Atmospheric CO₂ during the Mid-Piacenzian Warm Period and the M2 glaciation

Elwyn de la Vega, Thomas B. Chalk, Paul A. Wilson, Ratna Priya Bysani & Gavin L. Foster

The Piacenzian stage of the Pliocene (2.6 to 3.6 Ma) is the most recent past interval of sustained global warmth with mean global temperatures markedly higher (by ~2–3 °C) than today. Quantifying CO₂ levels during the mid-Piacenzian Warm Period (mPWP) provides a means, therefore, to deepen our understanding of Earth System behaviour in a warm climate state. Here we present a new high-resolution record of atmospheric CO₂ using the δ¹¹B-pH proxy from 3.35 to 3.15 million years ago (Ma) at a temporal resolution of 1 sample per 3–6 thousand years (kyrs). Our study interval covers both the coolest marine isotope stage of the mPWP, M2 (~3.3 Ma) and the transition into its warmest phase including interglacial KM5c (centered on ~3.205 Ma) which has a similar orbital configuration to present. We find that CO₂ ranged from ±394±34 ppm to ±330±14 ppm: with CO₂ during the KM5c interglacial being 391±30 ppm (at 95% confidence). Our findings corroborate the idea that changes in atmospheric CO₂ levels played a distinct role in climate variability during the mPWP. They also facilitate ongoing data-model comparisons and suggest that, at present rates of human emissions, there will be more CO₂ in Earth’s atmosphere by 2025 than at any time in at least the last 3.3 million years.

The Pliocene Epoch (2.588 to 5.3 Ma) was a time when global temperatures were ~3 °C warmer than the pre-industrial and sea level was ~20 m higher than present, largely due to the presence of smaller Greenland and Antarctic ice sheets. Given that many tectonic boundary conditions were similar (but not identical) to today, the Pliocene Epoch, and the mid-Piacenzian warm period (mPWP; 3 to 3.3 Ma) in particular, are useful targets for climate model validation studies (e.g. refs. 4–7). Phase 1 of the Pliocene Model Intercomparison Project (PlioMIP), found an overall agreement between climate model simulations of mPWP surface temperatures and the available data when run with a CO₂ of 405 ppm1. The North Atlantic and Pacific Oceans, however, are areas of consistently poor data-model agreement1,6. Haywood et al.4 noted that the experiment design of PlioMIP simulations precluded a determination of whether this result is attributed to poor model performance or poor data quality. This deficiency in experimental design, in part, resulted from the data collection time interval being from 3 to 3.3 Ma which spans a number of orbital climate cycles, whereas the models were run for less than 1,000 years with an invariant modern orbit.

To address this weakness, PlioMIP2 (phase 2)5 part of the model evaluations feeding into the 6th Assessment Report (AR) for the Intergovernmental Panel on Climate Change IPCC AR6, will focus on the KM5c interglacial interval at ~3.205 Ma which has a close-to-modern orbital configuration5. Other data compilation efforts with future data-model comparisons in mind, have targeted the interval from 3.3 Ma to 3.205 Ma5,15 because this also includes marine isotope stage M2, a prominent anomalously cold marine isotope stage (MIS) that provides a cold-to-warm transition within the overall warm background climate state of the late Pliocene (Fig. 1). A major limitation of these latest efforts, however, is the lack of data on atmospheric CO₂ during these rather narrow time intervals5,11. For instance, although ~40 δ¹³B-based determinations of CO₂ are available for the 3 to 3.3 Ma window12,13, the M2 to KM5 transition remains poorly sampled and disagreement between datasets from different analytical techniques persist (Fig. 1). Furthermore, the available δ¹¹B-CO₂ data exhibit relatively large short-term variability, which could signal orbital cyclicity (41 kyrs) aliased by low sampling resolution. Data from other CO₂ proxy systems such as stomata and palaeosol δ¹³C, are lacking in this interval and it has recently been shown that the marine-based alkenone-δ¹³C-CO₂ proxy underestimates CO₂ levels in the Pliocene15,16 therefore limiting its usefulness to providing a minimum CO₂ during the mPWP of >270 ppm16.

