RESEARCH PROJECT FINAL REPORT

PRESSURE AND TEMPERATURE CONDITIONS 1000 MILLION YEARS AGO IN AND AROUND BLACK ROCKS FOREST, CORNWALL, NY

Investigators: Albert Léger, Department of Earth and Planetary Sciences, American Museum of Natural History, New York, NY, 10024

Dates of operation: April 15, 1996 - April 15, 1997

Research Goals

The stated goals of the study were to:

1) conduct a field survey of BRF to find rocks with the appropriate mineral assemblage for temperature (T) and pressure (P) calculation,
2) prepare specimens for electron microprobe scanning electron microscope (SEM),
3) describe mineralogy and look for equilibrium criteria,
4) characterize mineral composition with electron microscope,
5) calculate T and P conditions at peak of metamorphism,
6) compare T and P with Cl-rich samples
7) publish results.

Summary of Results

Specimen collecting was successful in that I found rocks with the appropriate mineral assemblage for T and P calculation. Techniques used for characterization of these minerals were: (1) optical microscopy; (2) scanning electron microscopy; and (3) electron microprobe. Goals (1) through (5) have been achieved by this time. Results are presented below. We are still working on finding rocks with the right mineral assemblage to calculate the T and P of Cl-rich samples, but have not been successful so far.

Results to date include:

- successful collection of rock specimens
- preparation of thin sections
- description of mineralogy and texture
- mineralogy of specimens collected
- multiple analyses of the minerals from which T and P can be determined:
  garnet: $[(Fe,Mg, Mn,Ca)_3Al_2Si_3O_{12}]$,
  biotite: $[K(Fe,Mg)_3AlSi_3O_{10}(OH)_2]$,
  pyroxene: $[(Fe,Mg)_2Si_2O_6]$
  plagioclase feldspar series: $[CaAl_2Si_2O_8]$ - $[NaAlSi_3O_8]$
- calculation of "peak" conditions at 720° C and 6000 bars and "retrograde" conditions at 500°C and 3000 bars (peak refers to the maximum T and P experienced by the rock, usually corresponding to the greatest depth at which the rock crystallized; retrograde refers to the P,T conditions that the rock experienced on its way up to the surface, but still hot enough for the minerals to react).

Analysis of Minerals with the Electron Microprobe

The chemical compositions of minerals in the samples studied were determined by electron microprobe analyses conducted at the American Museum of Natural History. In July, 1996, a new electron microprobe was installed at AMNH, with funding from the National Science Foundation, AMNH and Columbia University. The instrument, a Cameca SX-100, is one of the most advanced electron microprobe in the world. Analysis of coexisting garnet, biotite, pyroxene, and plagioclase feldspar can yield estimate of T and P based on numerous experimental calibrations and the use of thermodynamic data bases. In short, we compare chemical compositions of coexisting minerals in natural samples to compositions obtained under fixed T and P conditions in the laboratory.

To obtain T and P conditions, the minerals have to coexist in the same area of the rock, so that we can be sure that they crystallized at the same time under the same conditions. The petrologist looks at the minerals with the optical microscope to determine if the minerals show an equilibrium texture (see Fig.1).

Calculation of Temperature and Pressure - Theoretical Considerations

Rocks from the Black Rock Forest (BRF) were metamorphosed during the Grenville Orogeny nearly 1000 Ma ago. The rocks that are now at the surface were buried deeply (ca. 15-20 km depth) and subjected to pressures around 6 kilobars (kbar) and temperatures between 700-800 degrees Celsius (°C). We know of these values from previous studies of Grenville rocks (Dodd, 1965; Dallmeyer and Dodd, 1971; Jaffe and Jaffe, 1973; Hall et al., 1975; Helenek and Mose, 1984; Aleinikoff and Grauch, 1990; Isachsen and Gates, 1991), but no such study has concentrated on BRF.

Geologists refer to the analyses to calculate temperature and pressure from rocks "geothermometry" and "geobarometry", respectively. Geothermometry and geobarometry calculations are based on equilibrium thermodynamics and rely on the chemical composition of coexisting minerals in rocks. Chemical compositions are determined with the electron microprobe, and those values are then compared to similar values that were achieved in the laboratory under known conditions.

