{-4}$ at visible wavelengths, and in the range from $-3 \times 10^{-4}$ to about $1.5 \times 10^{-3}$ at infrared wavelengths.

To understand how important the differences in $\Delta K_{\text{ext}}$ are, one can translate them into differences in optical depth. For a homogeneous dust layer located in the four lowest kilometers of the atmosphere (H=4 km) the differences in optical depths versus mass concentration are

$$\Delta \tau = \Delta K_{\text{ext}} \cdot H \cdot M,$$

where $\Delta K_{\text{ext}}$ is for $M=1 \, \mu g/m^3$. As an illustration, Figure 4 presents $\Delta \tau$ calculated at 0.5 and 9.5 μm (wavelengths used in remote sensing) versus mass concentration for the dust samples from Table 1. Figures 3 and 4 show that the uncertainties in the extinction coefficients (or optical depth) of a clay mixture due to composition change are larger at the infrared wavelengths than at visible wavelengths. However, for a heavy dust loading of about $M=10,000 \, \mu g/m^3$, which corresponds to a well-developed dust storm, the differences at visible wavelengths become important. Although the clay mixtures can have more complicated compositions, illite, kaolinite and montmorillonite are known to

Plate 3. Single scattering albedo of some minerals at solar wavelengths calculated for $r_0=0.25$, 0.5, and 0.7 μm.
Plate 4. Single scattering albedo of some minerals at IR wavelengths calculated for (a) $r_o = 0.25$ $\mu$m, (b) $r_o = 0.5$ $\mu$m, and (c) $r_o = 0.7$ $\mu$m.
Plate 5. Asymmetry parameter of some minerals at the solar wavelengths calculated for $\lambda=0.25$, 0.5 and 0.7 $\mu$m.

be the most abundant in terms of their mass fraction. Thus if only kaolinite is used to model optical properties of clay mixture, one can expect to underestimate or overestimate the extinction coefficient (and optical depth) for a given mass loading as illustrated in Figures 3 and 4.

The single scattering albedo of a mixture does not depend on total dust concentration, but depends instead on the relative abundance of absorbing constituents. In particular, iron oxides enhance absorption at UV and visible wavelengths, and quartz, calcite and gypsum change the spectral absorption features at infrared wavelengths.

As we discussed in section 2, there are very limited data on the amount of iron oxides species in dust samples. Therefore we model the optical properties for a range of possible weight fractions of hematite in the clay-size mode while the remaining mass was equally distributed among illite, kaolinite and montmorillonite. Figure 5 presents the cases of 1%, 10%, and 20% hematite by weight. The total mass concentration is $M=10 \text{ g/m}^3$. For these cases, we also calculated the single scattering albedo, which is shown in Figure 6. We assumed a lognormal size distribution with $r_0=0.5 \mu$m and $c=2$. For comparison, $\omega_0$ calculated for Sahara dust using refractive indices from Patterson et al. [1977] is about 0.8 [see Sokolik et al., 1997]. This low single scattering albedo implies that either Patterson's refractive indices are incorrect or hematite is not present in an external mixture as we have considered. In particular, we demonstrate below in section 4.2 that aggregation of hematite with quartz or clays can cause much higher absorption.

Quartz, calcite, or gypsum results in an increase of $\omega_0$ at solar wavelengths when externally mixed with clays. Also, these minerals can strongly influence the dust mixture properties at IR wavelengths because quartz, calcite, or gypsum often occur as larger sized particles and each has strong absorption features.

