



## Comment on “Magnetic effect on CO<sub>2</sub> solubility in seawater: A possible link between geomagnetic field variations and climate” by Alexander Pazur and Michael Winklhofer

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### 1. Introduction

[1] An experimental study [Pazur and Winklhofer, 2008] (forthwith referred to as PW2008) found a magnetic-field (MF) effect on CO<sub>2</sub> solubility  $K_0$ . They conclude that “the magnitude of the MF effect is such that CO<sub>2</sub> solubility reduces by a maximum of 0.5% per each % decrease in MF strength”. Such a relationship, if applicable to the global scale, would have profound consequences on the carbon cycle because of the large spatial and temporal variability of the geomagnetic field intensity over Earth’s surface.

[2] We question the experimental setup and the correctness of their conclusions mainly for four reasons. First, absolute CO<sub>2</sub> gas concentrations were not measured by the authors. Their method determines only relative amounts of gas concentration in setups with different applied MF, using an elastic light-scattering technique. Second, we are not sure that all dissolved carbon in their seawater samples was removed before the start each experimental run, which would have implications for the interpretation of the measurements in terms of CO<sub>2</sub> solubility. Third, if their suggested relationship between CO<sub>2</sub> solubility and MF is true, then the resulting effects on laboratory and field-based measurements of parameters of the oceanic carbonate system would be tremendous due to the variability of the Earth’s magnetic field intensity with latitude. Finally, the virtual axial dipole moment (VADM) of the Earth’s magnetic field has varied through time. Simulated changes in  $K_0$  as function of VADM lead to pre-anthropogenic changes in atmospheric CO<sub>2</sub> concentrations that disagree substantially with ice core based measurements.

### 2. Experimental Setup

[3] A major weakness in the experimental design is the lack of differentiation between the gaseous compounds

present in gas bubbles distributed in the test solutions and the dissolved gas pool in molecular form. Only the gaseous phase of gas bubbles in the liquid measured by the elastic light-scattering technique is described in the experiments. Thus, the use of light scatter intensity as a proportional unit for gas concentration is potentially misleading. PW2008 fail to support their conclusion “that MF strength affects the equilibrium concentration of dissolved gases in the liquid phase” (paragraph [16]). To do so requires that light scatter intensity are calibrated against measurements of absolute gas concentration measurements in mol/l in the presence of a reference MF strength. Furthermore, solubility of a gas is normally represented by an equilibrium constant expressing the ratio of the concentration of the gas in the liquid phase to that in the gas phase. The experiment described by PW2008 infers solubility ratios for CO<sub>2</sub> under different magnetic field conditions from the extent of removal of gas bubbles in the liquid without making clear the relative proportions of the initial amounts of gas and liquid. The (apparently untested) assumption seems to be made that the plateau in Figure 2 of PW2008 (after about 2 h) represents an equilibrium (for CO<sub>2</sub>) between the gaseous and aqueous phases. Furthermore, PW2008 measured the MF effect on bubble-size distribution under placid laboratory conditions, which raises further questions about how turbulent field conditions affect the applicability of the results.

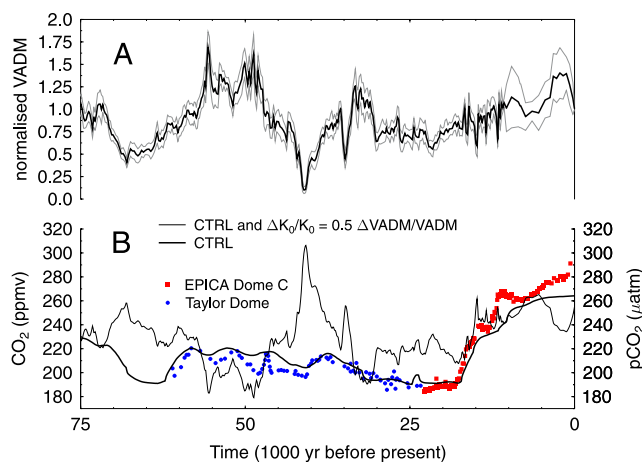
[4] Given that the gas content of the initial bubbles is a mixture; either air (a mixture of O<sub>2</sub>, N<sub>2</sub>, Ar, CO<sub>2</sub>, water vapor) or an air/CO<sub>2</sub> mixture (70:30) it is hard to interpret the changes in bubble distribution as a clear indication that the solubility of CO<sub>2</sub> changes; at best, its gas-transfer kinetics may have been affected. In addition, it would be necessary to know how the compositions of the bubbles change as the experiment progressed if one wished to draw more definitive conclusions.

