nodules appear to be the remnants of an old caliche horizon, not of a marine limestone. Erosion of the island's upper slopes has exposed and widely dispersed the caliche.

Altogether the evidence points to the formation of the lavas of Española Island in a subaerial environment. Furthermore, the presence of both ancient and contemporary caliche-bearing soils implies that the greater part of the island has always been emergent. Because the lavas of the north coast are dated at more than 3 million years and because these are stratigraphically younger than the buried cinder cone, it follows that the island is older than 3 million years. Consequently, it is possible that terrestrial life arrived or existed in the Galápagos Islands at least 3 million years ago, which is more than twice as long as had been assumed.

MINARD L. HALL
Facultad de Geología Escuela,
Politécnica Nacional,
Quito, Ecuador

References and Notes

1. C. Darwin, *Journal of Researches into the Natural History and Geology of the Countries Visited During the Voyage of H. M. S. Beagle Round the World Under the Command of Capt. Fitzroy* (Murray, London, 1845).
2. D. Lack, *Darwin's Finches, an Essay on the General Biological Theory of Evolution* (Cambridge Univ. Press, Cambridge, 1947).
3. P. Colinvaux, *J. Ecol.* **64**, 989 (1976).
4. A. Cox and B. Dalrymple, *Nature (London)* **209**, 776 (1966).
5. I. Thornton, *Darwin's Islands: A Natural History of the Galápagos* (Natural History Press, London, 1971).
6. K. Bailey, *Science* **192**, 465 (1976).
7. A. Cox, personal communication.
8. A. McBirney and H. Williams, *Geol. Soc. Am. Mem. 118* (1969).
9. J. Ayala, thesis, Escuela Politécnica, Quito, Ecuador (1979).
10. M. Hall, *Subaerial Origin of Española (Hood) Island and the Age of Terrestrial Life, Galápagos Islands* (National Geographic Society, Washington, D.C., 1982), final report.
11. V. Lorenz, A. McBirney, H. Williams, *An Investigation of Volcanic Depressions* (Manned Spacecraft Center, NASA, Houston, 1970), part 3.
12. G. Heiken, *J. Geophys. Res.* **76**, 5615 (1971).
13. G. Sigvaldason, *Contrib. Mineral. Petrol.* **18**, 1 (1968).
14. C. Wood, *J. Volcanol. Geotherm. Res.* **7**, 387 (1980).
15. ______, *Proc. 10th Lunar Planet. Sci. Conf.* (Houston, March 1979), p. 2815.
16. A. Waters and R. Fisher, *Proc. 2nd Columbia River Basalt Symp.* (Cheney, Washington, March 1969), p. 157.
17. G. Walker and R. Croasdale, *Bull. Volcanol.* **35**, 303 (1972).
18. J. Honnorez and P. Kirst, *ibid.* **39**, 441 (1975).
19. S. Porter, *Geol. Soc. Am. Bull.* **83**, 3607 (1972).
20. G. Heiken, *Bull. Volcanol.* **41-2**, 1 (1978).
21. G. Macdonald, *Volcanoes* (Prentice-Hall, Englewood Cliffs, N.J., 1972).
22. A. Swineford, A. Leonard, J. Frye, *Kans. State Geol. Surv. Bull.* **130**, 97 (1958).
23. P. Nagtegaal, *Leidse Geol. Meded.* **42**, 131 (1969).
24. R. Pike, *Proc. 9th Lunar Planet. Sci. Conf.* (Houston, March 1978), p. 3239.
25. The logistical help of the Charles Darwin Research Station and a NASA faculty fellowship is gratefully acknowledged. I also thank P. Ramon and H. Yepes for assistance in the field and T. Simkin, C. Wood, and M. Fieweger for help in revising the manuscript. Supported by a grant from the National Geographic Society.

