Reports

Biogenic Sulfur and the Acidity of Rainfall in Remote Areas of Canada

JEROME O. NRIAGU, DOUGLAS A. HOLDWAY,* ROBERT D. COKER

Sulfur released from any given natural or anthropogenic source carries an isotopic signature that can be used to trace its flow through the environment. Measurements of the concentration and isotopic composition of sulfur in weekly bulk precipitation samples collected over a 4-year period at a remote location in northern Ontario were recorded. The long-term isotopic data and the measurement on the production and release of dimethyl sulfide from boreal wetlands show that biogenic sources can account for up to 30 percent of the acidifying sulfur burden in the atmosphere in remote areas of Canada. The data suggest that significant biological reemission of anthropogenic sulfur is occurring. The role of this process in the continuing acidification of the environment for years to come must be a matter of concern.

THE CURRENT DEBATE ON ACID RAIN has focused on the role of sulfur compounds released from anthropogenic sources (*1*). Although the emission of large quantities of biogenic sulfur from the ocean is generally recognized (*2, 3*), the fluxes from continental aquatic ecosystems remain basically undefined. This report explores the possibility that bogs, marshes, and wetlands covering large areas of Canada represent an important source of atmospheric sulfur in remote regions of the country. Such a biogenic contribution may be identified on the basis of its isotopic signature.

Turkey Lakes Watershed is an undisturbed forested basin, about 10.5 km^2 in size, located approximately 50 km north of Sault Sainte Marie, Ontario. Since 1980, the chemical, biological, and physical properties of this basin have been monitored in order to elucidate the sensitivity and response of the watershed to the inputs of long-range transported atmospheric pollutants (*4*). Beginning from September 1982, bulk precipitation samples were collected every week from the basin for stable sulfur isotope measurement. The sampler was a Teflon-coated stainless steel square box, 0.25 m^2 in area, which was mounted on a wooden platform with its lip about 2.0 m above the ground. Each sample was boiled with H_2O_2, and the sulfate concentration was determined gravimetrically. The $BaSO_4$ was decomposed by heating the sample in a quartz tube, and the isotope ratio of the resultant SO_2 measured on a VG Micromass 602C mass spectrometer (*5, 6*). All isotope ratio results are expressed in the standard $\delta^{34}S$ notation:

$$\delta^{34}S \text{ (per mil)} = [(R_{ppt}/R_{std}) - 1] \times 1000$$

where R_{ppt} and R_{std} are the respective $^{34}S/^{32}S$ ratios for the precipitation sample and the standard reference material. Measurements on five to six replicate water samples collected at different locations (with different sulfate concentrations) or from the same location but at different times of the year show the reproducibility of sample collection and instrumental analysis to be ±5% (SD) for sulfate concentration and ±0.2 per mil (SD) for $\delta^{34}S$.

Water samples were also collected from 12 selected marshes, bogs, and wetlands in southern and north-central Ontario. The dimethyl sulfide (DMS) in each sample was immediately extracted by a purge and trap technique and measured on a gas chromatograph equipped with a dual-flame photometric detector and Chromosil 330 column (*7*). On the basis of diethyl sulfide as an internal standard, the method used had a detection limit of 0.8 ng $liter^{-1}$ of DMS and a precision (for sample collection and instrumental analysis) of better than ±5% (SD) of the reported DMS concentration.

Figure 1 shows a 4-year record of the isotopic composition of sulfur in atmospheric precipitation. The seasonal variation is striking, with the summer samples generally being depleted in ^{34}S compared to the winter ones. The yearly mean $\delta^{34}S$ values for winter samples were fairly constant, +4.5 to +5.3 per mil, and differed significantly from the corresponding annual means for summer samples, which varied from +1.9 to +3.4 per mil. The marked seasonality is further demonstrated by the monthly average $\delta^{34}S$ data (Fig. 1, inset). From the 4-year database, the difference in $\delta^{34}S$ between the winter (December to February) and summer (May to August) periods has been estimated to be 2.4 per mil.

