The Redox State of Iron: A Powerful Indicator of Hydrothermal Alteration

Paul A. Studemeister

Article abstract

The redox state of iron, \( \text{Fe}^{2+}/\text{Fe}^{3+} \), in rocks is a useful indicator of hydrothermal alteration. In general, rocks are resistant to shifts in \( \text{Fe}^{2+}/\text{Fe}^{3+} \) unless large volumes of fluid or high concentrations of exotic reactants such as \( \text{H}_2 \) or \( \text{O}_2 \) are present. The earth's surface in equilibrium with the atmosphere is an oxidizing environment; surface waters carry in solution \( \text{O}_2 \) plus \( \text{SO}_4^{2-} \). Laboratory experiments conducted at high temperatures reveal that water in the presence of ferrous minerals tends to dissociate and yield free hydrogen. At depths exceeding a few kilometres, waters are hot and reducing with \( \text{H}_2 \text{O} = 1/30 \) to \( 1/60 \). In a hydrothermal convection cell, rocks along the descending limbs will be oxidized whereas rocks along the ascending limbs will be reduced by the circulating water.
The Redox State of Iron: A Powerful Indicator of Hydrothermal Alteration

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Summary
The redox state of iron, (Fe\(^{2+}\)/Fe\(^{3+}\)), in rocks is a useful indicator of hydrothermal alteration. In general, rocks are resistant to shifts in (Fe\(^{2+}\)/Fe\(^{3+}\)) unless large volumes of fluid or high concentrations of exotic reactants such as H\(_2\) or Fe\(^{2+}\) are present. The earth's surface is in equilibrium with the atmosphere, and igneous and metamorphic rocks that form at high temperature are dissolved, hydrated, and oxidized at the surface. The end product is a residue of clay minerals, feldspar, hematite, pyrite, quartz, and sericite, somewhat depleted in silica and aluminosilicates.

The hydrophile interacts with the lithosphere at spreading centres where seawater convects through oceanic crust in response to heat emanating from hot magma. It is estimated that the entire ocean mass may circulate through the oceanic crust once every 3 to 10 ma, with an average discharge temperature of water between 100°C and 300°C (Spencer, 1980). Seafloor experiments have discovered hydrothermal vents with mounds of sulphide deposits at oceanic ridges. Sites of seawater discharge of convection cells. Turbulent jets of hot, reducing brine spew out onto the seabed, mixing with ambient seawater and precipitate iron and base metal sulphide minerals (Francis et al., 1979; Spiess et al., 1980). Hydrothermal convection and metal concentration are not restricted to the oceanic lithosphere. There are geothermal systems involving the convection of meteoric water through continental crust (White, 1981); these include the Salton Sea and Red Sea fields. The fluids in modern geothermal systems are saline waters with up to around 25wt% dissolved salts, mainly halite (White, 1981; Ellis, 1979; Le Bel and Ouden, 1962).

The convection of seawater through hot basalt leads to spectacular changes to produce an altered rock called a spilite (Spencer and Fyfe, 1973; Andrews and Fyfe, 1976). Spilite has a high Fe\(^{2+}\)/Fe\(^{3+}\) ratio and the gain of Mg, Na, plus H\(_2\)O in basalt. Along the narrow ascending limbs of convection cells, the elemental exchange trends are reversed when hot, modified seawater cools and reacts with basalt (Hajash and Archer, 1980). The alteration trends observed in basalt from the sea floor resemble those reported in laboratory experiments (Bishoff and Dickinson, 1975; Hajash and Archer, 1980) and in ophiolites (Spooner and Fyfe, 1973, Spooner, 1980).

Water exchange between the lithosphere and the mantle occurs on a grand scale in the subduction environment (Fyfe, 1981). The material subducted is a hydrated oceanic lithosphere of slippite plus serpentinite, different from the new crust forming at spreading ridges. Fyfe (1981) estimates that the oceanic mass is recycled by this process in a billion years or so at the present rate of subduction. The dehydration of the downgoing slippite-serpentinite slab would generate a hot viscous fluid laden with water, alkalis and silica. The chemical heterogeneity of the earth's mantle may reflect the association of such fluids exhalation from the oceanic slab.