30 November 1982; revised 8 April 1983

Boron in Sillimanite

Abstract. *Sillimanite in six granulite-facies, kornerupine-bearing rocks contains 0.035 to 0.43 percent* B_2O_3 *and 0.02 to 0.23 percent MgO (by weight). Substitution of boron for silicon and magnesium for aluminum is coupled such that the ratio of magnesium to boron is about 0.5. Sillimanite incorporates more than 0.1 percent* B_2O_3 *only at high temperatures in a boron-rich environment at very low partial pressures of water. In the amphibolite facies, the sillimanite boron contents are too low to appreciably affect the stability relations of sillimanite with kyanite and andalusite.*

Sillimanite usually occurs naturally as stoichiometric Al_2SiO_5. Analytical work has shown that Fe^{3+}, Cr^{3+}, or V^{3+} (mostly less than 2 percent oxide or 0.04 atom per three cations) and traces of titanium substitute for aluminum (*1–3*). This substitution has minimal effect on the thermodynamic properties of sillimanite and on its stability relations with the other Al_2SiO_5 minerals (*4*). Elements that have been reported present in sillimanite include boron, 0.006 to 0.05 percent B_2O_3 by weight [20 to 170 parts per million (ppm) boron by emission spectrographic analyses (*5*)] and magnesium, up to 0.3 percent MgO by weight [electron microprobe analysis (*6*)]. In contrast, the boron content in kyanite is reported not to exceed 10 ppm and that in andalusite, 25 ppm (*5*). On the basis of these boron contents, D. R. Wones (*4*, p. 208) suggested that boron's "effect on phase equilibria could be important."

Newly analyzed sillimanites from six kornerupine-bearing, granulite-facies rocks (*7*) contain 0.035 to 0.43 percent B_2O_3 (*8*), nine times the previously reported amount, and 0.02 to 0.23 percent MgO (Table 1). The atomic (Al + Fe + Cr)/Si ratio exceeds 2, the value for stoichiometric sillimanite. In contrast, sillimanite from two granulite-facies rocks lacking borosilicates (*7*), samples that were analyzed concurrently with the other six, contains only 0.02 percent MgO and is stoichiometric. We suggest that sillimanite found to contain magnesium should be suspected of containing boron as well, for example, the sillimanite containing 0.3 percent MgO in a borosilicate rock from Zambia (*6*).

The boron contents that we have found confirm that sillimanite is one of the very few anhydrous silicate minerals normally free of boron to incorporate boron in amounts greater than 0.1 percent B_2O_3. Another example is sapphirine; the sapphirine in our samples 1 and 2 contains 0.72 and 0.56 percent B_2O_3 (ion microprobe analyses). In contrast to sapphirine, sillimanite has a relatively simple crystal structure and chemical substitutions are very restricted.

The sillimanite structure consists of single chains of aluminum octahedra supported by double chains of ordered aluminum and silicon tetrahedra parallel to the *c* axis (*9*). In our sillimanite compositions recast to three cations (Table 1), the boron content varies inversely

