letters to nature

process can be applied to single-crystal growth of other materials that have hexagonality in their crystal structures. □

Methods

EPD evaluation by molten KOH etching

EPDs have been considered to be the density of dislocations exposed at the substrate surface. The molten KOH etching was performed at 773 K for 20–30 min in a nickel crucible. After the etching, etch pits were observed by optical microscopy. The field of view at each observation point was $870 \times 650\,\mu m$. The observation points were located in tetragonal grids, and the distance between each point was 2.0 or 3.0 mm.

Synchrotron monochromatic beam X-ray topography

The experiment was done at SPring-8 (BL20-B2). The topographies were taken with Berg-Barrett geometry with the diffraction plane of $11\bar{2}8$. Incident X-ray energy was 11.94 keV, and immersion depth of reflection beam was about $4\,\mu m$. The topographies in Fig. 3 were obtained by continuous scan of incident angle (ω), and the zebra patterns to evaluate the curvature radius of crystal lattice planes were taken by step scan of that. Dislocations in the topography appear as black or white lines or dots.

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Ionic liquids and eutectic mixtures as solvent and template in synthesis of zeolite analogues

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The challenges associated with synthesizing porous materials[1] mean that new classes of zeolites (zeotypes)—such as aluminosilicate zeolites[2,3] and zeolite analogues[4]—together with new methods of preparing known zeotypes[5], continue to be of great importance. Normally these materials are prepared hydrothermally with water as the solvent in a sealed autoclave under autogenous pressure[6]. The reaction mixture usually includes an organic template or 'structure-directing agent' that guides the synthesis pathway towards particular structures. Here we report the preparation of aluminophosphate zeolite analogues by using ionic liquids[7] and eutectic mixtures[8]. An imidazolium-based ionic liquid acts as both solvent and template, leading to four zeotype frameworks under different experimental conditions. The structural characteristics of the materials can be traced back to the solvent chemistry used. Because of the vanishingly low vapour pressure of ionic liquids, synthesis takes place at ambient pressure, eliminating safety concerns associated with high hydrothermal pressures. The ionic liquid can also be recycled for further use. A choline chloride/urea eutectic mixture[8] is also used in the preparation of a new zeotype framework.

Ionic liquid solvents are commonly defined as salts that are fluid at near-ambient temperatures (less than $\sim100\,^{\circ}C$)[7] and consist of predominantly ionic species. For the purposes of this work we can use a broader definition of an ionic liquid as any salt that melts below the temperature used in the synthesis of zeolites (typically $150-200\,^{\circ}C$). Even when an organic salt melts at a higher temperature, mixing it with other compounds (such as urea or metal chlorides) can depress the melting point to produce liquids with significant ionic character at suitable temperatures. These are known as eutectic mixtures. A particular example of this is the hydroxyethyltrimethylammonium chloride (choline chloride, melting point $\sim300\,^{\circ}C$) mixture with urea in a 1:2 ratio, which has a melting point of $12\,^{\circ}C$ (ref. 8).

There are very few examples of the use of ionic liquids in the preparation of porous materials, and no reports of zeolites or microporous solids prepared by using ionic liquids or eutectic mixtures, either as solvents or templates. High-melting dialkylimidazolium hydroxide salts, which are not ionic liquids, have been used as templates in aqueous solvents[9] and there is one report of the use of 1-alkyl 3-methyl imidazolium bromides to template a non-zeolitic porous solid, MCM-41, which is an amorphous silica material[10]. The pure organic salts in the latter example are ionic liquids. However, the actual solvent used in the preparation of MCM-41 is an aqueous solution containing only a small amount of the dialkylimidazolium salt. In this case the liquid phase is predominantly molecular, and the formation of MCM-41 relies on the water, which combines with the surfactant nature of the organic salt to produce the micelles required in the mechanism of the reaction. In both cases cited above the preparations use the traditional hydrothermal synthesis approach. However, ionic liquids have been used as solvents in the preparation of an aerogel[11]. Here we present the first use of ionic liquids and eutectic mixtures in the preparation of crystalline zeolites. Not only do the ionic liquids act as solvent, they also provide the template cations around which the

inorganic frameworks order. We show further that the syntheses rely on the solvent's being predominantly ionic, because sufficient quantities of molecular water disrupt the reaction, preventing the formation of zeolites. We term this procedure ionothermal synthesis to distinguish it from hydrothermal preparations, which take place in a predominantly molecular solvent. In addition we show that reactant quantities of mineralizers such as fluoride can be used to control the product of the reactions.

