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Antarctic Ice Sheet sensitivity to atmospheric CO₂ variations during the early to mid-Miocene

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Geological records from the Antarctic margin offer direct evidence of environmental variability at high southern latitudes and provide insight regarding ice sheet sensitivity to past climate change. The early to mid-Miocene (23 to 14 million years ago) is a compelling interval to study as global temperatures and atmospheric CO2 concentrations were similar to those projected for coming centuries. Importantly, this time interval includes the Miocene Climatic Optimum (MCO), a period of global warmth during which average surface temperatures were 3 to 4°C higher than today. Miocene sediments in the AND-2A drill core from the Western Ross Sea, Antarctica indicate that the Antarctic Ice Sheet (AIS) was highly variable through this key time interval. A multi-proxy dataset derived from the core identifies four distinct environmental "motifs" based on changes in sedimentary facies, fossil assemblages, geochemistry, and paleotemperature. Four major disconformities in the drill core coincide with regional seismic discontinuities and reflect transient expansion of grounded ice across the Ross Sea. They correlate with major positive shifts in benthic oxygen isotope records and generally coincide with intervals when atmospheric CO_2 concentrations were at or below pre-industrial levels (~280 ppm). Five intervals reflect ice sheet minima and air temperatures warm enough for substantial ice mass loss during episodes of high (\sim 500 ppm) atmospheric CO₂. These new drill core data and associated ice sheet modelling experiments indicate that polar climate and the AIS were highly sensitive to relatively small changes in atmospheric CO₂ during the early to mid-Miocene.

Antarctica | Ice Sheet | Climate Optimum | Ross Sea | Miocene

Introduction

Knowledge regarding Antarctic Ice Sheet (AIS) response to warming climate is of fundamental importance due to the role ice sheets play in global sea level change. Paleoenvironmental records from Earth's past offer a means to examine AIS variability under past climatic conditions that were similar to today and those projected for the next several decades (1, 2). In this respect, the early to mid-Miocene is a compelling interval to study as proxy reconstructions of atmospheric CO_2 , albeit uncertain, suggest that concentrations generally varied between pre industrial levels (PAL=280ppm) and values at or above 500ppm (3-9). Additionally, global mean surface temperature during peak Miocene warmth was up to 3 to 4 degrees higher than today (10), similar to 'best-estimate' temperatures expected by 2100 under the highest projected greenhouse gas concentration pathway (RCP 8.5) (1, 2). Finally, Miocene geography was similar to today (11) and major circum-Antarctic oceanic and atmospheric circulation patterns that dominate the modern Southern Ocean were well established (12, 13).

Much of our understanding regarding AIS history through the early to mid-Miocene comes from far field records from deep ocean basins. Benthic oxygen and carbon isotope proxies for global paleoclimate suggest that early to mid-Miocene climate and glacial environments were highly variable (14-19). These records include evidence for major transient glacial episodes and sea level fall, intervals of relative ice sheet stability, and periods of climatic warmth with major ice sheet retreat and sea level rise. Furthermore, reconstructions from sedimentary sequences on the Marion Plateau, offshore NE Australia (20), and New Jersey margin (21) suggest sea level varied by up to 100 m. Episodes of sea level maxima (+40 m) suggest loss of Antarctica's marine-

Significance

New information from the AND-2A drill core and a complementary ice sheet modelling study, show that polar climate and Antarctic Ice Sheet (AIS) margins were highly dynamic during the early to mid-Miocene. Changes in extent of the AIS inferred by these studies suggest that high southern latitudes were sensitive to relatively small changes in atmospheric CO_2 (between 280 and 500 ppm). Importantly, reconstructions through intervals of peak warmth indicate that the AIS retreated beyond its terrestrial margin under atmospheric CO_2 conditions that were similar to those projected for the coming centuries.

