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The influence of water-rock reactions and O isotope exchange with CO_2 on water stable isotope composition of CO_2 springs in SE Australia

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Abstract

Monitoring injected CO_2 in CCS sites using oxygen isotopes of water has been demonstrated in field and laboratory experiments. Here, we examine natural CO_2-rich springs in the Daylesford-Hepburn region, South East Australia, which show water ^{18}O depletion compared to local precipitation. Geochemical modelling shows that water-rock reactions are unlikely to have a significant effect on the observed $\delta^{18}O$ values, which can only be explained by isotopic exchange with CO_2. The water $\delta^{18}O$ shift can be used for monitoring CO_2 impact on shallow groundwater aquifers, provided that there is sufficient CO_2 and distinction between water and CO_2 $\delta^{18}O$ values exists.

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Keywords: **CCS; Monitoring; O isotopes; Natural analogues; Natural tracers**

Nomenclature

DIC	dissolved inorganic carbon
GMWL	Global Meteoric Water Line

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LMWL	Local Meteoric Water Line
V-SMOW	Vienna-Standard Mean Ocean Water
‰	per mille (parts per thousand)
ε	isotopic enrichment factor
δD	the ratio of the stable isotopes $^2H/^1H$ in ‰ relative to V-SMOW
$\delta^{18}O$	the ratio of the stable isotopes $^{18}O/^{16}O$ in in ‰ relative to V-SMOW
$\delta^{18}O^{i}_{H_2O}$	initial $\delta^{18}O$ value of H_2O in ‰
$\delta^{18}O^{i}_{CO_2}$	Initial $\delta^{18}O$ value of CO_2 in ‰
$\delta^{18}O^{f}_{H_2O}$	final $\delta^{18}O$ value of H_2O in ‰ (water in contact with CO_2)
$X^{o}_{CO_2}$	fraction of oxygen sourced from CO_2 in CO_2-H_2O system

1. Introduction

The stable isotope composition of CO_2 can be used as a tracer for verification and environmental monitoring of CO_2 in natural settings and of injected CO_2 in CCS projects [1]. The water-CO_2 oxygen isotope equilibration relationship presents a powerful tracing tool in conditions where CO_2 represents a major source of oxygen in a CO_2-water system and the isotopic composition of CO_2 is sufficiently different from that of brine in the storage reservoir and water in the overlying shallow aquifers [2]. Oxygen isotopes have been successfully used in CCS field projects [3] and at CO_2-enhanced oil recovery (EOR) sites [4,5] to monitor the movement of injected CO_2 plume. Their application has been confirmed in laboratory experiments at pressures and temperatures common in storage reservoirs [6,7] as well as at surface conditions [8]. This mechanism may also explain observed changes in the oxygen isotope composition away from the Local Meteoric Water Line (LMWL) in mineral spring waters from natural settings characterised by large amounts of CO_2.

Here we present a case study from CO_2-rich springs in the Daylesford-Hepburn region in Victoria, Australia, as a natural analogue of CO_2 migration to a shallow aquifer. We assess the relative importance of mineral reactions in the aquifer versus oxygen isotope equilibrium exchange between reservoir water and CO_2 for changes in the water stable isotope composition using geochemical data published by Cartwright et al. [9]. We provide evidence that equilibrium oxygen isotope exchange with CO_2 is the main mechanism responsible for the observed water oxygen isotope ratio ($\delta^{18}O$) depletion compared to the LMWL. Consequently we show that the oxygen isotope relationship observed in field sites and laboratory experiments is also observed in natural shallow aquifers where CO_2 is migrating to shallow groundwater aquifer from depth. We estimate the amount of CO_2 required to produce the observed isotopic shift and show that in cases where large amounts of CO_2 interact with water of sufficiently distinct isotopic composition, oxygen isotopes are a potential tracer for identifying CO_2 migration to the shallow subsurface.

