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A PALEOWEATHERING PROFILE FROM GRIQUALAND WEST, SOUTH AFRICA: EVIDENCE FOR A DRAMATIC RISE IN ATMOSPHERIC OXYGEN BETWEEN 2.2 AND 1.9 BYBP

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ABSTRACT. A core drilled near Wolhaarkop in Griqualand West, South Africa, intersected highly oxidized Kuruman Iron Formation below red beds of the Gamagara Formation. The lateral equivalents of the Kuruman Iron Formation in this drill hole consist largely of siderite, ankerite, magnetite, greenalite, and quartz. The oxidation of the Kuruman Iron Formation in WOL 2 occurred almost certainly during weathering prior to the deposition of the Gamagara Formation. The date of this weathering episode is bracketed between about 2.2 and 1.9 bybp by the age of the Ongeluk lavas in the Transvaal sequence below the unconformity and by the age of the Hartley lavas in the Olfantshoek Group above the unconformity.

The ratio of iron to SiO$_2$ in the several facies of the weathered Kuruman Iron Formation in WOL 2 is nearly the same as that in their unweathered equivalents. Since SiO$_2$ loss during weathering was almost certainly minor, the similarity of the Fe/SiO$_2$ ratio in the weathered and unweathered BIF indicates that nearly all the “FeO" in the Kuruman Iron Formation was oxidized and retained as FeO$_3$ during weathering. Such a high degree of iron retention is best explained by an O$_2$ content of the atmosphere $\geq 0.03$ atm at the time of weathering. Such an O$_2$ pressure is very much greater than that suggested by the composition of paleosols developed on basalt $\geq 2.2$ bybp but is consistent with the highly oxidized nature of the 1.85 by Flin Flon paleosol. The new data suggest that P$_{O_2}$ rose dramatically from about 1 percent PAL (present atmospheric level) to $\geq 15$ percent PAL between 2.2 and 1.9 bybp.

INTRODUCTION

In a remarkable series of papers on the oxygen content of the Precambrian atmosphere, Preston Cloud (1968, 1973, 1976) suggested that the Archean-Early Proterozoic atmosphere was oxygen deficient, and that a dramatic rise in the oxygen content of the atmosphere took place about 2 by ago, coincident with the disappearance of major iron-formations from the stratigraphic record. This hypothesis has been favorably received; it explains many geological observations, including the distribution of red beds and detrital uraninite deposits (for a review

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see Walker and others, 1983). The processes, the timing, and the specific events that were responsible for the rise in oxygen levels are still poorly understood, largely due to a lack of geological observations on which estimates of past oxygen levels can be based. Semiquantitative estimates by Grandstaff (1980) based on the survival of detrital uraninite in Archean and Early Proterozoic gold-uraninite ore deposits, and estimates by Kasting (in press) based on the requirements of models for the origin of iron-formations support the hypothesis of a low oxygen content in the Archean and Early Proterozoic atmosphere. However, Cloud's suggestion of a major rise in oxygen content about 2 by ago has never been tested quantitatively. Recent work by Holland, Feakes, and Zbinden (1989) on the 1.85 by old Flin Flon paleosol provides semiquantitative evidence in favor of a significant rise of P\textsubscript{O\textsubscript{2}} between 2.2 and 1.85 bybp. In this paper we present semiquantitative evidence for a dramatic rise in atmospheric oxygen about 1.9 to 2.2 by ago based on a paleoweathering profile developed on Kuruman Iron Formation and intersected in a deep diamond drill core in Griqualand West, South Africa.

REGIONAL GEOLOGIC SETTING

In Griqualand West, South Africa, red beds of the Olifantshoek Group unconformably overlie sedimentary rocks and lavas of the Transvaal Supergroup. Paleoweathering profiles were developed on several Transvaal lithologies immediately below the unconformity. These profiles are known from outcrop and from deep diamond drill cores for a strike distance of 350 km (fig. 1A). The unconformity is duplicated by a major thrust (fig. 1A). Apart from deformation along thrust planes, gentle folding, and normal faulting (Visser, 1944; Beukes and Smit, 1987), the Transvaal and Olifantshoek strata are little altered and virtually unmetamorphosed. Maximum regional metamorphic temperatures as low as 110° to 170°C at pressures of not more than 2 kb have been documented by Miyano and Beukes (1984).

In fresh drill cores the paleoweathering profiles are almost invariably characterized by the oxidation of gray to green, "FeO"-bearing Transvaal strata into red, hematite-rich paleoweathered material, the exact composition of which depends on the nature of the parent rock (Beukes, 1977; Van Wyk and Beukes, 1982). Parent rock textures tend to be preserved lower down in profiles and to be obliterated upward toward the paleoerosion surface. Recently, Wiggering and Beukes (in press) described one of these profiles at Drakenstein (fig. 1A), where Ongeluk basalt passes upward into a highly oxidized paleosol. In this paper we are concerned with a paleoweathering profile developed on Kuruman Iron Formation and on the conformably underlying Campbellrand dolomite of the Transvaal Supergroup. The composition of these units prior to weathering is very well known from the work of Beukes (1980, 1984), Miyano and Beukes (1984), Van Wyk (personal commun.), Klein and Beukes (1989), and Beukes and Klein (in press). Comparison
with their paleoweathered equivalents is therefore straightforward. The weathered profile that is the subject of this paper was intersected between 420 and 530 m in a subvertical diamond drill core (WOL 2) on the farm Wolhaarkop 448 to the southwest of Postmasburg (fig. 1A). Between 420 and 500 m the profile consists of highly oxidized Kuruman Iron Formation; between 500 and 530 m it consists of oxidized shale and dolomite of the Gamohaan Formation of the Campbellrand Subgroup (fig. 1B). The basic lithostratigraphic units of the Kuruman Iron Formation sequence can still be recognized. The original and early diagenetic iron carbonates, iron silicates, and magnetite have all been replaced by hematite without loss of the chert/iron mineral microbanding and mesobanding that is a prominent feature of their unoxidized equivalents. This is also true of the Gamohaan sequence, where hematite is the oxidation product of nodular and matrix sedimentary pyrite in shale and of contorted, microbiolaminated carbonates. Kerogen is conspicuous in fresh samples of the shale but is absent in oxidized shale. Below 530 m, the degree of paleoweathering rapidly decreases to the base of the core at a depth of 536.3 m (fig. 1B).

Oxidation of hematite-poor to hematite-rich iron-formation just below the Transvaal-Olifantshoek unconformity is very widespread. At the Rooinekke Mine, some 50 km to the south of Wolhaarkop (fig. 1A), manganese and iron carbonate-rich Rooinekke Iron Formation of the Koegas Subgroup has been transformed into high grade hematite ore with interbedded manganese oxide ore (Visser, 1954; Beukes, 1986). Wherever this iron-formation is cut by the unconformity in the Kalahari manganese field some 130 km to the north of Wolhaarkop (fig. 1A), siderite, magnetite, and minnesotaite have been converted to hematite (Kleyenstüber, ms: Beukes, 1985). In other areas, siderite lutite of the Griquatown Iron Formation has been oxidized to hematite-lutite. Good examples are preserved in core at the Sishen Iron Ore Mine (Van Schalkwyk and Beukes, 1986) and in core SMD3 on Constantia 309 to the west of the Kalahari manganese field (Beukes, 1985; Beukes and Smit, 1987) (fig. 1A). Some of the best exposures of hematitized iron-formation immediately below the unconformity are to be found on the Maremane dome between Sishen and Postmasburg. In this area the unconformity transects Campbellrand dolomite; hematitized Kuruman Iron Formation there slumped into large paleokarst features (fig. 1A). In this setting virtually all the original silica was leached from the iron-formation. This removal led to the formation of the giant, high grade hematite iron ore deposits of Sishen (Van Schalkwyk and Beukes, 1986) and Beeshoek (Grobbelaar and Beukes, 1986). Paleokarstic, bixbyite-rich ore of the Lohathla-type developed where the unconformity transects chert-free manganese-bearing dolomite of the Campbellrand sequence (Grobbelaar and Beukes, 1986). In contrast, braunitic ores of the Manganore-type developed in association with a ferruginous paleokarst chert breccia where the unconformity transects cherty dolomite units (Nel, 1929; De Villiers, 1960; Beukes, 1977, 1986).
Fig. 1. Regional geological map of Griqualand West (A) showing the lateral distribution of the Transvaal-Olifantshoek unconformity, iron and manganese deposits associated with paleoweathering profiles immediately below this unconformity, and the location of diamond drill core WOL 2. The stratigraphic setting of the paleoweathering profile intersected in WOL 2 is illustrated in (B). The Koegas Bif includes both the Kuruman and Griquatown Bifs.
The thickness of the paleoweathering profiles varies considerably along strike. They appear to be best developed on the Maremane dome, where thicknesses of several tens of meters are common (Van Schalkwyk and Beukes, 1986). The paleoweathered section at Wolhaarkop is one of the thickest in this region. At the Rooinekke mine the paleoweathering profiles are 20 to 30 m thick; in the Kalahari manganese field they are on
the order of 1 to 5 m thick; in a few drill cores paleoweathering profiles are completely absent.

