Sensitivity of ocean acidification and oxygen to the uncertainty in climate change

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Received 8 February 2014, revised 28 April 2014
Accepted for publication 2 May 2014
Published 5 June 2014

Abstract
Due to increasing atmospheric CO\(_2\) concentrations and associated climate change, the global ocean is undergoing substantial physical and biogeochemical changes. Among these, changes in ocean oxygen and carbonate chemistry have great implication for marine biota. There is considerable uncertainty in the projections of future climate change, and it is unclear how the uncertainty in climate change would also affect the projection of oxygen and carbonate chemistry. To investigate this issue, we use an Earth system model of intermediate complexity to perform a set of simulations, including that which involves no radiative effect of atmospheric CO\(_2\) and those which involve CO\(_2\)-induced climate change with climate sensitivity varying from 0.5 °C to 4.5 °C. Atmospheric CO\(_2\) concentration is prescribed to follow RCP 8.5 pathway and its extensions. Climate change affects carbonate chemistry and oxygen mainly through its impact on ocean temperature, ocean ventilation, and concentration of dissolved inorganic carbon and alkalinity. It is found that climate change mitigates the decrease of carbonate ions at the ocean surface but has negligible effect on surface ocean pH. Averaged over the whole ocean, climate change acts to decrease oxygen concentration but mitigates the CO\(_2\)-induced reduction of carbonate ion and pH. In our simulations, by year 2500, every degree increase of climate sensitivity warms the ocean by 0.8 °C and reduces ocean-mean dissolved oxygen concentration by 5.0%. Meanwhile, every degree increase of climate sensitivity buffers CO\(_2\)-induced reduction in ocean-mean carbonate ion concentration and pH by 3.4% and 0.02 units, respectively. Our study demonstrates different sensitivities of ocean temperature, carbonate chemistry, and oxygen, in terms of both the sign and magnitude to the amount of climate change, which have great implications for understanding the response of ocean biota to climate change.

Keywords: ocean acidification, oxygen, climate change, Earth system model

1. Introduction

Since the pre-industrial era, the concentration of carbon dioxide in the atmosphere has increased by about 40% (IPCC 2013). This increase in atmospheric CO\(_2\), mainly through its
influence on atmospheric radiative transfer, has a profound effect on global climate (IPCC 2013). Covering approximately 70% of the Earth surface, the ocean is an indispensable component of the climate system. With increasing CO$_2$ concentration in the atmosphere and associated climate change, the global ocean has undergone substantial physical and biogeochemical changes. For example, between year 1971 and 2010, near sea surface temperature has increased at a rate of about 0.11 °C per decade (Rhein et al 2013). Since the pre-industrial era, sea surface pH has declined by about 0.1 units with the concurrent decrease of [CO$_3^{2-}$] (Gattuso and Hansson 2011), and oxygen concentration in the upper global ocean decreased by 0.93 mmol m$^{-3}$ between the 1970s and 1990s (Helm et al 2011). These changes in ocean physical and biogeochemical properties have wide-ranging effects on marine organisms and ecosystems (Doney et al 2012).

Changes in ocean acidity and dissolved oxygen content are two of the most important stressors for ocean biology (e.g., Kleyapas et al 1999, Gray et al 2002, Feely et al 2004, Grantham et al 2004, Orr et al 2005, Kleyapas et al 2006, Pörtner and Knust 2007, Doney et al 2012). The change in ocean oxygen is mainly controlled by the change in ocean surface temperature, which alters the solubility of oxygen; the change in ocean ventilation, which alters the transport of oxygen from the surface to the ocean interior; and the change in marine biology, which alters the consumption of oxygen in the ocean (Keeling et al 2010, Helm et al 2011). However, ocean acidification, which refers to the reduction in ocean pH over an extended period, is mainly due to ocean’s uptake of anthropogenic CO$_2$ (Gattuso and Hansson 2011).