1.1. Geological background

CO_2-rich mineral water springs in the Daylesford-Hepburn region flow through a heavily faulted Ordovician shale and sandstone bedrock succession (Figure 1) and are separated from surface groundwater. The depth of circulation is unknown but historical records report spring water in mines up to 1.6 km depth [10]. The aquifer is overlain by basalts from the Newer Volcanics Province, active from 4.5 Ma to 5000 a [11]. CO_2 is reportedly mantle-sourced, based on the close proximity of the springs to eruptive centres [12], $^3He/^4He$ gas data [13] and DIC (dissolved inorganic carbon) $\delta^{13}C$ isotope ratios [9]. Spring water is high in HCO^{3-}, Ca^{2+}, Na^+ and Mg^{2+} but there is a significant solute variation between individual springs [9,14].

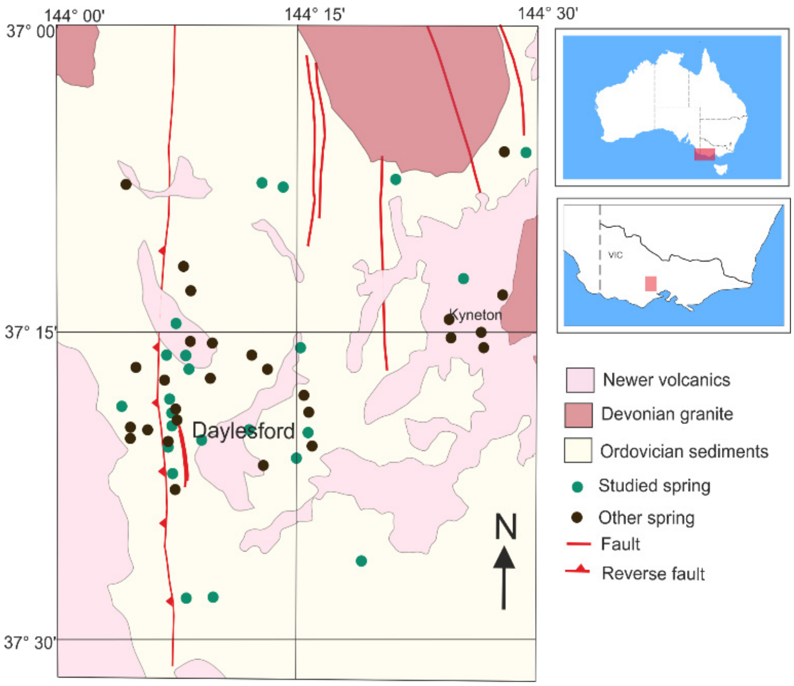

Figure 1. Map of the CO_2-rich mineral springs in the Daylesford-Hepburn region in central Victoria, Southeast Australia (adapted from Cartwright et al. [9]). The Ordovician basement (light yellow) is dissected by deep basement faults and overlain by recent basalts (pink). Mineral springs (studied ones by Cartwright et al. [9] in green) are in close proximity to major faults and eruptive centres.

1.2. Oxygen isotope change in spring waters

Cartwright et al. [7] reported highly variable oxygen ($\delta^{18}O$) and hydrogen (δD) isotope compositions from sampled springs in the Daylesford-Hepburn region (Figure 2). Stable isotope compositions are reported as delta notations in ‰ deviation relative to V-SMOW (Vienna-Standard Mean Ocean Water) according to Equation 1, where R represents the oxygen isotope ($^{18}O/^{16}O$) and hydrogen isotope ($^{2}H/^{1}H$) ratios of samples and standards, respectively.

$$\delta_{sample} = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000 \qquad (1)$$

The mineral water stable isotope ratios range from -7.8 to -5.8‰ V-SMOW for $\delta^{18}O$ and -44 to -31.8‰ V-SMOW for δD. Importantly, the spring waters show a depletion in $\delta^{18}O$ values in comparison to the LMWL, without a change in δD (Figure 2). Based on the principle presented in D'Amore and Panichi [15] to explain changes in the $\delta^{18}O$-δD composition of groundwater, such an isotopic shift can be the result of CO_2-water isotopic equilibrium exchange or low-temperature water-rock reactions.

