

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

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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 kornepupine, sillimanite, sapphirine, biotite, minor spinel and hemoilmenite, and traces of corundum and grandierite (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 kornepupine, 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 kornepupine. Sample 4 (3083D) collected by E. S. Grew from Ellammankovilpatti, India, is cordierite containing kornepupine, sillimanite, and traces of tourmaline (14). Sample 5 (RKH 73K-1) collected by R. K. Herd from the Gati-neau River, Quebec, and sample 6 (ON/WP-109-77) collected by S. Lonker in the Westport quadrangle, Ontario (19), are quartzofeldspathic gneisses containing kornepupine 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 kornepupine, tourmaline, and garnet. Sample 6 consists of layers about 1 cm thick. Kornepupine 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 grandierite (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 $^{16}\text{O}^+$ 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 $^{11}\text{B}/^{28}\text{Si}$ count ratios were corrected with a working curve based on grandierite, for which the B/Si ratio is unity [D. A. Stephenson and P. B. Moore, *Acta Crystallogr. Sect. B* **24**, 1518 (1968)]; $^{19}\text{F}/^{28}\text{Si}$ 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 kornepupine 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 kornepupine 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 kornepupine from Ellammankovilpatti [M. N. Balasubrahmanyam, *Mineral. Mag.* **35**, 662 (1965)] and 3.16 percent in sample 5 versus 3.29 and 3.51 percent in two kornepupines from the Gati-neau River [J. P. Girault, *Am. Mineral.* **37**, 531 (1952)]. Cation occupancies calculated from a crystal structure refinement of kornepupine 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.

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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].

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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 $\delta^{34}\text{S}$ 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 $\delta^{34}\text{S}$ values in sulfides in sedimentary rocks is consistent with and implies a lack of oxidative-reductive reactions.

Wide variations in $\delta^{34}\text{S}$ values have been used to postulate the onset of dissimilatory sulfate reduction in marine environments before $\sim 2.8 \times 10^9$ years ago (5, 6). The occurrence of bedded

sulfate deposits of $\sim 3.4 \times 10^9$ years confirms locally significant concentrations of sulfate in the Archean ocean (7). However, continental sedimentary rocks ranging from $\sim 2.7 \times 10^9$ to $\sim 2.3 \times 10^9$ years from Canada, South Africa, and Brazil have sulfides with $\delta^{34}\text{S}$ 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 $\delta^{34}\text{S}$ variations became significant.

The rocks of the Huronian Supergroup are $\sim 2.3 \times 10^9$ to $\sim 2.2 \times 10^9$ 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 fluvial, 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.

Sulfides, pyrite, and pyrrhotite constitute from 0.001 to 0.3 percent (by weight) of the rocks (13). Some of the quartzites and siltstone from the uppermost Cobalt Group did not contain sufficient sulfides (< 0.001 percent) for isotopic study. The sulfides have anhedral shapes, occur in interstitial spaces, and have grain sizes independent of the hydraulic equivalence of surrounding grains. They are not

associated with hydrothermal alteration, and in all respects they embody the features characteristic of authigenic or diagenetic accessory sulfides dispersed in sedimentary rocks.

The results of our $\delta^{34}\text{S}$ measurements (13) are shown relative to the stratigraphic sequence in Fig. 2. Sulfides from the three lower groups—Elliot Lake, Hough Lake, and Quirke Lake—have $\delta^{34}\text{S}$ val-

ues close to the meteoritic standard. In contrast, the uppermost Cobalt Group contains sulfides with significantly varying $\delta^{34}\text{S}$ values (−20 to +18 per mil). The consistency of the values near 0 per mil in the lower three groups cannot be attributed to secondary effects because even extreme metamorphism apparently does not homogenize sulfur isotope abundances in sulfides (5, 14).