A number of studies have examined changes in ocean acidity (e.g., Caldeira and Wickett 2005, Cao et al 2007, McNeil and Matear 2008, Steinacher et al 2009, RICE et al 2013, CAO et al 2014) or oxygen content (e.g., Plattner et al 2002, Schmittner et al 2008, Frölicher et al 2009, Keeling et al 2010, Duteil and Oschlies 2011) under the effect of increasing atmospheric CO$_2$ and/or climate change. These studies, in general, reported increased ocean acidity and decreased oxygen content in a future world with higher atmospheric CO$_2$ and temperature. However, it is not clear how climate change and its uncertainty would affect ocean acidification and oxygen content simultaneously. What is the effect of climate change on ocean oxygen content and different species of ocean carbonate chemistry at both the surface and sub-surface ocean? How would the uncertainty in the projection of future climate change translate into the uncertainty in the projection of ocean acidification and oxygen? In this study, we aim to address these questions through simulations using a coupled climate-biogeochemical cycle model.

2. Methods

2.1. Model description

The University of Victoria Earth System Climate Model (UVic) used here is a coupled climate-biogeochemical cycle model that simulates atmosphere and ocean climate, the ocean carbon and oxygen cycle, and the terrestrial carbon cycle. The model has a horizontal resolution of 1.8° latitude and 3.6° longitude with 19 vertical layers in the ocean. It has a three-dimensional general circulation model of the ocean that is coupled to a vertically integrated energy/moisture balance model of the atmosphere (Weaver et al 2001). Air-sea exchange of CO$_2$ and carbonate chemistry is simulated by a representation of inorganic carbon cycle module following the protocol of the Ocean Carbon-Cycle Model Intercomparison Project (Orr et al 1999). The CO$_2$ system thermodynamic constant K$_1$ and K$_2$ are from Dickson and Millero (1987) and K$_{1p}$, K$_{2p}$, K$_{3p}$ are from Millero (1995). Solubility K$_0$ is from Weiss and Price (1980). All constants are given on seawater pH scale, except for K$_s$, which is on the free pH scale. The inorganic carbon cycle is coupled to a simple marine ecosystem model that simulates phytoplankton, zooplankton, detritus, the nutrient of phosphate and nitrate, and oxygen (Schmittner et al 2008). The UVic model has been widely used in a variety of studies concerning the ocean biogeochemical cycles and climate change, such as projection of ocean acidification (e.g., Hoegh-Guldberg et al 2007, Cao and Caldeira 2008, Matthews et al 2009, Turley et al 2010), the global carbon cycle and its interactions with climate change (e.g., Friedlingstein et al 2006, Schmittner et al 2008, Zickfeld et al 2013), as well as the future evolution of the ocean oxygen cycle (Oschlies et al 2008, Schmittner et al 2008, Taucher and Oschlies 2011).

2.2. Simulation experiments

The UVic model was first spun up for 10,000 years with a prescribed constant pre-industrial atmospheric CO$_2$ concentration of 280 ppm to reach a quasi-equilibrium state of climate and the carbon cycle. Then a set of transient simulations were performed with prescribed atmospheric CO$_2$ concentrations: between year 1800 and 2005 atmospheric CO$_2$ concentration is taken from observational-based estimates, and after 2005 CO$_2$ concentration is taken from the representation concentration pathway (RCP) and its extensions up to year 2300 (Meinshausen et al 2011). Here we choose the high-end CO$_2$ concentration scenario of RCP 8.5 to illustrate future evolution of ocean acidification and ocean oxygen under a socioeconomic scenario with intense fossil fuel use. After year 2300 atmospheric CO$_2$ concentration is assumed to maintain at its year-2300 level of 1962 ppm. This assumption is not based on socioeconomic consideration but is simply used to illustrate long-term change in ocean acidity and oxygen under a potentially high atmospheric CO$_2$ concentration level. To investigate the effect of climate change on ocean acidification and oxygen, a set of transient simulations are performed with different values of climate sensitivity ($\Delta T_{2x}$, equilibrium global and annual mean change of surface air temperature in response to a doubling of atmospheric CO$_2$) that varies between 0.5 to 4.5 °C with an interval of 0.5 °C (i.e., $\Delta T_{2x}$ = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 °C). In addition, a simulation with no climate change is performed by setting climate sensitivity to zero (named as ‘noce’ to denote the simulation with no climate change). It is noted that in this
simulation the radiative effect of atmospheric CO2 is muted in the model, but increasing atmospheric CO2 causes a slight warming through CO2-induced vegetation change. The range of climate sensitivity used here includes the best estimate of climate sensitivity that ranges between 1.5 °C and 4.5 °C IPCC (2013).