A persistent hematite-pebble conglomerate and/or gritstone is widespread at the base of the Olifantshoek sequence immediately above the paleoweathering profiles (Nel, 1929; Strauss, 1964; Button, 1976; Van Schalkwyk and Beukes, 1986; Grobbelaar and Beukes, 1986). This unit also contains pebbles of oxidized, hematite-rich iron-formation and chert (fig. 2). Pebble type abundances are related to source rocks in the vicinity. Near high-grade iron ore deposits, like those at Rooinekke, Sishen, and Beeshoek, hematite pebbles are dominant. In the Kalahari manganese field pebbles of hematite-rich iron-formation are common. Some pebbles are very well rounded, others are extremely angular; sorting can range from very poor to intermediate. The paleomagnetic orientation of hematite pebbles in the basal conglomerate at the Sishen mine is random (Kirschvink and Beukes, in preparation). This indicates that the hematite was magnetized prior to the incorporation of the pebbles in the conglomerate and that the magnetic orientation of the pebbles was not reset by later thermal events. The conglomerate is absent in WOL 2 (fig. 1B). A 40-cm-thick shear zone in the Gamagara shale immediately above the paleoweathered profile suggests that the

Fig. 2. Hematite (A), hematitic iron-formation (B), and quartz pebble (C) conglomerate from the base of the Gamagara Formation in Drak 1 on Drakenstein. Note hematite granules in left part of sample (D).
conglomerate may have been faulted out. However, in core WOL 4 the contact is unsheared and is overlain by gritstone interbedded with shale. Granules and small, angular hematite pebbles are present in the gritstone.

The basal hematite-rich conglomerate of the Olifantshoek Group is normally overlain by red and cream colored shale coarsening upward into siltstone and fine-grained quartzite containing abundant grains of hematite (Van Schalkwyk and Beukes, 1986; Beukes and Smit, 1987). This is also the case in core WOL 2, but here the red shale grades upward into green shale, which is in turn overlain by hematitic quartzite. Hematite pigmentation defines the lamination in the red shales. When this pigment is leached, the shale becomes cream colored and massive (Van Schalkwyk and Beukes, 1986). Highly aluminous diaspare shales directly overlie the basal hematite-pebble conglomerate in places on the Maremane dome (Brabers, 1974). These are local features that are restricted to paleosinkhole structures along the pre-Olifantshoek erosion surface (Van Schalkwyk and Beukes, 1986).

Paleooxidation of the Transvaal strata is uniquely associated with the Transvaal-Olifantshoek unconformity. Older unconformities situated within the Transvaal sequence, like that at the base of the Makganyene diamicite in Griqualand West, the base of the Pretoria Group, and the top of the Hekpoort basalt in the Transvaal, lack any signs of ferric iron enrichment. In contrast, the pre-Olifantshoek hematitic paleoweathering profiles appear to have much in common with weathering profiles that developed immediately below the Mesozoic pre-Karoo, the Tertiary pre-Kalahari, and modern erosion surfaces. The Transvaal strata were oxidized below each of these unconformities (Kleyenstüber, 1984). Below the modern erosion surface, iron-formations of the Transvaal Supergroup are typically silicified and oxidized to depths of several tens of meters. Abundant ferric oxyhydroxides are developed, but there is no loss of silica banding (Beukes, 1980). Modern weathering has been so intense, that details of the pre-Olifantshoek oxidation profiles have been obliterated in outcrop and can only be studied in cores where the unconformity is intersected at depth.

THE AGE OF THE TRANSVAAL-OLIFANTSHOEK UNCONFORMITY

The unconformity is younger than the Ongeluk lava of the Transvaal Supergroup, and it is older than the Hartley lava of the Olifantshoek Group. Pb-Pb whole rock analyses from nine samples of Ongeluk lava define an isochron that indicates an apparent age of 2239 ± 90 my (Armstrong, ms; Walraven, Armstrong, and Kruger, 1990). This is in good agreement with the 2224 ± 21 my Rb-Sr age obtained for the Hekpoort basalt, its correlative in the Transvaal (Burger and Coertze, 1974). Rb-Sr whole rock analyses by Crampton(1974) indicated that the Hartley lava is 2070 ± 90 my old. This date has recently been recalculated by Armstrong (1987) to 2026 ± 180 my. Armstrong (ms) has also presented a new whole rock Rb/Sr age of
1881 ± 57 my and a Pb-Pb age of 1830^{+594}_{-454} my. The unconformity and its associated paleoweathering profiles therefore developed some 1.9 to 2.2 by ago.

**STRATIGRAPHY AND CORRELATION OF THE UNEARTHED AND WEATHERED KURUMAN IRON FORMATION**

Geologic mapping combined with aeromagnetic data have shown that the sequence in WOL 2 is a continuation of outcrops of the Kuruman Iron Formation immediately south of Postmasburg, along the southern margin of the Maremane dome (fig. 1A). Two major stratigraphic units of the Kuruman Iron Formation are developed in WOL 2 (fig. 3). The upper 16 m consist of very finely laminated and microbanded hematite iron-formation without distinct chert mesobands. The lower 63 m of the sequence consist of three units rich in hematite microbanded chert separated by two units of microbanded hematitic banded iron-formation (fig. 3). The banded iron-formation units display a cyclical repetition of lithofacies (fig. 3). The cycles, a meter to a few meters thick, are composed of centimeter thick hematite lutite microbands interbedded with hematite microbanded chert, overlain by thickly mesobanded hematitic banded iron-formation, which is in turn overlain by thinly mesobanded iron-formation (Beukes, 1980, 1983). Poddled chert mesobands are especially abundant in the latter lithofacies: wavy chert mesobands are characteristic of the thickly mesobanded facies. Two varieties of hematite microbands and mesobands are present. The first type has an earthy, red to reddish brown appearance: the second is hard, dark, and steel-gray. The earthy variety is more characteristic of the microbanded chert and thickly mesobanded iron-formation units: the hard, steel gray variety is more characteristic of the thinly mesobanded iron-formation units toward the top of each of the stacked sedimentary cycles. In the microbanded chert units disseminated, millimeter-sized euhedral rhombs of earthy hematite are especially conspicuous. These are pseudomorphs after carbonates.

Except for its mineralogical composition, the sequence in WOL 2 correlates very well with that of the Kuruman Iron Formation in the Danielskuil-Kuruman area to the east of Postmasburg. The Kuruman Iron Formation has a distinctive and consistent stratigraphy, which can be correlated over its entire strike length of more than 550 km in Griqualand West (Beukes, 1980, 1983, 1984; Beukes and Dreyer, 1986). The base of the unit is composed of ankeritic siderite microbanded chert and the siderite facies banded iron-formation known as the Kliphuis Member. This unit correlates with the hematite microbanded chert and thickly mesobanded hematitic iron-formation unit at the base of the succession in WOL 2 (fig. 3). The overlying Groenwater Member of the Kuruman Iron Formation is characterized by stacked sedimentary cycles, each composed of stilpnomelane lutite interbedded with siderite microbanded chert, which is overlain by siderite facies, siderite-magnetite facies, and magnetite-hematite facies banded iron-formation.
Fig. 3. Detailed stratigraphy of oxidized Kuruman Iron Formation and Campbellrand carbonate and shale in WOL 2. Composition and relative abundances of unweathered lithofacies are given for comparison. Codes are as follows: stipl. = stilpnomelane, sid. = siderite, mag = magnetite, hem = hematite.

Thicknesses of chert mesobands decrease upward in the cycles, so that the magnetite-hematite units are characterized by thin (<1 cm), wavy, and podded chert mesobands. This agrees almost exactly with the nature of the stacked sedimentary cycles in the Wolhaarkop core, which represent the oxidized equivalents of stilpnomelane lutite iron-formation cycles in the Kuruman-Danielskuil area. The stilpnomelane lutite banded iron-formation cycles are, however, not always fully developed. Especially in the presence of abundant stilpnomelane lutite beds, they often only extend into siderite facies banded iron-formation or siderite
microbanded chert units, which then constitute chert-rich zones within the sequence (Beukes, 1980). Most characteristic of these is the Elgan zone. The counterpart of this zone in the Wolhaarkop profile is a unit rich in hematite microbanded chert with interbeds of hematite lutite (fig. 3). The latter may represent hematitized stilpnomelane lutite macrobands.

