Title

Paleotemperature in the southwestern United States derived from noble gases in ground water

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(24). Given that *Rhizobium*-plant interactions may be modified pathogen-host relationships (25), it is interesting to note that NodRm-IV(S) is essentially a modified chitin tetramer. The optical and mechanical accessibility of root hairs, together with the possible use of bacterial genetics to modify signal molecules, will provide new opportunities to study the mechanism of action of these oligosaccharide signals.

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11. Alfalfa seeds (AS13, Ferry-Morse Seed, Modesto CA) were surface-sterilized and germinated as described (*26*). Seedlings (24 hours old) were transferred to the surface of square petri plates that contained buffered nodulation medium (BNM) (*27*) and 12% Bacto agar (Difco Laboratories, Detroit, MI). The plates were sealed with Parafilm, and the plants were grown for 2 days at 29°C under a cycle of 16 hours of light and 8 hours of dark. Whole seedlings were mounted in a custom perfusion chamber, and the zone of emerging root hairs was suspended in a 250-μl chamber. The chamber was perfused with alfalfa recording buffer (ARB) (1 ml/min). The root tips were excised halfway between the root cap and the point of root hair emergence to prevent movement of the root as a result of gravitropic bending. Because this procedure might interfere with nodule initiation, we spot-inoculated *R. meliloti* onto the root hair elongation zone at the same time. Nodules developed at the same frequency and emerged at the same time as they did on unexcised controls (*9*). After a 20-min recovery period under perfusion with ARB, emergent hair cells were impaled with a Prior (Stoelting, Wood Dale, IL) micromanipulator and a Wild (Technical Instrument Co., San Francisco) dissecting microscope at ×50 magnification. The equipment was set up on a vibration-resistant concrete table inside a Faraday cage. Glass microelectrodes were pulled from filamented glass capillaries (World Precision Instruments) on a Flaming/Brown micropipette puller (Sutter, model P-87). The final outer diameter of the tips was approximately 0.2 mm as measured by scanning electron microscopy. Pipettes were back-filled with 3 M KCl and placed in holders with a sintered Ag-AgCl pellet (World Precision Instruments). The reference electrode was connected to the recording bath with an agar bridge. Electrical potential was measured with a Getting model 5 amplifier, and the output was filtered through a six-pole Bessel filter at a 10-Hz corner frequency (Frequency Devices, Model 902LPF) and sent to an oscilloscope (Tektronix Instruments, Santa Clara, CA, model 5111A) and a chart recorder (Gould Electronics, Haywood, CA, model 2400S). When filled with 3 M KCl and placed in ARB, the electrodes had a resistance of approximately 30 megohms.
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15. *Rhizobium meliloti* strains 1021/pRMJT5, TJ1A3/pRMJT5, 1021/pMH36, and TJ1A3/pMH36 were grown to saturation in medium containing 5 g of tryptone, 3 g of yeast extract (Difco), and 0.5 g of $CaCl_2 \cdot 2H_2O$ per liter of solution at 30°C under tetracycline selection (10 mg/ml). Both 1021/pMH36 and TJ1A3/pMH36 cultures were induced throughout growth with 3 μM luteolin. The cells were pelleted, washed in 10 mM $MgSO_4$, diluted into *Rhizobium*-defined medium (1:100), and grown to a final absorbance of 0.7 at 600 nm. The cells were pelleted, and the supernatants were filtered through 0.45-μm Millipore filters. The filtrates were extracted with ethyl acetate, and the aqueous phase was extracted with butanol. The butanol phase was evaporated, and the precipitate was resuspended in distilled water.
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17. Tomato and alfalfa seeds were surface-sterilized and germinated on 12% water agar in inverted petri plates. After 2 days of growth, they were placed on the surface of a thin layer of solidified 0.6% agarose-BNM (2 ml) that was spread over the surface of a glass microscope slide. The radicles were covered with Spectra/Por6 dialysis membrane, and the slides were placed in 50-ml conical screw-cap tubes (Falcon, Becton Dickinson Labware, Lincoln Park, NJ) with 5 ml of BNM. After 2 days of growth, the dialysis membrane was removed, and the slides were placed in chambers under 1 mm of ARB.
18. Extracts were fractionated by HPLC on a Hewlett-Packard 1090M with a modified protocol (*28*). Samples were injected on a C_{18} reverse-phase column with a 2-mm inside diameter and eluted at 0.2 ml/min with a 20-min isocratic elution with 20% acetonitrile, followed by a 10-min gradient to 50% acetonitrile, and finally with a 15-min isocratic elution with 50% acetonitrile. Eluted species were detected by ultraviolet (UV) absorption at 215 nm. Fractions that contained the unique UV-absorbing peaks in 1021/pMH36 extracts were collected and pooled. The corresponding fractions were also collected from TJ1A3/pMH36 extracts.
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27. The BNM was composed of 2 mM Mes, 2 mM $CaSO_4 \cdot 2H_2O$, 0.5 mM KH_2PO_4, and 0.5 mM $MgSO_4 \cdot 7H_2O$, with the minor salts 50 nM Na_2EDTA, 50 nM H_3BO_3, 50 nM $FeSO_4 \cdot 7H_2O$, 50 nM $MnSO_4 \cdot H_2O$, 16 nM $ZnSO_4 \cdot 7H_2O$, 1 nM $Na_2MoO_4 \cdot 2H_2O$, 0.1 nM $CoCl_2 \cdot 6H_2O$, and 0.1 nM $CuSO_4 \cdot 5H_2O$. KOH (approximately 1.2 mM final concentration) was added to adjust the pH to 6.0. The ARB is the same composition but does not have the minor salts.
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29. We thank R. Scheller for equipment; J. Schroeder, E. Serrano, and B. Lucas for advice; K. Faull for assistance with HPLC and mass spectroscopy; and J. Dénarié for purified NodRm-IV(S). Supported by Department of Energy contract grant DE-A503-82ER12084 (S.R.L.), a National Science Foundation Predoctoral Fellowship (D.W.E.), and an NIH training grant in molecular biology awarded to Stanford University (E.M.A.).