The weekly sulfate concentrations (Fig. 2) show considerable scatter reflecting the well-known vagaries in the physical and chemical processes of atmospheric precipitation. In general, higher levels of sulfate were observed in the summer samples for the

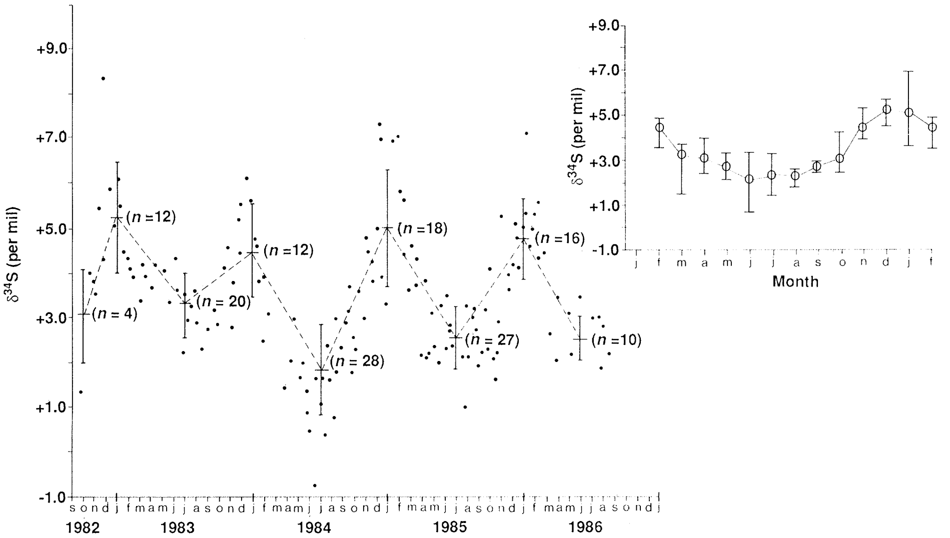

Fig. 1. Temporal variation in the isotopic composition of sulfur in bulk precipitation at a remote location in northern Ontario. The mean and standard deviation (error bars) of the $\delta^{34}S$ values as well as the number of measurements (*n*) for the cold months (mid-November to mid-March) and the warmer months (rest of the corresponding year) are indicated. Changes in the average monthly $\delta^{34}S$ values are shown as an inset; the error bars represent the range in annual mean values.

National Water Research Institute, Box 5050, Burlington, Ontario L7R 4A6, Canada.

*Present address: Office of the Supervising Scientist, Alligator River's Region Research Institute, Jabiru East, Northern Territory 5796, Australia.

duration of this study. The monthly average sulfate concentration is highest in late spring and remains fairly constant throughout the summer and early fall (Fig. 2, inset). By contrast, the minimum in monthly average δ^{34}S values occurs in summer (Fig. 1, inset).

Marked seasonal differences in both δ^{34}S and sulfate concentration in atmospheric precipitation have also been reported from many other locations (*6, 8, 9*). The seasonal trends observed may be attributed to (i) differences in intensity of sulfur emission from various sources (*6, 8*); (ii) differences in rates and mechanisms of SO_x oxidation, with faster oxidation accompanied by reduced isotopic fractionation during the warmer summer months (*9*); and (iii) changes in rates and processes of deposition of sulfur oxides from the atmosphere (*10*). The significance of each of these phenomena has been considered (*6*). Although atmospheric processes can lead to some fractionation of sulfur isotopes, and items (ii) and (iii) above may be contributing factors, the data nevertheless strongly suggest that an increased release of biogenic sulfur during the summer best explains the observed patterns in concentration and isotopic composition of the sulfur. The mean difference in sulfur contents of the summer and winter samples suggests that the biogenic contribution can account for up to 30% of the atmospheric sulfur burden. The fact that the emission of biogenic sulfur from terrestrial (*11*) and coastal marine (*12, 13*) ecosystems is particularly intensive during the warm summer months has been well documented. Further support for the biogenic origin of methylated atmospheric sulfur comes from a comparable seasonal variation in the levels of airborne methylarsenic compounds at remote continental locations (*14*). Methylated selenium compounds in the air may be expected to show a similar seasonal trend.

