

Supplementary material to the manuscript "Deep ice as a geochemical reactor: insights from iron speciation and mineralogy of dust in the Talos Dome ice core (East Antarctica)"

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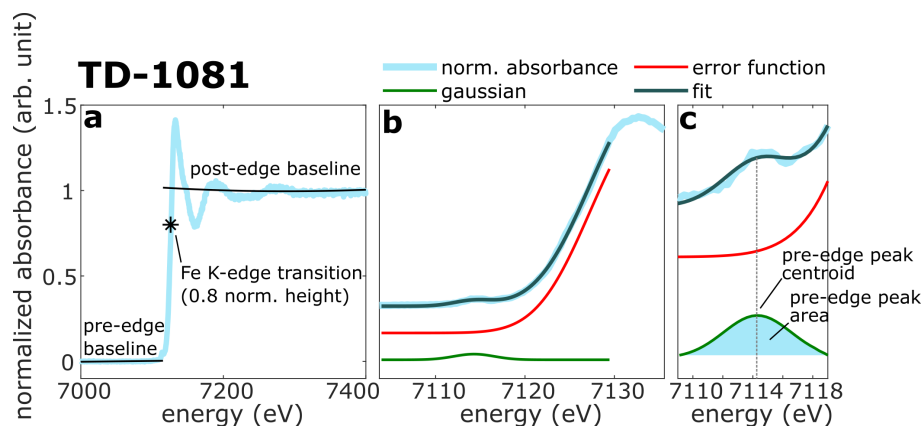


Figure S 1. Extraction of features from XANES spectra. Panel **a**: a full XAS spectrum (sample TD-1081) is presented along with the pre- and post-edge baselines used to normalize the data; the asterisk refers to the Fe K-edge transition, corresponding to the energy of the spectrum at the normalized height of 0.8. Panels **b**, **c**: enlargements of the pre-edge region; data are shown with the fits used to extract the pre-edge centroid energy and intensity.

1 X-ray absorption spectroscopy

1.1 Extraction of the Fe K-edge spectral features

An example of the procedure followed to extract the features of interest from Fe K-edge absorption spectra is shown in Figure S 1. Each spectrum, which corresponds to a mean signal obtained from multiple acquisitions, has been normalized considering its pre- and post-edge baselines (Figure S 1a). The pre-edge baseline has been fitted with a linear function, the post-edge one with a quadratic function. The position of the Fe K-edge transition has been defined as the energy along the main absorption jump, located at a normalized height of 0.8. Pre-edge peak features, strongly dependant on Fe oxidation and coordination (Wilke et al., 2001; Berry et al., 2003), have been obtained through curve-fitting (Figure S 1b, c). The near-edge section of the spectra has been fitted with an error function to take into account the main absorption jump and a gaussian one for the pre-edge peak. Pre-edge peak energy centroid and pre-edge peak intensity (integral area), have been determined considering the gaussian component of the fit.

1.2 Linear combination fitting

To evaluate the relative contribution of Fe-bearing minerals within the XAS spectra of TALDICE samples, a linear combination fitting approach was adopted. Through the combinatoric package of the Athena software (Ravel and Newville, 2005), the most efficient 4-elements linear combination constructed using the standard spectra (Figure S 2) and an ordinary least square algorithm (OLS), was identified for each sample. The R-squared parameter associated with the selected combinations always exceeded 0.9, confirming that the mineralogical standards were well representative of our samples. The OLS coefficients defining the selected combinations were related to the amount of information characterizing the fitted spectrum and associated