2.3. Analysis of ocean chemistry and oxygen

We calculate ocean carbonate chemistry fields, including pH, carbonate ion concentration, and saturation state of calcium carbonate based on the chemistry routine from the OCMIP-3 project (http://ocmip5.ipsl.jussieu.fr/OCMIP/) with the input of model-simulated temperature, salinity, concentrations of dissolved inorganic carbon (DIC), alkalinity (ALK), and phosphate. Silicate concentration is taken with the input of model-simulated temperature, salinity, and pH, carbonate ion concentration, and saturation state of calcium carbonate based on the chemistry routine from the World Ocean Atlas climatology (Garcia et al. 2004). The saturation state of calcium carbonate (Ω) for aragonite or calcite is calculated as Feely et al (2004): Ω = [Ca2+] [CO32−]/K*, where K* is the stoichiometric solubility product for aragonite or calcite that is estimated from Mucci (1983) with the effect of pressure adjustment based on Millero (1995). All constants are given at the seawater pH scale, except for Ks, which is on the free pH scale.

To quantify the combined effect of carbon dioxide and oxygen on the physiological limits of aerobic life, Brewer and Peltzer (2009) proposed the concept of ‘Respiration Index’ (RI) that is directly related to the available energy involved in the basic oxic respiration. Based on Brewer and Peltzer (2009), RI is defined as RI = \log_{10} (fO2/fCO2). We calculate the fugacity of carbon dioxide (fCO2) as a function of DIC, ALK, temperature, salinity, phosphate, and silicate, and the fugacity of fO2 as a function of modeled dissolved oxygen, temperature, and salinity (Sarmiento and Gruber 2006). We acknowledge that criticism of the concept of respiration index was raised (e.g., Seibel and Childress 2013), however, it might be too early to rule out the usefulness of RI as a potential indicator of physiological stress to marine organisms. Therefore, we calculate RI and present its change in response to climate change.

We also quantify the effect of climate change on ocean chemistry and oxygen due to climate-induced changes in different factors including temperature, salinity, DIC, ALK, and O2. To do this, we calculate carbonate chemistry fields and oxygen using one variable that is taken from the simulation with climate change and all other variables taken from the simulation without climate change. The difference between an ocean field calculated this way and that calculated with all input variables from the simulation without climate change represents the effect of climate-induced change in a certain factor on that ocean field. Similarly, the effect of climate change on RI is attributed to climate-induced change in fCO2 and fO2.

3. Results

We first present model-simulated DIC, ALK, and O2 with observational based estimates (figures S1 to S5). Figures S1, S2, and S3 present the latitude-depth distribution; figure S4 presents the vertical profile; and figure S5 presents the Taylor diagram (Taylor 2001) of model-observation comparison. As shown in these figures, the model captures reasonably well the observed large-scale pattern of DIC, ALK, and oxygen in different ocean basins. For example, the observed DIC and oxygen minimum in the mid-depth of the Indo-Pacific Ocean is simulated well by the model. The distinct pattern contrast between the Atlantic and Pacific Ocean is also captured by the model. Several apparent discrepancies between modeled fields and observational fields are observed at the sub-basin scale, especially for the simulation of alkalinity and oxygen. These discrepancies could be attributed to the model’s deficiency in the simulation of ocean circulation and/or marine biogeochemical cycle. A thorough investigation of the underlying reason for the model-observation discrepancy is beyond the scope of this study.

In the following we present model-simulated changes in ocean carbonate chemistry and oxygen. To demonstrate the effect of climate change, we focus on the simulation with no climate change and the simulation with climate sensitivity of 3.0 °C and 4.5 °C. We then present results in simulations with climate sensitivity varying from 0.5 to 4.5 °C. All results presented here are annual mean values.

