Evaluation of the phase detection limit on filter-deposited dust particles from Antarctic ice cores

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Abstract. The present investigation attempts optimization of laboratory X-ray powder diffractometry to investigate very small amount of filter-deposited mineral materials. Extensive tests were performed to select the optimal experimental conditions in reflection geometry. The results indicate that phase quantification can be performed down to 1-2 μg of absolute mass of each phase. The defined experimental protocols were successfully applied to the quantification of mineral phases contained in very small amounts (total mass in the range 10-15 μg) of polyphasic dust samples extracted from Antarctic ice cores.

Introduction

Antarctic ice cores are studied to reconstruct the past climatic changes, as they provide a mean to follow those changes with time. In fact, ice cores are naturally undisturbed archives of climatic information; Antarctic ice cap recorded biological and geological variations strictly correlated to climate since 800.000 years ago [1]. Aeolian mineral dust originated from a continental source area (Southern Hemisphere) and carried by wind are important climatic proxy data archived in Antarctic ice core; moreover, non glacial areas, called "dry valleys", depicts an alternative local dust source area [2-4]. Mineralogical and dimensional studies on aeolian insoluble particles allow to reconstruct dust mineral composition and to compare it with pedological data available for the source areas [3]. Insoluble dust mineral source areas changed during glacial and interglacial variations both in Southern [5] and Northern Hemisphere [6]. Changes in Principal Source Areas (PSAs) are possibly related to changes in atmospheric circulation, hydrological cycle and extent of deflation source areas [6]. The evaluation of the mineralogical composition of mineral dusts in Antarctic ice cores may greatly help the evaluation of PSAs changes, but, besides a few pioneering studies in the eighties, there is no recent research on mineralogical composition of the dust enclosed in Antarctic ice core [3, 5, 7, 8]. Dust phase composition is commonly evaluated indirectly by

means of recalculations from chemical analysis by PIXE method [9]. From this method, the main minerals found in ice samples appear to be clay minerals (kaolinite, illite, montmorillonite, etc.), quartz and K-feldspar [3]. Generally dust mineral concentration in ice core is about 20 ppb during the Holocene [4]. Due to the very limited amount of mineral material in the ice cores, it is very demanding to perform the analysis by means of powder diffraction: The total mass of powder in each sample is frequently in the range 1-100 µg, and often in the range 1-20 µg. Provided that the powder sample is a complex mineral mixture, each phase may well be present with a total amount of in the range 1-10 µg. Such amounts are at the lower limits of the technique and only with great care they can be actually detected by powder diffraction. The aim of this paper is to evaluate the lower limit of material detectable by routine laboratory X-ray equipment, and to define a protocol for the measurement of very small amounts of material. The measurements on the ice core dust samples are further complicated by the fact that they can not be deposited on zero-background plates, and they must be measured together with polycarbonate filters producing structured noise.

As a start, known quantities (comparable to those found in natural mixtures) of standard minerals (illite, quartz, and K-feldspar) were deposited on the same filters normally used for deposition of Antarctic ice particulate and then carefully measured. The optimal experimental geometry and conditions were selected by evaluating the peak/background ratio using various optical components and diffraction geometries. Variables included scan modes, different glancing angles, divergent and parallel beam geometry, slit openings, and scan times. During the second part of the investigation, different amounts of standard minerals were carefully measured using the selected geometry, with the aim of obtaining a standard protocol for the evaluation of mineral abundances in real ice core samples.

Experimental

Standard monophasic mineral samples (illite, quartz, and K-feldspar) were prepared in the class 1000 clean room of DISAT (Department of Environmental and Earth Sciences), University of Milano-Bicocca. Samples of 10 mg of mineral were weighed by an analytical balance (accuracy 10^{-5} g) in an ultra clean cuvette with 20 ml of ultra pure water (MilliQ water); they were homogenised by a mechanical shaker and then 1 ml of mineral suspension was further diluted in 20 ml of MilliQ water and analysed by a particle counter Beckman Counter©Multisizer III [10] to check the concentration and size of mineral particles. In fact, the particles trapped in Antarctic ice have diameters in the range 2.0-2.5 µm [2] and the standard samples used in the present work were prepared to have the same diameter class. Afterwards, the quota of the sample necessary to reach the correct final concentration was deposited on an ISOPORE polycarbonate filter (pore size 0.4 µm). The concentrations chosen for this work were 5 – 10 – 20 – 30 µg for all minerals. Another filter was prepared with 100 µg of K-feldspar, to be used to test the instrumental conditions. The filter area on which the sample was deposited has a diameter of about 8 mm, in order to provide a smaller background effect on the final diffraction pattern.