1-Methyl 3-ethyl imidazolium bromide (melting point 83 °C) was used as both solvent and template in the synthesis of four different aluminophosphate zeotype frameworks, depending on the synthesis conditions used (Fig. 1). At 150 °C a novel structure type, SIZ-1 (St Andrews Ionic Liquid Zeotype-1) was formed, and its structure was solved by single-crystal X-ray diffraction on Station 9.8 at the Synchrotron Radiation Source, Daresbury, UK (see Supplementary Information for details). The structure of SIZ-1 (Fig. 2) consists of hexagonal prismatic units known as double six rings joined to form layers that are linked into a three-dimensional framework by units containing four tetrahedral centres (two phosphorus and two aluminium) known as single four rings. The formula of the material is $Al_8(PO_4)_{10}H_3 \cdot 3C_6H_{11}N_2$ but the Al–O–P alternation is maintained. The framework is therefore interrupted, with some unusual intraframework hydrogen bonding (Fig. 2). The negative charge present on the framework (caused by the existence of terminal P–O bonds[12]) balances the charge on the 1-methyl 3-ethyl imidazolium templates that are present in the pores. The overall structure of SIZ-1 (Fig. 2) shows a two-dimensional channel system parallel to the a and b crystallographic axes.

The choline chloride/urea eutectic mixture (melting point 12 °C) can also be used to prepare a novel zeotype framework, which we name SIZ-2. The Al–O–P alternation is maintained, but the chemical formula $(Al_2(PO_4)_3 \cdot 3NH_4)$ indicates that SIZ-2 is also an interrupted structure (Fig. 3). In this case it is ammonium, formed on the partial decomposition of the urea, which acts to template the structure and balance the charge on the framework. The pore architecture displays three small intersecting channels parallel to the three crystallographic directions. These pores are too small to adsorb anything except the smallest molecules, but preliminary ion exchange experiments indicate that the ammonium can be at least partly exchanged for metal cations such as Cu^{2+}.

Interrupted aluminophosphate structures have the advantage of comprising anionic frameworks and can have interesting properties[13–16]. The disadvantage of interrupted materials is that they are
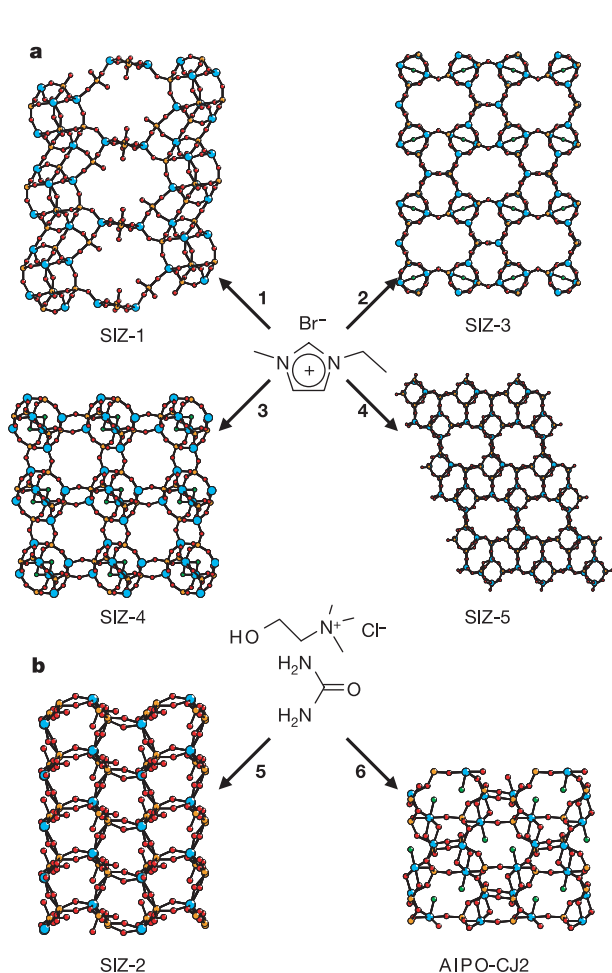