Where does all the biogenic sulfur come from? Bogs, marshes, and wetlands cover about 33% of the surface area of Ontario and about 14% (127.2 million hectares) of the country as a whole (*15*). We report here that the concentrations of DMS [the principal form of volatile organic sulfur compounds in natural waters (*2, 3*)] are surprisingly high in these ecosystems. The mean DMS concentration in 12 representative wetlands is 358 ng liter^{-1}, with the range being 109 to 823 ng liter^{-1} (Table 1). Considerably higher (600 to more than 70,000 ng liter^{-1}) concentrations of DMS, however, have been reported in a pond at Pullman, Washington (*11*); we are not aware of any other reported measurements of DMS in temperate freshwater bogs and wetlands. By applying the stagnant-film model of gas transfer across the air-water interface (*16*) and by using the mean DMS concentration and an exchange (or a piston) velocity of 5 cm hour^{-1} (*17*), we estimated an average emission rate for DMS sulfur from the wetlands of Ontario of 81 mg m^{-2} year^{-1}. As expected, this sulfur (in DMS) flux is less than the 500 to 3000 mg m^{-2} year^{-1} commonly observed in salt marshes (*12, 13, 18, 19*). Our data for sulfur flux out of shallow, highly organic rich wetlands are, however, comparable to the average value of 106 mg m^{-2} year^{-1} for the open ocean (*3, 20*), and to the sulfur emission rate of 50 to 135 mg m^{-2} year^{-1} from the tropical rain forest (*21*).

Table 1. Sulfate and DMS concentrations and calculated emission rates from Ontario swamps, wetlands, and bogs. Sulfur (in DMS) flux was calculated using exchange velocity of 5 cm hour^{-1} (*17*).

Name and location	Water sample depth (cm)	Sulfate (mg liter^{-1})	DMS (ng liter^{-1})	Sulfur flux (mg m^{-2} year^{-1})
	24 July 1986			
Wellington Rd. at Hwy. 34, E. Swamp; 5 km SE of Guelph, Ontario	15		200	45
Wellington Rd. at Hwy. 34, E. Pond; 5 km SE of Guelph	15		823	184
Wellington Rd. at Hwy. 34, W. Swamp; 6 km SE of Guelph	15		632	143
	28 July 1986			
Crawford Lake Swamp; 10 km E of Guelph	15		363	82
	90		280	63
Guelph Line Rd. Pond; 10 km ESE of Guelph	15		479	108
	45		450	102
	29 July 1986			
Swamp at junction of Hwys. 6 and 401; 6 km SE of Guelph	15		320	72
Beverley Swamp (Bronte Creek); 15 km SE of Guelph	15	1.6	308	47
	30 July 1986			
Beverley Swamp (Fletcher Creek); 17 km SSE of Guelph	15	2.3	165	37
Beverley Swamp (Spencer Creek); 18 km S of Guelph	5	1.2	355	80
	5 August 1986			
Luther Bog; 25 km NNW of Guelph	15	1.0	109	25
	6 August 1986			
Bog, Summit Muskeg Peat; near Copeland, Ontario	5	1.1	343	78
Bog, Mineral Springs Peat; near Copeland, Ontario	5	2.3	292	66

After correcting for the period of winter ice cover (*14*), and assuming that the average annual DMS concentration is only 75% of the mean July to August level, we estimated the total emission of DMS sulfur in Canada to be 100×10^6 kg year^{-1}. Hydrogen sulfide was also detected in all the samples analyzed, but it could not be quantified. From the size of the peaks, however, we could infer that H_2S concentration was at least comparable to that of DMS for most of the samples. Indeed, the rates of H_2S release from freshwater marshes of Florida (range 54 to 110, mean 80 mg m^{-2} year^{-1}) (*22*) and North Carolina (mean 60 mg m^{-2} year^{-1}) (*19*) are comparable to our DMS emission rates. Thus, we estimate the total emission of reduced sulfur compounds (DMS plus H_2S) from the wetlands of Canada to be 100×10^6 kg year^{-1}. This figure represents the upper limit since the wetlands studied are located in southern and north-central Ontario, which receive large amounts of pollutant sulfur from the atmosphere.

The deposition of sulfur in Canada typically varies from 3 to 0.5 g m^{-2} year^{-1} with the rate in the area studied generally being about 1 to 3 g m^{-2} year^{-1} (*22*). If we assume that the biogenic sulfur emission is proportional to the rate of atmospheric sulfur deposition, the total biogenic sulfur emission in Canada is estimated to be 25×10^6 to 100×10^6 kg annually. This potentially large natural source of sulfur has been ignored in reported inventories of sulfur emission in Canada (*23, 24*). Wetlands cover large areas of Scandinavia, Alaska, Russia, and the United Kingdom (*25*) and may represent a significant source of atmospheric sulfur in these areas as well.

