[AMERICAN JOURNAL OF SCIENCE, VOL. 298, OCTOBER, 1998, P. 621–672]

American Journal of Science

OCTOBER 1998

PALEOSOLS AND THE EVOLUTION OF ATMOSPHERIC OXYGEN: A CRITICAL REVIEW

ROB RYE and HEINRICH D. HOLLAND
Harvard University, Department of Earth and Planetary Sciences,
20 Oxford Street, Cambridge, Massachusetts 02138

* *Dedicated with affection to the memory of Bart Nagy*

ABSTRACT. **A number of investigators have used chemical profiles of paleosols to reconstruct the evolution of atmospheric oxygen levels during the course of Earth history (Holland, 1984, 1994; Kirkham and Roscoe, 1993; Ohmoto, 1996). Over the past decade Holland and his co-workers have examined reported paleosols from six localities that formed between 2.75 and 0.45 Ga. They have found that the chemical profiles of these paleosols are consistent with a dramatic change in atmospheric P_{O_2} between 2.2 and 2.0 Ga from ≤0.002 to ≥0.03 atm (Holland, 1994). Ohmoto (1996) examined chemical data from twelve reported paleosols ranging in age from 2.9 to 1.8 Ga.[1] He concluded that these chemical profiles indicate that atmospheric P_{O_2} has not changed significantly during the past 3.0 Ga. We seek to resolve the conflict between these reconstructions through a broader examination of the paleosol literature, both to determine which reported paleosols can be definitively identified as such and to determine what these definite paleosols tell us about atmospheric evolution.**

We here review reports describing over 50 proposed paleosols, all but two are older than 1.7 Ga. Our review indicates that 15 of these reported paleosols can be definitively identified as ancient soils. The behavior of iron during the formation of these 15 paleosols provides both qualitative and semiquantitative information about the evolution of the redox state of the atmosphere.

Every definitely identified pre-2.44 Ga paleosol suffered significant Fe loss during weathering. This loss indicates that atmospheric P_{O_2} was always less than about 5×10^{-4} atm prior to 2.44 Ga. Analysis of the Hokkalampi paleosol (2.44–2.2 Ga) (Marmo, 1992) and the Ville Marie paleosol (2.38–2.215 Ga) (Rainbird, Nesbitt, and Donaldson, 1990) yield ambiguous results regarding atmospheric P_{O_2}. Loss of Fe during the weathering of the 2.245 to 2.203 Ga Hekpoort paleosol (Button, 1979) indicates that atmospheric P_{O_2} was less than 8×10^{-4} atm shortly before 2.2 Ga. The presence of red beds immediately overlying the Hokkalampi, Ville Marie, and Hekpoort paleosols suggests that by about 2.2 Ga there was an unquantified but substantial amount of oxygen in the atmosphere. Iron loss was negligible during formation of the 2.2 to 2.0 Ga Wolhaarkop (Holland and Beukes, 1990) and Drakenstein (Wiggering and Beukes, 1990) paleosols and during formation of all the later paleosols we reviewed. Thus, atmospheric P_{O_2} probably has been ≥0.03 atm since sometime between 2.2 and 2.0 Ga.

INTRODUCTION

Paleosols, which form at the atmosphere-lithosphere interface, can provide semiquantitative data regarding atmospheric oxygen levels at the time they formed. A number of investigators have attempted to reconstruct the evolution of oxygen in Earth's atmosphere based on the series of snapshots that paleosols provide (Holland, 1984, 1994;

---

[1] The text in *Geology* contained data for nine reported paleosols. The appendices in GSA Data Respository Item 9666 contained data for several more reported paleosols including three from the time interval 2.9 to 1.8 Ga.

Kirkham and Roscoe, 1993; Ohmoto, 1996). Some of their conclusions have differed radically from one another.

Ohmoto (1996 and 1997) recently concluded that chemical profiles of paleosols indicate that atmospheric P_{O_2} has not changed significantly during the past 3.0 Ga. His conclusion was based primarily on data from ten proposed paleosols: the 2.9 to 2.8 Ga Dominion Reef paleosol, the 2.75 Ga Villebon paleosol, the ~2.45 Ga Denison, Pronto, and Quirke II DH 270 paleosols, the 2.44 to 2.2 Ga Hokkalampi paleosol, the 2.38 to 2.215 Ga Ville Marie paleosol, the 2.245 to 2.203 Ga Hekpoort paleosol, the 2.2 to 2.0 Ga Drakenstein paleosol, and the 1.9 to 1.8 Ga Flin Flon paleosol. Holland and co-workers have consistently concluded that atmospheric P_{O_2} was low ($\leq$0.002 atm) prior to about 2.2 Ga, and that it rose to at least 0.03 atm by about 2.0 Ga (see for example, Holland, 1994). This conclusion was based primarily on data from seven proposed paleosols: the two 2.775 to 2.755 Ga Mt. Roe paleosols, the 2.245 to 2.203 Ga Hekpoort paleosol, the 2.2 to 2.0 Ga Wolhaarkop paleosol, the 1.9 to 1.8 Ga Flin Flon paleosol, the 1.1 Ga Sturgeon Falls paleosol, and a suite of 0.45 Ga Arisaig paleosols. Here we review all the proposed paleosols cited by Ohmoto and by Holland and co-workers as well as over 30 other proposed paleosols to determine which of these reconstructions of atmospheric evolution is consistent with the available data.

In 1986 and 1990 Retallack reviewed the extant paleosol literature and sought to give an overview of all that paleosols might tell us about Earth history (Retallack, 1986b, 1990). This review is an update of Retallack's, drawing on the past 10 yrs' experience, both personal and published. Our goal is much more modest than Retallack's (1986b and 1990). We simply seek to reconstruct the redox history of the atmosphere. To that end we review the criteria for identifying paleosols, apply these criteria to over 50 reported pre-Devonian paleosols, and examine the chemical profiles of units that are definitely paleosols. For the sake of brevity we have focused almost exclusively on paleosols that formed before 1.7 Ga. We plan to review all the more recent Precambrian paleosols at a later date.

The use of paleosols as a means of reconstructing the chemical evolution of the atmosphere is suggested by their very nature. "A paleosol is a soil that formed on a landscape of the past" (Valentine and Dalrymple, 1976). Soils form at the interface of the atmosphere and the lithosphere. Chemical changes caused by weathering are driven by the acids and oxidants in soil waters. Atmospheric CO_2 and O_2 dissolved in rainwater contribute significantly to the acid and oxidant budgets of soil waters and therefore drive some of the chemical changes wrought by weathering.

Higher land plants are ubiquitous in modern soils. Fossil spore tetrads indicate that plants first appeared on the continents during the Mid-Ordovician (Kenrick and Crane, 1997). The continents were probably not fully colonized by rooted plants until the Devonian (Algeo and others, 1995). In a plant-colonized soil, respiration and decomposition significantly affect the amount of CO_2 and O_2 dissolved in soil waters. By producing and consuming O_2 and CO_2, organisms mask the effects of the ambient atmosphere on soil composition. Later on in this paper we will present an argument for why we believe that the oxidation state of pre-Devonian paleosols was largely unaffected by biology.

In the absence of biologic effects, subaerial weathering would have essentially involved the reaction of rocks with the ambient atmospheric gases. Pre-Devonian preserved soils or paleosols are therefore a potential source of semiquantitative data regarding the redox state of the atmosphere under which they developed. Unfortunately, it is not always possible to identify pre-Devonian paleosols with certainty. In the absence of root traces, some paleosols are indistinguishable from sedimentary rocks. Other paleosols may be identical to stratigraphically controlled alteration zones. Only those paleosols that can be clearly distinguished both from sedimentary rocks and from alteration zones are potentially useful as paleobarometers.

IDENTIFYING PRE-DEVONIAN PALEOSOLS

Soils that form in place on a homogeneous substrate such as an igneous or high grade metamorphic rock tend to exhibit unidirectional changes in texture, mineralogy, and bulk chemical composition from the unweathered parent rock to the top of the soil profile (Holland and Zbinden, 1988). At their base, such soils typically grade smoothly into the parent material. The top of a mature soil of this sort generally retains few, if any, of the parent rock's textural or mineralogical features. There is usually a continuum of intermediate stages of decomposition of the original minerals and textures. As the original minerals break down they are replaced by soil minerals. In a mature soil kaolinite, gibbsite, and amorphous silica often dominate the mineralogy near the top of the soil. Smectite and vermiculite are common in the lower portion of mature soils. The chemical compositions of the minerals in each soil zone are quite distinct. The several soil zones also have distinct textural characteristics. As a soil develops, the transition between soil zones may become quite sharp. Major textural, mineralogical, and chemical changes accompanying the transition from one soil zone to another may occur over a few centimeters in the middle of soil profiles. Sedimentary rocks generally do not show vertical changes in texture, mineralogy, and chemistry such as those found in undisturbed soils and tend not to reflect changes in the nature of the underlying materials. They also generally do not grade into the underlying materials. These soil properties can therefore be used to distinguish paleosols from most sedimentary rocks.

Soils often develop on sedimentary rocks. Most sedimentary rocks are vertically heterogeneous. Soils that develop on flat-lying clastic sediments and other heterogeneous substrates tend not to develop textural, mineralogical, and chemical profiles that distinguish them from other clastic sediments. Some sediments, particularly chemical sediments such as banded iron formations (BIFs), are fairly homogeneous along individual strata. When such sediments are tilted and then weathered, the resulting soil profiles can usually be distinguished from later sediments.

Many soils are transported during and after weathering. Transport typically destroys the mineralogical, textural, and chemical profiles of soils. Without root traces it is generally not possible to distinguish transported soils from sedimentary rocks and from soils that developed on heterogeneous parent rocks.

The changes in chemical composition produced during in-place weathering of most homogeneous parent rocks arise from differences in the mobility of their contained elements. During weathering, mobile elements go into solution. Once in solution, these elements either are lost from the soil or are reprecipitated as constituents of soil minerals in the lower portions of the soil. Immobile elements either never go into solution or are quickly reprecipitated as constituents of a highly insoluble phase. Ca, Mg, Na, K, and Mn are generally mobile elements. Under most weathering conditions, Ti, Al, and Zr are essentially immobile. The loss of mobile elements and the retention of immobile elements leads to significant differences between the ratios of mobile to immobile elements in soils and those in their parent rocks.

If a completely homogeneous rock is weathered, the immobile element ratios Ti/Al, Ti/Zr, and Al/Zr in the most weathered samples are usually equal to those in the parent rock. In reality, no rock is completely homogeneous, and no element is perfectly immobile, but Maynard (1992) has found that the Ti/Al ratio of modern in-place soils generally deviates from the Ti/Al ratio in their parent rocks by less than 50 percent, except in cases of extreme weathering. He also found that the Ti/Zr ratio in such soil samples never deviates by more than 40 percent from the value in the parent materials.

We can estimate the fractional loss of the mobile elements from soil samples during weathering by comparing their abundance with that of the immobile elements. In in-place soils derived from a homogeneous parent rock the Ca/Al, Na/Al, Mn/Al, and K/Al ratios generally decrease unidirectionally upward from those of the parent rock to those of the most weathered material, while the Ti/Al, Ti/Zr, and Al/Zr ratios remain essentially constant. In the top portion of such soils, the Mg/Al ratios are generally much lower than the Mg/Al ratios in the parent material. However, when smectite and/or vermiculite form in the lower portions of the soil, the depletion of Mg may be much less dramatic than than that of Ca, Na, and K. In fact, if smectites and vermiculites incorporate enough Mg from the soil waters that percolate down through the weathering profile, Mg/Al ratios in the lower portion of such soils may exceed the Mg/Al ratios in the parent materials. The movement of Mg during weathering can therefore lead to Mg enrichment in some portions of the soil.

In vertical sections through sediments immobile element ratios are rarely constant, and ratios of mobile to immobile element concentrations rarely vary as they do in soils developed *in situ* from a homogeneous parent. Thus, constant immobile element ratios and variations in mobile to immobile element ratios consistent with weathering of the underlying material are useful in distinguishing soils from sedimentary rocks.

The gradual replacement of parent textures and minerals, as well as variations in chemical composition similar to those found in in-place soils that developed on homogeneous parent materials, can all be produced by alteration below the contact between highly permeable and less permeable rock units. However, the process of covering a soil with later sediments or lava flows can produce features at the contact between the soil and the immediately overlying rock unit that are not found in alteration zones.

Soils are soft. Typically, they are eroded prior to the deposition of younger units. Occasionally, a soil is covered by prograding sediments or by a subaerial lava flow. Soils may be deformed prior to and during burial. Soft-sediment deformation features can serve to distinguish alteration zones from lithified paleosols (Holland and Zbinden, 1988). A significant number of soft-sediment deformation features have been recorded in the paleosol literature. Perhaps the most common are rip-up clasts of paleosol in the immediately overlying unit. When water inundates a soil, erosion is usually widespread. If the soil is dry enough prior to inundation, soil clasts may be formed and included in sediments deposited on top of the partially eroded soil. Lithified rip-up clasts of paleosol material, such as those found in an ironstone overlying the Hekpoort paleosol (fig. 1A), show that the proposed soil was indeed soft and friable when the overlying sediment was deposited. The parent rock was clearly altered prior to the deposition of the ironstone, which suggests a weathering origin for the rip-up clasts. The iron content of the rip-up clasts is less than that of the Hekpoort Basalt. The loss of iron must have preceded the deposition of the ironstone, as there is no plausible way to remove iron from a clast encased in sediment containing over 50 wt percent Fe_2O_3. If supposed rip-up clasts reside in sediments that are chemically similar to the most weathered portion of the proposed soil, the apparent weathering recorded in the rip-up clasts may be due to alteration that post-dates the deposition of the overlying sediment. The presence of rip-up clasts of both highly weathered and essentially unweathered parts of a paleosol, as found, for instance, in the basal Lorrain breccia above the Ville Marie paleosol (Rainbird, Nesbitt, and Donaldson, 1990), virtually rules out this possibility.

Subaerially weathered soils sometimes dry out. As they dry, desiccation cracks may form in the top portion of the profile. If these cracks are filled by sediment and are later lithified and compacted, they provide a clear testament to the subaerial origin of the soil (fig. 1B). Soils may also be covered by subaerial lava flows that entrain soft soil materials and produce mechanical mixtures of soil and lava. These mixtures can be preserved on a

Fig. 1. Photos of soft-sediment deformation features. (A) Rip-up clasts of the Hekpoort paleosol in the overlying oölitic iron stone (Core DPZ-2 courtesy of The Anglo-American Corporation). (B) Desiccation crack in the top of the sericite zone of the Hekpoort paleosol at Waterval Onder, South Africa. Polished slab courtesy of Andrew Button.

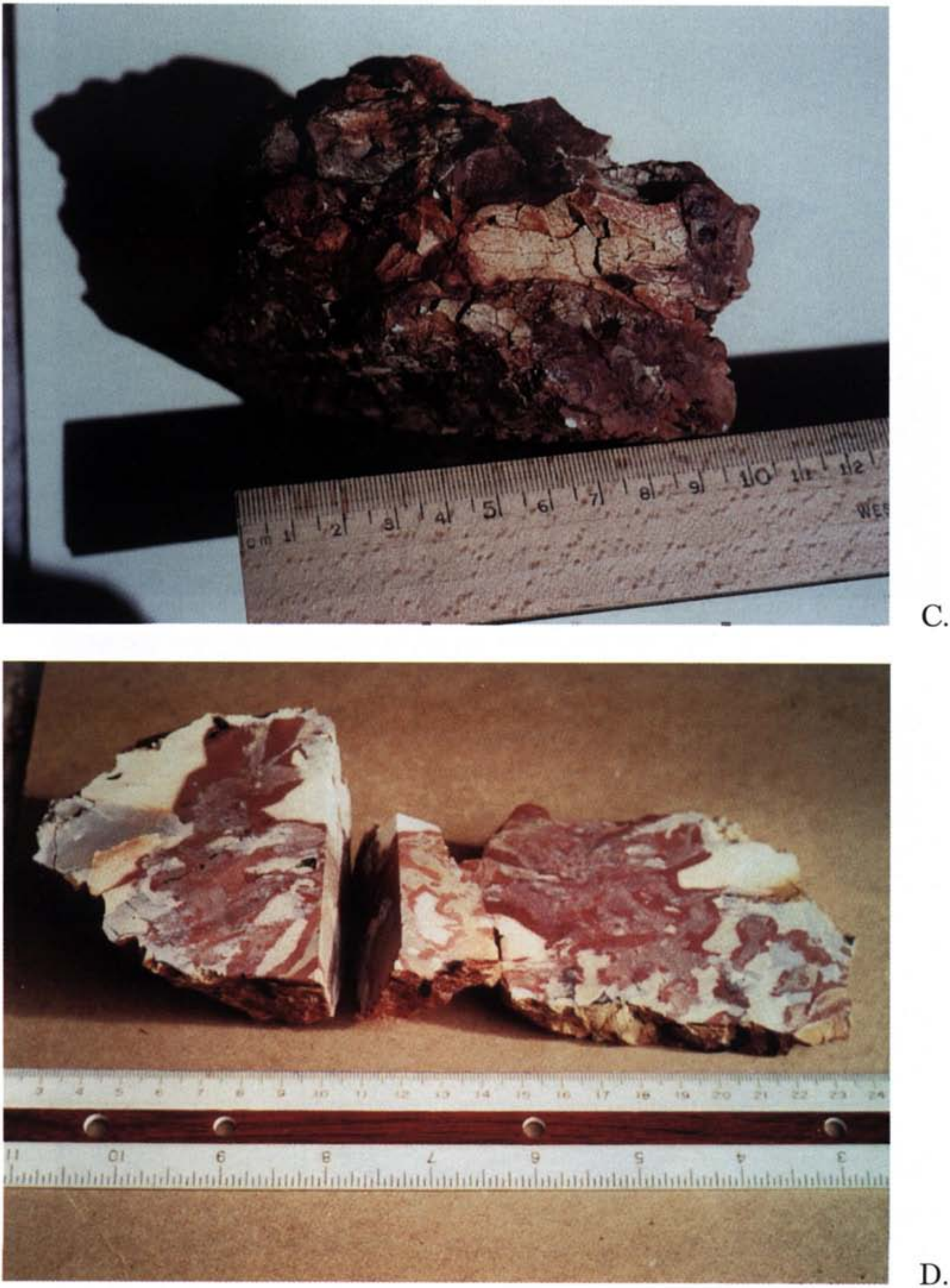


Fig. 1(C and D) Mechanical admixture of the Mt. Roe #2 paleosol with the overlying basalt flow.

E.

F.

Fig. 1(E) Mechanical admixture of the Arisaig paleosol with the overlying andesite flow. (F) Indurated balls of the Sturgeon Falls paleosol at the contact with Jacobsville sandstone.

small scale (fig. 1C and D) or on a large scale (fig. 1E) (Feakes, Zbinden, and Holland, 1989). When partially indurated, a soil may ball up during erosion. The resulting balls may be redeposited at the base of the overlying sediments, as in the Sturgeon Falls paleosol (fig. 1F) (Feakes, Zbinden, and Holland, 1989; Zbinden and others, 1988). These and other soft-sediment deformation features allow us to distinguish paleosols unequivocally from alteration zones of solid rock units below younger, permeable units.

A rock unit that formed prior to the development of vascular land plants must meet five criteria to be definitely classed as a paleosol. First, the unit must have developed on a homogeneous parent rock and have been preserved in place. Second, third, and fourth, the unit must exhibit changes in mineralogy, texture, and chemical composition from the parent rock to the top of the soil that are consistent with soil forming processes. Fifth, there must be identifiable soft-sediment deformation features along the contact between the unit and the immediately overlying rocks. If a rock unit meets all these criteria, it is classed here as a paleosol.

We have applied these five criteria for identifying paleosols to 50 pre-Devonian rock units that have been described as paleosols. The results of our analysis are summarized in table 1. We have listed the name, location, time of formation, and parent material for each proposed paleosol. Each paleosol was given a score of yes, no, or not available (N/A) for each of the five paleosol criteria. Metamorphic grade is listed to highlight the fact that most high grade metamorphic profiles described as paleosols do not meet the paleosol criteria outlined above. We also indicated whether or not each profile had experienced metasomatism, because we found that nearly every proposed soil in this review was enriched in K relative to its parent, a condition that certainly did not arise as a result of weathering.

In many profiles the K/Al ratios in samples from the top section of the paleosol are more than twice as high as the K/Al ratios in parent rock samples (Button, 1979; Feakes, Zbinden, and Holland, 1989; G-Farrow and Mossman, 1988; Hart, 1986; Macfarlane, Danielson, and Holland, 1994; Prasad and Roscoe, 1991; Sutton and Maynard, 1993; Wiggering and Beukes, 1990). Macfarlane and Holland (1991) showed that K addition in three paleosols was a result of short lived local or regional thermal disturbances. Potassium metasomatism is almost certainly responsible for high K levels in most of the other supposed paleosol profiles.

Some investigators suggest that the chemical changes induced by metamorphic events that introduced K into supposed paleosols obscured many of the chemical changes due to weathering (Palmer, Phillips, and McCarthy, 1989). In particular, Palmer, Phillips, and McCarthy (1989) concluded that Fe depletion in reported Archean and Paleoproterozoic paleosols in Canada and South Africa was probably due to metamorphism rather than to weathering. This conclusion cannot be supported for profiles that meet the textural, mineralogical, and chemical criteria for paleosols and that contain Fe-depleted rip-up clasts in overlying Fe rich sediments or lava flows. Furthermore, K enrichment in reported paleosols is ubiquitous both in pre-2.2 Ga paleosols that show Fe loss and in post-2.2 Ga paleosols that show Fe retention at the tops of the profiles. It would be fortuitous for all pre-2.2 Ga paleosols to have lost Fe during metamorphism and all post-2.2 Ga paleosols to have retained Fe during metamorphism. It is far more likely that in paleosols that meet all the criteria laid out above, K was added to a previously existing soil. We have therefore disregarded K in our evaluation of the chemical profiles of proposed paleosols.

We rated each of the 50 units according to the number of paleosol criteria they met. Paleosols that met the parental, textural, mineralogical, and chemical criteria listed above and that exhibit soft-sediment deformation features were given a rating of definite; they are almost certainly paleosols. Those that met all but one of these criteria were given a rating of likely. Those that met all but two were called possible. And those that failed

TABLE 1

50 Paleosol Candidates Evaluated

No.	paleosol name	location	date of weathering (Ga)	parent	textural evidence	mineralogical evidence	chemical evidence	soft-sediment features	metasomatism	metamorphic grade
Definite Paleosols										
1	Mt. Roe #1	Australia	2.775-2.755	basalt	Yes	Yes	Yes	Yes	Yes	lg
2	Mt. Roe #2	Australia	2.775-2.755	basalt	Yes	Yes	Yes	Yes	Yes	lg
3	Denison/Stanleigh	Canada	2.475-2.440	greenstone	Yes	Yes	Yes	Yes	Yes	lg
4	Quirke II	Canada	2.475-2.440	basalt	Yes	Yes	Yes	Yes	Yes	lg
5	Pronto/NAN	Canada	2.475-2.440	granodiorite	Yes	Yes	Yes	Yes - a	Yes	lg
6	Lauzon Bay	Canada	2.475-2.440	granite	Yes	Yes	Yes	Yes - a	Yes	lg
7	Cooper Lake	Canada	2.475-2.440	diabase	Yes	Yes	Yes	Yes - a	Yes	lg
8	Hokkalampi	Finland	2.44-2.2	granitoid	Yes	Yes	Yes	Yes	Yes	g
9	Ville Marie	Canada	2.38-2.215	granite	Yes	Yes	Yes	Yes	Yes	lg
10	Hekpoort	South Africa	2.245-2.059	basaltic andesite	Yes	Yes	Yes	Yes	Yes	g
11	Drakenstein	South Africa	2.235-1.924	basaltic andesite	Yes	Yes	Yes	Yes	Yes	lg
12	Wolhaarkop	South Africa	2.235-1.924	BIF	Yes	Yes	Yes	Yes	No	lg
13	Flin Flon	Canada	1.9-1.8	basalt	Yes	Yes	Yes	Yes	Yes	g
14	Sturgeon Falls	USA	1.1	basalt	Yes	Yes	Yes	Yes	Yes	g
15	Arisaig	Canada	0.45	basalt	Yes	Yes	Yes	Yes	Yes	g
Likely Paleosols										
16	pre-Pongola	South Africa	3.0-2.9	granite	Yes	Yes	Yes	No	Yes	g
17	Dominion Reef	South Africa	2.9-2.8	granite	Yes	Yes	Yes	No	Yes	?
18	Bird	South Africa	2.8-2.7	basalt	Yes	Yes	Yes	No	Yes	g
19	Krivoy Rog	Ukraine	2.8-2.6	granite	Yes	Yes	Yes	No	Yes	?
20	Island Lake	Canada	about 2.8	quartz diorite	Yes	Yes	N/A	Yes	N/A	N/A
21	Kalkloof	South Africa	2.7-2.55	Dunitic serpentinite	Yes	Yes	No	Yes	Yes	g?
22	Delmas	South Africa	2.7-2.55	granite	Yes	Yes	No	Yes	Yes	g
23	Jackson Lake	Canada	about 2.6	mafic volcanic	Yes	Yes	N/A	Yes	Yes	g
24	Denison	Canada	2.475-2.440	greenstone	Yes	Yes	No	Yes - a	Yes	lg
25	Pronto	Canada	2.475-2.440	granite	Yes	Yes	No	Yes - a	Yes	lg
26	Cooper Lake	Canada	2.475-2.440	sandstone	Yes	Yes	Yes	Yes - a	Yes	lg
27	pre-Sariola (Brattli	Norway	2.495-2.294	various	Yes	Yes	No - b	Yes	Yes	variable
28	sub-Thelon	Canada	1.85-1.7	granitic gneiss	Yes	Yes	No - b	Yes	No	lg
Possible Paleosols										
29	Steep Rock	Canada	3.0-2.7	granodiorite	No	Yes (?)	No - c	No	Yes	lg
30	Steep Rock	Canada	3.0-2.7	tonalite	Yes	Yes	N/A	No	N/A	lg
31	Kinojevis	Canada	about 2.7	basalt	Yes	Yes	No - d	No	N/A	N/A
32	Mertondale	Australia	2.58	granite	Yes	Yes	N/A	No	N/A	g
33	Hokkalampi	Finland	2.44-2.2	glaciogenic rock	Yes	Yes	No	Yes	Yes	g
34	pre-Jatulian	Karelia	>2.1	granite	Yes	Yes	No	No	Yes	g
35	Suodennieimi	Finland	> 2.0	diorite	Yes(?)	Yes(?)	No - d	No(?)	N/A	g/a
36	Wilson Island	Canada	about 1.9	gneiss	Yes(?)	Yes(?)	N/A	No	N/A	lg
37	Mistassini	Canada	Aphebian	tonalitic gneiss	Yes	No(?)	N/A	Yes	N/A	?
Unlikely Paleosols										
38	Point Lake	Canada	3.15-2.67	no column	No	No	No	No	Yes	lg
39	Steep Rock	Canada	3.0-2.7	carbonate	Yes	Yes	N/A	No	N/A	lg
40	Ada May	South Africa	3	quartzite	N/A	N/A	No	No	N/A	N/A
41	Laughland Lake	Canada	>2.95	no column	No	No	No	No	Yes(?)	lg
42	Vaal Reef	South Africa	2.9	quartzite	N/A	N/A	No	No	N/A	N/A
43	Villebon	Canada	about 2.75	no column	No	No	No	No	?	g
44	Ventersdorp	South Africa	about 2.3	basalt	N/A	N/A	No	No	Yes	N/A
45	Bathurst Inlet	Canada	about 2.0	sandstone	N/A	N/A	N/A	Yes	N/A	N/A
46	Mount Martin	Australia	Archean	komatiite	No	No	No	No	?	ug
47	Sonapahar	India	?	no column	No	No	No	No	N/A	a
48	Kakanuru	India	?	no column	No	No	No	No	?	gr
49	Bundelkhand	India	?	no column	No	No	No	No	?	g
50	Cod Island	Canada	1.88-2.0	granitic gneiss	No	No	No	No	?	g

Notation for metamorphic grade column: g = greenschist facies, l = lower. u = upper, a = amphibolite facies, gr = granulite facies, N/A = not available

Notes: (a) Soft-sediment deformation feature criterion for paleosol met by another profile under the same unconformity. (b) Some profiles under this unconformity fail on the chemical criteria for paleosols. Others are too sparsely sampled to tell whether they pass. (c) This profile is too thin to evaluate. (d) There are too few data published to determine whether these units pass the chemical criteria for paleosols.