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Paleotemperatures in the Southwestern United States Derived from Noble Gases in Ground Water

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A paleotemperature record based on measurements of atmospheric noble gases dissolved in ground water of the Carrizo aquifer (Texas) shows that the annual mean temperature in the southwestern United States during the last glacial maximum was about 5°C lower than the present-day value. In combination with evidence for fluctuations in mountain snow lines, this cooling indicates that the glacial lapse rate was approximately the same as it is today. In contrast, measurements on deep-sea sediments indicate that surface temperatures in the ocean basins adjacent to our study area decreased by only about 2°C. This difference between continental and oceanic records poses questions concerning our current understanding of paleoclimate and climate-controlling processes.

Paleoclimate records for the oceans and the continents during the last glacial maximum are inconsistent. The observation that the 0°C isotherm on mountains from almost all geographic settings and latitudes in both the Northern Hemisphere and the Southern Hemisphere dropped by about 950 m during the peak of the last glacial suggests that the temperature was lowered by 4.2° to 6.5°C at elevations between 3 and 5 km (*1*). On the other hand, paleoclimatic information derived from oxygen isotope measurements (on foraminifera) and faunal abundances indicate that most of the low-latitude ocean surface cooled by less than 2°C. No process has yet been identified that could cause marked high-

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altitude cooling in low latitudes if the sea surface cools by only 2°C (*2*). Therefore, either the paleoclimate records or our understanding of key climate processes appears to be wrong.

Whereas reconstructed faunal distributions in deep-sea sediments and oxygen isotope measurements are reasonably good tools for studies of the oceans' paleotemperatures (*3*, *4*), the situation for the continents is more complicated, because the paleothermometers that have been used are less accurate. Precipitation and temperature reconstructions for continents, for example, have used pollen data (*5*), beetle and land snail data (*6*), periglacial features (*7*), oxygen and hydrogen isotope ratios in lake sediments (*8*), soil carbonates (*9*), cave deposits (*10*), tree rings (*11*), ground water (*12*), and various other methods. Although the data are in qualitative agreement (all data indicate that most of the continents were colder during glacial time), these approaches suffer from major uncertainties stemming from the assumptions that must be made to convert the observations to temperatures.

