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# Neoarchean paleoweathering of tonalite and metabasalt: Implications for reconstructions of 2.69 Ga early terrestrial ecosystems and paleoatmospheric chemistry

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ABSTRACT

Field and laboratory investigations of a 2690.83 Ma ($^{207}Pb/^{206}Pb$ age of Saganaga Tonalite) unconformity exposed in outcrop in northeastern Minnesota, USA, reveal evidence for development of a deep paleoweathering profile with geochemical biosignatures consistent with the presence of microbial communities and weakly oxygenated conditions. Weathering profiles are characterized by a 5–50 m thick regolith that consists of saprolitized Saganaga Tonalite and Paulson Lake succession basaltic metavolcanic rocks retaining rock structure, which is cross-cut by a major unconformity surface marking development of a successor basin infilled with alluvial deposits. The regolith and unconformity are overlain by thick conglomerate deposits that contain both intrabasinal (saprock) as well as extrabasinal detritus. Thin-section microscopy and electron microprobe analyses reveal extensive hydrolysis and sericitization of feldspars, exfoliation and chloritization of biotite, and weathering of Fe-Mg silicates and Cu-Fe sulfides; weathering of Fe-Ti oxides was relatively less intense than for other minerals and evidence was found for precipitation of Fe oxides. Geochemical analyses of the tonalite, assuming immobile $TiO_2$ during weathering ($\tau_{Ti,j}$), show depletion of $SiO_2$, $Al_2O_3$, $Na_2O$, CaO, MgO, and MnO, and to a lesser degree of $K_2O$, relative to least-weathered parent materials. Significant Fe was lost from the tonalite. A paleoatmospheric $pCO_2$ of 10–50 times PAL is estimated based on geochemical mass-balance of the tonalite profile and assuming a formation time of 50–500 Kyr. Interpretations of metabasalt paleoweathering are complicated by additions of sediment to the profile and extensive diagenetic carbonate (dolomite) overprinting. Patterns of release of P and Fe and retention of Y and Cu in tonalite are consistent with recent laboratory experiments of granite weathering, and with the presence of acidic conditions in the presence of organic ligands (produced, for example, by a primitive microbial community) during weathering. Cu metal in the profile may document lower $pO_2$ than present day at the surface. Comparison with previous studies of weathered tonalite and basalt (Denison, 2.45–2.22 Ga) in Ontario, Canada, reveal general similarities in paleoweathering with our study, as well as important differences related to lower paleoatmospheric $pO_2$ and terrestrial biosignature for the older Minnesota profile. A falling water table in the Alpine Lake locality is presumed to have promoted formation of this gossan-like deep-weathering system that extends to 50-m depth.

## 1. Introduction

Unconformable surfaces separating Precambrian crystalline basement and overlying Archean or Proterozoic sedimentary rocks provide an exceptional opportunity to examine the role of primitive soil ecosystems on weathering and formation of *saprolite* (rock that has weathered to the extent that it has lost most of its primary feldspar minerals but still retains its original rock structure), and

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**Table 1**
Sample location information for rocks examined in this study. See Fig. 3 map for locations of two sample suites.

| Sample # | UTM Coordinates (in NAD83) | Rock type | Depth Below or Above the Unconformity | Comments |
|---|---|---|---|---|
| G357H | (648292E/5333489N) | Ogishkemuncie Conglomerate | ~ 6 m above unconformity surface | See outcrop photographs Fig. 4A–C |
| G357G | (648300E/5333480N) | Ogishkemuncie Conglomerate | ~0.15 m above unconformity surface | Includes quartz-rich gruss, Fig. 4D |
| G756 age of 2690.83 ± 0.26 Ma [0.0097%] 95% conf. | (645542E/5330796N) | Med-crs grained, equigranular tonalite to granodiorite from Saganaga Tonalite taken about 210m east of unconformity with Ogishkemuncie | Age of unconformity surface | New weighted mean $^{207}$Pb/$^{206}$Pb age provided by Boise State University lab using double Pb – double U dilution spike |
| G357F | (648300E/5333480N) | Weathered Saganaga Tonalite | ~0.3 m below unconformity surface | Adjacent to clastic dike in well developed saprolite |
| G357E | (648302E/5333455N) | Weathered Saganaga Tonalite | ~18 m below unconformity surface | Approximately in the middle of saprolite zone |
| G357D | (648332E/5333444N) | Weathered Saganaga Tonalite | ~46 m below unconformity surface | First macroscopic appearance of saprolite in zones and irregular alteration pods |
| G357C | (648347E/5333462N) | Fresh Saganaga Tonalite | ~49 m below unconformity surface | Similar to G357A |
| G357B | (648354E/5333468N) | Fresh Saganaga Tonalite | ~52 m below unconformity surface | Similar to G357A |
| G357A | (648351E/5333445N) | Freshest Saganaga tonalite | ~55 m below unconformity surface | |
| G362C | (647985E/5332140N) | Weathered basalt/basal conglomerate-breccia | Approximately at the unconformity (0.0 m depth) | Very difficult to place where weathered basalt ends and sediment begins |
| G362B | (647985E/5332140N) | Moderately weathered metabasalt | ~4.6–6.1 m below unconformity surface | Displays a sort of "elephant skin" texture of weathering |
| G362A | (647985E/5332140N) | Freshest metabasalt | ~15 m below unconformity surface | |