Figure 1 The synthesis of zeotypes by using ionic liquids and eutectic mixtures. **a**, 1-Ethyl 3-methyl imidazolium bromide can be used as both solvent and template to prepare SIZ-1, SIZ-3, SIZ-4 and SIZ-5. SIZ-3 and SIZ-4 are prepared in the presence of fluoride and SIZ-5 in the presence of excess water. **b**, A choline chloride/urea eutectic mixture can be used to prepare SIZ-2 in the absence of fluoride or excess water, and to prepare AIPO-CJ2 in the presence of fluoride or excess water. Conditions for reactions 1–6 are given in Table 1. Orange, cyan and red spheres correspond to phosphorus, aluminium and oxygen atoms respectively.
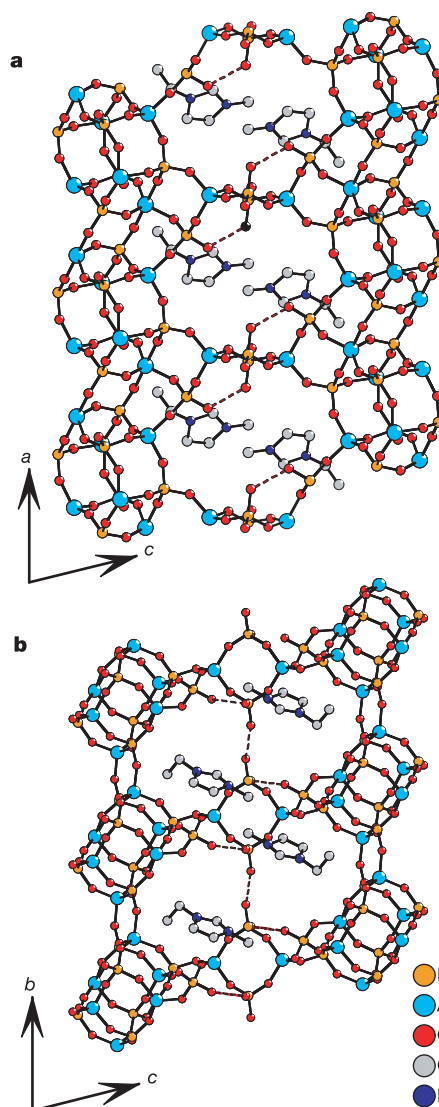

Figure 2 Two views of the SIZ-1 structure. **a**, Down the b-axis. **b**, Down the a-axis. In both views only one of the three disordered 1-ethyl 3-methyl imidazolium cations is shown for clarity. Intra-framework hydrogen bonds are shown as dotted lines.

invariably less thermally stable than their fully condensed counterparts. Mineralizing agents such as fluoride are known to promote T–O–T (where T represents a tetrahedral atom) bond formation[17]. Addition of fluoride to the synthesis mixtures does indeed lead to the formation of the fully condensed zeotype structure SIZ-3 ($Al_5P_5O_{20}F_2 \cdot 2C_6H_{11}N_2$), which has the AlPO-11 framework structure[18]. SIZ-4 ($Al_3P_3O_{12}F \cdot C_6H_{11}N_2$), which has the triclinic AlPO-34 structure[19,20], is also formed in the presence of fluoride but when

great care is taken to remove most of the water present in the starting materials by careful evaporation of the excess water in the reaction mixture before the reaction (Table 1). Addition of fluoride to the choline chloride/urea eutectic mixture results in the formation of a non-zeolitic aluminophosphate known as AlPO-CJ2 (Fig. 1)[21]. AlPO-CJ2 can also be prepared without fluoride but with excess water; hydroxide substitutes for fluoride in the final structure.

The lack of vapour pressure from the ionic liquid means that these synthetic procedures can be performed in open vessels, avoiding the high autogenous pressures (up to 15 bar at 200 °C) and associated safety concerns that accompany hydrothermal synthesis in sealed autoclaves[22]. SIZ-3 and SIZ-4 can both be prepared in round-bottomed flasks under ambient pressure by this method. In all cases the ionic liquid can be recycled and used in subsequent preparations.