References: 1,2 Macfarlane, Danielson, and Holland (1994); 3 Farrow (1987), G-Farrow and Mossman (1988), Mossman and Farrow (1992); 4 Prasad and Roscoe (1991 and 1996); 5 Farrow (1987), G-Farrow and Mossman (1988), Mossman and Farrow (1992); 6 Sutton and Maynard (1992); 7 Sutton and Maynard (1993); 8 Marmo (1992); 9 Rainbird, Nesbitt, and Donaldson (1990); 10 Button (1979), Hart (1986), Retallack (1986), Retallack and Krinsley (1993); 11 Wiggering and Beukes (1990); 12 Holland and Beukes (1990); 13 Holland, Feakes, and Zbinden (1989); 14 Zbinden and others (1988); 15 Feakes, Zbinden, and Holland (1989); 16,17 Grandstaff and others (1986); 18 Palmer, Phillips, and McCarthy (1989); 19 Kulish, Pokalyuk, and Reshetnyakov (1987); 20 Herd, Chandler, and Ermanovics (1976); 21 Martini (1994); 22 Ferraz (1989), Maynard and others (1995); 23 Falck, Donaldson, and Hall (1991); 24 Gay and Grandstaff (1980), Prasad and Roscoe (1996); 25 Gay and Grandstaff (1980); 26 Sutton and Maynard (1993); 27 Sturt, Melezhik, and Ramsay (1994); 28 Chiarenzelli (1983); LeCheminant and others (1983); Ross and Chiarenzelli (1985), Gall and Donaldson (1990), Gall (1994); 29 Schau and Henderson (1983); 30 Wilks and Nisbet (1988); 31 Kimberley and Grandstaff (1986); 32 Worden and Compston (1973); 33 Marmo (1992); 34 Koryakin (1971); 35 Rankama (1955); 36 Stanworth and Badham (1984); 37 Chown and Caty (1983); 38 Schau and Henderson (1983); 39 Wilks and Nisbet (1988); 40 Maynard (1992); 41 Schau and Henderson (1983); 42 Maynard (1992); 43 Vogel (1975); 44 Kimberley and Grandstaff (1986); 45 Grotzinger and others (1989); 46 Purvis (1984); 47 Golani (1989); 48 Kamineni and Rao (1988); 49 Sharma (1979); 50 Smyth (1976) three or more of the criteria were rated unlikely. These ratings are shown as headings for the four sections of table 1.

THE DEFINITE PALEOSOLS

Fifteen of the units we evaluated are rated as definite. They are listed in table 1, arranged chronologically from oldest to youngest. Their locations are shown on the map, figure 2. The times of formation of some of the definite paleosols are uncertain. Where age ranges overlap, we have listed the paleosols in the order of their maximum ages.

1 and 2.–Mt. Roe #1 and #2. The oldest definite paleosols, paleosols 1 and 2 in table 1, are the Mt. Roe #1 and Mt. Roe #2 paleosols. These paleosols developed on flows of the 2.765 ± 0.01 Ga Mount Roe Basalts of the Fortescue Group in Western Australia (Macfarlane, Danielson, and Holland, 1994). Both of the Mt. Roe paleosols are superbly exposed for strike lengths of 1 to 2 km near Whim Creek, Western Australia (Macfarlane, Danielson, and Holland, 1994). Original basaltic textures are clearly preserved in the unweathered material at the base of both paleosols, although many of the original minerals in the basalts have been replaced by chlorite and prehnite-pumpellyite facies minerals. Abundant plagioclase feldspar laths and some clinopyroxene are still present. Chlorite and quartz dominate the mineralogy of the lower portion of each paleosol. The upper portions of the two paleosols are dominated by sericite (Macfarlane, Danielson, and Holland, 1994). This mineralogical pattern is common to several of the definite and likely paleosols.

Relict basaltic textures persist into the lower sericite zones of both Mt. Roe paleosols, although all the original minerals at this level have been pseudomorphically replaced by sericite, rutile, and minor phosphate minerals. Original basaltic textures are flattened and gradually disappear toward the top of the sericite zones (Macfarlane, Danielson, and Holland, 1994). The gradual destruction of the original texture and mineralogy upward through the profile indicates a history of *in situ* weathering.

The contact between both Mt. Roe paleosols and the overlying unit is generally sharp (Macfarlane, Danielson, and Holland, 1994). In both profiles there are clear examples of clasts of paleosol material in the immediately overlying units (see fig. 1C and D). The Mt. Roe #1 paleosol is overlain by thin-bedded, laminated sediments that contain clasts of paleosol material up to 2 cm long and 3 mm thick. A basalt flow immediately overlies the Mt. Roe #2 paleosol. Macfarlane, Danielson, and Holland (1994) report that some of the paleosol material was entrained into the overlying flow during eruption. They also report field evidence of baking of the upper few decimeters of the sericite rich zone of the paleosol by the overlying flow. Together, these observations provide compelling evidence that both the Mt. Roe #1 and the Mt. Roe #2 paleosols were soft and highly weathered when they were covered.

The chemical profiles of the Mt. Roe #1 and Mt. Roe #2 paleosols are both consistent with the weathering of a homogeneous parent basalt. There is no evidence for the addition of a significant quantity of windblown or waterborne material. Sodium, magnesium, calcium, manganese, and iron are essentially absent from the sericite zone. From the top of the paleosol to the parent material the Ti/Al and the Ti/Zr ratios are nearly constant in both profiles (fig. 3). Thus, they meet all the criteria for paleosols. The difference between the immobile element ratios in the parent basalts at Mt. Roe #1 and Mt. Roe #2 (fig. 3) indicates that the paleosols developed on two different flows and are separate paleosols. The Mount Roe basalts and related lavas and tuffs above and below these paleosols are 2.765 ± 0.010 Ga by U-Pb zircon dating (Arndt and others, 1991).

3 to 7. Denison/Stanleigh, Quirke II, Pronto/NAN, Lauzon Bay, Cooper Lake.–The next oldest definite paleosols underlie the Matinenda Formation in the Elliot Lake area of Canada. These paleosols, numbered 3 to 7, developed on Archean greenstone (paleosol 3) (G-Farrow and Mossman, 1988; Gay and Grandstaff, 1980; Mossman and Farrow,

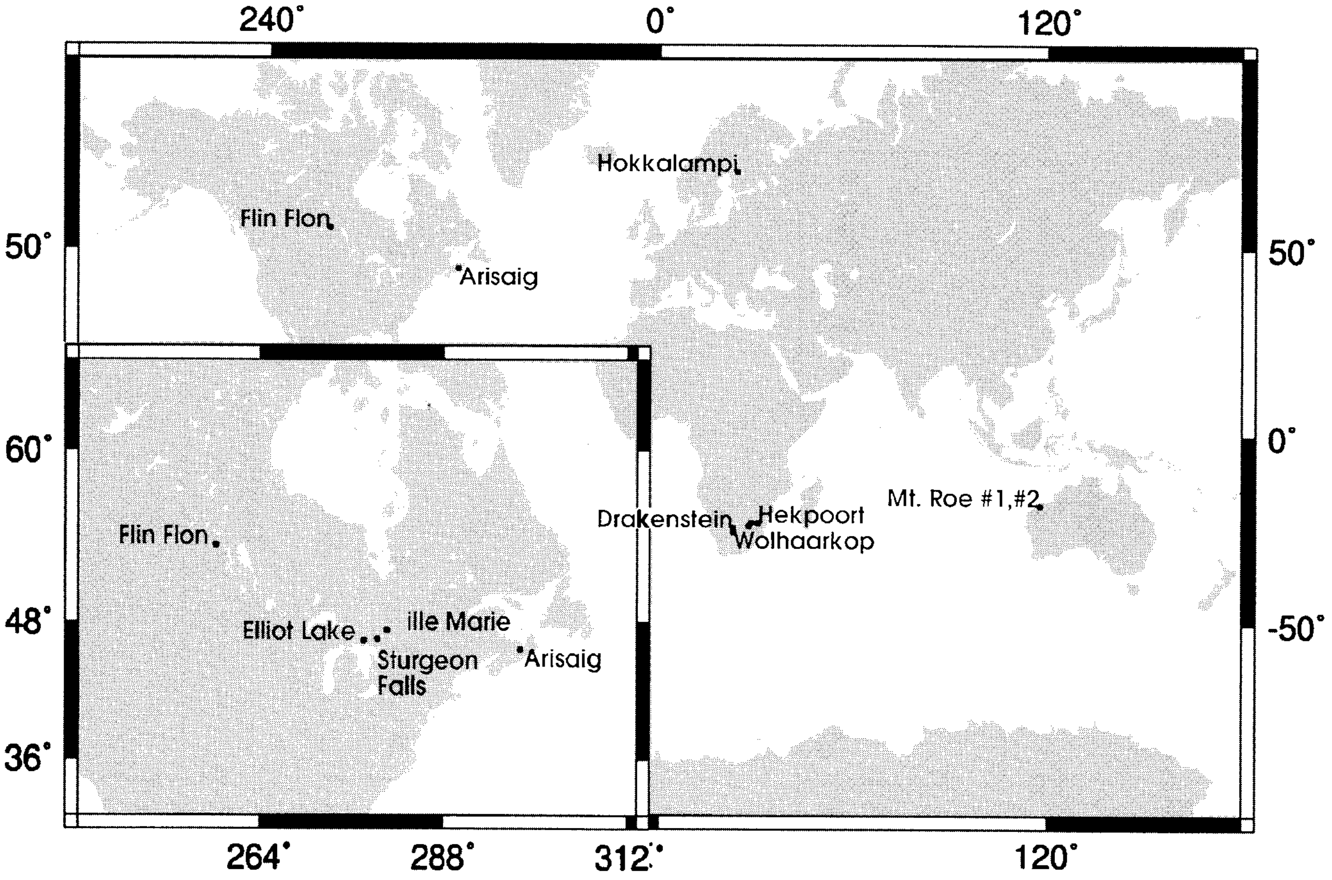


Fig. 2. World map depicting the locations of the 15 definite paleosols. The Denison, Quirke II, Pronto/NAN, Lauzon Bay, and Cooper Lake paleosols are all located at the point labeled Elliot Lake.

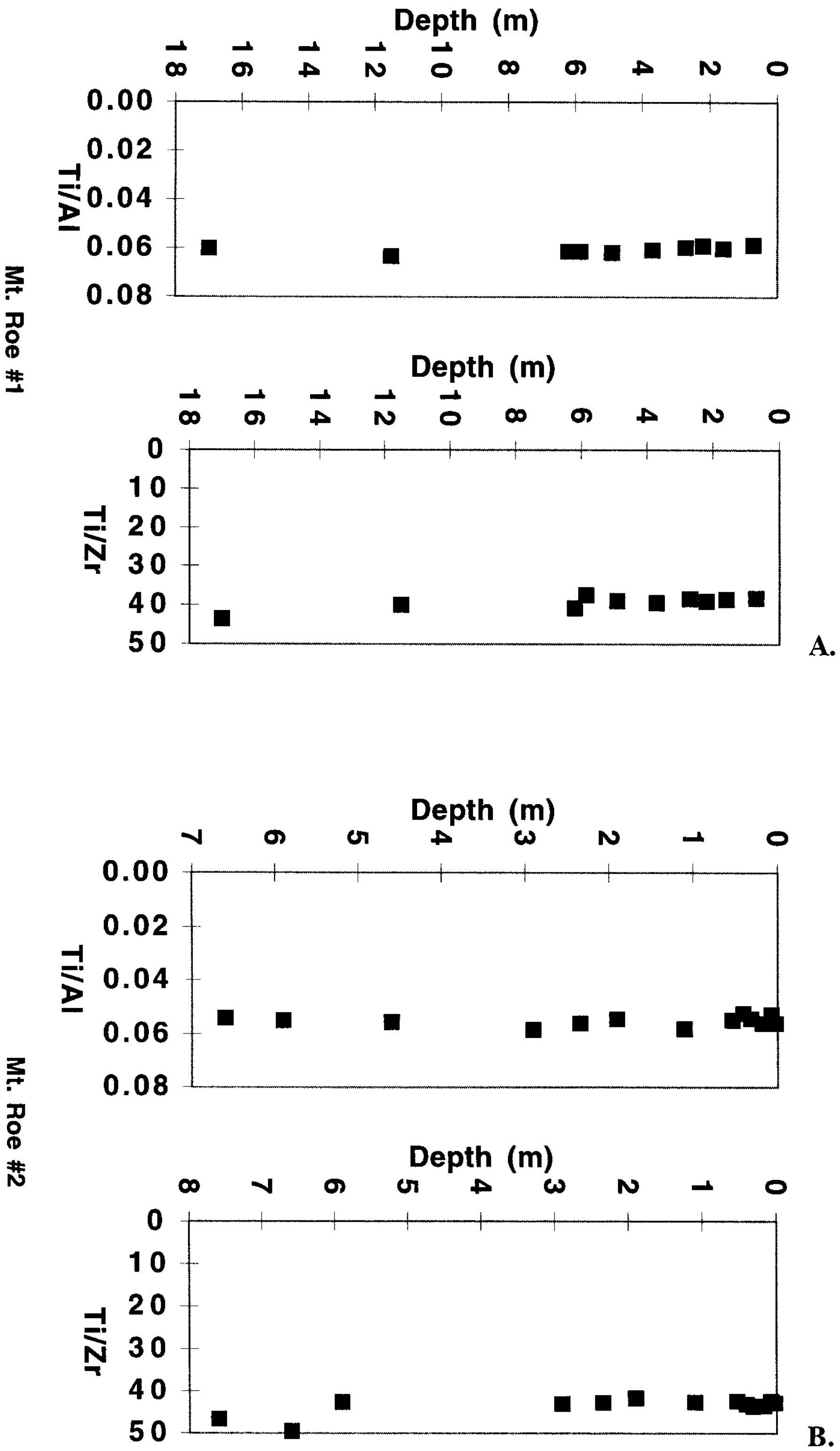


Fig. 3. Molar ratios of immobile elements versus depth in (A) the Mt. Roe #1 and (B) the Mt. Roe #2 paleosols (Macfarlane, Danielson, and Holland, 1994). In all but figures 5 and 12, 0 m depth represents the contact between the paleosol and the overlying unit.

1992), on Huronian basalt (paleosol 4) (Prasad and Roscoe, 1991), on Archean granodiorite (paleosol 5) (G-Farrow and Mossman, 1988; Mossman and Farrow, 1992), on Archean granite (paleosol 6) (Gay and Grandstaff, 1980; Sutton and Maynard, 1992), and on Archean diabase (paleosol 7) (Sutton and Maynard, 1993). The Huronian basalt, which is a member of the Dollyberry Formation, and the Matinenda Formation are considered to be nearly coeval with the Coppercliff Formation rhyolite which Krogh, Davis, and Corfu (1984) date at 2.450 (+0.025/−0.010) Ga using U-Pb zircon analysis (Prasad and Roscoe, 1991). Thus, these paleosols probably formed between 2.475 and 2.440 Ga.

All the reported Elliot Lake paleosol profiles show a gradual destruction of parent texture and loss of parent mineralogy from the bottom to the top of the profiles. Their chemical and soft-sediment deformation features are worth discussing on a case-by-case basis. G-Farrow and Mossman (1988), Goddard (1987), and Mossman and Farrow (1992) reported analyses of samples from two drill cores taken from the Denison and Stanleigh mines through the Matinenda Formation, through an apparent paleosol, and through its parent. The two cores penetrated the Denison paleosol (paleosol 3 in table 1), a weathering horizon that developed on a Denison Series greenstone. The immediately overlying conglomerate in the Stanleigh Mine core of the Denison paleosol contains 2 to 3 cm diam rip-up clasts of the paleosol (G-Farrow and Mossman, 1988). No rip-up clasts were found in the Denison mine core, but in mine drifts there are rip-up clasts of the paleosol in the immediately overlying Matinenda conglomerate.

The Ti/Al, Ti/Zr, and Al/Zr ratios are essentially constant in the paleosol of the Stanleigh Mine profile (fig. 4A). Unfortunately, the lowermost sample that G-Farrow and Mossman (1988) analyzed is still severely depleted in Ca and Mg. Thus, there are no samples of the unweathered parent greenstone in this Stanleigh Mine core. Nevertheless, the available data indicate that a paleosol developed on this greenstone at this site.

The distribution of Ti in the Denison Mine profile is odd. The Ti/Al and the Ti/Zr ratios both decrease steadily from the parent rock to the top of the profile, while the Al/Zr ratio is essentially constant throughout the profile (fig. 4B) (G-Farrow and Mossman, 1988; Mossman and Farrow, 1992). It seems likely that Ti was not distributed uniformly in the parent greenstone at this location prior to weathering. However, it is also possible that this profile contains a clastic component that was mixed with the altered greenstone. But if this is so, it is a remarkable coincidence that the clastic component has the same Al/Zr ratio as the underlying greenstone. Regardless of the reason for their variation, the Ti/Al and Ti/Zr ratio data indicate that this profile should be placed in the "likely," rather than in the "definite" paleosol category. This and the next two Denison profiles we describe are listed as paleosol 24 in table 1.

Gay and Grandstaff (1980) and Prasad and Roscoe (1996) have also reported paleosol profiles developed on greenstone in the Denison Mine. Most of the samples in these two profiles fail the immobile element criterion for paleosols (fig. 4C and D). Neither of these profiles qualifies as definite paleosols. However, they are apparently closely related to the definite Denison/Stanleigh paleosol described above.

Prasad and Roscoe (1991) identified paleosol 4, the Quirke II paleosol. They examined four drill cores from the Quirke II mine that penetrated the Matinenda formation and the underlying metabasaltic rocks (Prasad and Roscoe, 1991). The basalt immediately underlying the Matinenda conglomerate was clearly altered in all four cores. Prasad and Roscoe (1991) suggested that two of the cores, DH 75 and DH 270, may record multiple weathering events through more than one basalt flow and/or through Archean granite. Ohmoto (1996) concluded that DH 270 was hydrothermally altered and was not a paleosol. Samples from 8.5 to 5.5 m and from 2.5 to 0 m below the unconformity contain <0.5 wt percent Na_2O, while samples from 5.5 to 2.5 m depth contain >6.0 wt percent Na_2O (Prasad and Roscoe, 1991). Calcium is similarly distrib-

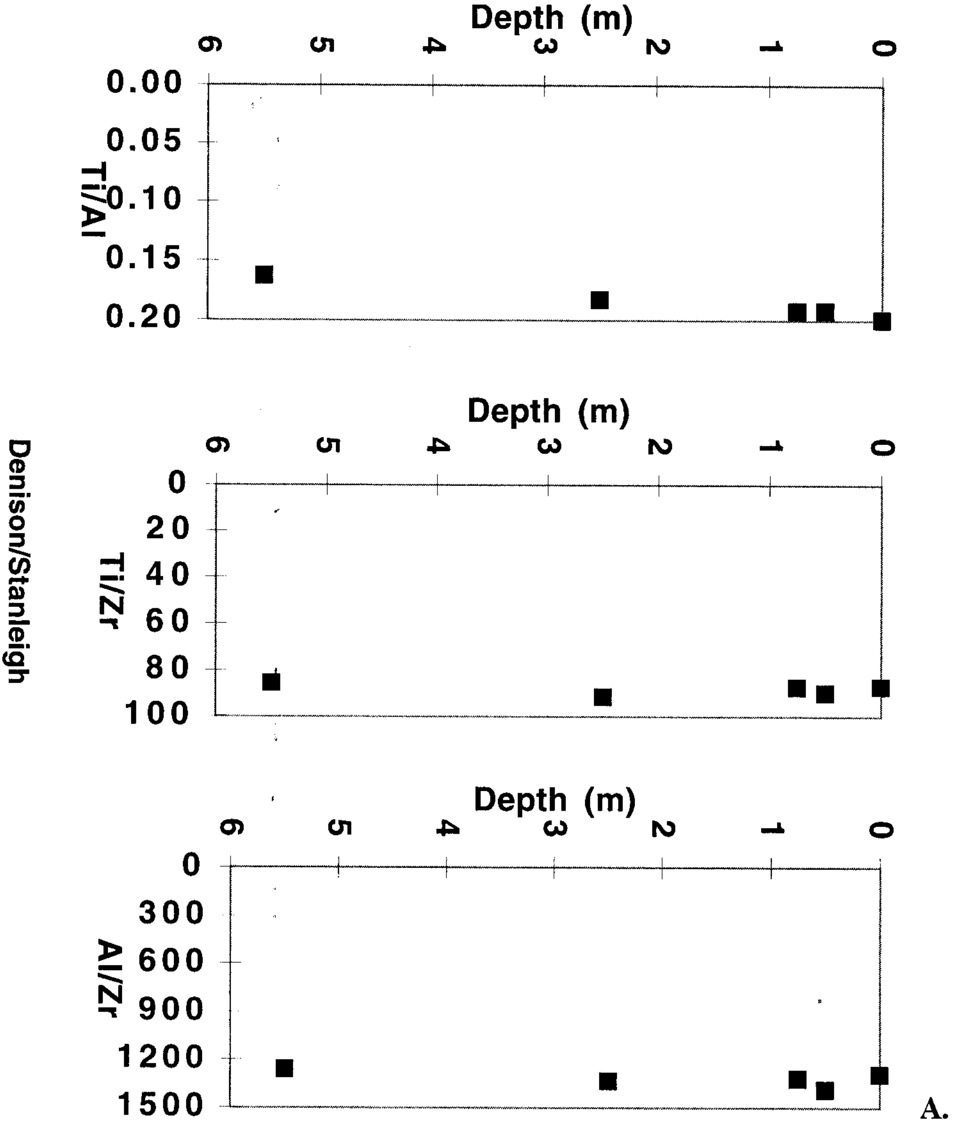
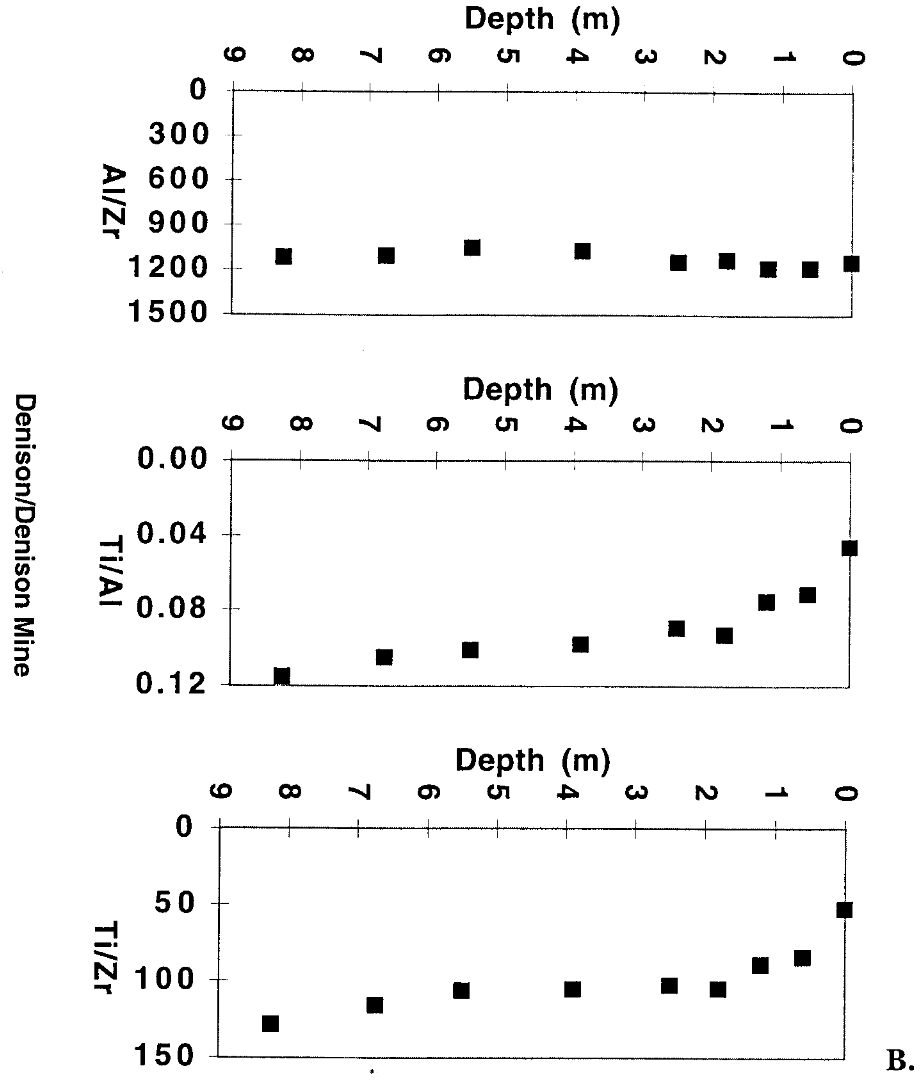


Fig. 4. Molar ratios of immobile elements versus depth in the Elliot Lake paleosols. (A) Stanleigh Mine profile of the Denison paleosol (Goddard, 1987; G-Farrow and Mossman, 1988).

uted. Whether or not this distribution was a result of hydrothermal alteration, this profile is clearly not a simple paleosol. On the other hand, the Ti/Al and the Ti/Zr ratios in core DH 268 are essentially constant from the parent basalt to the top of the paleosol (fig. 4E) and Na, Ca, and Mg are dramatically depleted throughout the paleosol relative to the parent. The presence of rip-up clasts of paleosol in the basal conglomerate at the unconformity in core DH 269 completes the strong case for a soil origin for the Quirke II Mine profiles, but the problems raised for most of the cores leave only DH268 as a viable tool for paleoatmospheric reconstruction.

