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Article abstract

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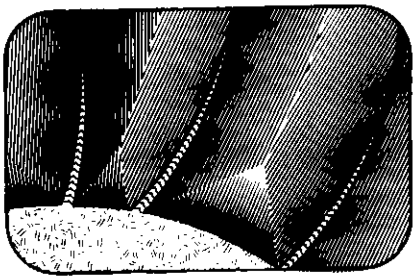

The Redox State of Iron: A Powerful Indicator of Hydrothermal Alteration

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Summary

The redox state of iron, (Fe^{+2}/Fe_t), in rocks is a useful indicator of hydrothermal alteration. In general, rocks are resistant to shifts in (Fe^{+2}/Fe_t) unless large volumes of fluid or high concentrations of exotic reactants such as H_2 or O_2 are present. The earth's surface in equilibrium with the atmosphere is an oxidizing environment; surface waters carry in solution O_2 plus 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 H_2 H_2O = 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.

Introduction

Water abounds in the uppermost layers of the earth where it participates in practically all sedimentary, metamorphic and igneous processes. The oceans now cover 70.8% of the earth's surface, but may have encircled the globe in the Archean (Fryer *et al.*, 1979). In the lithosphere water occurs in the pore spaces of rock formations, in the structure of silicate minerals and in minerals as inclusions. It is the dominant solvent, transporting agent and catalyst in rock-forming reactions. The chemical alteration of rock by water may involve the precipitation or solvation of mobile elements, hydration or dehydration of minerals and the oxidation or reduction of valence states.

The purpose of this paper is to focus attention on the changes in the redox state of iron that result from reaction with hydrothermal fluids. The (Fe^{+2}/Fe_t) of a rock is a sensitive indicator of the extent of alteration and it can distinguish spilitized from fresh igneous rock. The amount by which the (Fe^{+2}/Fe_t) was modified can be related to the integrated water to rock ratio. In the redox ratio Fe_t is the total primary iron and Fe^{+2} is the ferrous iron in the rock. It is assumed that during hydrothermal alteration there was no significant addition or leaching of iron from the rock.

Rock Alteration

The mechanical erosion and chemical weathering of surface rocks by interaction with air and water produces a vast array of sedimentary materials. In an attempt to reach equilibrium with the atmosphere, igneous and metamorphic rocks that formed at high temperature are dissolved, hydrated, and oxidized at the surface. The end product is a residual soil of clay minerals, limonite, hematite, chlorite, quartz and sericite, somewhat depleted in silica and alkalies.

The hydrosphere 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 (Spooner, 1980). Seafloor expeditions 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 seafloor, mix with ambient seawater and precipitate iron and base metal sulphide minerals (Franchetau *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 26wt% dissolved salts, mainly halite (White, 1981; Ellis, 1979; Le Bel and Oudin, 1982).

The convection of seawater through hot basalt leads to spectacular changes to produce an altered rock called a spilite (Spooner and Fyfe, 1973; Andrews and Fyfe, 1976). Spilitization along descending limbs of convection cells involves the loss of Si, Ca, plus K and the gain of Mg, Na, plus H_2O in basalt. Along the narrow ascending limbs of cells the elemental exchange trends are reversed when hot, modified seawater cools and reacts with basalt (Hajash and Archer, 1980). The alteration trends in basalt dredged from the seafloor resemble those reported in laboratory simulations (Bischoff and Dickson, 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 spilite plus serpentine, 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 spilite-serpentine slab would generate a hot viscous fluid laden with water, alkalies and silica. The chemical heterogeneity of the earth's mantle may reflect metasomatism by such fluids exhaling from the oceanic slab.

Redox Equilibria

The fundamental equilibrium for all redox reactions involving water is:

$$2\,H_2O = 2\,H_2 + O_2$$

The equilibrium constant at any temperature is (Reaction 1):

$$K = f^2_{H_2} f_{O_2}/f^2_{H_2O} = (P_{H_2}\gamma_{H_2})^2 (P_{O_2}\gamma_{O_2})/(P_{H_2O}\gamma_{H_2O})^2$$

where f_i is the fugacity, γ_i is the fugacity coefficient, and P_i is the partial pressure of species i.

