Sensitivity of atmospheric carbon dioxide to dust iron

solubility during the last glacial-interglacial cycle

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**Key Points:**

* List up to three key points (at least one is required)
* Key Points summarize the main points and conclusions of the article
* Each must be 140 characters or less with no special characters or acronyms.

**Abstract**

**1 Introduction**

**2 Methods**

2.1 General model description

We use a version of the Grid-ENabled Integrated Earth (GENIE) model focused on the carbon (C) cycle, cGENIE muffin v0.9, with three modules: (1) the 3D frictional–geostrophic ocean module, with 16 depth levels and a 36×36 equal-area horizontal grid (constant 10° in longitude and uniform in the sine of latitude), (2) marine biogeochemistry module BIOGEM (Ridgwell et al., 2007), and (3) an atmospheric component of the 2D energy–moisture balance model with prescribed climatological wind fields (Cao et al., 2009). The continental distribution and bathymetry are published in Ridgwell et al. (2007).

For this study, we focused on the biological pump of soft tissues. For this purpose, a co-limitation scheme of iron (Fe) and phosphorus (P) to the C cycle was implemented following Tagliabue et al. (2016). Additionally, a simplified scheme of organic complexing, nutrient removal, and particulate organic C (POC) sink was implemented following the methodology proposed by Parekh et al. (2004, 2006). Table S1 in the Supporting Information summarizes the data sets and values used. The circulation model uses both parameterized temperature (van de Velde et al., 2021), salinity and 33 biogeochemical tracers to describe the interactions between nutrients. In order to make a correct C inventory, tracers and pre-formed nutrients were used following the base configuration of Cao et al. (2009).

In BIOGEM, C sequestration is controlled by biological export. The biogenic uptake of dissolved nutrients, tracers and inorganic C occurs in the ocean euphotic zone (upper 81 m). Remineralization by ocean bacteria (at a 590-m depth) results in dissolution (i.e., regeneration) of inorganic nutrients and C. Finally, the efficiency of the biological pump (*P\**) is defined in terms of the ratio of the regenerated (*Preg*) to total *(Ptotal)* P concentration: .

2.2 Model nutrient limitation scheme

Both P and Fe have low ocean concentrations in many ocean basins, and in order to reproduce their limiting effects on primary productivity we use a colimitation scheme. The co-dependency between the concentration of dissolved phosphate ([PO43-]) and the biological uptake of C at the surface ocean is expressed as:

In cGENIE, the surface ocean is highly oxygenated and thus most of the Fe input is rapidly oxidized to Fe3+ (Figure 2). Iron dissolution is a determining factor in photosynthesis and it will depend on water temperature, salinity, and pH. Total dissolved Fe (TDFe) will be composed of (1) free Fe () and (2) ligand-bound Fe (). TDFe in the ocean is mostly present as (~99%), while is the only species that is susceptible to be scavenged by POC and eliminated from the system when TDFe is higher than the total concentration of ligands (*LT*). In turn, *LT* consists of a free ligand component () and that associated to Fe (), and is invariant and uniform in the water column (0.1 nM) following Parekh et al. (2005) and Doney et al. (2006).

**Diagram

Description automatically generatedFigure 2.** The iron (Fe) cycle in cGENIE. The only source of Fe to the ocean is dust. A fraction of supplied Fe will be complexed with organic ligands (), kept in free state (), and scavenged into particulate organic carbon (POC, Particulate Fe) to sink through the water column. The total dissolved Fe pool (TDFe) will be used by biology to generate particulate (POM) and dissolved (DOM) organic matter. The remineralization process will regenerate nutrients and carbon.

Finally, the Fe:C ratio is variable and parameterized to depend on TDFe, so that Fe requirements at the cellular level depend on Fe availability. Thus, under higher limitation, less Fe will be required and vice versa (a minimum ratio of 250,000 is imposed during maximum Fe limitation):

2.3 Experimental design

Six pairs of Holocene-Last Glacial Maximum (LGM) dust deposition rate fields were used as sources of soluble Fe to force cGENIE (for details see Lambert et al., 2021). One of these pairs (*Lambert*) is derived from paleo-dust observations compiled by Lambert et al. (2015), while the rest are derived from CMIP5 model simulations: *Albani* (Albani et al., 2014), *Takemura* (Takemura et al., 2009), *Ohgaito* (Ohgaito et al., 2018), *MIROC-ESM* (Sueyoshi et al., 2013) and *MRI-CGCM3* (Yukimoto et al., 2012).

Since the solubility of iron in dust is not well known, a sensitivity analysis was carried out by creating different dust iron solubility fields for each dust deposition rate field. To achieve this, we start by deriving a field of fractional Fe solubility (, %) in dust based on each of the twelve dust deposition rate fields described in the previous paragraph (i.e., six for the Holocene and six for the LGM), calculated as:

= ,

where is a scaling factor and is the concentration of dust in the surface ocean layer (see Text S1 of the Supplementary Information for further details). This relationship reflects observations that iron solubility of dust aerosols in weak acid solutions is inversely proportional to atmospheric dust load (Baker and Jickells, 2006).