Reserved for Publication Footnotes

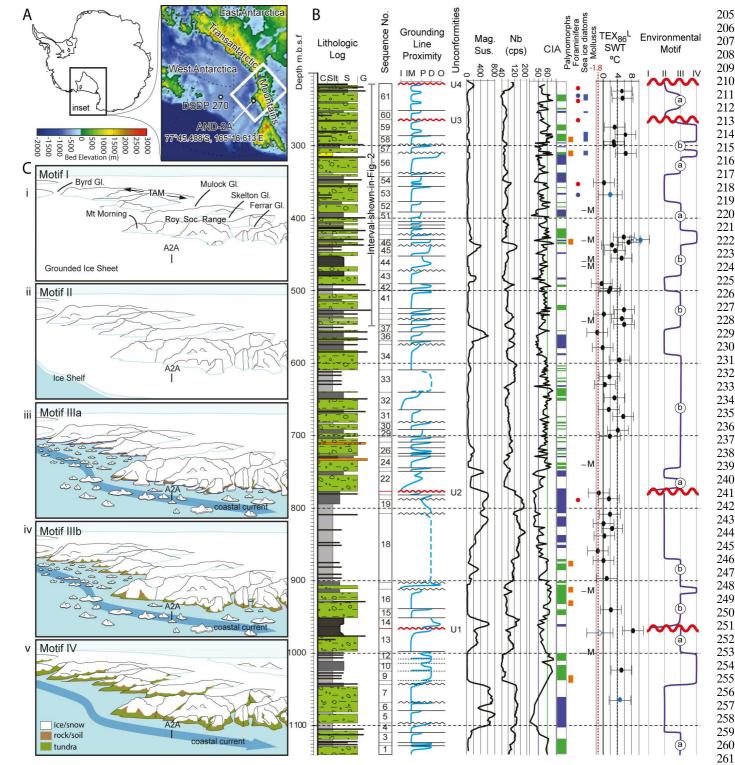


Fig. 1. A. Map showing Ross Sea area (inset) and AND-2A drill site (white box indicates approximate area for schematic reconstructions shown below). B. Stratigraphic summary of lower 925 m of AND-2A (214.13 to 1138.54 mbsf) showing 61 sedimentary cycles. Glacial proximity curve tracks relative position of the grounding line through ice-contact (I), ice-marginal (IM), ice-proximal (P), ice-distal (D) and open marine (O) environments. Continuously acquired data sets include magnetic susceptibility and Niobium (Nb) XRF-CS counts. Chemical Index of Alteration (CIA) (curve and bar) indicates arid (< 50, blue) and less arid (> 60, green) conditions. Intervals of peak palynomorph concentration shown by orange boxes. Foraminifera assemblages include cold water/ice marginal benthic species (red circles) and cool water planktonic species (blue circles). Blue bars = sea-ice diatoms. M=intervals with well-preserved molluscs. Sea water temperature estimates based on TEX₈₆^L(black circles) and Δ_{47} (blue circles, open = less well preserved specimens). Environmental Motif (LIV).

based ice sheets that, at present, occupy much of West Antarctica and large portions of East Antarctica (22), as well as substantial

