

Magnetic effect on CO₂ solubility in seawater: A possible link between geomagnetic field variations and climate

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[1] Correlations between geomagnetic-field and climate parameters have been suggested repeatedly, but possible links are controversially discussed. Here we test if weak (Earth-strength) magnetic fields can affect climatically relevant properties of seawater. We found the solubility of air in seawater to be by 15% lower under reduced magnetic-field (20 μ T) compared to normal field conditions (50 μ T). The magnetic-field effect on CO₂ solubility is twice as large, from which we surmise that geomagnetic field variations modulate the carbon exchange between atmosphere and ocean. A 1% reduction in magnetic dipole moment may release up to ten times more CO₂ from the surface ocean than is emitted by subaerial volcanism. This figure is dwarfed in front of anthropogenic CO₂ emissions. **Citation:** Pazur, A., and M. Winklhofer (2008), Magnetic effect on CO₂ solubility in seawater: A possible link between geomagnetic field variations and climate, *Geophys. Res. Lett.*, 35, L16710, doi:10.1029/2008GL034288.

1. Introduction

[2] Causal and non-causal connections between the Earth's magnetic field and climate have been proposed repeatedly, mostly on the basis of statistical analyses of time series of geomagnetic and climate (proxy) data (for a recent review, see *Courtillot et al.* [2007]). Potentially underlying mechanisms remain a subject of controversy, however. *Doake* [1977] suggested that rotational acceleration or deceleration due to waxing or waning ice sheets might trigger instabilities in the geodynamo and promote geomagnetic events of large magnitude (excursions or reversals). Although variations in the Earth's rotation rate affect the geodynamo [*Le Mouél et al.*, 1981], it is not known what magnitude is required for the change in angular frequency in order to critically perturb a stably running geodynamo, or how close the geodynamo has to be to the critical state to be susceptible for such perturbations at all. Also, there is no convincing statistical evidence for such a connection in the paleo-record, although possible correlations may be obfuscated by uncertainties in age models, as was already cautioned by *Doake* [1977].

[3] Since luni-solar precession may provide power to the geodynamo [e.g., *Vanyo*, 1991; *Tilgner*, 2007], all effects that perturb or modulate precession (such as obliquity variations) can potentially influence the geomagnetic field.

However, the statistical evidence for an orbitally modulated geodynamo from sedimentary paleomagnetic records is far from firm [*Guyodo et al.*, 2000; *Kent and Carlut*, 2001; *Roberts et al.*, 2003; *Heslop*, 2007; *Xuan and Channell*, 2008].

[4] Although absolute paleointensity records derived from terrestrial lava flows or archaeological artifacts are discontinuous in time, they have no climatic overprint, which makes them in principle better suited for studying such correlations. For example, *Gallet et al.* [2005] reported a remarkable coincidence between major cool episodes and periods of increased archeomagnetic field strength (AMF) since 700 AD. AMF variations during the four millennia BC appear to be interrupted by so-called archeomagnetic jerks, that is, periods of sharp intensity increase, which coincide with periods of fastest cooling rates [*Gallet et al.*, 2006]. Unfortunately, the archeomagnetic database is still too sparse to verify if periods of rapid warming are correlated with fast dropping AMF values.

[5] As *Courtillot et al.* [2007] remarked, the negative correlation between magnetic dipole moment and temperature is at odds with an often invoked mechanism, in which a diminishing dipole reduces the shielding capacity of the terrestrial magnetosphere against galactic cosmic radiation, which in turn enhances the nucleation rate of deep clouds, entailing a higher albedo and cooler temperatures.

[6] We test if this inverse correlation can be isolated from global time series constructed from instrumental records. The normalized correlation coefficient c_{TM} between global mean surface temperature T and magnetic dipole moment M (records shown in Figure 1a) amounts to -0.8 , which at first glance might suggest a significant anti-correlation. However, when the two curves are detrended or when comparing their time derivatives, the anti-correlation weakens ($c_{TM} \sim -0.5$ for detrended curves and $c_{TM} \sim -0.6$ for derivatives shown in Figure 1b), which implies that the inverse correlation between the original curves is due to the fact that M happens to continue decreasing during the upward trend in the temperature anomaly since the early 20th century, which in turn reflects the anthropogenic effect on global temperature. Although there appears to be some correlation between the derivatives shown in Figure 1b, the phase relationship between the curves is not consistent. It is clear that longer time series would be needed to clarify the nature of the correlations. Nevertheless, the possibility that geomagnetic field variations affect climate is worthwhile exploring, even though the instrumental records are unlikely to be useful here due to the human overprint.