The Groenwater Member of the Kuruman Iron Formation is overlain by the Riries Member. The lower part of this member, known as the Corheim zone (Beukes and Dreyer, 1986), is composed of finely laminated and microbanded greenalite-siderite and greenalite-siderite-magnetite facies iron-formation in the Danielskuil-Kuruman area (Beukes, 1980). A very distinctive feature of this facies is the virtual absence of well-defined chert mesobands. This is also the case in the finely laminated hematitic iron-formation intersected in the upper part of the Wolhaarkop core. This unit is thus correlated with the greenalitic iron-formations of the Corheim zone (fig. 3). The correlation implies that the upper part of the Corheim zone and the Bretby and Alphen zones of the Riries Member as well as the granular Ouplaas Iron Formation member at the top of the Kuruman Iron Formation (Beukes, 1980) are absent in WOL 2, presumably due to erosion prior to the deposition of the Gamagara red beds.

The thickness of the Kuruman Iron Formation varies considerably along strike. It reaches a maximum known thickness of approx 750 m in the basin toward the margin of the Kaapvaal craton near Koegas and thins onto the craton to a minimum known thickness of 110 m at Groenwater some 40 km to the west of Wolhaarkop and to 135 m near Danielskuil, some 30 km to the west of Groenwater (fig. 1A). Thinning is related to the Danielskuil-Postmasburg paleohigh, which was active during the deposition of the Kuruman sequence (Beukes, 1983). Individual stratigraphic units at Wolhaarkop are estimated to be some 10 to 13 percent thinner on average than their correlatives at Groenwater. This difference is most probably related to depositional processes and to the effects of paleoweathering.

The sequence of shale, dolomite, and microbanded chert that underlies the Kuruman Iron Formation at Wolhaarkop corresponds in very fine detail to the Tsineng member of the Gamohaan Formation of the Campbellrand Subgroup and represents a transition zone from carbonate to iron-formation deposition (Beukes, 1984; Klein and Beukes, in press). Sparitic, contorted, microbiolaminated dolomite like that intersected in WOL 2 characterizes the Gamohaan sequence immediately below the Tsineng member. The stratigraphy, mineralogy, and geochemistry of this transition zone are very well known (Beukes, 1980, 1984; Klein and Beukes, 1989) and are the basis for the comparison of oxidized and unoxidized material in figure 3.

An unsorted iron-formation breccia constitutes the upper 2.6 m of the Kuruman Iron Formation in WOL 2 (fig. 3). The fragments are angular and mainly of local origin, since they are similar in composition
to the laminated hematitic iron-formation of the Corheim zone. The matrix is composed of chert, finely distributed hematite, sand to grit-sized angular iron-formation fragments, and quartz sand grains. Centimeterwide fractures filled with fine to medium-sized, well rounded, and sorted quartz sand grains (fig. 4A) extend from the base of the breccia downward for more than 10 m into the laminated iron-formation. Minor angular hematite grains are present in the fracture fill: the cementing material consists of quartz and hematite. The fractures became filled with quartz sand after oxidation of the iron-formation, because fracture boundaries are sharp and cut across bedding without any indication of alteration of the iron-formation. The angular iron-formation clasts in the breccia must have accumulated after oxidation, because they are sharply defined from the matrix and show no signs of preferential alteration along their boundaries. Minor veins filled with quartz and sparry dolomite crosscut clasts and matrix in the breccia and bedding in the iron formation. These veinlets are clearly late tectonic/hydrothermal in origin.

MINERALOGY AND PETROGRAPHY

The iron-formation at Wolhaarkop is composed almost entirely of hematite and quartz (chert). Three varieties of hematite are present: cryptocrystalline red hematite dust, specularite needles <0.005 mm in length, and maghemite pseudomorphous after magnetite. The last two varieties are the dominant constituents of the hard, steel-gray mesobands. Earthy red hematite mesobands are composed of hematite dust and specularite cemented by chert and appear to be the typical oxidation product of iron carbonates. The shape of many euohedral iron carbonate rhombs was perfectly preserved by an infilling of chert-cemented hematite dust and specularite needles (fig. 4B).

The finely laminated facies of iron-formation in WOL 2 is probably the oxidized equivalent of greenalite–siderite–magnetite facies iron-formation. In this facies early diagenetic carbonate euohedra and nodules are completely replaced by chert (fig. 4C). The absence of hematite in the replaced euohedra suggests they may have been calcitic or dolomitic in composition. In some of the finely laminated units, chert laminae pigmented by red hematite dust alternate with steel-gray specularite laminae containing no maghemite. Original greenalite was probably replaced by specularite to form the steel-gray laminae. In contrast, the oxidation of iron carbonates seems to have given rise to the earthy red laminae. In units that originally represented oxide facies iron-formation, steel-gray laminae are composed of maghemite and specularite after original magnetite-specularite mesobands common in the Groenwater Member (Beukes, 1980). Original siderite-magnetite facies iron-formation is now composed of maghemite-rich microbands alternating with red cherty microbands. It is thus possible to identify original mineral assemblages with some degree of certainty. Other parameters that characterize the lithofacies, such as the distribution of disseminated
large carbonate euohedra, texture and style of microbanding, thickness and form of chert mesobands, and style of alternation between chert and iron-rich mesobands are also helpful (Beukes, 1980). Estimates of the abundances of various unweathered lithofacies are given in figure 3 and are summarized in table 1. Average compositions of various mineral phases from unweathered Kuruman Iron Formation are given in table 2. The compositions of hematite and magnetite are not given, because they are normally very pure phases (Van Wyk, personal commun). It should be noted that siderites in Kuruman Iron Formation contain on average 7.50, ankerites 8.45, and greenalites 5.48 percent MgO.

Dolomite of the Gamohaan Formation contains almost 6 wt percent FeO on average (table 2); this may explain the red hematite pigment in
<table>
<thead>
<tr>
<th>Facies Code</th>
<th>Unoxidized Facies</th>
<th>Oxidized facies Cumulative Thickness (m)</th>
<th>MINERALOGY</th>
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<tr>
<td>A</td>
<td>Greenalite-Siderite-Magnetite BIF</td>
<td>15.37  XXX   XX   X     X   XX</td>
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<td>B</td>
<td>Oxide BIF</td>
<td>14.80  XXX   XX   X     XX</td>
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<td>C</td>
<td>Siderite-Magnetite BIF</td>
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<td>D</td>
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<td>E</td>
<td>Siderite Chert</td>
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<tr>
<td>F</td>
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</tr>
<tr>
<td>G</td>
<td>Shale (Pyritic, Carbonaceous)</td>
<td>6.95   x      x     X     **x   x</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>Dolomite (Pink, Oxidized)</td>
<td>20.85  X      X     X     xxx</td>
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</table>

x: minor
xx: common
xxx: abundant
the pinkish, "oxidized" dolomites in the Wolhaarkop core. Hematite in the oxidized shale of this formation was most probably derived from chlorites, which contain on average 20.45 wt percent FeO (table 2). However, in both the shale and the dolomite some hematite is pseudomorphous after matrix and nodular pyrite (Klein and Beukes, 1989). Nodular pyrites are replaced by massive, earthy hematite with a rim of crystalline hematite displaying botryoidal growth forms.

The infilling of tectonic fractures by vein quartz was accompanied by the mobilization of some ferric iron. Hematite was leached from iron-formation along the margins of such veins. Some veins are infilled by quartz and hematite, indicating that some of the mobilized iron was reprecipitated in the veins. Along some of the veins, specularite has been transformed into red, earthy hematite.

**GEOCHEMISTRY**

A typical sample of each of the oxidized lithofacies in WOL 2 was analyzed (table 3) for comparison with the average chemical compositions of the equivalent, unweathered lithofacies of the Kuruman Iron Formation (table 4). During weathering most of the FeO was transformed into Fe$_2$O$_3$. Virtually no MgO, CaO, MnO, or CO$_2$ remain in the oxidized iron-formation. The loss of these components and of CO$_2$ accompanied the transformation of siderite and ankerite to iron oxides during weathering.