The equilibrium constant for reaction (1) can be derived from the relation ΔG° = -RTlnK where ΔG° = 113 kcal at 25 C (Robie and Waldbaum, 1968). Assuming ideal gas behaviour and pure water,

$$K = P^2_{H_2} P_{O_2}/P^2_{H_2O} = 10^{83}$$

If P_{H_2O} = 1 bar, then P_{O_2} = 10^{28} bar and P_{H_2} = 2 x 10^{-28} bar in a pure water system. At T = 500°C, the quilibrium constant is 2.2 × 10^{28}; P_{O_2} and P_{H_2} in a pure water system are, respectively, about 4 × 10^{-4} bar and 7 × 10^{13} bar.

These are very low pressures. Unless very large volumes of fluid or large concentrations of exotic reactants such as H_2 or SO_4^{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 Skippen, 1967). The buffer reaction for a basalt in equilibrium with water is:

$$\underset{\text{Fayalite}}{3\,Fe_2SiO_4} + \underset{\text{Water}}{2\,H_2O} = \underset{\text{Magnetite}}{2\,Fe_3O_4} + \underset{\text{Quartz}}{3\,SiO_2} + \underset{\text{Hydrogen}}{2\,H_2} \qquad (2)$$

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/H_2O in pure water is about 10^{26} according to reaction (1). However, if temperature is raised by, say, 300°C, reaction (2) proceeds faster and $H_2/H_20 = 1/30$ is attained (Eugster and Skippen, 1967). At elevated temperature the volume of water needed to change (Fe^{+2}/Fe_t) in rocks becomes considerably less.

Eugster and Skippen (1967) calculated the fugacities of H_2 and H_20 for the dissociation of water in the QFM and other buffer 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_t) 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 exotic reactants such as H_2, H_2S, 0_2, or $S0_4^{2}$. If the fluid and rock have the same temperature, P_{H_2}, and P_{0_2}, 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_t) 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 $(Fe^{+2}/Fe_t)_i$ to $(Fe^{+2}/Fe_t)_f$ with no appreciable loss or gain of iron. If $(Fe^{+2}/Fe_t)_f > (Fe^{+2}/Fe_t)_i$, then the rock must have reacted with a reducing fluid. Assuming the reducing agent is H_2, then the redox reaction is

$$Fe_20_3 + H_2 \rightarrow 2\,Fe0 + H_20 \qquad (3)$$

Mineral Fluid Mineral Fluid

If $(Fe^{+2}/Fe_t)_f < (Fe^{+2}/Fe_t)_i$, then the rock must have reacted with an oxidizing fluid. Assuming the oxidizing agent is 0_2, then the redox reaction is

$$2\,Fe0 + 1/2\,0_2 \rightarrow Fe_20_3 \qquad (4)$$

Mineral Fluid Mineral

The number of moles of redox agent, Δn, needed to change the valence state of a known amount of iron, m, by reaction (3) is

$$\Delta n = (0.5m)/(MW)$$

and by reaction (4) is

$$\Delta n = (0.25m)/(MW)$$

where MW is the atomic weight of iron, 55.85 g/mol.

The density of the carrier fluid is assumed to have changed little, so volume changes may be neglected. The volume of water needed to cause the shift in (Fe^{+2}/Fe_t) is

$$V_{H_20} = \Delta n / \mid c_i - c_f \mid$$

where c_i : concentration of reactant before alteration

c_f : concentration of reactant after alteration.

The integrated water to rock ratio becomes

$$V = V_{H_20}/V_{Rock}$$

where $V_{Rock} = (100\ g) / (\beta g/cm^3)$

β = rock density.

For most geological problems, c_i and c_f cannot be measured directly. One has to rely on laboratory data for the equilibrium concentrations in the appropriate buffer system. The application of experimental data requires knowledge of the temperature-pressure regimes of the initial and final states, coupled with the assumption of ideal gas behavior. The numerical results thus obtained are only a first-order approximation of the integrated water to rock ratio. The reactant removed corresponds to the difference between the equilibrium concentration at the initial and final states.

