

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

Paul A. Studemeister

Volume 10, numéro 4, december 1983

URI : https://id.erudit.org/iderudit/geocan10_4art04

[Aller au sommaire du numéro](#)

Éditeur(s)

The Geological Association of Canada

ISSN

0315-0941 (imprimé)

1911-4850 (numérique)

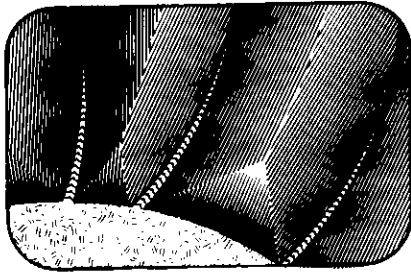
[Découvrir la revue](#)

Citer cet article

Studemeister, P. A. (1983). The Redox State of Iron: A Powerful Indicator of Hydrothermal Alteration. *Geoscience Canada*, 10(4), 189–194.

Résumé de l'article

The redox state of iron, (Fe₂/Fe₃), in rocks is a useful Indicator of hydrothermal alteration. In general, rocks are resistant to shifts in (Fe₂/Fe₃) unless large volumes of fluid or high concentrations of exotic reactants such as H₂ or O₂ are present. The earth's surface in equilibrium with the atmosphere is an oxidizing environment; surface waters carry in solution O₂ plus SO₂. 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 H₂ H₂O = 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

Paul A. Studemeister
 Dunraine Mines Ltd.
 Suite 506, 199 Bay Street
 Toronto, Ontario M5J 1L5

Summary

The redox state of iron, (Fe^{+2}/Fe_0) , in rocks is a useful indicator of hydrothermal alteration. In general, rocks are resistant to shifts in (Fe^{+2}/Fe_0) 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 hy-

drothermal fluids. The (Fe^{+2}/Fe_0) 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_0) was modified can be related to the integrated water to rock ratio. In the redox ratio Fe , 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 alkalis.

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).

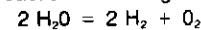
The convection of seawater through hot basalt leads to spectacular changes to produce an altered rock called a spilite (Spooner and Fyfe, 1973; Andrews and Fyfe, 1976). Spilitization along descending limbs of convection cells involves the loss of Si, Ca, plus K and the gain of Mg, Na, plus H_2O in basalt. 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, alkalis and silica. The chemical heterogeneity of the earth's mantle may reflect metasomatism by such fluids exhalting from the oceanic slab.

Redox Equilibria

The fundamental equilibrium for all redox reactions involving water is:



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

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

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

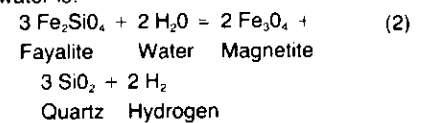
The equilibrium constant for reaction (1) can be derived from the relation $\Delta G^\circ = -RT \ln K$ where $\Delta G^\circ = 113$ kcal at 25°C (Robie and Waldbaum, 1968). Assuming ideal gas behaviour and pure water,

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

If $P_{H_2O} = 1$ bar, then $P_{O_2} = 10^{28}$ bar and $P_{H_2} = 2 \times 10^{28}$ bar in a pure water system. At $T = 500^\circ C$, the equilibrium 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:



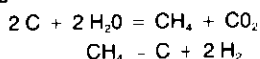
The extent of the dissociation of water to free hydrogen in the QFM buffer depends on the temperature. At surface temperatures reactions such as (2) are so slow that they can be disregarded. The H_2/H_2O in pure water is about 10^{28} according to reaction (1). However, if temperature is raised by, say, 300°C, reaction (2) proceeds faster

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 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 10⁹ 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 (Fe²⁺/Fe_T) around 0.7.

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



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).

Kerrick *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 (Fe²⁺/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 (Fe²⁺/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 convection 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 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⁺/Fe_T) value of each rock was determined with the method of Wilson, 1955 (APPENDIX I). A shift in (Fe²⁺/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 (Fe²⁺/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 x 10⁻² mol H₂ by reaction (3). The P_{H₂} in equilibrium with the QFM-H₂O system at T_i and P_i is about 11 bar; P_{H₂} is about 6 bar at T_f and P_f (Eugster and Skippen, 1967).

Assuming ideal gas behaviour, 2.15 x 10⁻² mol H₂ can be carried in about 126 cm³ of water at T_f = 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 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 maintained during reaction. However, as the reaction proceeds, rocks may become progressively more difficult to reduce (Kerrick *et al.*, 1977). Larger fluid volumes than those calculated may be required where (Fe²⁺/Fe_T) approaches 1 or 0.

