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CONTRIBUTION TO THE STUDY OF ATMOSPHERIC DUST SOURCES

A MINERALOGICAL APPROACH

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1 General introduction

The wind is responsible for an important erosion in most arid areas and the presence of mineral particles in the atmosphere is known since a long time (Darwin, 1846). Nevertheless, if cities of the northern Mediterranean Sea are used to colored rain events, the scientific community did not pay much interest to atmospheric dust until the last decades. The renewed attention of scientists for climatic processes and for geochemical cycles was however the reason for a new focus on mineral aerosol life-cycle since these particles appear to be an important constituent of the atmosphere. We present here the diverse effects of dust on environment, focusing on the importance of a good knowledge of dust mineralogy, and we explain then the aims of this study.

1.1 The importance of mineral dust

1.1.1 Interactions between mineral dust and climate

The evolution of the world climate is one of the most discussed question nowadays. Human activity leads to the emission of greenhouse effect gases (CO_2,CH_4 for instance) that are able to trap telluric infrared radiations, and therefore increase the energy incoming at the earth surface. At the same time, these human activities are also responsible for a large production of small particles (”aerosols”) which scatter and/or absorb radiative fluxes (the ”direct effect”) and have an influence on the clouds properties (the ”indirect effect”). These two effects globally tend to reduce radiative fluxes incoming at the surface and compete with the climatic impact of ”greenhouse” gases.

In the atmosphere, the aerosol population is a mixing of natural aerosol (volcanic ash, sea salt ...), of anthropogenic productions (sulfates, nitrates..) and of natural species enhanced by human activities (soot, dust..). All species have different properties with regards to radiative calculations : sulfates have a significant cooling effect since they scatter the solar energy back to space and have a large indirect effect, soot absorb the solar energy and heat therefore the atmosphere. Mineral particles affect the radiative transfer in a more complex way since they are likely to absorb and scatter the solar energy but also the infrared radiations. The radiative effect of dust particles is determined by their optical properties, which are calculated from the size and the mineralogical composition of the dust population. Different mineralogical species have distinct refractive indices, $m(\lambda)$, which can be written as follows :

$$m(\lambda) = n(\lambda) - i.k(\lambda) \tag{1}$$

λ being the wavelength, n being the ratio of the light velocity in the medium to the light velocity in the vacuum, and k characterising the absorption of the medium. The effect of the mineralogy on optical properties can be seen on figure 1 where the imaginary part of the refractive index (k) for hematite, quartz and a dust sample are shown. If we consider the dust sample as a simple mixture of the two minerals, the logarithmic scale reveals that little variations in the amount of iron oxides can strongly influence the absorption of light. For instance, in the visible range (550 nm), an increase of k lead to a large absorption of energy by dust and therefore to a local heating of the atmosphere. On the other hand, a decrease of k lead to more back-scattering of the solar energy to space, and therefore to a global loss of energy for the Earth. A precise assessment of the radiative direct effect of mineral dust is therefore impossible without a better knowledge of the mineralogy.

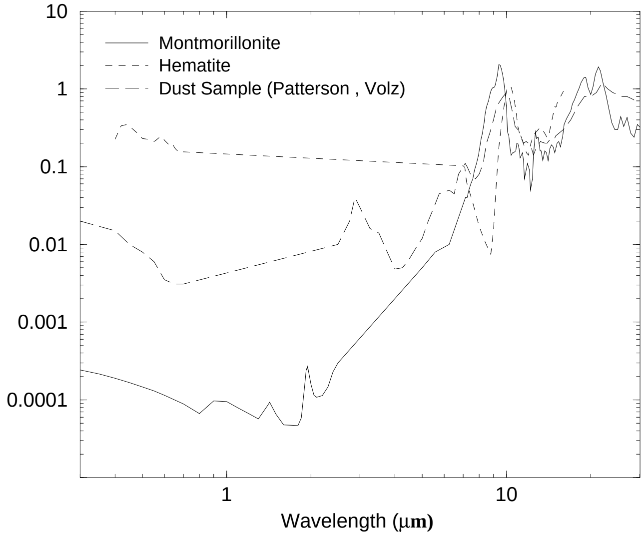

Figure 1: *Imaginary part of the refractive index for haematite, quartz and a dust sample.*

Besides, the ability of mineral dust to have an indirect effect is still unclear. To have an impact on cloud properties, particles have to be soluble and become Cloud Condensation Nuclei (CCN), which is not true as long as quartz, feldspar are considered. Yet carbonate minerals, such as calcite, and also gypsum are common components in dust and are soluble.