loss of mass from Antarctica's terrestrial ice sheets. Episodes

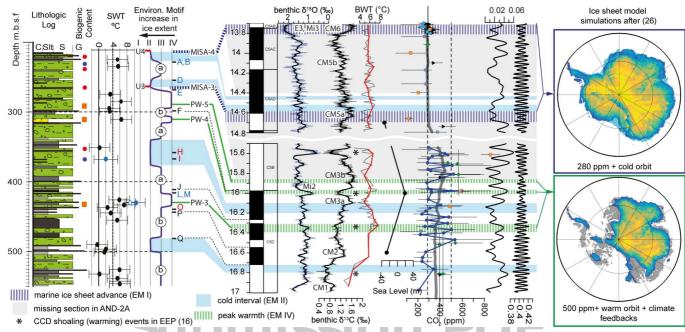


Fig. 2. Mid-Miocene section of AND-2A (557.35 to 214.13 mbsf) correlated to the Geomagnetic Polarity Timescale (46) and selected data sets. See Fig. 1 caption for description of AND-2A data. Letters A-Q indicate position of key age model constraints (see SI text, Fig. S2, and Table S1 for details). Benthic δ^{18} O and δ^{13} C isotope data with moving averages (thick lines) from IODP Sites U1338 and U1337 (14, 15). Mi events after (19) and E3 oxygen isotope excursion after (16). CM = carbon isotope maxima (18, 39). Asterisks = carbon minima events and intervals of major shoaling of the carbonate compensation depth in the eastern equatorial Pacific (15). Bottom water temperature reconstructions from (17) with 30 pt spline smooth (red line)(note: age model from (17) adjusted by ~+50kyrs for section between 15.5 and 17Ma). Sea level data from the Marion Plateau (20). Proxy atmospheric CO₂ data include boron isotopes (3-5) (blue circles), alkenones (3, 6) (black triangles), stomata (7) (green diamonds), and paleosols (orange squares). Thick grey line = 21 point weighted average. Grey shaded 'boxes' = time missing in unconformities; MISA (blue dashed line) = maximum ice sheet advance (EMI); blue shaded 'zones' = cold polar intervals (EMIV). Orbital eccentricity and obliquity from (48). Ice sheet simulations after (25).

of maximum sea level fall (up to -60m) suggest that the AIS occasionally grew and advanced across continental shelves.

Results

Geological records proximal to Antarctica's coastal margin provide direct evidence of past ice sheet variability in response to changing global climate. The AND-2A drill core, a 1,138 meterlong stratigraphic archive of climate and ice sheet variability from the McMurdo Sound sector of the western Ross Sea (77°45.488'S, 165°16.613'E), was recovered by drilling from an \sim 8.5 m thick floating sea-ice platform in 380 m of water, located ~30 kilometres off the coast of Southern Victoria Land (SVL) (Fig. 1A) (23). The drill core comprises lower Miocene to Quaternary glacialmarine strata deposited in the steadily subsiding Victoria Land Basin (VLB)(24). Paleogeography was broadly similar to today although continental shelves in the Ross and Weddell seas were likely shallower (SI text). Recovered core sediments, and proxies they contain, allow us to assess past ice sheet dynamics along a coastal margin influenced by ice flowing from East Antarctica and across the West Antarctic continental shelf. Through analysis of an integrated proxy environmental data set we derive a new environmental reconstruction, and combine this with a suite of global environmental data to establish a history of AIS response to global climate events and episodes during the early to mid-Miocene. This integrated data set allows us to evaluate key drivers of high latitude climate and ice sheet variability between 21 and 13 Ma. Outcomes from research reported here and in a companion ice sheet modelling study (25) suggest the AIS advanced across continental shelves during cold orbital configurations and retreated well inland of the coast under warm orbits. This large range of AIS variability occurred under a relatively low range in atmospheric CO₂ concentration (\sim 280 to 500 ppm) and indicates the Antarctic environment was highly sensitive during the early to mid-Miocene.

A near-continuous record spanning 20.2 to ~15 Ma is preserved in the lower 925 meters of AND-2A (Figs. 1B; S2; S3; Table S1). A diverse range of geological information including physical properties and sedimentological, paleontological, and geochemical data were collected (summarised in SI text and published (23, 26-33)). Here we present new data including sea surface water (upper 200 m) temperatures (SWTs) derived from archaeal lipids (TEX^L₈₆) and carbonate isotopes (Δ_{47}), whole rock inorganic geochemical data, and an integrated age model, and offer the first analysis of a combined proxy environmental data set derived from AND-2A (Figs. 1B; S3). These paleoenvironmental data are used to define four characteristic environmental motifs (**EM**) (Table S2) that reflect distinct climatic and glacial regimes (Fig. 1A and B).

Intervals of maximum ice sheet extent and cold polar conditions are assigned to **EM I (maximum ice)** and are characterised in AND-2A by four major disconformities. These disconformities are relatively rare and represent distinct and discrete times of major ice sheet advance beyond the drill site onto the continental shelf (Fig. 1Ci). Three disconformities AND2A-U1 (965.43 meters below sea floor, mbsf); -U2 (774.94 mbsf); and -U3 (262.57 mbsf) span the time intervals ~ 20 to 19.8 Ma, ~ 18.7 to 17.8 Ma, and ~15.8 to 14.6 Ma, respectively (Fig. S2). A fourth major disconformity AND2A-U4 (214.13 mbsf) separates middle Miocene rocks (> ~14.4 Ma, Fig. S2) from 214 meters of overlying upper Miocene to Quaternary strata.

