Evidence from Middle Ordovician paleosols for the predominance of alkaline groundwater at the dawn of land plant radiation

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ABSTRACT

Atmospheric carbon is estimated to have been ~500 times more abundant in Hadean time than at present, and its concentration has been gradually decreasing since then due to its storage in sedimentary rocks. Consequently, rain pH has been gradually increasing through geologic time, leading to the common assumption that groundwaters are less acidic today than they were in the distant past. However, this assumption overlooks the fact that root-forming land plants increase the carbonic acid concentration in soils by one or two orders of magnitude. In the absence of rooted land plants, reactions between minerals and rainwater are known to promote alkalinity. It is hypothesized that groundwater pH must have been, on average, highest shortly before the Late Ordovician to Silurian proliferation of root-forming land plants. To verify this hypothesis, we studied the mineralogy and geochemistry of the youngest known pre-Silurian paleosols to have developed on primary rocks, and provide evidence that they have evolved in predominantly alkaline groundwaters despite warm and humid paleoenvironmental conditions. Today, a lush vegetation cover would thrive in such a climate, and the system would be necessarily acidic due to large inputs of organic acids. Paired with previous observations indicating that early Paleozoic sedimentary rocks are especially rich in detrital illite and K-feldspar, there is now enough evidence to believe that there was a greater tendency for alkalinity during this time period than during previous and subsequent geologic periods.

INTRODUCTION

Because atmospheric carbon levels were especially high during the Hadean and the Early to Middle Archean, strongly acidic global weathering conditions are reported until 3.0 Ga (e.g., Sugitani et al., 1996). Continental growth during the Precambrian forced the gradual transfer of much carbon from the atmosphere to the lithosphere due to increasing rates of cation leaching from continental crust and the related increase in carbonate precipitation in the ocean (Kasting, 1993), which must have resulted in a decrease in rain acidity and a parallel increase in groundwater pH (vadose and phreatic). The latter may explain why paleosols became consistently enriched in K in Proterozoic time and generally remained so until the Silurian, when vascular land plants radiated over continental areas and subsequently promoted K leaching from soils due to the high solubility of this element in acidic solutions. Higher groundwater pH in Proterozoic to early Palaeozoic time may also explain why K-rich detrital illite is most abundant in marine mudrocks of that interval (Weaver, 1967).

Although the significant difference between the timing of pedogenesis and K enrichment in some pre-Silurian paleosols suggests that this enrichment occurred in, some cases, through metasomatic processes (MacFarlane and Holland, 1991), it should be pointed out that hydrothermal systems in continental crust involve deep groundwaters of meteoric origin, which are influenced by surface processes and by the burial of material derived from the surface. In Proterozoic time, buried continental sedimentary rocks would have been mostly devoid of organic material, possibly allowing deep groundwaters to maintain a higher pH than those of post-early Palaeozoic time.

The cold atmospheric conditions of ice house periods, which occur when atmospheric carbon levels (carbon dioxide and methane) become critically low (Kasting, 1993), do not promote the mineral-water reactions that lead to pH increase in groundwater (Schatz, 1963). Because solar luminosity increases with time, the Earth system needs less and less atmospheric carbon to prevent the development of ice house conditions (Kasting, 1993). It is therefore reasonable to think that atmospheric carbon levels at the eve of Late Ordovician glaciations (Saltzman and Young, 2005) were lower than during any previous nonglacial period. The Late Ordovician also roughly corresponds to the earliest introduction of root-forming land plants (Retallack, 2001), which radiated in Silurian time and which greatly influenced groundwater pH from then on through the release of organic acids. The pre-Silurian cover of lichen- and liverwort-like plants only affected the surface of the soils, and therefore had a very limited impact on groundwater chemistry compared to the deeper-reaching biomass of root-forming land plants. Moreover, it has been demonstrated that mineral-water reactions increase the pH of groundwater even in the presence of abundant acid-producing lichens (Schatz, 1963).