The filters were analysed by means of a PANalytical X'pert PRO diffractometer, which can be used both in divergent and parallel beam geometry. The instrument encompasses the X'celerator detector and has the possibility to mount a crystal monochromator on the incident beam. Different instrumental parameters were checked besides counting statistics, in

order to find the geometry with the best performances on the peak/signal ratio: scan mode, glancing angle, parallel vs divergent beam. In particular, different glancing angles were checked (8, 10, 12 °2θ), with both divergent and parallel beam. All scans were performed in exactly the same conditions, with angular steps corresponding to about 0.016 °2θ, a counting time of 25 s/step, an incident slit of ¼ °, an anti-scatter slit of ½ °, a mask of 10 mm, and soller slits on incident and diffracted beam of 0.02 rad. The patterns of the standard minerals at different concentrations were collected for about 2.5 hours, angular range 5-70 °2θ, steps of about 0.016 °2θ, and a counting time of 300 s/step. All data were collected with sample spinning at 2 rpm.

Results and discussion

The first part of the paper takes into account the testing of instrumental parameters' choice to optimize the signal-to-noise ratio. In this aim, different instrumental configurations were tried on a filter with 100 µg of K-feldspar, exploiting divergent and parallel beam geometry, together with a gonio scan or different glancing angle arrangements. The results of the tests are shown in Figure 1 where the peak/background ratio observed on two peaks is plotted against the diffraction angle 2θ. Only two peaks are considered here (with d=6.48 Å and d=3.24 Å, respectively), as they are the two peaks most visible above the complex background due to the polycarbonate filters. The peak/background ratio was evaluated using the profile fit routine in the software PANalytical HighScore Plus. In general, it can be observed that the patterns with the parallel beam geometry (open symbols and dotted lines) yield a better peak/background ratio. In both geometries, the gonio scan offers superior performances with respect to the various glancing angle arrangements, even though we are dealing with thin deposits of mineral powders. The use of a higher glancing angle (12°) provides results comparable to those of a gonio scan, but it must be reminded that only peaks at angles higher than the imposed glancing angle can be measured; in this case, for instance, the main peaks of clay minerals would remain undetected.
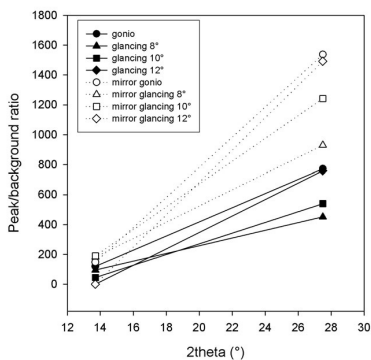

Figure 1. Comparison of peak-to-background ratios for parallel- and divergent beam geometries (empty and filled symbols, respectively).The connecting line is only a guide for the eye.