Miocene to Quaternary strata.401Eight stratigraphic intervals in AND-2A are assigned to EM402II (cold polar), as characterised by high magnetic susceptibility403(MS), high Niobium (Nb) content, and low Chemical Index of404Alteration (CIA), all of which reflect sediment derived from local405volcanic centers and unweathered outcrop in proximal regions406of the Transantarctic Mountains (TAM). We infer that relative407increases in local sediment are due to advance of ice from ex-408

409 panding ice caps on nearby Mount Morning and the Royal Society 410 Range under a cold polar climate. Five of the eight intervals are 411 dominated by massive to stratified diamictite facies that often 412 contain debris derived from local volcanic sources and were prob-413 ably deposited beneath a floating ice tongue or ice shelf proximal 414 to the grounding line of outlet or piedmont glaciers (Fig. 1Cii). 415 Each of these intervals is typically fossil-poor. TEX^L₈₆-derived 416 SWT's range between -1.4 and 2.6 ±2.8°C and are supported by a 417 Δ_{47} derived value of 2.1 ±3.7°C at 366 mbsf. We infer that proxies 418 in EM II reflect cold polar conditions with minimum grounding-419 line variability and persistent floating ice shelves and/or coastal 420 fast ice.

421 Twelve stratigraphic intervals are assigned to EM III (cold 422 temperate) as characterised by low to moderate MS, low to 423 moderate Nb content and moderate to high CIA. These data 424 indicate variable sediment provenance and periodic input from 425 local volcanic sources and/or unweathered outcrop. EM III is 426 divided into sub-types 'a' and 'b' based on variations in lithofacies 427 and fossil content. EM IIIa is dominated by stratified diamictite 428 and gravel with variable clast composition but including a high 429 proportion of rock fragments sourced from the region south of 430 Skelton and Mulock glaciers. Foraminifera vary in abundance and 431 are absent in many intervals but include up to ten species in others 432 (30). Marine diatoms and terrestrial palynomorphs are usually 433 absent but occur in low abundance in several discrete intervals. 434 Mollusc-bearing intervals are uncommon. TEX^L₈₆-derived SWTs 435 range between 2.2 and 5.4°C ±2.8°C. Intervals characterised by 436 EM IIIa likely reflect a sub polar climate and glacial regime with 437 tidewater glaciers. Periodic increase in gravel clasts derived from 438 regions south of Mount Morning reflect an increase in ice flux 439 through major East Antarctic Ice Sheet (EAIS) outlet valleys into 440 fjords under warmer conditions. During these intervals, calving 441 rates at the grounding-line increased and debris-laden icebergs 442 delivered sediment to the drill site as they drifted northwards 443 along the SVL coast (Fig. 1Ciii). 444

EM IIIb has persistently low Nb and MS, reflecting minimal 445 input from local volcanic sources. Lithofacies are diverse and 446 include massive and stratified diamictite and gravel; clast com-447 position is mixed, with a high proportion of lithologies derived 448 from the Skelton and Mulock glaciers and as far south as the 449 Carlyon and Byrd glaciers. Intervals of mudrock dominated se-450 quences are more common in EM IIIb than in EM IIIa. Terrestrial 451 palynomorphs are more abundant in several intervals of EMIIIb 452 (e.g., 947.54; 922.61; and 593.29 mbsf) and discrete intervals 453 bearing mollusc fossils occur occasionally (Figs. 1B; S3). TEX^L₈₆-454 derived SWTs range from 0.2 to 6.7°C ±2.8°C. We infer that EM 455 IIIb reflects a depositional setting similar to EM IIIa but with a 456 generally warmer climate, particularly during periods when SWTs 457 were 6-7°C ±2.8°C and local ice cap margins retreated to the coast 458 and had limited influence on marine sedimentation at the drill 459 site. Coarse clastic sediment was primarily delivered to the drill 460 site by debris-rich icebergs derived from large fast flowing outlet 461 glaciers to the south. Increased abundance of Podocarpites spp. 462 and Nothofagidites spp. pollen (Figs. 1B; S3) indicates local tundra 463 occupied ice-free regions along the coastal margin (Fig. 1Civ). 464