Figure 5 shows the range and the averages of the ratio of Fe to SiO$_2$ in samples of unweathered Kuruman Iron Formation compared to the values of this ratio in weathered Kuruman Iron Formation. The ratio of

<table>
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<th>Mineral</th>
<th>Ankerite</th>
<th>Siderite</th>
<th>Dolomite</th>
<th>Greenalite</th>
<th>Stilpnomelane</th>
<th>Fe-chlorite (in shale)</th>
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<td>7</td>
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<td>1.27</td>
<td>0.13</td>
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</tbody>
</table>

*Minimum Fe$_2$O$_3$ estimated from tetrahedral Fe$^{3+}$ assuming 8 tetrahedral cations.

Note: Magnetite and hematite are very pure Fe$_3$O$_4$ and Fe$_2$O$_3$, respectively. Averages computed from analyses given by Miyano and Beukes (1984), Van Wyk (personal comm.), Klein and Beukes (1989), and unpublished results of Beukes.
total iron to SiO$_2$ in samples of weathered material from WOL 2 falls within the range of this ratio in their unweathered facies equivalents. In greenalite–siderite–magnetite, siderite–magnetite, and oxide facies iron-formation, and in shale the ratio is somewhat greater in the weathered material than in average unweathered material. In siderite facies iron-formation and siderite microbanded chert the ratio is somewhat smaller than in fresh material. The SiO$_2$ content of the several iron-formation lithofacies is determined to a large degree by the rather variable number and thickness of SiO$_2$ mesobands relative to iron-rich mesobands. This variability explains the large standard deviations in the major element composition of banded iron-formation units, especially in the siderite-rich and chert units. Chert mesobanding in oxide-facies iron-formation is much more even and consistent; variations in the major element composition of this facies are therefore much smaller.

Changes in the stratigraphy of the Kuruman sequences in this region are largely due to changes in the relative thickness of the various lithofacies rather than to changes in their composition (Beukes, 1980). The Fe/SiO$_2$ ratios of the various Kuruman lithofacies at Wolhaarkop prior to the intense weathering 1.9 to 2.2 bybp were therefore almost certainly similar to the Fe/SiO$_2$ ratios of the same lithofacies within the region as a whole. A comparison of the Fe/SiO$_2$ ratios in the weathered facies of the Kuruman Iron Formation with those in their unweathered equivalents in the region is therefore meaningful, and the similarity of the ratios is highly significant.

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<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
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</table>

Table 3

Composition of oxidized facies of the Kuruman Iron Formation in WOL 2

Analyst: M. Sharpe, Rocklabs, Pretoria, South Africa
Table 4

Average composition of the unweathered facies of the Kuruman Iron Formation; standard deviations calculated by Lotus 1-2-3

<table>
<thead>
<tr>
<th>Facies</th>
<th>A</th>
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<th>C</th>
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<th>E</th>
<th>F</th>
<th>G</th>
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<td>16</td>
<td>2</td>
<td>3</td>
<td>8</td>
<td>4</td>
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<td>SiO₂</td>
<td>47.11±5.92</td>
<td>44.09±3.57</td>
<td>49.75±4.42</td>
<td>39.99±14.06</td>
<td>71.00</td>
<td>39.15±6.88</td>
<td>43.01±10.98</td>
<td>9.35±7.52</td>
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<td>TiO₂</td>
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<td>&lt;0.01</td>
<td>0.01</td>
<td>0.04</td>
<td>&lt;0.01</td>
<td>0.10±0.03</td>
<td>0.35±0.11</td>
<td>&lt;0.04</td>
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<td>Al₂O₃</td>
<td>0.15</td>
<td>0.04±0.01</td>
<td>&lt;0.1</td>
<td>0.10±0.06</td>
<td>0.11</td>
<td>4.22±1.26</td>
<td>9.09±2.37</td>
<td>1.73±0.68</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7.05±2.33</td>
<td>23.74±1.65</td>
<td>7.97±0.59</td>
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<td>8.89±5.41</td>
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<td>FeO</td>
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<td>4.30±1.95</td>
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<td>Na₂O</td>
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<tr>
<td>K₂O</td>
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<td>1.53±1.14</td>
<td>5.18±1.79</td>
<td>0.41±0.17</td>
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<td>H₂O⁺</td>
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<td>1.03±0.69</td>
<td>n.d.</td>
<td>0.0</td>
<td>3.31±0.44</td>
<td>n.d.</td>
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</tr>
<tr>
<td>H₂O⁻</td>
<td>0.11±0.09</td>
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<td>0.02±0.02</td>
<td>0.08±0.02</td>
<td>0.08</td>
<td>0.26±0.36</td>
<td>0.19±0.21</td>
<td>0.09±0.12</td>
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<td>CO₂</td>
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<td>13.90±2.71</td>
<td>23.89±5.95</td>
<td>11.48</td>
<td>6.94±2.93</td>
<td>14.05±4.34</td>
<td>39.85±4.33</td>
</tr>
</tbody>
</table>

Totals | 99.73 | 99.86 | 99.59 | 100.13 | 100.17 | 100.08 | 99.85 | 100.02 |

Averages computed from analyses given by Van Wyk (personal commun.), Klein and Beukes (1989), and Beukes and Klein (in press).
The standard deviations were computed by the relationship σ = \[\sqrt{\frac{\sum(x_i - m)^2}{n}}\] where
- \(x_i\) = individual concentrations
- \(m\) = mean of concentrations
- \(n\) = number of analyses
Fig. 5. The ratio Fe/SiO$_2$ (g/g) in the unweathered facies of the Kuruman Iron Formation (O) and in their oxidized equivalent in WOL 2 (□). Bars indicate probable upper and lower limits of the average ratios in the unweathered facies. These limits were calculated by the relationships

$$\frac{\text{Fe}}{\text{SiO}_2} = \frac{m_{\text{Fe}} + s_{\text{Fe}}}{m_{\text{SiO}_2} - s_{\text{SiO}_2}}$$

and

$$\frac{\text{Fe}}{\text{SiO}_2} = \frac{m_{\text{Fe}} - s_{\text{Fe}}}{m_{\text{SiO}_2} + s_{\text{SiO}_2}}$$

where

- $m_{\text{Fe}}$ and $m_{\text{SiO}_2}$ = mean concentrations of Fe and SiO$_2$.
- $s_{\text{Fe}}$ and $s_{\text{SiO}_2}$ = standard deviations of $m_{\text{Fe}}$ and $m_{\text{SiO}_2}$ from table 4.

**EVIDENCE FOR PALEWEATHERING**

Data from a single stratigraphic profile like that intersected in WOL 2 are usually insufficient to prove that oxidation was due to paleoweathering rather than to later alteration. However, the Wolhaarkop core contains three convincing indicators of paleoweathering. In the first place, the zone of oxidation was intersected at depth below fresh shale of the Gamagara sequence. This rules out recent weathering as a cause of the oxidation of the Kuruman Iron Formation in WOL 2. Secondly,
sand-filled fractures in the finely laminated, oxidized iron formation and breccia indicate that oxidation took place prior to the deposition of the overlying siliciclastics of the Gamagara sequence. The breccia at the top of the Kuruman sequence is probably a superficial breccia on the paleoeorosion surface developed prior to deposition of basal Gamagara gritstone and shale. Thirdly, hematitized pebbles, granules, and grains of iron-formation and chert derived from the underlying weathering profiles were incorporated in the basal conglomerates and gritstones of the Olifantshoek Group. The paleomagnetic directions of hematite in these pebbles are randomly distributed (Kirschvink and Beukes, in preparation). This indicates that the pebbles were oxidized and had obtained their magnetic orientations before incorporation in the basal Gamagara sediments.

On a regional scale, paleoweathering of the Kuruman Iron Formation in WOL 2 is indicated by the close relationship between paleoweathering profiles and the pre-Olifantshoek erosion surface. In many of these profiles alteration increases upward toward the plane of erosion; the profiles are always overlain at a sharp discontinuity by conglomerate, gritstone, or shale of the Olifantshoek sequence. No intersections are known where altered material changes to fresh material both upward and downward in the sequence. The iron ore-filled paleosinkhole structures along the pre-Olifantshoek erosion surface on the Maremane dome (fig. 1A) are further proof of paleoweathering. Alumina-rich diasporic shales partly fill some paleosinkholes; their presence indicates that a period of intense chemical weathering preceded the deposition of the Olifantshoek Group. The sinkhole structures must have developed before the deposition of the Olifantshoek Group, otherwise they could not have controlled the distribution of lithofacies in the basal part of the Gamagara Formation (Van Schalkwyk and Beukes, 1986).