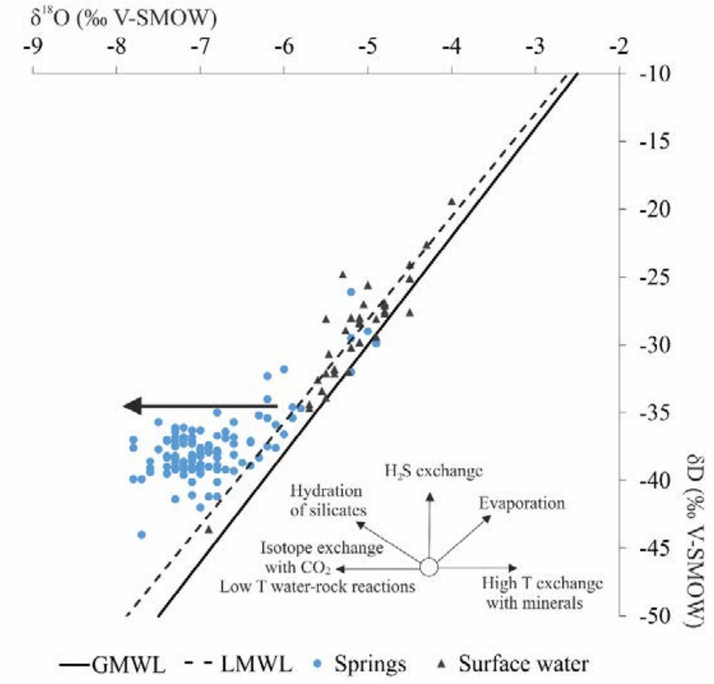

Figure 2. Stable isotope composition of Daylesford-Hepburn mineral spring waters (blue dots) and surface waters (black triangles) [9]. The Global Meteoric Water Line (GMWL) is shown as the black line, while the LMWL (defined as linear trend of surface waters) is shown as the dashed black line. The potential driving factors for simultaneous changes in $\delta^{18}O$ and δD are based on D'Amore and Panichi [15].

2. Methods

Mineral dissolution and precipitation reactions were simulated for three CO_2-rich springs (Sailors 1-3) in the Daylesford-Hepburn region using the geochemical modelling software PHREEQC [16] and the mineral spring geochemistry dataset published in Cartwright et al. [9] to test if precipitation of secondary minerals (clays) can explain the observed water $\delta^{18}O$ depletion. CO_2-promoted anorthite, forsterite and albite dissolution reactions represent the potential reactive minerals in Ordovician metasediments and Quaternary basalts as previously reported by Weaver et al. [14]:

$$CaAl_2Si_2O_8 + 4H_2O + 2CO_2 \rightarrow Al_2Si_2O_5(OH)_4 + 2HCO_3^- + Ca^{2+} \quad (2)$$

Anorthite Kaolinite

$$Mg_2SiO_4 + 4CO_2 + 2H_2O \rightarrow 2Mg^{2+} + 2HCO_3 + SiO_2 \quad (3)$$

Forsterite

$$2NaAlSi_3O_8 + 3H_2O + 2CO_2 \rightarrow Al_2Si_2O_5(OH)_4 + 4SiO_2 + 2Na^+ + 2HCO_3^- \quad (4)$$

Albite Kaolinite

All reactions were modelled using equations (2)-(4) and the weighted average Melbourne precipitation water (2007 – 2011) [17] as baseline water at 25 °C (Table 1). Water was reacted with fixed amounts of forsterite, albite and anorthite while maintaining equilibrium with kaolinite (Table 2).

Table 1. Weighted averages of monthly major ions concentrations in Melbourne, Australia (May 2007 - December 2011) [17].

pH	**Total Alkalinity (meq/L)**	**Cl^- (mg/ L)**	**SO_4^{-2} (mg/L)**	**Ca^{2+} (mg/L)**	**K^+ (mg/L)**	**Mg^{2+} (mg/L)**	**Na^+ (mg/L)**
5.85	0.12	5.36	1.76	1.14	0.48	0.42	3.11

Table 2. PHREEQC input parameters used for the water-rock reaction simulations for the Sailors springs.

	Sailors springs
$log(PCO2_{(g)})$	-0.5
Albite (mol)	0.012
Forsterite (mol)	0.004
Anorthite (mol)	0.006
Kaolinite (mol)	0
Quartz (mol)	0

3. Results

The geochemical simulations of reacting small amounts of anorthite, albite and forsterite with a defined CO_2 partial pressure while maintaining equilibrium with kaolinite and quartz closely match the published Ca^{2+}, Na^+, Mg^{2+}, HCO_3^- and CO_2 contents of the springs (Figure 3). In the modelled scenario for the Sailors springs, the total amount of kaolinite produced by albite and anorthite dissolution is 0.018 mol/L which represents 0.02% of the total oxygen in 1 litre of water.