The ionic liquid solubilizes the starting materials almost completely at the reaction temperatures, indicating that the synthesis mechanism is a crystallization from solution rather than a solid-to-solid transformation. The dependence of the products on water also gives some clues as to the mechanism of the reaction. Ionic liquids of this type are hydrophilic and it is almost impossible to dry them completely. However, infrared[23] and molecular dynamics studies[24] indicate that small amounts of water (for example at molar ratios of less than 10%) are present as isolated molecules that interact very strongly with the anions of the ionic liquids. The liquids in such situations are still overwhelmingly ionic in character. The interaction of water with the anions is probably so strong that it is effectively shielded from interaction with the Al- and P-containing ions that are solubilized by the cations of the ionic liquid. The interaction between the cations of the ionic liquid and the framework species (whether they are fully solubilized or at the surface of a growing crystallite) is the basis of the strong templating effect seen in these studies. The addition of fluoride ions helps to solubilize Al- and P-containing species in the ionic liquid even further through the formation of oxyfluoride anions in the solution, as well as catalysing the development of the Al–O–P bonds that are necessary for the crystallization of the solid[17].

Potentially the most important feature of this ionothermal synthesis mechanism is the removal of the competition between template–framework and solvent–framework interaction that is present in hydrothermal preparations. The structure-directing properties of templates are often not as specific as we should like[25], but in a system in which an ionic liquid is both solvent and template the negatively charged atoms at the surface of a growing framework will always be interacting primarily with the templating cation rather than with a mixture of template and solvent. Recent modelling studies indicate that the structure of imidazolium-based ionic liquids is characterized by long-range correlations and distributions that reflect the asymmetric structures of the cations[26]. Long-range asymmetric effects of this kind potentially increase the like-
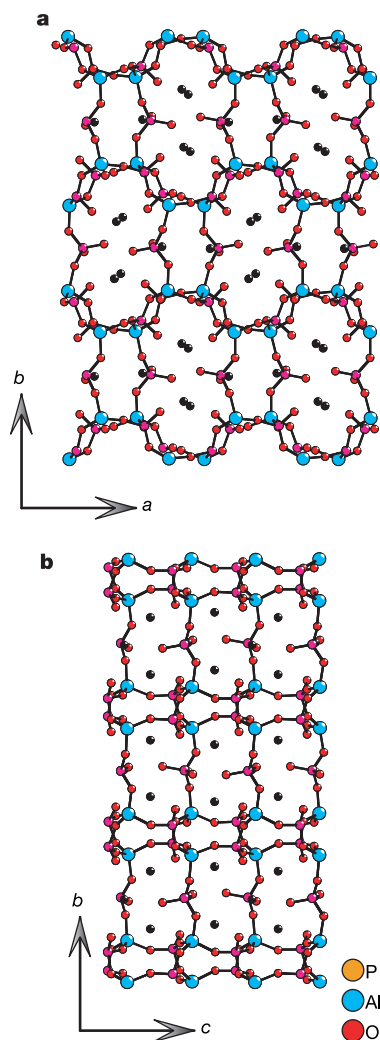

Figure 3 Two views of the structure of SIZ-2. **a**, Down the *c*-axis. **b**, Down the *a*-axis. The nitrogen atoms from the ammonium ions located in the pores of the structure are shown as black spheres.

Table 1 **Synthesis details and conditions for the preparation of materials**

Product	Al(OiPr)$_3$	H$_3$PO$_4$	HF	Water	IL	Temp. (°C)	Time (h)
			Mass of reagents added (g) (molar ratio of reagents)				
SIZ-1	0.1018 (1.0)	0.1732 (3.0)	0.00 (0.0)	* (2.9)	4.05 (43)	150	66
SIZ-3	0.1013 (1.0)	0.1732 (3.0)	0.015 (0.73)	* (3.8)	4.07 (43)	150	68
SIZ-4	0.1054 (1.0)	0.1772 (3.0)	0.015 (0.70)	* (0.0)	3.82 (39)	150	68
SIZ-5	0.0465 (1.0)	0.0858 (3.1)	0.00 (0.0)	0.495 (116)	2.03 (44)	150	19
Product	Al(OiPr)$_3$	H$_3$PO$_4$	HF	Water	EU	Temp. (°C)	Time (h)
SIZ-2	0.1007 (1.0)	0.171 (3.0)	0.00 (0.0)	* (2.9)	5.13 (40)	180	72
ALPO-CJ2†	0.1059 (1.0)	0.175 (2.9)	0.00 (0.0)	0.557 (62)	4.91 (37)	180	72
ALPO-CJ2‡	0.1024 (1.0)	0.178 (3.1)	0.015 (0.7)	* (3.8)	5.32 (41)	180	72