Geothermometry and geobarometry are based on the assumption of equilibrium at the time of metamorphism. We thus assume that the mineral compositions that we gather today are from minerals that coexisted under equilibrium conditions when they formed, and that they did not change significantly since then. The geologist looks at a series of parameters such as microstructure, microtexture, chemical zoning, and hydrothermal alteration to determine if equilibrium assemblages are present in rocks.

The fundamental equation relating mineral composition to pressure and temperature is:

$$\Delta G(P,T) = 0 = \Delta H(P,T) + P\Delta V(P,T) - T\Delta S(P,T) + RT \ln Keq,$$

where ΔG, ΔH, ΔS, and ΔV are known as the free energy, enthalpy, entropy, and volume of the reaction at the P and T of interest (see review by Spear, 1993). R is the gas constant. In an equation of this type, mineral compositions are needed for the term Keq, which refers to the equilibrium constant. Free energy, enthalpy, entropy, and volume of the reaction is known from experimental calibrations of thermodynamic data bases, leaving only P and T as unknowns. One

needs to fix one to get the other. Some mineral assemblages are better geothermometer, i.e., changes in P do not affect the results of T to a great extent. Other assemblages are better geobarometers, i.e., changes in T do not affect the results of P to a great extent. The best scenario is when two different mineral assemblages are found within the same rock. They then can define a point or a small area in P-T space, determining precisely equilibrium P-T conditions at the time to metamorphism.

The main geothermometer used in this study is the garnet-biotite exchange thermometer, used for coexisting minerals that exchange elements in known abundance with varying temperature. For example, coexisting garnet and biotite will exchange Fe and Mg in known proportions according to temperature of metamorphism. An exchange reaction between garnet and biotite can be written as:

$$\underset{\text{(Fe-garnet)}}{Fe_3Al_2Si_3O_{12}} + \underset{\text{(Mg-biotite)}}{KMg_3AlSi_3O_{10}(OH)_2} = \underset{\text{(Mg-garnet)}}{Mg_3Al_2Si_3O_{12}} + \underset{\text{(Fe-biotite)}}{KFe_3AlSi_3O_{10}(OH)_2} \ ,$$

or in short-hand:

$$FeMg_{-1}\,(\text{garnet}) = FeMg_{-1}\,(\text{biotite}).$$

Another geothermometer used in this study is the garnet-orthopyroxene exchange thermometer. Here, coexisting garnet and orthopyroxene will exchange Fe and Mg in known proportions according to temperature of metamorphism. The exchange reaction between garnet and orthopyroxene can be written as:

$$\underset{\text{(Fe-garnet)}}{Fe_3Al_2Si_3O_{12}} + \underset{\text{(Mg-opx)}}{Mg_2Si_2O_6} = \underset{\text{(Mg-garnet)}}{Mg_3Al_2Si_3O_{12}} + \underset{\text{(Fe-opx)}}{Fe_2Si_2O_6},$$

or in short-hand:

$$FeMg_{-1}\,(\text{garnet}) = FeMg_{-1}\,(\text{opx}).$$

A third geothermometer was used in this study. It calculates a temperature based on the composition of coexisting alkali [$(Na,K)AlSi_3O_8$] and plagioclase [$(Ca,Na)_{0-1}Al_{2-1}Si_{2-3}O_8$] feldspars.

Geobarometers (to calculate pressure) are almost all based on net-transfer equilibria. Net-transfer equilibria refer to equilibrium reactions written between coexisting mineral phases within a rock. The equilibria used in this study is: garnet-plagioclase-orthopyroxene-quartz.

Calculation of Temperature and Pressure - Results

The calculation of T and P in high-grade rocks (rocks that were metamorphosed at great depths) is not easy because the rocks are such at a high temperature that there is significant elemental diffusion and re-equilibration on their way up to the surface. This topic was reviewed in depth by Robinson (1991). In summary, to get the best estimates of "peak" conditions, one must use the composition of the garnet core with the composition of matrix biotite or the core

composition of orthopyroxene. We cannot use the composition of a biotite inclusion inside a garnet because there is too much ionic diffusion between the two minerals at the highest T and P and the compositions we measure today are not indicative of what they were during metamorphism. On the other hand, taking garnet and biotite compositions at the edge of the minerals give erroneously low temperatures because the minerals were resorbed during retrograde metamorphism. These lower temperatures are indicative of the final phase of equilibration, as the rocks moved up to the surface.