1.1.2 The sedimentary importance of mineral dust

Transport of dust by winds is an important source of material for the detritic sedimentation over oceans and continents. Biscaye (1965) showed that the mineralogical distribution of the sediments in the Atlantic Ocean is governed by the mineralogy of the West African soils. The localisation of dust sources, the relative abundance of minerals in dust raised from these sources, and the wind field implied in transport determine the magnitude and the place of deposition. The understanding of such mineralogical patterns can be of major interest : for instance, the ratio *kaolinite/chlorite* in sediments can be used used as an indicator for climate. Indeed, kaolinite is formed by alteration of feldspar in tropical conditions, whereas a mechanical alteration would rather lead to the formation of chlorite. The comprehension of the dust cycle during the last glacial period, in which mineral aerosols were supposed to have a large climatic role, requires therefore to understand how the different mineralogical species are transported.

Moreover, the input of mineral dust is able to modify significantly the geochemical equilibrium of many ecosystems. At the ocean surface or over poor continental areas, the deposition of atmospheric dust is necessary to achieve the nutrient balance. For instance, Swap et al. (1992) evaluated to 13 Mt/year the contribution of Saharan dust in the Amazonian and calculated that this deposition is an essential supply in nutrient for the rain forest. The authors assume further that the growth and the contractions of the Amazonian forest are controlled by the extend of the Sahara desert. Once again, this features underline the necessity of a mineralogical approach of the dust cycle.

1.2 Modelling mineral dust : a mineralogical approach

In the last decades, the understanding of the mineral dust life cycle has been considerably improved by the precision of satellite measurements but also by the growing quality of numerical models. These models are useful to understand the climatic impact of dust particles and to evaluate their deposition patterns. Nevertheless, all the current models are based on the hypothesis of a homogeneous mineral mixture though the variability of the mineral dust population is well known. This approximation is only due to the poor information available on the mineralogy of the arid areas. As a consequence, the sources formulation available for numerical models give dust vertical fluxes of a homogeneous mixture.

Two different parameterisations are currently used for the sources : the global map of Zobler (1986), which is a simplification of the first version of the FAO Soil Map of the World (FAO, 1974-1978), and the more refined physical formulation of Marticorena and Bergametti (1995) which is available for North Africa only. Our aim is not to develop a new formulation of the dust sources but only to assess their mineralogical composition, that is, for a given intensity of dust production at a certain place, we ought to predict its composition. Therefore, our formulation of the mineralogy of dust sources must be used with a source formulation, but it can be used with any of them. Our method is based on the latest digital version of the FAO World Soil Map and its legend (FAO, 1995), which constitutes the main database for this work.

A good mineralogical description of the dust mineralogy requires to know the amount of quartz, feldspar and clay minerals, which are the most important minerals in dust in terms of mass, calcite and gypsum, which have different optical and solubility properties, and iron oxides, which have a very important optical role. Iron can also strongly affect the operation of some ecosystems.. Among clay minerals, kaolinite, montmorillonite (or smectite), illite and chlorite are the most common and therefore their study is very important in simulation of marine sedimentation. It is noticeable that the mineralogical understanding of the dust sources was until now either local (Caquineau, 1997) or qualitative.

The present report present methods concerning iron oxides and, in a way, kaolinite.

2 Methods

2.1 The FAO World Soil Map(FWSM)

2.1.1 The Legend of 1974

The legend of the FWSM was published in 1974, together with the first paper version of the Map. It is divided into 10 volumes, among them 9 are devoted to 9 large regions of the world (for instance South East Asia). The most interesting information linked to soil mineralogy concern chemical analyses. They are given for each soil type observed in the region, and at different depths. We always consider the properties in the top horizon of the soil. Chemical analyses often consist in determining the amounts of different element oxides released after an acid attack (ex. : Al_2O_3, SiO_2, Fe_2O_3). However, these analyses are not always done.

