compound may undergo a spin crossover from one state to the other. The energy match between Δ and P can be achieved through a careful choice of ligands. The crossover may then be induced by several factors, such as temperature, pressure, or exposure to light. It is accompanied by a change in the optical and magnetic properties of the material (*10*). In the case of iron(II), the high-spin state is generally strongly colored and paramagnetic, whereas the low-spin state is generally pale yellow to colorless and diamagnetic. Several metal ions will undergo spin crossover behavior, but most known examples contain iron(II).

The fine control between Δ and P required for spin crossover is exhibited in the new complex of Halder *et al.* (*9*) in an unusual way. When the guest alcohol molecules are present in the lattice, roughly half of the iron atoms in the lattice undergo a spin crossover at low temperature. But when the guest molecules are removed, no spin crossover is observed, even though the guest alcohol molecules are not bound to any of the iron(II) atoms. One explanation is that hydrogen bonds between the alcohol guests and other ligands on the iron atoms are responsible for the change. A second possibility is the change induced in the lattice by the presence or loss of the guests.

It is not unusual for a host lattice to collapse upon loss of guest molecules. This collapse often leads to the irreversible destruction of the host lattice (*11*). In some systems, the cavities and pores are durable and do not change substantially in the absence of guest molecules (*12*). In unusual cases, the cavity may collapse to give an amorphous material and then regain crystallinity upon reintroduction of the guest (*13*), or crystallinity may be retained upon guest loss, but with a significant decrease in the cell volume (*14*).

The material of Halder *et al.* (*9*) is unusual in that the loss of guest molecules causes a substantial rearrangement of the lattice, with the crystals expanding in volume by 6%, even though the volume of the pores relative to the total volume of the crystal drops from 12% to 2%. Yet the sample remains crystalline throughout the transition. Crystallinity is retained even when the guest molecules are reabsorbed and the original structure regenerated. The material is composed of two interpenetrating lattices, and it may be the ability of these two lattices to slip past each other that provides the flexibility needed to allow such drastic changes without shattering the crystals.

Recent work has shown that the field of crystal engineering is entering a new age. Exciting results such as those of Halder *et al.* (*9*) demonstrate the versatility of solid-state structures and the ability of metal-organic structures to incorporate functionality that will allow for exciting magnetic, electrical, and optical properties. These advances will expand the uses of porous materials far beyond the well-developed catalytic systems.

References

1. A. Corma, *Chem. Rev.* **97**, 2373 (1997).
2. L. G. Beauvais, J. R. Long, *J. Am. Chem. Soc.* **124**, 12096 (2002).
3. O. M. Yaghi *et al.*, *Acc. Chem. Res.* **31**, 474 (1998).
4. M. Du *et al.*, *Inorg. Chem.* **41**, 4904 (2002).
5. G. Desiraju, *Acc. Chem. Res.* **35**, 565 (2002).
6. S.-I. Noro *et al.*, *Angew. Chem. Int. Ed.* **39**, 2081 (2000).
7. K. S. Min, M. P. Suh, *J. Am. Chem. Soc.* **122**, 6834 (2000).
8. J. A. Real *et al.*, *Science* **268**, 265 (1995).
9. G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science* **298**, 1762 (2002).
10. P. Gütlich, Y. Garcia, H. A. Goodwin, *Chem. Soc. Rev.* **29**, 419 (2000).
11. S. Subramanian, M. J. Zaworotko, *Angew. Chem. Int. Ed. Eng.* **37**, 1461 (1995).
12. M. Eddaoudi *et al.*, *Science* **295**, 469 (2002).
13. J. S. Seo *et al.*, *Nature* **404**, 982 (2000).
14. M. P. Suh, J. W. Ko, H. J. Choi, *J. Am. Chem. Soc.* **124**, 10976 (2002).

PERSPECTIVES: OCEANOGRAPHY

Oceanic Salt Switch

Ed Boyle

On page 1769 of this issue, Adkins *et al.* (*1*) report data constraining the salinity (and density) of ocean deep waters during the last glacial period. In contrast to today's ocean, they find that at the last glacial maximum, the saltiest waters formed in the Southern Ocean. Global ocean circulation must thus differ substantially between glacial and warm (interglacial) periods.

Knowledge of the salinity is important for understanding glacial circulation because the deep sea is filled with the densest waters formed at high latitudes. Whether the deep circulation is properly described as a density-driven "thermohaline circulation" or whether it should really be understood as a wind- and tide-driven "meridional overturning circulation" has been the subject of a recent Perspective (*2*). It is clear, however, that density gradients in the deep sea are a key characteristic of ocean circulation patterns and that the deep sea today is filled by the densest waters whose density was established at high latitudes (*3*).