School of Ocean and Earth Science, University of Southampton, National Oceanography Centre Southampton, Waterfront Campus Southampton, Southampton, SO14 3ZH, UK. E-mail: elwyn.de-la-vega@soton.ac.uk
To address this data deficiency, we developed δ\(^{11}\)B-based CO\(_2\) estimates from Ocean Drilling Program (ODP) Site 999 in the Caribbean (Supplementary Fig. 1) at a resolution of 1 sample per 3–6 kyr for the time interval 3.15 to 3.35 Ma, encompassing the M2 glacia tion and the KM5 interglacial (including KM5c). Although focusing predominantly on the mixed layer dwelling planktic species *Globigerinoides ruber* (45 new data points, 63 in total), we also present new measurements of *Trilobus sacculifer* (2 new data points, 5 total) on the same samples to provide a check on the consistency of the δ\(^{11}\)B-pH calibration for *G. ruber* which has been recently called into question\(^{12}\).

**Results**

Our new high-resolution CO\(_2\) record is shown in Fig. 2 (and Supplementary Fig. 2 and Supplementary Table 2) and is consistent with earlier studies\(^{12–14,20}\) in showing that CO\(_2\) was higher than the pre-industrial during the mPWP (mean = 360 ppm). Our more detailed record reveals that CO\(_2\) variations ranged from 330 to 394 ppm (based on the mean and distribution of CO\(_2\) in the <25% and >75% interquartile range during the whole studied period; ref. \(^{14}\)), with a peak-to-trough range of 56–75 ppm determined by a Welch T-test of the data within the upper and lower quartiles (at 95% confidence; p < 0.01). From a comparison with benthic δ\(^{18}\)O data from ODP 999 (Supplementary Table 2) and the δ\(^{18}\)O stack\(^{19}\) (LR04) we observe that cold marine isotope stages (e.g. KM2; Fig. 2) are typically closely associated with low CO\(_2\) and warm stages with high CO\(_2\) levels. However, during the prominent M2 cold stage and through the warming out of M2, CO\(_2\) appears to lag benthic δ\(^{18}\)O by ~10 kyr (Supplementary Fig. 5). This lag is not attributable to age model uncertainty because it is present when comparing δ\(^{11}\)B-derived CO\(_2\) and benthic δ\(^{18}\)O from the same samples (Fig. 2). CO\(_2\) during the interglacial KM5c, determined using the mean of the δ\(^{11}\)B of the five samples in this interglacial, is estimated at 391 ± 34 ppm (at 95% confidence). Using a broader time window (10 to 15 ky) for the KM5 interglacial moderately alters the estimate (see Supplementary Table 1).

Our estimates of borate ion, pH and CO\(_2\) derived from the δ\(^{11}\)B of *T. sacculifer* (without sac-like final chamber) from ODP 999 (our new data, and ref. \(^{14}\)) and ODP 926\(^{20}\) overlap well with those based on *G. ruber* from ODP 999 in the mPWP (Fig. 2 and Supplementary Fig. 3). Calculated CO\(_2\) does not exhibit substantive inter-species offset with a mean difference of 10 ± 29 ppm with no consistent bias towards higher or lower pH/CO\(_2\).

**Accuracy of δ\(^{11}\)B-CO\(_2\) from *G. ruber* in the Plio-Pleistocene.** Ref. \(^{17}\) suggested that the δ\(^{11}\)B-pH calibration of *G. ruber* may have evolved through time and that *G. ruber* may suffer from morphotype-differences in δ\(^{11}\)B-derived pH estimates for the surface Pliocene ocean resulting in underestimates of the true pH and corresponding overestimates of true CO\(_2\). The principal evidence presented for this assertion was the disagreement between Pliocene CO\(_2\) calculated using the *T. sacculifer* data of Bartoli et al.\(^{12}\) and the *G. ruber* data from Martinez-Boti et al.\(^{13}\) (Fig. 1). As shown here, when *T. sacculifer* and *G. ruber* are compared from the same samples and measured with the same analytical technique (in this case MC-ICPMS) there is no significant offset between the methods in terms of reconstructed borate ion δ\(^{11}\)B, pH or CO\(_2\) (Fig. 2 and Supplementary Fig. 3). This finding suggests that the *G. ruber* δ\(^{11}\)B-pH calibration has not evolved through time and therefore that the pH (and hence CO\(_2\)) we reconstruct here is an accurate record of the surface water carbonate system parameter. This finding indicates that disagreements between published Pliocene δ\(^{11}\)B-based datasets\(^{12,13,20,23}\) are likely attributable to either: (i) sampling driven aliasing due to the relatively large short-term CO\(_2\) variability in the mPWP (e.g.}
Figure 2. Top panel: Red circles and lines show $\delta^{11}$B-derived CO$_2$ data from *Globigerinoides ruber* at ODP Site 999 (this study and Martinez-Boti et al.\textsuperscript{13}, Chalk et al.\textsuperscript{18}), red squares are *Trilobatus sacculifer* at ODP 999 (this study and Seki et al.\textsuperscript{14}), purple squares are *T. sacculifer* from ODP 668 (Honisch et al.\textsuperscript{23}) and blue squares are *T. sacculifer* from ODP 926 (Sosdian et al.\textsuperscript{20}). Black solid line shows ice core-derived CO$_2$ from ref. \textsuperscript{30}.