Additionally, based on these twelve derived iron solubility reconstructions we created new fields by scaling all grid values by the same factor, as well as by scaling values of grid cells located within one of the five High-Nutrient, Low Chlorophyll (HNLC) ocean basins with respect to all other grid cells outside of any given HNLC ocean. In all cases the scaling factors used were 0.33, 0.67, 1.00 (i.e., no scaling factor applied), 2.00, and 3.00. Consequently, the model was forced with a total of 150 Holocene-LGM pairs of dust fields. As we are interested in performing a sensitivity analysis of aeolian iron inputs to ocean CO2 drawdown, all additional supplies of Fe associated with sedimentary processes in the ocean were not considered.

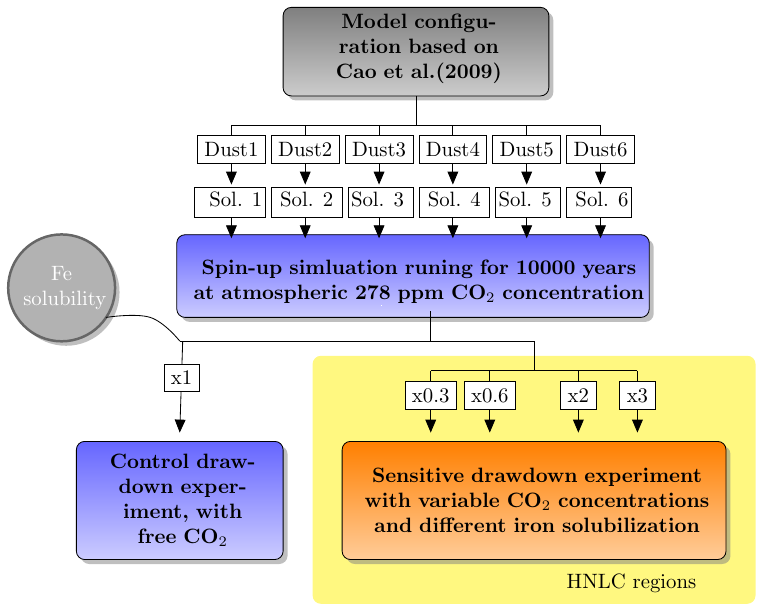
2.4 Simulation

We spun up cGENIE by performing six different 10,000-year pre-industrial experiments in which atmospheric carbon dioxide (CO2) concentration was fixed at 278 ppmv (Figure 3). Each of these six simulations was forced by a different Holocene dust field. Starting from the end of each spin-up, we ran global and regional sensitivity experiments as described in the previous section for the Holocene and LGM, allowing the model to run for an extra 10,000 years. Finally, we took the mean of the last 500 years of CO2 concentration and carbon export rate from each simulation.

**3 Results and discussion**

3.1 Nombre de esta sección

Figure 4 shows the mean fields of dust deposition rate considered in this study for the Holocene (Figure 4a) and LGM (Figure 4c), based on six Holocene-LGM pairs of individual fields as described in section 2.3, as well as the derived mean fields of in dust aerosols for the Holocene (Figure 4b) and LGM (Figure 4d). The latter constitute the base input fields of soluble Fe for our biogeochemical simulations.



**Figure 3.** Flow chart describing the experiment design. The gray box shows the general configuration used for spin-up and sensitivity experiment simulations. White boxes labeled *Dust 1-6* represent the six Last Glacial Maximum (LGM) and six Holocene dust deposition flux fields used as input to the simulations, while the associated input fields of dust fractional iron (Fe) solubility are represented by white boxes labeled *Sol. 1-6*. The top blue box represents the spin-up simulations run for each input field of dust flux, using a fixed value for atmospheric carbon dioxide (CO2) concentration. The bottom blue box represents the control simulations run with unprescribed CO2 for each input dust field (six for LGM and six for the Holocene). The bottom yellow box represents the main set of sensitivity experiment simulations, in which for all 12 input fields of dust fractional iron solubility, all grids of a given high-nutrient, low-chlorophyll (HNLC) ocean basin are multiplied by the same scalar factor.