Redox Equilibrium
The fundamental equilibrium for all redox reactions involving water is:
\[ 2H_2O = 2H_2 + O_2 \]

The equilibrium constant at any temperature is (Reaction 1):
\[ K = K_{H_2}K_{O_2}/K_{H_2O} = (P_{H_2}Y_{H_2})/(P_{O_2}Y_{O_2}) \]

where \( K \), \( f_{H_2} \), \( f_{O_2} \), \( f_{H_2O} \), \( Y_{H_2} \), \( Y_{O_2} \), and \( Y_{H_2O} \) are the fugacity, fugacity coefficient, and fugacity of species, respectively.

The equilibrium constant for reaction 1 can be derived from the relation 3Ga = RTlnK where 3Ga = 113 kcal at 25°C (Robie and Waldbauer, 1968). Assuming ideal gas behaviour and pure water,
\[ K = P_{H_2}P_{O_2}P_{H_2O} \]

If P_{H_2O} = 1 bar, then P_{H_2} = 10^{12} bar and P_{O_2} = 2 x 10^{-12} bar in a pure water system. At T = 500°C, the equilibrium constant is 2.2 x 10^{12}; P_{H_2} and P_{O_2} in a pure water system are, respectively, about 4 x 10^{-12} bar and 2 x 10^{-12} bar.

These are very low pressures. Unless very large volumes of fluid or large concentrations of exotic reactants such as H\(_2\) or S\(_2\) are present, rocks are resistant to changes in their redox state of iron.

Laboratory experiments conducted at high temperature reveal that water in the presence of minerals with ferrous iron tends to dissociate and yield free hydrogen (Eugster and Skippie, 1967). The buffer reaction for a basalt in equilibrium with water:
\[ 3Fe_2SiO_5 + 2H_2O = 2Fe_2O_3 + (2)Fayalite Water Magnetite 3SiO_2 + 2H_2 \]

Quartz Hydrogen

The extent of the dissociation of water to free hydrogen in the QFM buffer depends on the temperature. At surface temperatures reactions such as (2) are so slow that they can be disregarded. The H\(_2\)O in pure water is about 10^{12} according to reaction (1). However, if temperature is raised, say, 300°C, reaction (2) proceeds faster.
and \( H_2O \) is lost. At elevated temperature the volume of water needed to change \( Fe^{2+}Fe_2 \) in rocks becomes considerably less.

Eugster and Skippen (1967) calculated the fugacities of \( H_2O \) and \( H_2O \) for the dissolution of \( Fe^{2+}Fe_2 \) and \( Fe^{2+}Fe_2 \) systems at 327°C to 1027°C and at 500 bar to 2000 bar. Inspection of the data suggests that water moving from high to low temperature will tend to reduce rocks, whereas water moving from low to high temperature will tend to oxidize rocks.

In light of this discussion, the change in the \( Fe^{2+}Fe_2 \) of a rock by hydrothermal alteration is governed by:

1. The initial redox state of the rock.
2. The temperature-pressure regime of the initial and final states.
3. The water to rock ratio.

The redox reactions are modified if we are not dealing with pure water but with an aqueous fluid laden with reactive oxants such as \( H_2O \). If the fluid and rock have the same temperature, then there will be no change in the redox state of iron regardless of fluid composition or volume.

### Integrated Water to Rock Ratio

The extent by which hydrothermal alteration changes the \( Fe^{2+}Fe_2 \) of a rock is related to the water to rock ratio. Let us consider a rock of 100 g that has experienced a shift from \( Fe^{2+}Fe_2 \) to \( Fe^{2+}Fe_2 \), with no appreciable loss or gain of iron. If \( Fe^{2+}Fe_2 \), then the rock must have reacted with a reducing fluid. Assuming the reducing agent is \( H_2O \), then the redox reaction is:

\[
Fe_2O_3 + 3H_2O \rightarrow 2FeO + H_2
\]

### Mineral Fluid

If \( Fe^{2+}Fe_2 \), then the rock must have reacted with an oxidizing fluid. Assuming the oxidizing agent is \( O_2 \), then the redox reaction is:

\[
2FeO + 1.2O_2 \rightarrow Fe_2O_3
\]