**Implications for the composition of the atmosphere**

In the presence of an atmosphere that contains CO₂ but not O₂, siderite dissolves during weathering, and Fe⁺² released into solution is removed from the weathering profile. Under these conditions carbonate facies iron-formation that consist only of siderite and quartz and have a Fe/SiO₂ ratio of 0.5 g/g weather to a pure quartz residue when P₂CO₃ in the ambient atmosphere is ≥ about 5 PAL (1.7 × 10⁻³ atm). Quartz would also be the final product of the weathering of iron-formation that consist of more than one carbonate and greenalite. Most of the Kuruman Iron Formation exposed to weathering below the unconformity at Wolhaarkop would have been converted into a very quartz-rich rock, if O₂ had been absent from the atmosphere at the time of weathering and if atmospheric P₂CO₂ was ≥ about 5 PAL. The precise value of P₂CO₂ at which the rate of removal of iron carbonates by dissolution in groundwaters is equal to quartz dissolution depends on the degree to which a given groundwater is open to atmospheric CO₂. This in turn depends on the porosity of the weathering zone and on the depth to the water table.
The oxidation of much of the iron in the Kuruman Iron Formation and its retention in hematite can be explained only if \( \text{O}_2 \) was present in the atmosphere during weathering. The following is an attempt to define the level of atmospheric \( \text{O}_2 \) that is required to explain the observed degree of oxidation and retention of iron in the weathering profile of Kuruman Iron Formation at Wolhaarkop. In many ways the weathering of Kuruman Iron Formation is similar to that of the more common rock types, but the relative mineralogical simplicity and the near-absence of \( \text{Al}_2\text{O}_3 \) in the carbonate facies Kuruman sediments simplifies the application of the analytical approach developed by Holland and Zbinden (1988) and Pinto and Holland (1988) for relating the chemistry of weathering profiles to the composition of the atmosphere during their development.

**THE WEATHERING OF SIDERITE-QUARTZ IRON-FORMATION**

Consider first the weathering of a sediment consisting of pure siderite and quartz by reacting with groundwater that contains \( m^o_{\text{O}_2} \) moles of \( \text{O}_2/\text{kg H}_2\text{O} \) and \( m^o_{\text{H}_2\text{CO}_3} \) moles of \( \text{H}_2\text{CO}_3/\text{kg H}_2\text{O} \) before reacting with siderite. If this groundwater was initially in equilibrium with an atmosphere in which the \( \text{O}_2 \) and \( \text{CO}_2 \) pressures were \( P_{\text{O}_2} \) and \( P_{\text{CO}_2} \) respectively, then

\[
\begin{align*}
  m^o_{\text{O}_2} &= B_{\text{O}_2} \cdot P_{\text{O}_2} \\
  m^o_{\text{H}_2\text{CO}_3} &= B_{\text{CO}_2} \cdot P_{\text{CO}_2}
\end{align*}
\]

where \( B_{\text{O}_2} \) and \( B_{\text{CO}_2} \) are the Henry's Law coefficients for \( \text{O}_2 \) and \( \text{CO}_2 \) in water. The reaction of \( \text{H}_2\text{CO}_3 \) with \( \text{FeCO}_3 \) releases \( \text{Fe}^{+2} \). Since the kinetics of \( \text{Fe}^{+2} \) oxidation are rapid, \( \text{Fe}^{+3} \) would be generated within the weathering zone, and an iron hydroxide or iron oxyhydroxide would precipitate. The conversion of \( \text{FeCO}_3 \) into \( \text{Fe(OH)}_3 \) generates \( \text{CO}_2 \) via the overall reaction

\[
4\text{FeCO}_3 + \text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + 4\text{CO}_2
\]

During this process the concentration of \( \text{H}_2\text{CO}_3 \) in the groundwater increases to

\[
\begin{align*}
  m^i_{\text{H}_2\text{CO}_3} &= m^o_{\text{H}_2\text{CO}_3} + 4 \cdot m^o_{\text{O}_2}
\end{align*}
\]

if the reaction takes place in a closed system. This is not strictly true. However, some parts of the siderite facies iron-formation (unit D in table 1) were encountered as much as 80 m below the surface at the time of weathering (see fig. 1). The addition or loss of gases by diffusion at this depth is very slow compared to the rate of reaction of groundwater with carbonate sediments: saturation with respect to siderite requires only a few days (Smith, 1918). The assumption of a closed-system reaction is therefore almost certainly a good approximation.
After the groundwater has equilibrated with siderite

\[
\frac{m_{Fe^{2+}}^3}{(m_{H_2CO_3} - m_{Fe^{2+}})} = \frac{m_{Fe^{2+}}^3}{(m_{H_2CO_3}^o + 4m_{O_2}^o - m_{Fe^{2+}})} \\
\approx \frac{K_1 K_{Sid}}{4K_2} = 6.0 \times 10^{-8}
\]

(5)

where \( K_1 \) = first ionization constant of \( H_2CO_3 \)
\( K_2 \) = second ionization constant of \( H_2CO_3 \)
\( K_{Sid} \) = solubility product of siderite.

The values of \( K_1 \) and \( K_2 \) at 25\(^\circ\)C are well known (\( K_1 = 10^{-6.35} \), \( K_2 = 10^{-10.33} \); see for instance Stumm and Morgan, 1981, chap. 4); for \( K_{Sid} \) we have adopted the value \( 10^{-10.60} \) proposed by Robie, Hazelton, and Hemingway (1984). The product \( K_1 K_{Sid}/K_2 \) is not a strong function of temperature, and the value used here for 25\(^\circ\)C is probably adequate for interpreting the composition of the weathered Kuruman Iron Formation. The activity coefficients of the ions in solution have been set equal to unity, since the groundwaters were almost certainly quite dilute.

During the reaction of 1 kg of groundwater with siderite, \( m_{O_2}^o \) moles of \( Fe^{2+} \) are oxidized and retained as \( Fe_2O_3 \). The quantity of iron lost in solution from the weathering profile is equal to \( m_{Fe^{2+}} \). F, the fraction of iron retained during weathering is therefore

\[
F = \frac{4m_{O_2}^o}{4m_{O_2}^o + m_{Fe^{2+}}}
\]

(6)

The curves in figure 6 show the calculated values of the fraction of iron retained as a function of \( m_{O_2}^o \) for three values of the \( CO_2 \) pressure in the atmosphere. \( P_{CO_2} = 1 \) PAL (3.5 \( \times \) 10\(^{-4} \) atm) is a very strong lower

![Graph](image)

**Fig. 6.** The fraction of iron retained during the weathering of pure siderite as a function of the initial concentration of \( O_2 \) in groundwater and the \( CO_2 \) pressure in the atmosphere with which the groundwaters equilibrated before reacting with siderite.
limit, and $P_{CO_2} = 1000$ PAL (0.35 atm) is a reasonably strong upper limit for $P_{CO_2}$ during the weathering of the Kuruman Iron Formation about 1.9 bybp (see for instance Kasting, 1987 and in press). It is likely that $P_{CO_2}$ was about 100 PAL, but this estimate is still somewhat uncertain, because it is based on a model of the atmospheric response to changes in $P_{CO_2}$ that does not include cloud feedback.

The curves in figure 6 show that complete iron retention in such an iron-formation is impossible, even if the concentration of $O_2$ in the groundwater is equal to 250 $\mu$mol/kg, the $O_2$ content of groundwater equilibrated with $O_2$ in the present day atmosphere ($P_{O_2} = 0.2$ atm = 1 PAL). The fraction of iron retained is a rather weak function of $m_{O_2}$ between 250 $\mu$mol/kg and about 50 $\mu$mol/kg, that is, for groundwater equilibrated with an atmosphere containing 0.2 and about 0.04 atm $O_2$. Below 50 $\mu$mol $O_2$/kg, the fraction of iron retained in the weathering profile decreases rapidly.

The best indicator of the actual degree of iron retention in the Kuruman Iron Formation during weathering is probably the ratio of iron to SiO$_2$ in the iron-formation. Figure 5 shows the range of this ratio in samples of unweathered (O) and of weathered (□) Kuruman Iron Formation as calculated from the data in tables 3 and 4. The number of analyses of each facies refers to those of unweathered iron-formation: the error bars indicate standard deviations calculated as described in the captions of table 4 and figure 5. The ratio of total iron to SiO$_2$ in samples of weathered material from the several iron-formation facies falls within the range of this ratio in their unweathered equivalents. In most instances the Fe/SiO$_2$ ratio is somewhat greater in the weathered than in the unweathered material. If the Kuruman Iron Formation had consisted only of pure siderite and quartz, these data would suggest that $P_{O_2}$ in the atmosphere during weathering was in excess of 0.2 atm provided loss of SiO$_2$ during weathering was negligible.