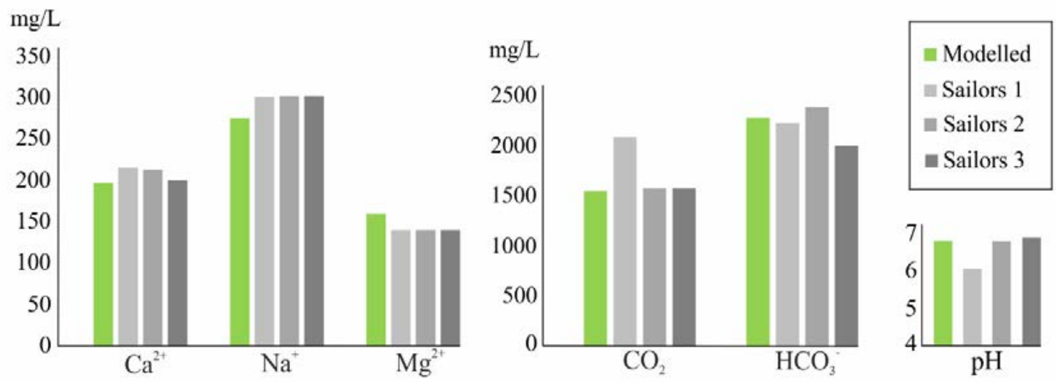

Figure 3. Ca^{2+}, Na^+, Mg^{2+}, HCO_3^- and CO_2 contents (mg/L) and pH of geochemical model (green bar) compared to Cartwright et al. [7] measurements from Sailors springs (grey bars). Silicate dissolution and clay precipitation simulation closely matches that the observed chemistry of Sailors springs.

4. Discussion

The fraction of oxygen involved in the modelled mineral reactions is too small to meaningfully influence the oxygen isotope ratio of the water body. Consequently, water-rock reactions cannot account for the depleted $\delta^{18}O$ values observed in Daylesford-Hepburn springs. CO_2 is in excess in the water, confirming results reported by Weaver et al. [14]. Mineral reactions are promoted by CO_2 but the water contains much more CO_2 than needed to account for the dissolution and precipitation reactions, meaning that the limiting factor in terms of cation and bicarbonate concentration is the availability of reactive minerals and not the CO_2 concentration. Since we can exclude mineral reactions as a source of oxygen to the waters, we assess the amount of CO_2 required to achieve the $\delta^{18}O_{H_2O}$ change observed in Daylesford (-1.7‰).

The magnitude of the shift in the water in contact with CO_2, $\delta^{18}O^{f}_{H_2O}$, relates to the fraction of oxygen sourced from CO_2 in the system ($X^{o}_{CO_2}$). The extent to which CO_2 can change water depends on the:

- Initial $\delta^{18}O$ value of CO_2 ($\delta^{18}O^{i}_{CO_2}$)
- Initial water $\delta^{18}O$ calculated from the LMWL ($\delta^{18}O^{i}_{H_2O}$)
- Relative proportions of CO_2 and H_2O equilibrating ($X^{o}_{CO_2}$)
- Temperature-dependant isotopic enrichment factor (ε)

This relationship is expressed in equation (5) [5]:

$$\delta^{18}O^{i}_{CO2} = \frac{\delta^{18}O^{f}_{H2O} - (\delta^{18}O^{i}_{H2O} \cdot (1 - X^{O}_{CO2})}{X^{O}_{CO2}} + \varepsilon \quad (5)$$

The value of $\delta^{18}O^{i}_{CO_2}$ in the Daylesford-Hepburn region is unknown. Thus we use a range of possible isotopic values for scenarios where CO_2 is sourced from mantle degassing [18] and where the CO_2 interacting with the reservoir waters have similar isotopic composition compared to nearby produced CO_2, such as the Caroline CO_2 field in Mount Gambier, SA [19] (Figure. 4). The fraction of oxygen sourced from CO_2 necessary to explain the oxygen isotope shift ranges between 7 and 12% for the maximum observed $\delta^{18}O^{f}_{H_2O}$ values.