Annual biogenic sulfur emission from Canadian soils has been estimated to be 246×10^6 kg year^{-1} (*24*). Estimates of DMS flux from the oceans into Canada range from 52×10^6 kg year^{-1} (*24*) to 200×10^6 kg year^{-1} (*26*). The emissions of

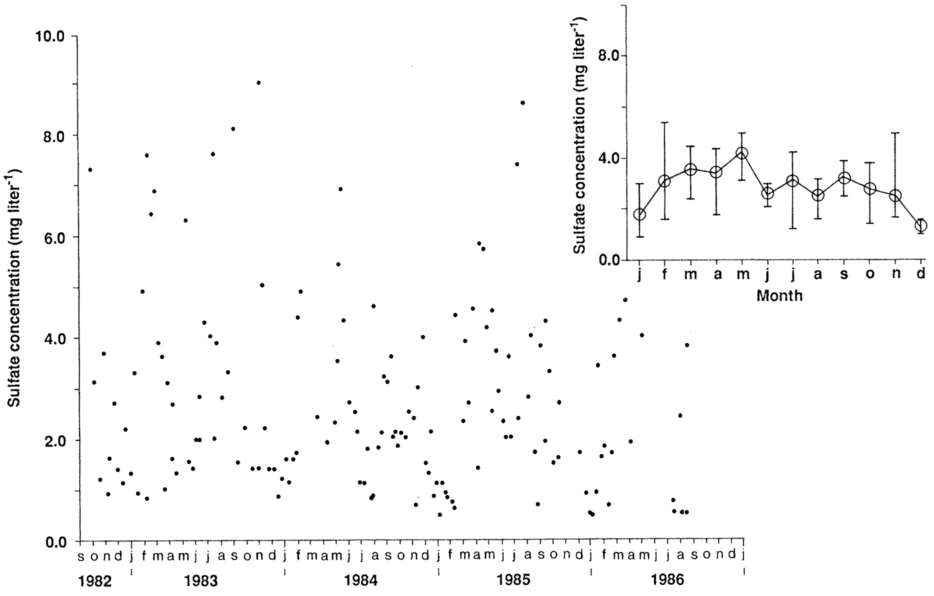

Fig. 2. Sulfate concentrations in the bulk precipitation samples. The graph of average monthly sulfate levels for the 4 years is shown as an inset; error bars represent the range in the annual mean values.

acidifying sulfur from all the natural sources thus total between 320×10^6 and 550×10^6 kg year^{-1}. The current emission of sulfur from industrial sources is about 2000×10^6 kg year^{-1} (*23*), implying that natural sources can account for about 14 to 21% of all the acidifying sulfur compounds emitted annually in Canada. This estimate of the contribution from natural sources is somewhat lower than the observed 34% increase in the sulfur content of bulk precipitation during the summer months. The release of pollutant sulfur is concentrated in the urban industrial centers, and the natural source contribution is accentuated at the remote locations. In other words, biogenic contributions to the atmospheric sulfur burden at remote areas should be higher than the countrywide average of 17%, as demonstrated in this study.

The production and loss of DMS reduces the sulfate concentrations in the wetlands to low levels during the summer (Table 1). Analysis of freshwater bogs (*27*), however, shows that the sulfur is not often stored in the sediments. The fact that the sulfate concentrations reach 5 to 10 mg liter^{-1} during the snowmelt (early summer) suggests that the input of anthropogenic sulfur, deposited in surrounding areas, is sustaining the biogenic sulfur flux from these ecosystems. Reemission of previously deposited pollutant sulfur in soils and wetlands may be an important phenomenon that has not been recognized previously. Its role in the continuing acidification of the environment even after reduction of the quantity of anthropogenic sulfur emissions should be a matter of concern.

