

# Oxygen fugacity variations and mineral reactions in sapphirine-bearing paragneisses, E. Grenville province, Canada

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## Abstract

Sapphirine-bearing assemblages occur in paragneisses in a 200 km long block in the Grenville province in Labrador–Quebec. The occurrence of some of these rocks was previously known, but their considerable extent is now recognised from regional mapping. The mineral assemblages, reactions, and compositions and the tectonic structure in the paragneisses of this block are surprisingly uniform. Within feldspar-quartz layers we recognise assemblages with sapphirine, quartz, iron titanium oxides, spinel, corundum, diaspore, orthopyroxene, sillimanite, cordierite, garnet, and biotite in metre to millimetre-thick layers. These minerals reacted with their matrix, especially quartz, during cooling and uplift. At least 11 retrograde reactions gave rise to spectacular corona textures and define a  $P$ - $T$ -time trajectory from *c.* 8 kbar at 900 °C to 6 kbar at 700 °C which changed from early isobaric to late isothermal. Based on successive generations of sapphirine and orthopyroxene with constant  $X_{Mg}$  and decreasing  $Fe^{3+}/Fe^{2+}$  ratio in recalculated formulae, we deduce an accompanying change from high to low oxygen fugacity along this trajectory. The isothermal section of the trajectory is consistent with predicted rapid uplift and with field evidence for thrust tectonics and mylonitisation.

KEYWORDS: sapphirine, paragneiss, oxygen fugacity, Grenville province, Canada.

SAPPHIRINE-BEARING assemblages occur throughout a 200 km long block within the late Proterozoic eastern Grenville province extending from Ptarmigan Lake (Emslie *et al.*, 1978) via Wilson Lake (Morse and Talley, 1971; Leong and Moore, 1972; Gittins and Currie, 1979; Nielsen and Gittins, 1977; Jackson and Finn, 1982) to Lac Ghyvelde and Lac Long (Thomas and Wood, 1983; Thomas *et al.*, 1984) (Fig. 1). Within this granulite facies terrain the major lithological units are in general paragneiss (containing the sapphirine rocks), gabbro, hypersthene granite and charnockitic gneiss, as well as late microcline granite (Fig. 1).

The sapphirine-bearing assemblages are often associated with oxide minerals in millimetre-scale layers which have a strong aeromagnetic signature (Thomas and Wood, 1983). At Wilson Lake, the oxide minerals form lenses which reach widths as great as 7 m (Leong and Moore, 1972). The rocks strike SW–NE, dip strongly to the SE or NW, and have a well developed lineation which plunges 40° S in the Ptarmigan Complex (Emslie *et al.*, 1978).