The volume of water is

$$V_{H_20} = \Delta n / \mid c_i - c_f \mid$$

where $c_i = n_i / V = P_i / RT_i$

$c_f = n_f / V = P_f / RT_f$

Here n is the number of moles at equilibrium, P is the partial pressure, T is the temperature in °K, V is the volume, and R is the Gas Constant.

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 21vol% 0_2 and only 5 x 10^{5} vol% H_2. Water in equilibrium with this exogenic atmosphere has about 10^{-7} mol 0_2 per cm^3 H_20, and only about 10^{12} mol H_2 per cm^3 H_20. Most surface waters have also about 10^{6} mol $S0_4^{2}$ per cm^3 H_20, an important oxidizing agent formed by the weathering of sulphide minerals. It is of no surprise that ferric minerals such as hematite, limonite and goethite are the stable iron-bearing minerals at the earth's surface. Hot spring and stagnant lagoon environments, reducing centres in disequilibrium with the atmosphere, are exceptions.

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:

$Fe_2Si0_4 + 1/2\,0_2 + H_20 \rightarrow$ (5a)
Fayalite Oxygen Water
$2\,Fe00H + Si0_2$
Limonite Quartz

$4\,FeSi0_3 + 0_2 + 2\,H_20 \rightarrow$ (5b)
Pyroxene Oxygen Water
$4\,Fe00H + 4\,Si0_2$
Limonite Quartz

$2\,Fe_30_4 + 1/2\,0_2 \rightarrow 3\,Fe_20_3$ (5c)
Magnetite Oxygen Hematite

$2\,FeS_2 + 15/2\,0_2 + 4\,H_20 \rightarrow$ (5d)
Pyrite Oxygen Water
$Fe_2O_3 + 4\,SO_4^{2} + 8\,H^{+}$
Hermatite Sulphate Hydrogen

The convection of seawater or meteoric water through the lithosphere fixes atmospheric oxygen in rocks. At spreading centres exogenic seawater with Cl^{-}, Na^{+}, CO_3^{2}, and SO_4^{2} evolves into a hot, reduced brine capable of transporting metals as chloride complexes (Andrews and Fyfe, 1976; Spooner and Fyfe, 1973). The spilitization of basalt removes HCO_3^{1}, CO_3^{2}, SO_4^{2}, and O_2 from seawater to form calcite, anhydrite, ferric oxide and hydrosilicate minerals.

The redox reactions that are pertinent to the removal of 0_2 and $S0_4^{2}$ from seawater during hydrothermal convection are

$Fe_2Si0_4 + 1/2\,0_2 \rightarrow Fe_20_3 + Si0_2$ (6a)
Fayalite Oxygen Hematite Quartz

$11\,Fe_2Si0_4 + 2\,S0_4^{2} + 4\,H^{+} \rightarrow$ (6b)
Fayalite Sulphate Hydrogen
$7\,Fe_3O_4 + FeS_2 +$
Magnetite Pyrite
$11\,Si0_2 + 2\,H_20$
Quartz Water

$22\,Fe_2Si0_4 + CaAl_2Si_20_8 +$
Fayalite Anorthite
$4\,H_20 + 4\,S0_4^{2} + 5\,Mg^{+2} \rightarrow$
Water Sulphate Magnesium
$Mg_5Al_2Si_30_{10}(OH)_8 + 14\,Fe_30_4 +$ (6c)
Chlorite Magnetite
$21\,Si0_2 + 2\,FeS_2 + Ca^{+2}$
Quartz Pyrite Calcium

The spilitization of basalt and gabbro by seawater convection has been studied in the ophiolites at E. Liguria, Italy by Spooner and Fyfe (1973) and Spooner *et al.* (1977). Spooner *et al.* (1977) report a regular increase with stratigraphic depth in (Fe^{+2}/Fe_t) of the spilitic lavas from 0.2 to 0.7. The oxidation of iron near the top of the lava series is attributed to descending, 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 x 10^{3} to 1 for the oxidation profile.

