The Origin and Significance of the Hematization of Silicic Rocks of Precambrian and Ordovician age in South Shropshire

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Abstract: Secondary hematite impregnates quartz-rich sandstones and acid to intermediate volcanics of Ordovician and Precambrian age in South Shropshire. A Triassic red-bed cover, or the sideritic Upper Carboniferous Coed-yr-Allt beds are proposed as the source of the iron. A comparison is made with similarly hematized silicic rocks of the Charnian Supergroup in the East Midlands. A geochemical model based on solution chemistry is proposed for the mobilization of iron from iron-rich minerals and rocks leading to the hematization of silicic rocks.

Spasmodic hematization as stains and cavity fill occurs along the Stiperstones ridge on the eastern margin of the Ordovician Shelve inlier (Moseley, 1991, 1992), within the Precambrian Longmyndian inlier and at Wart Hill (Moseley, 1981), a Uriconian inlier within the Church Stretton Fault System (Fig. 1).

This paper describes localities where hematization has occurred, discusses the source of the iron, and proposes a geochemical model to explain the preferential hematization of silicic rocks. The stratigraphical significance of this phenomenon is briefly reviewed. The hematite staining and cavity fill of silicic rocks is not a replacement process and is distinct from the hematite replacements seen in limestones in Cumbria (Rose and Dunning, 1977) and South Wales.

Location of hematization

The quartz-rich sandstones of the Stiperstones Quartzite Formation, Arenig Series (Lynas *et al.*, 1991) display hematite staining and infilling of silicified joints, fractures and small cavities. This is strongly developed near Manstone Rock (locality 1, SO 3675 9859, Fig. 1) where there are also traces of the secondary copper minerals malachite, azurite and bornite.