2.1.2 The digital version of 1995

The Soil Map of the World published by the FAO (Food and Agriculture Organisation of the United Nations) is nowadays the most complete global database of the world soils. It is a compilation of all the different soil maps published in different countries, and all the different legends have been unified. Because this map was originally done for agricultural purposes, it is not directly usable for dust studies, nevertheless, it includes informations on the granulometry and the chemistry of the soil that can be used to derive properties in respect to wind erosion. The FAO classification of soils is based on 106 **types** divided in 26 **classes**. Based on this classification, 4931 soil **units** are defined as combinations of 1 to 8 soil types. For each of these soil types, the granulometry (fine, medium, and coarse) and the slope (0-8%, 8-30% and >30%) of the surface are precisely defined. In the digital version of the FSMW, these data are available every 5 minutes of arc. The occurrence of mineralogical phases, like calcium carbonate or iron oxides accumulation, are also indicated for each soil unit, but these features usually appears in the deep soil and are not used in this study. Finally, the FSMW contains relationship between the soil types and classes and some useful chemical properties (pH, Cation Exchange Capacity,...)

2.2 Hypothesis and methods

The purpose of this work is to attribute mineralogical properties to each soil type, in order to combine them and then assess the mineralogical composition at the surface of each soil unit. However, in the FAO classification, mineralogy is not regarded as criterion to identify soils. Nevertheless, we assume here that the composition of the soil surface is not independent from the usual diagnostic properties (particles size, colour, chemical properties,...), and that the classification of the FAO is fine enough so that we can attribute a realistic mineralogy for each soil type. The attribution of a surface mineralogy to soil types can be done following two methods. The first method, called "systematic", and also the most direct, is the collection of large amount of soil descriptions for each soil type, this database being usable to define average mineralogies. This method has the advantage to check the validity of our approach and to avoid approximations, but is also limited by the small amount of mineralogical studies at the surface of arid areas. The second method, called "analytic", is based on relationships that exist between the surface mineralogy and soil properties that are better known. This method is fast when soil properties are already included in the FSMW, but also require a precise validation of the used relationship.

For both methods, we studied separately the clay ($< 2\mu m$) and the silt fraction ($> 2\mu m$, $< 20\mu m$). The three FAO size categories (fine, medium, coarse) have therefore to be converted to classical categories (clay, silt, sand). Particles larger than silt do not play a significant role in the large scale transport and were therefore not studied. Besides, the resolution of the map has been changed from 5×5 minutes to 1×1 degree cell, the averaging having, theoretically, to be weighted by the source strength of each soil unit. Since the formulation of the source is not the concern of this work, we used the clay content of each unit as a first guess to evaluate the source strength of each soil unit. The value attributed to a 1×1 degree cell is then the combination of 144 units contained in this cell. Soil units that are not "potentially arid" are excluded from the averaging procedure. Each 1×1 degree cell is kept in our processing if at least 72 soils units are "potentially arid". Some areas of the FSMW are referenced as "non-data" areas, but our averaging procedure eliminates them.

3 Systematic method

This approach is based on the constitution of a database containing the mineralogy of the 106 FAO soil types. Since our concern is related to wind erosion, we do not take into account all soils that are not significantly affected by wind erosion. Soil types that develop under diverse forests, tall grasses, meadows or humid environment are systematically excluded from our study (Acrisols, Cambisols, Chernozems, Podzoluvisols, Phaeozems, Gleysols, Rendzines, Rankers, Andosols, Greyzems, Luvisols, Nitosols, Ferralsols, Histosols). To limit the influence of local contributions, we based the database on global descriptions, i.e soil descriptions that take all kinds of profiles into account.

The major problem raised by this method is the collection of enough profiles for a peculiar soil type. Indeed, soil studies are seldom associated with mineralogical descriptions, these latest being often semi-quantitative (infrared spectra), not specifically realized for the soil surface or limited to the phyllosilicates. Furthermore, the FSMW is based on the FAO classification, whereas the described soils are often identified following other classifications (ex. : Soil Taxonomy used in the United States). Connections had then to be done between the different classifications. To use this hypothesis, we disposed of 206 soil profiles where the mineralogy of the 30 first centimetres were known.