[7] The intent of this Letter is to draw the attention to the widely unknown effects of magnetic fields on the physico-chemical properties of seawater, which may present an

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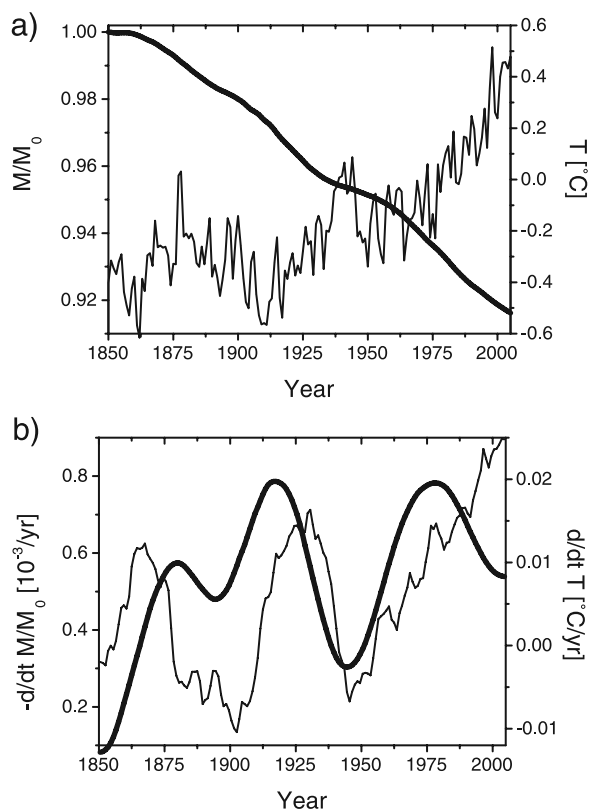


Figure 1. (a) Relative variation of the geomagnetic-field dipole moment M/M_0 (thick line, left scale), with $M_0 = M(1850)$, and globally averaged surface temperature anomaly, T (thin line, right scale). Data sources: M from Jackson *et al.* [2000], T from Brohan *et al.* [2006]. (b) Time derivatives of M/M_0 (thick, left scale) and T (thin, right scale), respectively. To emphasize a possible anti-correlation, the negative time derivative of M/M_0 is shown. T was smoothed before differentiation.

important mechanism linking geomagnetic field variations and climate, given the major role the ocean has on global climate. Several recent studies suggested that magnetic fields have a role on the physicochemical properties of aqueous electrolytic solutions [Beruto *et al.*, 2003; Vallée *et al.*, 2005], as well as on kinetics and thermodynamics of CaCO₃ precipitation [Holysz *et al.*, 2002; Barrett and Parsons, 1998]. Those experiments were done in a different context and the fields used were either strong static magnetic fields (≥ 100 mT) or weak alternating electromagnetic fields. Below we show that similar effects can also occur in weak (Earth-strength) static magnetic fields and propose a mechanism in which variations of the geomagnetic field strength affect the gas solubility of sea-water and thereby modulate the atmospheric CO₂ concentration.

2. Experiments

2.1. Magnetic Field Effects on Viscosity

[8] Viscosities of seawater and of a 0.62 M (3.5%) NaCl solution were determined from fluorescence polarization [Marangoni, 1992], for which purpose the solutions were dyed with Rhodamine-B (see Figures S1–S3 in the auxil-

iary material for setup and calibration¹). An electronically controlled pipette was periodically pumped up and down to induce a vertical flow in the solution (0–5 mm/s). The controlled application of a magnetic field (MF) was through Helmholtz coils, housed inside a permalloy box screening out the ambient field. When the Helmholtz coils were switched off, the residual field in the tank was about 1 μT . The effect of a MF on viscosity was investigated at $T = 5 \pm 0.1^{\circ}\text{C}$. After switching on a MF of 2 mT, the viscosity continuously increased. The effect is fully reversible when the MF is reduced to 1 μT again, with a decay time of less than 10 s (Figure S4). When the samples are agitated, the viscosity initially increases at much higher rates and reaches overall higher levels than without agitation. The increase of viscosity was 8–10% stronger for the 3.5% NaCl solution than for seawater. The viscosity enhancement due to a 2 mT field (relative to 1 μT) is equivalent to a temperature reduction of 0.7 $^{\circ}\text{C}$ (placid) or 1.5 $^{\circ}\text{C}$ (agitated). However, we were not able to quantify the viscosity enhancement due to an earth strength field (0.05 mT). Although the sign of the MF effect is the same, the signal-to-noise level here is too low to obtain decent estimates.