Conclusions

- 1) The redox state of iron, (Fe²⁺/Fe_T), 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⁺/Fe_T).
- 3) Surface waters in contact with the atmosphere are exogenic and have H₂/H₂O = 10⁻¹². Water in equilibrium with silicate rocks at depth have H₂/H₂O = 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 Fe²⁺ in a prepared rock solution with a known amount of ammonium metavanadate, and then quantitatively 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.

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

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 $Fe^{+2} (wt\%) = [(AMV_f - AMV_i) (55.85) (100)]/Rock$

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 negligible 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.

Acknowledgements

This research was funded by a grant from the Ontario Geological Survey. Many

thanks are extended to R. P. Sage and A. C. Colvine 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.

References

Andrews, A. J. and W. S. Fyfe, 1976, Metamorphism and massive sulphide generation in oceanic crust: *Geoscience Canada*, v. 3, p. 84-94.

Barnes, I., M. E. Hinkle, J. B. Rapp, C. Heropoulos, and W. W. Vaughn, 1973, Chemical composition of naturally occurring fluids in relation to mercury deposits in part of north-central California: *United States Geological Survey, Bulletin 1382-A*, 19 p.

Beach, A. and W. S. Fyfe, 1972, Fluid transport and shear zones at Scourie, Sutherland: Evidence of overthrusting: *Contributions to Mineralogy and Petrology*, v. 36, p. 175-180.

Bischoff, J. L. and F. W. Dickson, 1975, Sea water-basalt interaction at 200°C and 500 bars: implications for origin of sea-floor heavy metal deposits and regulation of sea water chemistry: *Earth and Planetary Science Letters*, v. 25, p. 385-397.

Ellis, A. J., 1979, Explored geothermal systems: in Barnes, H. L. (editor), *Geochemistry of Hydrothermal Ore Deposits*, 2nd Edition, John Wiley and Sons, New York, p. 632-683.

Eugster, H. P. and G. B. Skippen, 1967, Igneous and metamorphic reactions involving gas equilibria: in Abelson, H. P. (editor), *Researches in Geochemistry*, Volume 1, John Wiley and Sons, Inc., New York, p. 492-520.

Francheteau, J., H. D. Needham, P. Choukroune, T. Juteau et al., 1979, Massive deep-sea sulphide ore deposits discovered on the East Pacific Rise: *Nature*, v. 277, p. 523-528.

Fryer, B. J., W. S. Fyfe and R. Kerrich, 1979, Archean volcanogenic oceans: *Chemical Geology*, v. 24, p. 25-33.

Fyfe, W. S., 1981, Geosphere interactions and earth chemistry: in *Evolution of the Earth*, Geodynamic Series Volume 5, American Geophysical Union, p. 82-86.

Greenwood, H. J., 1976, Metamorphism at moderate temperatures and pressures: in Bailey, D. K. and R. Macdonald (editors), *The Evolution of Crystalline Rocks*, Academic Press, New York, p. 187-259.

Hajash, A. and P. Archer, 1980, Experimental seawater/basalt interactions: effects of cooling: *Contributions to Mineralogy and Petrology*, v. 75, p. 1-13.

Hawkes, H. E., 1980, Geothermal hydrogen: *Mining Engineering*, v. 32, No. 6, p. 671-675.

Kerrich, R., 1981, Archean gold-bearing chemical sedimentary rocks and veins: a synthesis of stable isotope and geochemical relations: in *Genesis of Archean Volcanogenic Hosted Gold Deposits*, Ontario Geological Survey, Miscellaneous Paper 97, p. 144-168.

Kerrich, R., W. S. Fyfe and I. Allison, 1977, Iron reduction around gold-quartz veins, Yellowknife District, Northwestern Territories, Canada: *Economic Geology*, v. 72, p. 657-663.

