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GR Focus Review

Secular changes at the Earth's surface; evidence from palaeosols, some sedimentary rocks, and palaeoclimatic perturbations of the Proterozoic Eon

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A R T I C L E I N F O

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A B S T R A C T

Secular changes in surficial processes and products are closely linked to plate tectonics, atmospheric composition, solar evolution and climate. Most siliciclastic sediments and rocks are derived from weathering profiles rather than directly from older rocks. Many palaeosols older than ~2.2 Ga show depletion in $Fe_{(T)}$, whereas in younger palaeosols, and modern soils, Fe is virtually immobile. This is thought to reflect the accumulation of free oxygen in the Earth's atmosphere, as is the 'disappearance' of iron formations after about 1.8 Ga. The temporal distribution of mature siliciclastic sedimentary rocks containing detrital pyrite and uraninite, and the subsequent appearance of fluvial and shallow marine red beds provide compelling evidence for oxygenation in early Palaeoproterozoic times. During periods of supercontinentality, especially at low palaeolatitudes, enhanced weathering of exposed rock surfaces led to production of thick, extensive quartzarenites, some of which are associated with glaciogenic rocks. Intense weathering during periods of supercontinentality would have decreased atmospheric CO_2, leading to extensive glaciations near the beginning and end of the Proterozoic Eon, and initiating a feedback loop that resulted in strong climatic oscillations until continental break-up brought stability to the climatic regime. It has been proposed that atmospheric oxygenation took place during warm climatic episodes between these glaciations when abundant nutrients were flushed into the oceans, stimulating unprecedented cyanobacterial blooms. Although many other supercontinents have been proposed, these unusual climatic conditions probably reflect rare critical relationships among solar luminosity, atmospheric composition and palaeolatitudinal distribution of continental lithosphere. Reappearance of iron formations associated with some Neoproterozoic glaciations may be explained by hydrothermal activity in semi-isolated rift basins.

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1. Introduction

Sedimentary rocks and their common progenitors, palaeosols, are surficial products that carry important information regarding the nature and evolution of the Earth's atmosphere. It is therefore appropriate to begin with a brief discussion of commonly held views about the nature of the early atmosphere and how it may have changed throughout geological time. Most ideas about the Hadean Earth are speculative because there are no known Hadean rocks on the planet. The Archaean–Hadean boundary was considered to be at 3.83–3.82 Ga by Moorbath (2005), about 30–40 Ma after the Late Heavy Bombardment. The Hadean encompasses the time period from about 4.56 Ga to 3.83 Ga, so that the first half billion years of Earth history is not represented in the planet's geological record. The surface of the early Hadean Earth was probably hot as a result of accretion and the abundance of radioactive elements, although this has become a contentious issue, following discovery of 4.2 Ga zircons in sandstones at Jack Hills in Western Australia. Geochemical investigation of these zircons has led to the suggestion (e.g. Watson and Harrison, 2005) that the Earth may have had surface water as early as 4.3 Ga and that plate tectonics and cycles of erosion and deposition took place much earlier than was previously thought to be the case. These interpretations are controversial and have been discussed in the literature (e.g. Moorbath, 2005 and references therein).

The nature of the first atmosphere is unknown (mostly H_2 and He?) for its remnants were probably lost to space during the Late Heavy Bombardment (~4.1–3.8 Ga). Because of the Earth's relatively weak gravitational pull, light gases tend to be lost, but with separation of the dense metallic core and development of a magnetic field, the planet achieved protection from the solar wind, which may have stripped other planets, such as Mars, of most of their atmospheres. The first atmosphere probably had little in common with the present one, which is mostly nitrogen but has a surprisingly high content of the highly reactive gas, oxygen (21% by volume). It is widely believed that the second atmosphere originated largely by degassing of the Earth's interior so that the major components most likely resembled those emanating from volcanoes today (H_2O, CO_2, SO_2, CO, S_2, Cl_2, N_2, H_2, NH_3 and CH_4). Noteworthy in this list is the absence of free oxygen so that it seems highly probable that the early atmosphere was anoxic. Free oxygen is believed to have been introduced to the atmosphere as a result of solar energy, either by photo-dissociation of water or (more importantly) as a by-product of the photosynthetic life style adopted by many micro-organisms, notably cyanobacteria. The importance of oxygen cannot be over-emphasised for it played a crucial role in the evolution of life, both in the opening up of new highly efficient metabolic pathways and in making possible the colonisation of shallow waters and land surfaces by development of the ozone layer which provides protection from harmful UV radiation. The appearance and growth of the ozone layer may also have encouraged many organisms (e.g. early armoured fishes, and cephalopods) to shed their protective exoskeletons (Fischer, 1965).

