Variations in the abundance of photosynthetic oxygen through Precambrian and Paleozoic time in relation to biotic evolution and mass extinctions: evidence from Mn/Fe ratios

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ABSTRACT

This paper reports new information about variations in the abundance of photosynthetic oxygen through Precambrian and Paleozoic time. Non-detrital marine sediments (cherts, limestones, and dolomite) were analysed for $\text{NH}_2\text{OH}\cdot\text{HCl}$ /acetic acid-extractable Mn and Fe, and the Mn/Fe ratio (a proxy for the oxidation-reduction potential of the sediment at the time of deposition) was plotted against geologic age. The method has never before been applied to ancient sediments, but previously published data produced independently by other methods confirmed its applicability and underlying assumptions. The Mn/Fe ratio was unexpectedly high ca. 3.416 Ga, implying localised oxidation due to oxygen production by cyanobacteria, but fell dramatically over the interval 3.416-3.298 Ga, suggesting mass mortality or mass extinction of early Archean cyanobacteria owing to asteroid impacts. However, the ratio increased continuously, though at episodically varying rates, from a minimum at ~1.8783 Ga to a maximum at ~0.680 Ga, signifying accumulation of oxygen in the atmosphere and hydrosphere. The rate of increase was relatively high at first but dropped abruptly at some point during the interval 1.8783-1.6 Ga, possibly signaling the appearance of eukaryotic herbivores. The ratio increased exponentially from 1.6 to 0.8 Ga and then rose more rapidly from 0.8 to 0.680 Ga, indicating a late Proterozoic upsurge of oxygen production, whereupon it fell catastrophically to a minimum in the Cambrian, reflecting widespread anoxia due to mass extinction of Ediacaran organisms. The crisis at the Precambrian-Cambrian boundary was followed by a logarithmic increase from the Cambrian to the Permian, indicating a resurgence of photosynthetic activity.

1. Introduction

There is general agreement among geologists that the Earth's atmosphere was originally devoid of oxygen (O_2) except for trace quantities generated by photodissociation of water, that it owes its present abundance of O_2 to photosynthesis, and that the earliest O_2 -generating photosynthetic organisms were cyanobacteria (Cloud, 1976; Schidlowski, 1983; Pavlov and Kasting, 2002; Bekker et al., 2004; Fike et al., 2006; Holland, 2006; Kaufman et al., 2007; Buick, 2008; Kump et al., 2011; Lyons et al., 2014). It is not known for certain when the cyanobacteria originated, but there is indirect evidence consistent with the possibility that they were in existence as long ago as 3.8 Ga (i.e. 3.8×10^9 years before the present) – at the beginning of the Archean aeon, when the earliest Precambrian sediments were laid down. The oldest microfossils that are reportedly identifiable with confidence as remains of cyanobacteria date back to ca. 2.5-2.7 Ga (i.e. the late Archean) (Altermann and Kazmierczak, 2003), and microscopic structures tentatively regarded as fossil cyanobacteria have been detected in sediments laid down ca. 3.5 Ga (Altermann and Kazmierczak, 2003; Schopf, 2006). The presumptive biological origin of the 3.5×10^9 year old structures has been questioned (Brasier et al., 2006); but geochemical evidence suggests that they are genuine fossil bacteria, and the occurrence of stromatolites formed ca. 3.5 Ga also constitutes a reasonable basis for inferring that microbial mats made up of cyanobacteria and other prokaryotes were in existence at least that long ago (Altermann and Kazmierczak, 2003; Komiya et al., 2008). Finally, there is a body of geochemical evidence, including stable isotope ratios of carbon in carbonaceous material and the occurrence of a banded iron formation, which implies that cyanobacteria were in existence as long ago as 3.8 Ga (Cloud, 1976; Dymek and Klein, 1988; Rosing, 1999; Katz et al., 2004; Buick, 2008).