We modeled the optical properties of a mixed aerosol with large particle sizes by assuming $r_0=0.7 \mu$m and $c=2$. We allowed the relative amount of quartz, calcite, and gypsum to vary. As was expected, the largest differences in the calculated optical properties were observed at IR wavelengths. As an illustration, Figure 7 presents the differences in the extinction coefficients, $\Delta K_{ext}$, between three types of mixtures and the extinction coefficient calculated for quartz. Type 1 is for a mixture of the equal weight fraction of quartz, calcite, and gypsum; type 2 is for a mixture of 80% quartz, 10% calcite, and 10% gypsum; and type 3 is for a mixture of 50% quartz, 30% calcite, and 20% gypsum.
Figure 3. The difference $\Delta K_{ext}$ between the extinction coefficient of a given clay mineral mixture from Table 1 and the extinction coefficient of kaolinite (see text).
We assume $M = 10 \, \mu g/m^3$. Quartz gives higher spectral extinction coefficients (or optical depth) at infrared wavelengths than the mixtures except a few small wavelength regions (see Figure 7). In particular, $K_{ext}$ of quartz is larger than those calculated for the mixtures in wavelength regions centered at 8.5 and 12.5 $\mu m$. Both these wavelength regions are used in satellite observations.

Summarizing the results of our modeling discussed above, some generalizations can be made about the optical properties of the mixtures of individual minerals.

1. At solar wavelengths the extinction coefficients calculated for mixtures of varying composition have relatively similar spectra, except for hematite. At infrared wavelengths significant differences are readily seen between the extinction coefficient spectra of individual minerals and their mixtures due to specific absorption bands.

2. At solar wavelengths the single scattering albedo is more sensitive to the presence of hematite than to other minerals. Clays have single scattering albedo from about 0.85 to 1, showing the smallest magnitudes at UV wavelengths. At infrared wavelengths the single scattering albedo varies from about 0 to 1 due to specific absorption features in each mineral.

3. At solar wavelengths the asymmetry parameter is in the range from about 0.65 to 0.75 for the mixtures considered. At infrared wavelengths, despite some specific features tied to absorption bands, the asymmetry parameter decreases with increasing wavelength.

4.2. Optical Properties of a Mixture of Mineral Particles in Aggregated Form

Airborne dust particles often occur in an aggregated form of two or more minerals. Moreover composition can vary with the size of aggregates and can undergo various chemical and physical transformations during the particle life-cycle. There is no general technique for modeling the optical properties of composite particles. We consider two effective medium approximations, referred to as Maxwell-Garnet and Bruggeman approximations. Both Maxwell-Garnet and Bruggeman approximations are derived from the same integral equation for propagation of electromagnetic waves in inhomogeneous medium but under a different set of approximations [Bohren and Huffman, 1983; Chylek et al., 1988]. We compare the refractive indices calculated from these approximations to refractive indices obtained by volume or mass mixing.

The simplest way to calculate an effective refractive index of a composite particle is to sum up the refractive indices of its individual constituents weighted by their volume (or mass) fractions:

$$ n_{eff} = \sum v_i n_i, $$

where $n_{eff}$ is the effective refractive index of the composite particle, $n_i$ is the refractive index of the $i$-th constituent, and $v_i$ is the volume fraction of the $i$-th constituent.

The Maxwell-Garnet approximation gives an effective dielectric constant, $\varepsilon_{eff}$, of a two-component mixture composed of inclusions embedded in homogeneous matrix [Bohren and Huffman, 1983]. The inclusions should be identical in composition but may be different in volume, shape and orientation. If all inclusions are spherical, it can be shown under some additional assumptions that

$$ \varepsilon_{eff} = \varepsilon_m \left( 1 + \frac{3 v_i (\varepsilon - \varepsilon_m) / (\varepsilon + 2 \varepsilon_m)}{1 - v_i (\varepsilon - \varepsilon_m) / (\varepsilon + 2 \varepsilon_m)} \right), $$

where $\varepsilon_m$ and $\varepsilon$ are complex dielectric constants of the matrix and inclusion, respectively. However, the Maxwell-Garnet approximation is not invariant with respect to interchanging the matrix and inclusions. It implies that a decision must be made as to which component is the matrix and which is an inclusion.

