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Interactive comment on "CO$_2$ air-sea exchange due to calcium carbonate and organic matter storage: pre-industrial and Last Glacial Maximum estimates" *by* A. Lerman and F. T. Mackenzie

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Received and published: 22 October 2004

Anonymous Referees Nos. 3, 2, and 1, in sequential publication order of their comments, observe that the paper is long and in places difficult to read. Some of the comments are highly constructive, and in the revision of the paper we have addressed these. However, we do believe that the language of the Anonymous Referees' writing would have been more balanced and therefore more credible and effective if it were not hidden behind anonymity. We also note that the published comment of Anonymous Referee 4 is identical to his comment on the earlier manuscript version of the paper. In both, the Referee mentions an unknown page number and states that we deal "with sea level rise" in the global carbon balance, which we do not do. At the same time we find it necessary to point out that if the background calculations in our paper (those now in Section 7, Appendix, and Section 4) were not easily available to the reader, then the parameter values for different processes would appear as produced out of nowhere, making the results difficult or impossible to understand and reproduce. Obviously it is

an editorial decision whether such supporting calculations should be appended to a published paper or kept on the Biogeosciences Web Site in an easily accessible form.

Anonymous Referee 3 seems to be critical of what he calls "classical geochemical approach", as opposed to coupled earth-system models that are "expected to further our understanding". Our approach to an understanding of the global system is *not* detached from the approach of coupled earth-system models and the two approaches are equally valid, compatible, and synergistic. In fact, we have written many papers using coupled earth-system biogeochemical-physical models. This Referee also suggests that we extend our approach to the future acidification of surface ocean waters. This is indeed a very important issue that ties with the change of the surface ocean as a CO_2 source in pre-industrial and early industrial time to it becoming a CO_2 sink due to the rising atmospheric CO_2 (e.g. Andersson and Mackenzie, 2004; Mackenzie et al., 2004). Clearly, this subject is beyond the scope of the present paper.

The choice of the initial conditions for our computations of CO_2 emission (Table 1 in the paper) is questioned by Anonymous Referee 1. Near the Last Glacial Maximum, we use the pH and atmospheric CO_2 concentration (Sanyal et al., 1995; Palmer and Pearson, 2003; Petit et al., 1999) to compute total alkalinity. For internal consistency of the results, we use the reported values of the pH and P_{CO_2} near LGM time over a range of temperatures (5 to 25°C) to calculate total alkalinities, rather than making a guess of one temperature. Then we use these alkalinity values to obtain the pH and other parameters at the higher atmospheric CO_2 concentrations. However, if the initial value of total alkalinity at 5°C and 195 ppmv atmospheric CO_2 (2.582×10^{-3} mol-equivalent/kg) was used throughout, the results would be very similar to those given in Table 1 of the paper: for example, the pH at 195 ppmv CO_2 and 25°C would decline from 8.35 to 8.32 and by even smaller amounts at the higher CO_2 partial pressures; DIC would be up to 7% to 8% lower than in the preceding case, which is well within the 10%-range of the DIC values in the modern surface ocean (Takahashi, 1989). In the paper we also show, as expected (Fig. 2), that effects of slight alkalinity differences on

the degree of calcite supersaturation of ocean water are much smaller than those of temperature. We also do not think that the nature of the available data justifies a choice of highly precise values for the initial conditions. Such choices are often subsequently ignored as, for example, in the much used application to a wide range of conditions of the value of what became known as the Revelle factor: originally, it was calculated by Bacastow and Keeling (1973) for an average surface ocean water of total alkalinity 2.435×10^{-3} mol-equivalent/liter, temperature $19.59°C$, chlorinity 19.24 per mil, and initial pH = 8.271.

Anonymous Referee 2 writes that our new parameter θ is identical to Ψ of Frankignoulle et al. (1994), whereas Anonymous Referee 1 states that the two factors are conceptually different and not comparable. We want to clarify this misunderstanding below.

1. Parameter Ψ is "released CO_2: precipitated carbonate ratio" that estimates the release of carbon dioxide from seawater (Frankignoulle et al., 1994). This parameter was calculated at different constant atmospheric CO_2 concentrations and different temperatures. In this respect, and as long as an equilibrium is assumed to exist between dissolved and atmospheric CO_2, Ψ defines carbon dioxide transfer across the air-sea interface due to calcium carbonate precipitation under certain conditions.

2. Our parameter θ includes the following conditions beyond those mentioned in the preceding paragraph: variable carbonate and organic carbon net removal rates from seawater, and CO_2 transfer to an atmosphere that increases its CO_2 content. Furthermore, θ also defines CO_2 transfer in the presence of dissolved inorganic and organic carbon inputs to the system.