### Oxidizing Fluids

The surface environment in equilibrium with the atmosphere is among the most oxidizing natural systems of the planet. The earth's atmosphere is 21% \( O_2 \) and only 5 × 10^6 vol% \( H_2O \). Water in equilibrium with this exogenic atmosphere has about 10^6 mol l^-1 per cm^2 H_2O. In 10^11 mol l^-1 per cm^2 H_2O. Most surface waters also have about 10^6 mol S_2O_3 per cm^2 H_2O. An important oxidizing agent is the oxidizing agent formed by the weathering of sulfide minerals. It is of no surprise that ferric minerals such as hematite, limonite and goethite are stable iron-bearing minerals at the earth's surface. Hot springs and stagnant lagoon environments, reducing centres in disequilibrium with the atmosphere, are exceptions.

### The Oxygen Balance

The oxygen balance of the earth is not simple. Oxygen is generated by photodissociation of water and by photosynthesis. It is consumed by biologic processes, decay and respiration, and by oxidation of rocks. Chemical weathering is an important sink for oxygen:

\[
Fe_2SiO_4 + 1.2FeO + H_2O \rightarrow Fe_2O_3 + 2FeO + SiO_2
\]

### Pyrite Oxygen Water

\[
Fe_2O_3 + 4SO_2 + H_2O
\]

### Hematite Sulfate Hydrogen

The covenant of seawater or meteoric water through the lithosphere fixes atmospheric oxygen in rocks. At spreading centres exogenic seawater with Cl, Na, CO_3^-, and NO_3^- evolves into a hot, reduced brine capable of transporting metals as chloride complexes (Andrews and Fyfe, 1975). The spilitization of basalt removes CO_3^-, SO_4^-, and Fe from seawater to form calcite, anhydrite, ferric oxide and hydroxides of minerals.

### Redox Reactions

The redox reactions that are pertinent to the removal of \( O_2 \) and \( S_2O_3^- \) from seawater during hydrothermal convection are:

\[
Fe_2SiO_4 + 1.2FeO + 4H_2O \rightarrow Fe_2O_3 + SiO_2
\]

### Fayalite Oxygen Hematite Quartz

\[
Fe_2O_3 + 2SO_2 + 4H_2O \rightarrow Fe_2O_3 + SO_2 + H_2O
\]

### Pyrite Sulphate Hydrogen

\[
7Fe_2O_3 + 2SO_2 + 4H_2O \rightarrow Fe_2O_3 + SO_2 + 2H_2O
\]

### Magnetite Pyrite

\[
11SiO_2 + 2Fe_2O_3 + 2H_2O
\]

### Quartz Water

\[
22Fe_2SiO_4 + 2CaAl_2Si_3O_8 + H_2O \rightarrow 2Fe_2O_3 + 2CaSiO_3 + 3SiO_2 + H_2O
\]

### Anorthite Sulphate Magnesium

\[
Fe_2O_3 + 4SO_2 + 2H_2O \rightarrow Fe_2O_3 + SO_2 + H_2O
\]

### Chlorite Magnesite

\[
21SiO_2 + 2Fe_2O_3 + Ca_2SiO_3 + H_2O
\]

### Quartz Oxide Calcium

\[
22Fe_2SiO_4 + 2CaAl_2Si_3O_8 + H_2O \rightarrow 2Fe_2O_3 + 2CaSiO_3 + 3SiO_2 + H_2O
\]

### Anorthite Sulphate Magnesium

\[
Fe_2O_3 + 4SO_2 + 2H_2O \rightarrow Fe_2O_3 + SO_2 + H_2O
\]

### Chlorite Magnesite

\[
21SiO_2 + 2Fe_2O_3 + Ca_2SiO_3 + H_2O
\]