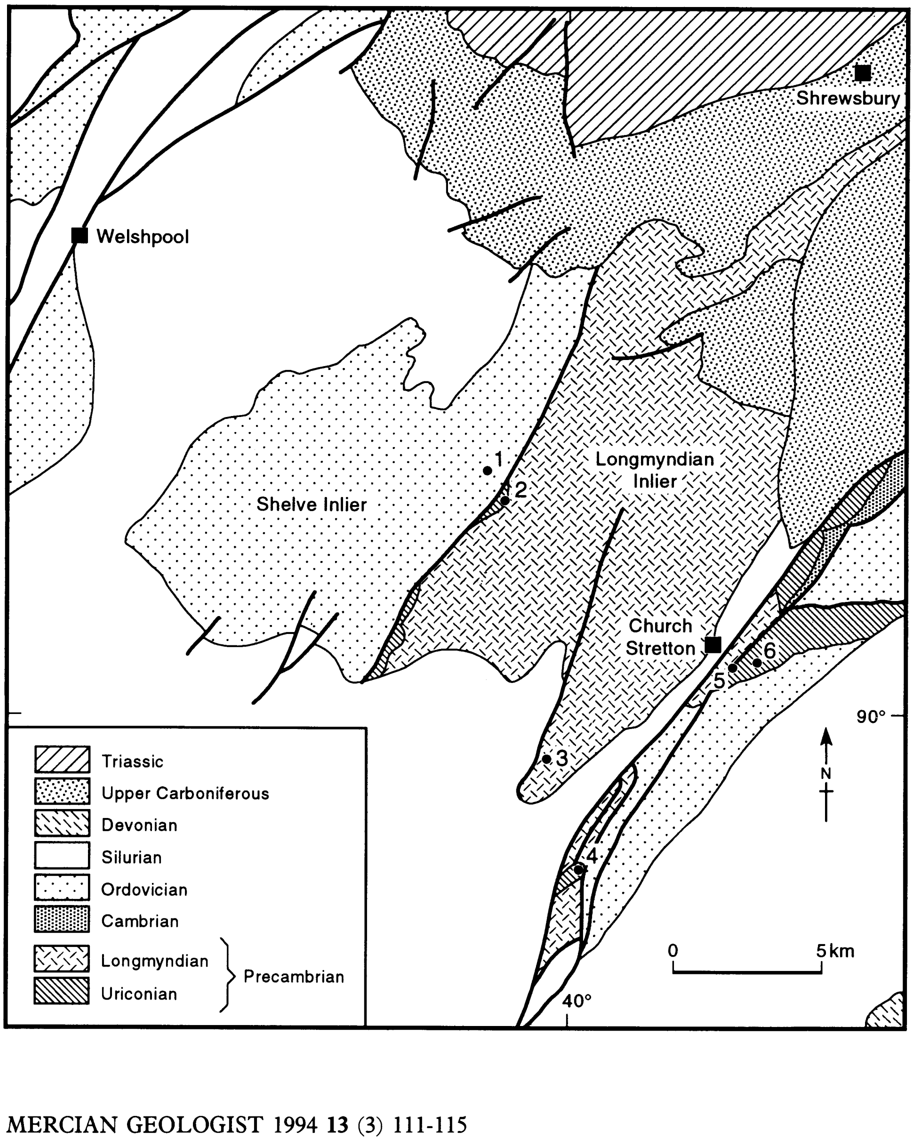

Fig. 1. Geological sketch map showing localities where Precambrian and Ordovician rocks have been hematized.

Two fault-bounded slivers of Precambrian volcanics, along the Pontesford Lineament at The Knolls (Linley Formation of Pauley, 1991; locality 2, SO 3711 9741, Figs 1 and 2) and within the Church Stretton Fault System at Wart Hill (Uriconian Volcanic Complex, locality 4, SO 4009 8471, Figs 1 and 3) display hematization. At The Knolls hematized rhyolitic crystal tuffs with malachite-stained fractures are faulted against coarse-grained Longmyndian sandstones. The fault gouge contains strings of tabular barite. At Wart Hill rhyolites and amygdaloidal andesites are hematized. The amygdales are hematite, although adjacent basalts show no evidence of hematization. Hematite in the rhyolites has been attributed to the weathering of magnetite (Greig *et al.*, 1968).