The second part of this paper deals with the detection limit in a laboratory powder diffraction experiment: small known amounts of standard minerals, deposited on polycarbonate filters, were collected using the best selected instrumental conditions as discussed above, and then the integrated area of the main peaks were correlated with the nominal weight of the deposited minerals. The peaks used were the main ones, in most cases the only well detectable against the background: d=3.24 Å for K-feldspar, d=10 Å for illite, and d=3.34 Å for quartz. The integrated areas were again evaluated using the peak fit routine of the software PANalytical HighScore Plus. The correlations for the three standard minerals are shown in Figure 2. As clearly seen in the diagrams, the correlation is reasonably good for all three minerals (with R^2 always over 0.92), and even the smallest amount (5µg) is clearly detectable against the background. In particular the diffraction peaks produced by 5 µg of K-feldspar were well measurable. Moreover, from the intercept of the regression line (which corresponds to 1 µg on the horizontal axis) it appears that even 1 µg of any of the three phases would be detectable.
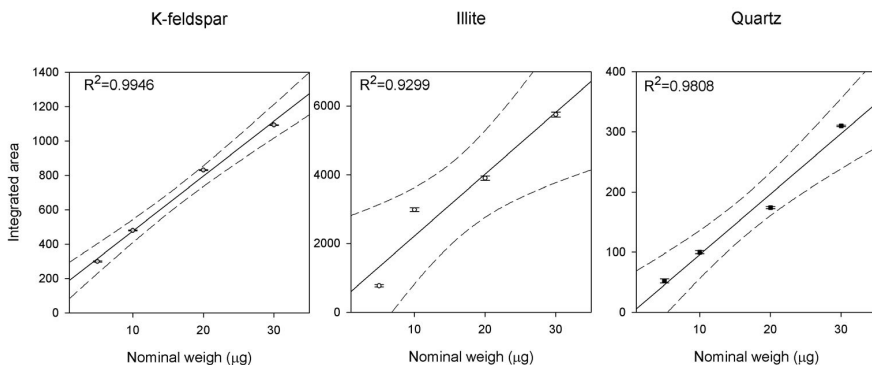

Figure 2. Correlation between integrated area and nominal weight on the filters. The R^2 for the linear correlation is shown on each diagram. The error bars on the data are from counting statistics alone, and the dotted line represent the 95% confidence interval.

This calibration is based on peak areas and it is therefore subject to the limits of single peak quantifications [11]: it should be applied with care, always in the same experimental conditions (regardless of the tube working hours) to mixtures containing minerals of the same chemical composition and with the same crystallinity degree of the standard samples. The latter conditions are reasonably met in K-feldspar and quartz, and less in illite, which has a variable chemical composition, together with various degrees of structural disorder. Nevertheless these data provide approximate estimation of the abundance of the various phases that can be detected in small mineral samples. The specific case of the dust particles from Antarctic ice cores are an extreme example of such samples, as they are commonly a few order of magnitudes more diluted than the air-filtered dust samples routinely collected for health tests in houses or working places. Two measurements on real Antarctic samples are presented, yielding the identification and quantification of mineral phases. TDC sample was drilled in 2001/2002 in Talos Dome Area [12]; GPS2 sample was recovered during the ITASE (Inter-

national Trans Antarctic Scientific Expedition) project in 1998/1999 [13] not far from Mario
Zucchelli Station – Terra Nova Bay. They were selected as representative of filters with a
small amount (sample TDC, with about 9 μg of dust) and a medium amount (sample GPS2,
with about 15 μg). The diffraction patterns of the two samples are shown in Figure 3 in
which the broad band between 15 and 20 °2θ is due to the polycarbonate filter supporting the
powders. Both the GPS2 and the TDC samples show measurable diffraction peaks and the
calibration lines obtained for illite, K-feldspar and quartz allow quantitative assessment of
these phases in the samples. The results of the quantitative estimation are listed in Table 1.
The standard errors in the table are set at the actual detection limit of each phase even
thought they are larger if estimated from the confidence intervals lines in Figure 2 (at least
twice as large): the errors on the integrated areas are very small, as the counting statistic was
extremely good and the peak fit excellent. As a matter of fact the main source for the disper-
sion of the points on the diagram is thought to be the loss of material during sample dilution
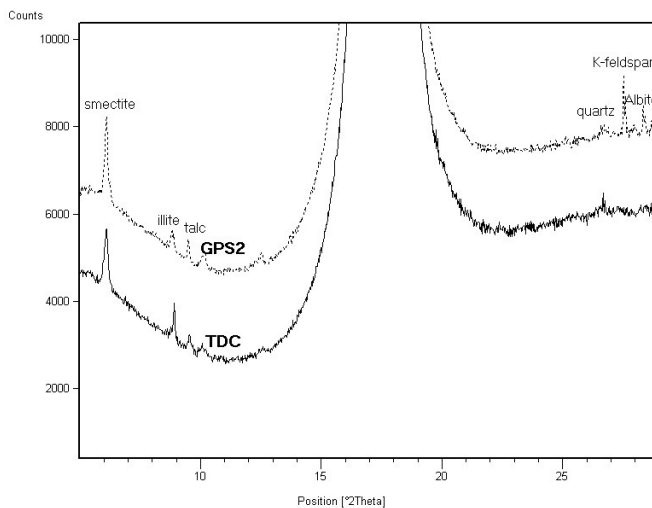and deposition on the filter, and this effect cannot be easily quantified.