For the above-mentioned reasons, we argue that the period preceding Late Ordovician glaciations and the radiation of root-forming land plants should have been most prone to developing alkaline groundwater conditions. This hypothesis is supported by the observation that detrital K-feldspars are substantially more abundant in early Palaeozoic sandstones than in those of other periods (Basu, 1981), as the solubility of these minerals is greatly reduced in mildly alkaline solutions (Blum and Stillings, 1995).

Paleosols of the Dunn Point Formation (Feakes et al., 1989) of Nova Scotia, Canada (Fig. 1), occur within a succession of volcanic host rocks that yielded a ca. 460 Ma (Llandeilian to lower Caradocian) U/Pb zircon date (Hamilton and Murphy, 2004). They therefore evolved shortly before the radiation of early root-forming Late Ordovician plants and Silurian vascular plants. This makes them potentially useful in determining the paleoenvironmental conditions in which early life on land first developed, before these conditions were transformed by biological activity itself.

ANALYTICAL METHODS

Field measurements and sampling were done in the Dunn Point Formation localities of Arisaig and McGillivray Brook, Nova Scotia (Fig. 1). Samples were taken at irregular intervals within the four best developed weathering profiles and their host rocks. Chemical compositions were determined with X-ray fluorescence (XRF) for both major and trace elements (Table DR1 in the GSA Data Repository[1]). Bulk density values for strain calculations were obtained by measuring the weight and volume of precisely cut cubic samples (Table DR2). Finally, X-ray diffraction (XRD) and thin-section analyses were also performed on most samples (Table DR3).

FIELD RELATIONSHIPS

The lower portion of the Dunn Point Formation is not exposed, but paleosols separate at least six 2–5-m-thick basalt flows, and occur on top of one 70-m-thick banded rhyolite flow, which tops the volcanic lava succession below volcanoclastic rocks (Fig. 1). The basaltic host rocks are thoroughly albitized and chloritized in

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[1]GSA Data Repository item 2009020, Tables DR1–DR3, is available online at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

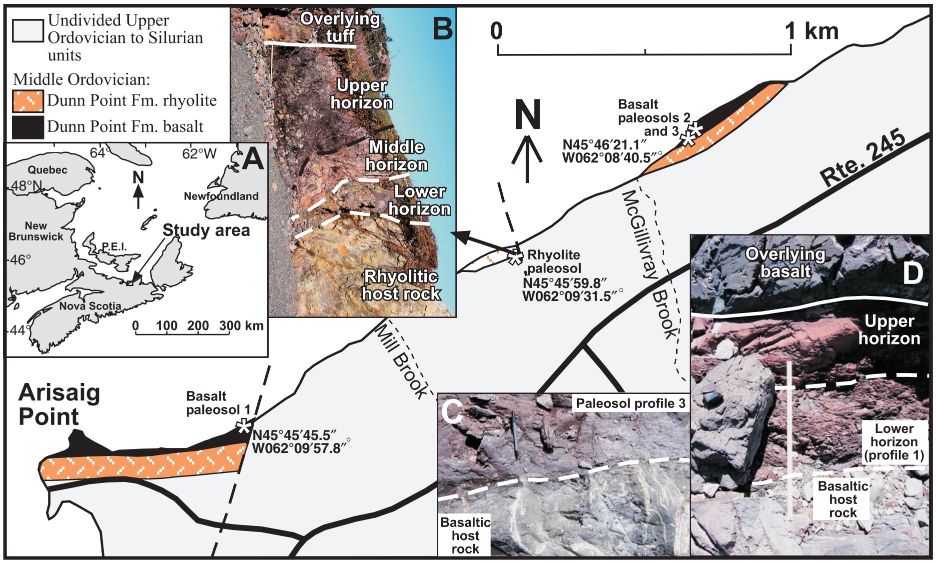

Figure 1. The Dunn Point Formation volcanics and associated weathering profiles in Arisaig, Nova Scotia, eastern Canada. A: General map. P.E.I.—Prince Edward Island. B: Weathering profile in rhyolite, rotated to the horizontal (meter stick for scale). C: Truncation of calcite veins by weathering (pen [~10 cm] for scale). D: Weathering profile in basalt paleosol 3 (meter stick for scale).

association with a dense network of calcite veins that is truncated by the weathering profiles, suggesting that alteration by hot fluids occurred prior to soil formation, during emplacement and cooling of the lavas (Fig. 1C).