Al(OiPr)$_3$, Al[OCH(CH$_3$)$_2$]$_3$; EU, eutectic mixture; IL, ionic liquid.
*No extra water was added in these preparations. Small amounts of water present came from the aqueous HF and H$_3$PO$_4$ solutions and the ionic liquid.
†No added fluoride.
‡Fluoride added.

lihood of transferring chemical information from the template cation to the framework, a situation that is desirable if full control over the templating process is to be achieved.

With the addition of larger quantities of water the liquid becomes less ionic and more molecular in character, and water molecules begin to form large hydrogen-bonded clusters and networks that percolate through the whole liquid phase[24]. This change in the molecular structure of the solvent changes the reactions drastically, and the dense phase berlinite ($AlPO_4$) becomes the favoured product. The presence of a hydrogen-bonded water network thus disrupts the ionic-liquid–framework interactions to such a degree that they are completely removed from the important crystallization steps in the reaction mechanism. As even more water is added so that it becomes by far the major chemical species, the solvent becomes predominantly molecular and cannot now be described as an ionic liquid. The reaction in such solvents is hydrothermal in nature and is similar to the traditional method of preparing zeolites.

The trends in reaction products are the same for both the fluoride and non-fluoride syntheses. Under ionothermal conditions (low or zero added water) the zeotypes described above are produced. At intermediate water concentrations only dense phases are produced and under hydrothermal conditions a different zeotype framework is formed; at water contents in which the ionic liquid/water ratio is less than 1:2.5, SIZ-5—which has the AlPO-41 framework[27]—is the major product, with a small amount of dense-phase impurity (Table 1).

Functional aluminophosphates require aliovalent doping to produce an anionic framework. Typically this is achieved by using silicon to produce silicoaluminophosphate materials. Silicon can be incorporated into the SIZ-4 structure with the use of this synthetic procedure, pointing to potential catalytic applications of such materials. Gallium can also be doped into the structure in the same way.

The use of ionic liquids and eutectic mixtures as solvent and template opens up many new possibilities in the preparation of zeolites and related porous solids. The relative lack of mineralizers in the pure ionic liquid solvent is probably the controlling reason why interrupted structures are formed when no fluoride is added. This gives us the possibility of selectively targeting interrupted frameworks (for example, for ion-exchange applications) or fully condensed zeotypes depending on which type of material is required. The scope for this preparative method is further emphasized if one realizes that there are at least a million binary ionic liquids and potentially more than 10^{18} ternary ionic liquids and eutectic mixtures[7] (compared with only about 600 molecular solvents, most of which have a polarity that makes them completely unsuited to this type of chemistry). Many of these ionic liquids will be structurally related to each other and might template the same frameworks (so-called default structures), so it is unlikely that 10^6 new materials will be prepared. However, the results reported here indicate that multiple frameworks are possible even from the same ionic liquid system. Computational enumeration predicts that several thousand zeolite structures are possible[28], and there is clearly scope for new synthesis methodologies to target these new materials. As long as kinetic considerations do not limit the method to the production of a small number of default structures, the ionothermal approach reported here might be a route for the preparation of many previously unknown materials. We are currently extending the ionic liquid chemistry to explore whether this is a general route to novel solids and to establish the chemical properties of the materials prepared. □

Methods

Synthesis of 1 ethyl 3-methyl imidazolium bromide

1-Ethyl 3-methyl imidazolium bromide (hereafter referred to as IL) was prepared in 94% yield from 1-methylimidazole and ethyl bromide as described[29].