Elemental zoning in garnet is indicative of conditions of growth. For low-grade rocks, the zoning of Mn in garnet shows high Mn-concentrations in the core and lower at the rim. For high-grade rocks, there is no perceptible zoning. Traverses across garnet grains were done to determine if zoning was present. As shown in Fig. 2, there is no zoning, except a slight reversal at the extreme edge, indicative of retrograde conditions. Another way to visualize elemental zoning is by doing X-ray mapping on the electron microprobe. X-ray maps give in 2-dimensions the elemental concentration of an element of choice. Such a map is shown in Fig. 3. These figures show that the garnets from BRF grew at a high temperature, certainly higher than 650° C (Robinson, 1991), which is in accord with our calculated values.

Calculated temperatures are based on mineral compositions listed in Table 1. The best estimate of true peak conditions is given by compositions of core garnet with core orthopyroxene. This geothermometer gives 720°C at 6 kbar. The core garnet and matrix biotite gives 770°C at 6 kbar but that is erroneously high due to re-equilibration of matrix biotite. Core garnet with adjacent biotite inclusion gives 550°C. This value is regarded as too low because of re-equilibration. The retrograde value given by garnet - orthopyroxene edges is 510°C. Below these temperatures, the minerals did not exchange cations any longer and "froze" those values as minimum temperatures.

The P,T results can be seen graphically in Fig. 4. Each geothermometer and geobarometer give a line in P-T space. Where these lines intersect is the best estimate of P and T in the rock. For example, the peak conditions in sample BRF96_1.1A are given by the intersection of curves (1) and (4). Reaction (1) is a barometer based on the garnet-plagioclase-orthopyroxene-quartz calibration of Newton and Perkins (1982) calculated with core garnet and core orthopyroxene compositions. Reaction (4) is a thermometer based on garnet-orthopyroxene Fe-Mg calibration of Harley (1984) with core garnet and core opx compositions. Retrograde conditions are at the intersections of curves (2) and (3). Reaction (2) is the same barometer as (1) but calculated with garnet and opx edge compositions; whereas reaction (3) is the same as (4), but based on garnet and opx edge compositions.

What this graph tells us is that the rocks cooled from a peak conditions of 720°C and 6 kbar (about 18 km depth inside the earth) to 500°C and 3 kbar (about 9 km depth) on their way up to the surface. The rocks are now at the surface (20°C and 1 bar), but still retain the higher P and T conditions because there is no more chemical exchange at temperatures lower than 500°C. These two points suggest that the rocks from in and around Black Rock Forest experienced a cooling period accompanied by de-compression. These data give us a first insight into the P-T history of the rocks from BRF. I will continue my work with other samples to place better constraints on the processes by which rocks from BRF were brought down to these depths in the Earth and then made their way up to the surface.

Table 1: Analyses of minerals in sample BRF96-1.1A used in P-T calculation.

	Garnet (core)	Biotite (matrix)	Plagioclase Feldspar	Orthopyroxene (core)
SiO_2	38.99	37.24	61.66	50.60
TiO_2	0.01	4.69	0	0.10
Al_2O_3	21.86	15.89	24.23	5.35
FeO	26.58	11.75	0	21.61
MnO	1.66	0.02	0	0.41
MgO	10.08	15.88	0	22.48
CaO	1.07	0.02	5.73	0.08
Na_2O	0	0.32	8.04	0
K_2O	0	9.24	0.35	0
H_2O*	-	4.60	-	-
Total	100.25	99.66	100.00	100.66

	Garnet (edge)	Biotite (inclusion)	Orthopyroxene (edge)
SiO_2	37.80	38.40	51.19
TiO_2	0.04	4.24	0.12
Al_2O_3	21.08	16.08	4.97
FeO	30.21	8.49	21.03
MnO	1.92	0.04	.37
MgO	7.05	19.05	23.06
CaO	1.08	0	0.06
Na_2O	0	0.37	0
K_2O	0	9.34	0
H_2O*	-	4.60	-
Total	99.22	100.62	100.82

*H_2O-contents were calculated for biotite.