The three best-developed basalt paleosols that were selected for this study are 1–2 m thick. They are characterized by a thoroughly oxidized upper horizon and a less oxidized lower horizon that partly preserved the greenish-gray color of the host rock (Fig. 1D). These well-developed paleosols with distinctive horizons contrast with the three profiles that were studied by Feakes et al. (1989) in the same region, which are more poorly developed.

The irregular weathering profile developed in rhyolite is over 8 m thick in some areas. The ~1-m-thick granular base of the rhyolite profile (green lower horizon) is strongly reduced below what we interpret as the paleo-redox line (Fig. 1B). The ~2 m reddish-brown middle horizon is also granular, but thoroughly oxidized. The ~5 m bright red upper horizon is massive, except for a granular uppermost 30 cm directly below the overlying felsic tuff.

MINERALOGY AND GEOCHEMISTRY

In the weathering profiles of both basaltic and rhyolitic host rocks, feldspar preservation is very low (0%–13% of the original host rock content; Fig. 2), which suggests penetrative chemical weathering in a warm and humid climate. Under such conditions, the observed accumulation of pedogenic calcite in the lower horizon of basalt paleosols 1 and 3 (Fig. 2; Table DR3) could not have occurred in an acidic solution.

The Dunn Point Formation paleosols described here were referred to as laterites by Boucot et al. (1974) and classified as Oxisols by Feakes et al. (1989). Analogy with modern Oxisols is based on the observation that the host rocks are deeply oxidized and chemically weathered, with little to none of their original mineralogy and textures remaining. However, whereas the upper horizons of modern Oxisols are systematically enriched in Ti, Al, and Fe, and correspondingly depleted in other major components, the upper horizons of the Dunn Point basalt paleosols are depleted in these elements, but enriched in K and Si, which are usually very mobile and therefore severely depleted in Oxisols (Fig. 2).

Mass gains and losses in Si, Al, Ti, Fe, K, Ca, and Na contents from host rock to paleosol were measured in relation to Zr (Fig. 3) by calculating the element-mass-transfer coefficient of Anderson et al. (2002; modified from Brimhall et al., 1992) to assess paleo-pH conditions. Although no element is truly immobile in tropical soils, laboratory experiments show that Zr is the least mobile and therefore the most appropriate element to use for assessing mobility in secondary environments (Hodson, 2002). Relative immobility of Zr in our samples is suggested by the lack of significant differences in Zr concentrations between the basalt paleosols and their host rock, and by nearly constant ratios of this element with other relatively insoluble high-field-strength elements, such as Nb (Fig. 2). In contrast, content ratios between Al, Fe, and Ti are not constant in any of the profiles (Figs. 2 and 3),