Five relatively short, lithologically diverse, stratigraphic intervals are assigned to **EM IV (minimum ice)** as characterised by low MS, low Nb content and high CIA, which indicate minimal sediment input from local volcanic sources and/or unweathered outcrop. Lithofacies are variable but sequences are usually dominated by mudrock, sandstone, and thin diamictite. A 46 meterthick section between 996.69 and 1042.55 mbsf incorporates five sequences dominated by sediments deposited within a marinedeltaic setting distal to the glacial margin (27). The interval between 428.28 and 436.18 mbsf incorporates a single sequence comprising a basal diamictite overlain by a sandstone unit with relatively abundant marine bivalves. Thick-shelled costate scal-

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lops as well as venerid clams recovered from this interval indicate 477 that water temperatures were at least 5°C warmer than in the 478 479 Ross Sea today (29). Relatively warm water temperatures are supported by TEX₈₆^L and Δ_{47} data, which indicate SWT at the 480 coastal margin reached a maximum between 7.0 ±2.8°C and 10.4 481 482 ±2.5°C. In-situ pollen and spores are abundant in this interval 483 and indicate a coastal vegetation of mossy tundra with shrub 484 podocarps and southern beech and suggest a cool terrestrial 485 climate (10°C January mean air temperature) (31-33). Evidence 486 for another interval of 'warm' climate is also preserved in a unique 487 diatom-rich unit at \sim 310 mbsf. This unit contains a 'typical' 488 tundra pollen assemblage recovered from other EM IV units but 489 also includes freshwater algae and cosmopolitan dinoflagellate 490 taxa that indicate much warmer temperatures than occur in the 491 Ross Sea today (32). Furthermore, TEX_{86}^{L} analyses from the 492 diatomite unit indicate maximum surface water temperatures of 493 \sim 6 to 7°C ±2.8°C, which is consistent with values inferred from 494 the fossils (29, 32) (SI text). EM IV records times when the AIS 495 margin retreated well inland and tundra occupied ice free regions 496 from the coast to at least 80 km inland (34)(Fig. 1Cv). 497

Discussion

Proxy environmental data derived from AND-2A indicate coastal environments in SVL were highly variable throughout the early to mid-Miocene (Figs. 1B; 1C). A robust age model for the AND-2A core (see methods and SI text) allows us to integrate environmental data from the Antarctic coastal margin with regional seismic data from the Ross Sea continental shelf (35), deep sea oxygen and carbon isotope data (14, 15), sea level records (20), and atmospheric CO_2 reconstructions (3-9)(Figs. 2; S5). We acknowledge that the age model for each data set has uncertainties and caution that both proxy CO₂ reconstructions and sea level records are presently limited in temporal resolution and subject to large uncertainties. Despite these limitations, our correlation framework (Figs. 2; S5) highlights several distinct episodes of: (1) cold climate and marine-based ice sheet advance, (2) peak warmth and maximum ice sheet retreat, and (3) cold climate with relatively stable terrestrial ice sheets, which are discussed in detail below.