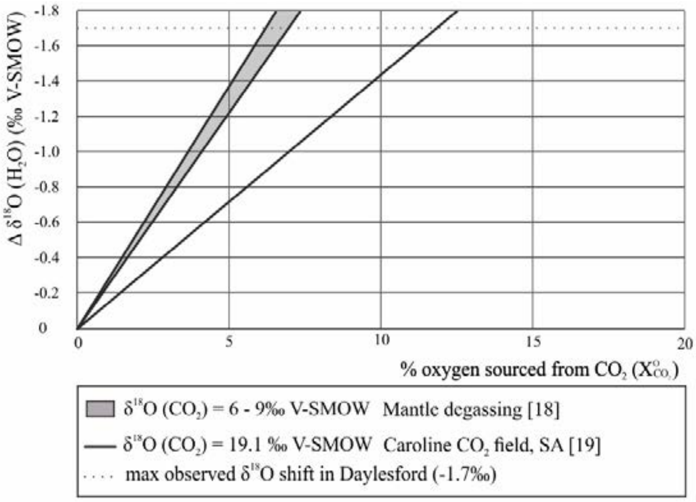

Figure 4. $\Delta\ \delta^{18}O_{H_2O}$ relative to $X^{o}_{CO_2}$ expressed as % following equilibrium oxygen isotope exchange with CO_2 in the Daylesford-Hepburn springs region. Range of potential $\delta^{18}O^{i}_{CO_2}$ values (grey filling for mantle degassing [18], solid black line for Caroline CO_2 field in South Australia [19] result in a range of 7 – 12% oxygen sourced from CO_2 to account for maximum observed shift of -1.7‰ in $\delta^{18}O_{H_2O}$ (dotted line).

In CCS settings, where the baseline $\delta^{18}O^{i}_{CO_2}$ values are known, this method can be used to quantify the amount of CO_2 that water interacted with. This simple model uses a closed system two-component mixing approach. In reality, both CO_2 and water move through the system at different rates. If CO_2 moves through a relatively stagnant water body at a continuous rate and degasses at the surface, the calculated $X^{o}_{CO_2}$ ranges represent the amount of CO_2 the water has interacted with rather than the amount of CO_2 currently present in the system. Consequently, our estimated range of fraction of oxygen sourced from CO_2 can be taken as a maximum value.

5. Conclusions

Mineral reaction modelling is a simple technique to assess the effect of primary mineral dissolution and secondary mineral precipitation on the mineral water oxygen isotope composition. A water $\delta^{18}O$ depletion relative to the Local Meteoric Water Line has been observed in CO_2-rich spring waters from the Daylesford-Hepburn region in central Victoria, Australia. This isotopic shift could be explained by either low-temperature water-rock reactions or CO_2-water equilibrium isotope exchange. Our geochemical modelling approach using published information from the Sailors springs in the Daylesford-Hepburn region shows that low-temperature water-rock reactions are unlikely to explain the observed water $\delta^{18}O$ depletion. Hence, we propose that the mineral spring water $\delta^{18}O$ values can be explained by oxygen isotope exchange with free-phase CO_2. This finding supports CO_2 injection field and laboratory experiments during which oxygen isotopes have been successfully used to track CO_2 migration in the subsurface. Our case study demonstrates that the water stable isotopic composition in CO_2-rich mineral springs can be used as a monitoring tool for studying the interaction with CO_2 in a shallow aquifer when CO_2-water ratios are high and when initial CO_2 and water $\delta^{18}O$ values are sufficiently different.

References

[1] Elodie J, Philippe S. The relevance of geochemical tools to monitor deep geological CO_2 storage sites. In: Panagiotaras D, editor. *Geochemistry - Earth's System Processes*, InTech; 2012, p. 81–104.

[2] Mayer B, Humez P, Becker V, Dalkhaa C, Rock L, Myrttinen A, Barth, JAC. Assessing the usefulness of the isotopic composition of CO_2 for leakage monitoring at CO_2 storage sites: A review. *Int J Greenh Gas Cont* 2015;37:46–60.

