Genesis of ferruginous concretions in a ferric soil and implications for past and present iron mobility

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Abstract
Theories on the genesis of ferruginous concretions in soils and weathering profiles continue to be debated. In particular, whether concretions represent *in situ* pedogenesis or are transported residues of 'laterite' weathering or ferricrete formation is unclear. In this study we use detailed field, micromorphological, geochemical and mineralogical investigations of a ferric soil profile from the Fraser Coast of Queensland to show that ferruginous concretions are of transported origin, and have been modified since deposition. The study found no evidence for a postulated Miocene 'laterite' weathering episode in this area; preserved primary minerals such as microcline show that the concretions are derived from reworked ferricrete rather than laterite.

Key Words
Pisolith, transport, ferricrete, laterite, iron mobilisation, in situ.

Introduction
As defined in the Australian Soil Classification (Isbell 2002), soils or soil horizons which contain a high proportion of ferruginous concretions (pisoliths) are 'ferric'. However, considerable controversy surrounds the origin of ferruginous concretions in soils and weathering profiles, in particular whether they have formed *in situ* or have been transported to their present locations (Bourman 1993b). Workers such as Tardy and Nahon (1985) and Muller and Bocquier (1986) propose *in situ* concretion formation. In this model the progressive formation of concretions in laterite weathering profiles can be traced from the mottled subsurface horizons to the surface. In contrast, other studies emphasise the role of erosion in the formation of concretions. Here, concretions result from the physical breakup of iron (Fe) duricrusts and ferruginised mottles, and their transport and modification in the soil and surface environments. In effect, this latter model considers concretions to be the breakdown product of either ferricrete or laterite materials (Bourman 1993a). These are dissected, eroded and redeposited at a lower landscape position, forming a new generation of mechanically accumulated ferricrete (Widdowson 2008). The current study investigates the genesis and processes currently affecting ferruginous concretions in the ferric soils of a coastal catchment in Australia. The concretions are considered the largest Fe reservoir in the surficial soils and sediments of the study area. Consequently, their genesis has clear implications for the past and current mobility of Fe. The potential for Fe remobilisation throughout the catchment has down-stream implications for coastal seawater chemistry and possible detrimental environmental ramifications. To this end, we determine field relationships, micromorphology, geochemistry and mineralogy of a soil profile exposed in an 'iron-stone gravel' quarry.

Setting
The 2.5 m deep soil profile investigated here is located in the Poona Creek catchment, on the Fraser Coast of Queensland (Figure 1A). The region lies 300 km north of Brisbane, and has a subtropical climate. Bedrock is quartzose sandstone of the Late Triassic-Early Jurassic Dunkinwilla Group (Cranfield 1994), which has been deeply weathered since the Miocene. Limited previous investigations suggest that soils in the study area are varied, but a sequence of Red Kandosols and Kurosols on hilltops, Red and Yellow Kandosols or Kurosols (often ferric) at midslope to footslope positions and Redoxic Hydrosols or Semi-Aquic Podosols in poorly drained valleys and on creek margins has been observed (Coaldrake 1961). Soils commonly feature a ferric horizon or, more rarely, a cemented ferruginous duricrust. In a recent survey of the catchment 60% of samples of the top 30 cm of the soil contained ferruginous concretions, ranging from 3-47 wt% (Löhr *et al.* 2010). The ubiquity of the ferruginous concretions and duricrust within the soil profile has previously been explained by resorting to a hypothetical 'laterisation' episode in the Miocene, which is thought to have led to the development of a deep weathering profile featuring extensive laterite duricrust (Cranfield 1994). Other workers have interpreted them as recent features of in situ pedogenesis (Coaldrake 1961).