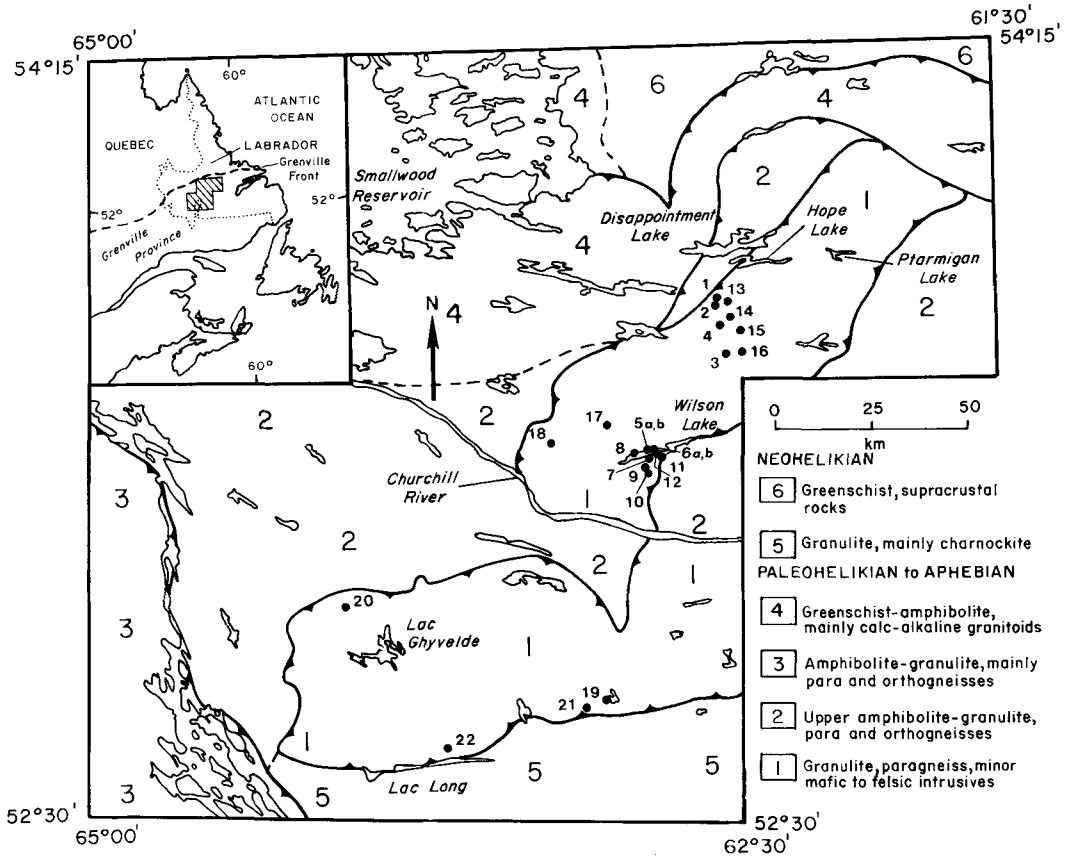


FIG. 1. General geological map of the area extending from Ptarmigan Lake via Wilson Lake to Lac Long showing the location of our analysed samples.

Quartz-feldspar segregations provide evidence of pervasive partial melting (Thomas *et al.*, 1984). Conformable veins of pseudo-tachylite and mylonite are widespread in the paragneiss.

Regional investigations consistently indicate that the oxide/sillimanite-rich layers are an early component of the granulite facies paragneiss. The sapphirine-bearing assemblages developed within and marginal to these layers.

The textural relations indicate many reactions, the most important of which are listed in Table 1 (reactions R1 to R11). Early Zn-rich (Table 2) magnesian spinel and iron-rich sillimanite were generated by R1. Phases produced by the oxidation reactions R1 and R2 are observed to participate in later reactions (e.g. R4). Hydrous phases in R8 and R10 overgrow phases produced in earlier reactions. The inferred reaction sequence is therefore: oxidation reactions; various non-oxidation reactions; and hydration reactions. Selective mineral analyses

are given in Table 2; these are representative point analyses which are remarkably consistent throughout the region.

The earliest reaction that we recognise is one favoured by high oxygen fugacity in which an Fe-rich spinel in contact with quartz forms a Mg-rich unzoned spinel with magnetite and sillimanite (R1). This Fe-rich spinel is not in contact with the reaction products and the resultant sillimanite (R1) has a distinctive high  $\text{Fe}_2\text{O}_3$  content of c. 2.0 wt. % (Grew, 1980; Fleet and Arima, 1985). At approximately the same time this Fe-rich spinel in contact with orthopyroxene reacted to form a magnesian spinel plus magnetite and sapphirine (R2). The relict orthopyroxene in R2 has a high  $\text{Al}_2\text{O}_3$  content of 9.4 wt. % which is consistent with a high  $T$  and  $P$  (Anastasiou and Seifert, 1972). In addition more magnesian spinel (not participating in the reactions) is present, and contains magnetite (?) exsolution. Rare sapphirine-quartz contacts are

Table 1: Selected reactions deduced from textural observation and analyses (Table 2). The order R1 to R11 is in general time sequence consistent with textures which show that there were several successive generations of Sa, Sp, Opx and Cd from early Sp-oxide layers in the quartz-bearing paragneisses.