The isotopic composition of biogenic sulfur in the atmosphere, to our knowledge, has never been determined. It can be estimated from the present data by using the isotope and mass balance relation:

$$\delta_t = \Sigma\delta_i C_i / C_t$$

where C_i is the concentration of the *i*th species, C_t is the total concentration in the mixture, and δ_i and δ_t refer to the corresponding isotopic values. If it is assumed that, other than the seasonal biogenic input, the yearly emission of sulfur flowing into the Turkey Lakes Watershed is fairly constant in rate and isotopic composition, the relation above would take the simpler form:

$$\delta_b = (C_w\delta_s - C_w\delta_w)/(C_s - C_w)$$

where the subscripts w, s, and b refer to winter, summer, and biogenic sulfur, respectively. This two-source model ignores the fact that space heating can engender the release of enough sulfur to significantly affect the isotopic signature of the atmospheric sulfur burden (*6*). The simplistic calculation is designed merely to demonstrate that sulfur of biogenic origin is isotopically different from anthropogenic sulfur at the study site. When the values $\delta_w = +4.9$ per mil, $\delta_s = +2.4$ per mil, $C_w = 2.1$ mg liter^{-1}, and $C_s = 3.2$ mg liter^{-1}, which are the average values observed between 1982 and 1985, are used in the calculation, the δ^{34}S for the biogenic sulfur is estimated to be −2.4 per mil. The depletion of ^{34}S in the biogenic sulfur pool and the approximately 5 per mil difference between the biogenic and anthropogenic sulfur seem reasonable (*28*) and tend to justify further applications of isotope ratio measurements in acid rain research.

REFERENCES AND NOTES

1. G. E. Likens, R. F. Wright, J. N. Galloway, T. J. Butler, *Sci. Am.* **241**, 43 (October 1979); J. R. Kramer, in *Sulfur in the Environment*, J. O. Nriagu, Ed. (Wiley, New York, 1978), pp. 325–370.
2. J. E. Lovelock, R. J. Maggs, R. A. Rasmussen, *Nature (London)* **237**, 452 (1972); B. C. Nguyen *et al.*, *ibid.* **275**, 637 (1978); T. S. Bates and J. D. Cline, *J. Geophys. Res.* **90**, 9168 (1985).
3. M. O. Andreae and H. Raemdonck, *Science* **221**, 744 (1983).
4. D. S. Jeffries *et al.*, *Water Air Soil Pollut.* **30**, 1033 (1986).
5. J. O. Nriagu and H. H. Harvey, *Nature (London)* **273**, 223 (1978); J. O. Nriagu and R. D. Coker, *ibid.* **303**, 692 (1983); J. O. Nriagu and Y. K. Soon, *Geochim. Cosmochim. Acta* **49**, 823 (1985).
6. J. O. Nriagu and R. D. Coker, *Tellus* **30**, 365 (1978).
7. D. A. Holdway and J. O. Nriagu, *Int. J. Environ. Anal. Chem.* in press.
8. D. Golomb, J. A. Fay, S. Kumar, *J. Air Pollut. Control Assoc.* **36**, 798 (1986); D. C. Grey and M. L. Jensen, *Science* **177**, 1099 (1972).
9. R. W. Shaw and R. J. Paur, *Atmos. Environ.* **17**, 1431 (1983); H. Rodhe and L. Granat, *ibid.* **18**, 2627 (1984); E. S. Saltzman, G. W. Brass, D. A. Price, *Geophys. Res. Lett.* **10**, 513 (1983); F. Caron *et al.*, *Appl. Geochim.* **1**, 601 (1986).
10. H. R. Krouse and R. O. van Everdingen, *Water Air Soil Pollut.* **23**, 61 (1984).
11. R. A. Rasmussen, *Tellus* **26**, 254 (1974); M. J. Bechard and W. R. Rayburn, *J. Phycol.* **15**, 379 (1979).
12. P. A. Steudler and B. J. Peterson, *Nature (London)* **311**, 455 (1984); *Atmos. Environ.* **19**, 1411 (1985).
13. D. F. Adams *et al.*, *Environ. Sci. Technol.* **15**, 1493 (1981).
14. H. Mukai, Y. Ambe, T. Muku, K. Takeshita, T. Fukuma, *Nature (London)* **324**, 239 (1986).
15. C. Tarnocai, *Peat Resources of Canada* (NRCC Publ. 24140, National Research Council of Canada and Land Resource Research Institute, Agriculture Canada, Ottawa, 1984); *Wetlands of Canada* (Ecological Land Classification Series, no. 14, Canadian Committee on Ecological Land Classification, Lands Directorate, Environment Canada, Ottawa, 1981).
16. P. S. Liss and P. G. Slater, *Nature (London)* **247**, 181 (1974); W. R. Bernard *et al.*, *J. Geophys. Res.* **87**, 8787 (1982).
17. R. Wanninkhof, J. R. Ledwell, and W. S. Broecker [*Science* **227**, 1224 (1985)] obtained a mean value of 2.2 cm hour^{-1} as the exchange velocity for sulfur hexafluoride in a lake with temperatures of 5° to 11°C. In bogs with escaping gas bubbles and vegetation at or near the water surface, the rate of gas escape should be expected to be higher than from the lake. We have assumed that the diffusion coefficients for DMS and sulfur hexafluoride are similar and have adopted an exchange velocity of 5 cm hour^{-1} (two times as high as the rate in a lake) for DMS in bogs. The use of a higher exchange velocity is further justified by the fact that the temperature of the bog water during the study was 20° to 30°C.
18. V. P. Aneja *et al.*, *Tellus* **31**, 174 (1979); S. G. Wakeham, B. L Howes, J. W. H. Dacey, *Nature (London)* **310**, 770 (1984).
19. V. P. Aneja, J. H. Overton, A. Aneja, *J. Air Pollut. Control Assoc.* **31**, 256 (1981).
20. M. O. Andreae and W. R. Barnard, *Mar. Chem.* **14**, 267 (1984).
21. M. O. Andreae and T. W. Andreae, *J. Geophys. Res.*, in press.
22. M. S. Castro and F. E. Dierberg, *Water Air Soil Pollut.* **33**, 1 (1987).
23. P. W. Summers and M. Lusis, *Assessment of the State of Knowledge of the Long-Range Transport of Air Pollutants and Acid Deposition*, part 2, *Atmospheric Sciences* (Federal/Provincial Research and Monitoring Coordinating Committee, Environment Canada, Ottawa, 1986).
24. *National Inventory of Natural Sources and Emissions of Sulphur Compounds* (Rep. EPS 3-AP-79-2, Air Pollution Control Directorate, Environmental Protection Service, Environment Canada, Ottawa, 1980).
25. D. I. Sebacher, R. C. Harriss, K. B. Bartlett, S. M. Sebacher, S. S. Grice, *Tellus* **38B**, 1 (1986).