Three lines of evidence indicate that SiO$_2$ loss from the Kuruman Iron Formation at Wolhaarkop was indeed small:

1. The individual stratigraphic units at Wolhaarkop are estimated to be only some 10 to 13 percent thinner on average than their correlates at Groenwater (see above). The small degree of thinning is easily explained solely in terms of the observed loss of CaO, MgO, and CO$_2$ during weathering. If a major amount of SiO$_2$ had been lost during weathering, the degree of thinning would have been much greater than 10 to 13 percent.

2. The beautiful preservation of delicate sedimentary features in the weathered Kuruman Iron Formation is very difficult to explain if a good deal of SiO$_2$ had been lost during weathering. Where SiO$_2$ loss has been extensive during modern weathering of this BIF, the original textures have been largely or completely destroyed.

3. The section of weathered Kuruman Iron Formation at Wolhaarkop is so thick, that groundwaters almost certainly became saturated with respect to quartz in the uppermost parts of the weathering horizon. SiO$_2$ loss was probably restricted to the upper few meters of the
weathered zone. This part of the profile may well have been stripped off prior to the deposition of the sediments that now overlie the weathered Kuruman Iron Formation. The hematite pebbles in the basal section of these sediments could well have been part of such a SiO₂-depleted paleosol.

We believe that these three lines of evidence are compelling, and that we are justified in concluding that SiO₂ loss from the section of Kuruman Iron Formation at Wolhaarkop was minor.

THE WEATHERING OF SIDERITE SOLID SOLUTION-QUARTZ IRON-FORMATION

In the derivation of the iron retention curves in figure 6 it was assumed that siderite and quartz were the only minerals in the unweathered BIF and that the siderite was pure FeCO₃. Neither assumption is valid for any of the facies of the Kuruman BIF. The siderite facies iron-formation contains ankerite in addition to siderite (see table 1), and the siderite contains significant quantities of MgO as well as small amounts of CaO and MnO. The siderite-magnetite facies contains a significant amount of magnetite in addition to impure siderite and ankerite. The above derivation of the degree of iron retention during weathering therefore needs to be modified. A completely quantitative treatment is impossible, because the solubility of minerals along the siderite-magnesite and along the ankerite-dolomite joins is not yet well defined, and because the degree of iron retention during weathering depends somewhat on the order in which the minerals within the iron-formation are weathered.

Consider first the weathering of a rock that consists of quartz and siderite with a composition equal to that of average siderite in the Kuruman BIF [Fe₀.₇₆Mg₀.₂₁Mn₀.₀₂Ca₀.₀₁][CO₃] (see table 2). This composition can be simplified without serious loss of accuracy to [Fe₀.₇₈Mg₀.₂₂][CO₃]. During dissolution, this phase reacts with H₂CO₃ to form

\[(\text{Fe₀.₇₈Mg₀.₂₂})\text{CO}_₃ + \text{H}_₂\text{CO}_₃ \rightarrow 0.78 \text{Fe}^{+²} + 0.22 \text{Mg}^{+²} + 2\text{HCO}_₃⁻.\]  

(7)

In the presence of dissolved O₂, Fe⁺² is oxidized to Fe⁺³ and is precipitated as a constituent of Fe(OH)₃ and/or FeO(OH). As above, 1 mol O₂ oxidizes 4 mol of Fe⁺². When all the O₂ has been removed by this process, the concentration of the important species in solution will be

\[m_{\text{Fe}⁺²} \approx 0\]  

(8)

\[m_{\text{Mg}⁺²} \approx 4 \times \frac{0.22}{0.78} m_{\text{O}_₂} = 1.13 m_{\text{O}_₂}\]  

(9)

\[m_{\text{HCO}_₃⁻} \approx 8 \times \frac{0.22}{0.78} m_{\text{O}_₂} = 2.26 m_{\text{O}_₂}\]  

(10)

\[m_{\text{H}_₂\text{CO}_₃} \approx m_{\text{H}_₂\text{CO}_₃} + 2.87 m_{\text{O}_₂}\]  

(11)
This solution is undersaturated with respect to the siderite solid solution. At saturation with respect to siderite

$$m_{\text{Mg}^+} = 1.13 m_{\text{O}_2}^0 + 0.28 m_{\text{Fe}^{2+}}^0$$

(12)

$$m_{\text{HCO}_3^-} = 2.56 m_{\text{Fe}^{2+}}^0 + 2.26 m_{\text{O}_2}^0$$

(13)

and

$$m_{\text{H}_2\text{CO}_3} = m_{\text{H}_2\text{CO}_3}^0 + 2.87 m_{\text{O}_2}^0 - 1.28 m_{\text{Fe}^{2+}}^0$$

(14)

The ratio $K_1/K_2$ will then be

$$\frac{K_1}{K_2} = \frac{(m_{\text{HCO}_3^-})^2}{m_{\text{H}_2\text{CO}_3} \cdot m_{\text{CO}_3^-}}$$

$$= \frac{(2.56 m_{\text{Fe}^{2+}}^0 + 2.26 m_{\text{O}_2}^0)^2}{(m_{\text{H}_2\text{CO}_3}^0 + 2.87 m_{\text{O}_2}^0 - 1.28 m_{\text{Fe}^{2+}}^0)(m_{\text{CO}_3^-})}$$

(15)

The $\text{CO}_3^-\text{H}_2\text{O}_4$ concentration depends on the solubility of the siderite solid solution. In the absence of pertinent solubility data for the siderite-magnesite solid solution, we will assume that

$$m_{\text{CO}_3^-\text{H}_2\text{O}_4} \approx K_{\text{Sid}}/m_{\text{Fe}^{2+}}^0.$$

(16)

It is unlikely that this approximation introduces a major source of error into the calculations.

Thus

$$\frac{K_{\text{Sid}}K_1}{K_2} \approx \frac{(2.56 m_{\text{Fe}^{2+}}^0 + 2.26 m_{\text{O}_2}^0)^2 m_{\text{Fe}^{2+}}^0}{(m_{\text{H}_2\text{CO}_3}^0 + 2.87 m_{\text{O}_2}^0 - 1.28 m_{\text{Fe}^{2+}}^0)}$$

$$\approx 2.4 \times 10^{-7}$$

(17)

The relationship between the initial concentration of $\text{O}_2$ in groundwater and the fraction of iron retained in the weathered iron-formation is shown in figure 7 for $P_{\text{CO}_2} = 1$, 10, and 100 times the present atmospheric level. At a given value of $m_{\text{O}_2}^0$, the curves are displaced to slightly higher degrees of iron retention from those in figure 6 for the weathering of iron-formation consisting of quartz and pure siderite. This displacement does not affect the conclusion reached earlier: that the quantitative retention of iron during weathering requires levels of $P_{\text{O}_2}$ in excess of 0.2 atm (1 PAL). It does, however, lower the value of $P_{\text{O}_2}$ required to explain any particular degree of iron retention during oxidative weathering. The groundwaters that have equilibrated with the siderite-magnesite solid solution in the above calculations are not saturated with respect to magnesite.

THE WEATHERING OF SIDERITE-ANKERITE-QUARTZ IRON-FORMATION

The carbonate facies Kuruman Iron Formation exposed below the unconformity at Wolhaarkop contains two carbonates. In parts of the
The fraction of iron retained during the weathering of siderite of composition $[\text{Fe}_{0.74}\text{Mg}_{0.22}]\text{[CO}_3\text{]}$ as a function of the initial concentration of $\text{O}_2$ in groundwater and the $\text{CO}_2$ pressure in the atmosphere with which the groundwaters equilibrated before reacting with siderite.

Stratigraphy, siderite and ankerite plus quartz account for nearly all of the sediment. In other parts of the iron-formation magnetite and/or greenalite are also abundant. In this section we explore the weathering of Kuruman Iron Formation consisting only of siderite, ankerite, and quartz. The analysis of the weathering of even this rather simple mineral assemblage is not straightforward, because the degree of iron retention during weathering depends somewhat on the relative rate of dissolution of ankerite and siderite. In this treatment we first assume that the two minerals dissolve at the same rate. We then explore the effects of the sequential dissolution of the two carbonates on the degree of iron retention at a given value of atmospheric $\text{P}_{\text{O}_2}$ and $\text{P}_{\text{CO}_2}$.

The average siderite facies (unit D) of the Kuruman Iron Formation consists of about 0.93 mol/kg of ankerite of approximate composition (Fe$_{0.52}$Mg$_{0.44}$Mn$_{0.05}$Ca$_{0.01}$)(Ca)(CO$_3$)$_2$ and about 3.74 mol/kg of siderite of approximate composition (Fe$_{0.76}$Mg$_{0.21}$Mn$_{0.02}$Ca$_{0.01}$)CO$_3$. The composition of these carbonates can be simplified, probably without a significant loss of precision, by combining the Mn in both carbonates with Mg.

