Canadian Mineralogist
Vol. 11, pp. 464-472 (1972)

SHARP COMPOSITIONAL ZONING IN AN ALMANDINE GARNET

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ABSTRACT

Sharp compositional variations, evidenced by electron microprobe analyses, occur in garnet crystals in chloritic schists from Pedrignano (Parma). Ca and Mn are enriched in the cores and Mg in the edges, whereas Fe is depleted both in the cores and in the outer rims. The unusual sharpness of the compositional zoning brings about the splitting, besides the broadening, of the diffractions from powdered individual crystals.

DESCRIPTION OF THE SAMPLES

The samples used for this research are from the Mineralogical Museum of the University of Parma and are labelled as occurring in Pedrignano (Parma). They consist of garnet-bearing chloritic schists in which garnets appear irregularly scattered about 30% by volume of the rock ; this is only an approximate value since the modal counting is affected by the widely varying size of garnet crystals ; the remaining part of the rock is entirely chlorite with a disseminated magnetite.

CHLORITE

Chlorite occurs as dark green flakes sometimes arranged in radial aggregates and characterized by high pleochroism (γ = very light green, almost colourless ; $\alpha \simeq \beta$ = emerald green), low birefringence and positive optic sign. The refractive index $\alpha \simeq \beta = 1.617 \pm 0.002$ was measured by the immersion method (Na light) accounting for the variations in different flakes. The specific gravity, measured with a Westphal balance by suspension in $CHBr_3$ and CH_2I_2 solutions, is 2.87 ± 0.02 ; the average of several measurements on flakes from two separations by isodynamic separator.

From optical and specific gravity data, this chlorite would be classified as *prochlorite* according to Troeger (1951), whereas it would be considered as *corundophilite* using the classification by Hey (1954) in Deer *et al.* (1962).

The lattice constants calculated from diffractometric data (Fe$K\alpha$/Mn radiation) are :

$d_{001} = 14.14 \pm 0.02$ Å (from diffractions 003, 004, 005)
$b = 9.25_8$ Å (from diffraction 060).

In order to obtain the distribution coefficient for Fe and Mg and the partition ratios for other elements between coexisting chlorite and garnet, chemical determinations were carried out on total Fe as (FeO), MgO, CaO and MnO in chlorite purified by hand using the stereo microscope after magnetic isodynamic and density separations. The results are (wt. %) : FeO (total) 21.0, MgO 20.7, CaO < 0.05, MnO 0.17.

GARNET

The crystals, isodiametric but never clearly euhedral, vary in diameter over a wide range up to 6-7 mm, their colour is constantly brownish red. In thin sections the light pink colour fades slightly from core to edges. Inclusions consisting only of chlorite, iron oxides and hydroxides, quartz and muscovite, are extremely scanty and scattered at random. Sometimes chlorite veinlets cross the garnet crystals, which appear always perfectly isotropic.

The refractive index was measured by the immersion method in a solution of stannic iodide in methylene iodide saturated with sulphur. Significant systematic differences were not found, neither between the rims and cores of individual chystals, or among different crystals. The mean value 1.805 ± 0.004 may be considered representative, accounting for the experimental errors.

Chemical composition

Material for a complete chemical analysis [1] was prepared by crushing garnet crystals, sieving and handling the portion in the range of 0.25-0.06 mm with density and magnetic techniques [2]; the final purification was accomplished by hand at the stereomicroscope.

The weight percent values of the oxides are reported together with the molecular percentages of end members and the atomic proportions on the basis of 12 oxygens in Table 1.

Microprobe investigation

Thin sections of the almandine from Pedrignano were studied on the electron microprobe at the Department of Geology and Mineralogy, Uni-

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[1] The methods used in chemical analysis of garnet and chlorite were as follows: gravimetric for SiO_2; volumetric for FeO (according to Pratt-Hillebrand) ; colourimetric for total iron (1-10 phenantroline), MnO (oxidation to Mn^{7+} by ammonic persulphate), TiO_2 (tiron) ; atomic absorption for Al_2O_3, CaO and MgO. Analysis powder dried at 110°C.