4 Analytical method

The contribution of this work to the analytical method essentially concernes the iron content in the top soil. Other methods based on size distributions and chemical properties concerning other minerals will not be developed in this report.

4.1 Iron compounds in soils

Iron is found in two major forms in soils. Either it is substituted in primary minerals (such as peridots) inherited from the parental material of the soil, and in secondary minerals formed by alteration of primary minerals (especially clay minerals), or it is present in iron oxides. These oxides are sometimes considered as free iron, though they can also be coated to silicate minerals. There are six naturally occurring iron oxides or hydroxides found in rocks and soils :

- Magnetite Fe_3O_4 is black and Hematite Fe_2O_3 is red. These are usually regarded as primary minerals.
- Maghemite Fe_2O_3 is a dark brown material and often in association with organic matter.
- Goethite and Lepidocrocite are hydrated iron oxides with the formula $FeOOH$. Both minerals are yellow-brown in colour.
- Limonite is another iron hydroxide ($Fe(OH)_3nH_2O$). This secondary component is amorphous and yellow in colour. It occurs as a coating material or absorbed on clay minerals.

Hematite and Goethite are the most common minerals and constitute therefore the most important form to be evaluated. Depending on the method used to determine the iron content, different measurements are obtained : the total iron content (HCl method), the free iron content (Deb and d'Hoore method) or the amorphous iron content (Segalen method). Iron amounts are low (hematite and goethite are mostly under 10 % of the soil surface mass) and therefore seldom measured. A first approach consist then in building an analytical method allowing to know iron amounts from other soil properties better described in the FSMW. To do this, we assume that the amount of free iron in a soil is close to that of iron oxides.

4.2 Element ratios

Chemical analyses of the soil content are more frequent than mineralogical studies in soil profiles descriptions. Our first idea was then to find a relationship between the chemical composition (SiO_2, Al_2O_3, K_2O, Fe_2O_3,..) and the iron oxides content. Actually, knowing the contents of a material in these different major elements, it is possible to estimate its mineralogy. This consists in changing basic vectors from the chemical analyses to the mineralogical composition. This can be done with the matrix of the mineralogical composition of chosen minerals.

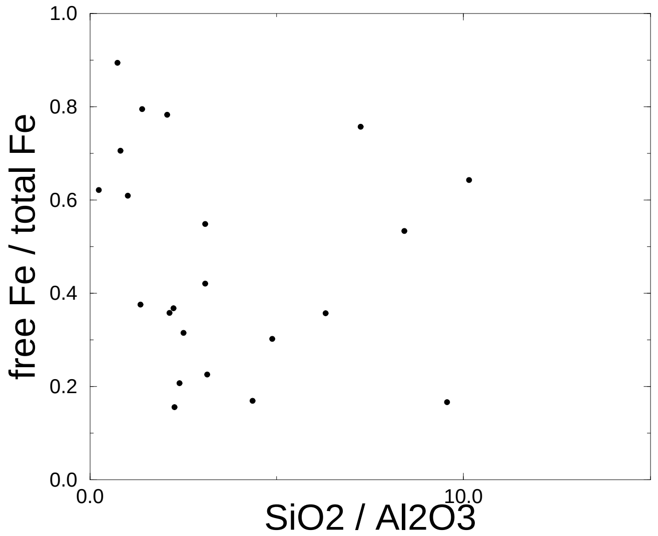

Figure 2: *Element ratios in top soils (from the FSMW legend).*

Considering that we focused on the iron oxides content and that chemical analyses are often limited to few elements, we had to consider a simplified mineralogy with three majors poles : tectosilicates (quartz and feldspars), phyllosilicates (clay minerals) and iron oxides (hematite, goethite) that we tried to re-compose from the contents in iron, silicium and aluminium.