In the modern ocean, the densest deep waters are found in the Mediterranean Sea. This water is not very cold, but it is very salty. Mixing near the Gibraltar Sill greatly reduces the density of this water as it enters the open Atlantic, and it therefore does not sink to great depths.

The densest waters filling the open ocean form in the Antarctic (Antarctic Bottom Water, AABW). These waters are extremely cold but less salty than the ocean average (see the table). The second densest water in the ocean is formed at several sites in the high-latitude North Atlantic and its adjacent seas (North Atlantic Deep Water, NADW). These waters are not as cold as the AABW but are more salty (due to an excess of evaporation over precipitation in the Atlantic Basin and its adjacent seas).

The NADW is only slightly less dense than the AABW despite a substantially warmer temperature. Both appear to form at approximately equal rates when integrated over the whole ocean overturning time (~1000 years) (*4*). In the Pacific Ocean, no deep water forms in the northern high latitudes, and deep waters are thus a mixture of Atlantic and Antarctic waters, slightly freshened by mixing with low-salinity water from intermediate depths.

It has been clear for some time that the deep ocean was much colder at the last glacial maximum (LGM) than it is today (*5*–*8*). In contrast to today's deep sea, the temperature gradients in the deep sea appear to have been subtle at the LGM. It has also been evident that in the glacial North Atlantic, nutrient-depleted northern source waters were found at shallower depths than today, and the deepest north Atlantic basin they fill today was instead occupied by nutrient-rich water from the Southern Ocean (*9*, *10*).

Adkins *et al.* now demonstrate that the saltiest water in the glacial deep ocean was found in the Southern Ocean, a dramatic change from modern conditions, where the saltiest deep-ocean water derives from the North Atlantic. This conclusion derives from data on the chlorinity (total concentration of silver-titratable halides) of pore waters in marine sediments sampled by the Ocean Drilling Program (ODP).

During the last glacial period, massive continental glaciers covered northern North America and Fennoscandia. The Antarctic ice sheet was also thicker than it is today. These glaciers and ice sheets stored so much water that the sea level was

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lowered by 120 to 135 m. The withdrawal of freshwater left the ocean about 3% saltier than it is today. This salty water diffused into the pore waters of deep-sea sediments by ionic diffusion.

Typical effective diffusion coefficients are $\sim 10^{-6}$ cm^2/s in marine sediments, an order of magnitude slower than in aqueous solutions, because of the blocking effects of sedimentary particles. Classical physics tells us that the average distance attained during a diffusive random walk will depend on the square root of the diffusion coefficient times the time (~10 m per ~20,000 years; ~100 m per 2,000,000 years). Although the deepest glaciation persisted for about 15,000 years (from 30,000 to 15,000 years before present), extensive glaciers also existed during the previous period (~70,000 to 30,000 years before present). The salty water therefore penetrated several tens of meters into marine sediments.

TEMPERATURE AND SALINITY OF OCEAN DEEP WATERS

	Present[1]		Last glacial maximum[2,3]	
	T (°C)	S (‰)	T (°C)	S (‰)
Atlantic	~2.0	~34.9	−1.5 ± 0.5	36.0 ± 0.2
Antarctic	~0.0	~34.7	−1.2 ± 0.5	37.2 ± 0.5
Pacific	~1.0	~34.6	−1.3 ± 1.0	36.2 ± 0.1

[1] Although temperature and salinity are measured extremely precisely in the modem ocean, the deep sea contains a range of values; these numbers are chosen as a "mode" in the volumetric distribution.

[2] Errors include the best estimate of propagation of uncertainties in data and curve fits; Altantic errors include the difference between two sites.

[3] The average LGM salinity is ~3% higher because of the withdrawal of water into massive continental ice sheets.

When glaciers melted at the end of the LGM, the waters overlying the sediments became fresher. This fresh water also began diffusing downward, continuing to the present day. This diffusive salt signal is mathematically analogous to the thermal diffusion signal observed in ice core and continental bore holes (*11*, *12*). A similar process has been occurring for the stable isotopic properties of seawater (δ^{18}O and δD). The lighter isotope of both of these isotope pairs was locked up in glaciers, leaving the ocean enriched in the heavier isotopes, which diffused downward into the sedimentary pore waters. When the glaciers melted, oceanic δ^{18}O and δD decreased, and this signal is now diffusing downward into the pore waters.

There are two key requirements for interpreting this signal. First, δ^{18}O, δD, and chlorinity must be measured with very high precision because diffusion from the modern ocean has erased a large part of the signal. Second, the primary signal must be extracted from the observations with a sediment pore water advection-diffusion model.