516 Four episodes of Maximum Ice Sheet Advance in the Ross 517 Sea (MISA-1 to MISA-4) are documented between 21 and 13 518 Ma (Figs. 2; S5). MISA episodes are recorded by stratigraphic 519 gaps in AND-2A that correlate approximately in time with one 520 of the major Ross Sea Unconformities (RSU's) that formed 521 during ice sheet advance across the continental shelf (35). Each 522 MISA episode also correlates generally with an interval of global 523 sea level fall, enrichment in deep-sea benthic $\delta^{\rm 18}O,$ increase in 524 benthic δ^{13} C values, and decrease in bottom water temperature 525 (BWT) (Figs. 2; S5). These patterns suggest episodes of maxi-526 mum ice sheet advance were not restricted to the Ross Sea but 527 represent continental scale expansion of the AIS. Importantly, 528 our correlation model suggests that these MISA episodes co-529 incided generally with eccentricity minima and intervals when 530 atmospheric CO_2 concentrations were below 300 ppm (4, 5). 531 MISA-3 (\sim 14.6 – 14.7 Ma) best illustrates these associations (Fig. 532 2) and is characterised by a \sim 30 m drop in sea level (20), a 2 533 to 3°C decrease in BWT in the Southern Ocean (17), a 0.75‰ 534 enrichment in δ^{18} O, a major increase in δ^{13} C (CM 5 of (18)) and 535 a decrease in atmospheric CO₂ concentration to \sim 300 ppm (4, 536 5). MISA-4 (\sim 13.7 –14.1 Ma)(Fig. S5) coincides with the major 537 Mi-3/E3 oxygen isotope excursion (16, 19), a drop in sea level of 538 \sim 60 m (20), a 2 to 3°C decrease in BWT (17), and a drop in CO₂ 539 below 300 ppm (3, 5)(Fig. 2; Fig. S5). MISA-3 and -4 correspond 540 in time with RSU 4, a surface that displays erosional features 541 with relief similar to bathymetric troughs that formed beneath 542 ice streams during recent glaciations (36). RSU 4 likely formed 543 during a phase of ice sheet advance and retreat that began ~ 14.6 544

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Ma and culminated in the Miocene Climate Transition (MCT) 545 and maximum ice sheet advance at 13.8 Ma. This phase of cold 546 547 climate and persistent marine based ice sheets ended at ${\sim}10$ Ma 548 when ice retreated to the terrestrial margins as revealed by upper 549 Miocene mud-rich sediments in AND-1B (37). 550

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Five episodes of Peak Warmth (PW-1 to PW-5), during which AIS grounding-lines retreated inland of the coastal margin, are also recorded. PW episodes are characterised by warm climate indicators in AND-2A (EM IV) that coincide generally with times of elevated BWT, depleted δ^{18} O values, eccentricity maxima, low δ^{13} C values, and relatively high atmospheric CO₂ concentrations (Figs. 2; S5). Intervals PW-3, -4, and -5 occurred between 16.4 and 15.8 Ma (Fig. 2) and offer insight into AIS response during the MCO. Ice-distal sediments in these intervals are relatively rich in terrestrial palynomorphs, and proxies indicate that SWTs in the Ross Sea were 6-10°C warmer than today. PW-4 (16 Ma) best illustrates these relationships as it correlates with a major (~ 0.5 ‰) decrease in δ^{18} O, a 0.4‰ decrease in δ^{13} C, a 2 to 3°C increase in BWT at ODP Site 1171 (17), and a 10 to 20 m rise in sea level across the Marion Plateau (20). Importantly, proxy data show that atmospheric CO_2 concentrations were >500 ppm during this warm episode (4, 7) (Fig. 2), which suggests that high latitude climate and Antarctica's terrestrial ice sheets were sensitive to CO_2 levels much lower than climate models suggest (38).

An unusual period of cold and relatively stable climate is suggested by proxies in the prominent thick interval of finegrained sediments between 901.54 to 774.94 mbsf in AND-2A (Sequence 18, Fig. 1B; S3). This unique stratigraphic interval is characterised by very low amounts of pollen and spores and persistently low SWTs (-1.3 to 2.6°C). Foraminifera and diatoms are rare to absent. We infer the mudstone accumulated in a dark environment beneath semi-permanent sea ice or an ice shelf. Interestingly, this interval correlates to upper Chron C6n, a time interval characterised by stable sea level (21) and low variability in orbital eccentricity (Fig. S2). Collectively these data suggest that global climate and the AIS remained relatively stable through several glacial-interglacial cycles spanning at least 500 kyrs.