3. Neither θ nor, as far as we understand, Frankignoulle et al. Ψ have anything to do with the specific ecological or hypsometric conditions or the physical scales of shallow and open sections of the ocean. Each parameter defines emission of CO_2 as a function of certain biogeochemical processes that are not specific to any particular site or

ecosystem. Biological precipitation of $CaCO_3$ with release of CO_2 occurs both in phytoplankton (coccoliths) and phytobenthos (calcareous algae), as well as in zooplankton (e.g. foraminifera, pteropods) and zoobenthos (e.g. foraminifera, molluscs, corals). If primary producers use only CO_2 in photosynthesis then the process has no effect on total alkalinity that in our paper is defined as comprising the bicarbonate, carbonate, borate, hydroxyl, and H^+ ionic species. In a more detailed definition of total alkalinity that includes nitrate, ammonium, and phosphate ions, photosynthesis and respiration do affect alkalinity (Stumm and Morgan, 1981, pp. 193–195; Zeebe and Wolf-Gladrow, 2001, pp. 7–8, 33–36, 51–52). If HCO_3^- in photosynthesis were taken from the environment and H^+ were produced within the cells or OH^- retained there, then total alkalinity of the external seawater might have been affected. However, carbon concentrating mechanisms in photosynthesizing cells produce higher CO_2 concentrations than are available to the organism in the surrounding water (Raven, 2003). The present state of knowledge of this mechanism indicates uptake of both HCO_3^- and H^+ from the external environment with no effect on total alkalinity (Raven, personal communication, 2004).

4. It is important to reiterate that our calculation of the CO_2 fluxes across the air-sea interface is based on the *net removal* of $CaCO_3$ and organic carbon from the surface layer. Inclusion in our calculation of such features as the physical separation of the surface layer from the sediments in the deep ocean, and the downwelling and upwelling fluxes would require better information and data on the mechanisms that may drive part of the produced CO_2 from the surface layer to the atmosphere and part into downwelling, and the return of alkalinity by upwelling to the surface layer. Although such processes may have to be considered in an analysis of a time-dependent course of the carbon cycle evolution, we point out on pp. 433, 447, and 458 that the transition history of the carbon cycle from LGM to pre-industrial time is outside the scope of our paper, primarily because the variations of individual fluxes are not sufficiently well known at centurial to dekamillenial time scales. It should also be noted that the methodology of the CO_2 emission calculation that is based on the volume of a global euphotic zone applies to any smaller section of a surface water layer of a reduced area or volume. We

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Discussion Paper

focus on the CO_2 production and emission across the air-sea interface due to calcium carbonate precipitation and organic carbon storage; we expand the theoretical treatment to an open system with inorganic and organic carbon inputs; and we estimate the CO_2 fluxes at the Last Glacial Maximum and the end of pre-industrial time, correcting some of the perceived atmospheric and land reservoir imbalances in the global carbon cycle.

References

Andersson, A. J. and Mackenzie, F. T.: Shallow-water oceans: a source or sink of atmospheric CO_2? Frontiers in Ecol. and Env., 2(7), 348-353, 2004.

Bacastow, R. and Keeling, C. D.: Atmospheric carbon dioxide and radiocarbon in the natural carbon cycle: II. Changes from A. D. 1700 to 2070 as deduced from a geochemical model, in Carbon and the Biosphere, edited by Woodwell, G. M. and Pecan, E. V., CONF-720510, National Technical Information Service, Springfield, Va., 86-135, 1973.

Frankignoulle, M., Canon, C., and Gattuso, J.-P.: Marine calcification as a source of carbon dioxide: positive feedback of increasing atmospheric CO_2, Limnol. Oceanogr., 39, 458-462, 1994.

Mackenzie, F. T., Lerman, A., and Andersson, A. J.: Past and present of sediment and carbon biogeochemical cycling models, Biogeosciences, 1, 11-32, 2004.

Palmer, M. R. and Pearson, M. N.: A 23,000-year record of surface water pH and PCO$_2$ in the Western Equatorial Pacific Ocean, Nature, 300, 480-482, 2003.

Petit, J.-R., Jouzel, J., Raynaud, D., Barkov, N. I., Barnola, J.-M., Basile, I., Bender, M., Chappellaz, J., Devis, M., Delaygue, G., Delmotte, G. M., Kotlyakov, V. M., Legrand, M., Lipenkov, V. Y., Lorius, C., Pepin, L., Ritz, C., Saltzman, E., and Stievenard, M.: Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, Nature, 399(6735), 4298722;436, 1999.

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Raven, J. A.: How photosynthetic organisms acquire carbon, http://www.dundee.ac.uk/biocentre/SLSBDIV7jr.htm, 1-3, 2003.

Sanyal, A., Hemming, G., Hansen, G., and Broecker, W.: Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera, Nature, 373, 234-237, 1995.

Stumm, W. and Morgan, J. J.: Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters, 2nd edit., Wiley, New York, xvi + 780, 1981.

Takahashi, T.: The carbon dioxide puzzle, Oceanus, 32(2), 22-29, 1989.

Zeebe, R. E. and Wolf-Gladrow, D.: CO_2 in Seawater: Equilibrium, Kinetics, Isotopes, Elsevier, New York, xiv + 346, 2001.

Interactive comment on Biogeosciences Discussions, 1, 429, 2004.

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