[5] The fact that the magnetic-field effect is absent in pure water seems problematic if it is to be interpreted as a solubility change. Why should the chemical potential of the dissolved CO<sub>2</sub> be affected so significantly by a magnetic field only in seawater? At 4°C, the solubility of CO<sub>2</sub> in seawater of salinity 35 (measured without regard to the Earth’s magnetic field) is about 20% less than it is in freshwater.

[6] There is no indication as to how the change in magnetic field will change the chemical potential of CO<sub>2</sub> (a diamagnetic substance) as a solute: a prerequisite for it to affect the solubility. This contrasts with O<sub>2</sub>, which is

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**Figure 1.** (a) Relative changes in the virtual axial dipole moment (VADM) based on a global paleointensity stack GLOPIS-75 [Laj *et al.*, 2005] plotted on the GICC05 age scale. Mean (thick line)  $\pm 1$  standard deviation (thin lines). (b) Ice core measurements of CO<sub>2</sub> (points, left scale) [Indermühle *et al.*, 2000; Monnin *et al.*, 2001, 2004] and carbon cycle simulation results (lines, right scale). CTRL: best-guess simulation with  $K_0$  independent of the Earth's magnetic field intensity [scenario S1.5 K as given by Köhler and Fischer, 2006]. An additional scenario is shown, in which  $K_0$  varies after equation (1) as function of VADM.

paramagnetic and displays a significantly higher magnetic susceptibility.

### 3. Degassing Seawater Samples

[7] Carbon dioxide exists in water in four different inorganic forms: as free carbon dioxide, CO<sub>2</sub>, bicarbonate, HCO<sub>3</sub><sup>-</sup>, as carbonate ion, CO<sub>3</sub><sup>2-</sup>, and as true carbonic acid, H<sub>2</sub>CO<sub>3</sub>. The sum of all forms is called total dissolved inorganic carbon (DIC). The different carbonate species are related to each other by chemical equilibria, whose dissociation constants depend on temperature, pressure, and salinity. Under ambient conditions the concentration of H<sub>2</sub>CO<sub>3</sub> is negligible, while the other species are typically found in the ratio [CO<sub>2</sub>]:[HCO<sub>3</sub><sup>-</sup>]:[CO<sub>3</sub><sup>2-</sup>]  $\sim$  1%: 90%: 9% [Zeebe and Wolf-Gladrow, 2001]. Only the 1% part of DIC found as CO<sub>2</sub> is in direct exchange with the atmosphere. To start experiments with essentially gas free samples, the water has to release all the carbon contained in DIC. This is not a trivial procedure as all the DIC has to pass through the bottleneck of dissolved CO<sub>2</sub>. In previous work on CO<sub>2</sub> solubility [Weiss, 1971, 1974] five extraction cycles were used to degas seawater, after which the partial pressure of CO<sub>2</sub> was reduced to less than 80  $\mu$ atm. The description of the degassing method of PW2008 does not contain sufficient details on the efforts undertaken to degas the water, nor on how much residual partial pressure of CO<sub>2</sub> was still present at the start of the MF experiments. It is our view that such controls are necessary before one can put the conclusion of PW2008 into the context of other work and, therefore, we strongly suggest that the solution be prepared using methods described in earlier studies [e.g., Weiss, 1971, 1974]. If a large quantity of DIC remained in the seawater samples at the start of the experiment the subse-

quent measured gas concentrations did not necessarily monitor CO<sub>2</sub> uptake (and thus CO<sub>2</sub> solubility) but were also affected by the DIC, which would have been converted from bicarbonate to carbon dioxide over time.