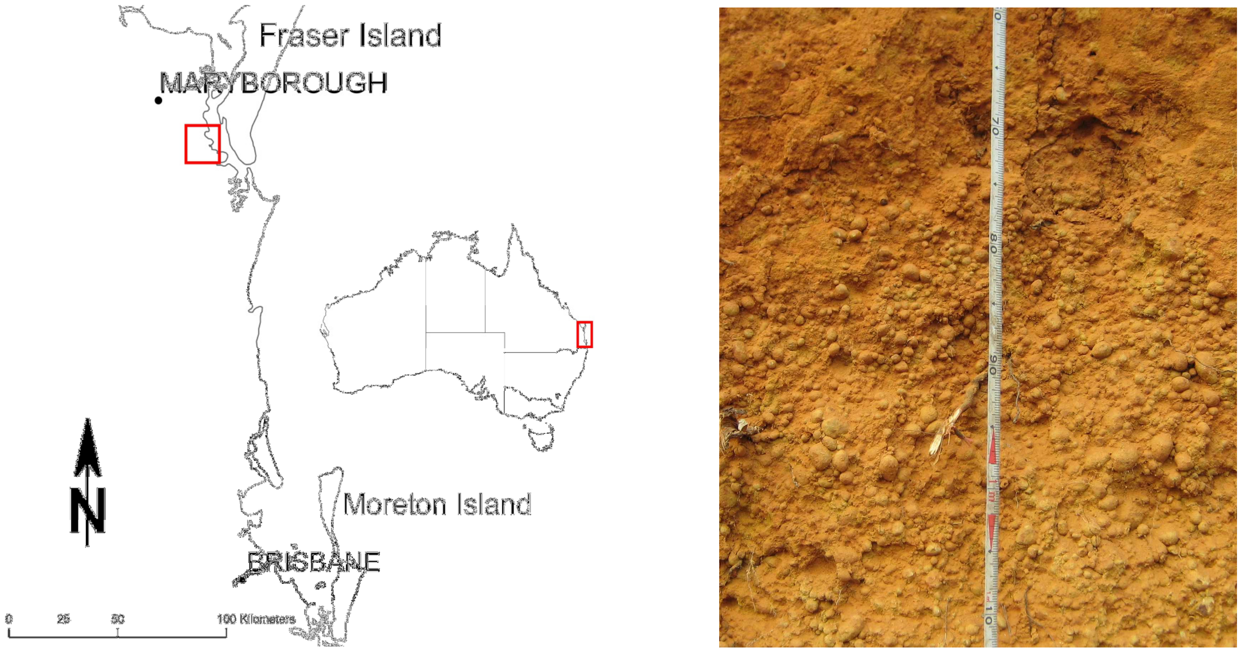

Figure 1. A) Location of the study area B) Soil profile showing ferruginous concretions in ferric horizon.

Results

The profile has been classified as a Ferric, Brown Kandosol. It features a 1 m thick ferric horizon at a depth of 75 cm (Figure 1B), as well as a surface horizon with up to 30 % concretions (Table 1). Angularity increases with depth in the ferric horizon, and occasional elongate concretions are dipping at less than 30^o or are clast supported. Ferruginised rock fragments only occur at the bottom of the profile.

Table 1. Soil profile description. Terminology after Australian soil and land survey field handbook (National Committee on Soil and Terrain, 2008).

Depth (cm)	Horizon	Colour	Description
0-15	A1	2.5 YR 4/6	Clay loam, sandy. Platy structure. Fine roots, faunal channels, bioturbation. Some concretions on surface, concentrated on bottom of horizon. 30 % concretions, matrix supported, 0.5-2 cm diameter. Subrounded –rounded. Sharp, smooth boundary.
15-55	A2	2.5 YR 4/6	Sandy clay loam. Massive, very firm structure. Fine-thick roots. Few concretions, < 5 %, 0.2-1.2 cm. Rounded, high sphericity. Diffuse boundary.
55-75	B1	2.5 YR 4/8	Clay loam. Concretions 10 % with gradual increase to bottom. 0.5 to 2 cm. Rounded, med-high sphericity. Clear, wavy boundary.
75-175	B2	7.5 YR 4/6	Clay loam. Ferric horizon. Concretions 80-90 %, clast supported. Decrease from rounded-well rounded at top, to angular-subrounded. Mostly medium-high sphericity. Elongate concretions horizontal or clast supported. Clear, irregular boundary.
175-210	CB	10 YR 5/6	Clay loam, sandy. Massive structure. Up to 50 % poorly sorted, ferruginised rock fragments, 4-8 cm in size. Sub angular-angular.
> 210	C	10 YR 5/6	As above, smaller and less frequent rock fragments. (Sandy) light-medium clay.

