MINERALOGY OF EPICA - DOME C ICE CORE DUST

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ABSTRACT

Optimization of analytical procedures for mineralogical characterization of aeolian dust trapped in Antarctic ice has been developed in this work. The analytical protocol includes X-Ray Powder Diffraction (XRPD) and High Resolution-Transmission Electron Microscopy (HR-TEM) coupled to Energy Dispersive X-Ray Fluorescence (ED-XRF) techniques. This procedure has been applied on standard minerals and Antarctic ice samples, in order to combine powder and single crystal results of aeolian particles archived in the EPICA Dome C (EDC) ice core during the last two climatic cycles. Diffraction measurements were also done on samples from Potential dust Source Areas (PSAs) collected in southern South America (sSA), South Africa (Saf), Australia (Aus), New Zealand (NZ), and some Antarctic (Ant) non-glaciated areas. Differences between the climatic periods has been observed in term of mineral assemblages. The more concentrated glacial periods seem to confirm the southern South America origin, while the provenance of interglacial particles seem to be a mixing between southern South America and Australia. This work highlight the potentialities of the XRPD coupled with HR-TEM techniques to help in the interpretation of the dust transport and deposition from the PSA to the Antarctic continent, and the possibility to understand the role of the atmospheric dust on the history of the southern Hemisphere climate in the last 200 kyrs.

INTRODUCTION

Ice cores can be considered undisturbed archives of climatic information, if drilled in the internal part of Antarctic Plateau, in the centre of Topographic Dome, and can permit to recover climatic and environmental records at different timescales (Petit *et al.*, 1999; EPICA Community Members, 2004). The EPICA Dome C (EDC) ice core provide information about the last 800 kyrs. Aeolian mineral dust trapped in the EDC core providing information about environment and climate, atmospheric circulation and the hydrological cycle of the Southern Hemisphere during last nine glacial and interglacial climatic periods (Lambert *et al.*, 2008). In this respect we could observe a high dust concentration value followed by a rapid decrease in dust mass and flux occurring during all the glacial to interglacial climatic variations, respectively from ~ 800 to ~ 15 ppb on average and a ratio of 50 to 1 over the last climatic cycle (Lambert *et al.*, 2008). The very low concentration of dust during interglacials is an analytical challenge in understanding the mineralogical properties of particles trapped in the ice cores.

The insoluble material reaching the Antarctic ice sheet is composed by extremely small particles, which display a diameter (spherical equivalent) smaller than 5 μm, and the size distribution typically shows modal values of about 2 μm, which is a characteristic dimension for long range transport (Delmonte *et al.*, 2002; Lambert *et al.*, 2008).

The environmental and climatic factors producing the increase in dust concentration during glacial times are: (1) dryness of the source areas, (2) variations in the hydrological cycle, (3) changes in the atmospheric circulation, and finally (4) efficiency during dust deposition (Petit *et al.*, 1999; Lambert *et al.*, 2008).

Mineral particles that compose the dust fraction suspended in the high troposphere that reach the Antarctic ice sheet are quartz, feldspars, salts, volcanic materials and mainly clay minerals (Pye, 1987). Due to the morphology, size and weight, clay materials are the most diffuse aeolian particles all over the Earth (Tegen & Fung, 1994). Moreover, several studies using isotopic tracers indicate that the major source for dust is southern South America (SSA) during cold periods (Grousset *et al.*, 1992; Basile *et al.*, 1997; Delmonte *et al.*, 2004). Conversely, for the last interglacial several studies provide evidence of large differences, with the strong contribution of the East Australia deflation areas (Revel-Rolland *et al.*, 2006).

An important contribution in understanding the climatic variations occurred in the Southern Hemisphere is obtained by applying mineralogical study on EDC ice core microparticles. In this respect, mineralogical and crystal-chemical studies provide information about the weathering occurred within the most important Southern Hemisphere source areas. Moreover, diffraction patterns obtained on the more recent aeolian sediments allow comparing the *present day* with the past environmental conditions at the same source.