Expenditures

The BRF grant award totaled $4000. Budgeted and actual expenditures are listed in the table below. Travel expenses were minor, so that money was used toward analysis.

	Budgeted	Actual
Electron microprobe and SEM	$2400	$3000
Field supplies	$ 400	$ 150
Travel expenses	$ 400	$ 0
Sample preparation	$ 800	$ 850
Total	**$4000**	**$4000**

Abstracts and Publications Resulting From Award

We have not yet submitted abstracts or papers directly related to the project. Work is continuing, however, and we intend to publish our results as soon as we are finished with the research. Copies of all abstracts or papers submitted will be sent to the Director of Black Rock Forest.

Future Plans

There are many investigators from the Department of Earth and Planetary Sciences at the American Museum of Natural History that are actively involved in research associated with the geology of Black Rock Forest (Léger, Harlow, Webster, and Rebbert). We plan to continue our studies of the rocks, minerals, and mineral deposits of Black Rock Forest. We are in a position now to put into physical context the formation of the area in and around BRF. The chemical compositions of rocks and minerals from BRF are extremely interesting and contain enough work for years to come. We will strive to share our results with scientific colleagues as well as students and anyone else interested in the geology of the Forest.

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Fig. 1: A) Back-scattered electron photograph of specimen BRF96-1.1A. The bright mineral in the center is garnet. It is surrounded by orthopyroxene (light gray). The dark gray mineral is biotite.
B) Optical microscope photograph of the same area as in (A) above.

Fig. 2: Traverse across a garnet from specimen BRF96-1.1B (same outcrop as BRF96-1.1A). End-member compositions show that the entire garnet is unzoned, except for a small region at the edges where Mn, Ca, and Fe contents go up, and Mg goes down. These trends are indicative that the garnet grew at a high temperature (above 650°C).

Fig. 3: X-ray maps of the same area as in Fig. 1. These maps show that the garnet in the center of the map is unzoned in Mg and Mn contents. These maps show well in 2-dimensions that there is no zoning in any part of the garnet, without having to analyze a large number of points all over the mineral.

Fig. 4: Final results of P-T determinations for sample BRF96-1.1A. These values should be indicative of the physical conditions experienced by rocks from in and around the Black Rock Forest during the Grenville Orogeny at 1000 million years ago. The rocks were buried to a depth of about 18 km and were metamorphosed to 720°C. They subsequently cooled down to about 500°C on their way up to 9 km depth. The rest of their way up to the surface, the mineral compositions did not change.