In contrast, the Bruggeman approximation allows for calculation of an effective dielectric constant of the multicomponent mixtures without distinguishing between matrix and inclusions. In other words, this approximation can be applied for a random inhomogeneous medium. For a two-component mixture the Bruggeman approximation can be written in the following way:

$$ v_1 (\varepsilon_1 - \varepsilon_{eff}) / (\varepsilon_1 + 2 \varepsilon_{eff}) + (1 - v_1) (\varepsilon_2 - \varepsilon_{eff}) / (\varepsilon_2 + 2 \varepsilon_{eff}) = 0, $$

where $v_1$ and $v_2$ are the volume fractions of the matrix and inclusion, respectively.
Figure 5. The differences between the normalized extinction coefficient calculated for a mixture of three clays and hematite and the normalized extinction coefficient calculated for a mixture of three clays at (a) visible and (b) infrared wavelengths (see text).
Figure 6. Same as Figure 5, except for the single scattering albedo (see text).
where $\varepsilon_1$ and $\varepsilon_2$ are dielectric constants of the mixture components. Also both approximations can be easily extended from a two-component to a multicomponent mixture. After effective dielectric constants are calculated by one of the approximations, the effective optical constants are given by equation:

$$n_{\text{eff}} = (\varepsilon_{\text{eff}})^{1/2}$$

(note that both $n_{\text{eff}}$ and $\varepsilon_{\text{eff}}$ are complex numbers).

The Maxwell-Garnet approximation was previously applied to dust by Longtin et al. [1988]. Longtin et al. considered mineral aerosol as a sand which can consist of two kinds of particles: pure quartz and quartz contaminated with a small amount of hematite. The optical constants of the latter particles were calculated by using the Maxwell-Garnet approximation for hematite contents of 5% and 10% by weight. Our calculations using the Bruggeman approximation give very similar effective refractive indices to those obtained with the Maxwell-Garnet approximation for these cases. However, we prefer to use the Bruggeman approximation because it seems more adequate for modeling of multicomponent (more than two components) mixtures with random inhomogeneities such as mineral aerosol aggregates.

It is important to stress that due both to various assumptions involved in the effective medium approximations and to poor knowledge of dust particle aggregation, much effort will be required to justify the applications of these approximations to mineral aerosols. Such studies have been conducted for cosmic dust grains, but we are not aware of any studies for eolian dust on the Earth [e.g., Perrin and Lamy, 1990].

Using the Bruggeman approximation we calculated effective refractive indices of aggregated particles and compared to the refractive indices calculated by volume mean mixing. We explore various possible mineralogical composition of composite particles based on reported measurements (see section 2).

The calculated effective indices of the aggregates made of clays (kaolinite, montmorillonite, and illite) give similar results for approximations considered due to the relatively small differences in the refractive indices of these minerals. The fact that the Bruggeman approximation and volume mean approximation give close results, and that these results are in a good agreement with measurements of refractive indices for a mixture of these clays by Querry [1987] is encouraging for using the effective medium approximations for dust aggregates.

The refractive indices of hematite are quiet different from those of other minerals. We considered various composite particles made of hematite and quartz or clays. Plates 6 and 7 present the spectral real and imaginary parts of the effective refractive indices calculated for the aggregates by the both Bruggeman and volume mean approximations. These refractive indices are for composite particles made of 99% quartz or kaolinite and 1% hematite, and for the aggregates made of 90% quartz or kaolinite and 10% hematite. Plates 6a and 7a provide the effective refractive index at solar wavelengths, while Plates 6b and 7b show the effective refractive index at infrared wavelengths. Examining these figures, one can point out various differences between the refractive indices of the four types of composite particles considered. For a given amount of hematite $n$ calculated by two approximations differs by a few percent. However, aggregation of quartz and hematite and kaolinite and hematite results in different dependencies of $n$ versus $k$ at solar wavelengths. The imaginary part, $k$, of the refractive index has the similar spectra shape for composite particles with the same amount of hematite, although $k$ calculated by two approaches differs by as much as 40%. This difference is illustrated in Figure 8, which shows the relative difference calculated as