[9] The MF effect on viscosity increases with decreasing temperature. Importantly, the viscosity effect vanished after degassing the salt solutions for 60 s under vacuum, and was re-established by gassing. The MF effects on the viscosity of the solution when O₂ or N₂ were used instead of air were similar, but slightly stronger with CO₂ and virtually absent with argon, in distilled water, and in a glucose solution (3.5 weight %). The fact that the MF effect is similar among the molecular gases suggests that effects seen with air are not due to the paramagnetic susceptibility of O₂, which is too small to explain the observed magnetic-field effects in terms of magnetization effects.

[10] The observed MF effect on viscosity obviously needs a combination of two components; namely, dissociated salts (electrolytes) and the presence of internal interfaces in the solution (due to air bubbles or particulate matter). Electrostatically, gas bubbles in water are similar to colloidal solutes. Both are coated by shells of ions and counterions, referred to as inner and outer Helmholtz layer, which together form a dielectric boundary layer (DBL). The potential that arises on removal of the outer Helmholtz layer, is called the zeta potential, a measure of the electric polarization. The zeta potential depends on pH and salt concentration [Creux *et al.*, 2007], but also on viscosity according to the Smoluchowski-Einstein equation. The observed changes in viscosity therefore are likely to represent a magnetic-field effect on the zeta potential.

2.2. Magnetic Field Effects on Gas Exchange Between Air and Seawater

[11] To measure gas concentration in sea-water, we used an elastic light-scattering technique [Vallée *et al.*, 2005] with a monochromatic (400 nm) light source. Elastic light scattering is sensitive to the presence of gas bubbles, which have a different refractive index than the solution and thus act as scatterers. The intensity of the scattered light depends not only on the concentration of the gas phase in the solution, but also on bubble size. To minimize the obfus-

¹Auxiliary materials are available in the HTML. doi:10.1029/2008GL034288.