In this work, we focus on the set-up and on the inter-calibration of XRPD and TEM, whose results were extensively tested with the use of certified standard samples, and we present the first data obtained by coupling diffraction and electron microscope analyses on a few samples from the EPICA (*European Project for Ice Coring in Antarctica*) ice core drilled at Dome C. Also an XRPD investigation on a few fine selected sediments from possible source areas collected in the more active dust sources of the Southern Hemisphere (Delmonte *et al.*, 2004; Revel-Rolland *et al.*, 2006) provide additional information about the provenance of mineral dust trapped in the Antarctic ice.

MATERIAL AND METHODS

Samples preparation and ice core dust deposition is an analytical challenge due to the very low amount of mineral materials, which is generally around 10-100 ng of mineral particles per g of ice; the extremely low quantity of solid particles in the Antarctic ice cap makes sample preparation for the different analytical techniques very difficult and prone to external contamination.

The ice core samples analysed in this research were selected from the European Project for Ice Coring in Antarctica-Dome C ice core (EDC, 3320 m long, 75º06'S, 123º21'E, 3233 m a.s.l., mean accumulation rate: 2.7 cm w.e. yr^{-1}) (Fig. 1). Two ice pieces are representative of Holocene, three from MIS2, two from MIS3, three from MIS4, two from MIS5.5 and three from MIS6 climatic periods. The ice samples were decontaminated using a microtome swamp and melted in Teflon pot in a 1000 class clean room at environment temperature. Afterwards, an estimation of dust concentration and size distribution of ice dust were made by a particle counter at DISAT, University of Milano Bicocca. The same procedure were also done on PSAs and certified standard minerals in order to check the size of mineral materials.

XRPD analyses were applied on (1) certified standard minerals, (2) Antarctic dust, and (3) on the bulk and fine fraction (FF, $\varnothing < 5$ μm) of airborne PSA sediments. Moreover, a crystallo-chemical characterization on ice core dust were done using HR-TEM at the Earth Science Dept. - University of Milano.

The former group of samples allows evaluating the lowest amount of mineral dust detectable through XRPD, obtaining also some calibration lines for semi-quantitative mineral phase estimation (Dapiaggi *et al.*, 2007) and creating a crystallographic dataset by means of HR-TEM investigation. The second group of samples allows the mineralogical characterization of extremely small amounts of

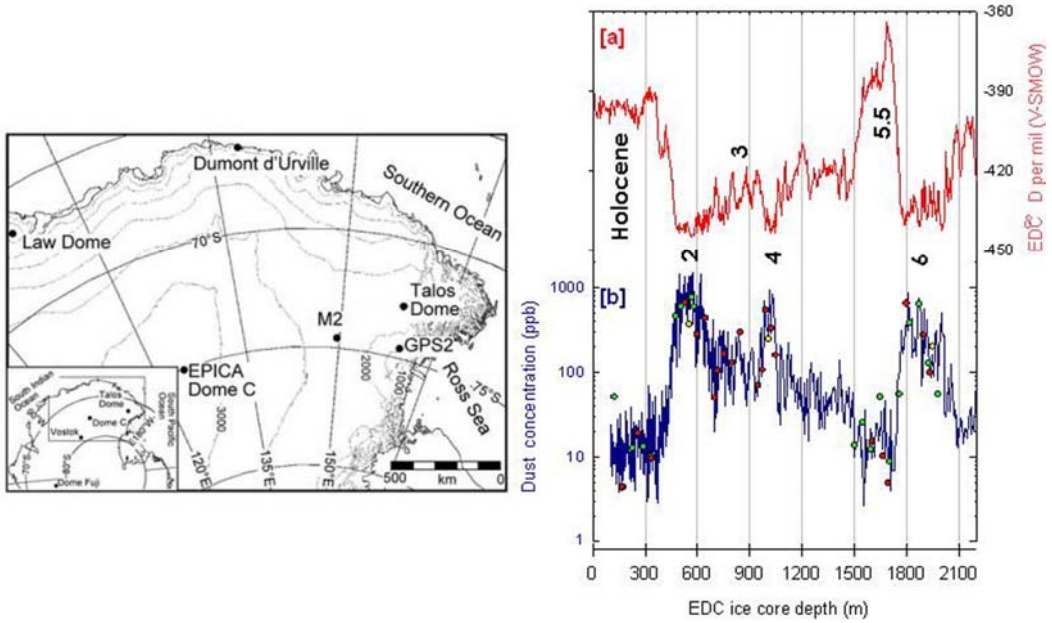


Fig. 1 - EDC drilling site and the EDC Deuterium (red) and dust (blue) record during the last 200 kyrs. Green dots show the I sampling, red dots the II and yellow dots the last (III) ice sampling.