![Figure 7. Differences between the extinction coefficients calculated for three types of mixtures and extinction coefficient calculated for quartz. Type 1 is for a mixture of equal weight fraction of quartz, calcite, and gypsum; type 2 is for a mixture of 80% quartz, 10% calcite, and 10% gypsum; and type 3 is for a mixture of 50% quartz, 30% calcite, and 20% gypsum.](image-url)
Plate 6. Real part of the effective refractive indices of aggregates calculated by the Bruggeman and volume mean approximations for aggregates made of 99% quartz and 1% hematite, 90% quartz and 10% hematite, 99% kaolinite and 1% hematite, and 90% kaolinite and 10% hematite.

\[ \frac{A(\text{Bruggeman}) - A(\text{volume mean})}{A(\text{Bruggeman})} \]

where the variable A is n or k. Figure 8 shows that the relative difference of n is negligibly small, while the difference is high for k. A maximum of the differences is centered at \( \lambda = 0.5 \) \( \mu \text{m} \) and is about 60% to 80% depending on composition of the aggregates.

Overall, for the aggregates considered, k calculated by the volume mean approximation is larger than that calculated by the Bruggeman approximation, except in a region of about \( \lambda < 0.3 \) \( \mu \text{m} \). Both approximations show that aggregation of even small amount of hematite with the less absorbing constituents causes an increase of k by almost an order of magnitude at solar wavelengths.

We also model aggregates made of quartz and calcite, quartz and gypsum, clays and calcite, and clays and gypsum. We found good agreement between refractive indices of these composite particles calculated by both approaches at solar wavelengths. However, various discrepancies were observed in infrared wavelengths. For instance, Figure 9 shows the imaginary part calculated by the Bruggeman approximation for composite particles made of 50% quartz and 50% calcite along with its differences relative to k calculated by the volume mean mixing. It is apparent that the volume mean mixing predicts greater absorption by the bands at the IR than does the Bruggeman approximation, but the differences are not great.

Using the effective refractive indices discussed above we model optical properties of aggregates in a similar manner to what we have done for a mixture of individual minerals. Plate 8 presents the normalized \( K_{ext}^* \) calculated for composite particles made of 90% quartz or kaolinite and 10% hematite, and for composite particles made of 99% quartz or kaolinite and 1% hematite. In turn, Plate 9 shows the single scattering albedo and asymmetry factor. The size distribution of aggregates was lognormal with \( r_s = 0.5 \) \( \mu \text{m} \) and \( \sigma = 2 \). The optical characteristics have similar features to what we pointed out for the imaginary part of the effective refractive index. For a given amount of hematite, aggregation with quartz or kaolinite has spectral optical properties calculated by a given effective medium approximation similar to each other. But they differ for the different effective medium approximations.

Comparing optical characteristics presented in Plates 8 and 9 to those calculated for a mixture of individual minerals (see section 4.1), one can notice that for a given mineralogical composition, mixtures of aggregates are characterized by much lower single scattering albedo and somewhat different \( K_{ext}^* \) than external mixtures. For instance, Figure 6a and Plate 9a show that an external mixture of kaolinite and 1% hematite has \( \omega_0 \) of 0.98 at \( \lambda = 0.5 \) \( \mu \text{m} \), in contrast to 0.83 or 0.89 calculated for aggregates by the two approximations. In turn, aggregates with 10% hematite
Figure 8. Relative differences of $n$ and $k$ calculated for composite particles by the Bruggeman approximation and by the volume mean approximation (see text).

Figure 9. Imaginary part, $k$, of the effective refractive index of composite particles made of 50% quartz and 50% calcite calculated by the Bruggeman approximations, and its differences, $\Delta k$, relative to one calculated by the volume mean mixing.
have $\omega_0$ of about 0.57 and have quite different single scattering albedo spectra at visible wavelengths compared to those calculated for a mixture of individual minerals.