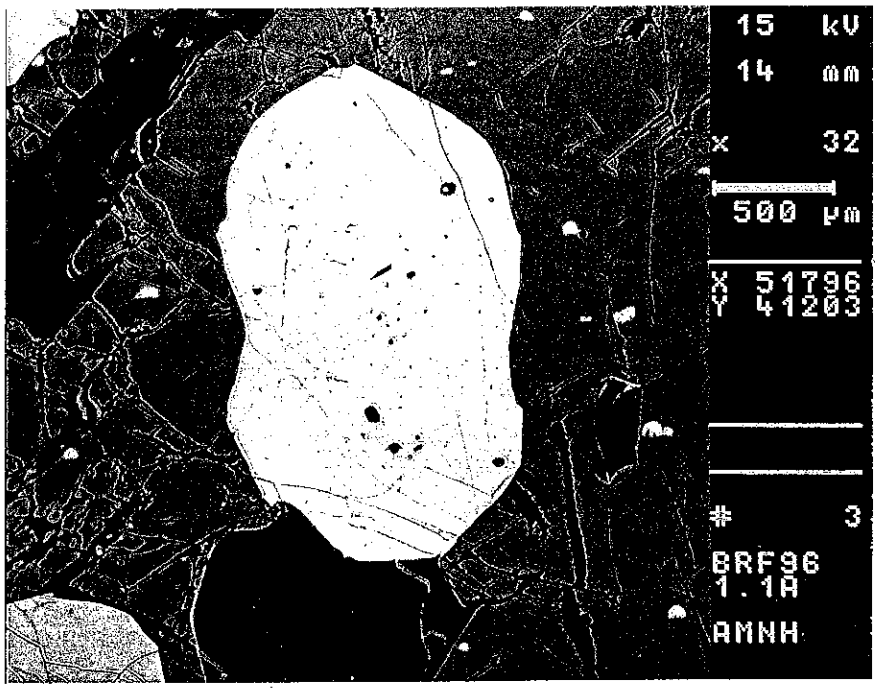

Fig. 1A

Fig 1B

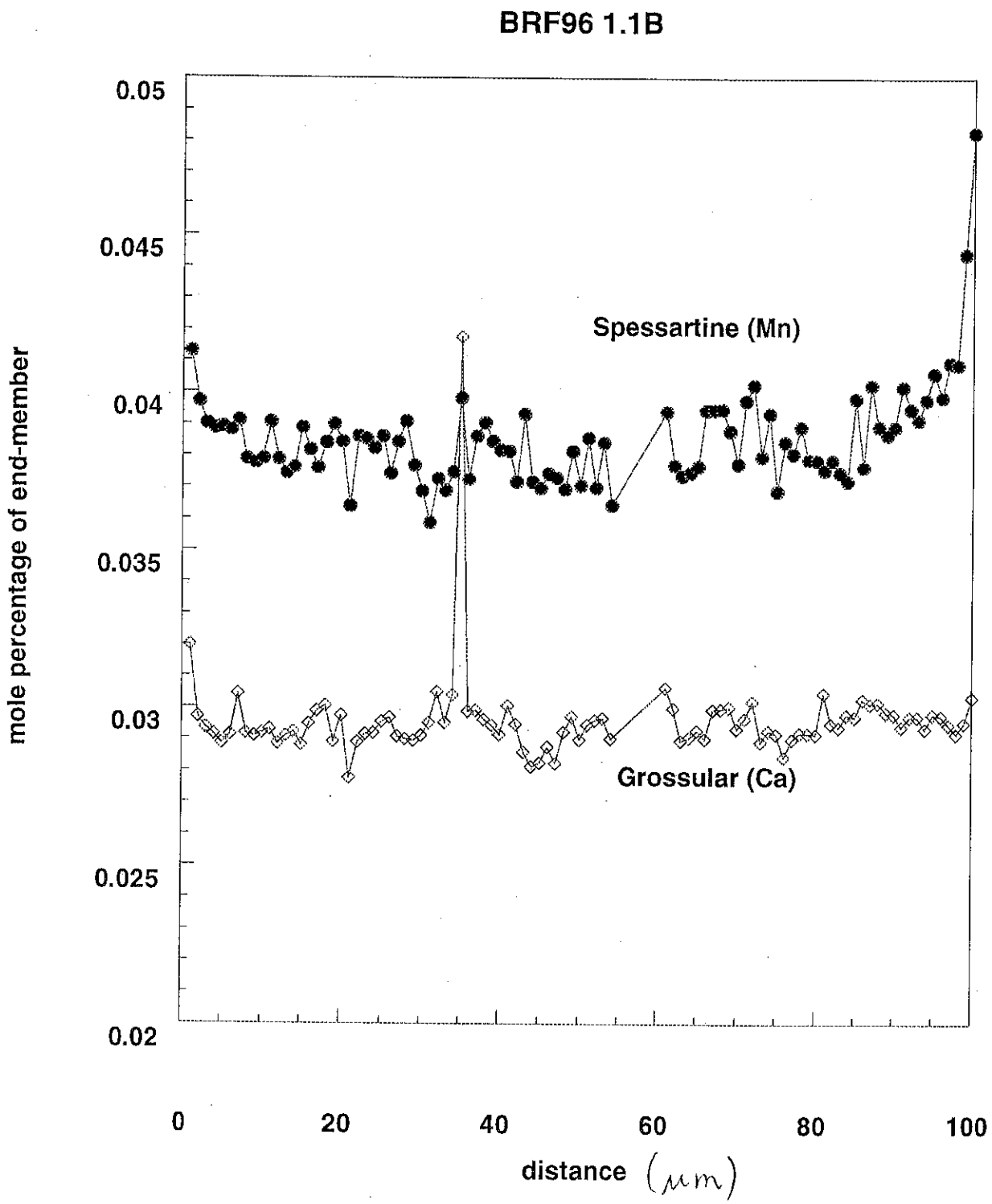
BRF96 1.1B
0.05
0.045
0.04
0.035
0.03
0.025
0.02
mole percentage of end-member
Spessartine (Mn)
Grossular (Ca)
0
20
40
60
80
100
distance (μm)