Antarctic dust samples. The latter group of samples (11 Ant, 5 NZ, 18 SSA, 11 Saf and 22 Aus sediments) allows the identification of clay minerals in order to evaluate the provenance of the aeolian mineral dust trapped in the Antarctic ice (Sala, 2008).

All the diffraction patterns on standard minerals and ice samples were collected in a parallel beam geometry following the procedure described in Dapiaggi *et al.* (2007). Moreover, the PSA samples were analyzed working in Bragg-Brentano geometry both for bulk and fine selected fraction (Sala, 2008). Fine selected sediments were analyzed twice, comparing diffraction patterns of air-dried and ethylene glycol-solvated preparation. This analytical step allow to identify presence of expandable clay minerals in the samples.

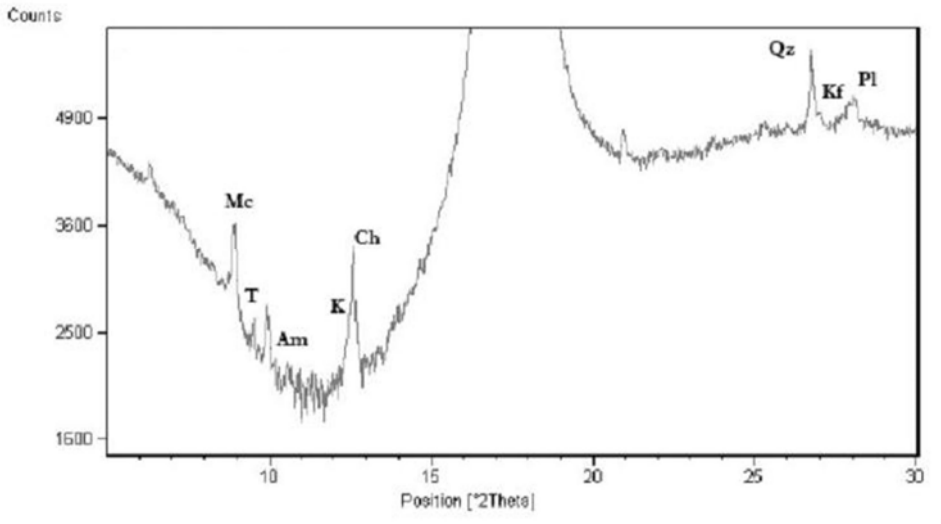
The crystal-chemical investigation were performed as follows: single particles were looked for on the copper carbon grid, trying to avoid polycrystalline aggregates; then the crystal is tilted until the zone axis is found, and its diffraction pattern is collected. Moreover, by using the ED-XRF data it was also possible to evaluated the chemical composition of the crystal. The electron diffraction and imaging data collection were applied in the Eucentric position and focus the image (moving the sample along the *z*-axes).

RESULTS AND DISCUSSION

Here mineralogical assemblages and crystal-chemical characteristics of Antarctic ice dust were presented. A semi-quantitative estimation based on the calibration line obtained by analysing a few certified standard mineral was applied on the EDC ice core dust in the same way described in Dapiaggi *et*

al. (2007). Unfortunately, due to the very low and various quantity of mineral materials deposited on filter and to the high variability in the chemical composition of each mineral phases trapped in the ice, the quantification by the calibration line reconstruction is not available and representative for all the mineral dust materials archived in the Antarctic ice. For these reasons a semi quantitative estimation, based on the integrated peaks area calculation was applied on the EDC mineral particles. These method allow to evaluate a few mineral phase ratio as clay mineral *versus* quartz and feldspars.

The XRPD analyses on the aeolian particles trapped in the EDC core highlight that the mineralogical composition of Antarctic dust is very similar for all glacial climatic periods investigated. The diffraction pattern show presence of a few mineral phases archived in the ice (Fig. 2) as chlorite (Ch), kaolinite (K), mica (Mc), talc (T), amphibole (Am), quartz (Qz), K-feldspar (Kf) and plagioclase (Pl).