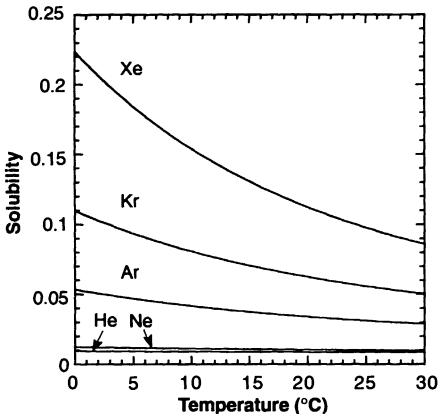

Fig. 1. Temperature dependence of the noble gas solubilities in distilled water expressed as the Bunsen coefficient (*33–35*).

Measurements of atmospheric noble gases dissolved in ground water offer a tool for estimations of continental paleotemperatures that can overcome many of the weaknesses of indirect paleotemperature indicators. The physical principle of the noble gas thermometer is the temperature dependence of the solubility of noble gases (Fig. 1), especially Ar, Kr, and Xe, in water. Laboratory measurements of the solubility of the individual noble gases as a function of temperature allow the observed noble gas concentration in a ground-water sample to be converted into a temperature at which the water was equilibrated with the atmosphere (*13–15*). Equilibration takes place during percolation of precipitation water through the unsaturated soil zone from the surface to the water table in the recharge area of the aquifer. Ground water is then often isolated from the atmosphere and migrates to the discharge area, carrying information on past climate in the concentrations of the dissolved atmospheric noble gases. The potential of atmospheric noble gases dissolved in ground water as a paleothermometer was recognized in the early 1970s (*15*), and pilot studies have demonstrated that paleotemperature records can be obtained with this method in carefully selected aquifers (with well-known hydrogeology, simple chemistry, and low dispersion and mixing rates) (*16–19*). The available data clearly show that a temperature shift between the last glacial and the present interglacial is documented in the noble gas pattern of old ground water (*16–19*). However, most of these studies are characterized by incomplete records, insufficient spatial resolution, or large errors in the noble gas temperatures that are due to analytical problems.

The advantage of the noble gas thermometer, as compared to the other paleothermometers, is that it is based on physical principles and measures an annual mean temperature with high accuracy. It averages the seasonal variations and smoothes out variability occurring on time scales of some years to about a thousand years. Because of intrinsic characteristics such as mixing processes, the noble gas method cannot resolve paleoclimate signals on time scales of several years to several hundred years. However, the noble gas record can be used to "calibrate" high-resolution records obtained by other methods that have weaknesses in the accuracy of the absolute temperature determination.

To establish a detailed paleotemperature record for the southwestern United States, we used the noble gas method on the well-studied Carrizo aquifer in Texas. The Carrizo sandstone in Atascosa and McMullen counties (Fig. 2; approximate location, 98°30'W, 29°00'N) is a confined, massive, medium-grained sandstone aquifer of Eocene age. The sandstone crops out across the northwestern corner of Atascosa County at an elevation of about 200 m above sea level and dips to the southeast with a more or less constant slope of about 20 m per kilometer (Fig. 3A). Rainfall recharges the aquifer at the outcrop, and the ground-water flow is driven gravitationally down the structural-depositional dip into the deeper subsurface layers (*20*). A systematic hydrochemical evolution occurs along the flow path: the concentrations of total dissolved solids gradually increase, and waters rich in calcium, sodium, bicarbonate, and chloride change to waters rich in sodium bicarbonate (*20*). In deeper parts of the aquifer, some ground water leaks upward into overlying layers. Just south of the border between Atascosa and McMullen counties (after a flow distance of about 75 km), cross-formational leakage along major faults causes mixing with ground water of deeper origin.

Noble gas samples were obtained from 22 wells (Figs. 2 and 3A), providing more or less even coverage across the sampled portion of the aquifer. The wells were chosen on the basis of earlier ^{14}C measurements (*21*) and hydrodynamic modeling (*22*). The ^{14}C ages were found to increase linearly from the recharge area at the northern border line of Atascosa County toward the southeast, where ages of more than 28,000 years were observed (Fig. 3B). Except for one well, the composition of the Carrizo waters has not changed *significantly*