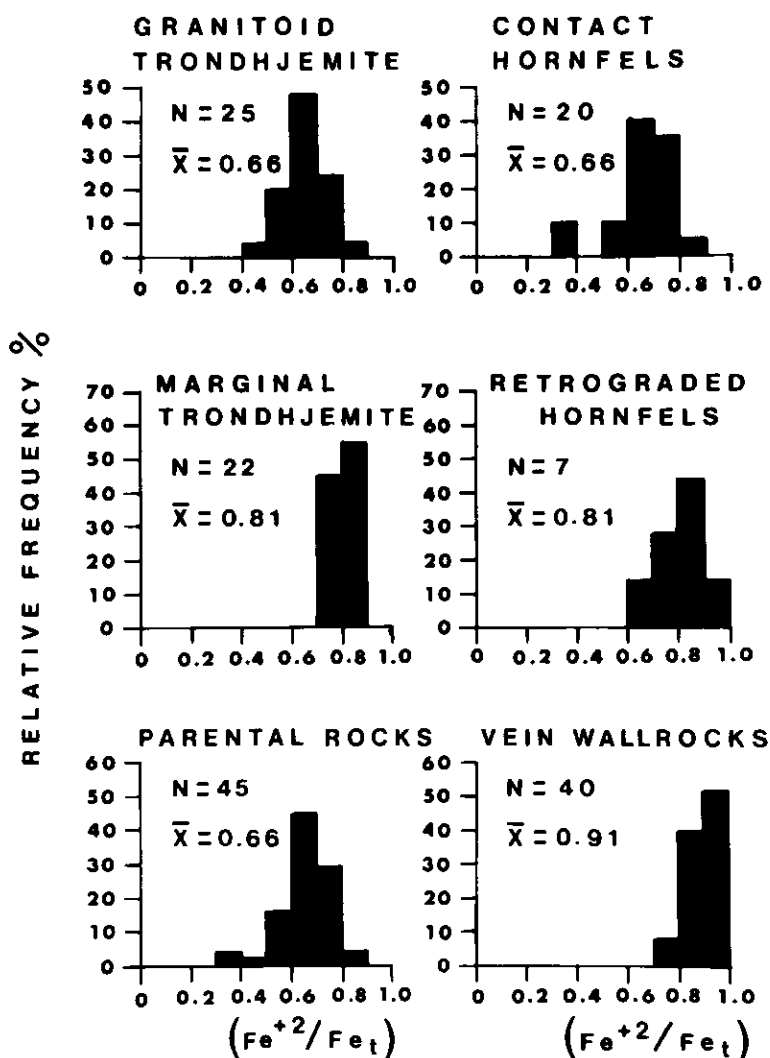


Figure 1 Histograms for the redox state of iron in rock suites from the Gutcher Lake area.

- Le Bel, L. and E. Oudin, 1982, Fluid inclusion studies of deep-sea hydrothermal sulphide deposits on the East Pacific Rise near 21°N: *Chemical Geology*, v. 37, p. 129-136.
- Levinson A. A., 1977, Hydrogen-A reducing agent in some uranium deposits: *Canadian Journal of Earth Sciences*, v. 14, p. 2679-2681.
- Robie, R. A. and D. R. Waldbaum, 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.
- Spiess, F. N., K. C. Macdonald, T. Atwater, R. Ballard, *et al.*, 1980, East Pacific Rise: hot springs and geophysical experiments: *Science*, v. 207, p. 1421-1433.
- Spooner, E. T. C., 1980, Cu-type mineralization and seawater convection in oceanic crust—the ophiolitic ore deposits of Cyprus: *in* Strangway, D. W. (editor), *The Continental Crust and its Mineral Deposits*, Geological Association of Canada, Special Paper 20, p. 685-703.
- Spooner, E. T. C., R. D. Beckinsale, and P. C. England, 1977, Hydration, ¹⁸O enrichment, and oxidation during ocean floor hydrothermal metamorphism of ophiolitic metabasic rocks from E. Liguria, Italy: *Geochimica et Cosmochimica Acta*, v. 41, p. 857-871.
- Spooner, E. T. C. and W. S. Fyfe, 1973, Sub-sea floor metamorphism, heat and mass transfer: *Contributions to Mineralogy and Petrology*, v. 42, p. 287-304.
- Studemeister, P. A., R. Kerrich, and W. S. Fyfe, 1982, Geochemistry and field relations of lode gold deposits in felsic igneous intrusions: *in* Pye, E. G. (editor), *Geoscience Research Grant Program, Summary of Research 1981-1982*, Ontario Geological Survey, Miscellaneous Paper 103, p. 185-209.
- White, D. E., 1981, Active geothermal systems and hydrothermal ore deposits: *in* 75th Anniversary Volume, *Economic Geology*, p. 392-423.
- Wilson, A. D., 1955, A new method for the determination of ferrous iron in rocks and minerals: *Geological Survey of Great Britain, Bulletin v. 9*, p. 56-58.
- Wolery, T. J. and N. H. Sleep, 1976, Hydrothermal circulation and geochemical flux at mid-ocean ridges: *Journal of Geology*, v. 84, p. 249-275.

MS received as revised, July 29, 1983

4th International Platinum Symposium & Field Trips

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

The tentative programme is:

- July 27-31 Convene at the Stillwater complex for field trip
- August 2-4 Symposium, University of Toronto
- August 5-7 Field trip, Sudbury, Ontario

Organizing Committee:

R.A. Alcock, L.J. Cabri, J.H. Crocket,
A.J. Naldrett (Chairman), N.J. Page

Papers presented at the conference will be published in *Economic Geology*, subject to prior critical reviews. Those who wish further information, please write to:

Professor A.J. Naldrett, Chairman • 4th International Platinum Symposium • Department of Geology • University of Toronto • Toronto, Ontario • M5S 1A1 • Canada •