We attribute the consistent $\delta^{34}\text{S}$ values near 0 per mil in the three lower groups to the lack of oxidation-reduction reactions of sulfur in the continental sedimentary cycle at the time of formation. The variations in $\delta^{34}\text{S}$ values in the uppermost group are similar to those from Phanerozoic sedimentary rocks (2), for which isotopic fractionation during oxidation-reduction reactions is well documented. The trend of $\delta^{34}\text{S}$ data in the sedimentary sequence, and in particular the spread of 38 per mil in the Cobalt Group, suggests the onset of sulfur oxidation in these continental environments at the time of their formation about 2.2×10^9 years ago.

The processes that form continental sedimentary rocks involve extensive interaction with the atmosphere during weathering, erosion, transportation, deposition, and diagenesis. Oxidation-reduction reactions involving sulfur in continental environments are dependent on the atmospheric O_2 pressure. A significant increase in O_2 in the atmosphere at the time of formation of the Cobalt

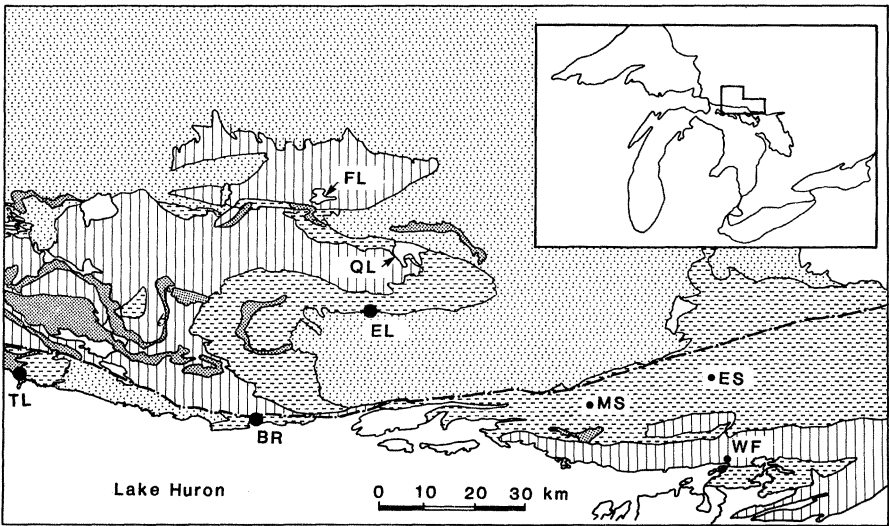


Fig. 1. Map showing the distribution of Huronian rocks: (horizontal dashed lines) lower Huronian rocks (Elliot Lake, Hough Lake, and Quirke Lake groups); (vertical stripes) uppermost Huronian Supergroup, Cobalt Group; (sparsely dotted area) Archean basement rocks; and (densely dotted area) Nipissing diabase. Samples for the isotopic study were collected mainly from two areas: Espanola (ES)–Whitefish Falls (WF) and Elliot Lake (EL)–Quirke Lake (QL)–Flack Lake (FL). Other samples were collected from north of Blind River (BR), northeast of Thessalon (TL), and the Massey (MS) area.