Early R1:	$\text{Fe} - \text{Sp} + \text{Qtz} + \text{O}_2$	=	$\text{Mg} - \text{Sp} + \text{Mt} + \text{Sill} (2.0 \text{ wt.}\% \text{ Fe}_2\text{O}_3)$
R2:	$\text{Fe} - \text{Sp} + \text{Opx} + \text{O}_2$	=	$\text{Mg} - \text{Sp} + \text{Mt} + \text{Sa}$
R3:	$\text{Rt} + \text{Mt} + ?$	=	$\text{Ilm} + \text{Hem} + \text{Cn} (2.1 \text{ wt}\% \text{ Fe}_2\text{O}_3)$
R4:	$\text{Sa} + \text{Qtz} + \text{Mt}$	=	$\text{Sill} (1.2 \text{ wt.}\% \text{ Fe}_2\text{O}_3) + \text{Opx} (+ \text{O}_2)$
R5:	$\text{Opx} + \text{Sill} + \text{Qtz}$	=	$\text{Cd} + \text{Mg} - \text{Sp}$
R6:	$\text{Opx} + \text{Sill}$	=	$\text{Cd} + \text{Sa} + \text{Mg} - \text{Sp}$
R7:	$\text{Sa} + \text{Sill}$	=	$\text{Cd} + \text{Cn} (1.5 \text{ wt.}\% \text{ Fe}_2\text{O}_3) + \text{Fe-Oxide}$
R8:	$\text{Kf} + \text{Opx} + (\text{Ti-phase}) + \text{H}_2\text{O}$	=	$\text{Bio} + \text{Sill/Qtz}$
R9:	$\text{Opx} + \text{Sa} + \text{Mt/Sp} + ?$	=	$\text{Gt} (+ \text{O}_2)$
R10:	Sa	=	$\text{Chl} + \text{Sp} + \text{Cn} (\text{now Dia})$
Late R11:	$\text{Cn} + \text{H}_2\text{O}$	=	Dia

Selected reactions deduced from textural observations. Different generations of Sa, Sp, Opx and Cd are indicated in bracketed numbers, which are also in Table 2. The order 1 to 10 is in general time sequence.

Abbreviations: Fe-Sp = Iron Spinel, Mg-Sp = Magnesian Spinel, Qtz = Quartz, H<sub>2</sub>O = Water, O<sub>2</sub> = Oxygen, Mt = Magnetite, Sill = Sillimanite, Opx = Orthopyroxene, Sa = Sapphirine, Rt = Rutile, Ilm = Ilmenite, Hem = Hematite, Cn = Corundum, Cd = Cordierite, Bio = Biotite, Kf = Potash feldspar, Gt = Garnet, Chl = Chlorite, Dia = Diaspore.

Table 2: Representative point analyses selected from over 600 mineral analyses.