The presence of rip-up clasts of paleosol material in the basal Matinenda conglomerate at three locations strongly indicates that there was a widespread weathering horizon



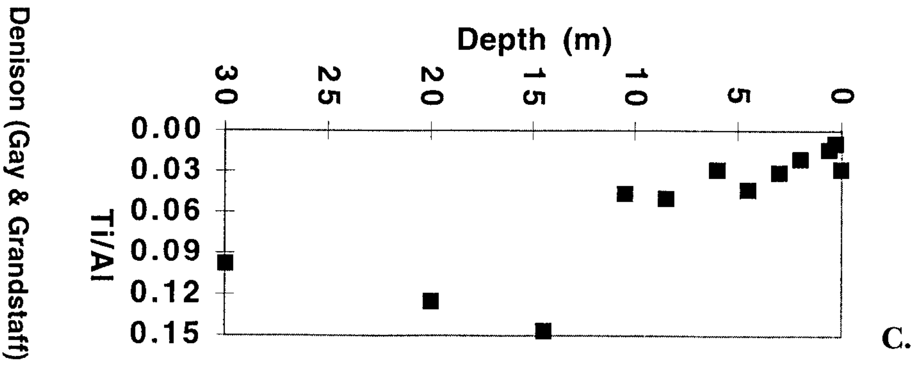


Fig. 4(B) Denison Mine profile of the Denison paleosol (Goddard, 1987; G-Farrow and Mossman, 1988); (C) Denison Mine profile of the Denison paleosol (Gay and Grandstaff, 1980).

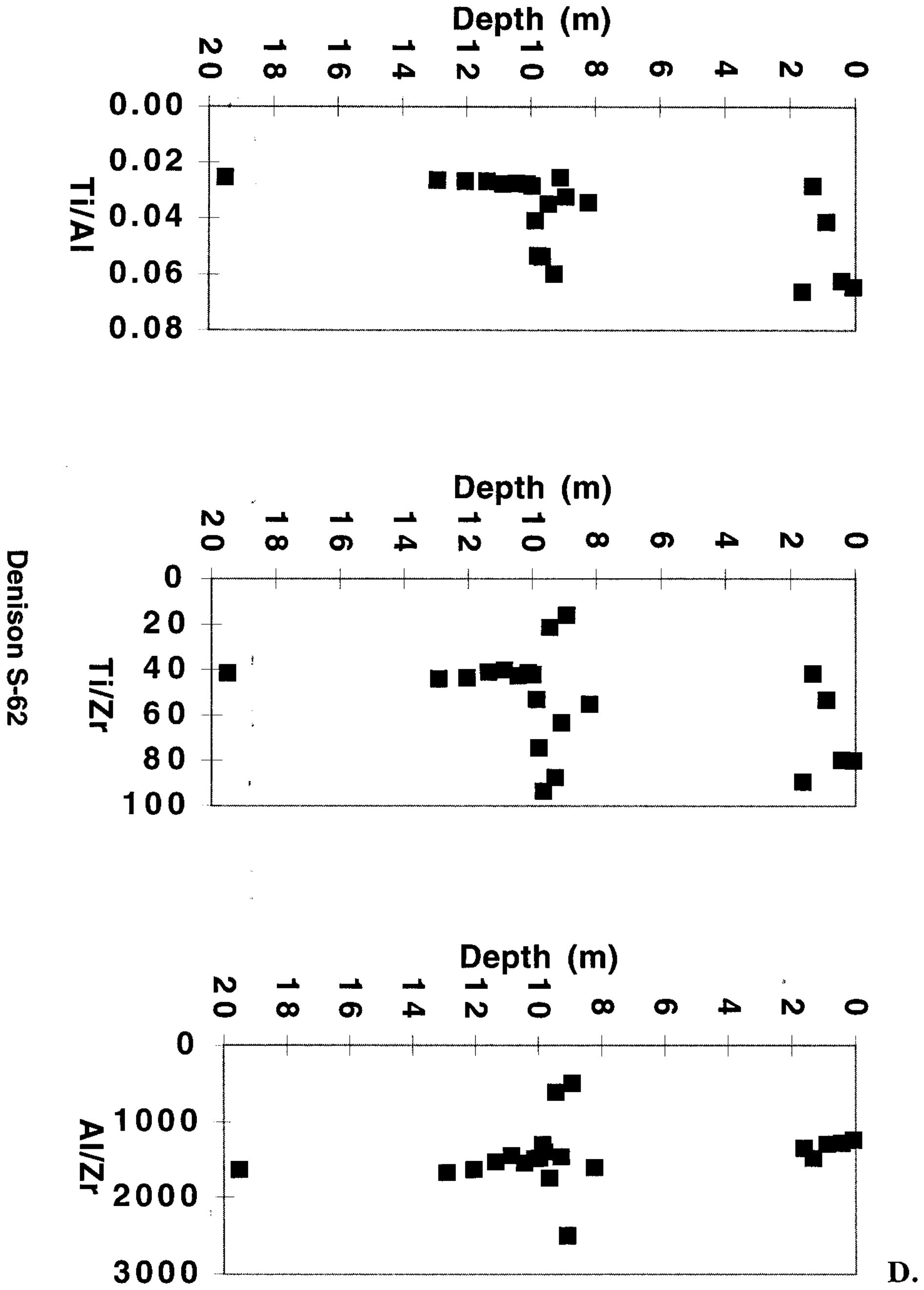
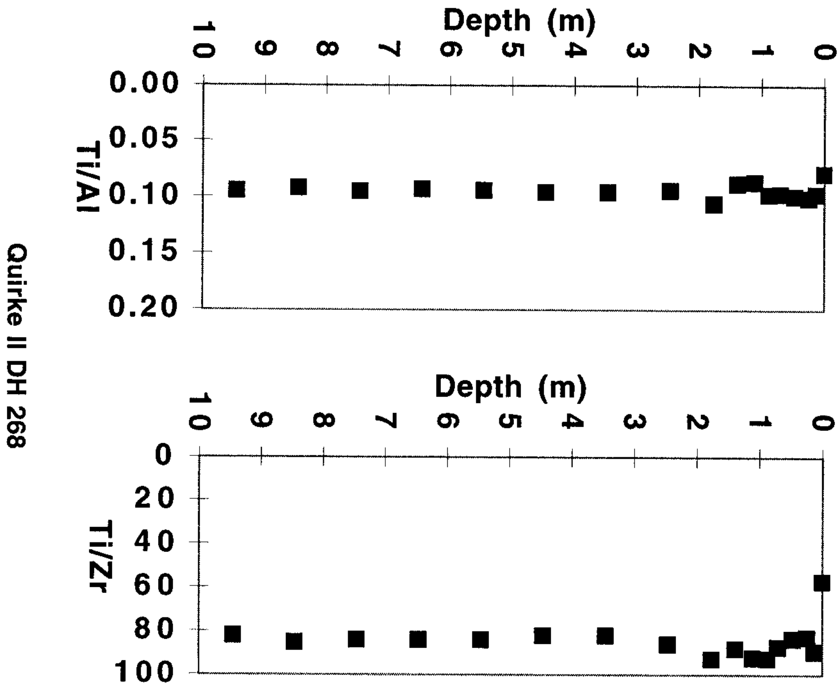
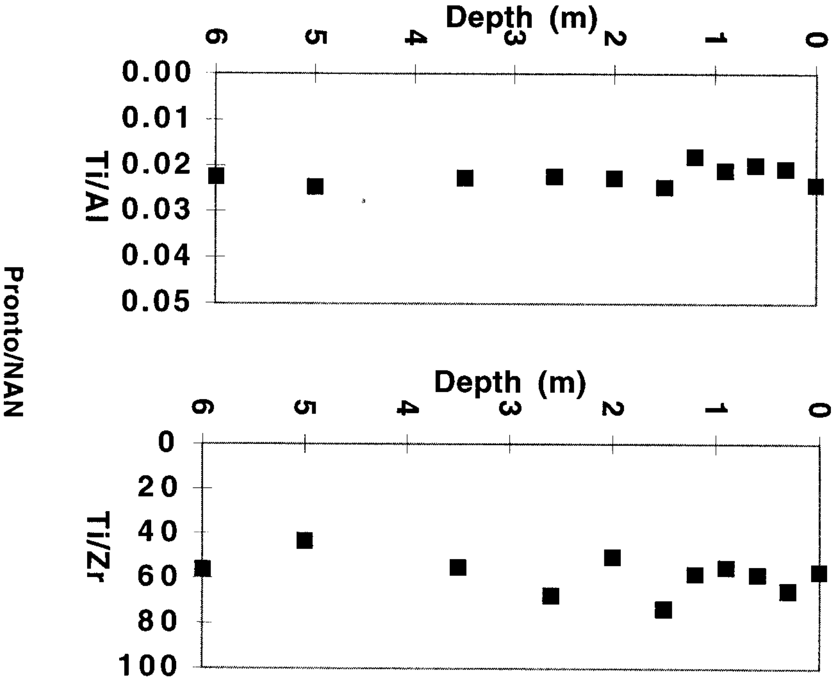


Fig. 4(D) Drill core S-62 from the Denison Mine (Prasad and Roscoe, 1996).

in the area when the overlying conglomerate was deposited. Sub-Matinenda profiles through units developed on a Pronto Series granite from a North American Nuclear Ltd drill site (paleosol 5 the Pronto/NAN paleosol; G-Farrow and Mossman, 1988), on a hydrothermally altered granite at Lauzon Bay, near Elliot Lake (paleosol 6, the Lauzon



E.



F.

Fig. 4(E) Quirke II DH 268 paleosol (Prasad and Roscoe, 1991 and 1996); (F) Pronto/NAN paleosol (Goddard, 1987; G-Farrow and Mossman, 1988).

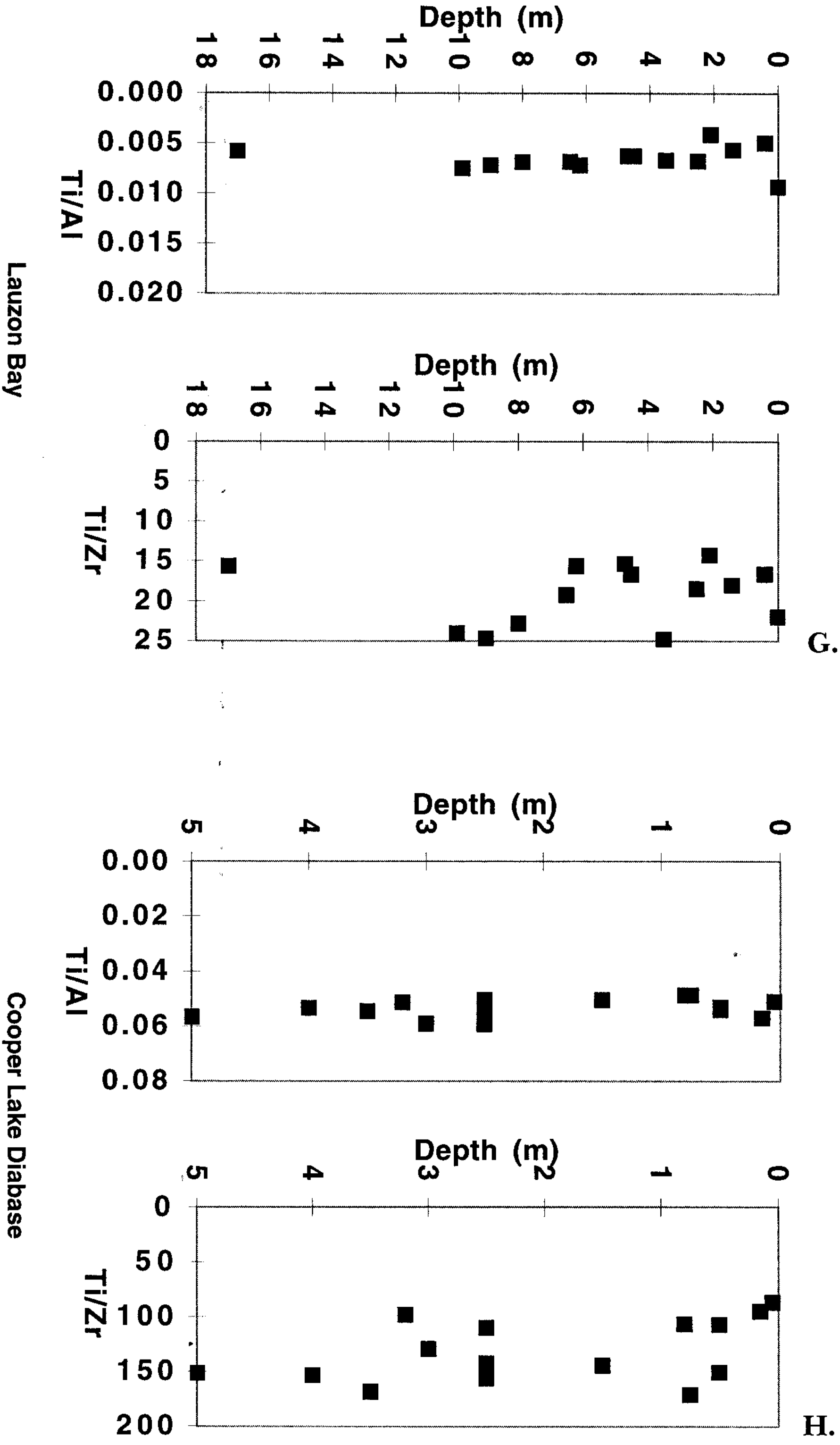


Fig. 4(G) Lauzon Bay paleosol (Sutton and Maynard, 1992); (H) Cooper Lake paleosol (Sutton and Maynard, 1993).

Bay paleosol; Sutton and Maynard, 1992), and on a diabase at Cooper Lake (paleosol 7, the Cooper Lake paleosol; Sutton and Maynard, 1993) that meet the textural, mineralogical, and chemical criteria for paleosols (table 1 and fig. 4F-H) are therefore classed as definite paleosols.

8. Hokkalampi.–Paleosol number 8, the Hokkalampi paleosol in the Koli-Kaltima area of eastern Finland, was intruded by 2.2 Ga mafic rocks (Marmo, 1992) and is younger than a 2.44 Ga layered gabbro (Sturt, Melezhik, and Ramsay, 1994). This paleosol developed on a number of parent rocks, including Archean granite. Marmo (1992) described three cores through the paleosol where it is developed on granite. He reported several analyses from each core. However, in each core only the bottom four analyzed samples were part of the paleosol. Marmo (1992) also analyzed overlying sediments that were apparently derived from the paleosol. Unlike Ohmoto (1996), we have excluded these samples from our analysis of the Hokkalampi paleosol, because they are not part of an in-place weathering profile.

The Hokkalampi paleosol is divided into three zones. The unweathered granitoid gradually gives way to a quartz-sericite schist and finally to a quartz-kyanite-andalusite schist (Marmo, 1992). The overlying breccia contains numerous clasts of the soil. Chemical data for each core are somewhat sparse, but paleosol samples in all three cores have immobile element profiles consistent with *in-situ* weathering of a homogeneous parent rock (fig. 5 and table 1). Unfortunately, the uppermost, presumably most heavily weathered zone of the soil, is missing in all three cores. This zone was almost certainly eroded in these locations prior to the deposition of the overlying sediments.

9. Ville Marie.–The Ville Marie paleosol, paleosol number 9, developed on Archean Algoman granite (Rainbird, Nesbitt, and Donaldson, 1990). The only known outcrop of this paleosol underlies the Lorrain Formation near Ville Marie, Québec, Canada. The albite in the parent granite gradually gives way to sericite upward in this paleosol. Microcline is preserved throughout the paleosol. The immobile element profiles (fig. 6) are consistent with in-place weathering of the granite. There are clasts of weathered as well as essentially unweathered granite in the overlying sediments. Granitic textures become less pronounced toward the top of the profile but are clearly recognizable throughout the paleosol. The persistence of parent textures at the top of the paleosol indicates that much of the soil was eroded prior to deposition of the Lorrain Formation.

The age of the Ville Marie paleosol is poorly constrained. The presence of rip-up clasts of the soil in the basal Lorrain Formation suggests that soil formation immediately preceded the deposition of this formation. The Nipissing diabase, which was dated, using U-Pb baddeleyite analyses, at 2.219 ± 0.004 Ga (Andrews and others, 1986), crosscuts the Lorrain elsewhere. The Gowganda Formation, which underlies the Lorrain Formation, has been loosely dated at 2.29 ± 0.09 Ga using Rb-Sr whole rock analyses (Fairbairn and others, 1969).

10. Hekpoort.–Paleosol number 10 is the Hekpoort paleosol. This Paleoproterozoic weathering horizon developed on the Hekpoort Basalt, a basaltic andesite in South Africa, and is preserved over an area of more than 100,000 km^2 (Button, 1979; Button and Tyler, 1981). The paleosol exposure at Waterval Onder was described by Button (1979); the exposure at the Daspoort Tunnel was described by Hart (1986). Retallack (1986a) and Retallack and Krinsley (1993) also examined the Waterval Onder locality. We are currently studying samples from a set of cores through the paleosol in the Bank Break area; these penetrate the immediately overlying ironstone, the paleosol, and the parent basaltic andesite. At all three sites, the texture and mineralogy of the paleosol have suffered from greenschist metamorphism. Nevertheless, textural and mineralogical patterns are consistent with a weathering origin. At all three sites immobile element ratios are essentially constant throughout the profile from the sericite zone down into the least altered samples of Hekpoort Basalt (fig. 7).

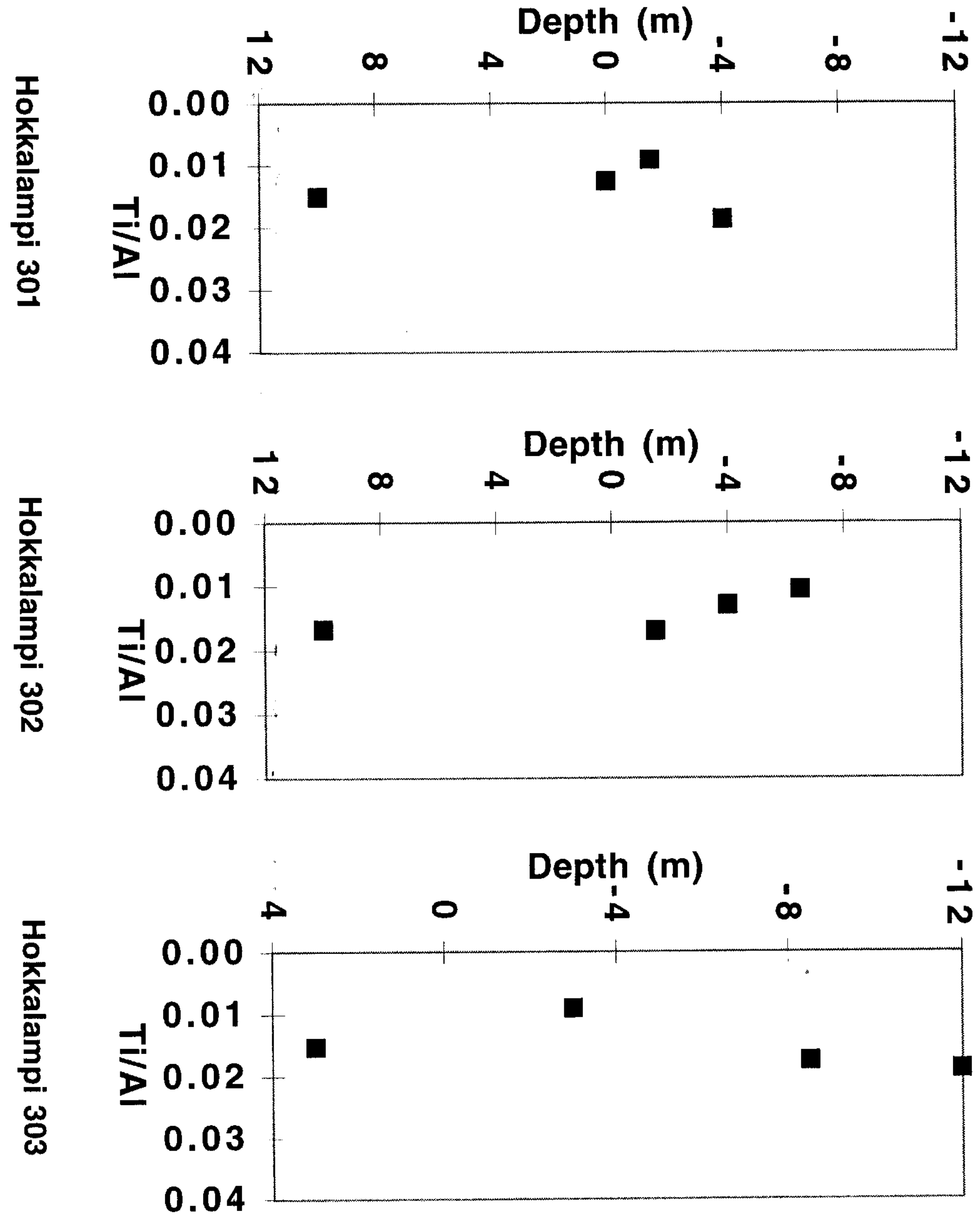


Fig. 5. Molar ratios of immobile elements versus depth in three cores through the Hokkalampi paleosol. 0 m represents the approximate location of the "contact" between the unweathered granite and the paleosol (Marmo, 1992).

Retallack and others have suggested that this paleosol developed on a sedimentary substrate, rather than on the Hekpoort Basalt (Retallack, 1986a; Retallack and Krinsley, 1993). This interpretation is based on textural observations of the paleosol at Waterval Onder. There are no samples of unweathered Hekpoort Basalt at this locality. Hart

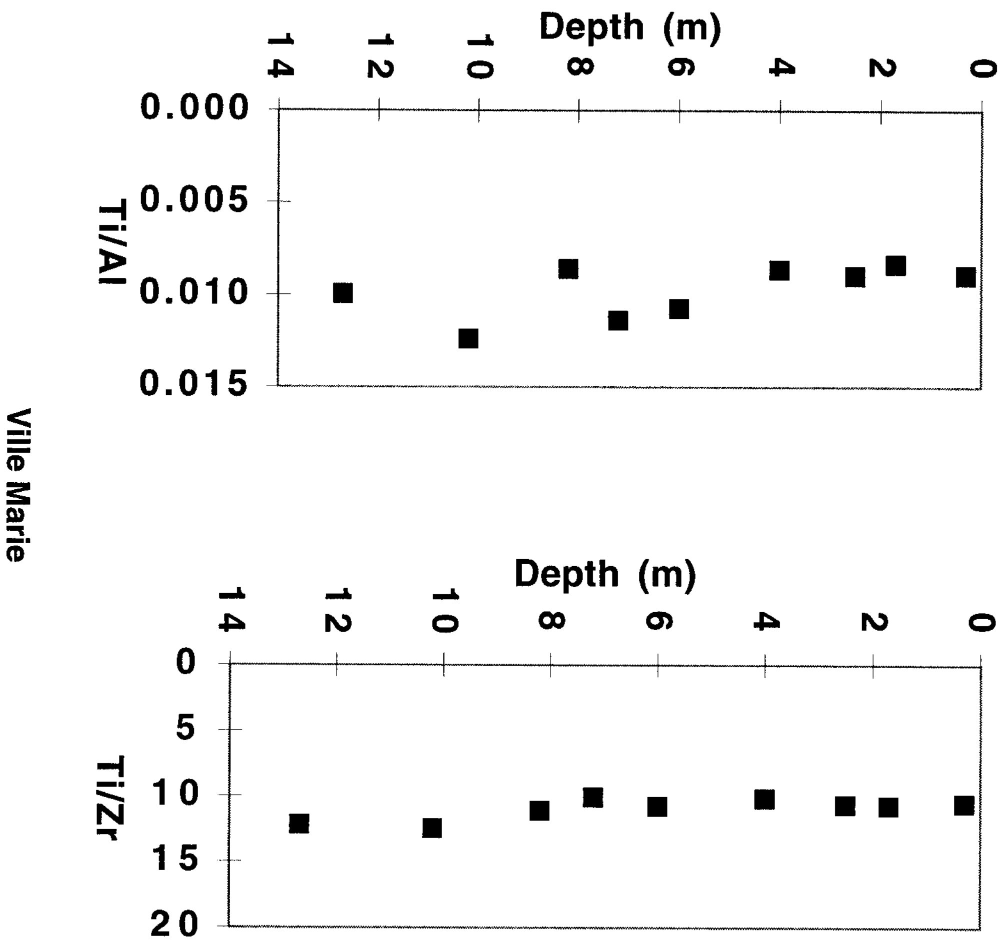


Fig. 6. Molar ratios of immobile elements versus depth in the Ville Marie paleosol (Rainbird, Nesbitt, and Donaldson, 1990).

(1986) examined a corestone of Hekpoort Basalt at the Daspoort Tunnel locality. In the Bank Break cores, we have complete core recovery showing a smooth, nondepositional transition from paleosol to unweathered Hekpoort Basalt. In these cores, the Ti/Al and Ti/Zr ratios are constant from the top of the sericite zone of the paleosol through the lowest sample of the Hekpoort Basalt several meters below the transition to the parent rock (fig. 7C–E). The preservation of the transition from unweathered to weathered material together with the constancy of the immobile element ratios from top to bottom essentially rules out the notion that this paleosol developed on a sedimentary substrate.

At Waterval Onder the paleosol is overlain by the Dwaal Heuvel sandstone. Sinuous sandstone dikes penetrate the top of the paleosol (fig. 1B). These dikes appear to have been desiccation cracks that were filled during the deposition of the overlying sand and were contorted during compaction (Button, 1979). In the Bank Break drill cores the upper contact of the paleosol is smooth, and the paleosol is overlain by an ironstone that contains rip-up clasts of the paleosol.