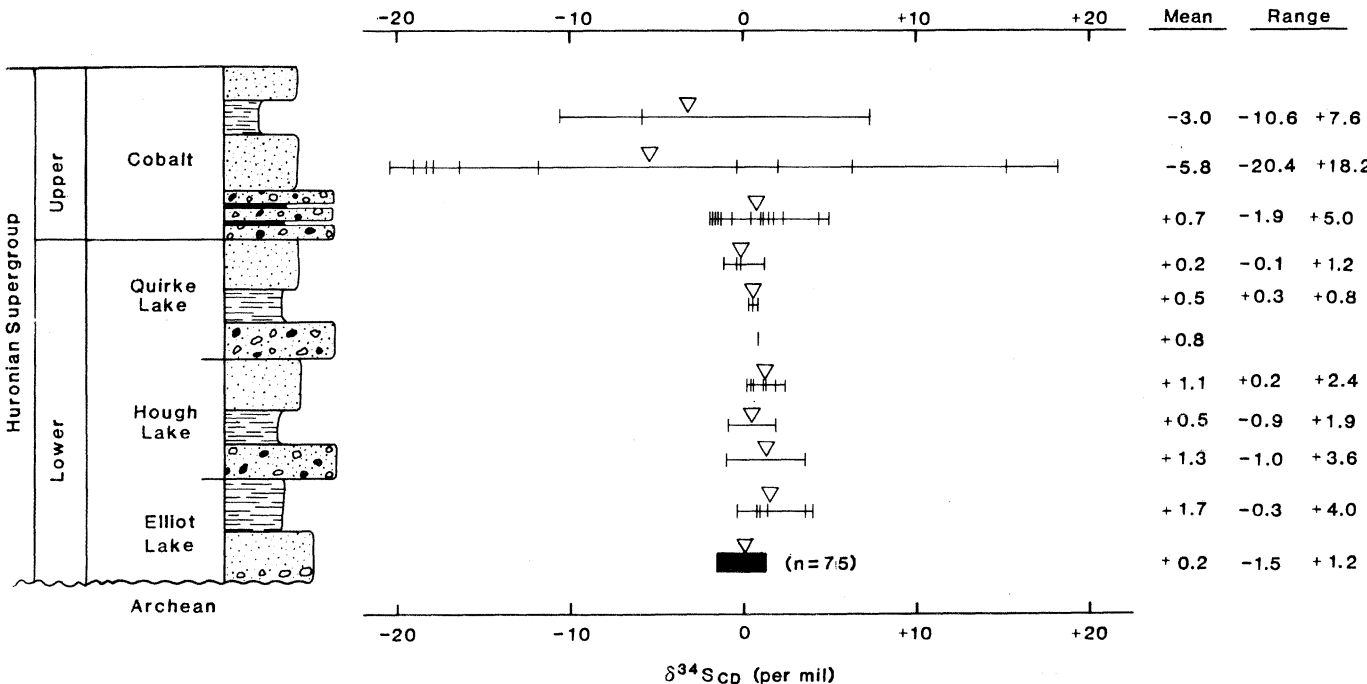


Fig. 2. The $\delta^{34}\text{S}$ values of sulfides from the Huronian Supergroup [with respect to the Cañon Diablo (CD) meteorite] with schematic lithological section. Each vertical bar represents a single sample. The average value of $\delta^{34}\text{S}$ for each formation is indicated by a triangle and is listed at the right along with the maximum and minimum values.

Group would induce oxidation of sulfur. Subsequent reduction would produce the $\delta^{34}\text{S}$ variations observed in the sulfide minerals.

The interpretation of a significant increase of atmospheric O_2 is consistent with the distribution of red coloration in the Huronian Supergroup. The color is due to hematite and iron hydroxides of nondetril origin, which are lacking in the three lower groups and occur in the uppermost group (11, 15). The $\delta^{34}\text{S}$ variation and the occurrence of iron oxides in the Cobalt Group are in accord with an increase in atmospheric O_2 at $\sim 2.2 \times 10^9$ years and its manifestation in the continental sedimentary cycle.

There has been considerable debate concerning the development of O_2 in the earth's atmosphere (16). Some arguments have led to the conclusion that the O_2 pressure was fairly high throughout Precambrian time (17). In contrast, our conclusion of a significant rise in the atmospheric O_2 content during this time is consistent with the models proposed by Cloud (18) and Garrels *et al.* (19).

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13. Sulfides in powdered rock samples were oxidized with $\text{HNO}_3\text{-Br}_2$ and then precipitated as BaSO_4 after the addition of BaCl_2 solution. The BaSO_4 was reduced to Ag_2S with either a mixture of HCl , H_3PO_4 , and HI [H. G. Thode, J. Monster, H. B. Dunford, *Geochim. Cosmochim. Acta* **25**, 159 (1961)] or graphite powder at 1100°C . Isotopic analyses of SO_2 produced by reacting the Ag_2S with Cu_2O at 900°C were performed on a mass spectrometer based on Micromass 602 components. The sulfide con-

tents were determined gravimetrically as BaSO_4 or Ag_2S . The isotope abundance data are expressed with respect to the Cañon Diablo (CD) meteorite standard in terms of the $\delta^{34}\text{S}$ notation:

$$\delta^{34}\text{S} = \left[\frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}}}{(^{34}\text{S}/^{32}\text{S})_{\text{CD}}} - 1 \right] \times 10^3$$