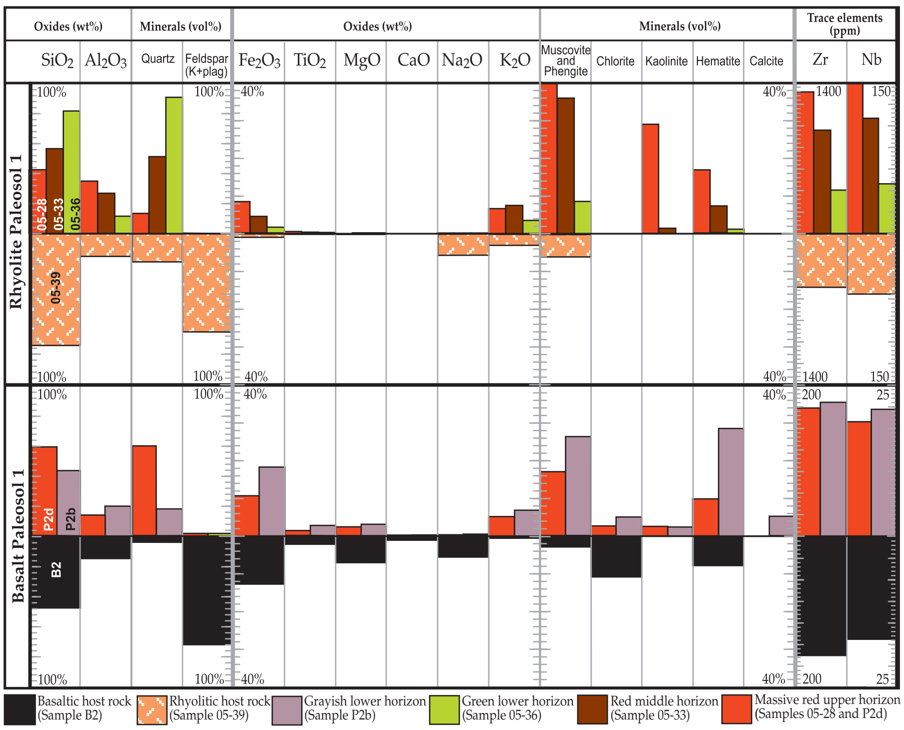

Figure 2. Mineralogical and geochemical contents in the Dunn Point Formation paleosols and host rocks from X-ray diffraction (vol%) and X-ray fluorescence (wt% for major oxides, and ppm for trace elements) data, respectively. Basalt paleosol 1 is used as a representative of the basalt paleosols, which all show very similar variations (Tables DR1 and DR3 [see text footnote 1]).