Knowing the distribution of iron in soil compounds described previously, we assumed that iron is present essentially in hematite, goethite and substituted in phyllosilicates. Aluminium and silica are present in tectosilicates (quartz and feldspar) and phyllosilicates (clay minerals), with aluminium being less substituted in primary minerals (tectosilicates) than in weathered secondary minerals (phyllosilicates). Thus, the ratio Si/Al seems to be linked with the relative abundance of tecto- and phyllosilicates : the more clay minerals are abundant, the lower the ratio is. Such a relationship has also been used by Gomes et al. (1990) to assess the clay/quartz ratio in dust samples. We assumed then that the ratio $freeFe/totalFe$ depends on the abundance of the clay minerals. Si/Al is known from the amounts of SiO_2 and Al_2O_3, whereas the amount of total iron is given by the one of Fe_2O_3. To validate this hypothesis, we had to determine a correlation beetween these two ratios. Yet, this method did not bring any satisfying results (see fig.2). It seems that this description does not take into account other phenomena such as scrubbing which tends to make the distribution of these elements more complex.

Others attempts to link the directly hematite-goethite contents to another chemical property of the soil were unsuccessful. Indeed, descriptions of the hematite-goethite contents of soil surfaces are usually qualitative (between 1 and 5 %, or ”present”) which seriously limit any numerical treatment. Besides, during this study, it appeared to us that the attribution of a chemical composition for each soil type is not straightforward since many soils have the same chemical contents but rather various mineralogy.

4.3 Colour of soils

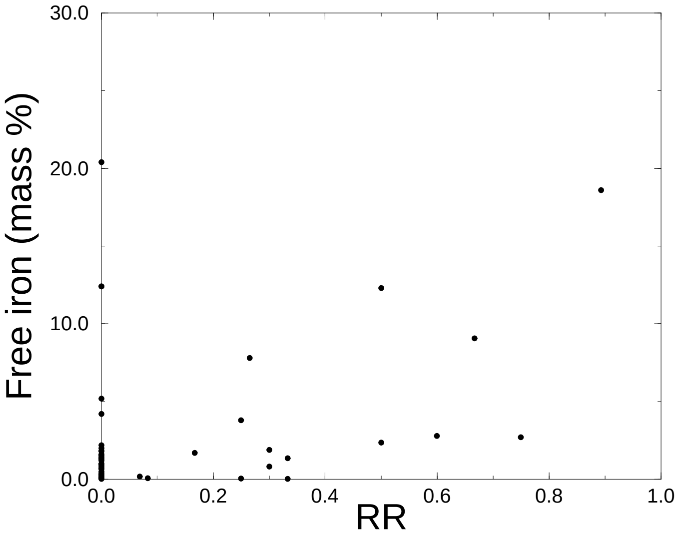

Figure 3: *Redness Ratio and free iron content (arid areas).*

The soil colour is classically the first observation made in all soils descriptions. The colour is given following the Munsell colour scale, which use three parameters : the **hue**, or tint, is represented with a letter (for soils : Y, YR or R, for (Y)ellow and (R)ed) and a number describing the evolution on the colour spectrum from red to yellow, the **value** indicates the lightness from 0 (black) to 10 (white) and the **chroma** measures the departure to the neutral colour (from weak to vivid). It is classically admitted that the colour of a soil depends mainly of the organic matter content and on the abundance of iron oxides. Since we focus here on arid and semi-arid areas, which are usually poor in organic matter, we considered here that iron oxides alone determine the colour of the soil.

Considering the colour properties of iron minerals, we first tried to determine an empirical relation between the free iron content of the top soil, and its colour. To do this, we used the redness ratio which is defined by $RR = \frac{(10-H)\times C}{V}$, where H is the hue, V the value and C the chroma. This variable is defined in Torrent et al. (1980) for soil having a hue between 0YR (yellow red) and 10YR. As described in figure 3, the redness ratio RR is not directly correlated to the free iron content, especially because of the different optical properties of these occurring iron oxides.

In fact, goethite is a yellowish brown mineral while hematite is a strong red mineral which affect more readily the colour of the soil. In a later article, Torrent et al. (1983) found a relationship between the hematite content of a soil and its colour. This relationship has not been specifically established for desert areas, neither for the top-soil profiles, nevertheless, we think it can be applied for our purpose.