With increasing atmospheric CO2 concentrations (figure 1(a)), the ocean becomes warmer (figure 1(b)), and ocean ventilation becomes weaker, as indicated by the reduced intensity of North Atlantic deep water formation (figure 1(c)) and reduced convective activities (figure 1(d)). At the same time, sea water becomes more acidic (figure 2) as a result of ocean’s absorption of atmospheric CO2. In the simulations with no climate change, relative to the pre-industrial values, by year 2100 and 2500 global mean surface ocean pH decreases by 0.43 and 0.75 units, and surface [CO32−] decreases by 55% and 77%, respectively (figures 2(b), (c)). Climate change modifies CO2-induced change in carbonate chemistry mainly through climate-induced changes in temperature, salinity, DIC, and ALK (figure S6). As shown in figure S6, climate-induced DIC change acts to mitigate surface acidification and climate-induced ALK change acts to increase surface acidification. The direct effect of temperature change is to decrease surface pH, but to increase surface [CO32−] and Ωaragonite. As a result, the net effect of climate change on surface pH is rather small but somewhat mitigates CO2-induced decrease in surface [CO32−] and Ωaragonite. This finding is consistent with previous studies on the effect of climate change on surface ocean acidification (Cao et al. 2007, McNeil and Matear 2007). By year 2500, in the simulation with climate sensitivity of 3 °C the inclusion of climate change increases surface mean [CO32−] and Ωaragonite by 21% and 15%, respectively (figures 2(c), (d)).
In the simulations here, increasing atmospheric CO₂ has no direct effect on the concentration of dissolved oxygen in the ocean. Simulated change in surface oxygen is mainly a result of increased sea surface temperature that decreases the solubility of dissolved oxygen in the ocean. By year 2100 and 2500 in the simulation with ΔT₂x = 3.0 °C surface-mean oxygen concentration decreases by 4.5 and 10.6%, respectively (figure 2(e)).
In the simulation with no climate change, global mean surface respiration index decreases from its pre-industrial value of 2.85 to 2.36 and 2.02 by year 2100 and 2500 (figure 2(f)). Here the decrease in RI is mainly a result of increased $fCO_2$ in the ocean. The net effect of climate change on surface RI is small: in the simulation with $\Delta T_{2x} = 3.0 \, ^\circ C$ by year 2500 the inclusion of climate change decrease RI by less than 1% (figure 2(f), figure S7).

Penetration of anthropogenic $CO_2$ from the ocean surface to the ocean interior makes the deep ocean more acidic (figures 2–4). Under the assumption of no climate change, by year 2500 global ocean pH decreases by 0.36 and $[CO_3^{2-}]$ decreases by 51% (figures 2(h), (i)). Climate change, mainly through reduced ocean ventilation and North Atlantic deep water formation (figures 1(c), (d)), reduces the transport of anthropogenic $CO_2$ from the surface to deep ocean (figure 3(b)), which mitigates deep ocean acidification (figure S8). In our simulation climate change decreases alkalinity concentration in the upper ocean and increases it in the deeper ocean (figure 3(c)) as a result of increased $CaCO_3$ production that is associated with the modeled increase in net primary production (figure S9). The climate-induced change in alkalinity distribution acts to increase upper ocean acidity and decrease deep ocean acidity (figure S8). Meanwhile, the direct temperature effect acts to decrease ocean pH but increase $[CO_3^{2-}]$ and $\Omega_{aragonite}$ (figure S8). Overall, climate change acts to mitigate acidification for the global ocean (figures 2, 3). In the simulation with $\Delta T_{2x} = 3.0 \, ^\circ C$, by year 2500 climate change increases ocean-mean pH and $[CO_3^{2-}]$ by 0.05 and 23%, respectively (figures 2(h), (i)). In our analysis, by year 2500, the fractional volume of the world ocean that experiences a pH reduction greater than 0.2 units is 64.0% in the simulation with no climate change, which shrinks to 48.9% when the effect of climate change ($\Delta T_{2x} = 3.0 \, ^\circ C$) is included.

Climate change, through increased surface temperature and decreased ocean ventilation, reduces the concentration of oxygen in the ocean interior (figures 2–4). By year 2100 and 2500, in the simulation with $\Delta T_{2x} = 3.0 \, ^\circ C$ mean $O_2$ decreases by 4.8 and 19.4%, respectively (figure 2(k)). The ocean with suboxic waters expands as well. Taking 10 $\mu mol$ kg$^{-1}$ as a threshold for suboxic waters (Shaffer et al. 2009), by year 2100 and 2500, in the simulation with $\Delta T_{2x} = 3.0 \, ^\circ C$ 1.95 $\times 10^7$ km$^3$ (1.5%) and 2.47 $\times 10^7$ km$^3$ (1.9%) of the world ocean is subject to suboxic condition, a 25% and 58% expansion of the suboxic water from the model-simulated pre-industrial suboxic volume ($1.56 \times 10^7$ km$^3$ or 1.2% of the world ocean).