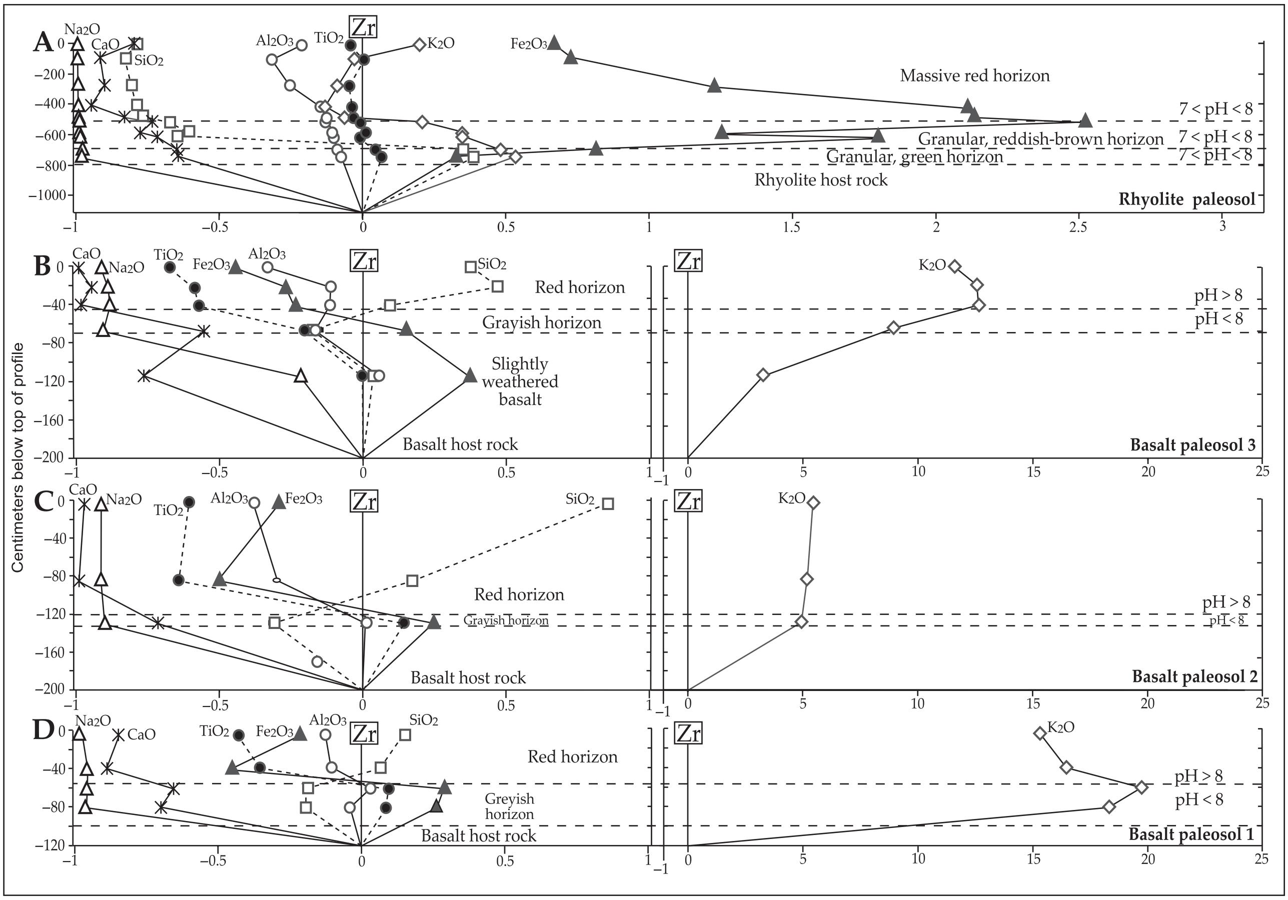

Figure 3. Vertical mass gains and losses in the Middle Ordovician Dunn Point Formation paleosols with respect to that of their host rocks. A: Rhyolite paleosol. B: Basalt paleosol 3. C: Basalt paleosol 2. D: Basalt paleosol 1. Based on the dimensionless element-mass-transfer coefficients of Anderson et al. (2002; modified from Brimhall et al., 1992), assuming Zr immobility.

suggesting that these elements showed different degrees of mobility during weathering.

Strain calculations (Brimhall et al., 1992) indicate that the basalt paleosols only experienced 1%–21% collapse, whereas the rhyolite paleosol experienced up to 71% collapse in its most deeply weathered upper horizon. This translates as a threefold increase in Zr and Nb concentrations from the host rhyolite to the overlying paleosol, in contrast with the relatively stable contents of these high-field-strength elements in the basalt paleosols, which seemingly underwent nearly isovolumetric weathering (Fig. 2).

Assuming Zr immobility, Ca and Na are strongly depleted throughout the four weathering profiles (Fig. 3), which again reflects penetrative chemical weathering and dominantly warm and humid conditions during pedogenesis. Silica is enriched in the upper part of the basalt paleosols, but depleted below, whereas Al, Fe, and Ti show the opposite pattern (Figs. 3B–3D). In contrast, Si is strongly depleted in the upper ~7 m of the rhyolite paleosol profile, and strongly enriched in the reduced lowermost horizon, whereas Al shows moderate depletion throughout the profile, and Ti shows moderate depletion in the upper horizon and moderate enrichment in the lower horizon (Fig. 3A). Such systematic patterns of eluviation and illuviation can be best explained by pedogenic processes.

Significant K enrichment in the thin lower and middle horizons of the rhyolite paleosol profile is paired with mild K leaching in the thick upper horizon, which is again best explained by pedogenic processes (Fig. 3A; note that K enrichment in Sample 05–27 from the uppermost 5 cm of the profile is interpreted to have been caused by contamination from the overlying tuff). In contrast, K is strongly enriched in the entire profile of each basalt paleosol, which suggests that other processes than pedogenetic mobilization must have been at work.

PALEOENVIRONMENTAL INTERPRETATIONS

In the rhyolite paleosol profile, K was surprisingly less mobile than Si and Al during pedogenesis, which is unlikely to occur in acidic conditions. On the other hand, greater mobility of Si than Al suggests that the soil pH was below 8 on average (Blatt et al., 1980). Mildly alkaline conditions are therefore inferred.

Although Si is less mobile than Al in both strongly acidic (pH < 4) and strongly alkaline (pH > 8) conditions (Blatt et al., 1980), the Si enrichment that is observed in the upper part of the basalt paleosol profiles is only possible by way of a concentration of the soil solution through evaporation, which promotes alkalinity. Replacement of Al by Si to form a siliceous duricrust is therefore interpreted as reflecting strongly alkaline conditions in the upper part of the basaltic soil profiles. Although the abundance of K in Proterozoic and early Palaeozoic paleosols suggests that neutral to mildly alkaline conditions may have been common throughout that time, the Dunn Point Formation paleosols are the only non-arid paleosols described in the literature that have been affected by the replacement of Al by Si, which necessitates strong alkalinity and which therefore corroborates with the hypothesis that Middle Ordovician time may have been especially prone to groundwater alkalinity.