Left; Late Pleistocene CO$_2$ from boron isotopes\textsuperscript{14,18,23,52} and ice core data. Also shown are CO$_2$ projections in line with RCP8.5 at current emission rates to the year 2040 (black broken line). Middle column; MPT CO$_2$ estimates\textsuperscript{18,23} including disturbed ice estimates\textsuperscript{14,25} (Note: age adjusted for scale). Right; mPWP estimates of CO$_2$ (this study combined with Martinez-Boti et al.\textsuperscript{13}), new data from *T. sacculifer* is shown in red squares and shows no offset from *G. ruber* estimates. Second panel: Time periods as above, LR04 and ODP 999 $\delta^{18}$O from *C. wuellerstorfi*\textsuperscript{18,19,53}.

Third panel: Iron mass accumulation rate from the Southern Atlantic ODP Site 1090\textsuperscript{28}. Fourth panel: % Northern Component Water (NCW) estimated from $\delta^{13}$C in benthic foraminifera (grey) and $\varepsilon^{15}$Nd from fish debris (dark green) in the deep North Atlantic (core U1313\textsuperscript{31}). Note the lag of ocean circulation and CO$_2$ relative to the M2 glaciation\textsuperscript{31}.

Figure 2), (ii) differences in core site location between studies (with possible different local CO$_2$ disequilibrium), (iii) the lack of a comparison between species on exactly the same sample, or (iv) the well-documented analytical offset between MC-ICPMS and negative-ion thermal ionization mass spectrometry (NTIMS; see refs. \textsuperscript{21,22}). We note that, if the offset is attributable to analytical issues, the agreement between data generated by both methodologies for the younger Pleistocene time slices examined here (Fig. 2) confirms the suggestion of Sosdian et al.\textsuperscript{20} that the *T. sacculifer* dataset of Bartoli et al.\textsuperscript{12} (measured with NTIMS) requires an additional analytical correction (see ref. \textsuperscript{16} for details), beyond that currently used for the NTIMS $\delta^{11}$B datasets of refs. \textsuperscript{17,23}.

mPWP CO$_2$ cycles – variability and causes. Our new high-resolution data set clearly demonstrates that the mPWP is an interval of relatively high CO$_2$ with a mean of 367 ppm whereas lower values are observed during the mid- and late-Pleistocene (262 ppm and 241 ppm\textsuperscript{18}, respectively Fig. 2). Our dense sampling permits, for
the first time, an assessment of CO2 variability during mPWP on orbital timescales, although the length of our record still precludes reliable time series analysis. The CO2 cycles (and derived climate CO2 forcing) we observe in the mPWP (including the M2 glaciation) are similar, yet smaller in amplitude, than those evident in δ18O-CO2 data from the Late Pleistocene (LP = 0–250 kyr; ref. 18) and early mid-Pleistocene Transition (eMPT = 1050–1250 kyr; Figs. 2 and 3). The variation in climate forcing between these different intervals correlates with the magnitude of δ18O variability, although there is an apparent increased response in δ18O during the late Pleistocene (δ18O range ~ 2‰) relative to the mPWP (δ18O range ~ 0.5–1‰ Fig. 3; ref. 13) likely reflecting the increased influence of ice-volume change on δ18O following the northern hemisphere glaciation 13.