The Hekpoort lava erupted subaerially. It has been dated by Rb-Sr whole rock analysis at 2.224 ± 0.021 Ga (Wiggering and Beukes, 1990, citing Burger and Coertze,

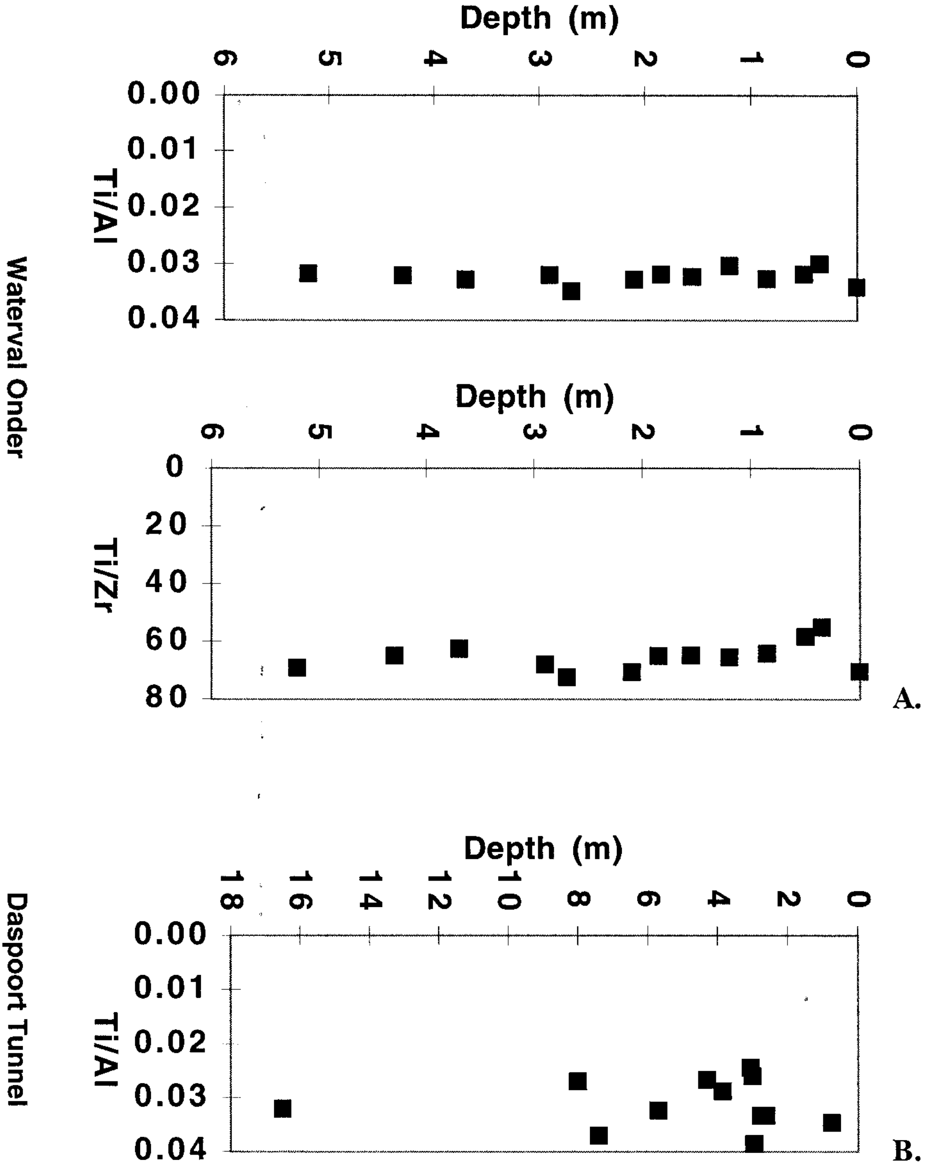


Fig. 7. Molar ratios of immobile elements versus depth in the Hekpoort paleosol. (A) Waterval Onder (Button, 1979); (B) Daspoort Tunnel (Hart, 1986).

1974). Walraven has confirmed this date with the single zircon evaporation technique (Reczo and others, 1995), but his data have yet to be published. The overlying sediments are members of the Pretoria Group of the Transvaal Supergroup. The felsic volcanic rocks of the Rooiberg Group unconformably overlie the Transvaal Supergroup (Cheney and de la R. Winter, 1995; Cheney and Twist, 1991; Schweitzer, Hatton, and de Waal, 1995) and have been dated at 2.061 ± 0.002 Ga (Schweitzer and Hatton, 1995). Therefore, the Hekpoort paleosol must have formed before 2.06 Ga. The Machadodorp Volcanic Member of the Silverton Group lies between the Hekpoort basaltic andesite

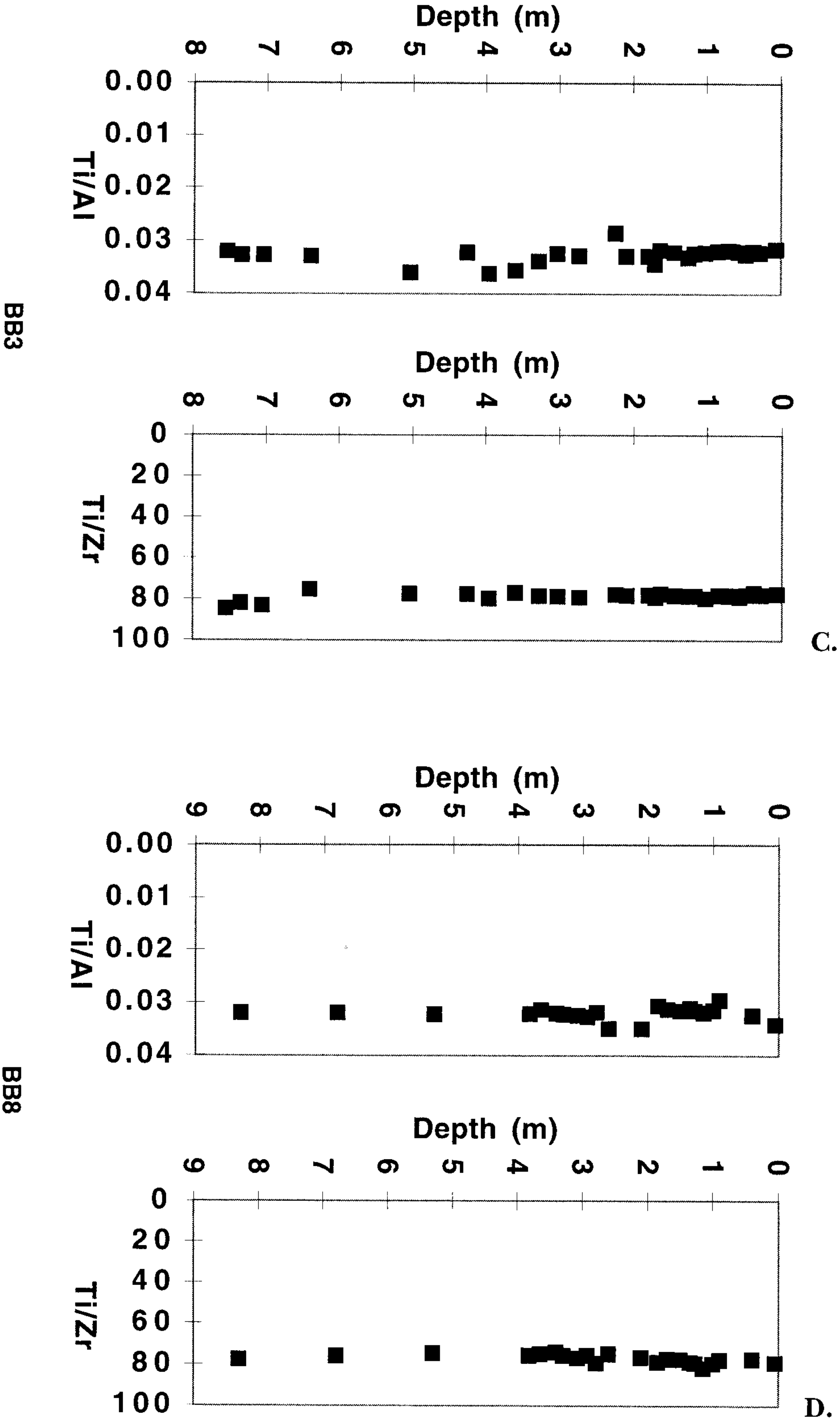


Fig. 7(C) Bank Break drill core number BB3 (Rye, unpublished data); (D) Bank Break drill core number BB8 (Rye, unpublished data).

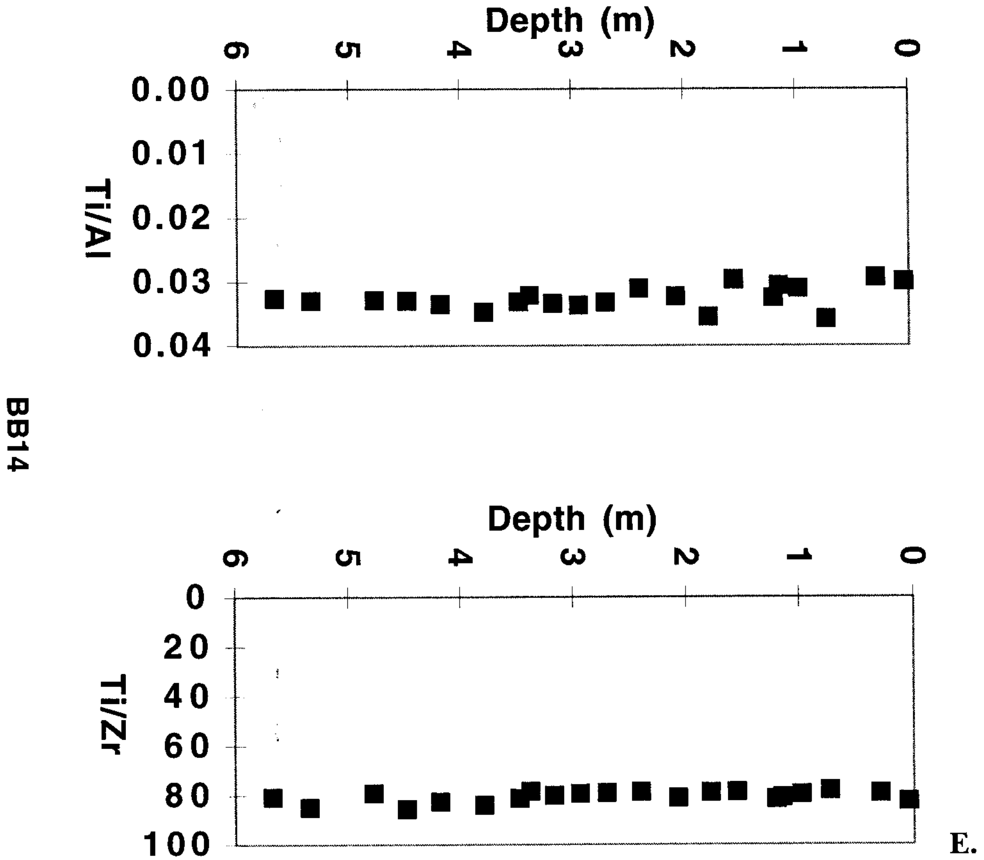


Fig. 7(E) Bank Break drill core number BB14 (Rye, unpublished data).

and the Rooiberg Group. An absolute age determination of the Machadodorp would help to constrain further the time of formation of the Hekpoort paleosol.

11. Drakenstein.–Paleosol number 11, the Drakenstein paleosol, developed on the Ongeluk basaltic andesite, which is the submarine equivalent of the Hekpoort. The Ongeluk has been dated using Pb-Pb whole rock analyses at 2.222 ± 0.012 Ga (Cornell, Schütte, and Eglington, 1996). The Ongeluk is overlain by basal sediments of the Olifantshoek Group. The unconformity is marked by an extensive weathering horizon that developed on multiple substrates and has been traced over a strike distance of about 350 km (Wiggering and Beukes, 1990). Wiggering and Beukes (1990) have studied a drill core through the Mapedi Formation of the Olifantshoek Group, the paleosol, and its parent Ongeluk lava at the farm Drakenstein 263, 20 km northwest of Hotazel in Griqualand West, South Africa. The profile meets the textural, mineralogical, and chemical criteria for a paleosol (fig. 8 and table 1). Though none was found in the core, rip-up clasts of the paleosol are common in the immediately overlying sedimentary rocks over the entire extent of the paleo-weathering horizon (Wiggering and Beukes, 1990).

The Ongeluk basaltic andesite was affected by submarine hydrothermal alteration prior to weathering (Cornell, Schütte, and Eglington, 1996; Wiggering and Beukes, 1990). None of the stratigraphically higher Transvaal Supergroup formations is present above the Ongeluk. The overlying Mapedi Formation of the Olifantshoek Supergroup is interbedded with the Hartley Basalt Formation. The basalts of the Hartley Basalt

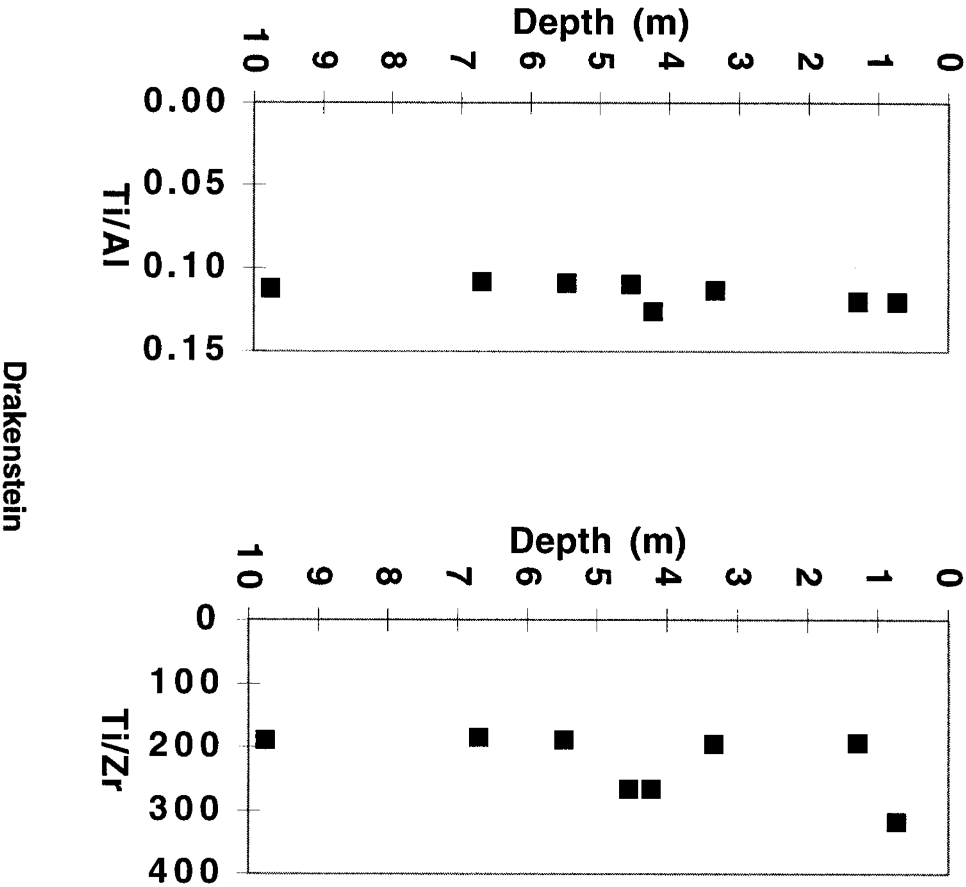


Fig. 8. Molar ratios of immobile elements versus depth in the Drakenstein paleosol (Wiggering and Beukes, 1990).

Formation have been dated by Rb-Sr analysis at 2.070 ± 0.090 Ga (Wiggering and Beukes, 1990, citing Crampton, 1974). Cornell, Armstrong, and Walraven (1998) have recently reinterpreted Crampton's Rb-Sr isochron to indicate the eruptions occurred at 2.026 ± 0.180 Ga. They have also dated a porphyritic andesite from the Hartley Basalt Formation at 1.928 ± 0.004 Ga using the U-Pb zircon evaporation method. If this andesite is coeval with the Hartley basalts, as suggested by Cornell, Armstrong, and Walraven (1998), then the deposition of the Olifantshoek Supergroup may not have started until about 1.92 Ga. Weathering of the Ongeluk that formed the Drakenstein paleosol could have occurred within a few million years of the eruption (about 2.22 Ga), if the submarine hydrothermal alteration was followed quickly by uplift and exposure of the altered lava. If, however, the overlying red beds were deposited about 1.92 Ga, which is permitted by the uncertainty in the age of the Hartley Basalts and the porphyritic andesite, then weathering of the Ongeluk may have been up to 0.3 Ga after the Ongeluk-Hekpoort eruptions. Better age constraints on this unconformity would clearly help to refine figures for the age of the paleosol.

12. Wolhaarkop.–Paleosol number 12, the Wolhaarkop paleosol, is also found at the 2.22 to 1.92 Ga Transvaal-Olifantshoek unconformity. This paleosol developed on the Kuruman Iron Formation. A drill core taken from the farm Wolhaarkop 448, southwest of Postmasburg in Griqualand West, South Africa penetrated the Gamagara Formation and the underlying paleosol (Holland and Beukes, 1990). During Precambrian weathering of an area at least 130 km along strike, iron carbonates, iron silicates, and magnetite were converted to hematite. Despite these transformations, banding was preserved in this paleosol (Holland and Beukes, 1990). Clasts of hematitized iron formation are common in the overlying Gamagara Formation breccia. Desiccation cracks filled with breccia are well preserved and extend more than 10 m into the paleosol (Holland and Beukes, 1990). The profile therefore meets all the physical paleosol criteria.

Chemically, the Wolhaarkop paleosol is very different from the other paleosols described above, because it contains essentially no Ti or Al. The mobility of silica during weathering was apparently minimal. Fe/Si ratios are essentially unaffected by weathering, suggesting that Fe was immobile (Holland and Beukes, 1990). Its stratigraphic position on the same horizon as the Drakenstein paleosol, together with its textural, mineralogical, and soft-sediment features indicate that the Wolhaarkop is a definite paleosol.

13. Flin Flon.–The Flin Flon paleosol is number 13 in our review. This soil developed on Amisk Group basaltic pillow lavas and was covered by 1.8 to 1.9 Ga Missi Group fluvial sediments near the town of Flin Flon, close to the southeastern corner of the Churchill Province of the Canadian Shield (Holland, Feakes, and Zbinden, 1989). The parent basalt is now a greenstone. The mineralogy of the greenstone is dominated by chlorite and includes minor amounts of quartz, carbonate, illite, and plagioclase feldspar. Upward in the paleosol, chlorite gives way to sericite and hematite. Textures change gradually from the parent greenstone up through the paleosol. There are numerous corestones within the paleosol (Holland, Feakes, and Zbinden, 1989), similar to the spheroidal masses of unweathered material in the Mt. Roe paleosols and in modern soils in Hawaii. A mixture of Missi sediments and paleosol material directly overlies the paleosol. The Ti/Al molar ratios in Holland, Feakes, and Zbinden's (1989) profile 1, from the greenstone to the unconformity atop the paleosol, scatter tightly around an average value of 0.024 (fig. 9A).

14. Sturgeon Falls.–The Sturgeon Falls paleosol, paleosol number 14, 25 km southwest of Baraga, Michigan was developed on hydrothermally altered Keweenawan basalt about 1.1 Ga, just before the deposition of the Jacobsville sandstone (Zbinden and others, 1988). Textural and mineralogical changes are gradual and unidirectional upward from the parent rock to the contact between the paleosol and Jacobsville sandstone. Rip-up clasts as well as partially indurated, balled-up chunks of paleosol are present in the overlying sandstone (Hamblin, 1958; Zbinden and others, 1988) (fig. 1F). The immobile element data indicate that this weathering profile developed *in situ* and contains no significant allochthonous components (fig. 9B).

15. Arisaig.–Several definite paleosols are preserved within a series of about 0.45 Ga andesite flows near Arisaig, Nova Scotia, Canada (Boucot and others, 1974; Feakes, Zbinden, and Holland, 1989). For the sake of brevity we have given these paleosols a single entry as paleosol 15 in table 1. There are two types of paleosols in this area: intact soil profiles and disrupted soils. The intact paleosols meet the textural and mineralogical criteria for a paleosol. The Ti/Al ratios are essentially constant in the intact Arisaig paleosols at Doctor's Brook (fig. 9C) and McGillivray Brook (fig. 9C) (Feakes, Zbinden, and Holland, 1989). The disrupted soils were clearly soft when they were covered and, therefore, meet the soft-sediment deformation criterion for a paleosol (fig. 1E).

THE LIKELY PALEOSOLS

Thirteen of the reported paleosols failed to meet one of the criteria for paleosols and have earned a rating of likely. We have arranged them from oldest to youngest and numbered them 16 through 28 in table 1. In some cases, published and informal reports

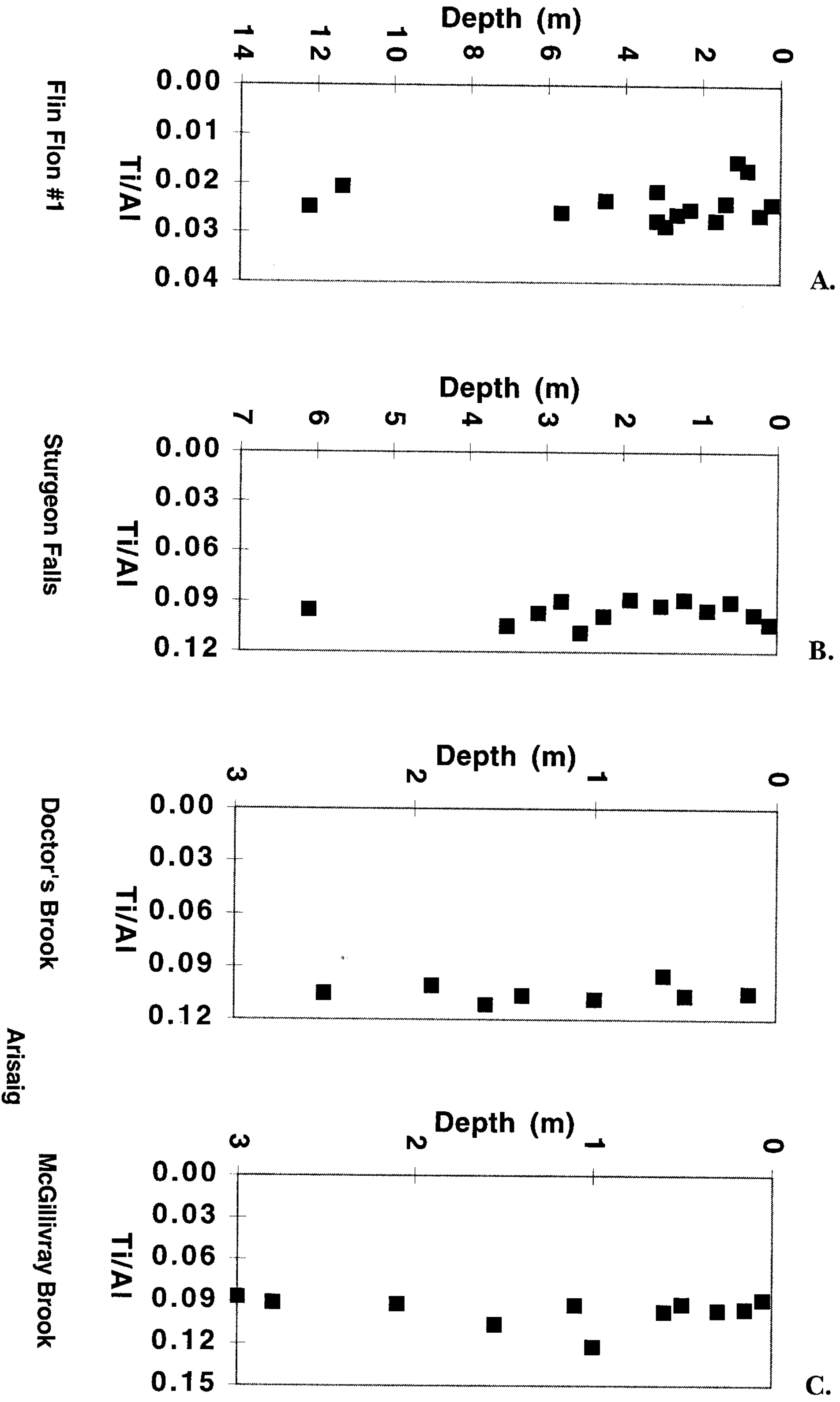


Fig. 9. Molar ratios of immobile elements versus depth in four paleosols. (A) the Flin Flon #1 paleosol (Holland, Feakes, and Zbinden, 1989); (B) the Sturgeon Falls paleosol (Zbinden and others, 1988); (C) the Arisaig paleosols at Doctor's Brook and McGillivray Brook (Feakes, Zbinden, and Holland, 1989).

on likely paleosols are silent about whether a profile actually meets the failed criterion. Thus, some of the likely paleosols may become definite paleosols with further study.

16 to 19. Pongola, Dominion Reef, Bird, Krivoy Rog.–Paleosols 16 and 17, the 3.0 to 2.9 Ga pre-Pongola and the 2.9 to 2.8 Ga Dominion Reef paleosols, are profiles on granites in the Transvaal, South Africa (Grandstaff and others, 1986). Paleosol 18, the Bird Basalt paleosol, is a profile developed on the 2.8 to 2.7 Ga Bird Basalt (DH 326) (Palmer, Phillips, and McCarthy, 1989) in the Central Rand Group of South Africa. Paleosol 19, the Krivoy Rog paleosol apparently developed on the Saksagan Granite between 2.8 and 2.6 Ga (Kulish, Pokalyuk, and Reshetnyakov, 1987). All the published descriptions of these four proposed paleosols are based on drill core samples. At least one core through each meets the parental, textural, mineralogical, and chemical criteria for a paleosol. However, there are no reported soft-sediment deformation features in these drill cores. In our experience, drill cores are the best source of samples for chemical analysis, but outcrops are usually essential for identifying paleosols, because they are large enough to permit the unequivocal identification of soft-sediment deformation features.

20,23. Island Lake and Jackson Lake.–Paleosol 20, the Island Lake paleosol, is an about 2.8 Ga profile on a quartz diorite at Island Lake, Canada (Herd, Chandler, and Ermanovics, 1976; and R. Herd, personal communication, 1997). Paleosol 23 is an about 2.6 Ga profile on Kam Group mafic volcanic rocks at Jackson Lake in Canada (Falck, Donaldson, and Hall, 1991, and J. A. Donaldson, personal communication, 1997). Both the Island Lake and Jackson Lake profiles meet the parental, textural, mineralogical, and soft-sediment deformation criteria for paleosols. Unfortunately, there are no published chemical analyses of these profiles (see table 1), although unpublished data do exist that may or may not confirm that these profiles are paleosols (R. Herd, personal communication, 1997, and J. A. Donaldson, personal communication, 1997).

21 and 22. Kalkloof and Delmas.–A regional unconformity has been identified underneath the about 2.55 Ga Black Reef Quartzite at the base of the Transvaal Supergroup in South Africa. There are several reports of granite- and one report of ultramafic-derived paleosols below this unconformity (Button and Tyler, 1981; Martini, 1994; Maynard and others, 1995). The two best documented potential paleosols under this unconformity are the Kalkloof paleosol (paleosol 21) (Martini, 1994) and the Delmas paleosol (paleosol 22) (Maynard and others, 1995).

The Kalkloof paleosol (21) is developed on ultramafic rocks (Martini, 1994). In some outcrops Martini (1994) has identified clasts of the proposed paleosol in the overlying conglomerate. However, in all the outcrops described, the ultramafic parent rock and the proposed paleosol have been extensively dolomitized, and the immobile element data are not consistent with an in-place origin of the soil.

The drill core profile from Delmas described by Maynard and others (1995) was developed on hydrothermally altered granite. This profile meets the parental, textural, and mineralogical criteria for a paleosol. There are rip-up clasts of the paleosol in the overlying quartzite (Ferraz, 1989). The Ti/Al and the Ti/Zr ratios in several of the paleosol samples in this core deviate by more than 50 and 40 percent from the Ti/Al and the Ti/Zr ratios in both the least altered sample in the core and deeper (more heavily metamorphosed) samples.