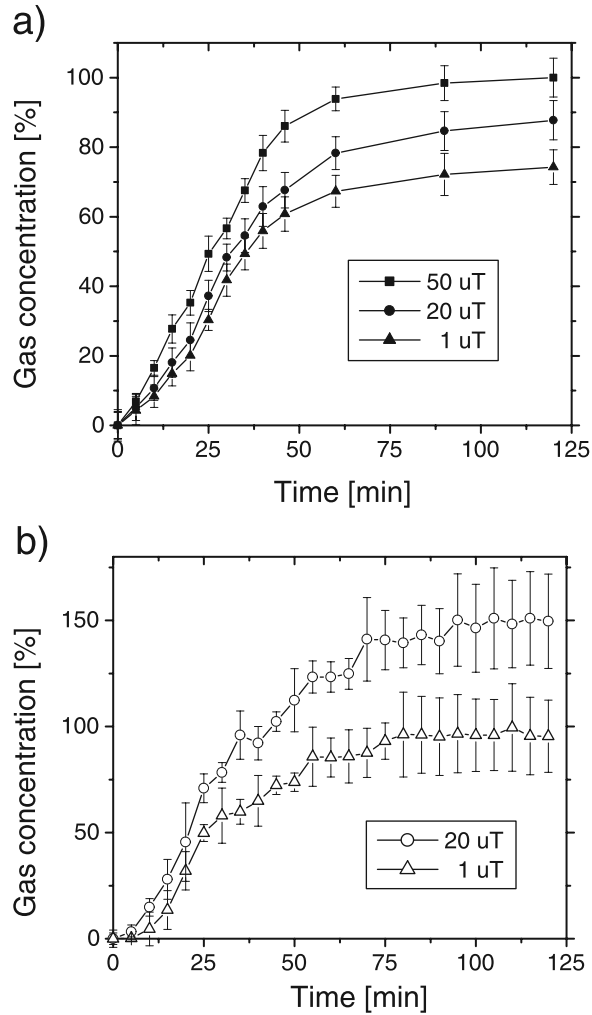


Figure 2. (a) Time course of air saturation of seawater at 1 μT , 20 μT , and 50 μT , respectively. Each curve presents the mean over five experiments each and their $\pm 1\sigma$ standard deviation (error bars). All curves are normalized to the saturation level obtained at 50 μT . (b) As in Figure 2a, but now for air with 30% CO₂. Averages of three experiments each, 100% is defined for normal air in 50 μT (see Figure 2a).

cating effects of a broad bubble-size distribution on the scattering intensity, the solution was not agitated in this experiment. Under placid conditions, the bubble-size distribution is narrow (bubble sizes well below 1 μm) and the bubbles are separated, whilst under turbulent conditions, bubbles are prone to interact and coalesce, which gives rise to a broad bubble-size distribution. Thus, for the placid solution, the scattering intensity can be considered to reflect the concentration of roughly monodisperse gas bubbles in the solution.

[12] The seawater was degassed before the experiment. Then the surface of the water container was allowed to exchange gas with the environment (ambient pressure) and the time course of the scatter intensity was recorded in 1 μT , 20 μT , and 50 μT , respectively. The solution was kept at 4°C. Each regassing experiment follows a similar time course, characterized by an initially linear increase in scatter intensity (gas concentration) up to 45 min, followed by an

approach-to-saturation behaviour, with saturation achieved after about two hours (Figure 2a). The curves are normalized by the saturation value for the curve taken at 50 μT . Importantly, re-gassing rate and saturation values increase with field strength. Additional experiments were conducted to determine the MF effect on CO₂ solubility. For ~30% (v/v) CO₂ enriched air, a reduction in field strength from 20 μT to 1 μT has an even more pronounced effect on gas solubility compared to normal air with 380 ppm CO₂ (Figure 2b). For pure CO₂, the extrapolated MF effect is twice as strong than for normal air, such that a 1% field change yields a 0.5% change in CO₂ solubility. Importantly, the magnetic-field effect is absent in purified water.

[13] The time course of the gas-solubility experiment represents the diffusion-limited, molecular transfer of gas across the air-solution interface. According to the classic models of air-sea gas exchange [Broecker and Peng, 1974; Liss and Slater, 1974], the main resistance to gas transport is due to the stagnant boundary layer, across which the exchanging gases transfer by molecular processes (diffusion) from the well-mixed atmosphere to well-mixed surface ocean and vice versa. The net flux F of gas into the salt solution is driven by the concentration gradient $\Delta c/d$ of gas across the stagnant film (thickness d),

$$F = D\Delta c/d = k(c_s - c_a) \quad (1)$$

where D is molecular diffusivity of gas in sea water, $k = D/d$ is the transfer velocity (“piston velocity”), c_a and c_s are the gas concentrations in air and in seawater (below the stagnant film), respectively. For O₂, N₂, and CO₂, D (at 4°C) is about 1×10^{-5} cm²/s [Himmelblau, 1964]. Under low agitation, Broecker and Peng [1974] obtained d values of 3×10^{-2} cm, resulting in k values of about 3×10^{-4} cm/s.

[14] With c_a in equation (1) kept constant during the experiment, the integration of equation (1) yields

$$c_s = c_s^{\text{sat}}(1 - \exp(-kt/L)), \quad (2)$$

where t is time and $L = V/A$ is the characteristic length, with V and A denoting the volume (1 cm³) and the surface area (1 cm²), respectively, of the liquid container. Fitting the measured time course to equation (2), we obtain experimental time constants of $L/k \sim 30$ min, that is, k values of about 5×10^{-4} cm/s, in good agreement with literature data.

3. Discussion

[15] The MF effect on viscosity and gas solubility requires the presence of dielectric boundary layers (DBL), because MF effects are absent when distilled water (or a glucose solution) is used instead of seawater. The MF effects therefore are expected to occur in the ocean as well, given the abundance of DBL in the surface ocean, be it due to submicrometre particles (10^8 – 10^9 particles per ml) [Wells and Goldberg, 1991], be it due to sub-100 nm colloidal particles (10^8 – 10^9 particles per ml) [Isao et al., 1990]. A conservative estimation of all DBL-generating matter yields a total surface of tens of m² per m³ seawater.