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High Efficiency DNA-Mediated Transformation of Primate Cells

Abstract. Tissue culture cells from several mammalian species, including three primate lines, were transfected with recombinant vectors carrying *Escherichia coli* xanthine-guanine phosphoribosyltransferase or Tn5 aminoglycoside phosphotransferase dominant selectable markers. Human HeLa and SV40-transformed xeroderma pigmentosum cells exhibited stable transformation frequencies of at least 10^{-3} (0.1 percent). CV-1, an African green monkey kidney cell line, could be stably transformed with the exceptionally high frequency of 6×10^{-2} (6 percent).

DNA-mediated introduction of genes into mammalian cells promises to be a powerful method for detecting sequences that control cell growth, confer resistance to toxic drugs, code for surface receptor proteins, or, indeed, alter cell phenotype in any clearly defined way. The importance of this method is well illustrated by the numerous recent publications reporting isolation of cellular oncogenes (1, 2). Further use of mammalian gene transfer is limited by the widespread impression that very few cell types are highly competent recipients for DNA-mediated transfection. Mouse NIH/3T3 and Ltk⁻ cells, which are commonly utilized in genomic DNA transfer experiments, are inappropriate for many

applications. We have systematically investigated DNA-mediated stable "transformation" of primate cells with mammalian vectors that carry dominant selectable markers. Our results indicate that primate cells can be equal or superior to murine cells as gene transfer recipients.

We previously described several mammalian vectors that carry the *Escherichia coli* chloramphenicol transacetylase (CAT) gene (3, 4). Expression of CAT may be readily assayed in higher eukaryotic cells, and therefore these vectors are useful for optimizing DNA transfection procedures as well as for measuring promoter function. Earlier experiments with CAT vectors indicated that the Rous sarcoma virus long terminal repeat (Rous LTR) directs accumulation of high levels of functional messenger RNA (mRNA) in various mammalian and avian cell types (4). This result prompted us to investigate mammalian vectors in which the Rous LTR promoter drives expression of *E. coli* xanthine-guanine phosphoribosyltransferase (gpt) (5) or Tn5 aminoglycoside phosphotransferase (neo) (6) dominant selectable markers.

The starting construct for these studies was the plasmid pRSVcat (4), which is composed of the ampicillin-resistance cistron and the origin of replication from plasmid pBR322 joined to a hybrid eukaryotic transcription unit. The transcription unit in this plasmid is composed of the Rous LTR, CAT coding sequence (cat), and simian virus 40 (SV40) mRNA processing signals, including the small-t intron and early region polyadenylation site. The gpt and neo coding regions, respectively, togeth-

Table 1. Comparison of pSV2neo and pRSVneo stable transformation frequencies. Form I plasmid DNA (5 μg) was added by the calcium phosphate-DNA cotransfection method (16, 17) to cells plated on the previous day at 3×10^5 per 25-cm² flask. After 48 hours cells were split and replated at the density indicated into medium containing G-418 (800 $\mu\text{g}/\text{ml}$; 39.5 percent active). Colonies (> 50 cells) were counted after 10 to 14 days in selection; transformation frequencies are shown in parentheses.

Recipient cell line	Colonies per 50-cm ² dish (No.)*	
	pSV2neo	pRSVneo
<i>10⁵ cells plated</i>		
NIH/3T3	25 (2×10^{-4})	91 (9×10^{-4})
CHO	120 (1×10^{-3})	90 (9×10^{-4})
Ltk ⁻	202 (2×10^{-3})	170 (2×10^{-3})
HeLa	29 (3×10^{-4})	215 (2×10^{-3})
<i>2×10^5 cells plated</i>		
XP2OS-SV40	22 (1×10^{-4})	150 (8×10^{-4})

*Approximate.