[2] The magnetic separations were carried out by Frantz II isodynamic separator, 15° forward and 25° side-tilt.

versity of Oxford. Chart recorder traces in Fig. 1 refer to traverses across two crystals of ca. 1,400μ and 2,000μ respectively. In Fig. 1*a* the compositional variations appear perfectly symmetric, whereas in 1*b* they are

TABLE 1. BULK COMPOSITION, STRUCTURAL FORMULA AND PROPORTIONS OF GARNET END-MEMBERS IN ALMANDINE FROM PEDRIGNANO, PARMA.

SiO_2	$35._9$	Si	2.926	3.000
TiO_2	0.1_2	$Al^{[4]}$	0.074	
Al_2O_3	$20._4$			
Fe_2O_3	$1._9$ [1]	$Al^{[6]}$	1.886	2.010
FeO	$34._9$	Ti[2]	0.007	
MnO	1.3_8	Fe^{3+}	0.117	
MgO	2.9			
CaO	2.2	Fe^{2+}	2.379	3.018
	99.7_0	Mg	0.352	
		Ca	0.192	
		Mn	0.095	
		O	12.000	

Physical Properties

	n_{core}	1.805 ± 0.004
	n_{rim}	1.805 ± 0.004
Film average	a_{core}	11.591 ± 0.007
	a_{rim}	11.531 ± 0.005
Diffractometer average	a_{core}	11.593 ± 0.004
	a_{rim}	11.533 ± 0.003

Molecular Proportions[3]

Almandine	78.8
Andradite	5.8
Grossular	0.6
Pyrope	11.7
Spessartite	3.1

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[1] As FeO may be low owing to incomplete attack, the highest value was chosen in a set of repeat determinations.

[2] We placed Ti in the R^{3+} group according to Deer *et al.* (1962) neglecting it in the calculation of the end-member proportions.

[3] Andratite calculated by Fe_2O_3 and grossularite by remaining CaO.

clearly skew. In all cases a very smooth and small decrease from rims to core appears for Mg and a stronger increase both for Ca and Mn, whereas Fe behaves more irregularly. Increase in Ca and Mn occurs abruptly in the first one, gradually in the second diagram, reaching "plateau" — values in the core. We decided, however, to use the charts only for qualitative zoning information, since calculations for quantitative values would require large corrections for the effects of atomic number, secondary fluorescence, mass obsorption, *etc.* to obtain some reliability.

The Mn-enrichment toward the core agrees with findings by Harte & Henley (1966), Hollister (1966), Blackburn (1969), Brown (1969) and Hietanen (1969), whereas the opposite behaviour of Mg is in agreement with evidence gathered by Dudley (1969), Harte & Henley (1966) and

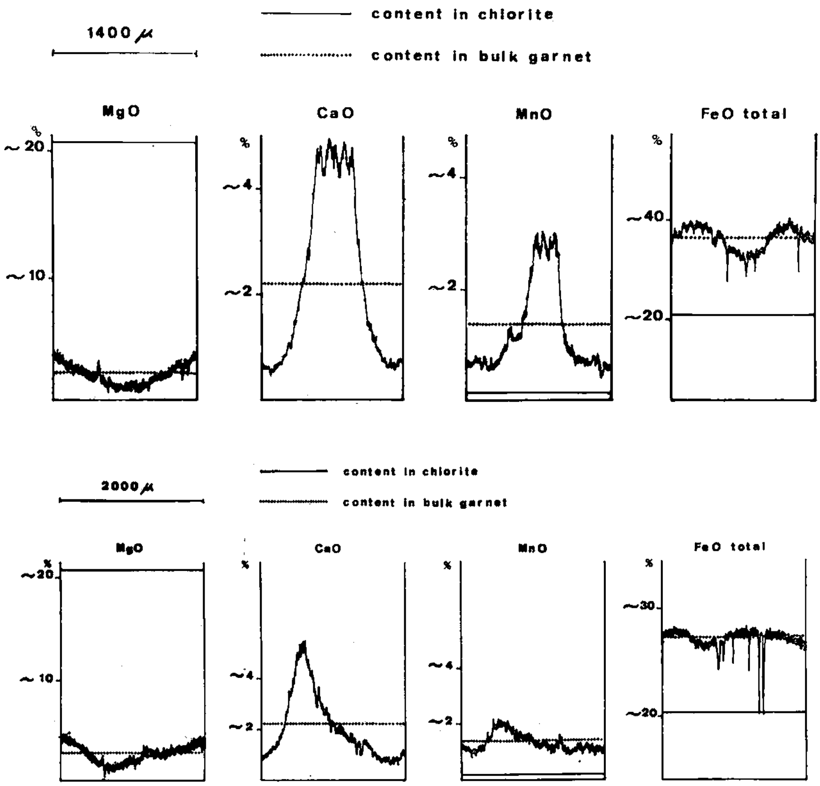

FIG. 1. Electron microprobe chart recorder traces on two crystals; a (top) 1,400μ b 2,000μ.