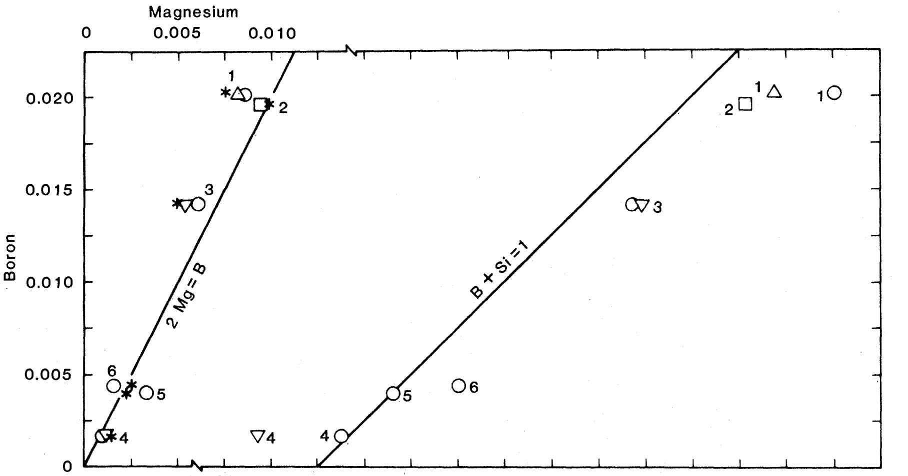

Fig. 1. The boron, magnesium, and silicon contents of sillimanite (in analyses recast to three cations). Asterisks indicate averages obtained during several sessions with the ion microprobe. Circles and squares designate electron microprobe data from Table 1. Triangles represent data from other sessions with the electron microprobe. Lines relating boron, magnesium, and silicon contents are for reference.

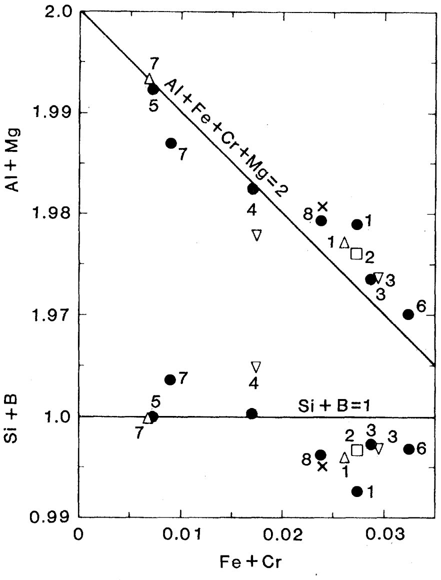

Fig. 2. Analyses of sillimanite recast to three cations. Numbers and symbols are the same as in Fig. 1. Samples 7 and 8 are Antarctic sillimanites (*7*). Lines refer to stoichiometric sillimanite for which B + Si = 1 and Al + Fe + Cr + Mg = 2. The symbol "X" indicates that this composition of sillimanite 8 is from Grew (*2*).

with the silicon content whereas the magnesium content increases linearly with the boron content at a fixed Mg/B ratio near 0.5 (Fig. 1) (*10*). Consequently, boron most likely replaces silicon. Magnesium may replace sixfold-coordinated aluminum. If we add boron to silicon and magnesium to aluminum, then B + Si $\approx$ 1 and Mg + Al + Fe + Cr $\approx$ 2 (Fig. 2).

However, the proposed coupled substitution requires a decrease in anionic charge, which in some minerals is compensated for by a substitution of fluorine or hydroxyl for oxygen. No fluorine was detected with the ion microprobe analyzer, which has a fluorine sensitivity of about 0.05 percent, nor was hydroxyl detected in an infrared scan of sillimanite from sample 2 (*11*). Substitution of boron for silicon also results in a charge imbalance of -0.5 on the oxygen [O_c in Burnham (*9*)] coordinated to tetrahedral silicon and aluminum. We suggest that the coupled substitution of boron for silicon and magnesium for aluminum involves a local rearrangement of the sillimanite structure, in which oxygen is lost to maintain charge balance. The volume of rearranged structure must be submicroscopic, for the analyzed areas of sillimanite are optically homogeneous and free, with rare exceptions, of visible inclusions. Moreover, there is no evidence in x-ray diffraction traces of sillimanite from sample 2 (*12*) of conversion to mullite, which might be expected as the Al/Si ratio increases and oxygen is lost. Incorporation of boron in sillimanite is thus distinct from other known substitutions in sillimanite.