*saprock* (rock that has started to weather but has not lost most of its primary feldspars; Graham et al., 2010). Both of these types of weathered material can comprise *regolith* (weathered rock overlying unaltered "parent rock"), but their use for such purposes has been questioned by many researchers because of common diagenetic and hydrothermal alteration associated with many of these surfaces (e.g., Morey, 1972; Duffin, 1989; Duffin et al., 1989; Nesbitt and Young, 1989; Rainbird et al., 1990; Maynard et al., 1995; Sutton and Maynard, 1996; Medaris et al., 2003). A common concern is whether diagenetic and metamorphic alteration overprints primary field, petrographic, and geochemical patterns related to subaerial exposure and paleoweathering, to the extent that primary paleoweathering features are not preserved. Potassium and sodium "metasomatism" of Precambrian paleosols has been previously discussed by Nesbitt and Young (1989), Palmer et al. (1989), Maynard (1992), Nesbitt (1992), and was revisited most recently by Nedachi et al. (2005) in their re-evaluation of the 2.45 Ga Pronto paleosol from Ontario, Canada, which was first reported by Gay and Grandstaff (1980) and is apparently the oldest reported paleoweathering profile formed on granitic parent material, and by Mitchell and Sheldon (2009) who discussed metasomatism in paleosols with mixed basalt-rhyolite parent material. The preceding authors have proposed a variety of field, petrographic and geochemical criteria (typically based on whole-rock analyses) for screening primary vs. altered paleosols, many of which are summarized in Retallack (1991) and Rye and Holland (1998).

Driese et al. (2007) proposed using detailed petrographic studies of purported weathered granitic rocks and overlying sedimentary cover rocks, and geochemical mass-balance applied to whole-rock samples, as two additional criteria with which to determine if alteration has occurred. They demonstrated for sub-Cambrian and Neoproterozoic granite paleoweathering profiles in North America that, in spite of the prevalence of diagenetic and hydrothermal alteration, most paleoweathering profiles formed on granitic basement can still provide important evidence for primitive terrestrial conditions, and are remarkably similar to modern weathering profiles. In a related study, Driese and Medaris (2008) examined a 1.7 Ga sub-Baraboo Quartzite paleoweathering profile formed on granite from Wisconsin and demonstrated that, even in spite of extensive potassium alteration, evidence for biological and hydrological controls on paleoweathering was still interpretable from both petrographic and geochemical investigations.

Recent work by Brantley and co-workers indicates that patterns of mobility of trace elements and rare-earth elements in paleoweathering profiles can be used as *biosignatures*, i.e., as indicators of a terrestrial biomass contributing organic compounds that enhanced mineral weathering (Neaman et al., 2005a,b, 2006; Hausrath et al., 2009). Their experiments involved laboratory weathering of basalt and granite, with and without simple organic compounds to serve as ligands for chelation of metals; their experiments were also conducted both in the presence and absence of significant $O_2$ in order to simulate a range of possible paleoatmospheric conditions. Their results indicated that there are specific suites of trace elements and rare-earth elements, and even some major elements, whose mobility (release) is enhanced by the presence of organic compounds, especially aliphatic ligands such as citrate, oxalate and malonate (Neaman et al., 2006; Hausrath et al., 2009). These organic compounds are commonly associated with microbial mats and simple soil microbiota. Graham et al. (2010) have shown that as crystalline rock converts to corestones, saprock and soil during weathering, significant porosity (both micro- and mesofractures) develops that can both store and conduct water, thus creating hospitable substrates for terrestrial ecosystems, with mycorrhizal hyphae that extend into microfractures and exude organic compounds. In fact, Buss et al. (2005) reported that a bacterial ecosystem grows to relatively high cell densities at about 5 m depth on weathering quartz diorite in the Puerto Rican rain forest. Brantley (2010) also pointed out the importance of pore formation for increasing the surface area of minerals in contact with soil water, thus potentially enhancing rock weathering. Whereas many of these fine-scale structures are unlikely to be preserved in