Our explanation for the differences between aggregates and external mixtures is the following. Hematite has a large imaginary part of the refractive index, but also a large real part. Therefore its single scattering albedo is not extremely low, and a large amount of hematite must be included in an external mixture with other minerals to have an overall low single scattering albedo. However, if hematite aggregates with less absorbing particles, the effective refractive index still has high $k$ for all the particles in the mixture but a relatively low real part of the effective refractive index. This combination results in low single scattering albedo for the mixture of aggregates with a relatively small amount of hematite.

5. Radiative Forcing by Mineral Aerosols

We used the dust optical properties calculated above to explore the importance of varying mineralogical composition and particle aggregation for the assessment of direct net (solar+infrared) forcing by mineral aerosols.

In particular, we calculate daily mean net radiative forcing by a mixture of individual minerals with varying weight fraction, and compare it to that by a mixture of aggregated minerals. We employ a one-dimensional radiative transfer code, based on the correlated K distribution technique incorporated into a two-stream code [Sokolik et al., 1998, Bergstrom et al., 1998]. We consider a surface albedo of 0.2. Atmospheric characteristics (water vapor profile, temperature profile, etc.) are from the "midlatitude summer" standard atmosphere. The dust vertical distribution was homogeneous up to 4 km, with a total particle number concentration of $N=400 \text{ cm}^{-3}$.

To illustrate Figure 10 shows the net radiative forcing calculated for several mixtures of varying proportion of clays, quartz and hematite. The figure shows daily mean net forcing, $\Delta F$ (W/m$^2$), calculated for the mixtures of individual minerals having composition of 90% clays, 5% quartz, and 5% hematite (Figure 10a); 75% clays, 20% quartz, and 5% hematite (Figure 10b); and 80% clays, 0% quartz and 20% hematite (Figure 10c). In Figures 10a and 10b, radiative forcing is negative leading to cooling. To have positive forcing, the hematite amount must be increased to about 15-20% which seems unrealistically high.

In contrast, Figure 10d demonstrates that a small amount of hematite (2% of a total mixture) aggregated with quartz, and then externally mix with clays gives positive $\Delta F$. We obtain similar results for a case when hematite is aggregated with one of the clays, and then externally mixed with quartz. These studies indicate that knowing whether or not hematite is aggregated with other minerals is crucial for modeling the dust optical properties, and for assessing dust radiative forcing.

6. Summary

In this paper we explored an alternative approach to incorporate the mineralogical composition of mineral aerosols into models of dust radiative properties. The approach considered has several advantages.

1. Refractive indices for individual minerals are better measured than refractive indices of mixtures.
2. Mixing the optical properties of minerals is more likely to yield correct optical properties than using the optical constants for a mixture of unknown composition.
3. Refractive indices of individual minerals may be better related to specific size modes than refractive indices of mixtures.
The major disadvantages of this approach are as follows.
1. There are not enough data on regional and global scales to quantify the size-resolved composition of dust at the moment.
2. There is no single welltested theory for modeling optical constants of the aggregated particles.

Nevertheless, we demonstrated that the optical properties of a mixture depend on the abundance of individual minerals and on their aggregation. In particular, we have selected seven major minerals based on their abundance and their absorption spectra. Using data on mineralogical composition of dust collected at several locations we calculated dust optical characteristics assuming a mixture of individual minerals or a mixture of aggregates. To calculate the effective refractive indices of aggregates, we employed the Maxwell-Garnet, Bruggeman, and volume mean approximations. Despite the lack of rigorous justification for these approximations, they indicate an absorption enhancement due to aggregation relative to an external mixture. Adequate treatment of particle aggregation is crucial for assessment of dust radiative effects because for a given composition and under similar atmospheric conditions a mixture of aggregates can cause the positive radiative forcing while a mixture of individual minerals gives the negative forcing.

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References