24 to 26. Denison, Pronto, Cooper Lake quartzite.–Paleosols 24 through 26 are three likely paleosols from the sub-Matinenda unconformity in the Elliot Lake area that is host to five of the definite paleosols. Paleosol 24, the Denison Mine profiles described by Gay and Grandstaff (1980), G-Farrow and Mossman (1988), and Prasad and Roscoe (1996), was discussed above together with paleosols 3 to 7. These profiles are examples of likely paleosols that are unlikely to be elevated to the definite category.

Paleosol 25, Gay and Grandstaff's (1980) Pronto paleosol profile, is apparently on the same stratigraphic horizon as the Pronto/NAN paleosol (5) (G-Farrow and Mossman,

1988) and meets the textural and mineralogical criteria for a paleosol. However, the Ti/Al ratios in the top samples of Gay and Grandstaff's profile are well over 50 percent higher than the Ti/Al ratio of the parent rock. This profile, even if it was a soil, is not simply an in-place weathering profile developed on a homogeneous parent rock. It probably contains a transported component.

Paleosol 26, the Cooper Lake quartzite profile, is in lateral contact with the Cooper Lake paleosol on diabase, paleosol 7 (Sutton and Maynard, 1993). Its position suggests that the profile is a paleosol. The textural, mineralogical, and immobile element patterns would all be consistent with a soil origin if the parent material was homogeneous. However, flat-lying clastic sediments are generally not homogeneous parents. Thus, while it is likely that this is a paleosol, we cannot definitively distinguish it from the sediment on which it apparently developed.

27. Pre-Sariola.—What we call paleosol 27, the pre-Sariola paleosol, is actually a group of proposed paleosols that have been identified on a major unconformity in the Baltic Shield beneath the Sariola Group. According to Sturt, Melezhik, and Ramsay, (1994), pre-Sariola weathering profiles have been described from at least 31 sites over a 700,000 km^2 area. They indicate that the granitic Hokkalampi paleosol, 8, is part of this preserved regional weathering horizon. The other profiles are developed on a variety of Archean and Paleoproterozoic rock types, including glaciogenic sediments, plagiogranites, and gabbros (Sturt, Melezhik, and Ramsay, 1994). Profiles developed on pegmatite in the Pasvik Valley near Brattli, Norway (Sturt, Melezhik, and Ramsay, 1994) meet the parental, textural, mineralogical, and soft-sediment deformational criteria for a paleosol. There are insufficient data to evaluate the chemical profiles. There are also too few chemical data for many of the other pre-Sariola profiles (see for example Kohonen and Marmo, 1992; Pekkarinen, 1979; Silvennoinen, 1972; Strand, 1988). Additional chemical analyses of profiles along this unconformity would surely be useful, as they might increase the list of definite paleosols.

28. Thelon.—Paleosol 28, the sub-Thelon paleosol, is developed on another proposed regional weathering horizon, which apparently developed on several rock types prior to the deposition of the 1.75 to 1.72 Ga Thelon Formation in the Northwest Territories, Canada (Chiarenzelli, 1983; Gall, 1994; Gall and Donaldson, 1990; LeCheminant and others, 1983; Ross and Chiarenzelli, 1985). Extensive silcretization apparently accompanied much of the sub-Thelon weathering in this area (Ross and Chiarenzelli, 1985). The proposed weathering profiles meet the mineralogical, textural, and soft-sediment deformation criteria for paleosols. However, the highly variable Ti/Al ratios in profiles developed on gneiss (Gall, 1994; Gall and Donaldson, 1990) suggest that either the parent rocks were inhomogeneous or that the weathering products contain an admixture of allochthonous components. There are too few data to evaluate the other published chemical profiles in the proposed sub-Thelon weathering horizon.

THE POSSIBLE AND UNLIKELY PALEOSOLS

Nine of the proposed paleosols in this review failed two paleosol criteria. These "possible" paleosols are numbered 29 to 37 in table 1. Paleosols 29 and 30 are profiles that apparently developed between 3.0 and 2.7 Ga near Steep Rock, Canada. Soft-sediment deformation features have not been reported in either of these profiles. Proposed paleosol 29 developed on granodiorite (Schau and Henderson, 1983). It is too thin (<1 m) to be of use. There are no published chemical data for paleosol 30, which is developed on tonalite (Wilks and Nisbet, 1988).

31, 32, 35, 36. Kirkland Lake, Mertondale, Suodenniemi, Wilson Island.—There is not enough information in published descriptions to evaluate the reports of paleosols 31, 32, 35, and 36: an about 2.7 Ga profile at Kirkland Lake, Canada (Kimberley and Grandstaff, 1986), a 2.58 Ga profile on the Mertondale Gneiss in Australia (Worden and Compston, 1973), a >2.0 Ga profile from Suodenniemi, Finland (Rankama, 1955), and an about 1.9 Ga (Bowring, Van Schmus, and Hoffman, 1984) profile in the Wilson Island Group in Canada (Stanworth and Badham, 1984).

33. Hokkalampi sediments.–Paleosol 33, a suite of profiles on glaciogenic sediments from the Hokkalampi paleosol (Marmo, 1992), is a possible paleosol. It fails both the parental and chemical criteria.

34 and 37. pre-Jatulian and Mistassini.–Drill cores through a pre-Jatulian (>2.1 Ga) unit in Karelia, which Koryakin described as a paleosol (number 34 in table 1), show no Ca, Mg, or Na loss and no soft-sediment deformation features (Koryakin, 1971). The Mistassini paleosol, number 37, is a proposed paleoweathering horizon between an Archean basalt and an Aphebian Mistassini Group dolomite (Chown and Caty, 1983). Unfortunately, no chemical data are available for the profile, and heavy dolomitization makes it unlikely that such data would be useful for studies of the ancient atmosphere.

38 to 50.–The remaining profiles, numbers 38 to 50, fail more than two of the criteria for paleosols. Several of the unlikely paleosols, including the units at Point Lake, 38, (Schau and Henderson, 1983), Laughland Lake, 41, (Schau and Henderson, 1983) and Villebon Township, 43, (Vogel, 1975), in Canada; Mount Martin, Australia, 46, (Purvis, 1984); and all of the reported paleosols in India, 47–49, (Golani, 1989; Kamineni and Rao, 1988, Sengupta and others, 1990; Sharma, 1979) lack a clearly identified parent rock and contain no weathering profile per se. There is little reason to expect that further study will allow these units to be upgraded to definite paleosols. The other unlikely paleosols, the Ada May, 40, and Vaal Reef, 42, in South Africa (Maynard, 1992); one of the profiles at Steep Rock, Canada, 39, (Wilks and Nisbet, 1988); and the profiles at Bathurst Inlet, Canada, 45, (Grotzinger and others, 1989) are developed on sedimentary rocks. All these fail multiple criteria for paleosols, including the homogeneous parent criterion. Some fail other criteria because of a lack of data.

WHAT DO THE DEFINITE PALEOSOLS TELL US ABOUT ATMOSPHERIC EVOLUTION?

The relationship between oxidant availability and Fe mobility during weathering is the primary tool for estimating paleoatmospheric oxygen levels using paleosols (Holland and Beukes, 1990; Holland and Zbinden, 1988; Pinto and Holland, 1988). The retention of Fe during weathering depends on the relative rates of supply and demand of oxidants and weathering acids. In most soils H_2CO_3 is the most important weathering acid. If oxygen is supplied much more rapidly to a weathering horizon than carbon dioxide is consumed, then essentially all Fe^{2+} in the weathering horizon will be oxidized to Fe^{3+} and retained as a component of ferric oxides and oxyhydroxides. The $\Sigma Fe/Al$ ratios in soils developed under such conditions are essentially constant from the top to the bottom of the soil. If carbon dioxide is supplied much more rapidly than oxygen, then Fe^{2+} will remain in the ferrous state. Under such conditions Fe^{2+} will behave like Mg. The $\Sigma Fe/Al$ ratios will be low in the top portion of the soil and can be high in the lower portion of the soil if Fe is reprecipitated there as a constituent of one or more soil minerals.

Although photochemically produced oxidants may be important at extremely low atmospheric oxygen levels, the relative rates of supply of oxidants and acids during subaerial weathering in the absence of higher land plants are generally directly related to the ratio P_{O_2}/P_{CO_2} in the atmosphere. For the weathering of any given rock, the oxygen demand is related to the acid demand by the ratio

$$R_c = \frac{(D_{O_2})}{(D_{CO_2})} = \frac{\Delta M_{FeO}}{8[\Delta M_{CaO} + \Delta M_{MgO} + \Delta M_{Na_2O} + \Delta M_{K_2O} + \Delta M_{MnO}]}$$

where D_i is the demand for the gas i during weathering of the rock, and ΔM_i is the difference between the concentration of the species i between the parent rock and the most weathered soil (Feakes, Zbinden, and Holland, 1989). If Fe was removed from the top of a paleosol during weathering, we can use the value of R_e for that paleosol to calculate a maximum value for the ratio P_{O_2}/P_{CO_2} for the atmosphere contemporaneous with its formation. If a paleosol retained Fe during weathering, we can use R_e to calculate a minimum value for that ratio (Pinto and Holland, 1988). Although the thickness of the soil profile and the rates of diffusion of CO_2 and O_2 also affect the calculations, Pinto and Holland (1988) found that the limiting value of P_{O_2}/P_{CO_2} during the weathering of most rock types under realistic conditions is generally fairly close to R_e. Thus, for paleosols where a full-up calculation of the limiting value for the ratio P_{O_2}/P_{CO_2} has not been published, we have assumed that it is equal to R_e.

Rye, Kuo, and Holland (1995) proposed an upper limit for atmospheric P_{CO_2} of about $10^{-1.7}$ atm, that is 60 times the present atmospheric level, for the time interval covered by all the known paleosols that lost Fe from their upper parts during weathering (2.75-2.25 Ga). This limit was based on the observation that some of the Fe liberated from the tops of these early soil profiles was probably reprecipitated as a constituent of a smectite rather than as a constituent of siderite in the lower portions of the soil profiles. In the absence of any other constraints, we will assume that this upper limit on P_{CO_2} holds for more recent paleosols as well.

Using Rye, Kuo, and Holland's (1995) maximum value for P_{CO_2} of $10^{-1.7}$ atm along with the limiting values of P_{O_2}/P_{CO_2}, we have calculated the maximum or minimum P_{O_2} indicated by the behavior of Fe in each paleosol. If Fe was mobile during weathering, the paleosol gives us a maximum value for P_{O_2}. If Fe was immobile during weathering, the paleosol gives us a minimum value for P_{O_2}.

In order to determine whether total Fe, Fe^{2+}, and Fe^{3+} were mobile during weathering we have plotted $\Sigma Fe/Al$, Fe^{2+}/Al, and Fe^{3+}/Al ratios versus depth for all the definite paleosols (figs. 10-16). Ohmoto prefers to normalize Fe to Ti (Ohmoto, 1996). In each of the definite paleosols both Ti and Al are essentially immobile, as demonstrated in the immobile element ratio versus depth plots in figures 3 to 9. Therefore, the Fe/Al and Fe/Ti plots for these paleosols are very similar. In paleosols developed on granite, initial Ti levels are low, so that small variations in the initial Ti distribution and small errors in Ti measurements can introduce significant variability in Ti normalized plots. Therefore, we have chosen to normalize to Al rather than to Ti.

The value of R_e for the Mt. Roe #1 paleosol profile is 0.039 (Macfarlane, Danielson, and Holland, 1994). The value of R_e for the Mt. Roe #2 paleosol is 0.049. Figure 10 shows the plots of $\Sigma Fe/Al$ versus depth in the Mt. Roe #1 and Mt. Roe #2 paleosols. Essentially all Fe, that is, both Fe^{2+} and Fe^{3+}, was removed from the upper portions of both of these paleosols during weathering. The loss of iron during the formation of Mt. Roe #1 indicates that the P_{O_2}/P_{CO_2} ratio in the atmosphere sometime between 2.775 and 2.755 Ga was no more than 0.016 (Macfarlane, Danielson, and Holland, 1994). Thus, atmospheric P_{O_2} was less than or equal to about 3×10^{-4} atm at that time. Analysis of data from Mt. Roe #2 yields similar results.

Ohmoto (1996 and 1997) concluded that Fe^{2+} had been oxidized to Fe^{3+} during weathering of three ~2.45 Ga pre-Matinenda paleosols in the Elliot Lake area. These supposed paleosols, the Pronto (25) profile described by Gay and Grandstaff (1980) and the Denison Mine (24) profiles described by Gay and Grandstaff (1980) and by Mossman and Farrow (1992) all fail the immobile element criteria for paleosols.

Iron depletion is ubiquitous in the upper portions of all of the ~2.45 Ga pre-Matinenda definite paleosols in the Elliot Lake area and at Cooper Lake, Canada (G-Farrow and Mossman, 1988; Prasad and Roscoe, 1991; Mossman and Farrow, 1992; Sutton and Maynard, 1992, 1993). The ratio of $\Sigma Fe/Al$ falls toward the top of each profile (see fig. 11).

The values of R_e for the basalt, diabase, and greenstone derived Elliot Lake profiles are 0.05, 0.07, and 0.08 in the Quirke II paleosol (profile DH 268) (4), the Cooper Lake

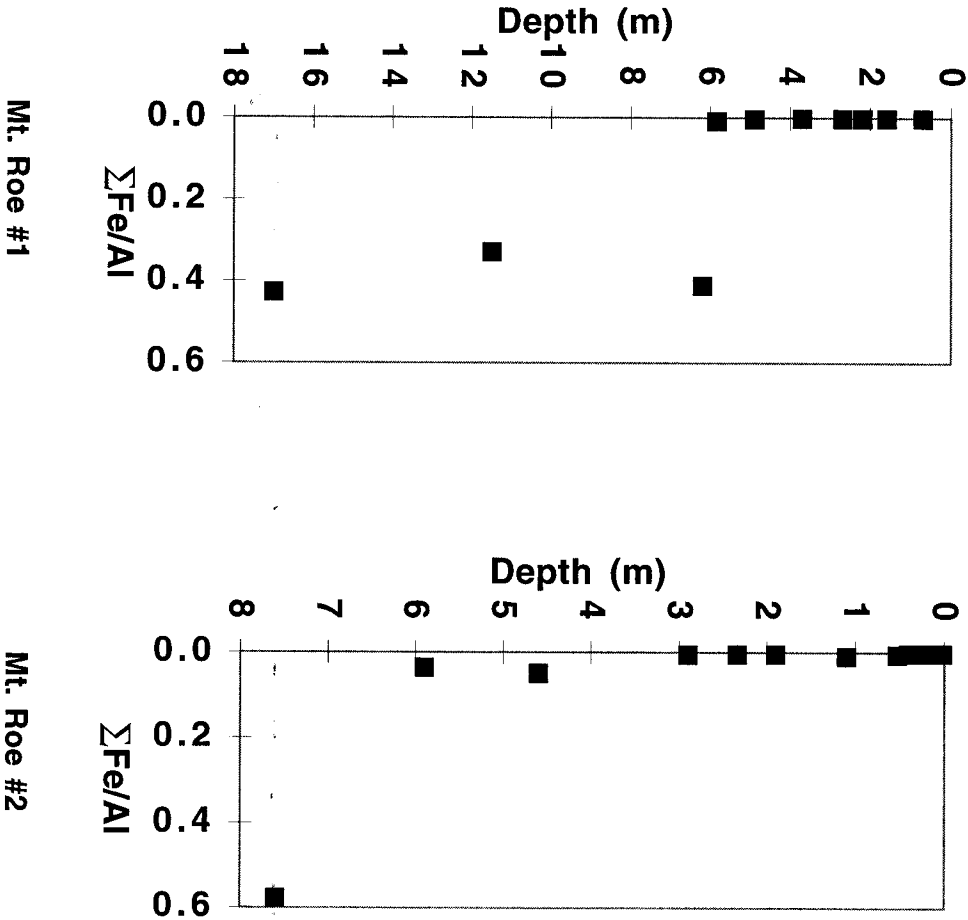


Fig. 10. ΣFe/Al molar ratio versus depth in the Mt. Roe #1 and Mt. Roe #2 paleosols (Macfarlane, Danielson, and Holland, 1994).

paleosol (7), and the Stanleigh Mine profile of the Denison paleosol (3) respectively. R_e values in the granite-derived Elliot Lake paleosols are 0.025 in the Pronto/NAN paleosol (5), and 0.007 in the Lauzon Bay paleosol (6). The greenstone, the diabase, the basalt, and the Pronto/NAN granite are high enough in iron that the metasomatic activity that led to potassium enrichment probably had little effect on the distribution of Fe in these profiles. Loss of Fe during weathering of these paleosol profiles indicates that the P_{O_2}/P_{CO_2} ratio in the atmosphere about 2.45 Ga was no higher than 0.025, and therefore that atmospheric P_{O_2} was less than or equal to about 5×10^{-4} atm.

The initial Fe content of the Lauzon Bay parent rock was only 1.12 wt percent (Sutton and Maynard, 1992). The ΣFe/Al ratio in the top paleosol sample is over 30 percent lower than the ΣFe/Al ratio in the parent rock, but the absolute loss of Fe is quite small and might be related to the metasomatic event that added K to the profile. Thus, although the apparent loss of Fe during the weathering of the Lauzon Bay paleosol suggests that atmospheric $P_{O_2} \leq 1.5 \times 10^{-4}$, this limit is uncertain.

The next three bona fide paleosols, the Hokkalampi paleosol, 8, the Ville Marie paleosol, 9, and the Hekpoort paleosol, 10, have overlapping ages, all having formed between 2.44 and 2.2 Ga. Ohmoto (1996 and 1997) concluded that all three of these paleosols formed under oxic conditions. Holland and Rye (1997) concluded that the Hekpoort formed under low oxygen conditions and the Hokkalampi and Ville Marie formed under higher oxygen conditions. We have reassessed the data for these three paleosol, examining the role of erosion in the development of the present Fe distribution.

The data for the Hokkalampi paleosol are somewhat equivocal. There are three cores through the paleosol. Core 303 shows an about 40 percent Fe loss from the top of the profile. Core 301 shows an about 50 percent Fe loss. Core 302 shows essentially no Fe loss (fig. 12). None of the cores includes the upper zone of the soil described by Marmo (1992), but the distribution of Mg in the cores can be used to estimate how close he came to sampling the top of the soil.

The tops of cores 303 and 301 show significant depletion in Mg relative to the parent rock. Mg depletion is also found in the top portion of all but one of the other paleosols. The top of core 302 is enriched in Mg with respect to the parent rock. Since Mg enrichment occurs in the lower portions of some paleosols, the Mg distribution in cores 303 and 301 suggests they contain material that was fairly near the surface during weathering, whereas core 302 only contains the lower portion of the soil. If cores 303 and 301 sample the upper portion of the soil, then the Hokkalampi paleosol gives us an upper limit on P_{O_2} of about 2×10^{-4} atm. Marmo (1992) analyzed cores that supposedly contained samples of the top of the paleosol. Iron levels are very low in these samples. However, these cores did not contain the whole paleosol profile; the relationship between these samples and the paleosol is therefore in doubt. Further study of the Hokkalampi paleosol may allow us to remove the ambiguity that remains regarding the conditions under which the Hokkalampi formed.

The distribution of Fe in the Ville Marie paleosol (9), which formed between 2.38 and 2.215 Ga is suggestive of oxidative weathering. There is no apparent Fe loss (fig. 13). However, the soil was deeply eroded prior to the deposition of the overlying Lorrain Formation. The initial Fe content of the granite is only 1.36 wt percent (Rainbird, Nesbitt, and Donaldson, 1990). Thus, the fluids that sericitized this soil could have affected the Fe budget of the paleosol. Taken alone, this paleosol does not make a good paleobarometer (personal communication, H. W. Nesbitt, and J. A. Donaldson, 1997).

The Hekpoort paleosol, 10, which has been dated at 2.224 ± 0.021 Ga, lost a great deal of Fe from the top portion of the Waterval Onder (Button, 1979), Daspoort Tunnel (Hart, 1986), and Bank Break profiles (fig. 14). Iron mobility during the weathering of this lava indicates that P_{O_2}/P_{CO_2} was less than or equal to 0.04, and that atmospheric P_{O_2} was no higher than 8×10^{-4} atm. This paleosol is the youngest paleosol that clearly lost a large part of its initial Fe during weathering.

All three of the paleosols that formed sometime between 2.44 and 2.2 Ga (paleosols 8-10) are directly overlain by red beds. The presence of these red beds suggests that atmospheric oxygen levels were fairly high shortly after the formation of each of these paleosols. Better dating and a quantitative model of red bed formation should allow us to determine whether these red beds and paleosols record a single rise in atmospheric P_{O_2} about 2.2 Ga or whether they indicate large P_{O_2} fluctuations between 2.44 and 2.2 Ga.

The 2.2 to 2.0 Ga Drakenstein paleosol, 11, the 1.85 Ga Flin Flon paleosol, 13, the 1.1 Ga Sturgeon Falls paleosol, 14, and the 0.45 Ga Arisaig paleosols, 15, have essentially constant $\Sigma Fe/Al$ ratios from the top to the base of the paleosols (fig. 15 and 16). Side-by-side plots of Fe^{2+}/Al versus depth and Fe^{3+}/Al versus depth indicate that ferrous iron was converted to ferric iron in the upper portions of the Drakenstein (fig. 15) and Flin Flon (fig. 16A) paleosols.

In the Drakenstein, Flin Flon, Sturgeon Falls, and Arisaig paleosols R_e is 0.04, 0.06 to 0.08, 0.09 to 0.27, and 0.05 to 0.12 respectively. Conservation of Fe and conversion of ferrous to ferric iron during weathering of these three basalts indicates that the ratio

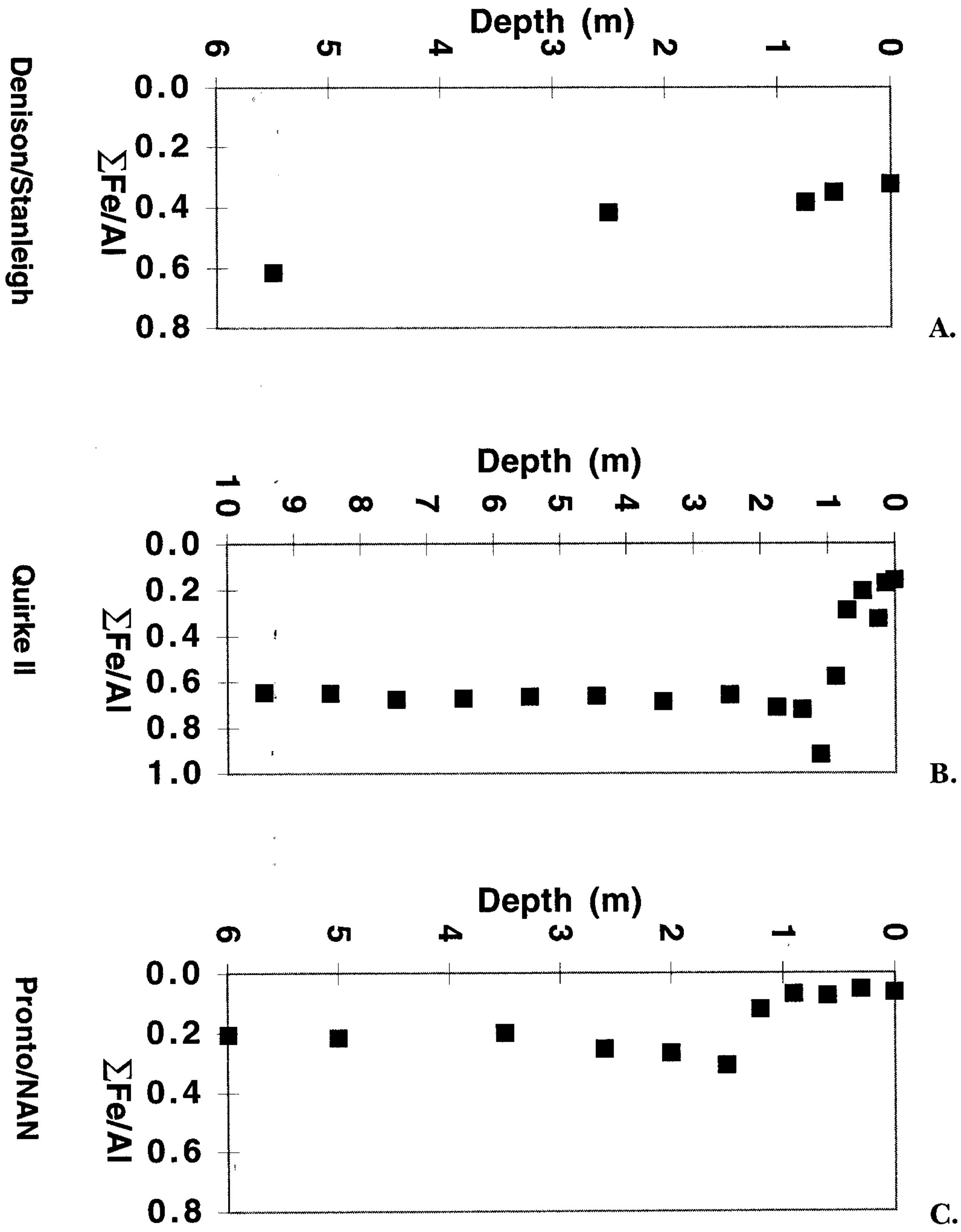


Fig. 11. Iron to aluminum molar ratios versus depth in the Elliot Lake paleosols. (A–C) ΣFe/Al molar ratio versus depth in (A) the Stanleigh Mine profile of the Denison paleosol; (B) the Quirke II DH 268 paleosol; (C) the Pronto/NAN paleosol.

P_{O_2}/P_{CO_2} has been greater than about 0.1, and that atmospheric P_{O_2} has been greater than about 2×10^{-3} atm since 2.0 Ga.