We suggest that the critical factor promoting the incorporation of boron in sillimanite is low partial pressure of water (P_{H_2O}) in the metamorphic fluid phase. High metamorphic temperatures are undoubtedly important, but differences among the samples (Table 2) are not sufficient to account for the tenfold difference in the sillimanite boron content. By analogy with the case for synthetic kornerupine (*13*), the high boron content (3.17 to 3.69 percent B_2O_3) of kornerupine in five of the samples (Table 2) implies a relatively high proportion of boron in the metamorphic fluid. The sillimanite boron content correlates not with the kornerupine boron content but with the kornerupine fluorine content (Tables 1 and 2). We doubt that the spread in the fluorine content among the six kornerupines (Table 2) is due to variations in the Fe/(Fe+Mg) ratio of the kornerupine, which ranges from 0.23 to 0.36 (*14–16*). By analogy with the case for biotite (*3*, *17*), we infer that the high fluorine contents are due to increased P_{HF}/P_{H_2O} in the fluid phase, probably as a result of decreased P_{H_2O}.

The marked correlation of the sillimanite boron content and the kornerupine fluorine content is thus due to the inverse correlation of these compositional features with P_{H_2O} and with the H_2O/B_2O_3 ratio in the fluid phase present in the rock during metamorphism. Under relatively more hydrous conditions, such as was the case for sample 4 and for Pearson and Shaw's (*5*) sillimanite-muscovite veinlet in andalusite, the boron contents of sillimanite would not be expected to exceed Pearson and Shaw's (*5*) value of 0.05 percent B_2O_3.

Such low boron contents would not have an appreciable effect on sillimanite stability relations. As P_{H_2O} decreases relative to P_{total}, sillimanite can incorporate an increasing amount of boron. In some granulite-facies terrains, such as south India (Paderu and Kondapalle, samples 1 through 3), where P_{H_2O} is a small fraction of the total pressure (*14*), the activity of boron in the fluid phase is somehow greatly enhanced and silliman-

Table 1. Ion and electron microprobe analyses of sillimanite. The oxide contents are in percentages by weight; the cation values are normalized to a total of three cations. N.A., not analyzed.

Oxide or cation	Sample 1	2	3	4	5	6
			Oxides			
SiO_2	35.78	36.13	36.49	37.00	36.89	36.52
TiO_2	0.05	N.A.	0.02	0.01	0.02	0.03
Al_2O_3	61.52	61.75	61.97	62.28	62.51	61.47
Fe_2O_3	1.29	1.30	1.39	0.76	0.32	1.56
Cr_2O_3	0.04	0.04	0.03	0.07	0.03	0.02
MnO	0.02	< 0.01	0.01	0.01	0.01	0.02
MgO	0.21	0.23	0.15	0.02	0.08	0.04
Na_2O	< 0.01	N.A.	< 0.01	< 0.01	< 0.01	< 0.01
K_2O	0.04	N.A.	0.04	0.03	0.03	0.04
CaO	0.01	N.A.	< 0.01	0.02	< 0.01	0.01
B_2O_3*	0.43	0.42	0.30	0.035	0.086	0.095
Total	99.39	99.87	100.40	100.24	99.98	99.81
			Cations			
Si	0.9724	0.9771	0.9832	0.9987	0.9959	0.9924
Ti	0.0011	N.A.	0.0004	0.0002	0.0005	0.0007
Al	1.9705	1.9668	1.9675	1.9815	1.9892	1.9685
Fe†	0.0265	0.0263	0.0281	0.0155	0.0065	0.0320
Cr	0.0008	0.0009	0.0006	0.0014	0.0007	0.0005
Mg	0.0086	0.0093	0.0061	0.0010	0.0033	0.0016
B	0.0202	0.0196	0.0142	0.0017	0.0040	0.0044

*All oxides except B_2O_3 were determined with a fully automated Applied Research Laboratories EMX electron microprobe at the University of California, Los Angeles. The B_2O_3 was determined with an Applied Research Laboratories ion microprobe mass analyzer at the Aerospace Corporation (*8*). †All Fe as Fe_2O_3.