Mc:Qz	T:Qz	Am:Qz	K:Qz	Ch:Qz	Mc:F	T:F	Am:F	K:F	Ch:F	K:Ch	K:Mc	Ch:Mc
1:1.7	1:19	1:50	1:5	1:2	1:2	1:18	1:50	1:5	1:2	1:3	1:3	1:1

Fig. 2 - EDC-MIS2-I diffraction pattern and mineral phases ratio.

The low concentrated mineral dust filtered trough Nuclepore membrane make the diffraction peak identification for interglacial samples an analytical challenge; in this case only mica, talc and amphibole (Fig. 3) are detected against the background. The other mineral phases trapped are probably under the detection limit of 1 µg for each kind of materials. Due to the very low concentration of dust deposited on filter it's impossible to obtain the ratio between the mineral phases detected in the sample. The mineral ratios reported in Table 1 show the mean values of each clay material detected in the glacial ice against quartz and feldspar.

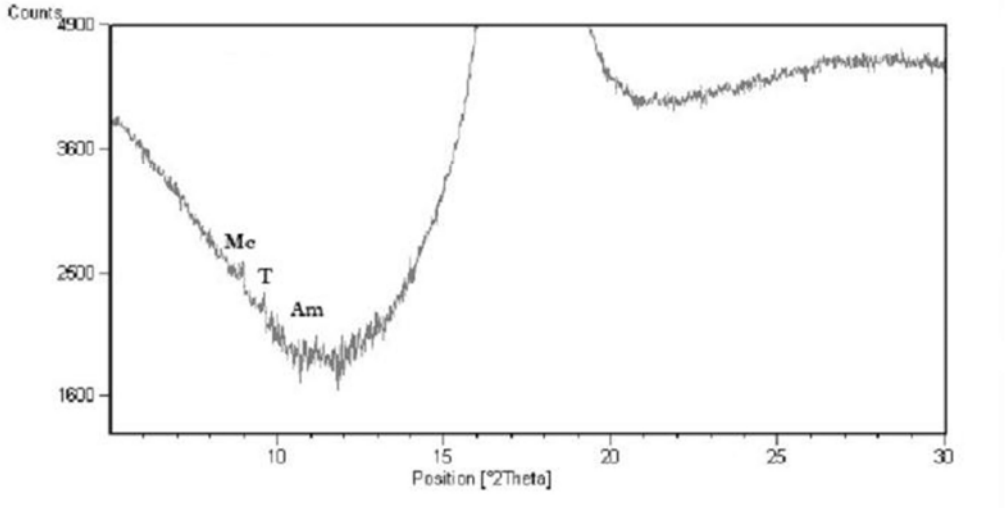


Fig. 3 - EDC-Holocene-I diffraction pattern.

The coupling with electron microscopy techniques on a shared quota of the same ice sample provide supplementary information about the structure of each mineral particle and also confirm the mineralogical results described above for the bulk fraction during Glacial periods (Table 2). Moreover, only single crystal HR-TEM analyses coupled to ED-XRF investigation allowing the mineralogical characterization of Interglacial Antarctic ice core dust are also presented in Table 2.

The most important characteristics observed during Glacial periods are summarized as follow:

- chlorite, mica, illite-smectite, quartz and feldspars are the most abundant mineral phases trapped in the ice samples. Mica and illite-smectite are detected in a very high concentration in all the climatic stages. In all the samples many polycrystalline illite-smectite, probably an interstratified layer, were observed using electron diffraction;

- only one particle of kaolinite was detected both in MIS2 and MIS4 climatic stage, to low for any statistical analyses, but significant in term of source characterization;

- comparing the XRPD and the HR-TEM abundances of calcite is clearly visible a large discrepancies both for MIS2 and MIS6 climatic periods;

- talc, pyrophyllite and titanium oxide are observed in a very low quantity, while for the iron oxide we have more or less the same percentage with the exception of MIS4 that show a little increase.

Table 1 - Mean mineral phases ratio of EDC ice core dust archived during Glacial periods obtained from XRPD investigation.