Whereas soil water pH must have been, on average, above 8 in the upper horizon of the basalt paleosols to account for a greater mobility of Al than Si, it must have averaged below 8 in the lower horizon to account for an inversion of the Al-Si relationship at that level (Blatt et al., 1980; Figs 3B–3D). Higher pH in the upper part of the profile may be achieved by higher evaporation rates near the surface, which would have also contributed to generate Si saturation and precipitation.

The upward migration of Si in the basalt paleosol profiles is indicative of frequent and prolonged periods of soil saturation in this zone during pedogenesis, which can be explained by a combination of high precipitation rates and low infiltration rates in the relatively impermeable basaltic host rocks. This process would have been best achieved under a climate with concentrated seasonal precipitations that would have allowed Si to be mobilized toward the top of the saturated profiles, followed by extended periods that were moderately wet and dominated by evaporation, which would have allowed soil water pH to increase in the upper part of the profile. This inferred tendency for a high water table is consistent with the observation that the basalt flows were thoroughly albitized, chloritized, and veined following emplacement and preceding pedogenesis, suggesting that they were emplaced very close to or slightly above base jlevel. The shallow marine succession (Arisaig Group) that directly overlies the volcanic and volcanoclastic succession is also consistent with the hypothesis that the basalt flows may not have been emplaced on dry ground, although most of them were exposed to subaerial weathering shortly after emplacement.

Potassium enrichment in the basalt paleosols is unlikely to have occurred by a pedogenic concentration of the meager K contents of the basaltic host rocks. It is also unlikely to have occurred during deep burial, as mesodiagenetic compaction would have made these muddy paleosols quite impermeable, and veins are too scarce to justify substantial enrichments by post-compaction metasomatism. Hence, K enrichment in the basalt paleosols most likely occurred through the illitization of other types of pedogenic clays in shallow burial conditions, after a substantial source of K was provided to phreatic water by the emplacement of the thick overlying rhyolite. In contrast, the relative stability of K in the rhyolitic weathering profile (Fig. 3A) suggests that illite formation occurred during pedogenesis in this profile, using available K from the host material and keeping it in the system.

Deep burial of the succession under volcanoclastics and Silurian marine sediments probably largely contributed to the estimated threefold reduction of volume in the rhyolite paleosol, whereas Si enrichment made the basalt paleosol less compressible. It should also be noted that the lack of substantial volume strain in the basalt paleosols is further proof that the enforcement provided by Si enrichment occurred prior to burial. The pedogenic and eodiagenetic illite of all profiles converted to muscovite and phengite (Fig. 2; Table DR3) during deep burial and a subsequent regional event of low-grade metamorphism that occurred in Middle Devonian time in relation to the Acadian Orogeny (Hamilton and Murphy, 2004).

CONCLUSION

The Middle Ordovician Dunn Point Formation paleosols show an apparent dichotomy between penetrative chemical weathering, which suggests warm and humid conditions, and (1) the stability of K during the weathering of a rhyolitic host rock, (2) the stronger mobility of Al than Si during the weathering of basaltic host rocks, and (3) the accumulation of calcite in the latter, which suggest alkalinity and which could therefore not occur under such a climate in today's vegetated context. In the modern world, soil acidity is mainly controlled by organic activity, and hence, alkaline soils are now found only in settings that are too arid to support significant plant life. Because soil water involved in the weathering of these rocks was apparently able to maintain alkalinity even under a warm and humid climate, these thoroughly weathered Middle Ordovician soils developed pedogenic facies that have no modern equivalents. This ability of soils to develop alkalinity in the absence of land plants, even under humid conditions, implies that early land plants may have evolved in a predominantly alkaline world during the Ordovician and the Silurian, when atmospheric carbon was down to a fraction of its Precambrian levels, although their radiation subsequently led to a rapid lowering of global groundwater pH. This may explain why primitive land plants have an affinity for alkalis, a trait that should be taken into consideration in models of early land plant evolution.

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