26. J. N. Galloway and D. M. Whelpdale, *Atmos. Environ.* **14**, 409 (1980).
27. J. O. Nriagu, unpublished results.
28. R. D. Fuller, M. J. Mitchell, H. R. Krouse, B. J. Wyskowski, *Water Air Soil Pollut.* **28**, 163 (1986); D. R. Hitchcock and M. S. Black, *Atmos. Environ.* **18**, 1 (1984).

29. We thank R. Semkin and D. Jeffries for assistance in collecting the bulk precipitation samples. Invaluable comments on an early draft of the manuscript were provided by M. O. Andreae, J. N. Galloway, and F. Elder.

2 January 1987; accepted 15 May 1987

Lateral Isotopic Discontinuity in the Lower Crust: An Example from Antarctica

RUTH I. KALAMARIDES, JONATHAN H. BERG, ROBERT A. HANK

The lower continental crust is one of the least known variables in the crust-mantle evolutionary equation. In order to study the nature and compositional heterogeneity of the lower crust, more than 20 inclusions of lower crustal granulites in volcanic rocks from the McMurdo Sound region of Antarctica were analyzed for strontium and oxygen isotopes. These inclusions were erupted from volcanic centers covering an area of 12,000 square kilometers. Along with results from analyses of major and trace elements, the isotopic data reveal a profound discontinuity in the composition and probably the age of the lower crust that coincides with the boundary between the Transantarctic Mountains and the Ross Embayment. Although this topographic boundary between East and West Antarctica is largely a Cenozoic development, which apparently reflects a simple subvertical faulting relationship due to crustal rifting, the isotopic differences in the lower crust across the boundary suggest that the current faulting and rifting may coincide with an older crustal suture, the age of which is uncertain.