5 Results

We only present here results for the map of Africa, since it is the arid area which has been the most extensively studied and can therefore most readily be validated. Though this study mainly focused on iron oxides, the map of hematite is presented here together with the map of kaolinite. Indeed, hematite and kaolinite are formed under similar hydrolysis conditions, and the comparison between these two maps will give use a "first step" validation.

5.1 Distribution of hematite in Africa

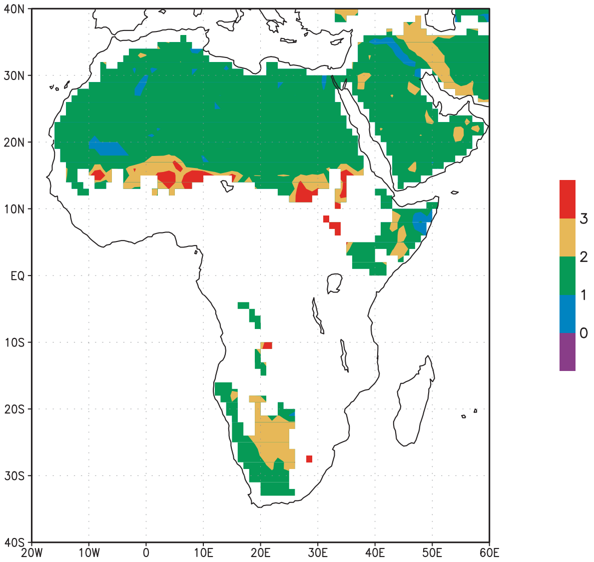

Figure 4: *Hematite in the top soil for the clay size fraction (mass %).*

The map on figure 4 concerns the distribution of hematite in the top soil of Africa for the clay size fraction. The repartition of hematite is strongly influenced by climatic conditions. Humidity favours the alteration of silicate minerals and therefore the formation of hematite. Hence the amount of hematite increases toward the equator, and occurs in dust source regions which experience a wet season : for instance the Lake Chad, and in general the whole Sahel are areas where hematite can be found. Contents in haematite (between 0 and 8%) are low, because this iron oxide is seldom a major component in soils mineralogy at these latitudes. It is also noticeable that hydrolysis is not the only process that can "produce" (or liberate) hematite. For instance, it has been observed in desert that the hematite content increases with the age of the dunes. It might indicates that wind could also be responsible for an increase of hematite content. Apparently, this phenomenon is poorly reproduced in this map.

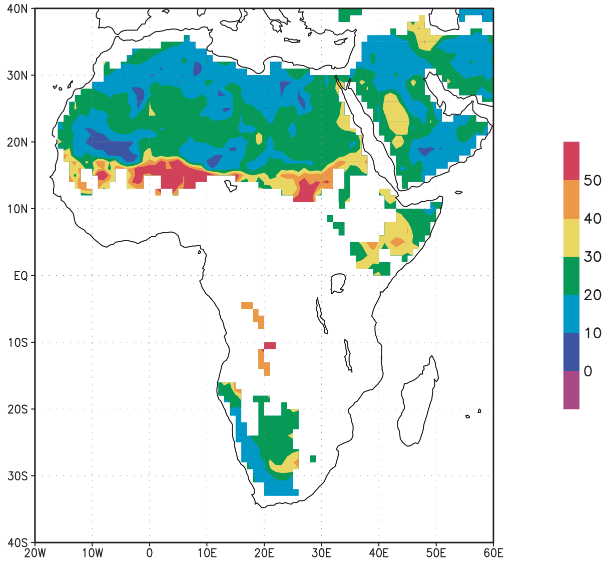

Figure 5: *Kaolinite in the top soil for the clay size fraction (mass %).*

5.2 The repartition of kaolinite in Africa

On figure 5, the map shows the abundance of kaolinite determined following the systematic method for the clay size fraction . For latitude lower than 10 degrees and larger than 40 degrees, white areas are non-source areas, while in the Northern part of the continent (ex. Algeria, Mauritania) white areas corresponds to soils where our database is still incomplete. Moreover, one should remember that this map does not describe dust sources but the mineralogical content of potential sources : for instance, the West part of the Congo Basin, where kaolinite is dominant (see figure 5), is not a dust source on the global scale.