Table 2. Metamorphic conditions and kornerupine compositions [in percentages by weight (ion microprobe data (*8*)] for six samples containing sillimanite

Sample	Metamorphic: Temperature* (°C)	Metamorphic: Pressure* (kbar)	Kornerupine: B_2O_3	Kornerupine: Fluorine
1	800 to 850	7 to 8	3.17	0.60
2			3.33	0.90
3			3.67	0.50
4	700 to 800	8 to 9	2.21	0.04
5	650 to 800	4 to 7	3.16	0.25
6			3.69	0.20

*Estimated from petrologic studies on associated rocks (*14*, *18–20*).

ite incorporates significant amounts of boron despite the crystal chemical constraints.

EDWARD S. GREW
Department of Earth and Space Sciences, University of California, Los Angeles 90024
JAMES R. HINTHORNE
Department of Geology, Central Washington University, Ellensburg 98926

References and Notes

1. G. A. Chinner, J. V. Smith, C. R. Knowles, *Am. J. Sci.* **267A**, 96 (1969); A. L. Albee and A. A. Chodos, *ibid.* **267**, 310 (1969); G. R. Rossman, E. S. Grew, W. A. Dollase, *Am. Mineral.* **67**, 749 (1982).
2. E. S. Grew, *J. Petrol.* **21**, 39 (1980).
3. J. A. Speer, *Can. J. Earth Sci.* **19**, 1888 (1982).
4. P. H. Ribbe, in *Reviews in Mineralogy*, vol. 5, *Orthosilicates*, P. H. Ribbe, Ed. (Mineralogical Society of America, Washington, D.C., 1980), p. 189.
5. G. R. Pearson and D. M. Shaw, *Am. Mineral.* **45**, 808 (1960).
6. S. Vrána, *Neues Jahrb. Mineral. Monatsh.* **1979**, 22 (1979).
7. Samples 1 and 2 (original numbers E 2730 and E 2724), collected by C. S. Middlemiss near Paderu, India, are medium- to coarse-grained (to 1 cm) rocks containing kornerupine, sillimanite, sapphirine, biotite, minor spinel and hemoilmenite, and traces of corundum and grandidierite (*14, 15*). Sillimanite prisms 0.3 to nearly 2 mm in diameter are colorless or chatoyant and light brown from patches of abundant acicular inclusions. Sample 3 (J-21) collected by J. K. Nanda near Kondapalle, India, consists of kornerupine, corundum, magnetite, and hemoilmenite isolated by borders of garnet and tourmaline from a quartz matrix [J. K. Nanda, V. Natarajan, A. Purushottam, R. Prabhavathi, *Neues Jahrb. Mineral. Monatsh.* **1983**, 103 (1983)]. Sillimanite forms rare inclusions about 0.1 mm in diameter in kornerupine. Sample 4 (3083D) collected by E. S. Grew from Ellammankovilpatti, India, is cordierite containing kornerupine, sillimanite, and traces of tourmaline (*14*). Sample 5 (RKH 73K-1) collected by R. K. Herd from the Gatineau River, Quebec, and sample 6 (ON/WP-109-77) collected by S. Lonker in the Westport quadrangle, Ontario (*19*), are quartzofeldspathic gneisses containing kornerupine and tourmaline. In sample 5, sillimanite prisms 0.07 to 0.15 mm in diameter are concentrated in a layer a few millimeters thick between thicker layers containing kornerupine, tourmaline, and garnet. Sample 6 consists of layers about 1 cm thick. Kornerupine and tourmaline occur in a layer with garnet and cordierite, whereas prismatic sillimanite 0.15 to 0.2 mm in diameter is abundant in layers with biotite, garnet, cordierite, rare tourmaline, and rare grandidierite (*15*). Samples 7 and 8 in Fig. 2 were collected by E. S. Grew in Antarctica: sample 7 (410A) is a sapphirine granulite from the Schirmacher Hills, and sample 8 [556(3)] is a single crystal fragment from a pegmatite at Reinbolt Hills (*2*); borosilicates are absent in these rocks.