THE OVERALL COMPOSITION AND the degree and scale of heterogeneity of the earth's continental lower crust are vital to our understanding of the tectonic and petrologic evolution of continents and the development of the earth's crust-mantle system (*1*). Direct studies of the lower crust are rare, and studies that assess regional variation of the lower crust are rarer still. Most studies that purport to document regional chemical variation of the lower crust have involved uplifted and exposed granulite terranes (*2, 3*), which may or may not be representative of the lower crust. We report isotopic results determined directly on lower crustal inclusions transported to the surface over a broad region by relatively young (Cenozoic) volcanic eruptions. Because of the wide areal distribution of these inclusions, they play a crucial role in delineating horizontal variation in the composition of the lower crust.

The eastern boundary or "front" of the Transantarctic Mountains (TM), whose peaks in places rise from sea level to elevations greater than 5000 m, marks the boundary between East and West Antarctica. The nature of this boundary has been debated for many years. Since the advent of plate tectonic theory, most interpretations have fallen into two groups: one is a convergent-margin scenario of subduction, collision, and suturing, and the other is a divergent-margin scenario of continental rifting and block faulting. The geologic-tectonic history of the McMurdo Sound–Royal Society Range area of Antarctica is summarized in Fig. 1. Uplift of the TM and subsidence of the Ross Sea have apparently occurred primarily from the late Cretaceous to the present (*4, 5*). On the basis of gravity studies, which indicate that the thickness, density, and compositional characteristics of the crust change dramatically at the boundary between the TM and the Ross Sea, Smithson (*6*) suggested that this boundary marks a crustal suture that formed by continental collision during the convergence associated with the Ross Orogeny in the early Paleozoic. He suggested that the TM crust was thickened by underplating the margin of East Antarctica with the crust of West Antarctica [see also (*7*)]. Others (*8–12*) have suggested that the TM front is a normal fault boundary separating the uplifted block of the TM from the recently rifted and subsided Ross Embayment (RE). In this latter case, there is no lateral discontinuity in the geology across the front, only a subvertical displacement along a fault or faults, with the thinner crust of the RE having been caused by listric faulting and stretching.

Cenozoic volcanics of the Erebus Volcanic Province (*8*) were erupted through older crust that is partially exposed in the uplifted TM and completely unexposed in the RE (Fig. 2). The lavas have brought to the surface an extensive suite of crustal inclusions (*13*). These inclusions are the only direct evidence of the nature of the lower crust; in the case of the RE crust, the inclusions represent virtually the only evidence for the nature of the upper crust as well. The most abundant inclusions in both the TM and RE are lower crustal two-pyroxene granulites. Although rare relict igneous textures have been found, the more common textures range from an annealed texture with 120° angles at grain-boundary junctions, to a classic mortar texture, to a highly sheared and granulated texture with bent cleavages and lamellae. The TM two-pyroxene granulites locally contain garnet or spinel and do not contain coexisting primary olivine and plagioclase, indicating that they originated at depths ranging from about 17 to 45 km (*14, 15*). The RE two-pyroxene granulites commonly contain coexisting primary olivine and plagioclase, and spinel is present only locally, consistent with a crustal thickness of no more than 20 to 25 km (*14, 15*). Quantitative thermobarometry based on mineral compositions largely confirms the above conclusions and indicates that the geothermal gradient in the upper crust is very high, ranging from 60° to 100°C per kilometer (*14*).

The studied samples cover as much as possible of the range of two-pyroxene–granulite compositions in order to evaluate the extent of compositional diversity. Those samples analyzed represent a wide range in mineralogy, and the selection of samples for analysis has been weighted in a manner that would probably overemphasize the similarities between the two suites.

Plots of Rb-Sr data for the granulite inclusions are shown in Fig. 3A. A previous Sr isotope study of the RE granulites (*16*) indicated an age for the xenoliths (158 million years) that was roughly contemporaneous with the Jurassic Ferrar magmatism evident at or near the surface in this region. However, data on a large number of inclusions were disregarded, and we believe that the determined age is fortuitous. Our data do not form an isochron for either the RE or TM granulites. Because the samples have a wide areal distribution and are derived from varying depths within the crust, the lack of an isochron is not unreasonable.

In the following discussion on Sr initial ratios (I_{Sr}), all such ratios were calculated from a selected age of 900 million years. This age is arbitrary, but is probably close to the minimum age for the TM granulites, which we assume to be represented by the maximum age of the overlying metamorphic rocks, that is, 675 to 950 million years (*17*).

Department of Geology, Northern Illinois University, DeKalb, IL 60115.