We conclude that environmental data from AND-2A and key far-field records suggest that Antarctica's climate and ice sheets were highly variable during the early to mid-Miocene. Whereas orbital variations were the primary driver of glacial cycles (28, 33, 39), atmospheric CO_2 variations modulated the extent of ice sheet advance and retreat. Specifically, coldest conditions and maximum ice sheet growth (MISA episodes and EM II) occurred generally during eccentricity minima and when atmospheric CO₂ was low (<400 ppm). Peak warmth and maximum AIS retreat occurred during eccentricity maxima and intervals of high CO₂ (≥500 ppm). Numerical climate and ice sheet model simulations produced in our companion study (25) (Fig. 2) support these observations and simulate grounding line advance across Antarctica's continental shelves under cold orbits and low CO2 (280 ppm) but maximum retreat under warm orbital configuration and high CO_2 (500 ppm). Together, these studies suggest that polar climate and the AIS were highly sensitive to relatively small changes in atmospheric CO_2 during the early to mid-Miocene.

Summarv

Our analysis of the AND-2A drill core and synthesis with regional and global data show that the early to mid-Miocene Antarctic coastal climate was highly variable. During relatively short-lived intervals of peak warmth summer land surface air temperature was at least 10°C, tundra vegetation extended to

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locations 80 km inland (34, 40), surface water temperatures in 613 the Ross Sea were between 6 and 10°C, and the AIS retreated 614 inland. During intermittent intervals of peak cold climate, vegetation vanished and the AIS grew and advanced into the marine environment, expanding across the continental shelf.

Whereas glacial cycles were paced by orbital variability through the early to mid-Miocene, maximum ice sheet retreat occurred when atmospheric CO₂ was \geq 500 ppm and maximum advance when CO₂ was \leq 280 ppm (Figs. 2; S5) (4). New numerical ice sheet simulations (25) also show that the Miocene AIS expanded across the continental shelf when atmospheric CO_2 was low (280 ppm) and retreated well inland of the coast when CO_2 was high (500 ppm). These ice sheet proximal data and model simulations support inferences from benthic deep sea records that suggest the global climate system and AIS were 628 highly sensitive during the mid-Miocene (14-16). These results 629 are consistent with observations and numerical climate and ice sheet simulations based on the warm Pliocene (41-44), which 630 631 indicate that sustained levels of atmospheric $CO_2 > 400$ ppm may 632 represent a stability threshold for marine-based portions of the West and East Antarctic ice sheets. Furthermore, outcomes from our complementary drill core analysis and ice sheet modelling indicate that Antarctica's terrestrial ice sheets were vulnerable when atmospheric CO₂ concentrations last exceeded 500 ppm. Given current atmospheric CO₂ levels have risen above 400 ppm (45) and are projected to go higher (2), paleoclimate reconstructions such as this one for the early to mid-Miocene imply an element of inevitability to future polar warming, Antarctic ice sheet retreat, and sea level rise. 642

Methods and Materials

Methods are presented in detail in SI text and (23). AND-2A was described using standard sedimentological techniques to produce detailed stratigraphic logs (27). An age model for the core (SI text, Fig. S2) utilises magnetostratigraphy, biostratigraphy, ⁸⁷Sr/⁸⁶Sr dating of macrofossils, and ⁴⁰Ar-³⁹Ar ages on lava clasts and tephra layers to correlate rock units to the Global Polarity Timescale (46). Assemblages of fossil pollen, dinoflagellates, diatoms, foraminifera, and molluscs were used to constrain paleoenvironmental conditions. A standard suite of continuous physical properties was collected on whole and split core and in the borehole. Whole rock inorganic geochemical data were collected at high sampling resolution using an X-ray fluorescence core scanner (XRF-CS). Additional chemical data were collected from discrete bulk sediment samples at lower resolution to provide calibration points for near-continuous non-invasive sampling obtained via XRF-CS. Concentrations of Al₂O₃, Na₂O, CaO, K₂O, P₂O₅, and total organic carbon (TOC) from bulk sediment samples were used to calculate the CIA (47). Samples for TEX^L₈₆ were prepared at Utrecht University and LC-MS analyses performed at the Royal Netherlands Institute for Sea Research. Samples for Δ_{47} (clumped isotopes) were prepared and analysed at the California Institute of Technology.

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