However, the O_2 produced by cyanobacteria in the earlier phases of the Precambrian was scavenged by reducing agents, notably Fe(II), in the hydrosphere (hence the widespread deposition of vast quantities of the uniquely Precambrian BIFs) (Cloud, 1976; Schidlowski, 1983) and did not start accumulating in the atmosphere until ~2.5-2.3 Ga (in the early Proterozoic) (Bekker et al., 2004; Holland, 2006; Kaufman et al., 2007; Buick, 2008; Canfield et al., 2013; Lyons et al., 2014; Planavsky et al., 2014), or possibly as early as ~2.95 Ga (Planavsky et al., 2014). Oxygenation of the atmosphere and hydrosphere, in turn, fostered the evolution of eukaryotes, leading eventually to the rise of metazoans (Margulis et al., 1976). Yet O_2 levels in the atmosphere

and hydrosphere are thought to have increased in stages or episodes characterised by different net rates of increase rather than at a constant rate (Fike et al., 2006; Holland, 2006; Canfield et al., 2013; Lyons et al., 2014). These variations included fluctuations ca. 2.3-2.0 Ga owing to episodes of enhanced primary production and subsequent decomposition of organic matter known as the Lomagundi (or Lomagundi-Jatulian) and Shunga events (Medvedev et al., 2009; Canfield et al., 2013; Strauss et al., 2013). The initial upsurge in O₂ levels starting ca. 2.5-2.3 Ga and the subsequent fluctuations were reportedly followed by a long mid-Proterozoic interval (ca. 1.85-0.85 Ga) in which there was no significant change in O₂ levels over time, and this this period of supposed stasis was followed by a renewed upsurge in the late Proterozoic ca. 0.85 Ga (Fike et al., 2006; Holland, 2006; Lyons et al., 2014). There is also evidence of a sharp decrease, leading to worldwide anoxia in ocean waters, associated with mass extinction of Ediacaran organisms at the end of the Precambrian (Hsu et al., 1985; Logan et al., 1995; Amthor et al., 2003; Schröder and Grotzinger, 2007; Wille et al., 2008; Laflamme et al., 2013), although some members of the Ediacaran biota appear to have survived until the Cambrian (Glaessner, 1984; Hagadorn et al., 2000; Kimura and Watanabe, 2014).

The purpose of the present study was to acquire new information about temporal variations in the O₂ content of the atmosphere and oceans and related aspects of biological evolution in the Precambrian and Paleozoic by analysing non-detrital marine sediments ranging in age from early Archean to Permian for a geochemical parameter – the manganese/iron (Mn/Fe) ratio of the sediment's oxide (or oxyhydroxide) fraction – which served as a proxy for the oxidation-reduction potential (Eh) of the sediment at the time of deposition and was, therefore, assumed to vary with the O₂ concentration in the overlying seawater. The Mn/Fe ratios of Recent sediments, or solvent-extractable oxides in the sediments, tend to increase with the Eh values of the sediments (Kjensmo, 1968; Engstrom and Wright, 1984; Jackson, 1988; Jackson and Bistricki, 1995; Jackson et al., 2013), and basic geochemical principles provide grounds for supposing that this generalisation is applicable to ancient sedimentary rocks as well (Lepp, 1963; Degens, 1965; Mason, 1966). The reason for the correlation between the Mn/Fe ratio and the Eh is that Fe oxide is precipitated at lower Eh values and dissolved O₂ concentrations than Mn oxide at any given pH. Hence, the more highly oxidising the environment of deposition, the higher the Mn/Fe ratio of the oxide fraction of a sedimentary rock would be expected to

be, on the simplifying assumption that the ambient pH at the time of deposition did not vary greatly either spatially or temporally – a reasonable assumption for seawater, whose pH values were probably confined to a range of ~6.5-8.1 (i.e. circumneutral to mildly alkaline) from the Archean to the present time (Grotzinger and Kasting, 1993; Krupp et al., 1994; Arvidson et al., 2013).