### 4. Consequences of MF-Dependent CO<sub>2</sub> Solubility for the Present Carbon Cycle

[8] Although PW2008 give no proper relationship between solubility,  $K_0$ , and magnetic field strength, they use a value of 0.5% change in solubility per 1% change in  $B$  to estimate the possible effect on the modern carbon cycle. By doing so the authors assume that

$$\frac{\Delta K_0}{K_0} = 0.5 \frac{\Delta B}{B}. \quad (1)$$

[9] For reasons of simplicity we use in the following equation (1), but it should be pointed out that the equation is not defined for  $B = 0$ .

[10] In the geocentric axial dipole approximation [Merrill *et al.*, 1998] the variation in  $B$  is given by ( $\phi$  is the magnetic latitude)

$$B(\phi) = B(\phi = 0) \sqrt{1 + 3 \sin^2 \phi}. \quad (2)$$

Thus, the intensity of the Earth's magnetic field at the surface today varies by a factor of two according to the latitude and the position of the geomagnetic poles. Higher order moments tend to increase this factor.

[11] The large latitudinal dependent variations in magnetic induction observed over the Earth would after equation (1) lead to variations in  $K_0$  and thus of aquatic CO<sub>2</sub> concentrations with location that cannot be explained by variations in environmental parameters (temperature, salinity, pressure), DIC, and total alkalinity (TA) alone. Up to date, information about these parameters were sufficient to completely describe the carbonate system and to calculate other quantities, such as the concentrations of the different carbonate species and pH [Zeebe and Wolf-Gladrow, 2001]. Large measuring programs addressing the marine carbonate system and the exchange with the atmosphere (GEOSECS, WOCE, CARINA, CARBOOCEAN, etc.) gave no hint to large discrepancies between observations and calculations that have to be explained by a "missing factor" as suggested by PW2008. For example, Weiss [1974] suggested good agreement (0.1–0.2%) between measurements made in La Jolla, CA (33°N), with those made in Liverpool, England (53°N).

[12] PW2008 relate 1 ppmv CO<sub>2</sub> increase per decade to 0.35 PgC yr<sup>-1</sup> which would imply that 1 ppmv atmospheric CO<sub>2</sub> corresponds to 3.5 PgC. The correct value is, however, 2.12 PgC per ppmv CO<sub>2</sub>.

### 5. Implications of MF-Dependent CO<sub>2</sub> Solubility Over Time

[13] During the last 75,000 years palaeomagnetic reconstructions show that the VADM has ranged between a value that is approximately double today's and about one tenth of it (Figure 1a). If we implement the experimentally observed

relationship between solubility and MF (equation (1)) in the carbon cycle box model BICYCLE [Köhler and Fischer, 2006] and perform transient simulations over this time window, we produce a rise in atmospheric  $p\text{CO}_2$  to 300  $\mu\text{atm}$  across the Laschamp geomagnetic excursion, which was centred at 41,000 yr before present (Figure 1b). Our simulation using the conclusions of PW2008 implies a rise of more than 100  $\mu\text{atm}$  with respect to the control run, which contradicts ice core measurements of around 200 ppmv  $\text{CO}_2$  across the Laschamp excursion (Figure 1b).