To properly interpret these results, it is important to clearly identify what processes of Fe solubilization are being captured by our methodology, and which are not. As was mentioned previously, the inverse relationship between in dust and atmospheric dust load used to derive our fields is based on laboratory Fe leaching experiments of aerosol samples collected over the ocean using a weakly acidic solution (Baker and Jickells, 2006). Under these conditions, Fe extracted into solution consists of a highly labile Fe fraction that may be extracted in pure water, and a water-insoluble fraction that is solubilized under weakly acidic conditions. Together, these two fractions constitute the so-called *labile* Fe (Perron et al., 2020). The highly labile fraction of Fe represents non-structural Fe adsorbed onto mineral surfaces, the so-called *soluble* Fe (Perron et al., 2020), so that leaching experiments performed with pure water (or seawater) mimic Fe solubilization during transport in non-acidic air masses (e.g., Chomchoei et al., 2005; Cosentino et al., 2020; Simonella et al., 2022). This Fe fraction may be considered the source-inherited Fe in dust, readily available without the need of atmospheric processing (Cosentino et al., 2020; Simonella et al., 2020). In turn, the water-insoluble, weak acid-soluble Fe represents structural Fe predominantly in clay minerals (Journet et al., 2008; Marcotte et al., 2020; Simonella et al., 2022), so that Fe leaching experiments with weak acids mimic proton-induced Fe processing during transport in acidic atmospheres (e.g., Cosentino et al., 2020; Simonella et al., 2022). Because soluble Fe is usually a small fraction of labile Fe, as low as 1% even in close-to-source dust aerosols (e.g., Simonella et al., 2022), and because the relationship we used to derive our input fields represents labile Fe (Baker and Jickells, 2006), these fields mainly represent Fe solubility enhancement due to progressive fining of dust with greater distance traveled and associated rises in particle reactivity due to higher surface-to-volume ratios (Baker and Jickells, 2006; Cwiertny et al., 2008). Instead, our input fields do not capture differences in source-inherited Fe solubility of dust.

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**Figure 4.** Mean field of (a) Holocene and (c) Last Glacial Maximum (LGM) dust deposition rate derived from the six Holocene-LGM field pairs used in this study, and calculated fractional Fe solubility in deposited dust for the (b) Holocene and (d) LGM.

Table 1 shows mean global dust for the Holocene and LGM, as well as regional averages for the main HNLC ocean basins, for each of the dust fields used in this study. Given the higher dust loads during the LGM, dust reaches a global mean of 0.38% which is lower than that of the Holocene (0.65%). Although the solubility of Fe is considered to vary between 1-10%, for values only coming from the relationship between dust flux and time deposition, numerous works use global measures below or close to 1% (Lambert et al., 2021; Odalen et al., 2020; Saini et al., 2022; Tagliabue et al., 2016). The MIROC-ESM model shows the highest average values (~0.77% on average for both periods), except for the Ohgaito model which reaches ~1% during the Holocene. During the LGM all models show much greater variability. The relationship between the Ohgaito, Takemura and MIROC-ESM models is not unexpected, as these models either do not include or tend to underestimate source of dust at latitudes south of 30°S of glaciogenic origin or otherwise, which could provide greater heterogeneity. Nevertheless, although the Lambert model is the farthest from the average it has the best adjustment with the core datasets for the LGM. Regionally, the Eastern Central Pacific (CEP) along with the Southern Oceans (SO, South Pacific (SP) and South Indian Atlantic (SAI)) show the highest dissolved iron inputs, with medians of 1.01% (CEP), 1.71% (SP) and 0.93% (SAI) and 0.62% (CEP), 1.1% (SP) and 0.43% (SAI) during the Holocene and LGM, respectively. Since all models tend to reproduce CEP conditions well, it is the region with the best adjustment between models for both periods.

**Table 1.** Mean fractional iron solubility (%) in deposited dust aerosols. NA: North Atlantic, NP: North Pacific, CEP: Central East Pacific, SP: South Pacific, SAI: South Atlantic and South Indian, PI: Pre-Industrial, LGM: Last Glacial Maximum. MMM: Multi-Model Mean

| **Model/Region** | **Global** | **HNLC ocean basin** | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| **NA** | **NP** | **CEP** | **SP** | **SAI** |
| MMM\_PI | 0.65 | 0.42 | 0.27 | 0.93 | 1.67 | 1.12 |
| MMM\_LGM | 0.38 | 0.21 | 0.13 | 0.62 | 1.10 | 0.59 |
| Albani PI | 0.73 | 0.34 | 0.23 | 0.60 | 1.86 | 1.13 |
| Albani LGM | 0.27 | 0.18 | 0.09 | 0.63 | 0.53 | 0.28 |
| Lambert PI | 0.36 | 0.30 | 0.15 | 0.66 | 0.51 | 0.68 |
| Lambert LGM | 0.15 | 0.12 | 0.06 | 0.35 | 0.20 | 0.44 |
| Ohgaito PI | 0.99 | 0.49 | 0.29 | 1.18 | 3.68 | 2.04 |
| Ohgaito LGM | 0.35 | 0.19 | 0.11 | 0.73 | 0.83 | 0.37 |
| Takemura PI | 0.70 | 0.51 | 0.41 | 0.96 | 1.50 | 1.32 |
| Takemura LGM | 0.65 | 0.31 | 0.31 | 0.62 | 1.47 | 1.63 |
| MIROC-ESM PI | 0.77 | 0.44 | 0.30 | 1.04 | 2.39 | 1.40 |
| MIROC-ESM LGM | 0.76 | 0.22 | 0.14 | 0.60 | 2.67 | 2.06 |
| MRI-CGCM3 PI | 0.58 | 0.38 | 0.23 | 1.06 | 1.44 | 0.85 |
| MRI-CGCM3 LGM | 0.49 | 0.29 | 0.16 | 0.89 | 1.44 | 0.70 |

**4 Conclusions**

**Acknowledgments**

**Open Research** 

**References**