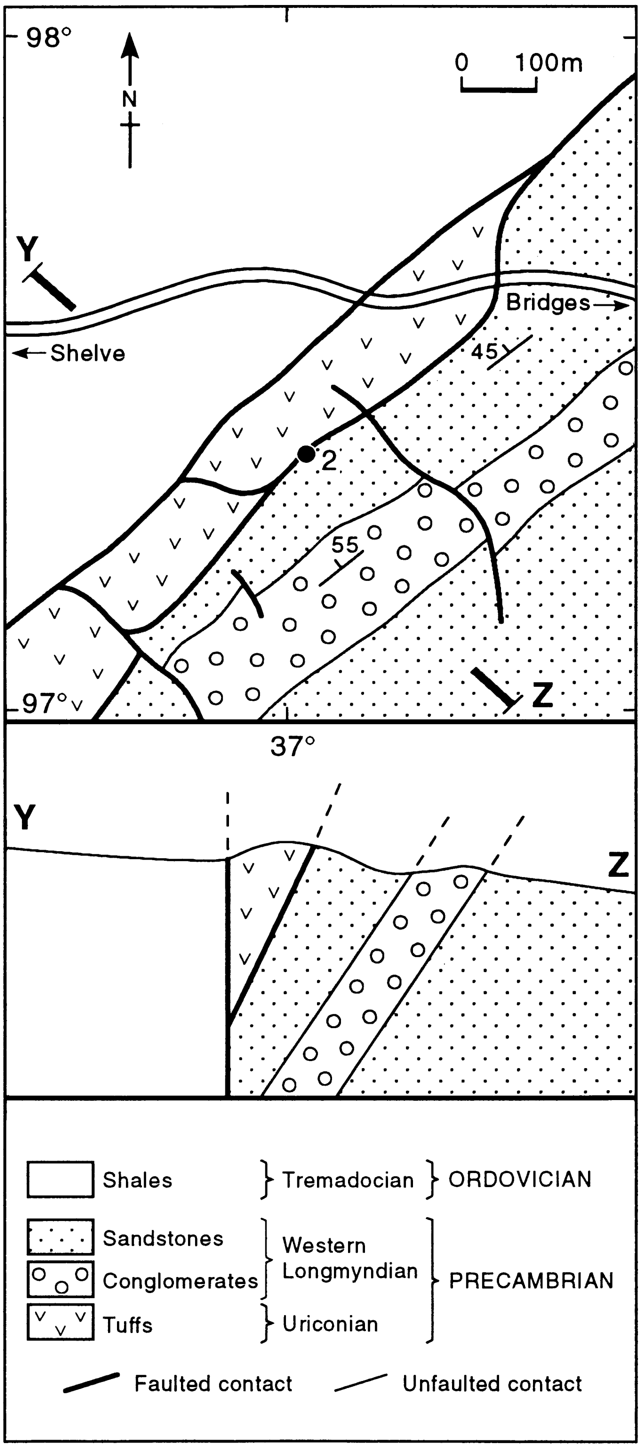

Fig. 2. Geological sketch map of part of The Knolls area showing the position of locality 2.

Hematization of the Uriconian Volcanic Complex is evident next to the B4371 between Church Stretton and Hope Bowdler where andesites are hematite-stained (locality 6, SO 4712 9268, Fig. 1). At Hazler Quarry (locality 5, SO 4631 9243, Fig. 1) the Caradoc infill of Neptunian dykes within Uriconian basalts displays a hematite matrix. Near Myndtown (locality 3, SO 3896 8873, Fig. 1) along part of the line of the Western Longmynd boundary fault, Longmyndian shales and sandstones with sparse malachite-barite occurrences are hematized.

All of these localities are adjacent to faults or within fault complexes and duplexes (Cocks, 1989; Lynas, 1988, 1991; Woodcock and Fischer, 1986), which may have acted as channels for migrating solutions containing iron and copper. None of these hematite occurrences are economically viable.

Possible sources of iron

A hematite-rich or sideritic sedimentary cover now removed by erosion may have been the source of the iron. Red Triassic strata and the partly sideritic Coed-yr-Allt beds of Upper Carboniferous age crop out adjacent to the northern margins of the Shelve and Longmyndian inliers, and the Coed-yr-Allt beds also occur within the Church Stretton Fault System 3 km north of Church Stretton (Fig. 1). Old Red Sandstone strata crop out 15 km to the east and south-east of the Longmyndian inlier.

Oxidation of sedimentary pyrite in the Mytton Flags Formation, which overlies the Stiperstones Quartzite Formation, may also have mobilized iron. Near Stiperstones village (SO 3562 9973) mudstones contain traces of sedimentary pyrite, and are strongly limonitized. The limonite is an oxidation product of the pyrite. Similarly, alteration of the small quantities of pyrite and chalcopyrite found in association with the galena-sphalerite-barite-calcite-quartz veins that cut the Mytton Flags Formation might have made iron available. This may explain the association of hematite with secondary copper minerals in the Stiperstones Quartzite Formation, with these minerals deposited in a zone of weak oxidation.

Dolerites cut the Ordovician succession of Shelve and the Longmyndian Supergroup, and also occur in the Uriconian Volcanic Complex. There may well be more that are not exposed (Dines, 1958). The weathering of these dolerites, well advanced at some localities, would have released iron compounds through the alteration of olivine and pyroxenes. Deeply weathered dolerites at Wart Hill cut hematized rhyolites and are 150m south-east of the hematized andesites (Fig. 3).

The quartz-arenites of the Stiperstones Quartzite Formation contain detrital magnetite, the decomposition of which produces purple-red hematite stains and 'blushes'. However, a red-bed or sideritic cover is the most likely source of most of the iron. The other possible sources are of only limited extent.