## 6. Conclusions

[14] The potentially important conclusions of PW2008 on the MF effect on  $\text{CO}_2$  solubility and its consequences for the global carbon cycle contradict evidences from oceanic field programs, marine chemistry, paleomagnetic reconstructions, and carbon cycle modeling. Experimental details did not consider the effect of the marine carbonate system on  $\text{CO}_2$  partial pressure, nor are the gas concentrations measured on a partial pressure or volume mixing ratio basis. The suggested magnitude of the effect is not sustainable if our remarks are taken into consideration. If there is any effect between MF and solubility it is very likely much smaller. Until similar laboratory experiments are trustable, experimentalists should follow with more care earlier setups on  $\text{CO}_2$  solubility, e.g. those carried out by Weiss [1971, 1974]. Furthermore, the whole matrix of variability in temperature, salinity, and magnetic field strength should be covered to come to unequivocal conclusions. The present day the VADM has a value of  $8 \times 10^{22} \text{ A m}^2$ , which equates to maximum surface magnetic field intensity (as  $B$ ) of c. 60  $\mu\text{T}$  situated in the polar regions and a minimum of c. 30  $\mu\text{T}$  somewhere between the tropics. According to GLOPIS-75 [Laj et al., 2005] VADM varied in the past 75,000 years between approximately 1 and  $14 \times 10^{22} \text{ A m}^2$ , corresponding to a range of magnetic field intensity between 4  $\mu\text{T}$  and more

than 100  $\mu\text{T}$ . This might also be the range of interest for future laboratory experiments.

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## References

- Indermühle, A., E. Monnin, B. Stauffer, T. F. Stocker, and M. Wahlen (2000), Atmospheric  $\text{CO}_2$  concentration from 60 to 20 kyr BP from the Taylor Dome Ice Core Antarctica, *Geophys. Res. Lett.*, 27, 735–738.
- Köhler, P., and H. Fischer (2006), Simulating low frequency changes in atmospheric  $\text{CO}_2$  during the last 740,000 years, *Clim. Past*, 2, 57–78.
- Laj, C., C. Kissel, and J. Beer (2005), High resolution global paleointensity stack since 75 kyr (GLOPIS-75) calibrated to absolute values, in *Time-scales of the Paleomagnetic Field*, *Geophys. Monogr. Ser.*, vol. 145, edited by J. E. T. Channell et al., pp. 255–265, AGU, Washington, D.C.
- Merrill, R. T., M. W. McElhinney, and P. L. McFadden (1998), *The Magnetic Field of the Earth: Paleomagnetism, the Core and the Deep Mantle*, *Int. Geophys. Ser.*, vol. 63, 531 pp., Academic, San Diego, Calif.
- Monnin, E., A. Indermühle, A. Dällenbach, J. Flückiger, B. Stauffer, T. F. Stocker, D. Raynaud, and J.-M. Barnola (2001), Atmospheric  $\text{CO}_2$  concentrations over the last glacial termination, *Science*, 291, 112–114.
- Monnin, E., et al. (2004), Evidence for substantial accumulation rate variability in Antarctica during the Holocene, through synchronization of  $\text{CO}_2$  in the Taylor Dome, Dome C and DML ice cores, *Earth Planet. Sci. Lett.*, 224, 45–54.
- Pazur, A., and M. Winkhofer (2008), Magnetic effect on  $\text{CO}_2$  solubility in seawater: A possible link between geomagnetic field variations and climate, *Geophys. Res. Lett.*, 35, L16710, doi:10.1029/2008GL034288.
- Weiss, R. F. (1971), Solubility of helium and neon in water and seawater, *J. Chem. Eng. Data*, 16, 235–241.
- Weiss, R. F. (1974), Carbon dioxide in water and seawater: The solubility of a non-ideal gas, *Mar. Chem.*, 2, 203–215.
- Zeebe, R. E., and D. A. Wolf-Gladrow (2001),  *$\text{CO}_2$  in Seawater: Equilibrium, Kinetics, Isotopes*, *Elsevier Oceanogr. Book Ser.*, vol. 65, 346 pp., Elsevier Sci., Amsterdam.
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