### Quartz Oxide Calcium

The spilitization of basalt and gabbro by seawater convection has been studied in the ophiolites at E. Liguria, Italy. By Spooner and Fyfe (1975) and Spooner et al. (1977), Spooner et al. (1977) report a regular increase with stratigraphic depth in \( Fe^{2+}Fe_2 \) of the spilitic lavas from 0.2 to 0.7. The oxidation of iron near the top of the lava series is attributed to desegregation, exogenic seawater during ocean-floor hydrothermal metamorphism (Spooner et al., 1977). As seawater was heated along the descending limbs of convection cells, oxygen was progressively consumed. Spooner et al. (1977) estimate an integrated water to rock ratio of about 2 × 0^3 to 1 for the oxidation profile. A decrease in the \( Fe^{2+}Fe_2 \) value of rocks generally implies alteration by an exogenic fluid originating at the surface. However, similar shifts in the redox state of iron may occur in shear zones where large volumes of fluid flow up a thermal gradient. At Scourie in Scotland granulite with \( Fe^{2+}Fe_2 \) = 0.84 passes into a foliated rock with \( Fe^{2+}Fe_2 \) = 0.55 at the centre of some shear zones (Beam and Fyfe, 1972). Beach and Fyfe propose that the progressive oxidation was caused by
water flowing from a lower to a higher temperature regime when hot granulite
thrust-over colder, wetter rocks. Water will tend to oxidize with increase in tempera-
ture (Eugster and Skippen, 1967).

Reducing Fluids

Fluids originating at depths of a few kilo-
metres or more are probably hot, reducing,
and H₂-bearing. This environment is in
great contrast to the surface environment
where oxidizing conditions prevail. Hawkes
(1980) estimates that the contrast in the
ratio of hydrogen to water between a depth of
15 km and the surface is about 10⁶ to 1. Hydrogen gas is present in measurable
amounts in most volcanic gases and geothermal fluids emanating from frac-
tures at the surface (Barnes et al., 1973; White,
1982; Ellis, 1979). The presence of free
hydrogen in the metamorphic realm is at-
tested to by hydrogen trapped in fluid
inclusions of metamorphic or hydrothermal
minerals (Hawkes, 1980; Greenwood,
1976). Most high grade metamorphic rocks
and fresh igneous rock have (Fe²⁺/Fe³⁺)
around 0.7.

Hydrogen may be generated in the crust
by several processes. It is well known in
microbiotology that there exist bacteria that
produce hydrogen by means of the
decomposition of organic compounds.
These anaerobic bacteria are known to
thrive in reducing environments in rocks at
shallow depths (Hawkes, 1980; Levinson,
1977). Hydrogen may be generated during
regional metamorphism by reactions such as

\[ 2C + 2H_2O \rightarrow CH_4 + CO_2 \]

\[ CH_4 + C \rightarrow 2H_2 \]

The limiting factor for the generation of
methane, and ultimately hydrogen, by these
reactions is the amount of graphite or
organic matter in rocks. The dissociation
of water in the presence of minerals with
ferrous iron is probably the dominant reac-
tion at depth that yields free hydrogen
(Eugster and Skippen, 1967; Wolery and
Sleep, 1976).

Kerrich et al. (1977) document the
change in the redox state of iron around
gold-bearing quartz veins in the Yellowknife
District, Northwestern Territories. The au-
tors report a shift in (Fe²⁺/Fe³⁺) from 0.75 in
background epidote amphibolite to 0.95 in
gold-bearing schist around the veins.
The observed reduction of primary iron is
attributed to the reaction of vein wallrocks
with an ascending, cooling hydrothermal
fluid. Kerrich et al. (1977) estimate a
minimum water to rock ratio of about 3:1 by
quantitatively evaluating the (Fe²⁺/Fe³⁺) data
with reference to the quartz-fayalite-
magnetite-water buffer system.

The Gutcher Lake Stock: A Test Case

A survey of the redox state of iron was
conducted over an Archean felsic stock in the
Wawa greenstone belt of Ontario.
The stock of trondhjemite intrudes a pil-
lowed series that is metamorphosed to the
regional greenschist facies at Gutcher
Lake, 25 km north of Wawa. The stock is 4
km² in plan and is partly enveloped by an
aureole of chloride-epidote-amphibole horn-
ffels up to 1 km wide. In the contact au-
reole, biotite is partly altered to chlorite;
amphibole and epidote are mottled with
chlorite, quartz, and calcite, and some
hornblende porphyroblasts have actinolite
rims (Studemeister et al., 1982). The stock is
generally a granoid trondhjemite that has
chlorite pseudomorph after biotite and
plagioclasic mottled with sericite plus cal-
cite (Studemeister et al., 1982). The inten-
sity of sericite and calcite alteration
increases toward the margin of the stock.
The stock and its aureole are traversed by
fractures now filled with quartz, ankerite,
calcite, sericite, chlorite and pyrite. These
veins are fringed by schistose chlorite-
sericite-calcite-quartz rock that pass into
mottled hornfels or trondhjemite.