We also compare the δ11B-derived CO2 data with ice-core based CO2 for the Pleistocene intervals 18,23 (Supplementary Fig. 4). We expect the range of CO2 variability from the various Antarctic ice cores to be narrower than our marine-based records because of the greater precision associated with the ice core records (±6 ppm vs. ±20–30 ppm) and the CO2 data from blue ice from the mid-Pleistocene may not capture a full climate cycle 24,25. Despite these caveats, and as discussed elsewhere 18,25, there is good agreement between the ice-core and δ11B-derived CO2, providing confidence in the accuracy of the distribution (and absolute values) we determine here for the mPWP.

Three phenomena are suggested to exert a major control over glacial-interglacial CO2 change in the Late Pleistocene record: (i) changes in stratification south of the Antarctic Polar Front influencing the ventilation of CO2-rich circumpolar deep water; 19 (ii) variations in the magnitude of dust-borne Fe fertilization in the sub-Antarctic that influences the strength of the biological pump in this region; 27,28 (iii) changes in the extent to which southern component deep water fills the North Atlantic increasing deep ocean carbon storage 29. Ref. 30 proposed that polar waters in the North Pacific and the entire Southern Ocean (SO) were destratified prior to the onset of Northern Hemisphere Glaciation at 2.7 Ma. This mechanism may contribute to elevated CO2 during the mPWP 30, but it would also rule out water mass ventilation in the high-latitude SO as an important driver of the CO2 cycles we observe in the mPWP. Both the accumulation and variability of dust-borne Fe at ODP Site 1090 (Fig. 2) were reduced during the mPWP to a fraction of that observed in the other time intervals examined (~600 kyr; Figs. 2 and 3). The variation in climate forcing between these different intervals correlates with the magnitude of δ18O variability, although there is an apparent increased response in δ18O during the late Pleistocene (δ18O range ~ 2‰) relative to the mPWP (δ18O range ~ 0.5–1‰ Fig. 3; ref. 13) likely reflecting the increased influence of ice-volume change on δ18O following the northern hemisphere glaciation 13.

M2 Glaciation – the role of CO2. Marine Isotope Stage M2 (at 3.3 Ma) is an anomalously cold stage clearly evident in the LR04 δ18O stack 33 and many other temperature records, such as arctic air temperature 33 and sea surface temperature 34,35 (including site ODP 999, supplementary Fig. 6) It is also often described as a failed attempt at Northern Hemisphere Glaciation 34,36,37, that eventually initiated ~600 kyr later at ~2.6 Ma. Refs. 13,14 used δ11B-CO2 to suggest that CO2 dropped below 280 ppm for the first time during the intensification of Northern Hemispheric
Glaciation (INHIG), consistent with the suggestion that 280 ppm CO2 is an important threshold below which extensive glaciation of continents in the northern hemisphere develops. Our new data reveal that while the lower bound of the error envelope in our smoothed CO2 record approaches this value, atmospheric CO2 during M2 is unlikely to have crossed this threshold. Furthermore, in our records, CO2 variability associated with M2 lags δ18O by 10 kyr, which also means that minimum CO2 is not coincident with minimum northern hemisphere orbital forcing (Supplementary Fig. 5). Additional support for CO2 playing a secondary role in M2 is that other periods of low CO2 are evident in the mPWP (Fig. 2). For instance, the KM2 glaciation is clearly evident in the benthic δ18O data, Mg/Ca-SST at site 999 (Fig. 2 and Supplementary Fig. 6) and our CO2 record, but is not considered to be a major glacial interval (Fig. 2). This therefore suggests that other boundary conditions, such as orbital configuration, were perhaps dominant in triggering the M2 cold stage.

M2 Glaciation - CO2 lags δ18O. Minor dephasing between εNd, δ13C and benthic δ18O has been observed in the late Pleistocene, with carbon budget change lagging δ18O and preceding the change in ocean circulation, but with smaller lags than we observe during M2 (~2.5 ky vs. ~10 ky).

Similarly, while variations in atmospheric CO2 are not entirely in phase with ice volume changes over the late Pleistocene, the leads-lags are small (<3 ky) and are not readily observed when comparing δ13C-derived CO2 and benthic foraminiferal δ18O time series (e.g. Figure 2 left panels). This therefore either requires the operation of subtly distinct carbon-cycle dynamics during the Pleocene, and M2 in particular, or implies some other driver operated to explain the observed ~10 kyr lag of CO2 during M2.