Rock No.	18	6b	18	18	3	3	14	14	6b	21	14	17
Reaction No. (1)	2	6	1,2	1,2	2,3	4	8	8	5,6	7	9	10
	Sapphirine		Spinel		Orthopyroxene			Biotite	Cordierite		Garnet	Chlorite
SiO <sub>2</sub>	13.3	13.1	-	-	48.3	51.4	52.4	38.8	49.5	49.9	39.1	37.2
TiO <sub>2</sub>	0.01	0.02	0.01	0.04	0.08	0.02	0.03	2.37	-	-	0.02	-
Al <sub>2</sub> O <sub>3</sub>	58.4	60.3	58.4	63.0	9.4	5.3	6.28	18.1	32.8	33.4	21.9	14.1
Cr <sub>2</sub> O <sub>3</sub>	0.03	0.05	0.06	1.31	0.02	-	0.04	0.03	-	-	-	-
FeO(2)	9.1	9.2	30.1	11.2	16.8	15.9	12.4	10.4	3.45	2.30	21.2	15.4
MnO	0.90	0.27	0.21	0.60	1.36	1.50	1.25	0.10	0.16	0.19	3.70	0.50
MgO	17.2	16.7	8.7	16.7	23.7	25.6	27.5	17.9	11.5	12.3	11.9	21.9
Anhydrous Total	98.94	99.64	98.69	100.05	99.66	99.72	99.90	97.60	97.41	98.09	99.17	89.10
Cations O-BASIS	14	14	3	3	4	4	4	-	-	-	-	-
Si	1.603	1.567	-	-	1.756	1.862	1.866	5.508	5.029	5.010	5.959	7.170
Ti	0.000	0.001	0.000	0.000	0.002	0.000	0.000	0.253	-	-	0.002	-
Al	8.296	8.502	1.910	1.929	0.403	0.226	0.264	3.028	3.927	3.952	3.934	3.202
Cr	0.002	0.004	0.001	0.026	0.000	-	0.001	0.003	-	-	-	-
Fe <sup>3+</sup>	0.488	0.352	0.088	0.043	0.077	0.046	-	-	-	-	0.142	-
Fe <sup>2+</sup>	0.429	0.568	0.610	0.200	0.433	0.434	0.369	1.234	0.293	0.193	2.559	2.482
Mn	0.091	0.027	0.004	0.013	0.041	0.046	0.037	0.012	0.013	0.016	0.477	0.081
Mg	3.090	2.977	0.359	0.646	1.284	1.382	1.460	3.787	1.741	1.840	2.703	6.291
	-	-	Zn 0.025	0.138	-	-	-	K 1.792	-	-	Ca 0.220	-
Total	14.002	14.001	3.000	3.000	4.000	4.000	4.000	15.619	11.006	11.013	15.999	19.228
X <sub>Mg</sub> (4)	0.85	0.83	0.37	0.75	0.73	0.74	0.78	0.75	0.85	0.89	0.47	0.71

(1) Representative point analysis related by textures to the reactions of table 1.

(2) Total Fe as FeO.

(3) Sa :  $\text{Fe}^{3+} = \text{Al}^{[4]} - (\text{Al}^{[6]} + \text{Cr} + 2\text{Ti})$ ; Sp :  $\text{Fe}^{3+} = 8 - [2(\text{Fe} + \text{Mg} + \text{Mn} + \text{Zn}) + 4\text{Ti} + 3\text{R}^{3+}]$ ;

Opx :  $\text{Fe}^{3+} = \text{Al}^{[6]} - (\text{Al}^{[4]} + \text{Cr} + 2\text{Ti})$ ;

(4)  $X_{\text{Mg}} = \text{Mg}/(\text{Mg} + \text{Fe}^{2+} + \text{R}^{2+})$ .

Where two analyses of the same phase are given, they represent different generations deduced from textural observations and differences in mineral chemistry.

Abbreviations as in Table 1.

preserved indicating the early stability of this association, but mostly we see evidence of their reaction to sillimanite (with a  $\text{Fe}_2\text{O}_3$  content of 1.2 wt. %), orthopyroxene and  $\text{O}_2$  (R4). Magnetite is involved in this reaction, indicating a change to lower oxygen fugacity, and the resultant orthopyroxene has an alumina content lower than that of the earlier orthopyroxene reflecting lower  $P$ - $T$  conditions. Reactions R5 and R6 involve the reaction of orthopyroxene and sillimanite with or without quartz to give rise to cordierite and Mg-rich spinel, with or without sapphirine. This second generation sapphirine has a lower  $\text{Fe}^{3+}$  content than the earlier sapphirine of reaction R2; this is consistent with reaction R4 in which we have evidence of a change to lower oxygen fugacity. Reaction R7 gives rise to cordierite, and corundum which has a lower Fe content than the corundum produced by reaction R3. Biotite bordering sillimanite-oxide layers has been produced with sillimanite/quartz by the reaction of K feldspar, orthopyroxene and an unknown Ti phase (R8). Biotite dehydration and replacement has occurred locally. By reaction R9 garnet develops as an overgrowth on sapphirine-oxide layers, suggesting late crystallisation. Garnet also occurs within the quartzo-feldspathic matrix as small idiomorphs on isolated oxide grains; these late garnets show no zoning and probably formed under conditions of low oxygen fugacity (Hsü, 1968). Throughout the block, sapphirine consistently shows late alteration; sapphirine relics in optical continuity are veined by chlorite and relict spinel and corundum (R10). Corundum has reacted with water (and a small amount of Si?) to form diaspore (R11).