Synthesis of choline chloride/urea eutectic mixture

Choline chloride/urea eutectic mixture was prepared from choline chloride and urea in a 1:2 ratio as described[8].

Synthesis of zeolite analogues in sealed autoclaves

A typical synthesis procedure was as follows: a Teflon-lined autoclave (volume 23 ml) was charged with IL or choline chloride/urea eutectic mixture, $Al[OCH(CH_3)_2]_3$ (Aldrich) and H_3PO_4 (85 wt% in water; Aldrich). Distilled water or HF (48 wt% in water; Aldrich) was added if required. The stainless steel autoclave was then heated in an oven to the required temperature. The reagent masses, temperatures and length of time left in oven needed to produce the pure phase materials are as detailed in Table 1. These conditions were optimized by changing the reaction compositions (for example, the water content) slightly and characterizing the resulting products. The yields for the reactions, quoted with respect to the aluminium-containing starting material, range from 50–60% for SIZ-1 (51%), SIZ-3 (56%) and SIZ-4 (50%) to almost 100% for SIZ-1 and SIZ-5. However, it should be noted that both SIZ-1 and SIZ-5 samples tend to contain small amounts of amorphous phosphate-rich material.

For the SIZ-4 synthesis the $Al[OCH(CH_3)_2]_3$, H_3PO_4 and HF were added to the Teflon liner. This was then heated to 50 °C on a hotplate for 2 h to remove the water and any propan-2-ol formed during the initial reaction. This was confirmed by following the mass of the mixture until no more mass loss was observed. The IL was then added and the synthesis proceeded as normal.

After the autoclave had been cooled to room temperature the product was suspended in distilled water, filtered by suction and washed with acetone. The products were all white crystalline solids.

Replacement of the IL with the symmetric ionic liquid (1,1′-dimethyl 3,3′-hexamethylene diimidazolium dibromide) also leads to the production of SIZ-3 or SIZ-4 under the same conditions as those in Table 1. Silicon can be incorporated into the SIZ-4 framework structure by adding about 0.06 mol equivalents of a silica source (Cab–O–Sil) into the reaction listed in Table 1. Similarly gallium can be incorporated by adding Ga_2SO_4 to the reaction mixtures.

^{13}C magic-angle spinning NMR indicates that the 1-methyl 3-ethyl imidazolium cation is intact in the pores in SIZ-1, SIZ-3, SIZ-4 and SIZ-5; its presence is confirmed by single-crystal X-ray diffraction studies in SIZ-1 and SIZ-4. SIZ-3, SIZ-4 and SIZ-5 are all very thermally stable. Heating in oxygen at 500 °C leads to the removal of the organic cation and the fluoride to leave the empty zeotype frameworks. The interrupted structures, SIZ-1 and SIZ-2, are less thermally stable and collapse at ~250 °C as the organics are removed from the structures (see Supplementary Information for full characterization details of all materials).

Synthesis of zeolite analogues in round-bottomed flasks

SIZ-3 and SIZ-4 can be prepared in an open container using the conditions from Table 1. A round-bottomed flask fitted with a condenser, magnetic stirrer and drying tube was charged with the starting materials and then heated to the target temperature (150 °C) for the required duration. The products were recovered as described above.

Recycling of ionic liquid

After the zeotype had been filtered off, the filtrate was centrifuged to remove any remaining small solid particles. The water and acetone were removed from the ionic liquid by rotary evaporation. The remaining product was dissolved in excess dichloromethane and magnesium sulphate was added. This was stirred for 30 min and then filtered under suction. The dichloromethane was removed by rotary evaporation. Ethyl acetate was added and the solidified ionic liquid precipitated from solution. This was filtered, then washed with ethyl acetate and dried under vacuum at 25 °C for 10 h to give IL. About 80% of the mass of ionic liquid used in the original preparation could be recovered. Note, however, that some was used up as a template and so was not available for recycling; the real recycling efficiency was therefore greater than 80%. The ionic liquid was characterized by ^{1}H NMR. The IL was then used successfully in the preparation of zeotypes SIZ-3 and SIZ-4.