During the simultaneous dissolution of siderite and ankerite, Fe$^{3+}$ released from these carbonates will be oxidized to Fe$^{3+}$ and will be precipitated as a constituent of one or more hydrous ferric oxides until all the $\text{O}_2$ dissolved in the groundwater has been consumed. The oxidation of each mole of Fe$^{3+}$ requires a quarter mole of $\text{O}_2$. Hence the increase in the $\text{H}_2\text{CO}_3$ concentration due to the conversion of FeO in siderite and ankerite will again be $4\text{m}_{\text{O}_2}$. During this process Mg$^{2+}$ and Ca$^{2+}$ are released into solution. Their release uses $\text{H}_2\text{CO}_3$ via the reactions

\[
(Mg\text{CO}_3)_{s,s} + H_2\text{CO}_3 \rightarrow Mg^{2+} + 2\text{HCO}_3^-
\]

and

\[
(Ca\text{CO}_3)_{s,s} + H_2\text{CO}_3 \rightarrow Ca^{2+} + 2\text{HCO}_3^-
\]
The concentration of $H_2CO_3$ at the end of $Fe^{+2}$ oxidation will therefore be

$$m_{H_2CO_3}^i = m_{H_2CO_3}^0 + 4m_{O_2}^0 \left[ 1 - \frac{b}{a} - \frac{c}{a} \right]$$  \hspace{1cm} (20)

where

- $a = \text{mol of FeO in siderite plus ankerite per kg of siderite facies iron-formation}$
- $b = \text{mol of MgO in the same}$
- $c = \text{mol of CaO in the same}$

From the compositional data for average siderite facies iron-formation in table 4 it then follows that

$$m_{H_2CO_3}^i = m_{H_2CO_3}^0 + 1.29 m_{O_2}^0$$  \hspace{1cm} (21)

This shows that the concentration of $H_2CO_3$ at the end of $Fe^{+2}$ oxidation is greater than the initial concentration of $H_2CO_3$ in the groundwater. That is not true for all iron-formations. When the concentration of FeO in the carbonates is sufficiently small so that $[(b + c)/a] > 1$, then $m_{H_2CO_3}^i < m_{H_2CO_3}^0$. In extreme cases

$$m_{H_2CO_3}^0 + 4m_{O_2}^0 \left( 1 - \frac{b}{a} - \frac{c}{a} \right) < 0.$$  \hspace{1cm} (22)

The $H_2CO_3$ in groundwater is then potentially exhausted before all the $Fe^{+2}$ released by the dissolution of the carbonates can be oxidized. In that case, groundwaters become saturated with respect to calcite, dolomite, or both before all their contained $O_2$ has been removed by the oxidation of $Fe^{+2}$ to $Fe^{+3}$.

During the weathering of siderite facies Kuruman Iron Formation, some siderite and ankerite are dissolved after all the $O_2$ has been removed from solution. The approximate composition of the groundwaters after steady state has been reached can be calculated in the same manner as the composition of groundwaters saturated with respect to siderite only. The ratio of the first to the second ionization constants of $H_2CO_3$ is given by the expression

$$\frac{K_1}{K_2} = \frac{(m_{HCO_3})^2}{(m_{H_2CO_3})(m_{CO_3}^{+2})}$$  \hspace{1cm} (23)

In this expression

$$m_{HCO_3} \approx 2m_{Fe^{+2}} + 2m_{Mg^{+2}} + 2m_{Ca^{+2}}$$  \hspace{1cm} (24)

The concentration of $Mg^{+2}$ at steady state is equal to the concentration of $Mg^{+2}$ at the end of $O_2$ loss plus the amount added subsequently: thus

$$m_{Mg^{+2}} = 0.39 m_{Fe^{+2}} + 1.55 m_{O_2}^0.$$  \hspace{1cm} (25)
Similarly

\[ m_{\text{Ca}^{2+}} = 0.29 \, m_{\text{Fe}^{2+}} + 1.16 \, m_{\text{O}_2} \]  \hspace{1cm} (26)

so that

\[ m_{\text{HCO}_3^-} \approx 3.36 \, m_{\text{Fe}^{2+}} + 5.42 \, m_{\text{O}_2}. \]  \hspace{1cm} (27)

The concentration of \( \text{H}_2\text{CO}_3 \) at steady state is equal to \( m_{\text{H}_2\text{CO}_3} \) minus the quantity of \( \text{H}_2\text{CO}_3 \) neutralized by reaction with siderite and ankerite after \( \text{O}_2 \) exhaustion:

\[ m_{\text{H}_2\text{CO}_3} = m_{\text{H}_2\text{CO}_3}^0 + 1.29 \, m_{\text{O}_2}^0 - 1.68 \, m_{\text{Fe}^{2+}}. \]  \hspace{1cm} (28)

The concentration of \( m_{\text{CO}_3^2-} \) at steady state is poorly defined, but is probably close to

\[ m_{\text{CO}_3^2-} \approx \frac{K_{\text{Sid}}}{m_{\text{Fe}^{2+}}} \]  \hspace{1cm} (29)

It follows that

\[ \frac{K_1 \, K_{\text{Sid}}}{K_2} \approx \frac{[3.36 \, m_{\text{Fe}^{2+}} + 5.42 \, m_{\text{O}_2}^0]^2}{[m_{\text{H}_2\text{CO}_3}^0 + 1.29 \, m_{\text{O}_2}^0 - 1.68 \, m_{\text{Fe}^{2+}}]^2} \approx 2.4 \times 10^{-7} \]  \hspace{1cm} (30)

The calculated fraction of Fe retained during the weathering of the siderite-ankerite mixture in the siderite facies of the Kuruman Iron Formation is shown in figure 8 as a function of \( m_{\text{O}_2}^0 \) for \( P_{\text{CO}_2} = 1, 10, \) and 100 PAL. The assumption made in the above derivation that \( \text{HCO}_3^- \) is the only quantitatively important anion in the groundwaters within this system is valid for the three curves except at very low values of \( m_{\text{O}_2}^0 \) at
$P_{CO_2} = 1$ PAL. Under these conditions the pH of the groundwaters is sufficiently high that the concentration of $CO_3^{2-}$ and $OH^-$ cannot be neglected.

The fraction of iron retained in the iron-formation during weathering at a given value of atmospheric $P_{O_2}$ and $P_{CO_2}$ is greater than the fraction of iron retained during the weathering of siderite-magnesite solid solutions under the same conditions. Nevertheless, iron retention in excess of 80 percent requires $O_2$ concentrations in the groundwater in excess of 50 $\mu$mol/kg and hence levels of $P_{O_2}$ in excess of 0.04 atm, that is, 0.2 PAL.

The degree of iron retention will be somewhat different if ankerite and siderite react sequentially rather than simultaneously with groundwater. If siderite reacts more rapidly with groundwater than ankerite, the degree of iron retention during siderite dissolution will be given by the curves in figure 7 for iron retention in iron-formation consisting only of siderite-magnesite solid solution. The retention of iron during ankerite dissolution is more complete than the retention of iron during the dissolution of siderite-magnesite solid solutions. However, even if iron retention is complete during ankerite dissolution, the fraction of iron retained during the weathering of the siderite-ankerite mixtures will be intermediate between the iron retention during the weathering of siderite iron-formation alone and the fraction of iron retained following the simultaneous dissolution of siderite and ankerite during the weathering of the two-carbonate iron-formation.

**THE WEATHERING OF SIDERITE-ANKERITE-MAGNETITE-QUARTZ IRON-FORMATION**

All the unweathered facies of the Kuruman Iron Formation contain some magnetite, a mineral that enhances the degree of iron retention during the weathering of carbonate facies iron-formation. Each mol of magnetite contains one mol of Fe$^{+2}$ and two moles of Fe$^{+3}$. In the absence of $O_2$, all the Fe$^{+2}$ released during the dissolution magnetite is apt to be removed in solution via the reaction

$$Fe_3O_4 + 2H_2CO_3 + (n - 1) H_2O$$

$$-Fe^{+2} + 2HCO_3^- + Fe_2O_3 \cdot nH_2O \quad (31)$$

The fraction of iron retained is 0.67. When $O_2$ is present in the weathering groundwaters, $F$ lies between 0.67 and 1.00, and nearly complete iron retention is readily attainable. However, precise calculations of $F$ require a knowledge of the phase or phases containing the Fe$^{+2}$ formed by the oxidation of Fe$^{+2}$ released during the weathering of magnetite. This information is not available. All the Fe$^{+3}$ in the weathered Kuruman Iron Formation is now a constituent of hematite, which was probably not the original Fe$^{+3}$ mineral precipitated during weathering.