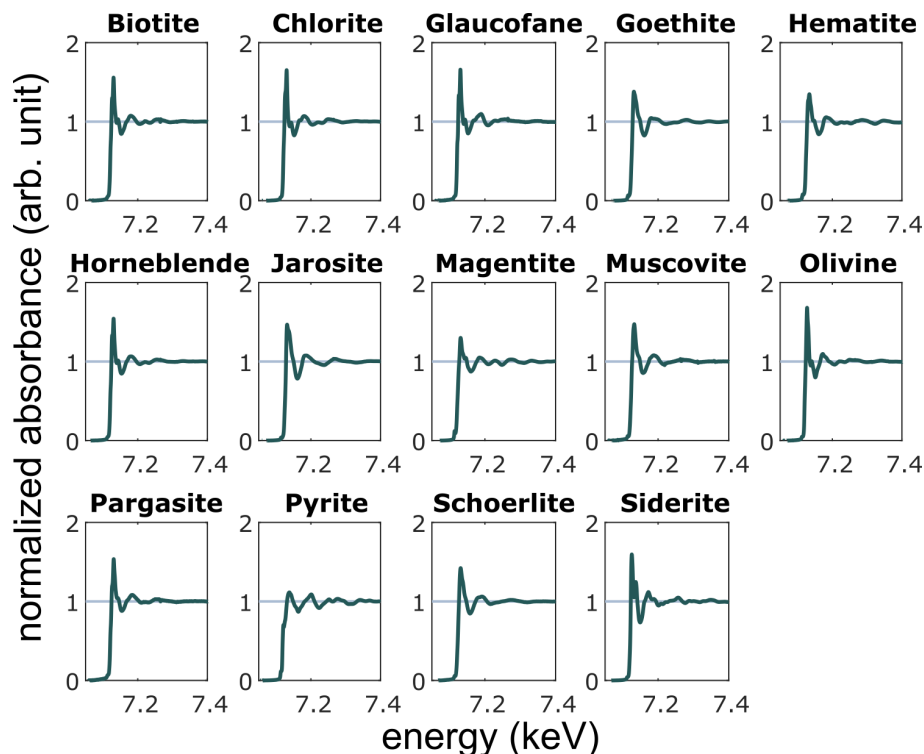


Figure S 2. XAS spectra of the Fe-bearing mineralogical standards considered in this study.

to the considered mineralogical standards. Their sum within a single combination is always equal to 1. They were thus converted
 20 in % coefficients and interpreted as a relative abundance index. For example, if one sample is fitted by a combination where
 a given Fe-bearing mineralogical standard has a OLS coefficient of 0.6, it means that the considered standard explain ~60 %
 of the information present in the sample spectrum. The exact amount of information associated with OLS coefficients is the
 product between the coefficient itself and the R-squared parameter, which corresponds to the fraction of information contained
 into the sample spectrum, reproduced by the considered linear combination. If in the above example, we assume a R-squared
 25 parameter of 0.9, the relative amount of information explained by the standard is 0.6×0.9 (54 %). A graphical presentation of
 the procedure is shown in Figure S 3.

We highlight that adopting this approach, it is not possible to obtain an absolute quantification of Fe-bearing mineral within
 the samples. This is because the XAS Fe signal is not related to the total mass of samples, but only to the crystalline Fe fraction
 present in minerals.