2. Materials and methods

The samples comprised a collection of non-detrital sedimentary rocks (limestones, dolomite, and carbonate-bearing cherts) of marine origin ranging in age from early Precambrian to late Paleozoic and representing formations located in many different parts of the world (Table 1). (Fine-grained detrital sediments (shales, mudstones, and argillites) were also analysed (Jackson, T.A., unpublished data) but were found to be unsuitable for this investigation, presumably because such sediments commonly have anoxic or reducing environments regardless of whether the overlying water and atmosphere are enriched in O₂.) The samples had previously been used for research on major events and trends in biotic evolution – Precambrian evolution in particular – as represented by variations in quantifiable properties of extractable and non-extractable organic constituents and illite through geologic time (Jackson, 1973, 1975, 1977; Jackson and Moore, 1976; Jackson et al., 1978).

The weathered surfaces of the specimens were removed, and the fresh rock was broken or sawed into pieces ~1 cc in size, pulverised in a tungsten carbide disc mill (Spex “Shatterbox”), and analysed for readily reducible Mn and Fe oxides using the method of Tessier et al. (1979), which involves extraction of sediment samples with an aqueous solution of hydroxylamine hydrochloride acidified with acetic acid. A similar technique employing HNO₃ instead of acetic acid (Chao, 1972; Gupta and Chen, 1975) has also been used for analyses of this kind.

The analytical procedure was as follows. Approximately 2.0000 gram portions of the powdered rock samples were weighed out, transferred to 50 mL centrifuge tubes, and pretreated with hot concentrated acetic acid added one drop at a time until there was no visible effervescence in order to dissolve the carbonate minerals. Thereupon the readily reducible Mn and Fe were extracted by suspending each sample in a 20 mL aliquot of a 0.04 M hydroxylamine hydrochloride (NH₂OH·HCl) solution in 25% (v/v) acetic acid and incubating the mixture in a hot water bath at 96-100°C for ~6 hours with occasional agitation to ensure uniform mixing. The

extract was then cooled to room temperature and centrifuged, and the clear supernatant solution was transferred by Pasteur pipette to a 100 mL volumetric flask. The residue was rinsed with 25% acetic acid and centrifuged, the supernatant solution was added to the original extract, and the extract was made up to a final volume of 100 mL with 25% acetic acid. The extract was analysed for total Mn and Fe with a Perkin Elmer 2380 atomic absorption spectrophotometer employing an air/acetylene flame, and the Mn/Fe ratio was calculated. All sample dilutions and calibration standard solutions were made up to 25% acetic acid, and the Mn and Fe concentrations were calculated as mass of element per unit weight of the rock. Selected rock samples were analysed in duplicate to check the precision of the method.

The hypothetical possibility that the proportions of Mn and Fe depended to a significant extent on the abundance of organic matter in the sediment – in particular, humic matter, which could have played a part in the transport of Mn and Fe to the basin of deposition (Engstrom and Wright, 1984) – was checked by plotting the Mn/Fe ratios and the Mn and Fe concentrations separately against the previously published total organic C concentrations, which represent the kerogen in the sediments (Jackson and Moore, 1976). In general, kerogen (non-extractable organic matter) accounts for > 95% of the organic C in sedimentary rocks and is thought to consist primarily of diagenetically altered humic matter (Degens, 1965).

The Mn/Fe ratio was plotted against the geologic age of the sample expressed in Ga units (10^9 years before the present), and the observed variations were interpreted as representing variations in the abundance of photosynthetic O_2 in the overlying water and atmosphere at the time of deposition. Until now the use of this parameter has been limited to Recent sediments and soils, but the assumption that it is applicable to ancient sediments is consistent with well known, long established facts about the geochemistry of Mn and Fe (Degens, 1965; Mason, 1966) and is supported by the discovery that the Mn/Fe ratio of Precambrian BIF correlates with the degree of oxidation of the Fe as represented by the proportion of Fe_2O_3 to Fe_3O_4 (Lepp, 1963).