The interpretation is that the stock ema-
nated heat that started seawater convect-
ing and generated a contact aureole of
epidote-hornblende hornfels. Subsequent
regional metamorphism partly retrograded
the stock and its hornfels aureole. The carbo-
inate-hydroxysilicate mineral assem-
blage of alteration suggests retrogression
by a CO₂-H₂O fluid. The inherent slow rates
of reaction in retrograde metamorphism
explain the disequilibrium assemblages and
textures that prevail in the trondhjemite
and its hornfels aureole.

A suite of rocks at various stages of
greenschist alteration was collected over the
stock. The (Fe²⁺/Fe³⁺) value of each rock
was determined with the method of
Wilson, 1955 (APPENDIX I). A shift in
(Fe²⁺/Fe³⁺) from about 0.66 up to 0.90 in
vein wallrocks suggests retrogression by
a reducing fluid (Figure 1). Partly altered
trondhjemite and hornfels have (Fe²⁺/Fe³⁺)
around 0.8. The integrated water to rock
ratio in vein wallrocks can be calculated
assuming that there was no significant ad-
dition or leaching of iron. The reducing
agent is assumed to have been free hydro-
gen from the dissociation of water in con-
tact with silicate minerals.

Retrogression of the stock is modelled
by an initial state of T, = 500 C and P,
= 1 kb at the peak of contact metamor-
phism to a final state of T, = 300 C and P,
= 2 kb during regional metamorphism
(Studemeister et al., 1982). Epidote-amphi-
bolite hornfels and its retrograde product
veins have a primary iron content of
about 10% of which about 66% and 90%,
respectively, is ferrous iron. Hence, 2.40
grams of ferric iron was reduced to ferrous iron
per 100 g of rock near the veins, requiring

2.15 x 10⁻⁷ mol H₂ by reaction (3).
The Pᵥₑ in equilibrium with the QFM-H₂O system
at T and P, is about 11 bar; Pᵥₑ is about 6
bar at T and P, (Eugster and Skippen,
1967).

Assuming ideal gas behaviour, 2.15 x
10⁻⁷ mol H₂ can be carried in about 126 cm³
of water at T, = 500°C. About 25% of the
hydrogen would be available for reduction, the
residual remains in the fluid at the
Pᵥₑ = 300°C buffer pressure. The volume of
water required to reduce 2.40 g of ferric iron
per 100 g of rock is about 475 cm³.
This corresponds to an integrated water to
tock ratio of about 15:1 in the vein wall-
rocks.

The value calculated with experimental
data may be a minimum estimate of the
integrated water to rock ratio. It is assumed
that the rocks are on a constant oxygen
buffer system and that equilibrium is main-
tained during reaction. However, as the
reaction proceeds, rocks may become pro-
gressively more difficult to reduce (Kerrich
et al., 1977). Larger fluid volumes than
those calculated may be required where
(Fe²⁺/Fe³⁺) approaches 1 or 0.

Conclusions

1) The redox state of iron, (Fe²⁺/Fe³⁺), in
rocks is a sensitive indicator of alteration
by water.

2) Unless excess volumes of water or large
concentrations of exotic reactants (H₂, O₂,
SO₂, H₂S) are involved, rocks are resistant
to shifts in (Fe²⁺/Fe³⁺).

3) Surface waters in contact with the at-
mosphere are exogenic and have H₂,H₂O =
10⁻¹⁷. Water in equilibrium with silicate
rocks at depth have H₂,H₂O = 1.3 to 1.60.

4) In the lithosphere free hydrogen is gen-
erated by the dissociation of water and
oxygen is consumed by oxidation of rocks.
5) Rocks along the descending limbs of
convection cells are progressively oxidized
as the water is heated. Rocks along the
ascending limbs of hydrothermal systems
are reduced as the water cools.
6) Retrograde metamorphism of an Ar-
chean stock and its contact aureole near
Wawa, Ontario was caused by a hot,
reducing fluid. The integrated water to rock
ratio in the wallrocks to fractures now
filled with quartz was 15:1 or greater.