Sapphirine-quartz became unstable in reaction R4 at a  $T$  of 1000–800 °C and a  $P$  of 11–8 kbar (Newton, 1972). Using the thermodynamic model of Sen and Bhattacharya (1984) for  $T$ , and the  $P$  model of Harley (1984), we estimate 7 kbar and 700 °C for the garnet-producing reaction R9. Reaction R4 is controlled by  $T$  decrease, but reactions R5 and R6 reflect a  $P$  decrease. Thus early isobaric cooling gave way to later isothermal uplift, coincident with decreasing oxygen fugacity shown by successive parageneses.

These sapphirine-bearing assemblages are developed throughout a wide segment of the Grenville province in central Labrador and the successive generations of phases described above are remarkably constant throughout this wide region. Field evidence for widespread thrusting and mylonitisation (Emslie *et al.*, 1978; Thomas *et al.*, 1985) agrees with the isothermal section of our  $P$ - $T$ -time trajectory and the predictable rapid uplift.

### Acknowledgement

We thank NATO for research grant number 289.81 on the petrology of sapphirine-bearing rocks.

### References

- Anastasiou, P., and Seifert, F. (1972) *Contrib. Mineral. Petrol.* **34**, 272–87.
- Emslie, R. F., Hulbert, L. J., Brett, C. P., and Garson, D. F., (1978) *Geol. Surv. Canada, Current Research Part A*, Pap. 78-1A, 129–34.
- Fleet, M. E., and Arima, M. (1985) *Am. Mineral.* **70**, 1232–7.
- Gittins, J., and Currie, K. L. (1979) *Geol. Surv. Canada, Current Research Part A*, Pap. 79-1A, 77–82.
- Grew, E. S. (1980) *J. Petrol.* **21**, 39–68.
- Harley, S. L. (1984) *Ibid.* **25**, 697–712.
- Hsü, L. C. (1968) *Ibid.* **9**, 40–83.
- Jackson, V., and Finn, G. (1982) *Newfoundland and Labrador Dept. of Mines and Energy, Open File Lab.* 13E/7(40), 22 pp.
- Leong, K. M., and Moore, J. M., Jr. (1972) *Can. Mineral.* **11**, 777–90.
- Morse, S. A., and Talley, J. H. (1971) *Can. Earth Planet. Sci. Lett.* **10**, 325–8.
- Nielsen, P. A., and Gittins, J. (1977) *J. Geol. Soc. Am. Abst. with Prog.* **9**, 305.
- Newton, R. C. (1972) *J. Geol.* **80**, 398–420.
- Sen, S., and Bhattacharya, A. (1984) *Contrib. Mineral. Petrol.* **88**, 64–71.
- Thomas, A., and Wood, D. (1983) *Geol. Surv. Canada, Current Research Part A*, Pap. 83-1A, 305–12.
- Culshaw, N. G., Mannard, G., and Whelan, G. (1984) *Ibid.* Pap. 84-1A, 485–93.
- Nunn, G. A. G., and Wardle, R. J. (1985) *NATO ASI Series C*, **158**, 151–61.

[Manuscript received 23 June 1986]