Concretions can be sorted into two types, based on their appearance. Most concretions are brown, with a burnished outer surface. These range from <2 mm to > 16 mm in diameter. Black concretions which are harder and often magnetised are also common. These are typically much smaller than the brown concretions and do not exceed 8 mm in diameter. The fine earth fraction, the black and the brown concretions are characterised by distinct mineralogy and composition (Table 2). Major differences are the low concentration of iron oxides and total iron in the fine earth fraction compared to the concretions, and the higher concentration of siderophile trace elements in the concretions. Polished thin sections of undisturbed material collected from all horizons, as well as representative concretions, show evidence of four types of internal arrangement. This includes: a) concentric concretions (alternating bands of distinctly coloured cementing material, sharp boundaries between bands), b) uniform concretions (uniform texture and colour, or diffuse changes), c) nucleic concretions (formed around a nucleus or incorporating a fragment or another concretion) and d) ferruginised rock fragments. Concentric and uniform concretions are most common.

Micromorphological study of the undisturbed samples and selected concretions shows: a) compound concretions, b) incomplete or broken surface coatings, c) laminae free of quartz grains, d) lenses featuring quartz grains of different size to core, surrounded by quartz-free cement. Angular concretions at depth display iron and aluminium oxyhydroxide overgrowths.

Table 2. Mineralogical (A) and selected compositional data (B) of fine earth fraction, black concretions and brown concretions. Data shown are ranges, compiled from multiple samples. Mineralogy obtained by XRD and Rietveld pattern refining, compositional data obtained by XRF.

A	Quartz^A	Microcline^A	Anatase^A	Kaolinite^A	Maghemite^A	Hematite^A	Goethite^A	Gibbsite^A	Amorph^A
Fine Earth <2mm	57-60	0-5.5	1	17-27	0	1-1.5	0-2	2-11	4-9
Black	38-39	0-1.4	0	6	17	26-31	0-2	1	5-11
Brown	28-36	0-7	0-1	16-23	0-6.5	2-7	17-24	4-12	7-20

B	SiO_2^A	$Al_2O_3^A$	$Fe_2O_3^A$	MnO^A	MgO^A	Ti^B	V^B	Cr^B	Mn^B	Co^B	Ni^B	Cu^B	Zn^B	Pb^B
Fine Earth <2mm	71.3-78.9	10.9-15.3	2.5-3.47	0.01	0.24	6524-8794	80-102	82-95	<4-15	<2-5	6-8	<3	13-14	<10
Black	40.1-43.9	11.8-12.7	36.7-41.5	0.01	0.24-0.25	5255-5391	643-752	378-439	50-52	<2-6	19-21	<3	9-10	86-100
Brown	37.7-46.5	16.4-22.1	19-28.6	0.01	0.22-0.23	4103-5927	456-557	177-321	<4-19	<2-12	12-18	<3	11-15	26-53

^{a} wt %; ^{b} mg/kg

Discussion

Field-based evidence such as a high proportion of elongate concretions lying horizontally, as well as a high proportion of sub-rounded to rounded clasts indicate a transported origin for the concretions investigated here. This is further supported by the marked differences between fine earth fraction and concretions. However, the compositional and mineralogical differences between morphologically distinct concretions suggest a different origin or source for different concretion types. The multiple bands or concentric rings which are typical of the larger, brown concretions also suggest a complex growth history, while the smaller concretions generally show less structural variation.

Coventry *et al.* (1983) used a range of micromorphological features to distinguish *in situ* from transported concretions. Those features which indicate a transported origin include a) incomplete or broken surface coatings, b) different particle size distributions of sand and silt grains in concretions and non-cemented matrix, c) different particle size distributions of sand and silt grains in adjacent concretions and d) compound or nucleic concretions. Milnes *et al.* (1987) also described a series of depositional multiple laminar goethite rinds on concretions, with occasional gibbsite, incorporating individual quartz grains or lenses between them as evidence of their accretionary origin. Micromorphological study of the concretions in the Poona Creek soil profile shows many of the same features, consistent with a transported origin. In fact, Milnes *et al.* (1987) suggested that deposition of the laminae and incorporation of the quartz occurs in a succession of pedogenic environments, which would be consistent with a long history of exposure, transportation and weathering.