One possible non-carbon cycle driver for the observed lag at M2 could be a preservation bias in our data because partial dissolution of planktic foraminiferal tests drives δ11B towards more negative isotopic composition (lower pH, higher CO2) in some species. However, while our chosen species for pH/CO2 reconstruction, G. ruber, is known to be relatively susceptible to partial dissolution on the seafloor, its δ11B signal has been observed to be robust. Furthermore, a recent study of test weight and fragmentation at ODP 999 showed that tests become better preserved during M2 (Supplementary Fig. 7), as observed during glacial periods of the late Pleistocene. This is inconsistent with the high CO2 observed during the descent into M2 maximum (especially given fragmentation and δ18O are in phase, Supplementary Fig. 7), ruling out an effect of partial dissolution on our CO2 reconstruction and observed lag.

An alternative explanation for the delayed pH change observed at ODP 999 during M2 lies in local water mass changes during this glacial episode. Although the Central American Seaway was closed to deep water by this time, it is possible that limited exchange of surface water was still occurring around M2 and the early Pleistocene. Temperature data from Mg/Ca in T. sacculifer and G. ruber at site 999 (this study, Supplementary Fig. 6, data from the East Equatorial Pacific site 1241 is also shown for comparison) show a cooling prior to the M2 maximum. A connection between the East Equatorial Pacific and the Caribbean, or local intensification in upwelling could have brought cold, nutrient- and carbon-rich waters (low Mg/Ca, low pH) to Site 999, potentially explaining the apparent high CO2 at the inception of M2. However, because no noted decline in the abundance of G. ruber occurred, this is a species known to favour oligotrophic conditions, it is seems unlikely this was accompanied by a significant influx of such water. Also, a mechanism for increased influx of EEP water during sea level regression is lacking. Importantly, during KM5c (3205ky), the CAS likely remained closed impeding the influx of Pacific waters to site 999, as shown by elevated temperature (relatively to the M2 interval) in the Caribbean (Supplementary Fig. 6), hence local changes in hydrography are unlikely to have unduly impacted our CO2 estimates for this central interval.

The cause of the apparent lag of CO2 compared to δ18O during the inception of M2 therefore remains uncertain, but because this lag is also present in North Atlantic εNd records we favour a carbon cycle-based interpretation. A Southern Ocean-driven explanation for the CO2 lag during M2 is perhaps indicated by the observation that the tail of the CO2 decline during M2 is out of phase with decline in northern hemisphere insolation, but apparently in-phase with insolation decline at 65°S (i.e. offset by one half precession cycle, Supplementary Fig. 5).

Past to future – when will we exceed mPWP CO2 levels? Atmospheric CO2 has been increasing since the industrial revolution from a background of ~280 ppm, reaching 411 ppm in 2019. The mPWP is often cited as being the last time CO2 levels were as high as today, although we note methane and other greenhouse gases remain poorly constrained and may contribute to extra radiative forcing.

Our refined view of CO2, during this interval however reveals that in terms of the mean (367 ppm), mPWP values were exceeded in the mid-1990s. Our upper quartile range (394–39 ppm) suggests that CO2 during the mPWP is very likely to have been <427 ppm (using the distinctions of the IPCC). Atmospheric CO2 rose by 2.5 ppm from 2017 to 2018, if this rate is sustained, our new data indicate that CO2 will surpass even the highest mPWP values within the next 5 to 6 years (2025–2026).