The 2.2 to 2.0 Ga Wolhaarkop paleosol, 12, also retained essentially all its Fe during weathering (Holland and Beukes, 1990). Retention of Fe during the weathering of the

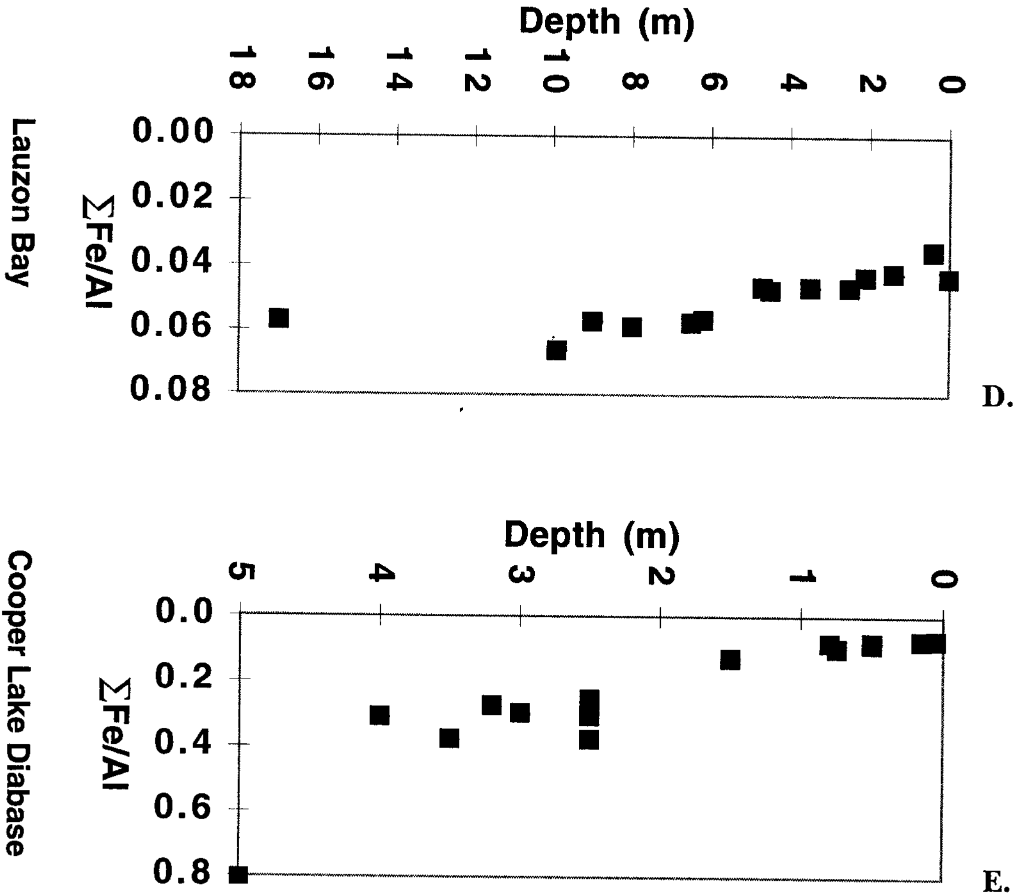


Fig. 11(D and E) ΣFe/Al moles ratio versus depth in (D) the Lauzon Bay paleosol; (E) the Cooper Lake paleosol.

siderite facies of the Kuruman Iron Formation that produced the Wolhaarkop paleosol suggests that atmospheric P_{O_2} was greater than 0.03 atm (Holland and Beukes, 1990) by 2.0 Ga.

We have plotted the age range and the limiting value for P_{O_2} during weathering for each paleosol as a horizontal bar in figure 17. Each bar has a vertical arrow. If Fe was removed from the top of the paleosol during weathering, a downward arrow has been attached to indicate that this paleosol gives us a maximum value for P_{O_2}. If Fe was retained in the top of the paleosol during weathering, an upward arrow was attached to indicate that the paleosol gives us a minimum value for P_{O_2}. Altogether the ΣFe/Al profiles of the 15 definite paleosols indicate that oxygen levels were below 5×10^{-4} atm until at least 2.45 Ga, that they may have fluctuated significantly between 2.44 and 2.2 Ga but were certainly below 8×10^{-4} atm at some point during this interval, and that they rose to at least 0.03 atm by about 2.0 Ga and have probably stayed high since then.

Ohmoto (1996) concluded that the behavior of Fe during the weathering of all paleosols of all ages give us minimum values for P_{O_2}. According to him, Fe^{2+} was essentially quantitatively oxidized to Fe^{3+} and reprecipitated as a constituent of ferric hydroxides during the formation of every paleosol. In his model, essentially all ΣFe loss is due to the reductive dissolution of ferric hydroxides either by hydrothermal fluids or

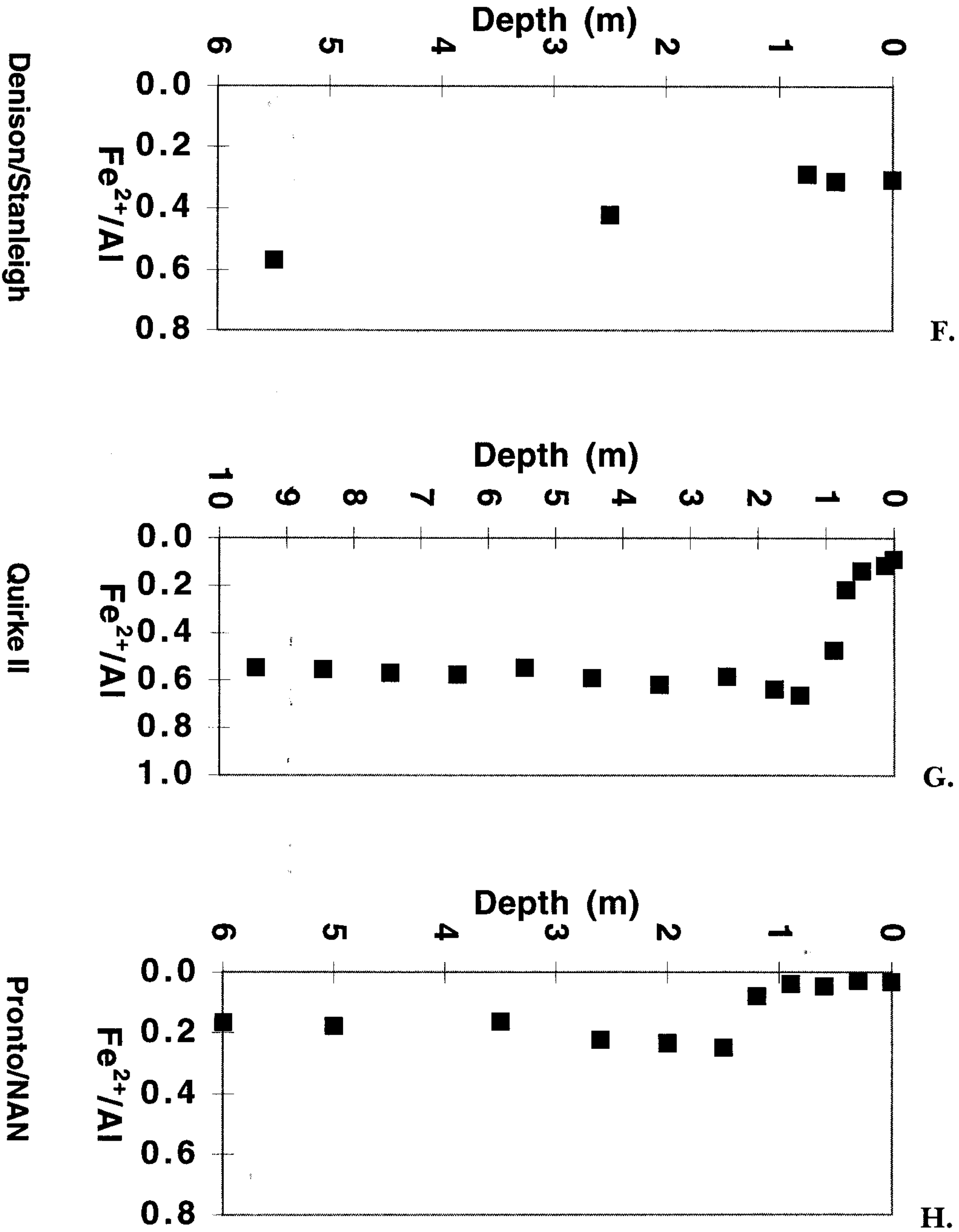


Fig. 11(F–H) Fe^{2+}/Al molar ratio versus depth in (F) the Stanleigh Mine profile of the Denison paleosol; (G) the Quirke II DH 268 paleosol; (H) the Pronto/NAN paleosol.

by organic acids generated from the decay of terrestrial organic matter. This conclusion is not supported by the available evidence.

Massive Fe loss at the top of paleosols is restricted to paleosols that formed before 2.2 Ga. In all cases where material from a pre-2.2 Ga paleosol was entrained in the

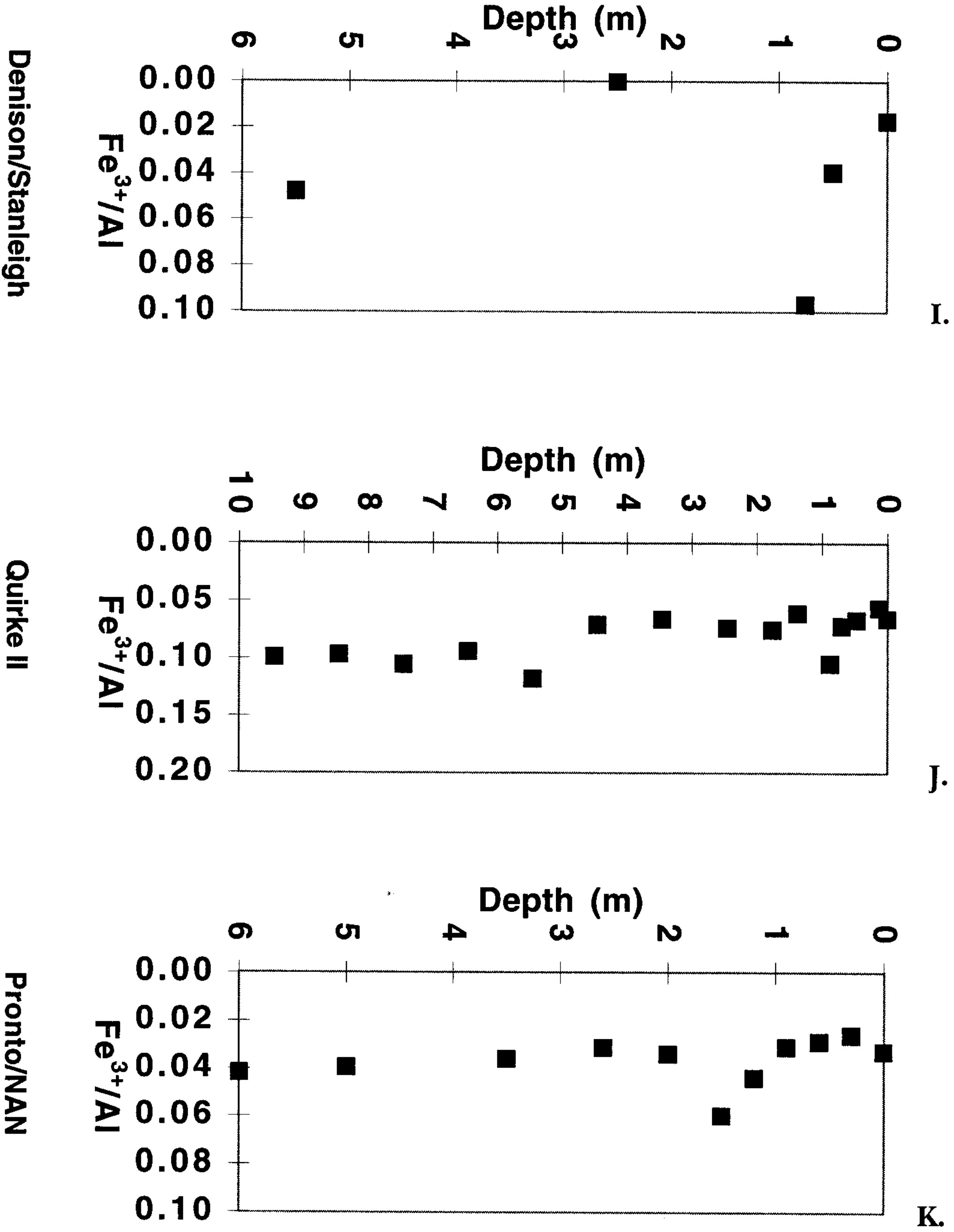


Fig. 11(I–K) Fe^{3+}/Al molar ratio versus depth in (I) the Stanleigh Mine profile of the Denison paleosol; (J) the Quirke II DH 268 paleosol; (K) the Pronto/NAN paleosol. References: A, C, F, H, I, and K: Goddard (1987), G-Farrow and Mossman (1988); B, G, and J: Prasad and Roscoe (1991); D: Sutton and Maynard (1992); E: Sutton and Maynard (1993).

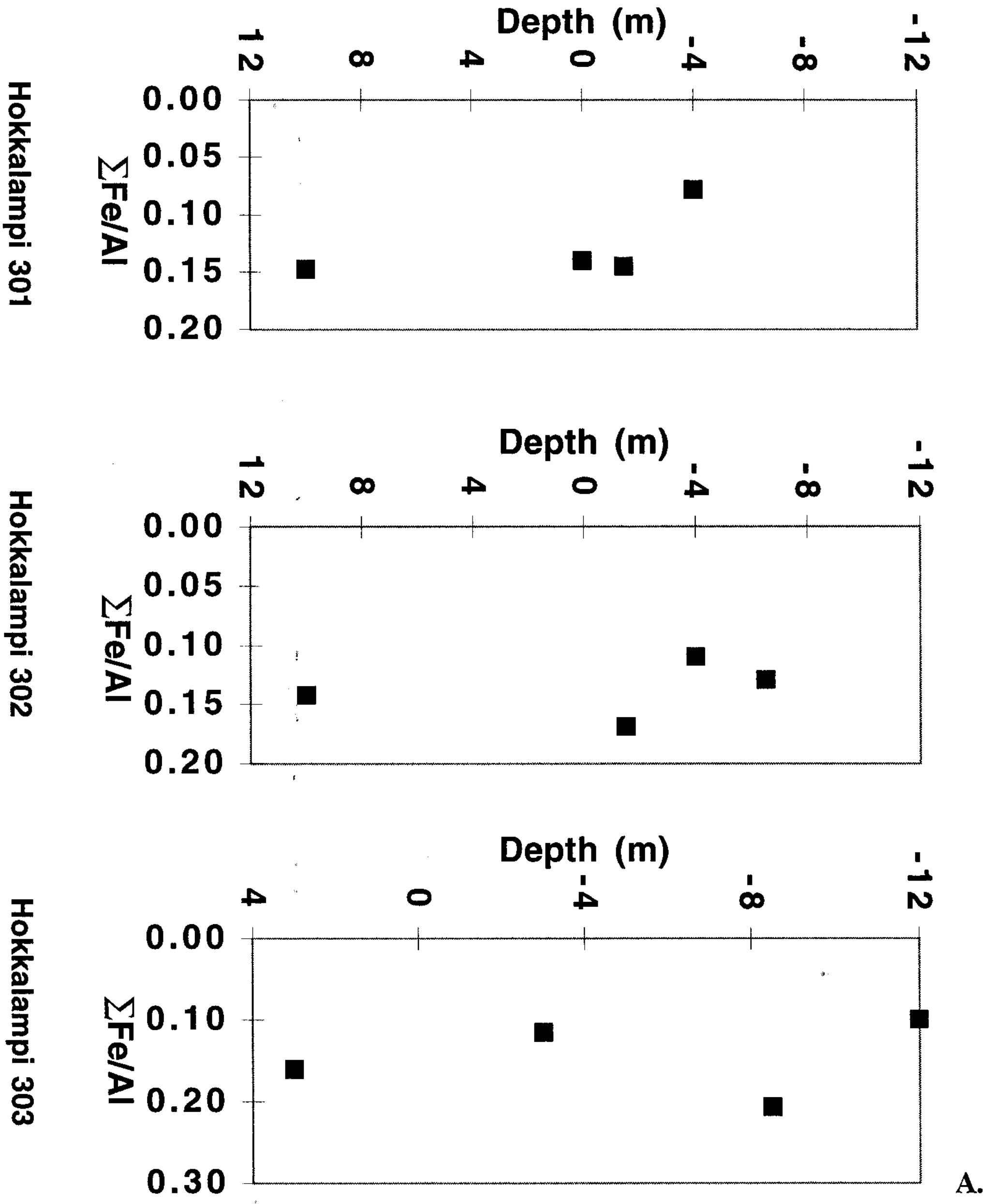


Fig. 12. Iron to aluminum molar ratios versus depth in three cores through the Hokkalampi paleosol (see fig. 5). (A) ΣFe/Al molar ratio versus depth.

overlying sediment or lava flow the entrained material clearly shows that Fe loss in the paleosol preceded the deposition of the overlying unit (see for example fig. 1A, C, and D). Hydrothermal fluids could not have been responsible for the Fe loss in these paleosols. That leaves the possibility that biological activity caused the massive Fe loss in all the earliest paleosols.

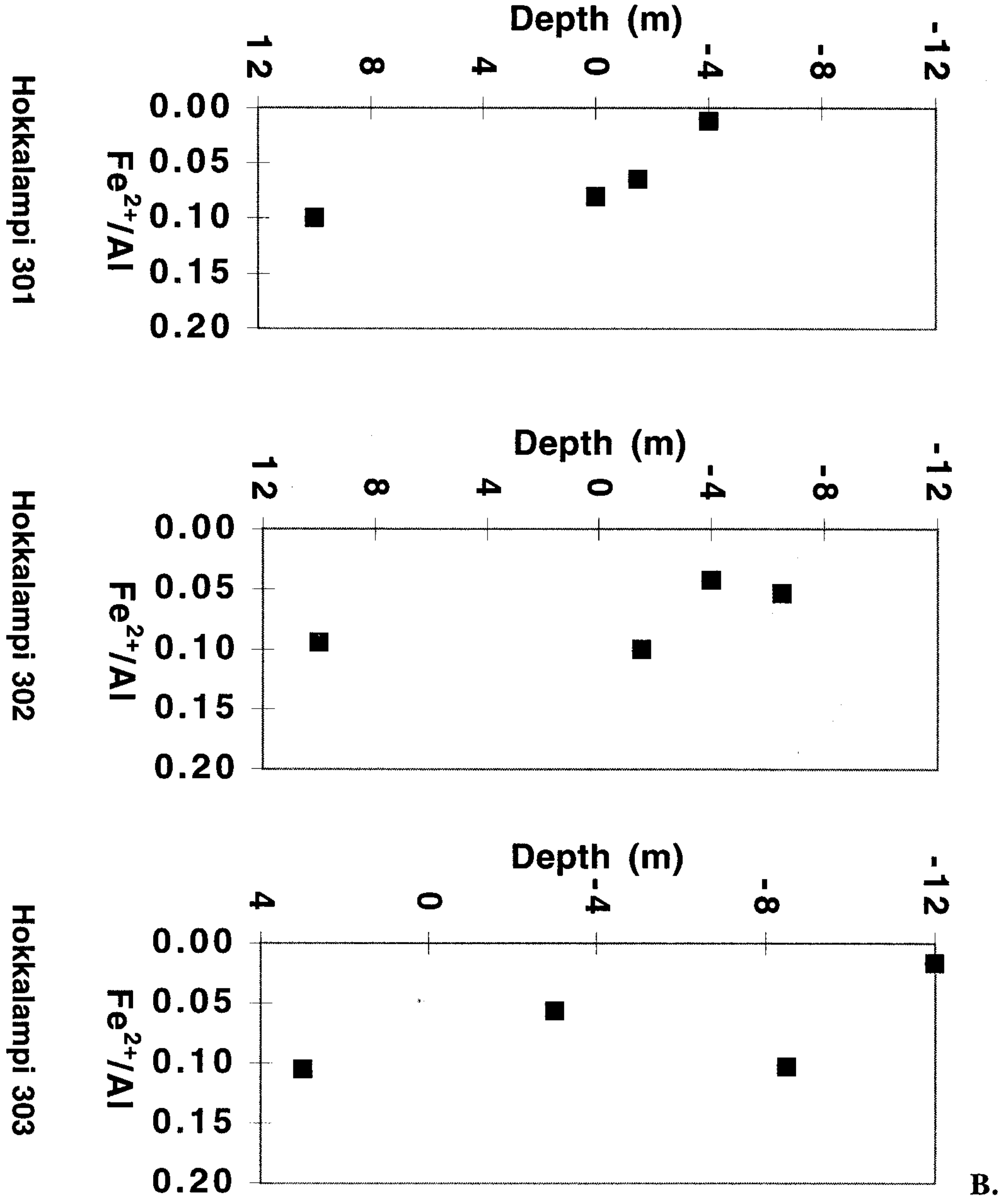


Fig. 12 (B) Fe^{2+}/Al molar ratio versus depth.

Although the evidence for the existence of an algal and/or bacterial land cover during the Precambrian has been rather weak, the recent discovery of what appear to be the remains of a methanotrophic mat at the top of the Mt. Roe #2 paleosol (Rye, 1998) strengthens the contention that such mats were a common feature on the continents during the last 2.2 Ga of the Precambrian. It is very difficult to estimate the quantitative effects of such mats on soil air and water composition. Pinto and Holland (1988) have estimated the rate at which these mats generated dissolved organic carbon (DOC). They

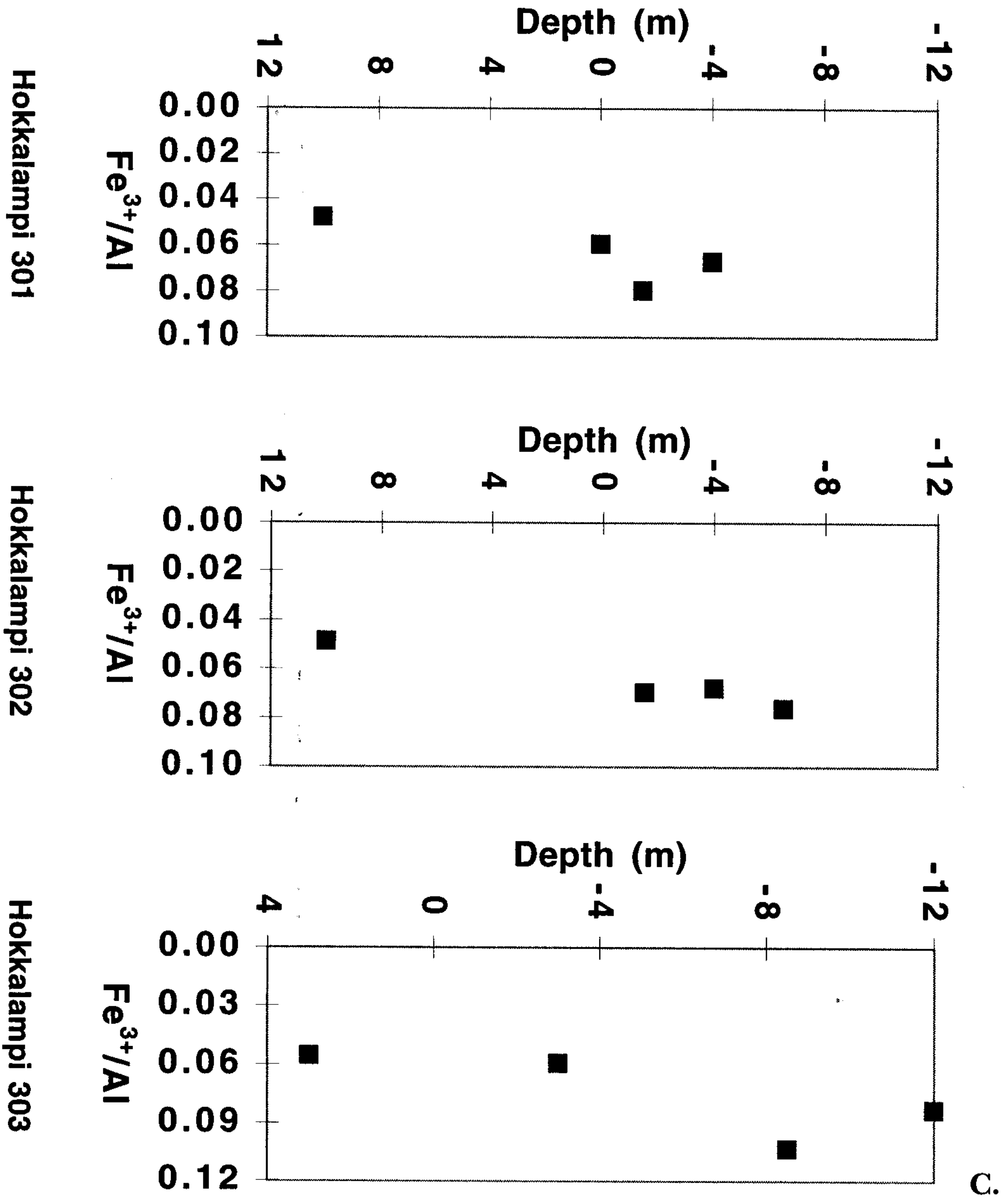


Fig. 12 (C) Fe^{3+}/Al molar ratio versus depth (Marmo, 1992).

concluded that the downward flux of oxygen required to destroy the flux of DOC from such mats was smaller than and possibly trivial compared to the oxygen flux required to oxidize Fe^{2+} released during the weathering of many igneous rocks. They pointed out, however, that there is ample room to doubt the validity of their calculations. Since then Raven (1995) has proposed values for the potential rate of organic carbon production in cyanobacterial mats that are considerably larger than those used by Pinto and Holland (1988). Thus, in principle, bacterial and/or algal mats could have had a significant impact on the oxidation state of pre-Devonian paleosols.

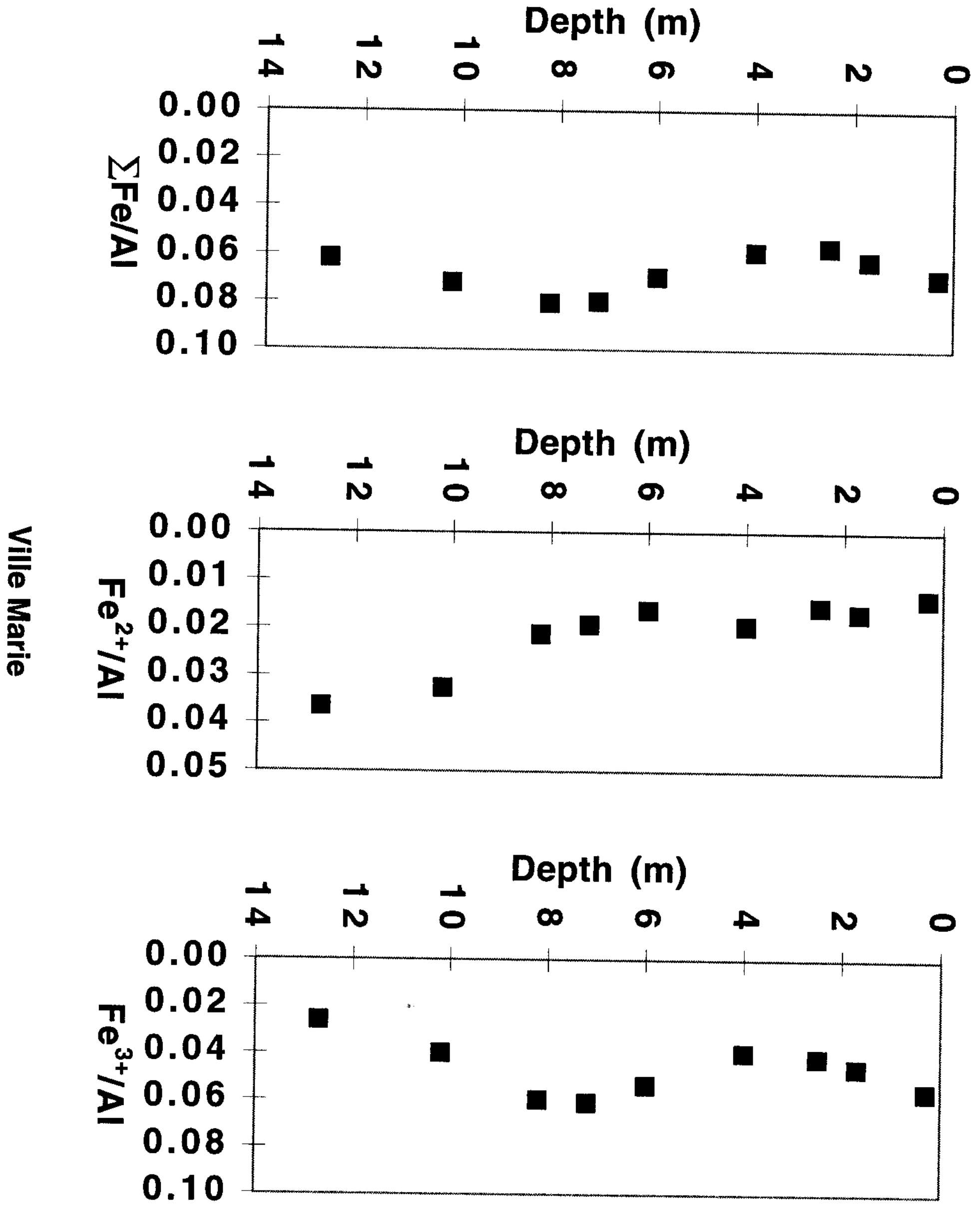


Fig. 13. Iron to aluminum molar ratios versus depth in the Ville Marie paleosol (Rainbird, Nesbitt, and Donaldson, 1990).