	MIS2	MIS3	MIS4	MIS6
Mc:Qz	1:1.3	2:1	1:1.1	1:1.2
T:Qz	1:11	1:1	1:20	1:12
Am:Qz	1:27	0	1:4	1:19
K:Qz	1:5.3	0	1:2.6	1:10
Ch:Qz	1:1.8	1:1.5	1:1.8	1:1.7
Ca:Qz	1:8.7	0	0	1:2
Mc:F	1:1.2	2.5:1	1:1.4	1:1.1
T:F	1:10	1.3:1	1:13	1:14
Am:F	1:25	0	1:2.8	1:23
K:F	1:5	0	1:1.7	1:12
Ch:F	1:1.6	1:1.3	1:1.3	1:2.1
Ca:F	1:8	0	0	1:2.4
K:Ch	1:3	0	1:1.4	1:6
K:Mc	1:4	0	1:2.7	1:11
Ch:Mc	1:1.3	1:3	1:2	1:2

Table 2 - Mineral phases detected during Glacial and Interglacial periods coupling HR-TEM and ED-XRF investigation. Numbers and percentage are referred to the number of particles analysed.

Mineral	Glacial				Interglacial	
	MIS2	MIS3	MIS4	MIS6	Holocene	MIS5.5
chlorite	8 (10.5%)	7 (26.9%)	7 (18%)	4 (9.1%)	3 (5.6%)	13 (19.1%)
kaolinite	1 (1.3%)	0	1 (2.6%)	0	4 (7.6%)	2 (3.1%)
quartz	10 (13.2%)	1 (3.8%)	6 (15.4%)	5 (11.4%)	5 (9.4%)	5 (7.3%)
feldpsar	7 (9.2%)	1 (3.8%)	0	3 (6.8%)	4 (7.6%)	6 (8.8%)
illite-smectite	23 (30.3%)	7 (26.9%)	12 (30.8%)	19 (43.2%)	7 (13.2%)	14 (20.5%)
mica	15 (19.7%)	8 (30.8%)	5 (12.8%)	6 (13.7%)	21 (39.7%)	18 (26.5%)
talc	1 (1.3%)	0	1 (2.6%)	0	2 (3.7%)	0
calcite	6 (7.9%)	0	0	0	4 (7.6%)	4 (5.8%)
pyrophyllite	1 (1.3%)	0	1 (2.6%)	3 (6.8%)	0	0
titanium oxide	0	0	1 (2.6%)	1 (2.2%)	0	2 (3.1%)
iron oxide	4 (5.3%)	2 (7.8%)	5 (12.6%)	3 (6.8%)	3 (5.6%)	4 (5.8%)
TOTAL dust	76	26	39	44	53	68

In opposition to the mineral assemblages observed mainly during the Last Glacial time (MIS2) and also along the other three Glacial periods (MIS3, MIS4 and MIS6) we could observe a considerable increase in kaolinite and a decrease in illite-smectite and chlorite during Holocene. Also quartz and feldspars percentage decrease from MIS2 to the Holocene. The concentration of iron oxide is like the same of Glacials as well as talc and calcite. Contrarily to the ice core dust identification discussed for the Holocene ice samples, during MIS5.5 are visible some differences. In this respect we could observe an increase in chlorite and illite-smectite, while mica was detected in low concentration than during Holocene; quartz and feldspars did not show strong variation. Iron oxide and calcite do not vary, while kaolinite is very scarce and an increase in titanium oxide is appreciable.

Comparing the EDC ice core dust with the mineral assemblages observed in the Southern Hemisphere (Table 3) continental land some clear differences are appreciable:

- sSA sediments show an high concentration of smectite, feldspars, quartz, illite and chlorite; moreover a considerable concentration of kaolinite and amphibole is detected but not in all the samples analysed;

- SAf sediments highlight a very high concentration of kaolinite besides quartz and illite. Kaolinite should be considered as tracer SAf sediments;

- Aus sediments show a dominant concentration of kaolinite. As in the case of SAf and sSA sediments, quartz and illite are detected in high concentration and represents the mean mineral composition of Aus samples;

- NZ sediments show a common mineral assemblages formed by chlorite, illite and quartz;

- Ant sediments display the most variable mineralogical composition of the Southern Hemisphere; high concentrations of quartz and illite have been observed as in the case of all the other continents and a relevant abundances of smectite, talc, pyrophyllite, amphibole, chlorite and feldspars.