If goethite was the Fe$^{+3}$ mineral precipitated during weathering, and if the groundwaters became saturated with respect to this phase and
magnetite, then equilibrium was attained in the reaction

$$\text{Fe}_3\text{O}_4 + 2\text{H}_2\text{CO}_3 \rightarrow \text{Fe}^{+2} + 2\text{HCO}_3^- + 2\text{FeOOH}$$  \hspace{1cm} (32)

The equilibrium constant for this reaction is approximately

$$\frac{m_{\text{HCO}_3^-}^2 \cdot m_{\text{Fe}^{+2}}}{m_{\text{H}_2\text{CO}_3}^2} \approx 10^{-5.06}$$  \hspace{1cm} (33)

Since in these groundwaters

$$2m_{\text{Fe}^{+2}} \approx m_{\text{HCO}_3^-}$$  \hspace{1cm} (34)

their composition can be calculated readily. The fraction of iron retained can then be determined from the expression

$$F = \frac{12m_{\text{O}_2}^0 + 2m_{\text{Fe}^{+2}}}{12m_{\text{O}_2}^0 + 3m_{\text{Fe}^{+2}}}$$  \hspace{1cm} (35)

where $m_{\text{O}_2}^0$ is the concentration of $\text{O}_2$ in the groundwaters before reacting with magnetite. The results are plotted in figure 9. The degree of iron retention is in excess of 0.80 for all values of $P_{\text{CO}_2}$ between 1 PAL and 100 PAL provided $m_{\text{O}_2}^0 > 17 \mu\text{mol/kg}$, that is, $P_{\text{O}_2} > 0.014$ atm. (0.07 PAL). These calculations go far toward explaining the high degree of iron retention during the oxidation of oxide facies Kuruman Iron Formation at Wolhaarkop. They are, however, incomplete, because this facies contains a significant amount of siderite and ankerite in addition to magnetite.

The effect of the presence of magnetite on the degree of iron retention in iron-formation that contain siderite and ankerite depends on the order in which the minerals are attacked by groundwater. If they

![Graph](image_url)

**Fig. 9** The fraction of iron retained during the weathering of magnetite to goethite as a function of the initial concentration of $\text{O}_2$ in groundwaters and the $\text{CO}_2$ pressure in the atmosphere with which the groundwaters equilibrated before reacting with magnetite.
are attacked simultaneously, the presence of magnetite enhances the degree of iron retention, because two-thirds of its iron is already in the Fe$^{2+}$ state, and because CO$_2$ is not generated during the dissolution of magnetite. The amount of CO$_2$ added to groundwaters during the oxidation of Fe$^{+2}$ in iron formations is therefore not 4mO$_2$ but 4 $\eta$mO$_2$, where $\eta$ is the fraction of Fe$^{+2}$ in the unweathered iron formation present in carbonate phases:

$$\eta = \frac{(m_{Fe+2})_{carb.}}{(m_{Fe+2})_{carb.} + (m_{Fe+2})_{mag.}}.$$  

(36)

In the siderite facies Kuruman Iron Formation $\eta \approx 0.84$. It can be shown that the reduction of CO$_2$ generation by 16 percent due to the presence of magnetite in this facies produces a small increase in iron retention. The increase is too small to be of significance in the interpretation of the oxidized Kuruman Iron Formation. A similar, small increase in F would be observed if magnetite reacted with groundwaters after, rather than together with, siderite and ankerite.

THE WEATHERING OF IRON-FORMATIONS CONTAINING GREENALITE

Greenalite is common in facies A of the Kuruman Iron Formation. Unfortunately, the experimental data for the solubility of greenalite are still rather unsatisfactory (see, for instance, Klein and Bricker, 1977), and the fate of SiO$_2$ released during the weathering of greenalite in the Kuruman Iron Formation is hard to gauge. It does not seem worthwhile, therefore, to calculate Fe retention curves for the greenalite-siderite-magnetite facies of the Kuruman Iron Formation.

CONCLUSIONS

The calculations described above relate the degree of iron retention during the weathering of Kuruman Iron Formation to the composition of the atmosphere during the time of weathering. For a given value of PO$_2$ and PCO$_2$ in the atmosphere during weathering of the iron-formation, the degree of iron retention was found to increase from iron-formation consisting of quartz plus pure siderite, to quartz plus siderite-magnesite solid solution, to quartz plus siderite and ankerite, to quartz plus siderite, ankerite, and magnetite. The last of these assemblages corresponds most closely to that of several of the facies of Kuruman Iron Formation weathered at Wolhaakop. As pointed out above, the calculated values of the iron retention as a function of PO$_2$ and PCO$_2$ for these facies can only be regarded as reasonable approximations.

Comparison of the Fe/SiO$_2$ ratio of the weathered facies with that of the corresponding unweathered facies of the Kuruman Iron Formation indicates that iron loss during weathering was minor in all the facies. In several facies, the Fe/SiO$_2$ ratio of the weathered iron-formation is greater than the mean value of the Fe/SiO$_2$ ratio in their unweathered equivalent, but all the Fe/SiO$_2$ ratios in the weathered iron-formation
fall within the likely range of the Fe/SiO$_2$ values in their unweathered counterparts. If iron retention during weathering of the Kuruman Iron Formation were essentially complete, the O$_2$ content of the atmosphere must have been equal to or greater than the present value of 0.2 atm. The most likely estimate of the minimum value of P$_{O_2}$ during weathering may be derived from the degree of iron retention in the siderite facies iron-formation. The Fe/SiO$_2$ ratio of a weathered section of this facies is about 70 percent of the mean Fe/SiO$_2$ ratio for the unweathered siderite facies. This indicates an initial O$_2$ concentration of 37 $\mu$mol/kg in groundwater at an atmospheric CO$_2$ pressure of 10 PAL and about 100 $\mu$mol/kg groundwater at an atmospheric CO$_2$ pressure of 100 PAL. Other oxidants, such as H$_2$O$_2$, were probably present in much lower concentrations (Kasting, Holland, and Pinto, 1985). P$_{O_2}$ values at equilibrium with such groundwaters are about 0.03 atm (0.15 PAL) and 0.08 atm (0.40 PAL) respectively. These values are somewhat uncertain, but they are consistent with the minimum value of P$_{O_2}$ suggested by the complete oxidation of iron in the 1.85 by old Flin Flon paleosol (Holland, Feakes, and Zbinden, 1989). They are much higher than the value suggested for P$_{O_2}$ 2.2 by ago by the extensive loss of iron during the weathering of the Hekpoort paleosol (Button, 1979; Button and Tyler, 1981; and Hart, ms).

These data, taken together, indicate that the O$_2$ content of the atmosphere rose dramatically about 1.9 bybp. As pointed out earlier, Preston Cloud proposed such a rise a number of years ago. It now appears that the Sokoman Iron Formation, the youngest of the large Early Proterozoic iron-formation, may well have been deposited just before the rise of atmospheric O$_2$ 1.9 bybp (Hoffman, 1988). This is consistent with the view that iron-formation form only when the deeper parts of the oceans are oxygen-free, a condition that probably prevailed more than 2.0 by ago, but that may well have disappeared after the rise in P$_{O_2}$ about 1.9 bybp. The late Precambrian Urucum and Rapitan Iron Formations (James and Trendall, 1982) may signal a relatively brief return to the marine conditions that prevailed more than 2.0 bybp.

The changes in the geochemistry of uranium ores approx 2.0 bybp are also consistent with a major increase in P$_{O_2}$ at that time (see for instance Holland, 1984, chap. 7). The formation of large uranium deposits containing what is almost certainly detrital uraninite is difficult to explain in the presence of current levels of P$_{O_2}$ (Grandstaff, 1980). On the other hand, the large hydrothermal uranium deposits that began to be formed at least as long ago as 1.5 bybp are difficult to explain without invoking very significant O$_2$ levels in the atmosphere. It has always been difficult to quantify the upper limit of P$_{O_2}$ that permits the formation of Blind River and Witwatersrand-type uranium ores and the lower limit of P$_{O_2}$ that is required for the formation of the hydrothermal Athabasca-type uranium ores. It now appears that the evidence for P$_{O_2}$ levels in the atmosphere from normal paleosols and from weathered iron-formation will finally set at least semiquantitative limits on the O$_2$ content of the
atmosphere during the Precambrian. The data from the oxidized Kuruman Iron Formation at Wolhaarkop suggest that $P_{O_2}$ was at least 0.03 atm 1.9 bybp and that it may have been comparable to the $O_2$ content of the present atmosphere at that time.

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