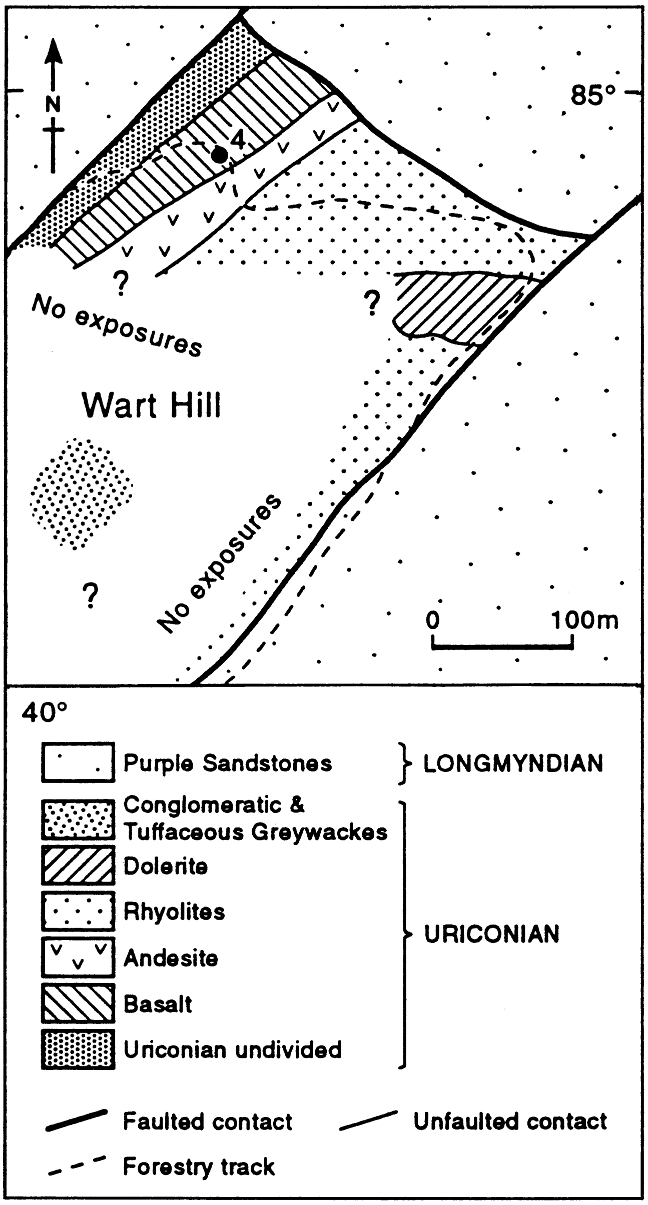

Fig. 3. Geological sketch map of Wart Hill showing the position of locality 4.

A geochemical model for the mobilization of iron from a red-bed or iron-rich cover

Although Fe_2O_3 is a stable mineral, hydrated Fe_2O_3 is susceptible to acid attack by H_2CO_3, H_3O^+ (Krauskopf, 1989) and presumably weak acids where pK_a values are small.

The following cycle is proposed as iron is carried downwards mainly in solution from the parent red bed. The letters in parentheses denote the state of compounds, (l) — liquid, (s) — solid, (g) — gas and (aq) — in solution.

$$Fe_2O_3.H_2O(s) + 6H_3O^+(aq) = 2Fe^{3+}(aq) + 10H_2O(l)$$

$$Fe^{3+}(aq) + 6H_2O(l) = [Fe^{III}(H_2O)_6]^{3+}(aq) + H_3O^+(aq)$$

$$[Fe^{III}(H_2O)_6]^{3+}(aq) + 3H_2O(l) \rightleftharpoons [Fe^{III}(H_2O)_3(OH)_3]^0(aq) + 3H_3O^+(aq)$$

$$2[Fe^{III}(H_2O)_3(OH)_3]^0(aq) = Fe_2O_3.nH_2O + (9-n)H_2O(l)$$

The mobility of $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$ is controlled by acidity and carbonation. The usually weakly acidic character of groundwater enhances the solubility, and hence migration, of both $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$. Once in solution the polarising potential of $Fe^{2+}(aq)$ and especially $Fe^{3+}(aq)$, even with concentrations of only $1 \times 10^{-5}M$, will continue to enhance acid conditions according to the following equation:

$$[Fe^{III}(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe^{III}(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$$

and on the basis of the ionic product of H_2O, $Kw = [H^+]\,[OH^-] = 10^{-14}mol^2l^{-2}$ where $[H^+] = [OH^-] = 10^{-7}\ mol.l^{-1}$ but $Fe^{3+}(aq) + 3OH^-(aq) = Fe(OH)_3(s)$, so $[H^+] > [OH^-]$. Within any of these systems iron hydroxide (hydrated Fe_2O_3) compounds and complexes are not necessarily lost by precipitation. $Fe(OH)_3$ is precipitated only when $pH \simeq$ or > 3. Colloid chemistry allows for the mobilization of $Fe(OH)_3$ by peptization or as hydrated Fe_2O_3 as a stable sol with associated ions or organic matter.