Mineralogical characterization of aeolian mineral dust trapped in the EDC ice core coupling powder and single crystal investigation confirms and improve the results obtained by Gaudichet *et al.* (1992) on the old Dome C and Vostok ice core using electron microscopy. The XRD and HR-TEM results revealed that the mineral assemblages of dust reaching the inland East Antarctica during Glacial periods is composed mainly by chlorite, mica, illite-smectite, quartz and feldspar, while during the Interglacials we could observe a decrease in illite-smectite and chlorite, an increase in mica and the detection of a considerable concentration of kaolinite.

The comparison of the EDC ice core dust with the aeolian sediments collected in the Southern Hemisphere continental lands suggests that sSA is the most probable dust source area during Glacial periods, while the mineralogical evidence observed for the Interglacial ice core dust highlights a mixed provenance from sSA and Aus during warm periods.

Table 3 - Mean mineral phases ratio obtained from XRPD analyses of southern South America (sSA), southern South Africa (SAf), Australia (Aus), New Zealand (NZ) and Antarctic (Ant) sediments.

	SSA	SSAf	AUS	NZ	ANT
Sm:Qz	1.7:1	1:1.4	1:1	1:5	1:1.8
I:Qz	4.3:1	3:1	3:1	3:1	3.7:1
T:Qz	1:61	1:23	1:92	0	1:13
Py:Qz	0	1:68	0	0	1:5.5
Am:Qz	1:13	0	0	1:10	1:17
K:Qz	1:3.2	1.7:1	6.4:1	0	1:20
Ch:Qz	1:1.5	1:2	0	1.5:1	1:3.5
Sm:F	4:1	47.5:1	17.2:1	2.7:1	1.8:1
I:F	10:1	207.1:1	47:1	40.2:1	12:1
T:F	1:26	3:1	1:6	1:9	1:4
Py:F	0	1:1	0	0	1:1.3
Am:F	1:5	0	0	1.3:1	1:5.5
K:F	1:1.3	119:1	99:1	0	1:8
Ch:F	1.4:1	35:1	0	19.4:1	1:1.3
K:I	1:14	1:2	2.1:1	0	1:90
Ch:I	1:7.3	1:6	0	1:2	1:14
Sm:I	1:2.3	1:4.2	1:3	1:15	1:6
K:Ch	1:1.9	3.2:1	0	0	1:6.5

Moreover, this mineralogical observation are also confirmed by a few complementary information concerning the atmospheric circulation models and the system of air trajectories (Mahowald *et al.*, 1999) over the Antarctica, the material supplies in the source areas and many other studies applied on Antarctic ice core dust (Delmonte *et al.*, 2004, 2007; Revel-Rolland *et al.*, 2006; Basile *et al.*, 1997; Grousset *et al.*, 1992; Gaudichet *et al.*, 1992).

CONCLUSION

The analytical protocol developed in this work provides an improved way to evaluate the mineralogical phase composition of dust trapped in the Antarctic ice cores. The very sensitive X'Celerator detector mounted on the X-Ray diffractometer allows to investigate a very tiny quantity of material, down to 1 µg for each mineral species deposited on the polycarbonate substrate.

The mineralogical and crystal-chemical composition of dust trapped in the EDC ice core highlight a dominant provenance from sSA during Glacial time and a mixing of Aus and sSA mineral particles

during warm Interglacial periods. This results were also confirmed by atmospheric circulation model (Mahowald *et al.*, 1999), isotopic signature of dust particles (Delmonte *et al.*, 2004; Revel-Rolland, 2006) and some other complementary information strictly related to the environmental and climatic condition of the Potential dust Source Areas during the last 200 kyrs as described in Delmonte *et al.* (2004).

The coupling of XRPD and HR-TEM allows to understand the role of the atmospheric dust from the southern Hemisphere continents during the last two climatic cycles, and provides new dataset of boundaries conditions for the general models used for the hydrological cycle and the Circum Antarctic atmospheric circulation studies.

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