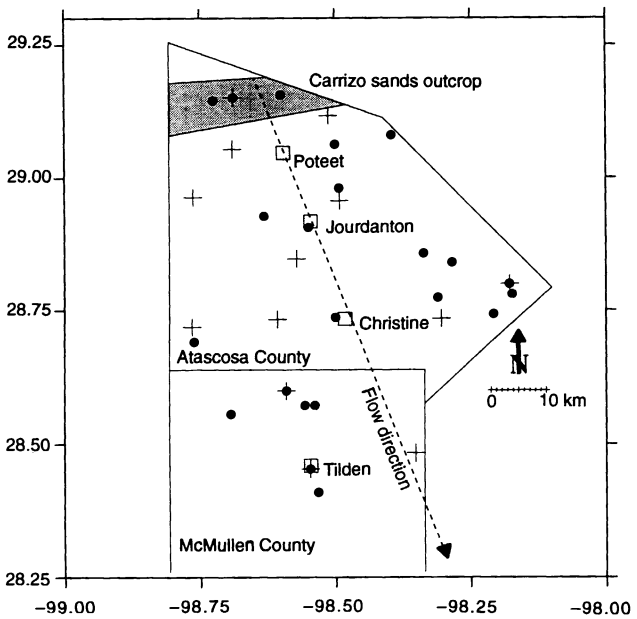

Fig. 2. Map of the area of investigation in south Texas with sampling locations. The *x* and *y* axes indicate longitude and latitude, respectively. Closed circles represent noble gas data; crosses, ^{14}C data (*21*). Also indicated is the average direction of flow as defined by ^{14}C and hydraulic age gradients and the direction of maximum inclination of the Carrizo sandstone.

during the last 30 years (*23*); thus, the climate signal in the aquifer should not have been disturbed by leaking wells or high withdrawal rates. Therefore, it seemed justifiable to use the ^{14}C data (*21*) to provide a chronology for our paleotemperatures, although the data were not collected simultaneously.

We measured the noble gas contents of the waters at the Institute of Environmental Physics, University of Heidelberg, Germany, using a specially designed mass spectrometric system (*17, 24*). Measurement precision was about ±3.4% for He, ±2.1% for Ne, ±1.7% for Ar, ±1.6% for Kr, and ±1.4% for Xe. We calculated noble gas paleotemperatures (Fig. 3C) from Ne, Kr, and Xe concentrations after correcting for excess air (*25*). The Ar data were omitted for the paleotemperature calculations because of analytical problems (*26*). After subtraction of the excess air, the noble gas temperatures reflect the mean annual temperature of the ground air at the water table (*27*), which for the continental United States (except in extremely warm, cold, or dry regions) is about 1°C higher than the mean annual temperature of the air (*28*). The analytical uncertainty of the noble gas temperatures (Fig. 3C) was ±0.5°C (1σ error).

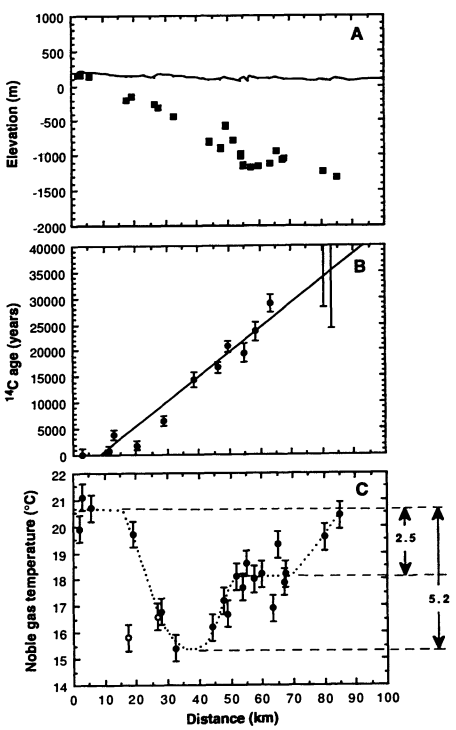

Fig. 3. (**A**) Vertical section along the above described flow line including topography and location of the well screens within the Carrizo sandstone. (**B**) ^{14}C ages as a function of distance from the recharge area. The slope of the linear fit corresponds to a flow velocity of about 2 m/year. (**C**) Noble gas temperatures as a function of distance from the recharge area. The open circles represent samples influenced by mixing as a result of a leaky well casing (25 km) or originating from a deeper layer (18 km). The noble gas paleotemperatures are plotted as a function of distance from the recharge area, which serves as a measure of age. The northern edge of the Carrizo outcrop in Atascosa County (Fig. 2) is set to zero. The direction of the distance vector (162°) is identical to the direction of the ground-water flow as defined by ^{14}C and hydraulic age gradients (*21, 22*) and the direction of maximum inclination of the Carrizo sandstone (*20*). The noble gas temperature is 5.2°C lower for the last glacial maximum and 2.5°C lower for the middle Wisconsin period (22,500 to 33,500 years ago) than today.