However, the paleosol record itself argues that the impact of the mats was probably small. While Fe loss is the rule in pre-2.2 Ga paleosols, Fe retention is ubiquitous in paleosols that formed after 2.2 Ga. The highly oxidized state of the younger paleosols suggests that the effect of mats on their oxidation state was minor. If so, the effect of mats on the pre-2.2 Ga paleosols was probably minor as well. We have, therefore, neglected the effect of mats in this review. However, this complete neglect may turn out to be unjustified.

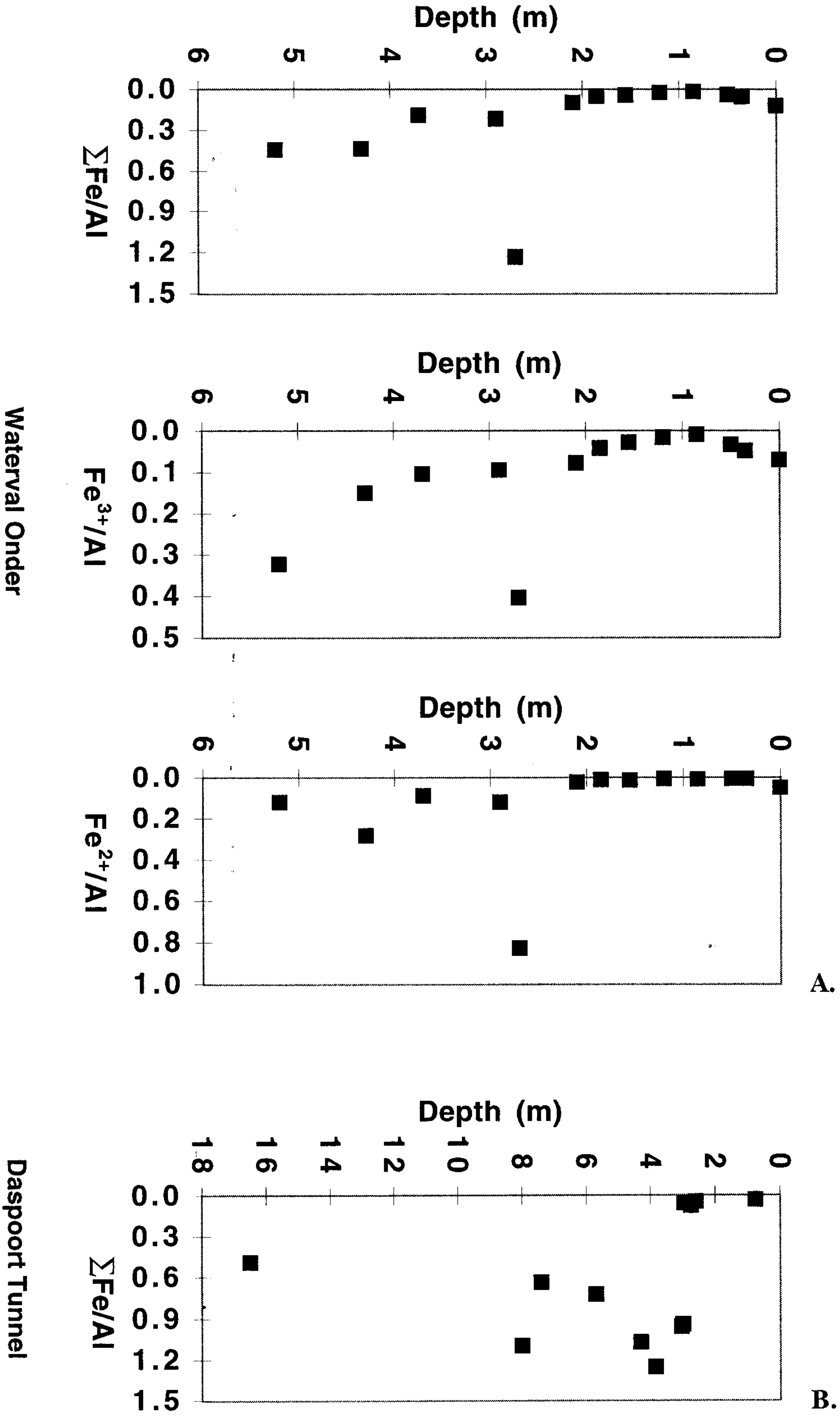


Fig. 14. Iron to aluminum molar ratios versus depth in the Hekpoort paleosol. (A) Waterval Onder (Button, 1979); (B) Daspoort Tunnel (Hart, 1986).

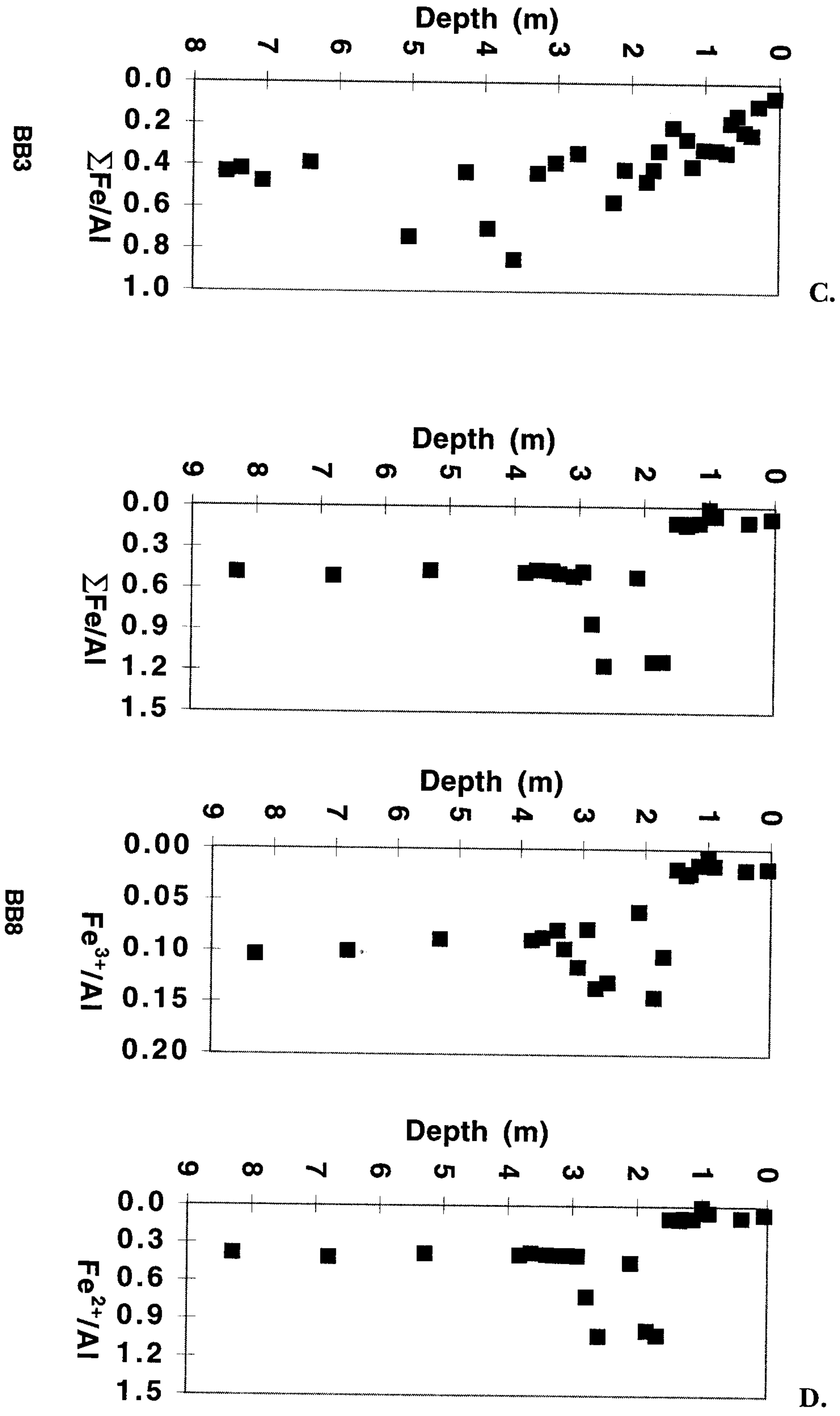


Fig. 14(C) Bank Break core BB3 (Rye, unpublished data); (D) Bank Break core BB8 (Rye, unpublished data).

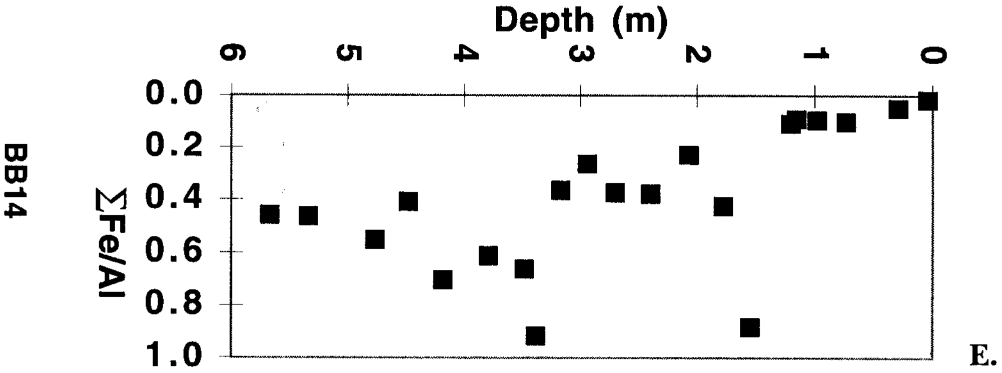


Fig. 14(E) Bank Break core BB14 (Rye, unpublished data).

Although biological activity is most likely not responsible for ΣFe depletion in pre-2.2 Ga paleosols, it may have played a role in mobilizing Fe^{3+} that was present prior to the onset of weathering in some paleosols. The top portions of both Mt. Roe paleosols, 1 and 2, contain 0.04 to 0.20 wt percent total Fe oxides, measured as Fe_2O_3. Our unpublished titration data indicate that the unweathered basalt contains more than 1 wt percent Fe_2O_3. Thus, ferric iron was apparently lost during the formation of the Mt. Roe paleosols at about 2.75 Ga. Among the pre-Matinenda paleosols in the Elliot Lake area, iron speciation data are available for the Stanleigh Mine profile of the Denison paleosol, 4, the Quirke II (DH 268) paleosol, 5, and the Pronto/NAN paleosol, 6. In all three profiles the Fe^{3+}/Al ratios are essentially constant from bottom to top. In the Stanleigh Mine profile the Fe^{2+}/Al ratios drop by about 50 percent from the bottom to the top, while the Fe^{2+}/Al ratios drop sharply toward the top of the other two profiles (fig. 11).

The upper about 1.5 m of the Hekpoort paleosol in the Bank Break core, BB8, has lost both Fe^{3+} and Fe^{2+} relative to the parent rock (>3 m) (fig. 14C). The lower, chlorite rich portion of the soil (1.5-3 m) is enriched in both Fe^{3+} and Fe^{2+} (fig. 14C). In the Waterval Onder roadcut we see the same general pattern (fig. 14A), but unfortunately the parent rock is not exposed at this site (Button, 1979).

Ohmoto has argued that Fe^{3+} in magnetite and other primary igneous minerals would only be mobilized during weathering if attacked by organic acids (Ohmoto, 1996). The discovery that the Mt. Roe #2 paleosol was probably colonized by bacteria allows for the possibility that the dissolution of magnetite near the top of this paleosol was driven by biological processes. We are currently exploring whether Fe^{3+} depletion during weathering requires the involvement of land-based organisms. One of us (RR) will discuss the issue in detail in manuscripts on the Hekpoort and Mt. Roe #2 paleosols.

CONCLUSIONS

Ohmoto's (1996) suggestion that oxygen levels have not changed significantly during the past 3.0 Ga is not supported by the available data for paleosols. His conclusion relied in part on analyses of five of the units (Dominion Reef, 18; Denison, 24; Villebon, 43; Pronto, 25; and Ville Marie, 10) that are not suitable for paleoatmospheric reconstructions. This reliance clearly skewed his results. On the other hand, Holland and co-workers' conclusion that atmospheric P_{O_2} increased during the Paleoproterozoic (Holland, 1994) is supported, although the history of atmospheric oxygen that is emerging may be more complicated than previously thought.

Chemical profiles in the fifteen definite paleosols described in this review clearly indicate that atmospheric P_{O_2} rose between 2.75 and 2.0 Ga. ΣFe/Al ratio profiles suggest

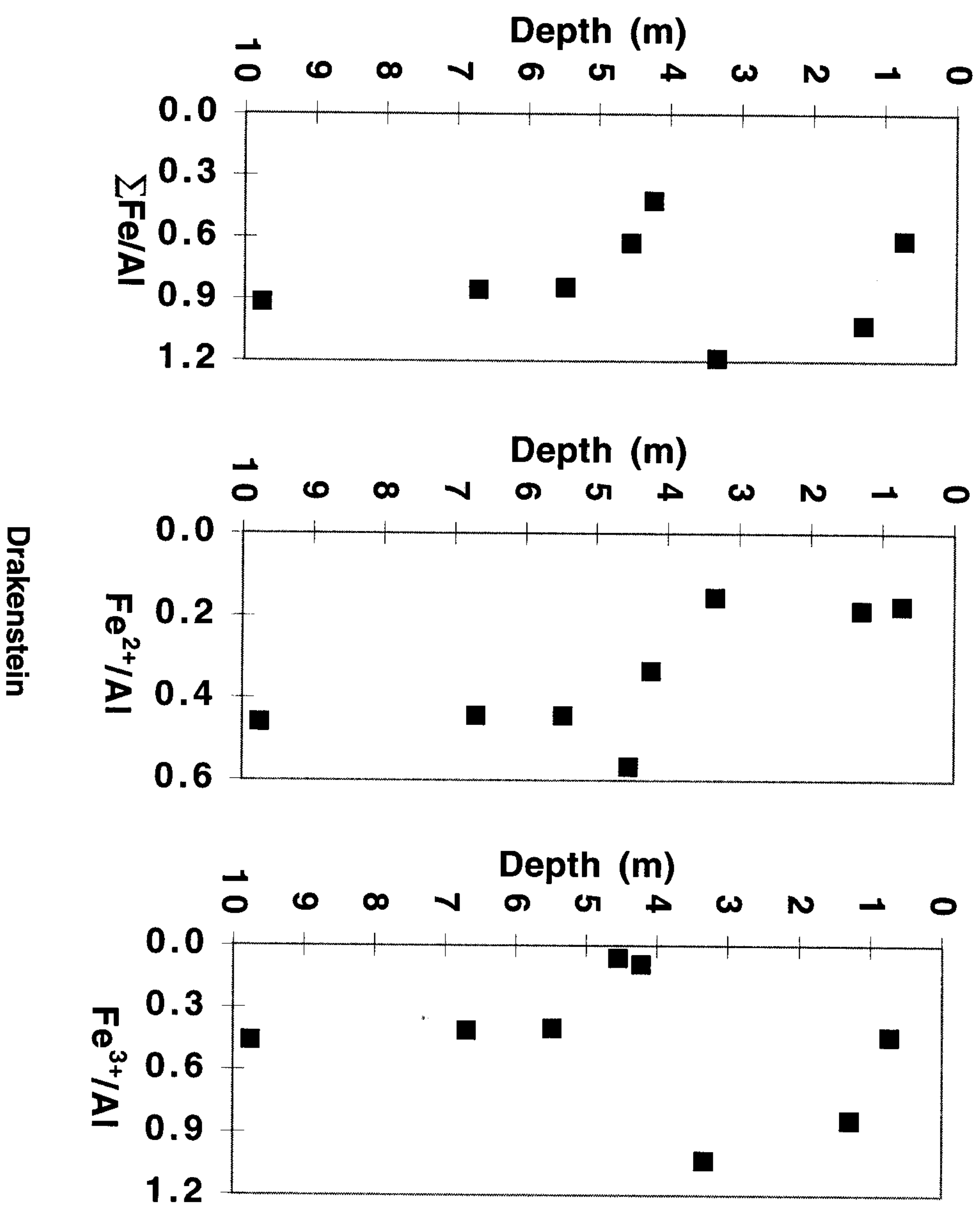


Fig. 15. Iron to aluminum molar ratios versus depth in the Drakenstein paleosol (Wiggering and Beukes, 1990).

that atmospheric P_{O_2} rose from $\leq 8 \times 10^{-4}$ atm to ≥ 0.03 atm between the formation of the Hekpoort paleosol between 2.245 and 2.203 Ga and the formation of the Wolhaarkop paleosol between 2.2 and 1.92 Ga. This picture is consistent with the marine $\delta^{13}C_{carb}$ record, which indicates that a large amount of oxygen was added to the atmosphere between 2.22 and 2.06 Ga (Karhu and Holland, 1996). The presence of detrital uraninite (Ramdohr, 1958a,b; Robb, Davis, and Kamo, 1990; Robb and others, 1992; Robb and Meyer, 1990; Schidlowski, 1966) and detrital pyrite (Kirkham and

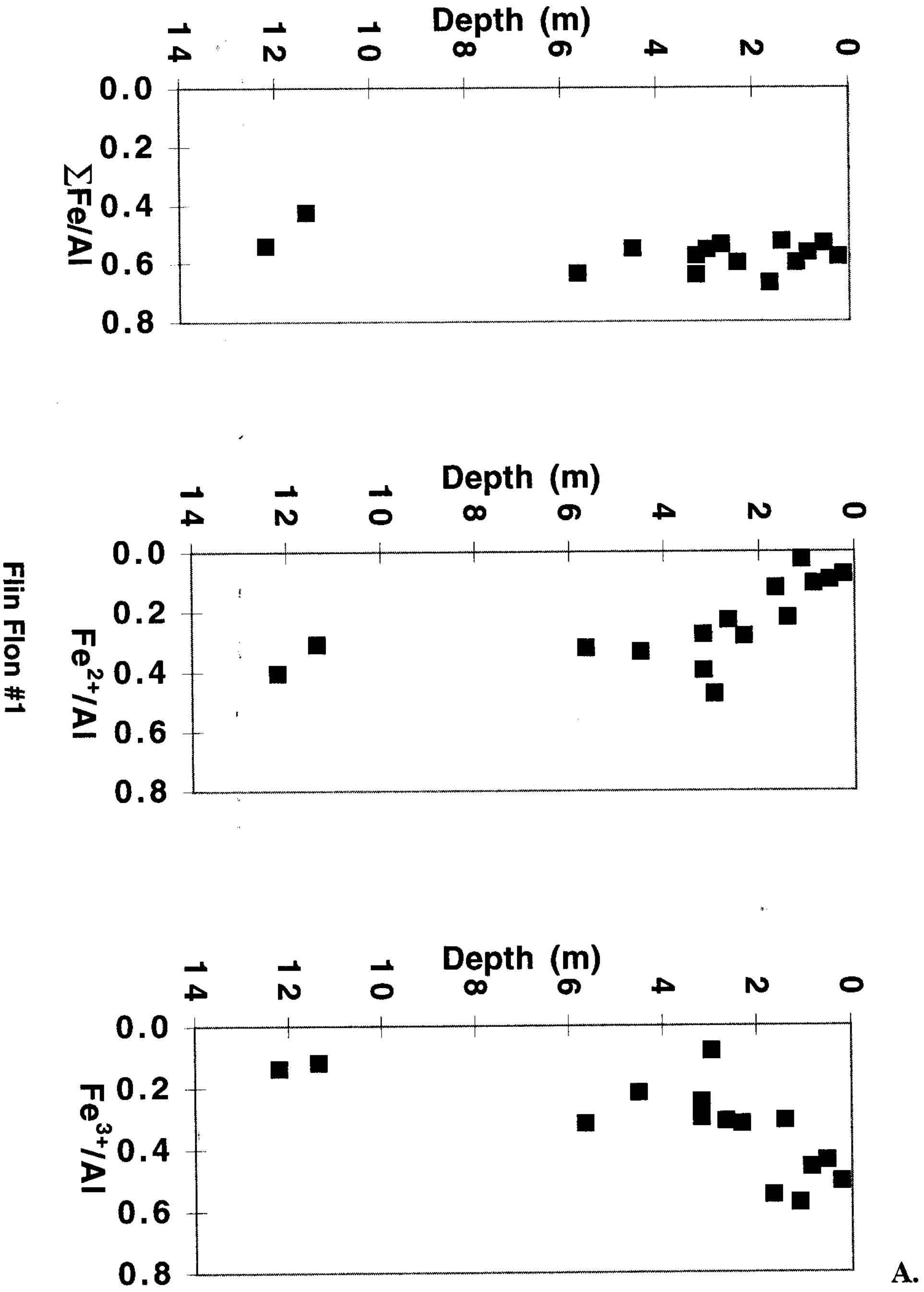


Fig. 16. Iron to aluminum molar ratios in four paleosols. (A) the Flin Flon #1 paleosol (Holland, Feakes, and Zbinden, 1989).

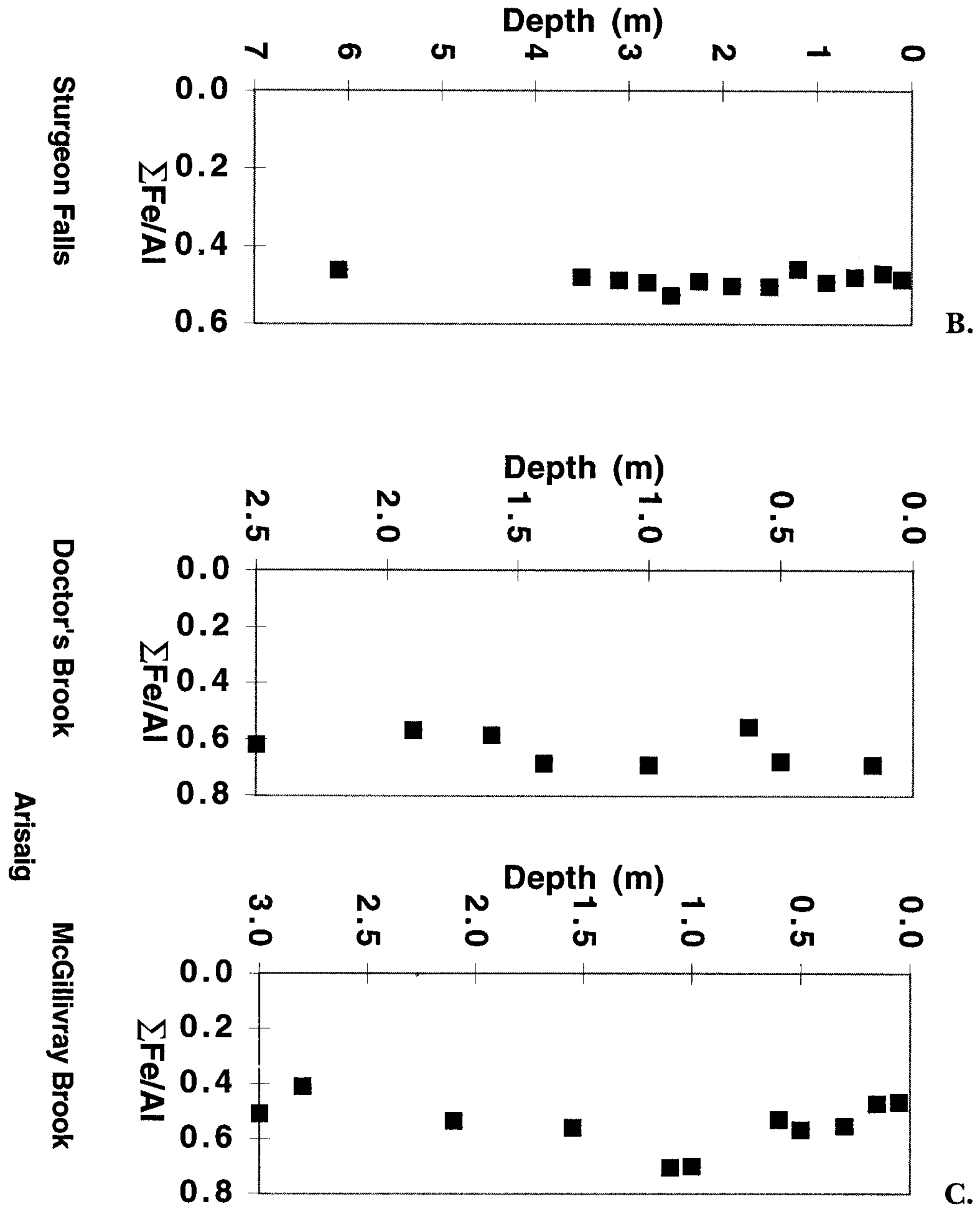


Fig. 16(B) the Sturgeon Falls paleosol (Zbinden and others, 1988); (C) the Arisaig paleosols at Doctor's Brook and McGillivray Brook (Feakes, Zbinden, and Holland, 1989).