3. Results and discussion

The Mn/Fe ratios showed a complex but systematic pattern of decreases and increases through geologic time (Fig. 1; Table 1), suggesting a series of events and trends in global atmospheric and biotic evolution. These

variations reveal significant new information and provide a basis for new insights; yet several major features of the observed pattern of variation are in remarkably good agreement with postulated temporal variations in the abundance of atmospheric O₂ which have been reported independently elsewhere by others on the basis of other kinds of evidence (see below). This corroboration has three important implications: [1] It validates the premise that the Mn/Fe ratio is a function of the sediment Eh and the O₂ concentration of the overlying water at the time of deposition; [2] it implies that the signatures of the original Eh values of the sediments have not been masked, obliterated, or significantly distorted by diagenesis; and [3] it verifies the assumption that cherts and carbonate rocks can legitimately be treated as a single population of samples (cf. Jackson, 1973, 1975; Jackson and Moore, 1976; Jackson et al., 1978). Another important generalisation which emerged from the data is the fact that samples from widely separated geographical locations yielded a single coherent pattern of variation, implying that the observed effects were of worldwide extent. Furthermore, the Mn/Fe ratio does not correlate significantly with the total organic C concentration in the sediment ($r = 0.403$; $P > 0.1$), nor does the Mn concentration ($r = 0.509$; $P > 0.05$, < 0.1) or the Fe concentration ($r = 0.424$; $P > 0.1$) alone [not shown; see the Mn and Fe data and Mn/Fe ratios in Table 1 and the total organic C data of Jackson and Moore (1976)]. This appears to rule out the hypothetical possibility that organic matter affected the Mn/Fe ratios to a significant degree. It should also be noted that the standard error for samples analysed in duplicate was invariably 1-2 orders of magnitude lower than the mean, demonstrating that the precision of the analytical method was highly satisfactory (Table 1).

The major features of the plot shown in Fig. 1 may be described and interpreted as follows:

1. The Mn/Fe ratio was higher than might be expected in the early Archean (ca. 3.416 Ga), probably owing to localised oxidation of reduced aqueous Fe and Mn species by photosynthetic O₂ generated by cyanobacteria, a process that was presumably confined to microenvironments in the immediate vicinity of the organisms and did not involve escape of O₂ into the atmosphere (Cloud, 1976; Schidlowski, 1983; Pavlov and Kasting, 2002). However, the ratio dropped abruptly to a much lower value over the relatively brief interval 3.416-3.298 Ga. Ostensibly it continued to decline, but at a lower rate, until 1.8783 Ga, although its actual trajectory within the interval 3.298-1.8783 Ga is unknown owing to the total absence of samples in that age range. The dramatic decrease from 3.416 to 3.298 Ga, which is in

agreement with total Mn and Fe data published previously by Dungworth and Schwartz (1974), was accompanied by pronounced changes in the properties of the organic matter in the sediments (Nagy and Nagy, 1969; Jackson, 1973, 1975; Jackson et al., 1978), suggesting a major change in the nature of the biota. These results are consistent with mass extinction (or, at the very least, mass mortality) of the dominant early Archean cyanobacterial species owing to a series of asteroid impacts which occurred during the Archean and early Proterozoic, including the period 3.4-2.0 Ga (Gogarten-Boekels et al., 1995; Koeberl, 2006; Bottke et al., 2012). Furthermore, it is important to note that the two samples which revealed the sudden change during the interval 3.416-3.298 Ga came from the same uninterrupted stratigraphic sequence (the Onverwacht Group) and the same environment of deposition (a deep marine basin) and were sediments of the same kind (dark grey chert containing sulphide and carbonate minerals) (Jackson, 1975; Byerly et al., 1996), implying that the observed effect is unlikely to have been caused by a mundane geological process such as a temporal shift in the origin or nature of the sediments. In short, the Mn/Fe ratios together with other kinds of evidence documented in the literature suggest mass mortality, and possibly mass extinction, of cyanobacteria caused by an asteroid impact. Thus, the observed effect casts doubt on the hypothesis that the prokaryotic microorganisms which predominated during much of Precambrian time were not subject to mass extinction (Butterfield, 2007), though further research is needed to verify it and to test my interpretation of it.