The noble gas temperatures show a systematic trend with age in the aquifer except for one sample (which will be omitted from consideration) at about 18 km from the recharge area. This well is deeper than the surrounding wells and might contain significantly older water from the underlying aquifer (*20*). The scatter of the data points around the curve in Fig. 3C does not exceed the accuracy of measurement (±0.5°C).

Ground-water samples taken in the recharge area show an average noble gas temperature of 20.6° ± 0.6°C. This value is 1.2°C lower than the present annual mean ground temperature in the recharge area, 21.8°C {annual mean air temperature of 20.7° and 20.9°C measured at two meteorological stations near the recharge area [Hondo and Floresville (*29*)] plus 1°C average ground temperature–air temperature difference (*28*)}. However, noble gas temperatures represent a mean value over several decades to a few hundred years. A small deviation between the temperature recorded by the noble gases dissolved in the ground water and the currently observed ground temperatures is not surprising in view of slight variations in the mean annual air temperature (*30*). There is a clear minimum in the noble gas temperature record (15.4° to 16.2°C) at a distance of about 35 km from the recharge area. Between 50 and 70 km from the recharge area, a plateau was observed (average noble gas temperature of 18.1° ± 0.6°C). Toward the end of the record (distance from the recharge area >70 km) there was a significant increase toward values similar to those in the outcrop area.

If we convert the distance into an age using the ^{14}C data (Fig. 3B), the noble gas temperature minimum corresponds to an age between 12,000 and 17,000 years ago and the plateau to an age between 20,000 and 30,000 years ago. The two noble gas temperatures at the high end of the age scale most likely reflect temperatures well beyond 30,000 years ago because the corresponding ^{14}C activities fall below the detection limit and because the two wells are located in the fault zone, where mixing with older formation water probably occurs.

Considering uncertainties in the determination of ^{14}C ages (*31*), we interpret the noble gas temperature minimum as representative for the last glacial maximum (LGM), which probably occurred about 18,000 (^{14}C) years ago, and the plateau as representative for the middle Wisconsin period [22,500 to 33,500 years ago (*5*)].

The data thus suggest that the annual mean temperature in southern Texas was about 5°C lower during the LGM and about 2.5°C lower during the middle Wisconsin period than in the Holocene. The noble gas temperature record established here is qualitatively consistent with eight earlier measurements for the Carrizo aquifer (*32*).

There are few estimates of paleotemperatures for south Texas with which to compare our data, mainly because of the scarcity of well-preserved pollen records in that area. However, an LGM summer temperature about 5°C lower than today was estimated from geological and hydrological studies on the Llano Estacado and from pollen analyses in the Boriack Bog near Austin (*5*).

The recharge area of the Carrizo aquifer is located at 200 m above sea level, at a distance of 200 km from the Gulf of Mexico and 750 km from high mountains. The Gulf of Mexico is characterized by a small temperature drop between the last glacial and the present interglacial, whereas the retreat of the snow lines indicates higher temperature variations for the mountains. The temperature shift of 5°C between Holocene and LGM, as derived from noble gas concentrations, resembles closely the temperature change in the high mountains obtained from the snow line lowering and pollen assemblages. These data indicate that the southwestern United States was uniformly cooler and that the lapse rate remained unchanged during the LGM. However, sea surface temperatures in the Gulf of Mexico are characterized by a small temperature drop, 2°C, between the last glacial and the present interglacial. Model calculations indicate that these differences are not consistent with the 5°C temperature change on the adjacent continents. Our noble gas temperatures strengthen the estimates of cooler continental paleotemperatures during the LGM. The inconsistency of the oceanic and continental paleorecords indicates that there are still gaps in our understanding of fundamental climate processes.