Less certain than any of these speculations is the question of timing of oxygenation of the atmosphere. Because of the largely qualitative nature of geology, most ideas are hotly debated and the history of oxygenation of Earth's atmosphere is no exception. Almost all of the lines of evidence (and conclusions drawn from there) outlined in this contribution have proponents and opponents. In this paper evidence from palaeosols and certain sedimentary rocks is used in an attempt to elucidate some aspects of secular change near the surface of the Earth.

Early proponents of an anoxygenic Archaean atmosphere include Cloud (1968, 1973, 1976); Roscoe (1969) and Holland (1973). An important early paper that cited *geological* evidence for atmospheric change was published by Roscoe (1973). Based on investigation of rocks of the Palaeoproterozoic Huronian Supergroup (2.45–2.2 Ga), Roscoe suggested that there was a change in the atmosphere during deposition of the thick (up to ~12 km) Huronian succession. He suggested the name, "oxyatmoversion" for this putative change. His interpretation was based on several lines of evidence, including:

a. The presence of what were interpreted to be clastic grains of pyrite and uraninite in mineralogically mature quartz–pebble conglomerates and sandstones near the base of the Huronian Supergroup.
b. Unusual palaeosols developed on Archaean basement rocks beneath the Huronian lack the concentration of iron (especially ferric iron) commonly seen in modern weathering profiles.
c. The drab (green and grey) colours of fluvial deposits in the lower part of the Huronian succession, in contrast to red and purple hues, due to finely disseminated hematite, in similar rocks in the upper part of the supergroup.

These important observations were strengthened by reports of similar occurrences in other continents but over the succeeding forty years their interpretation has sparked considerable debate (e.g. Dimroth and Kimberley, 1976; Clemmey and Badham, 1982; Holland, 1999).

2. Palaeosols

Palaeosols are considered to be ancient weathering profiles, although there is a significant difference in the conditions under which older (pre-Devonian) examples and younger ones formed; namely the absence of a plant cover during formation of the older ones. A plant cover can add organic acids that may accelerate rates of chemical weathering. Plant roots also tend to stabilise the soil and make it less susceptible to erosion.

It is generally easier to identify modern soils than ancient alteration profiles (palaeosols) for, in addition to weathering processes, ancient profiles may be the result of metasomatic or metamorphic processes, guided in some cases by unconformities or faults. In addition, true weathering profiles have commonly been altered in a manner that makes them difficult to identify (Nesbitt and Young, 1989; Retallack, 1991; Fedo et al., 1995; Driese et al., 2007). Weathering profiles signify a period of exposure to the atmosphere. They represent unconformities of variable magnitude and are most confidently identified at contacts between basement rocks of crystalline aspect and sedimentary cover rocks, but they commonly occur within sedimentary sequences that have been periodically exposed to the atmosphere.

Palaeosols have received much study. Previous reviews of palaeosols include those of Gall (1999), Retallack (2001) and Sheldon and Tabor (2009). Geochemical techniques developed by Nesbitt and Young (1982, 1984, 1989), Nesbitt and Wilson (1992), and Fedo et al. (1995) have been used in an attempt to quantify the weathering process and gain insight into some aspects of palaeoclimatology. Several authors have noted that palaeosols can provide evidence regarding conditions at the surface of the Earth — particularly the oxygen content of the atmosphere (Macfarlane et al., 1994; Rye and Holland, 1998; Murakami et al., 2001; Yang and Holland, 2003). In the following section, 426 published analyses from weathering profiles developed on mafic igneous rocks are used to compare palaeosols and soil profiles ranging in age from Archaean (>2.5 Ga) to recent. The analyses were divided into three age groups; those that are forming at the present day, those between about 1.1 Ga and 1.7 Ga, and profiles older than ~2.2 Ga. These subdivisions were chosen in order to make comparisons between recent and ancient weathering profiles and, in particular, to compare some aspects of the major element chemistry of profiles that developed before and after the time of the supposed 'oxyatmoversion' (Roscoe, 1973) or 'Great Oxidation Event' of Karhu and Holland (1996), loosely dated at about 2.2 Ga.

Values for the Chemical Index of Alteration (CIA), introduced by Nesbitt and Young (1982, 1984, 1989) reflect the proportion of secondary aluminous minerals relative to primary minerals such as feldspars. The CIA is calculated as follows:

$$CIA = \left[Al_2O_3/\left(Al_2O_3 + CaO^* + Na_2O + K_2O\right)\right] \times 100$$