2. Having declined to a minimum, which, in Figure 1, appears to have occurred ca. 1.8783 Ga, the Mn/Fe ratio increased continuously but at episodically varying rates, as indicated by abrupt changes in the slope of the curve, until 0.680 Ga (Fig. 1), reflecting the progressive but stepwise accumulation of photosynthetic O₂ in the atmosphere, which started ca. 2.5-2.3 Ga (Pavlov and Kasting, 2002; Holland, 2006; Canfield et al., 2013; Lyons et al., 2014). The actual position of the minimum is uncertain, as no other data are available for the interval 3.298-1.6 Ga. However, considering the evidence that the oxygenation of the atmosphere and hydrosphere began ca. 2.5 Ga (Pavlov and Kasting, 2002; Holland, 2006; Canfield et al., 2013; Lyons et al., 2014), we may tentatively infer that the minimum occurred ca. 2.5 Ga or that a period of uniformly low O₂ concentrations stretching from the Archean to the early

Proterozoic came to an end ca. 2.5 Ga. The onset of atmospheric oxygenation was soon followed by the evolution of eukaryotic photoautotrophs (i.e. algae), which appear in the fossil record ca. 2.0-1.8 Ga (Teyssdre, 2006, 2007; Javaux, 2007; Parfrey et al., 2011) or possibly as early as 2.1 Ga (Riding, 1992), although a diverse, well preserved fossil microflora found in chert laid down ca. 1.9 Ga apparently consists solely of cyanobacteria and other prokaryotes (Hofmann, 1976). The occurrence of this profoundly important stage in atmospheric evolution during the Proterozoic has been established independently by other kinds of evidence published elsewhere (Cloud, 1976; Schidlowski, 1983; Pavlov and Kasting, 2002; Bekker et al., 2004; Holland, 2006; Kaufman et al., 2007; Buick et al., 2008; Kump et al., 2011; Canfield et al., 2013; Lyons et al., 2014). According to recently proposed theories of atmospheric evolution, however, the O₂ concentration in the atmosphere, following a rapid initial upsurge that began ca. 2.5-2.3 Ga, levelled off and remained virtually constant over much of mid-Proterozoic time (ca. 1.85-0.85 Ga) before rising again in the late Proterozoic (Holland, 2006; Lyons et al., 2014), whereas my data show a continuous increase, though at a reduced rate, during this interval. Thus, the net rate of increase, which was relatively high initially, dropped sharply at some point no later than 1.6 Ga (more specifically, during the interval 1.8783-1.6 Ga), lowering the slope of the curve (Fig. 1), possibly owing to the appearance of eukaryotic primary consumers (i.e. herbivores) which fed on algae and cyanobacteria, thereby reducing the net rate of photosynthetic O₂ production in the middle to late Proterozoic (Javaux, 2007). From 1.6 to 0.8 Ga the Mn/Fe ratio increased at a uniform, highly significant exponential rate ($r = -0.999$; $P \approx 0.001$; $N = 4$), testifying to the persistence and consistency of the natural process responsible for the trend and the high degree of precision and sensitivity of the analytical method. (Note that separate chert and dolomite samples dated 1.3 Ga gave nearly the same result. This, too, attests to the precision of the data, and it validates the assumption that the data for cherts and carbonate rocks were equivalent and could therefore be lumped together as a single population and plotted on the same graph, as demonstrated elsewhere in studies of Precambrian and Phanerozoic organic matter (Jackson, 1973, 1975; Jackson and Moore, 1976; Jackson et al., 1978).) From 0.8 to 0.68 Ga, however, the Mn/Fe ratio increased more rapidly, indicating a late Proterozoic upsurge in O₂ production, as postulated independently elsewhere (Fike et al., 2006). This could

represent an important development in the continuing evolution and proliferation of algae or enhancement of primary production owing to an increase in the rate of nutrient recycling largely as a consequence of bioturbation by the earliest species of benthic invertebrates (Martin et al., 2008).