In the simulation with no climate change by year 2100 and 2500 ocean-mean RI decreases by 4.3 and 16.5%, respectively, mainly as a result of increased $fCO_2$ of the ocean. Climate change, through its effect on both $fCO_2$ and $fO_2$, further decreases ocean RI (figure 2(l)). In our analysis, by year 2500 in the simulation with no climate change, 2.7% of the world ocean experiences a value of RI less than 1, compared to the value of 3.9% in the simulation with $\Delta T_{2x} = 3.0 \, ^\circ C$. In the deep ocean the effect of climate change acts to decrease both $fCO_2$ and $fO_2$ (figures S10(a), (b)). The decrease of $fCO_2$ tends to increase RI whereas the...
decrease of $fO_2$ tends to decrease RI (figure S10(c)). Therefore, the change of $fCO_2$ and $fO_2$ due to climate change has compensating effect on the change in RI in the deep ocean (figure S10(c)).

To illustrate the overall effect of climate change on ocean acidification and oxygen, we calculate the change at year 2500 (relative to the pre-industrial time) for surface-mean and ocean-mean DIC, pH, $[CO_3^{2-}]$, $\Omega_{aragonite}$, $O_2$, $pCO_2$, and $pH$. The model-simulated horizontal mean pH, $[CO_3^{2-}]$, $O_2$, and RI as a function of year and depth for simulations with no climate change and $\Delta T_{2x} = 3.0^\circ C$ are shown in Figure 4.
and RI for simulations with climate sensitivity ranging from 0.5 to 4.5 °C as well as the simulation with no climate change. Changes in these ocean biogeochemical fields as a function of climate sensitivity are given in terms of both absolute values (figure 5) and percent values (figure S11). It is observed that different fields show different sensitivities to the amount of climate change. Linear regression of the change in an ocean variable against climate sensitivity shows that for every degree increase of climate sensitivity, changes in surface-mean pH, $[\text{CO}_3^{2-}]$, $\Omega_{\text{aragonite}}$, $O_2$, and RI are $-0.001$ (or $-0.01\%$), $3.2 \mu\text{mol kg}^{-1}$ (or $1.5\%$), $0.06$ (or $1.8\%$), $-8.1 \mu\text{mol kg}^{-1}$ (or $-3.3\%$), and $-0.003$ (or $-0.10\%$), respectively. Averaged over the whole ocean, for every degree increase of climate sensitivity, changes in pH, $[\text{CO}_3^{2-}]$ and RI are $0.015$ (or $0.19\%$), $3.4 \mu\text{mol kg}^{-1}$ (or $3.4\%$), $0.03$ (or $3.1\%$), $-8.5 \mu\text{mol kg}^{-1}$ (or $-5.0\%$), and $-0.01$ (or $-0.26\%$), respectively. Meanwhile, by year 2500 every degree increase of climate sensitivity causes an ocean warming of 0.8 °C.

**4. Discussion and conclusions**

In this study we use an Earth system model of intermediate complexity to project future changes in ocean physical and biogeochemical fields. Our projection, under the ‘business as usual’ scenario RCP 8.5, can be compared with the simulation results under the same scenario from 10 Earth system models (Bopp et al 2013) in the framework of Coupled Model Intercomparison Project 5, CMIP5 (Taylor et al 2012). Under a climate sensitivity of 3.0 °C, the UVic model-simulated change in sea surface temperature, sea surface pH, and global ocean $O_2$ content in the 2090s (relative to the 1990s) is $2.11$ °C, $-0.33$ units, and $-3.41\%$, respectively. These results are in close agreement with the corresponding projected changes from 10 Earth system models of $2.73$ (±0.72) °C, $-0.33$ (±0.003) units, and $-3.45$ (±0.44) %, respectively (Bopp et al 2013). However, in our simulations ocean net primary production (NPP) increases, which is in sharp contrast with the results of Bopp et al (2013), who reported a decrease in NPP of $8.6$ (±7.9) % for the same period under RCP 8.5. By year 2500 model-simulated NPP has increased by $85\%$ (figure S9). Our result is also in contrast with that from four climate-carbon cycle model simulations (Steinacher et al 2010) that reported a decrease in NPP of $2\%$ to $13\%$.
from 1860 to 2100 under SRES A2 scenario. As discussed in Bopp et al (2013), two studies using UVic model (Schmittner et al 2008, Taucher and Oschlies 2011) found an increase in NPP during the 21st century. As augured in Bopp et al (2013), the discrepancy might be attributed to different parameterizations used for temperature dependency of biological production and/or remineralization rate or different routing functions of living organic matter to particulate or dissolved matters. Given the importance of NPP change in ocean carbon cycle, the exact reasons for the discrepancy in modeled NPP response, at both the global and regional scales, merit further studies.