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Similar meltwater contributions to glacial sea level changes from Antarctic and northern ice sheets

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The period between 75,000 and 20,000 years ago was characterized by high variability in climate[1–12] and sea level[13,14]. Southern Ocean records of ice-rafted debris[15] suggest a significant contribution to the sea level changes from melt water of Antarctic origin, in addition to likely contributions from northern ice sheets, but the relative volumes of melt water from northern and southern sources have yet to be established. Here we simulate the first-order impact of a range of relative meltwater releases from the two polar regions on the distribution of marine oxygen isotopes, using an intermediate complexity model. By comparing our simulations with oxygen isotope data from sediment cores, we infer that the contributions from Antarctica and the northern ice sheets to the documented sea level rises between 65,000 and 35,000 years ago[13] were approximately equal, each accounting for a rise of about 15 m. The reductions in Antarctic ice volume implied by our analysis are comparable to that inferred previously for the Antarctic contribution to meltwater pulse 1A (refs 16, 17), which occurred about 14,200 years ago, during the last deglaciation.

Greenland ice-core records show strong climate fluctuations between 75 and 20 kyr BP: the Dansgaard–Oeschger (DO) cycles[1–3]. Abrupt warmings of 6–10 °C occurred throughout the mid- to high-latitude North Atlantic region at a spacing of about 1,500 yr (refs 4, 5). Each initiated a relatively warm DO interstadial, during which a gradual cooling trend developed that eventually culminated in rapid 'collapse' to the next cold DO stadial. DO-style variability was widespread throughout the northern hemisphere and beyond[5–9].

Antarctic ice-core records follow a different 'rhythm', with fewer and temporally more symmetrical climate fluctuations. The timing relationship between DO-style and Antarctic-style fluctuations was established with the use of atmospheric methane data from ice cores[10] and was corroborated by work on marine sediment core MD952042 from 3,146 m depth off Portugal[12]. The $\delta^{18}O$ record for surface-water planktonic foraminifera in MD952042 shows DO-style variability, whereas that for bottom-dwelling benthic foraminifera mimics Antarctic-style variability[12]. The latter is observed also in SW Pacific core MD972120 from 1,210 m depth[9], showing the global nature of the benthic signal.

The widespread benthic $\delta^{18}O$ signal suggests a relationship between variations in southern high-latitude climate and global ice volume (sea level). However, benthic $\delta^{18}O$-based sea level reconstructions might be biased by deep-sea temperature changes: 1 °C error translates to about 30 m uncertainty in sea level. Efforts to separate ice volume from temperature influences on benthic $\delta^{18}O$ indicate rapid and high-amplitude ice-volume variability during the last glacial cycle[14]. Independent sea level quantification from the Red Sea method is coherent with both the absolute values from fossil reef data and the structure of benthic $\delta^{18}O$ records[13]. It indicates that sea level rose by about 30 m, at 2 m per century, in association with the 2–3 °C warming of Antarctic climate events A1–4 (Fig. 1a)[13].

Although the Antarctic-style timing of sea level change might imply Antarctic ice-volume variations, it is equally possible that southern high-latitude climate fluctuations were driven by oscillations in climate and ice volume on the Northern Hemisphere[18,19], because Antarctic ice volume is often considered relatively stable, with its full glacial–interglacial variability contributing less than 25 m to the roughly 120 m global sea level change[20–24], and because models forced with meltwater additions into the North Atlantic and Arctic show interhemispheric temperature fluctuations similar to those observed in ice cores[18,19]. However, recent work has challenged the notion of Antarctic stability on the basis of distinct ice-rafted debris (IRD) peaks in Southern Ocean records, preceded by −0.5‰ to −0.9‰ shifts in surface-water foraminiferal $\delta^{18}O$ (ref. 15; Fig. 1c). A predominantly Antarctic origin has also been inferred for meltwater pulse (mwp) 1A, a sea level rise of about 20 m in about 500 yr during the last deglaciation[16,17].

Here we assess the origins of the meltwater pulses that caused sea level rises associated with Antarctic warming events A1–4 (Fig. 1a), by using marine $\delta^{18}O$ as a sensitive tracer for input of isotopically light high-latitude melt water. Away from its surface-bound source and sink terms, $\delta^{18}O$ in sea water behaves as a conservative, passive tracer. Crucially, past seawater $\delta^{18}O$ changes are reflected in $\delta^{18}O$