3. Having peaked at or near the end of the Proterozoic (ca. 0.680 Ga), the Mn/Fe ratio fell abruptly and catastrophically to a minimum in the Cambrian period. This momentous event at the Precambrian-Cambrian boundary evidently reflects the mass extinction of the majority of the mysterious, highly distinctive multicellular eukaryotic organisms which comprised the late Proterozoic Ediacaran biota and confirms the observation that it involved an episode of widespread anoxia (Hsu et al., 1985; Logan et al., 1995; Schröder and Grotzinger, 2007; Wille et al., 2008; Laflamme et al., 2013). Evidently the catastrophe which exterminated most of the Ediacaran biota caused a sudden drop in the O₂ concentration of the atmosphere and oceans, probably owing to [1] consumption of O₂ by bacteria decomposing the remains of vast numbers of dead organisms and [2] decimation of O₂-generating photosynthetic organisms, notably algae. Accordingly, it caused sediments of the Precambrian-Cambrian transition zone to have anomalously low $\delta^{13}\text{C}$ values, implying a sharp drop in biological productivity (Hsu et al., 1985). The sediments are characterised by another geochemical anomaly (enrichment in iridium, osmium, and gold) which is consistent with the possibility that the mass extinction resulted from an asteroid impact (Hsu et al., 1985).
4. Finally, the Mn/Fe ratio, after dropping to a minimum at the Precambrian-Cambrian boundary, rebounded and showed a continuous, highly significant logarithmic increase from the Cambrian to the Permian ($r = -0.996$; $P > 0.001$, < 0.01 ; $N = 4$), probably reflecting rapid recovery and progressive expansion of planktonic algal populations – green algae in particular (Katz et al., 2004) – in the ocean and other aquatic habitats. The observed trend may be due in large part to a continuous rise in the rate of primary production by the marine phytoplankton owing to enhanced recycling of nutrients by processes such as bioturbation and the decomposition of the remains of marine organisms throughout the Paleozoic (Martin et al., 2008). The evolution and proliferation of plants, which evolved from green

algae and colonised the land in the Ordovician (Kenrick and Crane, 1997), probably contributed to the observed effect. The overall result of these processes was a progressive rise in photosynthetic O₂ production spanning the entire Paleozoic era.

In conclusion, the results of the research reveal significant new information about major events and trends in atmospheric evolution and related aspects of biotic evolution, including mass extinctions, during the Precambrian and Paleozoic. These findings also appear to confirm, extend, and refine a number of observations reported independently by others. However, they include evidence suggesting an early Archean mass mortality or mass extinction event, thus casting doubt on the hypothesis that prokaryotic organisms such as cyanobacteria have not been prone to mass extinction, and they contradict the theory that the O₂ concentration in the atmosphere was constant during much of Proterozoic time (i.e. the interval 1.85-0.85 Ga).

More generally speaking, the research data suggest that the Mn/Fe ratio of the readily reducible oxide fraction of non-detrital sediment is a precise and sensitive measure of the redox potential or degree of oxygenation of the sedimentary environment at the time of deposition and is not significantly altered by diagenesis. Thus, the analytical method employed in this investigation is potentially capable of providing important information about temporal variations in atmospheric and oceanic O₂ levels, along with information about related developments in biotic evolution and paleoecology, throughout geologic time. Furthermore, the method has the advantage of being relatively simple and inexpensive.

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Table 1

Table 1. Information about the sediment samples, including the results of the chemical analyses.