Laboratory studies show that OH-containing Fe complexes are attacked by $H_2CO_3(aq)/CO_2(g)$ producing $Fe^{3+}(aq)$ suggesting a cycle as indicated by

$$[Fe^{III}(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe^{III}(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$$

$$[Fe^{III}(H_2O)_5OH]^{2+}(aq) + CO_2(g) + H_2O(l) \rightleftharpoons [Fe^{III}(H_2O)_6]^{3+}(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) + H_3O^+(aq) \rightleftharpoons CO_2(g) + 2H_2O(l)$$

Should overlying strata be sideritic, then $Fe^{2+}(aq)$ may be mobilized according to

$$FeCO_3(s) + H_2CO_3(aq) \rightleftharpoons Fe^{2+}(aq) + 2HCO_3^-(aq)$$

Eventually $Fe^{2+}(aq)$ will be oxidized according to $2Fe^{2+}(aq) + 4HCO_3^-(aq) + \tfrac{1}{2}O_2 + H_2O(l) = Fe_2O_3(s) + 4H_2CO_3(aq)$ (Krauskopf, 1989).

Slight shifts in Eh-pH conditions for groundwater can influence the equilibrium, $Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq)$, which represents an essentially closed system utilizing the bridging ligand/outer sphere transfer theory. A bridging H_2O – ligand is seen as a 3d-electron carrier so that $(OH_2)_5Fe^{3+}(H_2O)$ —≡— $Fe^{2+}(H_2O)_5$. A shift in Eh-pH may disrupt this equilibrium system so that the Fe can be circulated as suggested above.

The role of anaerobic bacteria as agents acting as siderophores, which bind Fe^{3+} in soluble complexes or oxidize Fe^{2+} to Fe^{3+} so as to release iron in the soluble form of salts of weak organic acids, should not be overlooked. Some modern bacteria are known to fulfil these functions, e.g. *Thiobacillus thiooxidans*, *T. ferrooxidans*, *Gallionella ferruginea* and *Leptothrix ochracea* (Schegel, 1986). An impermeable horizon, or a water table level within a red bed, may promote local anaerobic conditions.

Laboratory studies carried out by the writer involving porous hematized sand/iron-deficient sand and Fe_2O_3/sand systems showed that percolating groundwater may be capable of carrying fine material, e.g. clay/Fe_2O_3 mixes, downwards with no chemical change. Thus eluvial Fe_2O_3 may be carried below the parent red bed before suffering anaerobic or non-organic chemical action.

The deposition of Fe_2O_3 is most likely accomplished by the dehydration of $Fe(OH)_3$, or OH-containing iron complexes mainly in the zone of oxidation. This goes some way to explaining the hematite-malachite association at some localities.

$$2Fe(OH)_3(s) = Fe_2O_3(s) + 3H_2O(l)$$

$$2[Fe^{III}(H_2O)_3(OH)_3]^0(aq) = Fe_2O_3(s) + 9H_2O(l)$$

The preferred hematization of silica-rich rocks is not easily explained. An almost monomineralic environment of stable SiO_2 seems to promote Fe_2O_3 deposition. The negative dipole on the SiO_4^{4-} unit cell in quartz may attract iron complexes and sols with a positive dipole. The examples of iron as the major impurity in citrine as colloidal $Fe(OH)_3$ and in amethyst as Fe_2O_3 possibly support this interpretation.