Our simulations show that for a given atmospheric CO2 concentration if climate sensitivity is higher, that is, in a warmer and more stratified ocean, the extent of global ocean acidification (in terms of both [CO3^2−] and pH) would be less severe, but the reduction of dissolved oxygen would be greater. However, if climate sensitivity is lower, that is, in a less warm and less stratified ocean, the extent of global ocean acidification would be more severe, but the reduction of dissolved oxygen would be smaller. At the ocean surface, larger climate sensitivity results in smaller reduction in [CO3^2−] and Ωaragonite, but has negligible effect on pH. Ocean warming, ocean acidification, and reduction in dissolved oxygen all pose a potential threat to marine biota (e.g., Eppley 1972, Pörtner and Knust 2007, Hoegh-Guldberg et al 2007, Hutchins et al 2009, Doney et al 2012). Also, the change in ocean temperature, pH, [CO3^2−], Ωaragonite and dissolved O2 does not occur in isolation and changes in these variables could have synergistic effects on marine organisms Gruber (2011). For example, the sensitivity of marine organisms to ocean acidification may depend on ocean temperature (Pörtner, 2008), and for some marine organisms, ocean acidification and reduced oxygen content may reduce the level of tolerance to thermal stress Pörtner (2010). Our results demonstrate the complex interconnection of changes in ocean temperature, acidity, and oxygen, which would inevitably affect the response of marine biota.

We have also disentangled the net effect of climate change into the effect of climate-induced changes in individual factors. It is found that climate-induced changes in temperature, dissolved inorganic carbon, and alkalinity all play a key role in the net effect of climate change on ocean acidification. These factors can act in either the same or opposite direction in modifying carbonate chemistry, depending on the region and chemistry species considered. Among these factors, climate-induced change in alkalinity, which would depend on the change in CaCO3 production and dissolution, is of relatively high uncertainty.

Several caveats should be noticed when interpreting the simulation results here. For example, Oschlies et al (2008) found that a potential increase in the stoichiometry of carbon-to-nitrogen drawdown due to increased pCO2 (Riebesell et al 2007) would increase respiration of excess organic carbon in the deep ocean and thus reduces oxygen inventory. This direct effect of atmospheric CO2 on ocean oxygen is not included in the simulations here. Also, it is possible that the production of CaCO3 would decrease in response to a CO2-induced decrease in saturation state of carbonate material (Ridgwell et al 2007). This potential feedback of ocean acidification on CaCO3 production is not considered here. The above processes involved in the response of ocean biogeochemical cycles to climate change, together with probably a few others that have not been discussed, may further complicate the simulated changes of ocean oxygen and carbonate chemistry species. In addition, here we limit our analysis to the annual mean results. Variability in ocean physical and geochemical fields could have great implication for marine biology. For example, Shaw et al (2013) showed that natural variability of pCO2 in coral reef system plays an important role in determining the response of coral reef fish to ocean acidification. The change in the variability of ocean physical and biogeochemical fields in response to climate change merits future studies using more comprehensive climate-biogeochemistry models. Nonetheless, our study demonstrates that climate change, mainly through its impact on temperature, ocean ventilation, DIC, and alkalinity, would affect ocean oxygen and various carbonate chemistry fields in different ways, which has implication for understanding the effect of climate change on marine biota.

Acknowledgments

We thank two anonymous reviewers for their constructive suggestions. This work is supported by National Natural Science Foundation of China, (Grant 41276073) and by the Fundamental Research Funds for the Central Universities (Grant. 2012XZZX012).

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