Supporting Information for

Physical weathering intensity controls bioavailable primary Fe(II) silicate content in major global dust sources

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Introduction

This supporting information includes an extended description of the methods, and five figures supplementary to those in the main text. These include a map of sample locations (Figure S1), the near-edge Fe K-edge X-ray absorption spectra for the set of standards used (Figure S2), the reconstruction of Fe(II)/Fe_total and Fe mineralogy in non-glacially-impacted Saharan dust (Figure S3), the first three principal components of the samples and standards (Figure S4), and the cumulative contribution to variance by the first three principal components of the samples and standards (Figure S5). The raw Fe K-edge XAS data files for the previously unpublished samples (see Materials and Methods) are deposited with the Columbia Academic Commons and are freely available for download.

Text S1.
All Fe K-edge X-ray absorption spectroscopy (XAS) spectra were collected in fluorescence mode at the Stanford Synchrotron Radiation Lightsource (SSRL), beamline 4-1, with a Passivated Implanted Planar Silicon (PIPS) detector, and an Fe foil standard in transmission mode. The first derivative of the XAS spectra for the Fe foil was used to calibrate the monochromator to 7,112.0 eV. To mount samples in front of the beam, dry marine sediments were wrapped in Kapton tape, and small pieces (~3 cm by ~1.5 cm) of the filter samples were mounted from the corners. Samples were run for 1-2 scans each. Spectra were analyzed using Larch (Newville, 2013), and the energies were shifted such that the foil edge for each scan was at 7,112.0 eV. The necessary shifts were typically within the resolution of the instrument (~0.7 eV). Spectra in the X-ray absorption near-edge structure (XANES) region from 7,110-7,140 eV and 7,100-7,180 eV were used for linear combination fitting with standards (LCF) and principal components analysis (PCA), respectively. We also used Larch (Newville, 2013) for PCA (Manceau, Marcus, & Lenoir, 2014), to take advantage of the group-based data structure, using the numpy singular value decomposition function. Here, principal components are indicated with capital letters, e.g. PC1. Loading factors, or the sample's position on the principal component axis, are indicated with lowercase letters, e.g. pc1. For this paper, Fe speciation data was collected for the Greenland, West African Margin, and North Pacific samples. The mineral standards were 1) run on the same beamline and with the same detector as the samples (Shoenfelt et al., 2018), 2) ground from hand samples in a ceramic mortar and pestle, and 3) diluted ~1:20 with boron nitride powder to make the Fe concentration appropriate for XAS collected in fluorescence mode, except for bentonite which was undiluted and ferrihydrite which was a previously published standard (Shoenfelt et al., 2017). The Fe(II)/Fe total and mineral compositions of the sediment samples were determined with XANES, using LCF to determine the best fit 5 of 10 standards, similar to Shoenfelt et al. 2018.
Figure S1. Map of the sample locations for this study. The blue stars are the core locations in the South Atlantic and South Pacific that capture the Fe speciation signal from glacially impacted Southern Hemisphere dust. The green stars are the locations of the Labrador Sea marine sediment samples that capture the Fe speciation signal from glacial Greenland sediments. The purple star is the core location in the North Pacific that captures the Fe speciation signal from East Asian dust. The red star is the core location at the West African Margin that captures the Fe speciation signal from Saharan dust.
Figure S2. The Fe K-edge X-ray absorption spectra for the standards used in this paper.
Figure S2. The Fe K-edge X-ray absorption spectra for the standards used in this paper

Figure S3. (a) Fe(II)/Fe_total and mineral composition of dust-borne Fe in the West African Margin core, with (b) dust fluxes and organic carbon fluxes to the core. (a) Filled blue squares are Fe(II)/Fe_total. Open yellow upwards triangles, open brown downwards triangles, open light blue circles, and blue ×'s are contributions to the total mineral composition from the Fe(II)-rich minerals pyrite (~100% Fe(II)), bentonite (~33% Fe(II)), hornblende (~100% Fe(II)), and biotite (~100% Fe(II)), respectively. Colors match those in Figure 2 and Figures S2. Note that the limits of the y-axis in (a) are 0-20% total Fe. The periods of wet, warm climate are indicated in purple bars and the periods of dry, cool climate are indicated in yellow bars, and all are labeled (AHP = African Humid Period; YD = Younger Dryas; BA = Bølling-Allerød warm period; HS1 = Henrich Stadial 1) (Bradtmiller et al., 2016).
The first three principal components fit to the samples and standards (loadings shown in Figure 2).

**Figure S4.** The first three principal components fit to the samples and standards (loadings shown in Figure 2).
**Figure S5.** The cumulative contribution to the variance in the spectra by the first three principal components (Figure 2 and Figure S4).