Conclusions
Our new δ11B-data for the mPWP provide a tightly constrained and robust estimate of CO2 during KM5c of 391–39 ppm (at 95% confidence), and documents CO2 variability during the mPWP from 330 to 34 ppm. This extended view suggests that changes in ocean carbon storage may play an important role in natural variability in CO2 on orbital timescales in warmer than present climate states. By better constraining the upper levels of CO2 during the mPWP we conclude that, given current rates of CO2 increase, we will very likely surpass mPWP values within 4 to 5 years, meaning that, by 2024/2025 levels of atmospheric CO2 will be higher than any point in the last 3.3 million years.
Methods
ODP Site 999 is located in the Caribbean Sea and has been reliably used to reconstruct past atmospheric CO2 in a number of previous studies. Air-sea disequilibrium for CO2 in the surface waters in the region of ODP Site 999 are close to 0 (+20 ppm) today and ref. 13 suggest this remained the case for at least the last 3.3 million years. An age model for the interval 3.15 to 3.35 Ma studied here was constructed by analyzing the epibenthic foraminifera Cibicidoides wuellerstorfi for δ18O in each sample, combining these data with similar data from ref. 33, and tuning the combined record to the LR04 benthic δ18O stack19 (Fig. 1). From each sample, ~120 individual tests of the mixed layer dwelling species Globigerinoides ruber white sensu stricto (300–355 μm) were hand separated, clay removed, oxidatively cleaned and analyzed for boron isotopic (δ11B) and trace element composition (e.g. Mg/Ca, Al/Ca) at the University of Southampton using well-established procedures21,52. These data were converted to pH using the G. ruber δ11B-pH calibration of ref. 39 and a modern δ11B of seawater44 (39.6‰). Sea surface temperatures (SST) were derived from each sample Mg/Ca ratio using the calibrations of ref. 55 corrected for the changing Mg/Ca for seawater following ref. 36 based on ref. 36.

It was recently suggested7 that the δ11B-pH calibration for G. ruber may have varied over the last 3.5 million years. We therefore also analyse T. sacculifer (300–355 μm) from two samples from ODP 999 to combine with existing T. sacculifer data14,20,52 to provide a test of the G. ruber δ11B-pH calibration of ref. 39. Following previous studies14, uncertainty relating to the following factors, including uncertainty in the δ11B-pH calibration, were propagated using a Monte Carlo approach (n = 10,000): temperature (±1.5 °C, 2σ), salinity (± 3 psu, 2σ), δ11Bsw (± 0.2, 2σ; refs. 20,57), analytical uncertainty (± 0.12–0.3‰, 2σ; see Supplementary Table 2).

In order to calculate atmospheric CO2 from the reconstructed surface water pH we use dissolved inorganic carbon (DIC) from the reconstructions of ref. 39. Uncertainty in this term is also propagated into CO2 uncertainty using a Monte Carlo approach (n = 10,000), but with a uniform distribution encompassing the range of the reconstructed DIC for our study interval (1765 to 1840 μmol/kg). CO2 was then determined by the maximum probability of all 10,000 realisations.

To obtain CO2 during the KM5c interglacial the mean and associated uncertainty of the reconstructed borate δ11B and SST of the data lying within ±7 kyr of the peak of KM5c (n = 5) was determined. In our age model we defined that the peak of KM5c was at 3212 kyr, although expanding the window to ±15 kyr, or uncertainty in the identification of the peak of KM5c to within 10 kyr, did not have a significant effect on our calculated mean (Supplementary Table 1).

This average was then used to calculate pH and CO2, but only considering the uncertainty in δ11Bsw and DIC detailed above. This approach was chosen because it allows the random uncertainties arising from SST and δ11B measurement error to be reduced through replication, whilst still realistically accounting for the systematic uncertainties in δ11Bsw and DIC.

In order to place our new data into a Plio-Pleistocene context, we recalculated the δ11B data of ref. 13 from 3.0 to 3.3 Ma using the same methodology outlined here and combined it with our new data. The difference in the method is the choice of the second carbonate parameter where constant modern alkalinity is used in ref. 13 whereas we use DIC20 in this study. These new and published data are then combined into a single record with an average temporal resolution of 1 sample every 4 kyr. This was then interpolated to 1 kyr resolution and a 6-point running mean was used to reduce the influence of analytical uncertainty on our reconstructed CO2 record. Uncertainty in the smoothed record was determined using the output of the original Monte Carlo simulation.

CO2 forcing was calculated relatively to preindustrial CO2 (278 ppm) and is defined as:

\[ (R_{\text{CO2}}) = \ln \frac{\text{CO2}}{\text{CO2}_{\text{preind}}} \]

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Author contributions
E.d.l.V., G.L.F. and T.B.C. wrote the manuscript. E.d.l.V. generated boron isotope and element data. R.P.B. and T.B.C. generated oxygen and carbon isotope data. P.A.W. provided input on the manuscript. All authors contributed to the interpretation of the data.

Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to E.d.l.V.

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