*Figure 3. Diffraction patterns of sample TDC (solid line) and sample GPS2 (dotted line): the broad
band between about 15 and 20° 2θ is due to the polycarbonate filter.*

	K-feldspar (μg)	Illite (μg)	Quartz (μg)	Weight on filter (μg)
TDC	-	5 (1)	1 (1)	9
GPS2	2 (1)	3 (1)	2 (1)	15

*Table 1. Estimated weights on the two samples for the three minerals studied. The numbers in paren-
thesis represent the standard error derived from peak area integration and counting statistics alone.*

Concluding remarks

Very small amounts (of the order of a few μg) of crystalline material deposited on polycarbonate filters proved to be detectable by powder diffraction. The comparison between the various instrumental parameters showed superior performances of the parallel beam geometry with respect to the divergent beam one for such thin samples. A calibration using various known amounts of standard minerals allowed the estimation of the absolute quantity of selected phases on real dust samples from Antarctic ice cores down to 1-2 μg. Such ice-derived samples have been quantified by X-ray diffraction for the first time, and the data are crucial to expand on a statistical basis the single-grain methods based on transmission electron microscopy [3, 5, 7]. The results are of general application, although extreme care must be used in the control of the reproducibility of the experimental conditions.

References

1. EPICA community members, 2004, *Nature*, **429,** 623-628.
2. Delmonte, B., Petit, J.R., Andersen, K.K., Basile-Doelsch, I., Maggi, V. & Lipenkov, Y.V., 2004, *Climate Dynamics*, **23,** 427-438.
3. Gaudichet, A., De Angelis, M., Lefevre, R., Petit, J.R., Korotkevich, Y.S. & Petrov, V.N., 1988, *Geophysical Research Letters*, **15,** 1471-1474.
4. Delmonte, B., Basile-Doelsch, I., Petit, J.R., Maggi, V., Revel-Rolland, M., Michard, A., Jagoutz, E. & Grousset, F., 2004, *Earth Science Reviews*, **66,** 63-87.
5. Briat, M., Royer, A., Petit, J.R. & Lorius, C., 1982, *Annals of Glaciology*, **3,** 27-31.
6. Maggi, V., 1997, *Journal of Geophysical Research*, **102,** 26,725-26,734.
7. Gaudichet, A., De Angelis, M., Joussaume, S., Petit, J.R., Korotkevich, Y.S. & Petrov, V.N., 1992, *Journal of Atmospheric Chemistry*, **14,** 129-142.
8. Gaudichet, A., Petit, J.R., Lefevre, R. & Lorius, C., 1986, *Tellus*, **38B,** 250-261.
9. Marino, F., Maggi, V., Delmonte, B., Ghermandi, G. & Petit, J.R., 2004, *Annals of Glaciology*, **39,** 110-118.
10. Delmonte, B., Petit, J.R. & Maggi, V., 2002, *Climate Dynamics*, **18,** 647-660.
11. Cruciani, G. & Guagliardi, A., *Analisi quantitativa*, in *Analisi di materiali policristallini mediante tecniche di diffrazione*, N. Masciocchi and A. Guagliardi, Editors. 2006. p. 146-161.
12. Stenni, B., Proposito, M., Gragnani, M., Flora, O., Jouzel, J., Falourd, S. & Frezzotti, M., 2002, *Journal of Geophysical Research*, **107,** doi:10. 1029/2000JD000317.
13. Frezzotti, M., Pourchet, M., Flora, O., Gandolfi, S., Gay, M., Urbini, S., Vincent, C., Becagli, S., Gragnani, M., Proposito, M., Severi, M., Traversi, R., Udisti, R. & Fily, M., 2005, *Journal of Glaciology*, **51,** 113-124.