[3] Serno S, Johnson G, LaForce TC, Ennis-King J, Haese RR, Boreham CJ, Paterson L, Freideld, BM, Cook PJ, Kirste D, Haszeldine S, Gilfillan SMV. Using oxygen isotopes to quantitatively assess residual CO_2 saturation during the CO2CRC Otway Stage 2B Extension residual saturation test. *Int J Greenh Gas Cont* 2016;52:73–83.

[4] Kharaka YK, Cole DR, Hovorka SD, Gunter WD, Knauss KG, Freifeld BM. Gas-water-rock interactions in Frio Formation following CO_2 injection: Implications for the storage of greenhouse gases in sedimentary basins. *Geology* 2006;34:577–80.

[5] Johnson G, Mayer B, Nightingale M, Shevalier M, Hutcheon I. Using oxygen isotope ratios to quantitatively assess trapping mechanisms during CO_2 injection into geological reservoirs: The Pembina case study. *Chem Geol* 2011;283:185–93.

[6] Johnson G, Mayer B. Oxygen isotope exchange between H_2O and CO_2 at elevated CO_2 pressures: Implications for monitoring of geological CO_2 storage. *Appl Geochem* 2011;26:1184–91.

[7] Becker V, Myrttinen A, Nightingale M, Shevalier M, Rock L, Mayer B, Barth JAC. Stable carbon and oxygen equilibrium isotope fractionation of supercritical and subcritical CO_2 with DIC and H_2O in saline reservoir fluids. *Int J Greenh Gas Cont* 2015;39:215–24.

[8] Barth JAC, Mader M, Myrttinen A, Becker V, Van Geldern R, Mayer B. Advances in stable isotope monitoring of CO_2 under elevated pressures, temperatures and salinities: Selected results from the project CO_2ISO-LABEL. In: Liebscher A, Münch U, editors. *Geological Storage of CO_2 – Long Term Security Aspects*. Zürich:Springer International Publishing; 2015. p. 59-71.

[9] Cartwright I, Weaver T, Tweed S, Ahearne D, Cooper M, Czapnik K, Tranter, J. Stable isotope geochemistry of cold CO_2-bearing mineral spring waters, Daylesford, Victoria, Australia: Sources of gas and water and links with waning volcanism. *Chem Geol* 2002;185:71–91.

[10] Shugg A. Hepburn Spa: Cold carbonated mineral waters of Central Victoria, South Eastern Australia. *Environ Geol* 2009;58:1663–73.

[11] Boyce J. The Newer Volcanics Province of southeastern Australia: a new classification scheme and distribution map for eruption centres. *Aust J Earth Sci* 2013;60:449–62.

[12] Lawrence CR. Hydrogeology of the Daylesford Mineral District with special reference to the mineral springs. Dept of Mines. Geological Survey Victoria, Undergroud Water Investigation Report 1969.

[13] Chivas, AR, Barnes IE, Lupton JE, Collerson K. Isotopic studies of south-east Australian CO_2 discharges.*Geol Soc Aust Abstr*1983;12:94-

[14] Weaver TR, Cartwright I, Tweed SO, Ahearne D, Cooper M, Czapnik K, Tranter, J. Controls on chemistry during fracture-hosted flow of cold CO_2-bearing mineral waters, Daylesford, Victoria, Australia: Implications for resource protection. *Appl Geochem* 2006;21:289–304.

[15] D'Amore F, Panichi C. Geochemistry in geothermal exploration. *Appl Geotherm* 1987;9:69–89.

[16] Parkhurst DL, Appelo CAJ. User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations.Water-resources investigations report 99-4259 1999.

[17] Crosbie R, Morrow D, Cresswell R, Leaney F, Lamontagne S, Lefournour M. New insights to the chemical and isotopic composition of rainfall across Australia. CSIRO Water for a healthy country flagship, Australia 2012.

[18] Bindeman I. Oxygen isotopes in mantle and crustal magmas as revealed by single crystal analysis. *Rev Min Geochem* 2008;69:445–78.
[19] Chivas AR, Barnes I, Evans WC, Lupton JE, Stone JO. Liquid carbon dioxide of magmatic origin and its role in volcanic eruptions. *Nature* 1987;326:587–9.