Roscoe, 1993; Poujol, Robb, and Respaut, 1998; Ramdohr, 1958a,b; Sturt, Melezhik, and Ramsay, 1994) in pre-2.3 Ga sedimentary rocks indicates oxygen levels were low prior to about 2.3 Ga. The emergence of red beds, which are found in the >2.215 Ga Lorrain Formation (Rainbird, Nesbitt, and Donaldson, 1990), the ≥2.142 +0.004/ −0.002 Ga (Hoffman and Grotzinger, 1989) Chakonipau Formation in the Labrador

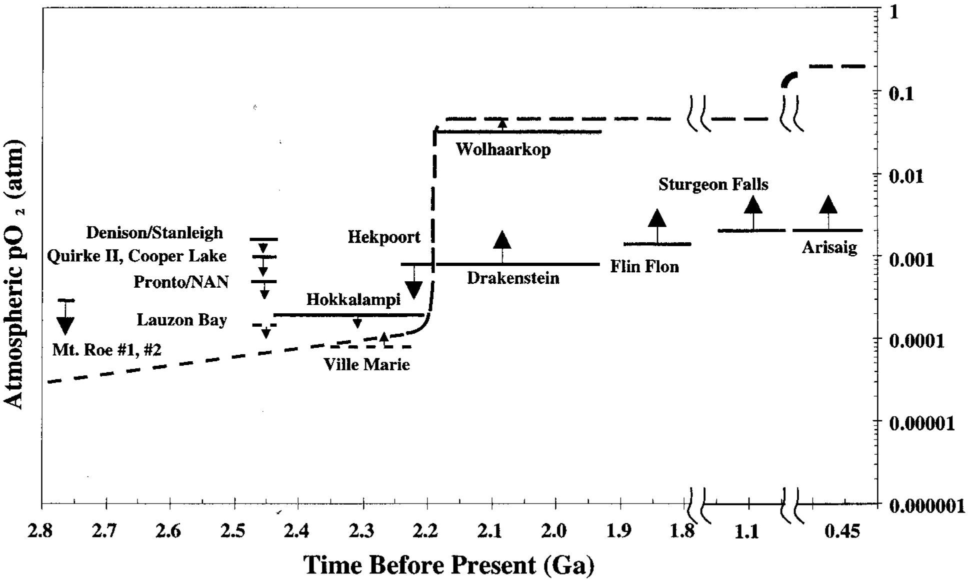


Fig. 17. Atmospheric pO_2 during the last 2.8 Ga. The maximum or minimum value for atmospheric pO_2 was estimated on the basis of the mobility of Fe during weathering of the 15 definite paleosols. Paleosols that lost Fe during weathering have a downward arrow indicating atmospheric pO_2 was equal to or less than the value depicted. Paleosols that retained Fe during weathering have an upward arrow indicating atmospheric pO_2 was equal to or greater than the value depicted. The dashed curve is the approximate trajectory of atmospheric pO_2 as constrained by a variety of data (Holland, 1994). The history of pO_2 during the Phanerozoic is based on the results of Berner and Canfield (1989).

Trough and in the Lower Jatulian (Melezhik and others, 1997) which is crosscut by and intercalated with groups of dikes and sills up to 2.215 Ga in age (Perttunen, 1991), indicates oxygen levels were already fairly high about 2.2 Ga. Thus, the sedimentary record is broadly consistent with the rise in oxygen that is seen in the paleosol record.

The presence of red beds immediately overlying all three paleosols that formed between 2.44 and 2.2 Ga–the Hokkalampi paleosol, the Ville Marie paleosol, and the Hekpoort paleosol–suggests that either these paleosols formed nearly simultaneously near the end of this time interval, or that atmospheric P_{O_2} may have oscillated between 2.44 and 2.2 Ga. The apparent differences in the behavior of Fe^{3+} during weathering of the various pre-2.2 Ga paleosols is tantalizing. Hopefully the subtleties in the paleosol-based picture of atmospheric evolution will shortly come into sharper focus.

ACKNOWLEDGEMENTS

The authors would like to thank Nick Beukes, Al Donaldson, Barry Maynard, Wayne Nesbitt, and Alec Trendall for many thoughtprovoking discussions and for the trenchant comments that shaped this manuscript. Paul Falkowski, Jacques Martini, Carolyn Olson, Neil Phillips, Nirankar Prasad, Greg Retallack, and Elizabeth Zbinden also contributed significantly through written comments on earlier versions. We would like to thank Barry Maynard (again) and Hiroshi Ohmoto for their formal reviews. We would especially like to thank Manfred Schidlowski for his many contributions to the development of this manuscript. Support for this project came from NASA grants NAGW-599 and NAG5-4174 and from Harvard University's Shaw Fund.

REFERENCES

Algeo, T. J., Berner, R. A., Maynard, J. B., and Scheckler, S. E., 1995, Late Devonian oceanic anoxic events and biotic crises: "Rooted" in the evolution of vascular land plants?: GSA Today, v. 5, p. 45, 64–66.

Andrews, A. J., Masliwec, A., Morris, W. A., Owsiacki, L., and York, D., 1986, The silver deposits at Cobalt and Gowganda, Ontario. II: An experiment in age determination employing radiometric and paleomagnetic measurements: Canadian Journal of Earth Sciences, v. 23, p. 1507–1518.

Arndt, N. T., Nelson, D. R., Compston, W., Trendall, A. F., and Thorne, A. M., 1991, The age of the Fortescue Group, Hamersley Basin, Western Australia, from ion microprobe zircon U-Pb results: Australian Journal of Earth Sciences, v. 38, p. 261–281.

Berner, R. A., and Canfield, D., 1989, A new model of atmospheric oxygen over Phanerozoic Time: American Journal of Science, v. 289, p. 333-361.

Boucot, A. J., Dewey, J. F., Dineley, D. L., Fletcher, R., Fyson, W. K., Griffin, J. G., Hickox, C. F., McKerrow, W. S., and Ziegler, A. M., 1974, The geology of the Arisaig area, Antigonish County, Nova Scotia: Geological Society of America, Special Publication 139, 191 p.

Bowring, S. A., Van Schmus, W. R., and Hoffman, P. F., 1984, U-Pb zircon ages from Athapuscow aulacogen, East Arm of Great Slave Lake, N.W.T., Canada: Canadian Journal of Earth Sciences, v. 21, p. 1315-1324.

Burger, A. J., and Coertze, F. J., 1974, Age determinations–April 1972 to March 1974: Geological Survey of South Africa Annals, v. 10, p. 135-141.

Button, A., 1979, Early Proterozoic weathering profile on the 2200 M.Y. old Hekpoort basalt, Pretoria Group, South Africa: preliminary results: Johannesburg, University of the Witswatersrand, Economic Geology Research Unit, Information Circular, 133, 19 p.

Button, A., and Tyler, N., 1981, The character and economic significance of Precambrian paleoweathering and erosion surfaces in Southern Africa: Economic Geology, 75th anniversary volume, p. 686–709.

Cheney, E. S., and de la R. Winter, H., 1995, The late Archean to Mesoproterozoic major unconformity-bounded units of the Kaapvaal Province of southern Africa: Precambrian Research, v. 74, p. 203–223.

Cheney, E. S., and Twist, D., 1991, The conformable emplacement of the Bushveld mafic rocks along a regional unconformity in the Transvaal succession of South Africa: Precambrian Research, v. 52, p. 115-132.

Chiarenzelli, J. R., ms, 1983, Mid-Proterozoic chemical weathering, regolith, and silcrete in the Thelon Basin, Northwest Territories: M.S. thesis, Carleton University, Canada.

Chown, E. H., and Caty, J.-L., 1983, Diagenesis of the Aphebian Mistassini regolith, Quebec, Canada: Precambrian Research, v. 19, p. 285–299.

Cornell, D. H., Armstrong, R. A., and Walraven, F., 1998, Geochronology of the Proterozoic Hartley Basalt Formation, South Africa: constraints on the Kheis tectonogenesis and the Kaapvaal Craton's earliest Wilson Cycle: Journal of African Earth Sciences, v. 26, p. 5–27.

Cornell, D. H., Schütte, S. S., and Eglington, B. L., 1996, The Ongeluk basaltic andesite formation in Griqualand West, South Africa: submarine alteration in a 2222 Ma Proterozoic sea: Precambrian Research, v. 79, p. 101–123.

Crampton, D., 1974, A note on the age of the Matsap Formation in the northern Cape Province: Transactions of the Geological Society of South Africa, v. 77, p. 71–72.

Fairbairn, H. W., Hurley, P. M., Card, K. D., and Knight, C. J., 1969, Correlation of radiometric ages of Nipissing diabase and Huronian metasediments with Proterozoic orogenic events in Ontario: Canadian Journal of Earth Sciences, v. 6, p. 489–497.

Falck, H., Donaldson, J. A., and Hall, L., 1991, Regolith beneath the Archean Jackson Lake Formation: its implications for Yellowknife Volcanic Belt stratigraphy, Slave Province, NWT: Geological Association of Canada–Mineralogical Association of Canada Abstracts with Programs, p. A35.

Feakes, C. R., Zbinden, E. A., and Holland, H. D., 1989, Ordovician paleosols at Arisaig, Nova Scotia, and the evolution of the atmosphere, in Bronger, A., and Catt, J. A., editors, Paleopedology: Nature and Application of Paleosols: Catena Supplement 16, p. 207-232.

Ferraz, M. F., ms, 1989, The nature of the Archean basement in the provenance areas of the East Rand and Evander Goldfields: M.S. thesis, University of the Witwatersrand, South Africa.

G-Farrow, C. E., and Mossman, D. J., 1988, Geology of Precambrian paleosols at the base of the Huronian Supergroup, Elliot Lake, Ontario, Canada: Precambrian Research, v. 42, p. 107–139.

Gall, Q., 1994, The Proterozoic Thelon paleosol, Northwest Territories, Canada: Precambrian Research, v. 68, p. 115–137.

Gall, Q., and Donaldson, J. A., 1990, The sub-Thelon Formation paleosol, Northwest Territories: Geological Survey of Canada, Current Research, Part C, Paper 90-1C, p. 271–277.

Gay, A. L., and Grandstaff, D. E., 1980, Chemistry and mineralogy of Precambrian paleosols at Elliot Lake, Ontario, Canada: Precambrian Research, v. 12, p. 349–373.

Goddard, C. E., ms, 1987, The geology of paleosols at the Archean-Lower Huronian unconformity, Elliot Lake, Ontario: B.S. thesis, Mount Allison University, Canada.

Golani, P. R., 1989, Sillimanite-corundum deposits of Sonapahar, Meghalaya, India: a metamorphosed Precambrian paleosol: Precambrian Research, v. 43, p. 175–189.

Grandstaff, D. E., Edelman, M. J., Foster, R. W., Zbinden, E., and Kimberley, M. M., 1986, Chemistry and mineralogy of Precambrian paleosols at the base of the Dominion and Pongola groups (Transvaal, South Africa): Precambrian Research, v. 32, p. 97–131.

Grotzinger, J. P., Adams, R. D., McCormick, D. S., and Myrow, P., 1989, Sequence stratigraphy, correlations between Wopmay Orogen and Kilohigok Basin, and further investigations of the Bear Creek Group (Goulburn Supergroup), District of Mackenzie, N.W.T.: Geological Survey of Canada, Current Research, Part C, Paper 89-1C, p. 107–119.

Hamblin, W. K., 1958, The Cambrian Sandstones of Northern Michigan: Lansing, Michigan, Michigan Geological Survey, Publication 51.

Hart, T. J., ms, 1986, A Petrographic and Geochemical Study of the 2.2 b.y. Hekpoort Paleosol at the Daspoort Tunnel, Pretoria, in the Republic of South Africa: Senior honors thesis, Harvard University.

Herd, R. K., Chandler, F. W., and Ermanovics, I. F., 1976, Weathering of Archean granitoid rocks, Island Lake, Manitoba: Geological Association of Canada–Mineralogical Association of Canada Abstracts with Programs, p. 72.

Hoffman, P. F., and Grotzinger, J. P., 1989, Abner/Denault reef complex (2.1 Ga), Labrador Trough, N.E. Québec, in Geldsetzer, H. H. J., James, N. P., and Tebbutt, G. E., editors, Reefs, Canada and Adjacent Area: Canadian Society of Petroleum Geologists Memoir 13, p. 49–54.

Holland, H. D., 1984, The Chemical Evolution of the Atmosphere and Oceans: Princeton Series in Geochemistry: Princeton, New Jersey, Princeton University Press, 582 p.

——— 1994, Early Proterozoic atmospheric change, in Bengtson, S., editor, Early Life on Earth: Nobel Symposium 84: New York, Columbia University Press, p. 237–244.

Holland, H. D., and Beukes, N. J., 1990, A paleoweathering profile from Griqualand West, South Africa: Evidence for a dramatic rise in atmospheric oxygen between 2.2 and 1.9 bybp: American Journal of Science, v. 290-A, p. 1–34.

Holland, H. D., Feakes, C. R., and Zbinden, E. A., 1989, The Flin Flon paleosol and the composition of the atmosphere 1.9 bybp: American Journal of Science, v. 289, p. 362–389.

Holland, H. D., and Rye, R., 1997, Evidence in pre-2.2 Ga paleosols for the early evolution of atmospheric oxygen and terrestrial biota: Comment: Geology, v. 25, p. 857–858.

Holland, H. D., and Zbinden, E. A., 1988, Paleosols and the evolution of the atmosphere: Part I, in Lerman, A., and Meybeck, M., editors, Physical and Chemical Weathering in Geochemical Cycles: Dordrecth, The Netherlands, Kluwer Academic Publishers, p. 61–82.

Kamineni, C. C., and Rao, A. T., 1988, Sapphirine granulites from the Kakanuru area, Eastern Ghats, India: American Mineralogist, v. 73, p. 692–700.

Karhu, J., and Holland, H. D., 1996, Carbon isotopes and the rise of atmospheric oxygen: Geology, v. 24, p. 867–870.

Kenrick, P., and Crane, P. R., 1997, The origin and early evolution of plants on land: Nature, v. 389, p. 33–39.

Kimberley, M. M., and Grandstaff, D. E., 1986, Profiles of elemental concentrations in Precambrian paleosols on basaltic and granitic parent materials: Precambrian Research, v. 32, p. 133–154.

Kirkham, R. V., and Roscoe, S. M., 1993, Atmospheric evolution and ore deposit formation: Resource Geology Special Issue, v. 15, p. 1–17.

Kohonen, J., and Marmo, J., 1992, Proterozoic lithostratigraphy and sedimentation of Sariola Jatuli-type rocks in the Nunnanlahti-Koli-Kaltimo area, eastern Finland; implications for regional basin evolution models: Bulletin of the Geological Survey of Finland, v. 364, p. 1–67.

Koryakin, A. S., 1971, Results of a study of Proterozoic weathering crusts in Karelia: International Geology Review, v. 13, p. 973–980.

Krogh, T. E., Davis, D. W., and Corfu, F., 1984, Precise U-Pb zircon and baddelyite ages for the Sudbury area, in Pye, E. G., Naldrett, A. J., and Giblin, P. E., editors, Geology and ore deposits of the Sudbury Structure: Ontario Geological Survey, Special Volume 1, p. 431–446.

Kulish, Y. A., Pokalyuk, V. V., and Reshetnyakov, V. V., 1987, Mineralogical-geochemical features of the upper Archean weathering profile in the Krivoy Rog region: International Geology Review, v. 29, p. 1327–1336.

LeCheminant, A. N., Ashton, K. E., Chiarenzelli, J., Donaldson, J. A., Best, M. A., Tella, S., and Thompson, D. L., 1983, Geology of Aberdeen Lake map area, district of Keewatin: Preliminary report: Geological Survey of Canada, Current Research, Part A, Paper 83-1A, p. 437–448.

Macfarlane, A. W., Danielson, A., and Holland, H. D., 1994, Geology and major and trace element chemistry of late Archean weathering profiles in the Fortescue Group, Western Australia: implications for atmospheric P_{O_2}: Precambrian Research, v. 65, p. 297–317.

Macfarlane, A. W., and Holland, H. D., 1991, The timing of alkali metasomatism in paleosols: Canadian Mineralogist, v. 29, p. 1043–1050.

Marmo, J. S., 1992, The lower Proterozoic Hokkalampi paleosol in North Karelia, Eastern Finland, in Schidlowski, M., Golubic, S., Kimberley, M. M., McKirdy, D. M., and Trudinger, P. A., editors, Early Organic Evolution: Implications for Mineral and Energy Resources: Berlin, Springer-Verlag, p. 41–66.

Martini, J. E. J., 1994, a Late Archaean-Paleoproterozoic (2.6 Ga) palaeosol on ultramafics in the Eastern Transvaal, South Africa: Precambrian Research, v. 67, p. 159–180.

Maynard, J. B., 1992, Chemistry of modern soils as a guide to interpreting Precambrian paleosols: Journal of Geology, v. 100, p. 279–289.

Maynard, J. B., Sutton, S. J., Robb, L. J., Ferraz, M. F., and Meyer, F. M., 1995, A paleosol developed on hydrothermally altered granite from the hinterland of the Witwatersrand Basin: characteristics of a source of basin fill: Journal of Geology, v. 103, p. 357–377.

Melezhik, V. A., Fallick, A. E., Makarikhin, V. V., and Lyubtsov, V. V., 1997, Links between Palaeoproterozoic palaeogeography and rise and decline of stromatolites: Fennoscandian Shield: Precambrian Research, v. 82, p. 311–348.

Mossman, D. J., and Farrow, C. E. G., 1992, Paleosol and ore-forming processes in the Elliot Lake District of Canada, in Schidlowski, M., Golubic, S., Kimberley, M. M., McKirdy, D. M., and Trudinger, P. A., editors, Early Organic Evolution: Implications for Mineral and Energy Resources: New York, Springer-Verlag, p. 67–75.

Ohmoto, H., 1996, Evidence in pre-2.2 Ga paleosols for the early evolution of the atmospheric oxygen and terrestrial biota: Geology, v. 24, p. 1135–1138.

——— 1997, Evidence in pre-2.2 Ga paleosols for the early evolution of atmospheric oxygen and terrestrial biota: Reply: Geology, v. 25, p. 857–858.

Palmer, J. A., Phillips, G. N., and McCarthy, T. S., 1989, Paleosols and their relevance to Precambrian atmospheric composition: Journal of Geology, v. 97, p. 77–92.

Pekkarinen, L. J., 1979, The Karelian formations and their depositional basement in the Kiihtelysvaara-Väntsilä area, east Finland: Bulletin of the Geological Survey of Finland, v. 301, p. 1–141.

Perttunen, V., 1991, Kemin, Karungin, Simon ja Runkaukse kartta-alueiden kallioperä. Pre-Quaternary rocks of the Kemi, Karunk, Simo and Runkaus map-sheet areas. Explanation to the maps of pre-Quaternary rocks, sheets 4541, 2542 + 4524, 2543 and 2544. Geological Map of Finland 1:100,000, 80 p.: Espoo, Geological Survey of Finland.

Pinto, J. P., and Holland, H. D., 1988, Paleosols and the evolution of the atmosphere, Part II., in Reinhardt, J., and Sigleo, W., editors, Paleosols and Weathering Through Geologic Time: Geological Society of America, Special Paper 216, p. 21–34.

Poujol, M., Robb, L. J., and Respaut, J. P., 1998, U-Pb and Pb-Pb isotopic studies relating to the origin of gold mineralization in the Evander Goldfield, Witwatersrand Basin, South Africa: Johannesburg, University of the Witwatersrand, Economic Geology Research Unit, Information Circular 320, 19 p.

Prasad, N., and Roscoe, S. M., 1991, Profiles of altered zones at ca. 2.45 Ga unconformities beneath Huronian strata, Elliot Lake, Ontario: evidence for early Aphebian weathering under anoxic conditions: Geological Survey of Canada, Current Research, Part C, Paper 91-1C, p. 43–54.

Purvis, A. C., 1984, Metamorphosed altered komatiites at Mount Martin, Western Australia–Archaean weathering products metamorphosed at the aluminosilicate triple point: Australian Journal of Earth Sciences, v. 31, p. 91–106.

Rainbird, R. H., Nesbitt, H. W., and Donaldson, J. A., 1990, Formation and diagenesis of a sub-Huronian saprolith. Comparison with a modern weathering profile: Journal of Geology, v. 98, p. 801–822.

Ramdohr, P., 1958a, Die Uran- und Goldlagerstätten Witwatersrand, Blind River District, Dominion Reef, Serra de Jacobina: Erzmikroskopische Untersuchungen und ein geologischer Vergleich: Abhandlungen der Deutschen Akademie der Wissenschaften zu Berlin Klasse für Chemie, Geologie und Biologie, Jahrgang 1958, no. 3, 35 p.

——— 1958b, New observations on the ores of the Witwatersrand in South Africa and their genetic significance: Geological Society of South Africa Transactions, v. 61, p. 1–50.

Rankama, K., 1955, Geologic evidence of chemical composition of the Precambrian atmosphere: Geological Society of America Special Paper, v. 62, p. 651–664.

Raven, J. A., 1995, The early evolution of land plants: aquatic ancestors and atmospheric interactions: Botanical Journal of Scotland, v. 47, p. 151–175.

Reczo, B. F. F., Oberholzer, J. D., Res, M., Erikkson, P. G., and Schreiber, U. M., 1995, A re-evaluation of the volcanism of the Palaeoproterozoic Pretoria Group (Kaapvaal craton) and a hypothesis on basin development: Journal of African Earth Sciences, v. 21, p. 505–519.

Retallack, G. J., 1986a, Reappraisal of a 2200 Ma-old paleosol near Waterval Onder, South Africa: Precambrian Research, v. 32, p. 195–232.

——— 1986b, The Fossil Record of Soils, in Wright, V. P., editor, Paleosols: Their Recognition and Interpretation: Princeton, New Jersey, Princeton University Press, p. 1–57.

——— 1990, Soils of the Past: London, Unwin Hyman, 520 p.

Retallack, G. J., and Krinsley, D. H., 1993, Metamorphic alteration of a Precambrian (2.2 Ga) paleosol from South Africa revealed by backscattered electron imaging: Precambrian Research, v. 63, p. 27–41.

Robb, L. J., Davis, D. W., and Kamo, S. L., 1990, U-Pb ages on single detrital zircon grains from the Witwatersrand Basin, South Africa: Constraints on the age of sedimentation and on the evolution of granites adjacent to the basin: Journal of Geology, v. 98, p. 311–328.

Robb, L. J., Davis, D. W., Kamo, S. L., and Meyer, F. M., 1992, Ages of altered granites adjoining the Witwatersrand Basin with implications for the origin of gold and uranium: Nature, v. 357, p. 677–680.

Robb, L. J., and Meyer, F. M., 1990, The nature of the Witwatersrand Hinterland: Conjectures on the source area problem: Economic Geology, v. 85, p. 511–536.

Ross, G. M., and Chiarenzelli, J. R., 1985, Paleoclimatic significance of widespread Proterozoic silcretes in the Bear and Churchill Provinces of the northwestern Canadian Shield: Journal of Sedimentary Petrology, v. 55, p. 196–204.

Rye, R., 1998, Highly negative $\delta^{13}C$ values in organic carbon in the Mt. Roe #2 paleosol: Terrestrial life at 2.765 Ga?: Mineralogical Magazine, v. 62A, p. 1308–1309.

Rye, R., Kuo, P. H., and Holland, H. D., 1995, Atmospheric carbon dioxide concentrations before 2.2 billion years ago: Nature, v. 378, p. 603–605.

Schau, M., and Henderson, J. B., 1983, Archean chemical weathering at three localities on the Canadian Shield: Precambrian Research, v. 20, p. 189–224.

Schidlowski, M., 1966, Beiträge zur Kenntnis der radioaktiven Bestandteile der Witwatersrand-Konglomerate: I. Uranpecherz in den Konglomeraten des Oranje-Freistaat-Goldfeldes: Neues Jahrbuch fuer Mineralogie. Abhandlungen, v. 105, p. 183–199.

Schweitzer, J. K., and Hatton, C. J., 1995, Chemical alteration within the volcanic roof rocks of the Bushveld Complex: Economic Geology, v. 90, p. 2218–2231.

Schweitzer, J. K., Hatton, C. J., and de Waal, S. A., 1995, Regional lithochemical stratigraphy of the Rooiberg Group, upper Transvaal Supergroup: A proposed new subdivision: South African Journal of Geology, v. 98, p. 245–255.

Sengupta, P., Dasgupta, S., Bhattacharya, P. K., Fukuoka, M., Chakraborti, S., and Bhowmick, S., 1990, Petro-tectonic imprints in the sapphirine granulites from Anantagiri, Eastern Ghats mobile belt, India: Journal of Petrology, v. 31, p. 971–996.

Sharma, R. P., 1979, Origin of the pyrophyllite-diaspore deposits of the Bundelkhand Complex, Central India: Mineralium Deposita, v. 14, p. 343–352.

Silvennoinen, A., 1972, On the stratigraphy and structural geology of the Rukatuntury area, northeastern Finland: Bulletin of the Geological Survey of Finland, v. 257, p. 1–48.

Smyth, W. R., 1976, Geology of the Mugford Group, Northern Labrador: St. John's, Newfoundland, Canada, Mineral Development Division, Report of Activities. 76-1, p. 72–79.

Stanworth, C. W., and Badham, J. P. N., 1984, Lower Proterozoic red beds, evaporites and secondary sedimentary uranium deposits from the East Arm, Great Slave Lake, Canada: Journal of the Geological Society of London, v. 141, p. 235–242.

Strand, K., 1988, Alluvial sedimentation and tectonic setting of the early Proterozoic Kurkikylä and Kainuu Groups in northern Finland: Geological Survey of Finland, Special Paper, v. 5, p. 75–90.

Sturt, B. A., Melezhik, V. A., and Ramsay, D. M., 1994, Early Proterozoic regolith at Pasvik, NE Norway: palaeoenvironmental implications for the Baltic Shield: Terra Nova, v. 6, p. 618–633.

Sutton, S. J., and Maynard, J. B., 1992, Multiple alteration events in the history of a sub-Huronian regolith at Lauzon Bay, Ontario: Canadian Journal of Earth Sciences, v. 29, p. 432–445.

Sutton, S. J., and Maynard, J. B., 1993, Sediment- and basalt-hosted regoliths in the Huronian supergroup: role of parent lithology in middle Precambrian weathering profiles: Canadian Journal of the Earth Sciences, v. 30, p. 60–76.

Valentine, K. W. G., and Dalrymple, J. B., 1976, Quaternary buried paleosols; a critical review: Quaternary Research, v. 6, p. 209–220.

Vogel, D. E., 1975, Precambrian weathering in acid metavolcanic rocks from the Superior Province, Villebon Township, South-Central Québec: Canadian Journal of Earth Sciences, v. 12, p. 2080–2085.

Wiggering, H., and Beukes, N. J., 1990, Petrography and geochemistry of a 2000–2200-Ma-old hematitic paleo-alteration profile on Ongeluk Basalt of the Transvaal Supergroup, Griqualand West, South Africa: Precambrian Research, v. 46, p. 241–258.

Wilks, M. E., and Nisbet, E. G., 1988, Stratigraphy of the Steep Rock Group, northwest Ontario: a major Archaean unconformity and Archaean stromatolites: Canadian Journal of Earth Sciences, v. 25, p. 370–391.

Worden, J. M., and Compston, W., 1973, A Rb-Sr isotopic study of weathering in the Mertondale granite, Western Australia: Geochimica et Cosmochimica Acta, v. 37, p. 2567–2576.

Zbinden, E. A., Holland, H. D., Feakes, C. R., and Dobos, S. K., 1988, The Sturgeon Falls paleosol and the composition of the atmosphere 1.1 Ga BP: Precambrian Research, v. 42, p. 141–163.