Name and location of rock formation ¹	Sample no. ²	Rock type ³	Age (Ga) ⁴	NH ₂ OH·HCl/acetic acid-extractable elements			
				Mn (μg·g ⁻¹)	Fe (μg·g ⁻¹)	Mn/Fe ratio (wt./wt.)	
						Individual values	Mean of duplicate values ± standard error
Kromberg Formation, Onverwacht Group (South Africa)	14	chert	3.416 (3.411-3.421) ⁵	572	3,750	0.153	
Mendon Formation ⁶ , Onverwacht Group (South Africa)	15	chert	3.298 (3.295-3.301) ⁵	43	837	0.051	
Gunflint Iron Formation (Ontario, Canada)	11	chert	1.8783 (1.8770-1.8796) ⁷	348	16,600	0.0210	
Paradise Creek Formation (Queensland, Australia)	17	chert	1.6 (1.5-1.7)	86	944	0.091	
Beck Spring dolomite (California, U.S.A.)	4	dolomite	1.3 (1.2-1.4)	131	822	0.159	
Beck Spring dolomite (California, U.S.A.)	5	chert	1.3 (1.2-1.4)	150	880	0.170	
Bitter Springs Formation (Northern Territory, Australia)	12+13	chert	0.8 (0.7-0.9)	98	202	0.485	0.477 ± 0.008
				122	260	0.469	
Kuibis Formation, Nama system (Southwest Africa)	20	limestone	0.680 (0.640-0.720)	311	384	0.810	0.784 ± 0.026
				340	448	0.759	
Conococheague [Elbrook] limestone (Virginia, U.S.A.)	39	limestone	0.510 (0.500-0.530) [Cambrian]	81	1,700	0.048	0.048 ± 0.000
				89	1,860	0.048	
Chambersburg limestone (Maryland, U.S.A.)	38	limestone	0.475 (0.450-0.500) [Ordovician]	44	535	0.082	0.075 ± 0.007
				49	727	0.067	
Givetian limestone (Belgium)	40	limestone	0.360 (0.340-0.400) [Devonian]	443	1,530	0.290	
Kupferschiefer (Germany)	29	limestone	0.250 (0.240-0.260) [Permian]	3,180	833	3.82	

¹More detailed information about the rock formations is given elsewhere (Jackson, 1975; Jackson and Moore, 1976; Jackson et al., 1978).²The sample numbers are the same ones that were used in previous publications (Jackson, 1973, 1975, 1977; Jackson and Moore, 1976; Jackson et al., 1978).³All chert samples contained carbonate minerals.⁴Ga = 10⁹ years before the present. The geochronological data were obtained from P. Cloud (personal communication) except where otherwise noted.⁵Source of geochronological data: Byerly et al. (1996).⁶Previously called the Swartkoppie Formation (or Swartkoppie Horizon) but currently called the Mendon Formation and assigned to the Onverwacht Group (Lowe and Byerly, 1999).⁷Source of geochronological data: Fralick et al. (2002).

Fig. 1. Plot showing variation in the Mn/Fe ratio of the readily reducible oxide fraction of non-detrital sedimentary rock as a function of the geologic age of the rock. The figure includes interpretive notes that are consistent with independent evidence in the literature. Explanation of symbols and terminology: chert, ■; carbonate rock (limestone or dolomite), ▲; Ga = 10^9 years before the present. The logarithms of the Mn/Fe ratios were used to make the plot, because the ratio values span three orders of magnitude. The geochronological data were obtained from the late Preston Cloud (personal communication) except for the ages of the Archean Kromberg and Mendon Formations, which were obtained from Byerly et al. (1996), and the age of the Proterozoic Gunflint Iron Formation, which was obtained from Fralick et al. (2002) (see Table 1). The error bars for geologic age represent the range of possible dates according to the available radiometric data. The error bars for duplicate Mn/Fe ratios (mean $\pm$ standard error) and for some of the geologic ages were too small to be shown in the plot (see Table 1).

Figure 1