Contents in kaolinite range from about 10 to 60% in dust sources and mainly follow latitudinal bands, especially because kaolinite is an indicator of alteration in tropical conditions and therefore follows the change of climatic conditions. The main sources for kaolinite are located in the Southern Sahara (especially Sahel), and the south west of the continent. These are actually potential sources (the location of "real" sources also depend on the wind field, the number of stones on the top soil,. . .).

These results can be compared with the distribution of kaolinite in dust on the West African coast as measured by Chester et al. (1972). The graph shown on figure 6 reveals that the amount of kaolinite in dust samples have monotonous variations on each side of the equator : maximal at the equator and decreasing with the latitude. This figure also gives the average kaolinite amount against latitude for all dust potential sources, according to the map. The maximum at the equator is not present, whereas we notice two maxima on each side of the equator. These two extrema are located at both 20 degrees of latitude. One should remember that trade winds blow toward the Equator from North-East to South-west in the Northern hemisphere, and from South-East to North-West in the Southern hemisphere. It is therefore reasonable to assume that the presence of a maximal content in kaolinite for the dust at the equator is the result of its transport by trade winds.

The map on figure 7 shows the distribution of kaolinite in recent sediments for the clay size fraction following Biscaye (1965). Once again, it is interesting to compare the major boundaries in the distribution of the mineral in the top soil with the boundaries in oceanic sediments. Near the West African coast, near the coast of Guinea and in the Gulf of Guinea for instance, continental and oceanic areas correspond to the highest contents in kaolinite. With these two maps, we can compare the location of dust sources and places of deposition. For the African West coast, the location of sources and the direction of major winds blowing from East to West could explain the main deposition pattern.

Due to a lack of a better dataset to compare with our results, we cannot propose a better validation. Nevertheless, the distribution of hematite in African soils seems to be satisfying. The good correlation between the hematite map and the kaolinite map, and the similarity between the processes which lead to the formation of these two minerals let us think that the results are also realistic for hematite.

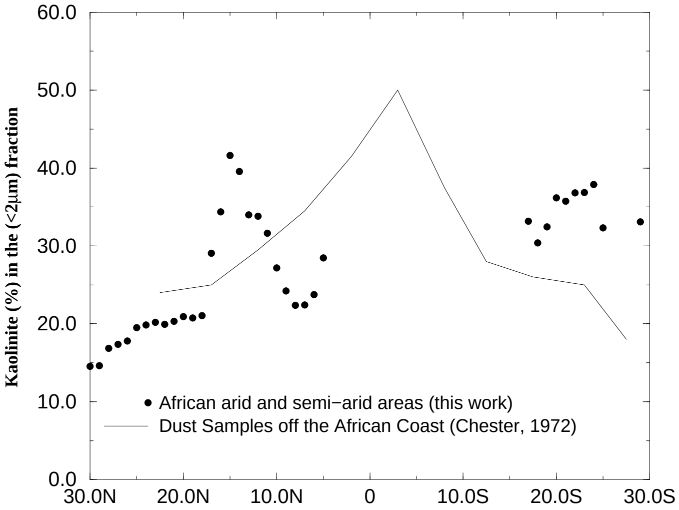

Figure 6: *Distribution of kaolinite with latitude in dust samples collected over the Atlantic Ocean off-African Coasts (Chester et al., 1972) and at the surface of arid soils in our maps.*

6 Conclusion

This work contributed to the premises of the first quantitative evaluation of the mineralogy of the atmospheric dust source. We developed two different methods