8. We obtained the ion microprobe data by using a primary beam of $^{16}O^-$ ions accelerated to 20 keV, a 2.5-nA current, and a beam spot size about 0.035 mm in the largest dimension. We scanned the secondary ion spectra in the mass range 1 to 150 (through cerium) of each of the analyzed minerals and collected quantitative data in the ion-counting mode. The $^{11}B/^{28}Si$ count ratios were corrected with a working curve based on grandidierite, for which the B/Si ratio is unity [D. A. Stephenson and P. B. Moore, *Acta Crystallogr. Sect. B* **24**, 1518 (1968)]; $^{19}F/^{28}Si$ count ratios were corrected with a working curve based on biotite containing 3.45 percent fluorine (electron microprobe analyses). The SiO_2 values used in the calculations are from the electron microprobe data in Table 1 and (*14–16*). Working curves for ion microprobe analyses were used by J. R. Hinthorne and C. A. Anderson [*Am. Mineral.* **60**, 143 (1975)] for fluorine and hydrogen. We reduced the sillimanite magnesium data using relative secondary ion sensitivity factors calculated from the model of C. A. Anderson and J. R. Hinthorne [*Anal. Chem.* **45**, 1421 (1973)]. The spread of values for three to five ion microprobe determinations of boron and magnesium in the two sillimanites richest in boron (samples 1 and 2) is 15 to 20 percent of the value reported, and for three determinations of boron in kornerupine in samples 1 and 2 is about 5 percent. The MgO contents obtained with the ion microprobe are in good agreement with those obtained with the electron microprobe (Fig. 1). The kornerupine B_2O_3 contents determined with the ion microprobe are comparable to B_2O_3 values obtained by wet chemical methods on other samples from the same localities: 2.21 percent in sample 4 versus 2.40 percent for a kornerupine from Ellammankovilpatti [M. N. Balasubrahmanyan, *Mineral. Mag.* **35**, 662 (1965)] and 3.16 percent in sample 5 versus 3.29 and 3.51 percent in two kornerupines from the Gatineau River [J. P. Girault, *Am. Mineral.* **37**, 531 (1952)]. Cation occupancies calculated from a crystal structure refinement of kornerupine in sample 6 yield 3.65 percent B_2O_3 [L. W. Finger and R. M. Hazen, *Carnegie Inst. Washington Yearb.* **80**, 370 (1981)], in good agreement with our ion microprobe value of 3.69 percent.
9. C. W. Burnham, *Z. Kristallogr.* **118**, 127 (1963).
10. Using the SAS method [A. J. Barr, J. H. Goodnight, J. P. Sall, J. T. Helwig, *A User's Guide to SAS* (SAS Institute, Inc., Raleigh, N.C., 1976)], an anonymous reviewer obtained a correlation factor $r^2 = 0.962$ between the ion microprobe boron contents and electron microprobe magnesium contents.
11. G. R. Rossman (personal communication) detected no hydroxyl in an infrared trace run on a crystal of sillimanite 100 μm thick; this result indicates that no more than 0.01 percent H_2O is present.
12. Two traces include four sillimanite peaks [(101), (020), (121), and (231)] absent in the standard powder pattern of mullite [H. E. Swanson, M. C. Morris, E. H. Evans, L. Ulmer, *Natl. Bur. Stand. (U.S.) Monogr. 25* (1964), section 3, p. 3].
13. G. Werding and W. Schreyer, *Contrib. Mineral. Petrol.* **67**, 247 (1978).
14. E. S. Grew, *J. Geol. Soc. India* **23**, 469 (1982).
15. ———, *Mineral. Mag.* **47**, 401 (1983).
16. ——— and J. R. Hinthorne, unpublished data.
17. J. L. Munoz and S. D. Ludington, *Am. J. Sci.* **274**, 396 (1974).
18. D. Ackermand, R. K. Lal, P. Raase, M. Raith, *Fortschr. Mineral.* **59** (No. 1), 6 (1981); M. Raith, P. Raase, D. Ackermand, R. K. Lal, *Geol. Rundsch.* **71**, 280 (1982).
19. S. Lonker, *Can. J. Earth Sci.* **17**, 1666 (1980).
20. D. Perkins III, E. J. Essene, L. A. Marcotty, *ibid.* **19**, 1759 (1982).
21. This research was supported by NSF grant DPP80-19527 to the University of California, Los Angeles. E.S.G's field work in India was supported by a grant under the Indo-American Fellowship Program; J.R.H's travel to Los Angeles was financed by the Faculty Research Fund of Central Washington University. We thank R. I. Gait for samples E 2730 and E 2724 from the Royal Ontario Museum; R. K. Herd, S. Lonker, and J. K. Nanda for samples; A. S. Janardhan for arranging E.S.G's collecting at Ellammankovilpatti; N. Marquez for operation of the ion microprobe facility at the Aerospace Corporation; G. R. Rossman for infrared data; an anonymous reviewer for the SAS data; and P. C. Grew for constructive comments.