Fig. 2

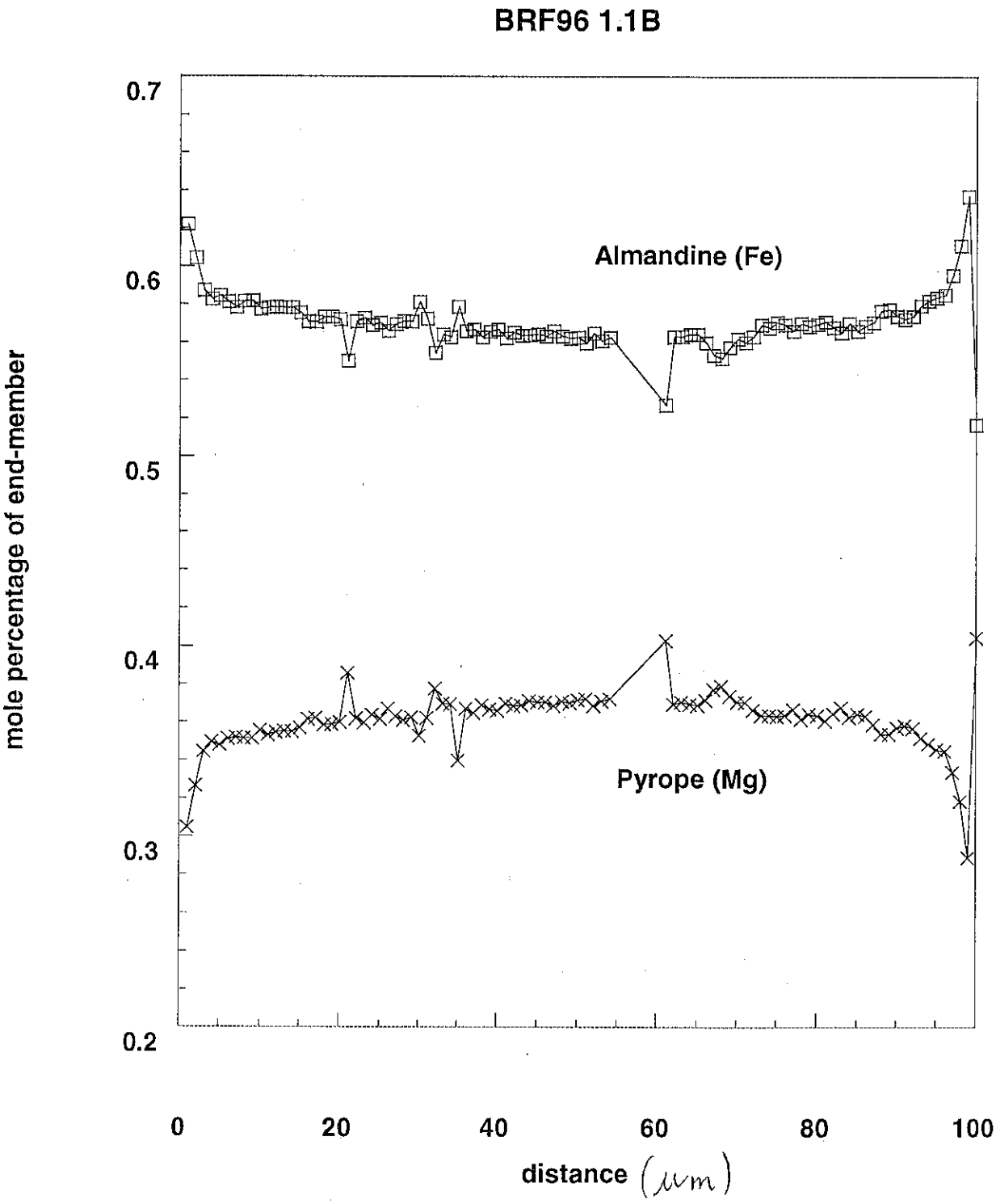
BRF96 1.1B
mole percentage of end-member
0.7
0.6
0.5
0.4
0.3
0.2
Almandine (Fe)
Pyrope (Mg)
0
20
40
60
80
100
distance (μm)