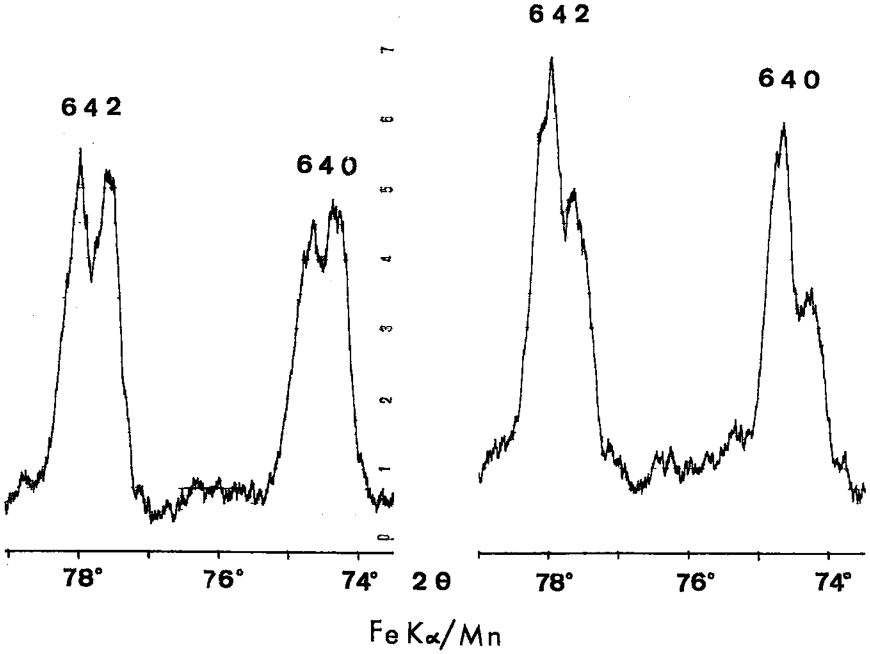

FIG. 2. Diffractometer records of two magnetic fractions from an individual crystal: a (left) not magnetic at 0.40 amp; b magnetic at 0.40 amp.

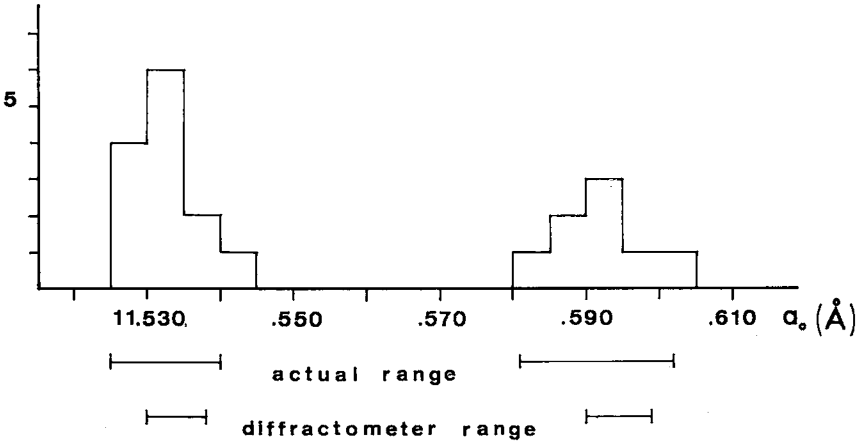

FIG. 3. Distribution of *a* values from powder photographs on very small crystall fragments.

other authors. The remarkable increase of Ca toward the core is perhaps the most interesting feature of these garnets, as Brown (1969) says that "many garnets are zoned strongly in Fe and Mn but not in Ca". The Ca trend we found is in agreement with the plots reported by Harte & Henley (1966), although these authors declare that this element, (as Mg too), may either increase or decrease, whereas Hietanen (1969) states that Ca generally behaves contrary to Mn, though much more irregularly.