[16] The MF effect on gas-solubility in seawater does not seem to be directly related to the MF effect on viscosity, since the latter is much less pronounced. This is also suggested by the fact that the time scale of gas uptake in our experiments shows no discernible difference between normal and reduced MF. The single-most important difference between gas uptake under normal and reduced MF is the magnitude of the flux and the saturation level. This implies a lower gas solubility in seawater in weaker magnetic fields and we may conclude that MF strength affects the equilibrium concentration of dissolved gas in the liquid phase. It is therefore conceivable that geomagnetic field strength may act as an additional factor that modulates the air-sea exchange of gas.

[17] An important unknown is the magnetic-field effect on the reaction rates in the dissolved inorganic carbon system. CO₂ as a reactive gas may become hydrated already in the stagnant film, whereupon concentration gradients of other inorganic carbon species (HCO₃⁻, CO₃²⁻) would be set up immediately (given the rapid dissociation of carbonic acid, compared to the slow hydration reaction under typical seawater pH conditions), which leads to well-known CO₂ exchange enhancement [Hoover and Berkshire, 1969; Wanninkhof and Knox, 1996]. The fact that the MF effect on solubility is more pronounced for a CO₂ enriched atmosphere than for the standard atmosphere might also result from MF effects on the equilibrium constants in the marine carbonate system, but more experiments are needed for clarification.

[18] The theoretical framework describing effects of a weak static MF on electrolyte solutions, gas solubility, and equilibrium constants is at a level that does not even allow us to make qualitative predictions. Obviously, the MF effect is related to the presence of ionic solutes. Salinity reduces solubility of hydrophobic gases, and it is possible that the magnetic field (by exerting a Lorentz force on ionic solutes at DBL) partly undoes the adverse effect of salinity on gas solubility. We speculate that under higher fields, the relative influence of thermal fluctuations on ion movement becomes weaker (particularly at DBL, where gyration of ions may be stabilized), which would lead to lower effective temperatures, hence higher gas solubility.

4. Conclusions

[19] We have measured viscosity and gas solubility of seawater at different magnetic field (MF) strengths. While the MF effect on seawater viscosity is probably too small to be relevant under naturally occurring field variations, the MF effect on gas solubility may present a physical link between geomagnetic field and climate. Our small-scale laboratory experiments indicate lower solubility of CO₂ in seawater under reduced MF intensity. The extra amount of CO₂ not dissolved due to reduced CO₂ solubility in a weaker MF would add to the greenhouse effect. This mechanism therefore has the right sign to qualitatively explain the observed anti-correlation between archeomagnetic field strength and global temperature estimates.

[20] However, the magnitude of the mechanism is small compared to the magnitude of the preponderant mechanisms driving the exchange of carbon between ocean and atmosphere, such as water temperature, biological pumping,

overturning circulation. The effect of geomagnetic-field variations therefore is to modulate the air-sea exchange of carbon.

[21] The magnitude of the MF effect is such that CO₂ solubility reduces by a maximum of 0.5% per each % decrease in MF strength. To provide a quantitative assessment of the MF effect on the global carbon dioxide budget, we assume that our experimental results can be extrapolated to the global scale and that a reduction in CO₂ solubility by 0.5% is equivalent to an emission of 0.5% of the total amount of dissolved inorganic carbon (DIC) in the surface ocean (700 Pg C) [see Sigman and Boyle, 2000, Figure 2]. A 1% decrease in magnetic dipole moment occurring over a decade would then add 1 ppm CO₂ per decade to the atmosphere, that is, 0.35 Pg C/yr. This figure is a magnitude larger than the CO₂ discharge from subaerial volcanism (0.03 Pg C/yr) [Kerrick, 2001], from which we surmise that the MF effect may have played a role in pre-industrial times.

[22] Given the high anthropogenic emission rate of CO₂ (7 Pg C/yr), it would be preposterous to make the weakening Earth's magnetic field responsible for global warming. Yet, by lowering the capacity of the surface ocean to absorb excess CO₂ from the atmosphere, the diminishing field acts in the same direction as the increase in sea-surface temperature and acidity, thereby exacerbating the effects of global warming.

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