Fig 2

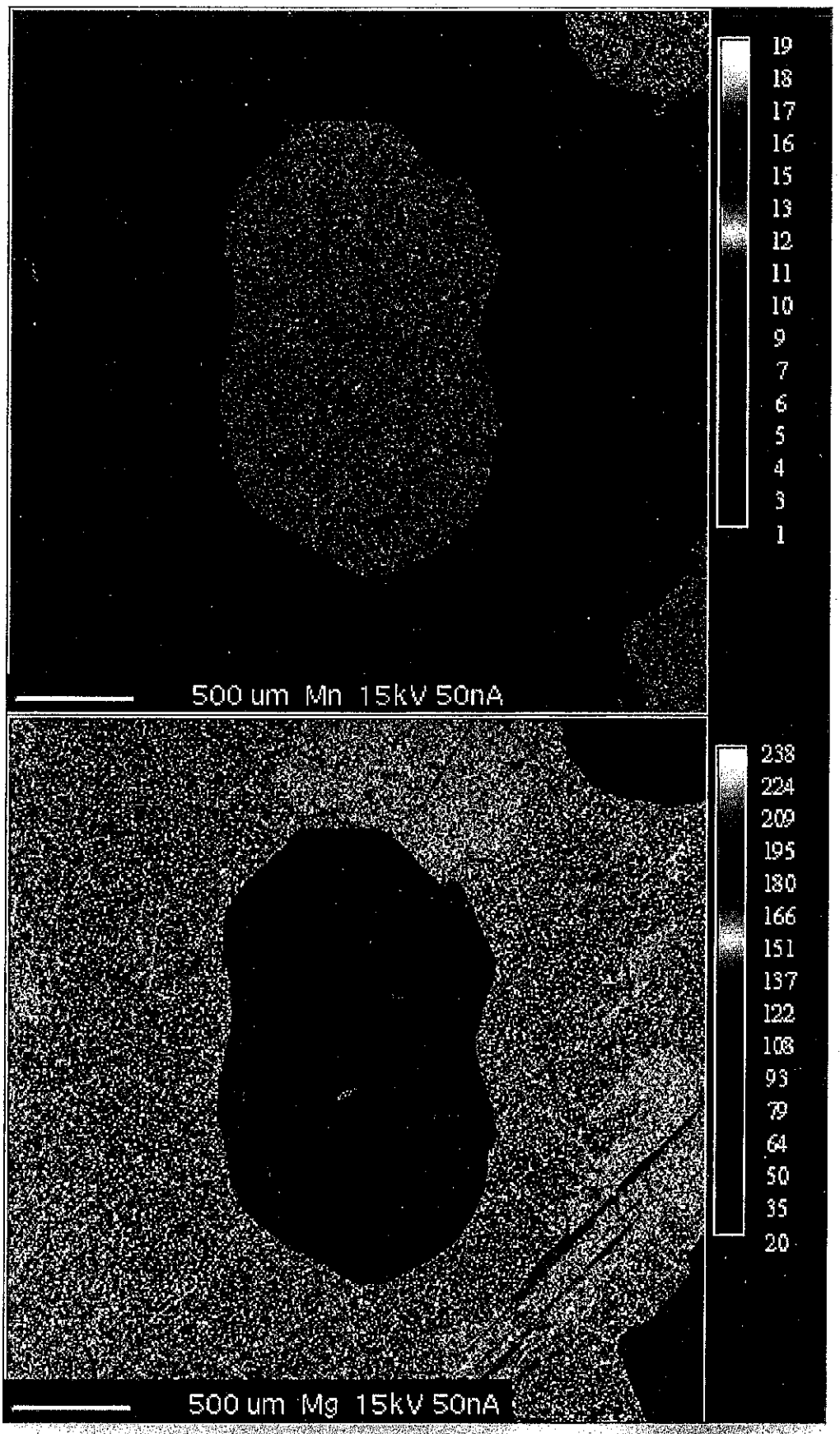
19
18
17
16
15
13
12
11
10
9
7
6
5
4
3
1
500 um Mn 15kV 50nA
238
224
209
195
180
166
151
137
122
108
93
79
64
50
35
20
500 um Mg 15kV 50nA