A decrease in the (Fe^{+2}/Fe_t) 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 $(Fe^{+2}/Fe_t) = 0.84$ passes into a foliated rock with $(Fe^{+2}/Fe_t) = 0.55$ at the centre of some shear zones (Beach 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 temperature (Eugster and Skippen, 1967).

Reducing Fluids

Fluids originating at depths of a few kilometres or more are probably hot, reducing, and H_2-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 10^9 to 1. Hydrogen gas is present in measurable amounts in most volcanic gases and geothermal fluids emanating from fractures at the surface (Barnes *et al.*, 1973; White, 1982; Ellis, 1979). The presence of free hydrogen in the metamorphic realm is attested 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 (Fe^{+2}/Fe_t) around 0.7.

Hydrogen may be generated in the crust by several processes. It is well known in microbacteriology 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

$$2\,C + 2\,H_2O = CH_4 + CO_2$$

$$CH_4 = C + 2\,H_2$$

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 reaction 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 authors report a shift in (Fe^{+2}/Fe_t) 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 (Fe^{+2}/Fe_t) 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 pillowed 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 chlorite-epidote-amphibole hornfels up to 1 km wide. In the contact aureole, 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 granitoid trondhjemite that has chlorite pseudomorphic after biotite and plagioclase mottled with sericite plus calcite (Studemeister *et al.*, 1982). The intensity 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 emanated heat that started seawater convecting and generated a contact aureole of epidote-hornblende hornfels. Subsequent regional metamorphism partly retrograded the stock and its hornfels aureole. The carbonate-hydrosilicate mineral assemblage of alteration suggests retrogression by a CO_2-H_2O 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 (Fe^{+2}/Fe_t) value of each rock was determined with the method of Wilson, 1955 (APPENDIX I). A shift in (Fe^{+2}/Fe_t) 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 (Fe^{+2}/Fe_t) around 0.8. The integrated water to rock ratio in vein wallrocks can be calculated assuming that there was no significant addition or leaching of iron. The reducing agent is assumed to have been free hydrogen from the dissociation of water in contact with silicate minerals.

Retrogression of the stock is modelled by an initial state of $T_i = 500°C$ and $P_i = 1$ kb at the peak of contact metamorphism to a final state of $T_f = 300°C$ and $P_f = 2$ kb during regional metamorphism (Studemeister *et al.*, 1982). Epidote-amphibole hornfels and its retrograde product near veins have a primary iron content of about 10% of which about 66% and 90%, respectively, is ferrous iron. Hence, 2.40 g of ferric iron was reduced to ferrous iron per 100 g of rock near the veins, requiring 2.15×10^{-2} mol H_2 by reaction (3). The P_{H_2} in equilibrium with the QFM-H_2O system at T_i and P_i is about 11 bar; P_{H_2} is about 6 bar at T_f and P_f (Eugster and Skippen, 1967).

Assuming ideal gas behaviour, 2.15×10^{-2} mol H_2 can be carried in about 126 cm³ of water at $T_i = 500°C$. About 25% of the hydrogen would be available for reduction, the residual remains in the fluid at the $T_f = 300°C$ buffer pressure. The volume of water required to reduce 2.40 g of ferric iron per 100 g of rock is about 476 cm³. This corresponds to an integrated water to rock ratio of about 15:1 in the vein wallrocks.

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 maintained during reaction. However, as the reaction proceeds, rocks may become progressively more difficult to reduce (Kerrich et al., 1977). Larger fluid volumes than those calculated may be required where (Fe^{+2}/Fe_t) approaches 1 or 0.

Conclusions

1) The redox state of iron, (Fe^{+2}/Fe_t), in rocks is a sensitive indicator of alteration by water.
2) Unless excess volumes of water or large concentrations of exotic reactants (H_2, O_2, SO_4^{-2}, H_2S) are involved, rocks are resistant to shifts in (Fe^{+2}/Fe_t).
3) Surface waters in contact with the atmosphere are exogenic and have $H_2/H_2O = 10^{-12}$. Water in equilibrium with silicate rocks at depth have $H_2/H_2O = 1:30$ to $1:60$.
4) In the lithosphere free hydrogen is generated 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 Archean 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 quantitatively oxidizing the Fe^{+2} in a prepared rock solution with a known amount of ammonium metavandate, and then quantitatively reducing excess V^{+5} 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 metavandate, AMV,