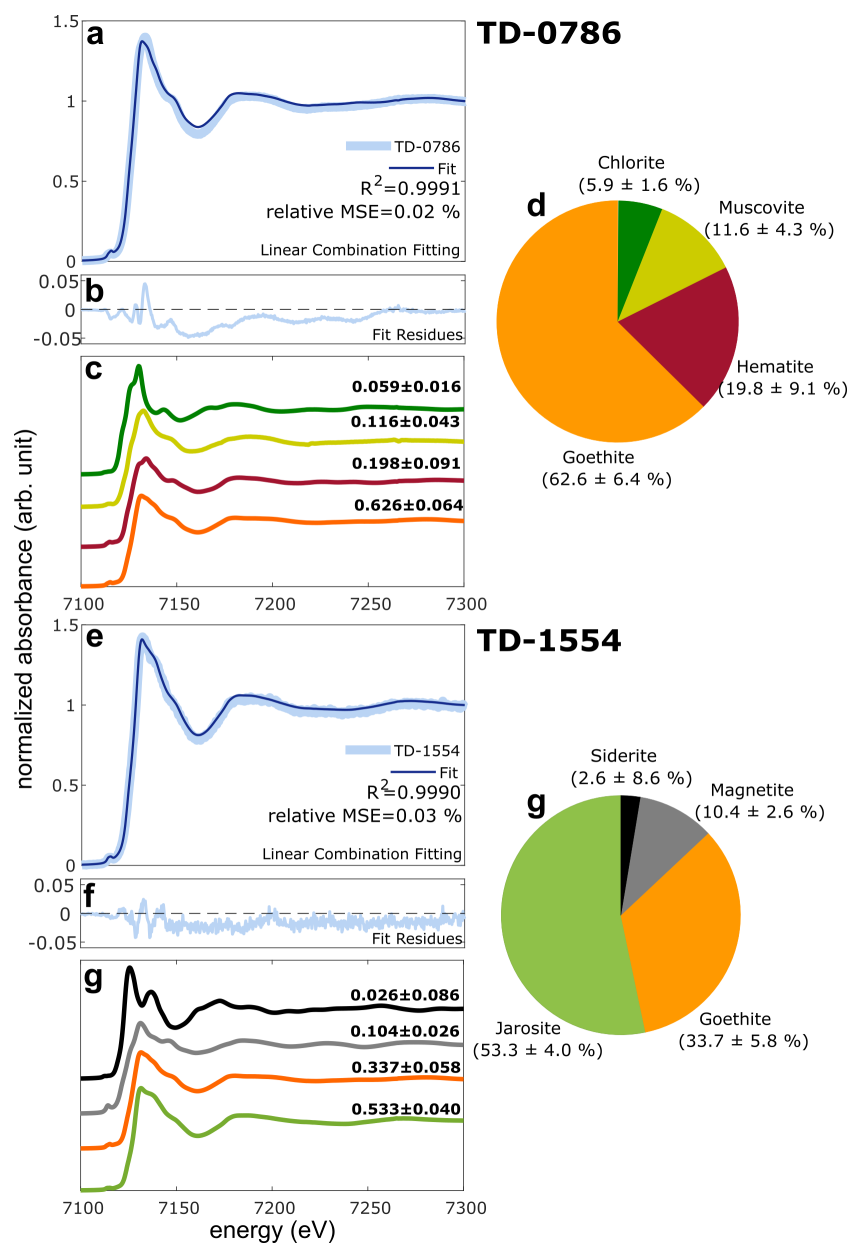


Figure S 3. Graphical examples of the procedure followed to estimate the relative contribution of Fe-bearing mineral standards within the spectra of TALDICE samples. A sample from the upper part of the ice core (TD-0786) and one from the deep part (TD-1554) are considered. Panels **a, e**: sample spectra and the fit corresponding to the linear combination obtained considering the spectra of the standards. Goodness of fit is evaluated through R-squared and relative Mean Square Error (MSE). Panels **b, f**: residuals of the fit. Panels **c, g**: spectra of the standards used to define the linear combination used to fit the two samples, numbers refer to the regression coefficients applied to each standard within the combination (errors are statistical only). Panels **d, h**: pie charts obtained converting the regression coefficients in %; these values, being directly related to the importance of standards within the sample spectra, were used as an estimator of the relative abundance of the associated minerals within the samples.

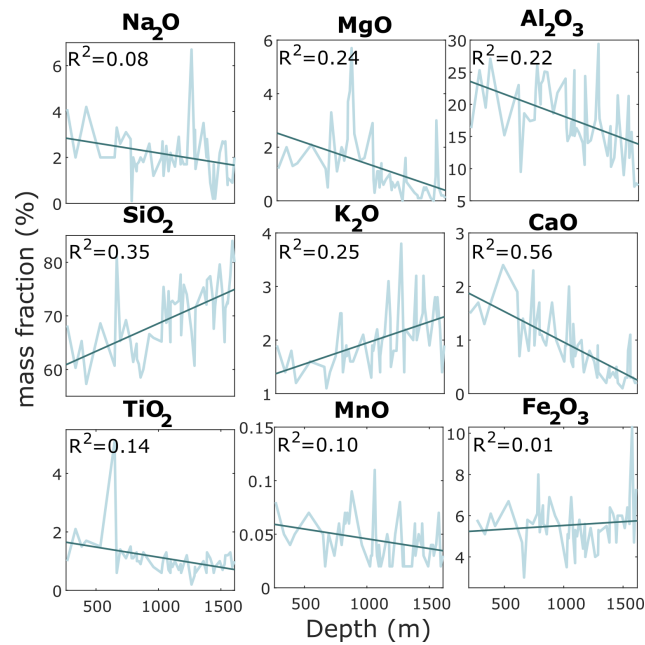


Figure S 4. Major element composition of TALDICE dust samples. Each graph refers to a major element, showing how it behaves with respect to depth. Linear regression, including the R-squared parameter, are also presented.

References

Berry, A. J., O'Neill, H. S. C., Jayasuriya, K. D., Campbell, S. J., and Foran, G. J.: XANES calibrations for the oxidation state of iron in a silicate glass, *American Mineralogist*, 88, 967–977, 2003.

35 Ravel, B. and Newville, M.: ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT, *Journal of synchrotron radiation*, 12, 537–541, 2005.

Wilke, M., Farges, F., Petit, P.-E., Brown Jr, G. E., and Martin, F.: Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study, *American Mineralogist*, 86, 714–730, 2001.