Appendix I: Redox Titration For Ferrous
Iron

The ferrous iron content in rock powders
was determined volumetrically by quantita-
tively oxidizing the Fe²⁺ in a prepared
rock solution with a known amount of am-
monium metavanadate, and then quantita-
tively reducing excess V⁵⁺ with a
standardized ferrous ammonium sulphate
titrant (Wilson, 1955). Between 0.25 g
and 0.50 g of rock powder was added to
0.05 g of ammonium metavanadate, AMV,
**Table 1** The redox state of iron in rocks from the Gutcher Lake area.

<table>
<thead>
<tr>
<th>Sample Site Description</th>
<th>Sample Number</th>
<th>Statistical Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>III) Granoïd-textured rocks from the core of the Gutcher Lake stock</td>
<td>3a 0.65</td>
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<td></td>
<td>3b 0.72</td>
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<td></td>
<td>3c 0.68</td>
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<td>3d 0.61</td>
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<td>3e 0.63</td>
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<td>3f 0.74</td>
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<td>3g 0.60</td>
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<td>3h 0.66</td>
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<td>3i 0.77</td>
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<td>3j 0.72</td>
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<td>3k 0.66</td>
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<td>3l 0.57</td>
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<td>3m 0.73</td>
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<td>3n 0.70</td>
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<td>3o 0.08</td>
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<td>3p 0.75</td>
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<td>3w 0.86</td>
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<td>3x 0.66</td>
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<td>3y 0.57</td>
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<tr>
<td>IV) Fine-grained, fissile rocks from the border zone of the Gutcher Lake stock</td>
<td>4a 0.78</td>
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<td>4b 0.86</td>
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<td>4c 0.75</td>
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<td>4h 0.84</td>
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<td>4s 0.80</td>
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<td>4t 0.76</td>
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<td>4u 0.85</td>
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<td></td>
<td>4v 0.74</td>
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<tr>
<td>V) Wallrocks and core of sulphide-mineral-bearing quartz-carbonate veins</td>
<td>5a 1.00</td>
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<td></td>
<td>5b 0.90</td>
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<td>5c 0.74</td>
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<td>5d 0.96</td>
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<td>5e 0.95</td>
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<td>5f 0.87</td>
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<td>5g 0.81</td>
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<td>5h 1.00</td>
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<td>5i 0.86</td>
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and the mixture digested for 24 hours in 5 ml to 10 ml of concentrated HF acid. The solution was then titrated against ferrous ammonium sulphate, FAS, previously standardized against ceric sulphate.

The amount of ferrous iron in the rock is $\text{Fe}^{2+}$ (wt%) = $[(\text{AMV} - \text{AMV}) / (100)] / \text{Rock}$

where AMV: initial moles of AMV
AMV: final moles of AMV
Rock: weight of rock powder

Specimens were run in duplicates and some in quadruplicates; the variation in replicate Fe$^{2+}$ determinations was less than 2%.

The ferrous iron refers to the iron locked in HF soluble silicate, carbonate and oxide minerals. Pyrite does not readily dissolve in cold HF and therefore does not contribute to Fe$^{2+}$. The (Fe$^{2+}$/Fe) value in rocks with negligible sulphide minerals was calculated by substituting for Fe, the iron content determined by XRF analysis. For rocks with significant pyrite, Fe, was determined by AA analysis. About 0.25 g of rock powder was digested for 24 hours in cold HF, and then diluted aliquots of this solution were analyzed for total iron by AA.

Acknowledgements
This research was funded by a grant from the Ontario Geological Survey. Many thanks are extended to R. P. Sage and A. C. Colvin of the Ontario Geological Survey for assistance in carrying out the field work. I thank also R. W. Hodder, R. Kerrich, W. S. Fyfe, B. Barnett and B. McKinnon of the University of Western Ontario for important discussions and technical assistance.

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Figure 1 Histograms for the redox state of iron in rock suites from the Gutcher Lake area.


Robie, R. A. and D. R. Waldbauer, 1968. Thermodynamic properties of minerals and related substances at 298.15 K (25.0°C) and one atmosphere (1,013 bars) pressure and at high temperatures. United States Geological Survey Bulletin 1259.


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This symposium will be held in Canada and the USA in July-August, 1985.

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- July 27-31: Convene at the Stillwater complex for field trip
- August 2-4: Symposium, University of Toronto
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