Table I *The redox state of iron in rocks from the Gutcher Lake area.*

Sample Set Description	Sample Number	(Fe^{+2}/Fe_t)	Statistical Function
I) Mafic metavolcanics in the regional greenschist facies (quartz-albite-epidote-actinolite-calcite-chlorite)	1a	0.76	
	1b	0.76	
	1c	0.83	
	1d	0.78	
	1e	0.61	
	1f	0.73	
	1g	0.76	
	1h	0.90	
	1i	0.89	$N_1 = 18$
	1j	0.87	
	1k	0.84	$\bar{X}_1 = 0.82$
	1l	0.82	
	1m	0.76	$S_1 = 0.08$
	1n	0.91	
	1o	0.87	
	1p	0.92	
	1q	0.78	
	1r	0.89	
II) Mafic metavolcanics in the epidote-hornblende hornfels facies (magnetite-biotite-epidote-hornblende ± pyrrhotite with incipient calcite-actinolite-chlorite)	2a	0.32	
	2b	0.69	
	2c	0.69	
	2d	0.68	
	2e	0.73	
	2f	0.75	
	2g	0.67	
	2h	0.75	
	2i	0.51	$N_2 = 20$
	2j	0.37	
	2k	0.76	$\bar{X}_2 = 0.66$
	2l	0.80	
	2m	0.83	$S_2 = 0.13$
	2n	0.71	
	2o	0.74	
	2p	0.66	
	2q	0.64	
	2r	0.59	
	2s	0.70	
	2t	0.69	
Mafic metavolcanics in the epidote-hornblende hornfels facies extensively retrograded to the regional greenschist facies (sphene-magnetite-calcite-actinolite-chlorite-biotite-epidote-hornblende)	2xa	0.90	
	2xb	0.81	
	2xc	0.91	$N_{2x} = 7$
	2xd	0.67	
	2xe	0.89	$\bar{X}_{2x} = 0.81$
	2xf	0.71	
	2xg	0.76	$S_{2x} = 0.10$
III) Granitoid-textured rocks from the core of the Gutcher Lake stock (chlorite-quartz-feldspar with accessory epidote, white mica, and calcite)	3a	0.65	
	3b	0.72	
	3c	0.68	
	3d	0.61	
	3e	0.83	
	3f	0.74	
	3g	0.60	
	3h	0.66	
	3i	0.77	
	3j	0.72	
	3k	0.66	$N_3 = 25$
	3l	0.57	
	3m	0.73	$\bar{X}_3 = 0.66$
	3n	0.70	
	3o	0.68	$S_3 = 0.08$
	3p	0.76	
	3q	0.63	
	3r	0.66	
	3s	0.49	
	3t	0.52	
	3u	0.61	
	3v	0.59	
	3w	0.66	
	3x	0.66	
	3y	0.57	
IV) Fine grained, fissile rocks from the border zone of the Gutcher Lake stock (chlorite-calcite-albite-white mica-quartz ± pyrite)	4a	0.78	
	4b	0.80	
	4c	0.73	
	4d	0.84	
	4e	0.84	
	4f	0.89	
	4g	0.82	
	4h	0.84	
	4i	0.87	
	4j	0.84	$N_4 = 22$
	4k	0.79	
	4l	0.83	$\bar{X}_4 = 0.81$
	4m	0.82	
	4n	0.75	$S_4 = 0.04$
	4o	0.75	
	4p	0.85	
	4q	0.82	
	4r	0.79	
	4s	0.80	
	4t	0.78	
	4u	0.85	
	4v	0.74	
V) Wallrocks and core of sulphide-mineral-bearing quartz-carbonate veins (chalcopyrite-pyrrhotite-pyrite-calcite-albite-white mica-chlorite-quartz-ankerite)	5a	1.00	
	5b	0.90	
	5c	0.74	
	5d	0.96	
	5e	0.95	
	5f	0.87	
	5g	0.81	
	5h	0.90	
	5i	1.00	
	5j	0.86	$N_5 = 22$
	5k	0.95	
	5l	0.95	$\bar{X}_5 = 0.92$
	5m	0.97	
	5n	0.93	$S_5 = 0.06$
	5o	0.94	
	5p	0.90	
	5q	0.87	
	5r	0.98	
	5s	0.99	
	5t	0.93	
	5u	0.96	
	5v	0.97	
VI) Wallrocks and core of barren quartz-carbonate veins (albite-chlorite-white mica-quartz-ankerite)	6a	0.81	
	6b	0.74	
	6c	0.78	
	6d	0.83	
	6e	0.83	
	6f	0.84	
	6g	0.84	
	6h	0.86	$N_6 = 19$
	6i	0.86	
	6j	0.87	$\bar{X}_6 = 0.89$
	6k	0.88	
	6l	0.90	$S_6 = 0.08$
	6m	0.91	
	6n	0.96	
	6o	0.97	
	6p	0.98	
	6q	0.99	
	6r	0.99	
	6s	1.00	