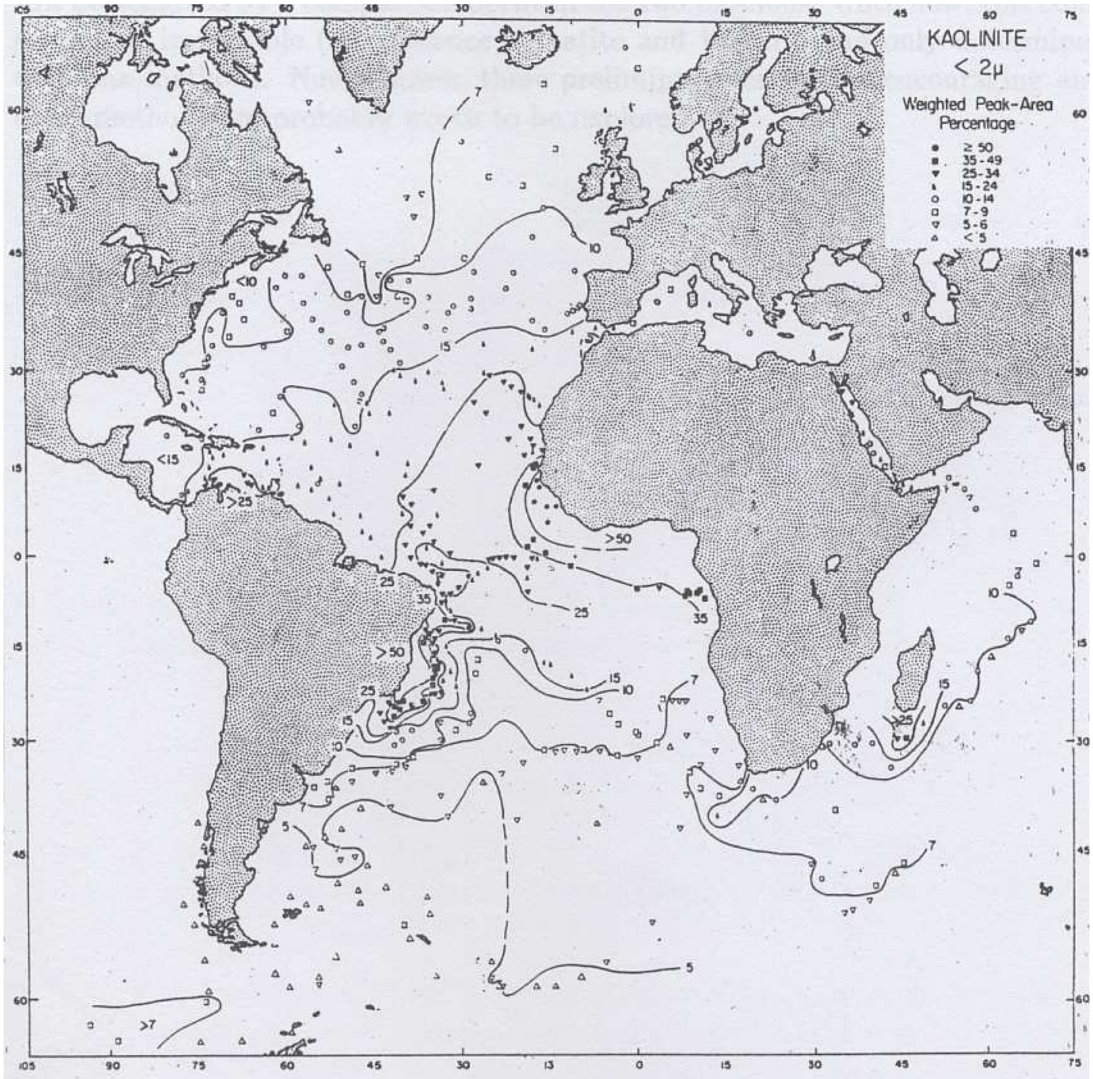

Figure 7: *Kaolinite in marine sediments for the clay size fraction following Biscaye (1965).*

in order to estimate the amount of quartz, kaolinite, smectite, montmorillonite, chlorite, calcite, gypsum and hematite at the soil surface, with a special focus on hematite. As exposed in the last section of this report, the results are correct in a qualitative way, which is certainly not enough, and further developments are necessary. First, the "systematic" method withstands on a database which still requires improvements (concerning sand dunes, Lithosols..). Secondly, the validity of the relationship used in the "analytic" method also need to be more precisely validated. Third, we belive that the first validation of our work will be achieved by a comparison between the two methods. Until now, this comparison is impossible (for instance hematite and kaolinite are only determined with one method). Nevertheless, these preliminary results are encouraging and these methods are probably worth to be explored.

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