Knowledge of such chlorinity and isotopic gradients dates back to measurements on Deep Sea Drilling Project (DSDP) cores in the 1980s (*13*, *14*). McDuff (*15*) laid out the theoretical basis for the interpretation of this evidence with respect to glacial/interglacial fluctuations. Diffusion and advection of isotopes and ions must be modeled in a sedimentary diffusion model with time-dependent boundary conditions, based on an understanding of variable diffusion coefficients (which depend on sediment type and compaction) and pore water advection (induced by compaction upon burial everywhere in the ocean and in some places by thermal gradients from the underlying sea floor).

The problem with this early work was that the DSDP used rotary drilling, a process that compromises sample integrity by mixing sediments with drilling fluid and ambient seawater. Furthermore, strict limits on the DSDP sample size made it difficult to obtain enough pore water for a precise measurement. Although the early data showed the chlorinity and δD signals, the data were not precise enough to be of much use.

The situation changed with the advent of hydraulic piston coring and multiple-hole coring in the new ODP phase. In the 1990s, Dan Schrag realized that this new system provided better pore water samples. He obtained high-quality δ^{18}O and δD samples, which he used (along with physical evidence for sea level) to constrain glacial/interglacial changes in oceanic δ^{18}O due to glaciation/deglaciation. On the basis of these data, he estimated that the waters of the glacial deep ocean were near the freezing point of seawater at the surface (*5*). Shackleton and others had previously reached this conclusion (*6–8*), but the new pore water constraint was more powerful than the previous approaches.

But the most important dynamical property of seawater—its density—cannot be established from temperature alone because density is a strong function of salinity at very cold temperatures. That is where chlorinity comes into the picture. Inspired by the work of McDuff and Gieskes and presented with the opportunity to sample 50-m-long piston cores with the French research vessel Marion Dufresne in the mid-1990s, Adkins began a study of the paleosalinity of the ocean based on pore water chlorinity measurements. With an electrochemical titration technology inherited from Gieskes and McDuff, Adkins could make extremely precise measurements of chlorinity and observe chlorinity variations in long cores throughout the Atlantic.

Adkins, McIntyre, and Schrag then teamed up to make paired chlorinity and δ^{18}O measurements on ODP samples. The result of the first four ODP holes studied are presented in this issue (*1*). A major new discovery about glacial ocean circulation comes out of this work. In the glacial ocean, the densest water of the ocean (densest because of the salt content, not the temperature, which was uniformly cold everywhere in the deep sea) is found in the Antarctic. The saltiness likely derives from brine release during the formation of sea ice in winter months. The cold, salty, nutrient-rich waters found throughout the lower half of the ocean during glacial maxima must therefore originate in the Antarctic.

This study is probably not the end of the story. So far, there are only four cores with joint high-precision δ^{18}O and chlorinity data. As more sites are explored, there may be further surprises. Furthermore, the results are model dependent, and as these models are improved, somewhat different solutions may prove possible.

But at this point in the game, the evidence provides a landmark change in our understanding of deep-ocean circulation. During the shift from glacial conditions ~20,000 years ago to the interglacial conditions of the past ~10,000 years, the salt source of the deep sea switched from the Antarctic to the North Atlantic. This finding is sure to be a major feature in modeling studies of the glacial climate.

References and Notes

1. J. F. Adkins, K. McIntyre, D. P. Schrag *Science* **298**, 1769 (2002).
2. C. Wunsch, *Science* **298**, 1179 (2002).
3. B. A. Warren, in *Evolution of Physical Oceanography*, B. A. Warren, C. Wunsch, Eds. (MIT Press, Cambridge, MA, 1981), pp. 6–41.
4. W. S. Broecker *et al., J. Geophys. Res.* **103**, 15833 (1998).
5. D. P. Schrag, G. Hampt, D. W. Murray, *Science* **272**, 1930 (1996).
6. N. J. Shackleton *Q. Sci. Rev.* **6**, 183 (1987).
7. L. D. Labeyrie, J. C. Duplessy, P. L. Blanc, *Nature* **327**, 477 (1987).
8. P. A. Martin *et al., Earth Planet. Sci. Lett.* **198**, 193 (2002).
9. E. Boyle, L. D. Keigwin, *Nature* **330**, 35 (1987).
10. J.-C. Duplessy *et al., Paleoceanography* **3**, 343 (1988).
11. K. M. Cuffey *et al., Science* **270**, 455 (1995).
12. R. N. Harris, D. S. Chapman, *Science* **275**, 1618 (1997).
13. I. Friedman, K. Hardcastle, *J. Geophys. Res.* **93**, 8249 (1988).
14. J. R. Lawrence, *Init. Rep. Deep Sea Drill. Proj.* **20**, 891 (1973).
15. R. E. McDuff, *Init. Rep. Deep Sea Drill. Proj.* **86**, 675 (1985).

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