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
Fe^{+2} (wt%) = $[(AMV_i - AMV_f)(55.85)(100)]/Rock$
where AMV_i : initial moles of AMV
AMV_f : 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_t) value in rocks with negligeable sulphide minerals was calculated by substituting for Fe_t the iron content determined by XRF analysis. For rocks with significant pyrite, Fe_t 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.

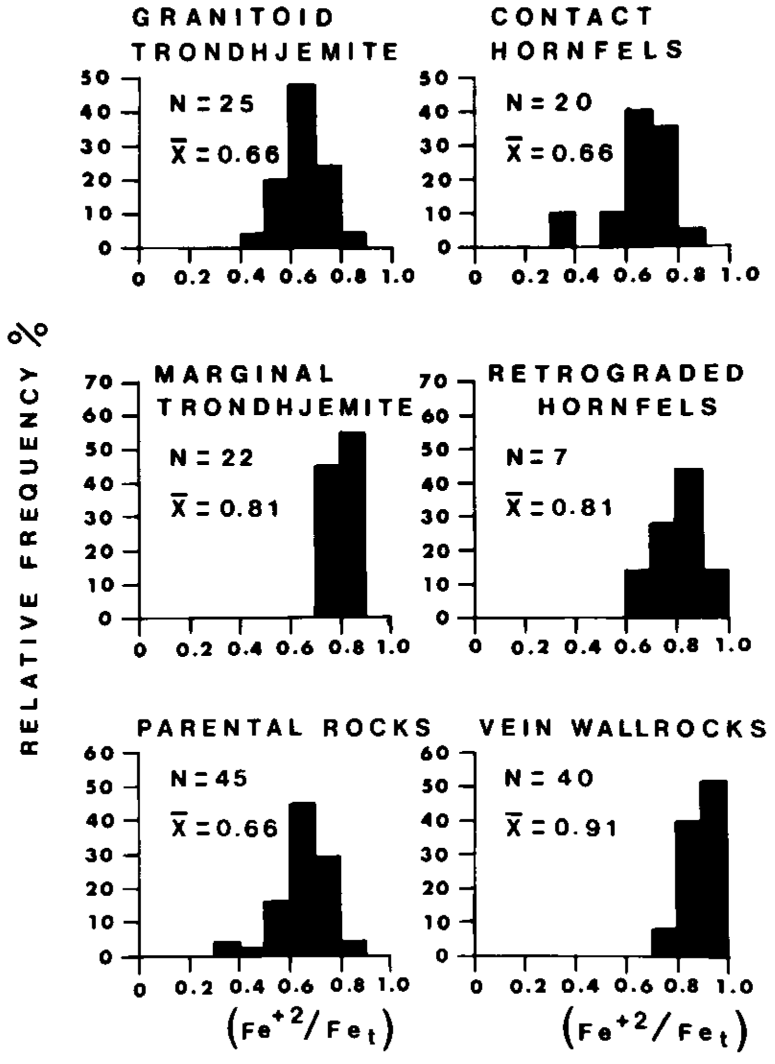

Figure 1 *Histograms for the redox state of iron in rock suites from the Gutcher Lake area.*

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