4 April 1983; revised 5 May 1983

The Start of Sulfur Oxidation in Continental Environments: About 2.2 × 10^9 Years Ago

Abstract. *Whereas dissimilatory sulfate reduction in marine environments has been postulated on the basis of sulfur isotope abundances as commencing before about 2.8 × 10^9 years ago, data from the Huronian Supergroup, Canada, suggest that oxidative-reductive reactions involving sulfur in continental environments were not significant before about 2.2 × 10^9 years ago.*

Phanerozoic sedimentary rocks and modern sediments, both marine and continental in origin, are known to contain sulfides of widely varied $\delta^{34}S$ values (*1, 2*). This wide variation is attributed to sulfur isotope selectivity during various processes in the sulfur cycle. In particular, large kinetic isotope effects are identified with bacterial sulfate reduction (*3*). Whereas small isotope fractionations are occasionally encountered in unique circumstances, for example, during very rapid sulfate reduction (*3, 4*), it does not necessarily follow that the lack of sulfur isotope variations is evidence for the absence of oxidative-reductive processes. Nonetheless, the maintenance of such unique conditions in natural systems over substantial periods of time is highly unlikely. Therefore, the absence of a spread in the $\delta^{34}S$ values in sulfides in sedimentary rocks is consistent with and implies a lack of oxidative-reductive reactions.

Wide variations in $\delta^{34}S$ values have been used to postulate the onset of dissimilatory sulfate reduction in marine environments before ~ 2.8 × 10^9 years ago (*5, 6*). The occurrence of bedded sulfate deposits of ~ 3.4 × 10^9 years confirms locally significant concentrations of sulfate in the Archean ocean (*7*). However, continental sedimentary rocks ranging from ~ 2.7 × 10^9 to ~ 2.3 × 10^9 years from Canada, South Africa, and Brazil have sulfides with $\delta^{34}S$ values close to the meteoritic standard (Cañon Diablo), independent of modes of formation or the association of organic matter (*8*). We have studied younger strata in the Huronian Supergroup in Ontario, Canada (Fig. 1), to ascertain the time at which $\delta^{34}S$ variations became significant.

The rocks of the Huronian Supergroup are ~ 2.3 × 10^9 to ~ 2.2 × 10^9 years old; this estimate is based on the ages of rhyolite intercalating with the lowermost Matinenda Formation (*9*) and Nipissing dolerite intruding the sedimentary rocks (*10*). They are largely of fluviatile, glacial, and deltaic origins and therefore were formed mainly in continental environments (*11, 12*). The samples (locations shown in Fig. 1) represent almost the entire Huronian succession and cover an extensive area of sedimentary rocks of continental origin.