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25. During its underground passage, ground water accumulates nonatmospheric noble gases that are produced in the soil matrix by nuclear processes or diffused from deeper layers of the earth's crust or mantle. Excesses of Ne, Ar, Kr, and Xe due to these processes are rarely detected and can easily be separated from the atmospheric noble gases owing to their different isotopic composition. However, He may show concentrations several orders of magnitude above the solubility equilibrium level and the amount of atmospheric He cannot be isolated. Also, the solubility of He is relatively insensitive to temperature. Therefore, He cannot be used in paleotemperature studies. The other process contributing to the concentrations of all noble gases is excess air formation due to dissolution of small air bubbles caused by fluctuations of the ground-water table [T. H. E. Heaton and J. C. Vogel, *J. Hydrol.* **50**, 201 (1981)]. In most cases this process can be easily corrected for, because the noble gas concentration ratio of the excess air component equals that of air, whereas the solubility equilibrium component is fractionated with respect to air as a result of the different solubilities of the single noble gases. For the data set from the Carrizo aquifer described below, excess air contributes on average (numbers in parentheses. maximum) 22(34)% to the Ne, 8(13)% to the Ar, 4(8)% to the Kr, and 3(5)% to the Xe concentration of the water sample. Because solubility and its temperature dependence increase with atomic mass, the Ne concentrations are most sensitive to the addition of excess air whereas the Xe concentrations are mainly controlled by temperature. To separate the two unknowns, two noble gas concentrations, ideally Ne and Xe, are needed.
26. The Ar concentrations appear to be on the average 2% too low to be consistent with the other noble gases. The reason is probably an incomplete removal of chemically active gases from the gas sample, these gases influence the sorption characteristics of the charcoal trap used to separate the individual noble gases. If the Ar value is used for calculation of the noble gas temperatures, error bars become slightly larger and the noble gas temperatures are shifted to lower values, on average by 0.37°C This shift would not affect our conclusions.
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31. Dating of ground water by ^{14}C is complicated by the complex hydrochemistry of C in the groundwater system We applied several recent ^{14}C correction models [see F M Phillips, M. K. Tansey, L. A. Peeters, S Cheng, A Long, *Water Resour. Res.* **25**, 2259 (1989) for a summary] to Pearson and White's data (*21*) and obtained a standard deviation of ±2000 years, which may serve as an estimate of the uncertainty in ^{14}C ages due to C hydrochemistry.
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Geothermal Evidence from Canada for a Cold Period Before Recent Climatic Warming

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Three deep boreholes in a small area in Quebec, each having two high-accuracy temperature logs separated by 22 years, allow reliable determination of the ground surface temperature history during the past few centuries. The temperature logs show that the recent climatic warming was preceded by a cold period near the end of the 19th century in this area. The presence of such a cold period is also suggested by borehole temperature data from other areas in Canada.

Whether the climatic warming during the past hundred years is caused entirely by human activities is uncertain. Early instrumental observations indicate that surface air temperatures were low near the end of the 19th century (*1*, *2*), but the scarcity of meteorological stations before 1880 precludes a meaningful global analysis (*3*). However, the presence of a cold period in various parts of the world at that time has also been suggested by some but not all studies using proxy methods (*4*–*6*). These data suggest that the recent warming might be partially or mostly a return from a cold period. In this report, we describe geothermal evidence from Quebec and other areas in Canada for the presence of a cold period before warming near the end of the 19th century. The estimation of ground surface temperature (GST) histories from precise borehole temperature measurements was first attempted in 1969 (*7*) and 1971 (*8*), but its importance had not been widely appreciated until Lachenbruch and Marshall (*9*) provided evidence from the Alaskan Arctic for climatic warming during the past several decades. Recent developments include the use of a model that realistically simulates lithologic layers in the crust and flexible inversion methods (*10*–*12*) and estimation of GST over a vast area (*13*). Compared to proxy methods, this technique involves simple physics (heat conduction) and is not subject to uncertainties related to calibration. However, the estimated GST history is necessarily a highly smoothed version of the real one and provides an interesting contrast with temperature records that are based on proxies.

In 1990, we relogged 12 boreholes that had been logged in 1968 as part of a detailed geothermal study (*14*) near Lac Dufault, Quebec (Fig. 1), in an Archean volcanic belt of the Superior Province of the Canadian Shield. Repeat temperature logs, especially those separated by more than 20 years, are desirable for three reasons. (i) They better constrain the GST estimation because not only the curvatures in each temperature profile, but also the temperature changes with time at given depths, contain information on the past GST. (ii) They help to identify transients in subsurface temperatures that are due to climatic changes as opposed to curvatures in the temperature profiles caused by terrain effects and conductivity variations. (iii) They allow accurate identification of disturbances by water flow. Three of the 12

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