The Charnian Supergroup: a red-bed cover analogue

A red bed origin for the hematite impregnations described above is supported by comparison with the highly silicic rocks of the Precambrian Charnian Supergroup of Leicestershire which are overlain unconformably by red Triassic breccias, sandstones and mudstones. In the Charnian it is the rocks high in silica that are the most strongly hematized. Euhedral quartz phenocrysts in rhyolitic and dacitic porphyries of the Whitwick Complex at High Sharpley, near Whitwick, are fractured, probably due to rotation in the plane of the cleavage. The fractures are strongly hematized giving a red colouration to the phenocrysts, and the porphyries are also hematized along the slaty cleavage. Silicified rhyolitic dust tuffs of the Blackbrook Group are hematized along the cleavage, bedding and minor fractures. Quartz-rich sandstones of the Stable Pit Quartz Arenite Member of the Brand Group are locally hematized. Charnian pelites and intermediate volcanics are only reddened very close to the Precambrian/Triassic unconformity; elsewhere such rocks are only limonitized (Moseley and Ford, 1985, 1989).

Discussion: age of a red-bed cover for part of South Shropshire

There are a number of possible ages for the postulated red-bed cover of the Shelve and Longmyndian inliers.

Llandovery strata rest unconformably on the Ordovician strata of Shelve and on the Longmyndian Supergroup and may have been succeeded by the unbroken Silurian to Lower Devonian (partly red-bed) succession seen elsewhere in the Welsh Borderland. The Shelve inlier is immediately adjacent to sandstones and conglomerates of the Wentnor Group (Longmyndian) which contains detrital magnetite, sometimes weathered to hematite (Greig *et al.*, 1968). It seems unlikely however that Precambrian might have overlain Ordovician as this would involve a complex structural re-interpretation of the Pontesford Lineament, which juxtaposes the Shelve and Longmyndian inliers. The Pontesford Lineament is an element of the Welsh Borderland Fault System which is now interpreted as a possible terrane boundary (Woodcock, 1984; Woodcock and Gibbons, 1988).

A red-bed cover of Triassic strata and/or the Upper Carboniferous Coed-yr-Allt beds which contain sideritic nodules presents the most tenable explanation for the hematization. The Coed-yr-Allt beds are unconformable on Arenig and Longmyndian strata on the northern edges of the Shelve and Longmyndian inliers and are faulted against Uriconian Volcanics within the Church Stretton Fault System (Fig. 1). Triassic strata crop out 10 km to the north near Shrewsbury, and extend northwards into Cheshire and Merseyside. Natural bitumens that stain barite-sulphide deposits in Shelve, some Stiperstones sandstones (Murchison, 1854; Ricketts, 1885) and some Longmyndian rocks are thought to have been sourced from Carboniferous sediments (Parnell, 1987). On this evidence it is probable that at least some of the iron that promoted the hematization described above originated from siderite in Upper Carboniferous strata.

Although now occurring in areas topographically lower than some Lower Palaeozoic and Precambrian formations the former extent of the Coed-yr-Allt beds remains uncertain. Parnell (1987) suggested the possibility of a lateral or obliquely upward migration of hydrocarbons to allow for the possibility that the Longmyndian and Shelve inliers were not completely covered by Carboniferous strata. It is uncertain if iron-containing solutions, derived from some of the sideritic Coed-yr-Allt beds, would have followed a similar pathway. The stratigraphically and topographically higher Triassic strata might therefore be the more likely source of iron.

Locality 1 on the Stiperstones ridge is topographically only 8 m lower than Manstone Rock, which is the highest point of both the Shelve and Longmyndian inliers. If evolved from a sideritic or red bed cover, hematization at this elevation suggests at least an almost complete former submergence of Ordovician and Precambrian areas by Carboniferous or Triassic strata.

Conclusions

(i) Hematization of silicic rocks in parts of the Shelve and Longmyndian inliers is derived from a cover of sideritic Coed-yr-Allt beds (Upper Carboniferous) and/or red beds of Triassic age.
(ii) Some iron may have been derived from the oxidation of local pyrite and chalcopyrite and the alteration of dolerites.
(iii) Quartz-rich rocks display a greater susceptibility to hematization than mineralogically more complex rocks.

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