Fig. 3

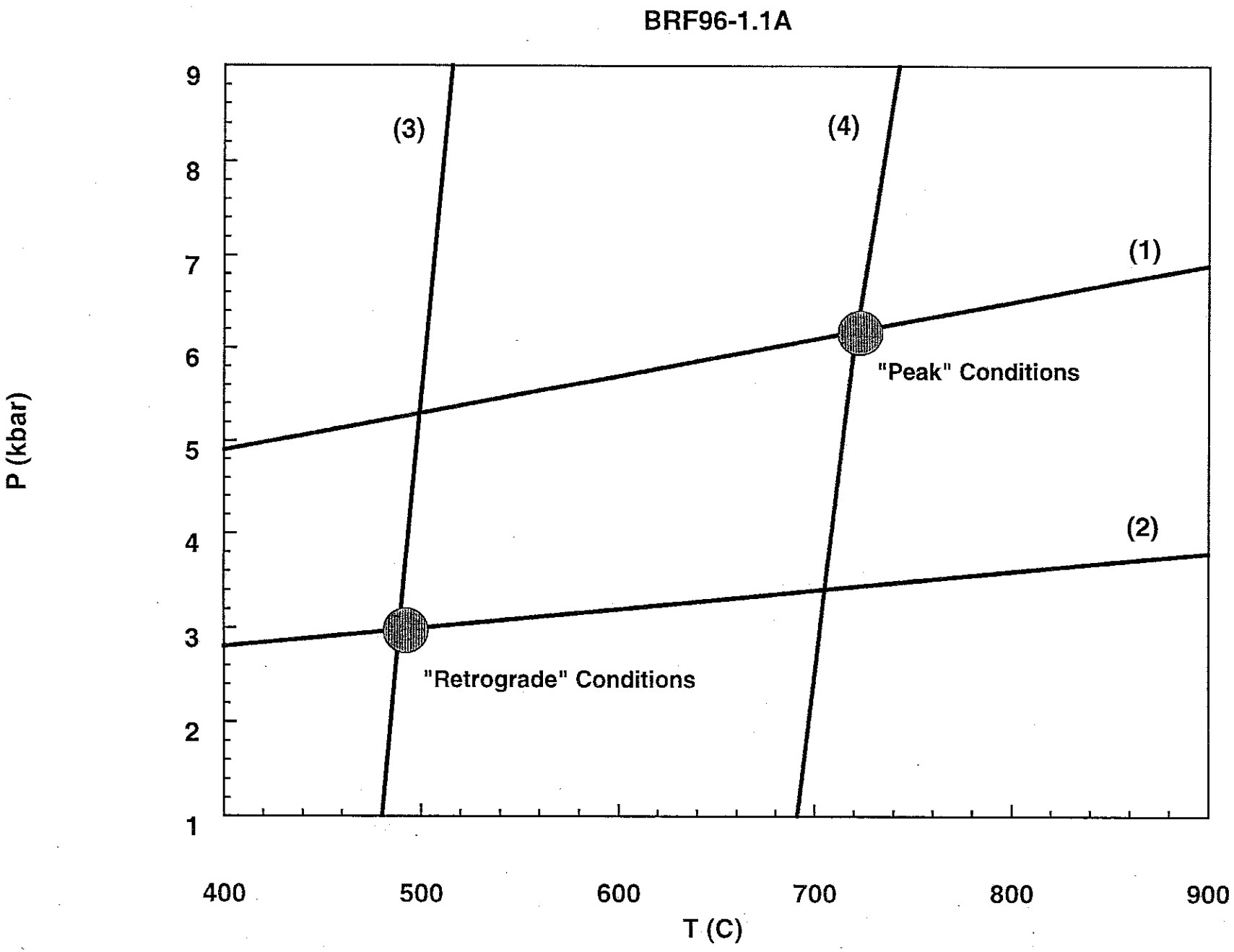
BRF96-1.1A
P (kbar)
9
8
7
6
5
4
3
2
1
(3)
(4)
(1)
(2)
"Peak" Conditions
"Retrograde" Conditions
400
500
600
700
800
900
T (C)

Fig. 4