We do not, at present, have sufficient data from other profiles to fully place this study into a landscape context (i.e. toposequence). Nevertheless, based on the micromorphological, geochemical, mineralogical and field evidence presented here, it is likely that the concretions have been transported prior to deposition and that they were formed by the physical break-up of pre-existing ferruginous materials. There is also sufficient evidence to identify the original type of ferruginous material. Microcline is a relatively unstable mineral, especially in the aggressive weathering conditions of the upper laterite weathering profile in which residual laterite duricrust forms. The fact that microcline has been identified in some of the concretions suggests that the concretions are the reworked residuum of earlier generations of ferricrete, in which microcline was preserved by coating with Fe oxides, rather than a lateritic residuum (Widdowson 2008). Comparison of the chemical composition and mineralogy of the concretions in this study with those in other studies (mostly formed by lateritic weathering) show that the Poona catchment Fe-concretions are similar in mineralogy but relatively poor in most trace elements. They are, however, within the compositional range expected, assuming that they have formed through ferruginisation by allochthonous inputs of iron into the Duckinwilla Group parent material. ‘Laterisation’ is very unlikely to have been widespread in the study area, as the quartz- and kaolinite-rich sandstones of the Duckinwilla Group are unlikely to have contained sufficient iron for laterite duricrust formation (Widdowson 2008).

Based on this information and the evidence that the concretions are indeed transported residuum, it is unlikely that the study area has in fact been subject to a deep lateritic weathering event, as previously suggested (Cranfield 1994). A more suitable explanation is perhaps that of Bourman (1993b), which provides a model of long-term continual weathering that leads to ferruginisation and the formation of ferricrete in lower landscape positions. Bourman argues that this better explains the occurrence of ferruginous materials in much of southern and eastern Australia. There is also evidence of more recent mobilisation of iron within the profile. The increase in angularity of concretions at lower levels of the ferric horizon, as well as the occurrence of ferruginised rock clasts in the bottom horizons, suggests that mobilisation of iron has occurred since deposition of the concretions, and has resulted in overgrowths and ferruginisation of the rock fragments.

Conclusions

The concretions are most likely to be of transported origin and can be regarded as clastic components, which formed outside the material in which they are currently found. They have been modified since their deposition by re-mobilisation of iron and re-precipitation further down the profile. These processes have resulted in iron oxyhydroxide overgrowths on some concretions and the ferruginisation of rock fragments in lower horizons. Thus, the concretions are contributing to Fe cycling processes in many ferric soils. Mineralogical and geochemical evidence suggests the concretions are originally derived from reworked ferricrete duricrust, rather than reworking of laterite duricrust. There is therefore no evidence for a Miocene ‘laterite’ weathering episode preserved in the study area.

References

Bourman RP (1993a) Modes of ferricrete genesis-evidence from southeastern Australia. *Zeitschrift für Geomorphologie* **37,** 77-101.

Bourman RP (1993b) Perennial Problems in the Study of Laterite-A Review. *Australian Journal of Earth Sciences* **40,** 387-401.

Coaldrake JE (1961) 'The Ecoystem of the Coastal Lowlands ("Wallum") of Southern Queensland'. (CSIRO: Melbourne)

Coventry RJ, Taylor RM, Fitzpatrick RW (1983) Pedological significance of the gravels in some red and grey earths of central North Queensland. *Australian Journal of Soil Research* **21,** 219-240.

Cranfield LC (1994) '1:250000 Geological Series-Explanatory Notes. Maryborough, Queensland. Sheet SG56-6'. (Geological Survey of Queensland: Department of Minerals and Energy).

Isbell RF (2002) 'The Australian Soil Classification'. (CSIRO Publishing: Melbourne).

Löhr SC, Grigorescu M, Hodgkinson JJ., Cox ME, Fraser SJ (2010). Iron occurrence in soils and sediments of a coastal catchment. A multivariate approach using self organising maps. Geoderma **156,** 253- 266.

Milnes AR, Bourman RP, Fitzpatrick JW (1987) Petrology and mineralogy of 'laterites' in southern and eastern Australia and southern Africa. *Chemical Geology* **60,** 237-250.

Muller JP, Bocquier G (1986) Dissolution of kaolinites and accumulation of iron oxides in lateritic-ferruginous nodules: mineralogical and microstructural transformations. *Geoderma* **37,** 113-136.

National Committee on Soil and Terrain (2008) 'Australian soil and land survey field handbook'. (CSIRO Publishing: Melbourne).

Tardy Y, Nahon D (1985) Geochemistry of laterites, stability of Al-goethite, Al-hematite and Fe-kaolinite in bauxites and ferricretes: an approach to the mechanism of concretion formation. *American Journal of Science* **285,** 865-903.

Widdowson M (2008) Laterite and Ferricrete. In 'Geochemical Sediments and Landscapes'. (Eds DJ Nash, SJ McLaren) pp. 46-94. (Wiley-Blackwell: Chichester).