Whereas Hietanen (1969) observed Fe to remain fairly constant, Harte & Henly (1966), Hollister (1966) and Brown (1969) found that it increased toward the edges. In our diagrams, going from core to edges, total iron increases first, then decreases at the outer rims. This could be related to an opposite behaviour of Fe^{2+} and Fe^{3+}, with a decreasing trend for the first toward the core (see Mg) and for the second toward the edges ; a sympathetic variation for Ca and Fe^{3+} is actually in agreement with crystal chemical features of garnets. In the hypothesis of opposite trends, occurring smoothly for Fe^{3+} and somewhat abruptly for Fe^{2+}, a diagram would result, by overlapping, quite close to the experimental one.

X-RAY STUDIES

Diffractometer

Diffractometer records have been carried out on powders from individual crystals and also on two different magnetic fractions of powdered single crystals. In agreement with the electron microprobe data, diffractions are always remarkably broad and, from 521 onward, appear clearly split into two peaks. By comparing the records of two different magnetic fractions from an individual crushed crystal, variations appear in the intensity ratio of the two peaks of each diffraction (Fig. 2 *a* and *b*). This proves that the magnetic separations cause at least a partial separation of materials with different chemical composition : a further magnetic separation was not achieved, possibly due to the total Fe depletion both in the core and in the outer rims.

From the diffractometer records on powders from individual crystals, two sets of *a* values were obtained, definitely different from one another, by reading the Bragg angle in reference to the two distinct peaks of each broad diffraction, *i.e.* 11.533 ± 0.003 and 11.593 ± 0.004 respectively (Table 1 and Fig. 3).

Powder photographs

Powder photographs were taken by Fe$K\alpha$/Mn radiation on fragments smaller than 1/8 mm, randomly chosen by crushing three crystals from a single rock hand-specimen[1].

The results obtained can be split also in this case into two sets, averaging 11.531 ± 0.005 and 11.591 ± 0.007 respectively, both with symmetric distribution pattern (Fig. 3, and Table 1). In particular, powder photographs of a fragment from the rims and another from the core, picked by hand from a microscope slide, gave values close to 11.53 and 11.59 respectively.

The *a* averages from films agree quite well with those from diffractometer (Table 1).The wider ranges obtained for photographic values are obviously due to the fact that the fragments were chosen at random, whereas the diffractometer readings were accomplished in reference to the two distinct peaks of each split diffraction, corresponding to the two more abundant compositions.

SUMMARY AND CONCLUSIONS

Electron microprobe investigations evidence sharp compositional variations in almanditic garnets of chloritic schists from Pedrignano. The Mn-impoverishment towards the rims, in agreement with most findings on zoned garnets and possibly to be related to Mn-depletion from the equilibrium system during their growth (Brown 1969) is here almost sharp, whereas Mg shows an opposite behaviour, increasing smoothly towards the edges.

The most peculiar feature is, however, the very strong and sharp enrichment of Ca in the cores, which could possibly be related to the lack of minerals other than chlorite and garnet in the rock.

The depletion of total iron both in the rims and in the cores is to be related to the Fe^{2+}—Mg diadochy in the rims, whereas in the cores a higher impoverishment of Fe^{2+} by the Ca and Mn^{2+} diadochy possibly is partially counterbalanced by Fe^{3+} proxying for Al.

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[1] For this purpose both a conventional camera (Siemens, 57.3 mm in diameter) and a Gandolfi camera (same diameter, GANDOLFI 1967) were used, the latter using single grains down to 30μ. The *a* values were calculated by extrapolating to $\theta = 90°$ the regression line $\frac{1}{2}$ $(\cos^2 \theta/\theta + \cos^2 \theta/\sin \theta) / a$ in the case of the conventional camera; for the Gandolfi camera, in which absorption is negligible on account of the small specimens used, *a* values were obtained by reading at high Bragg angles, where the α_1 and α_2 diffractions are clearly resolved. The photographs taken by the Gandolfi camera show lines remarkably sharper, in agreement with the compositional homogeneity of the extremely small samples used.

In this scheme all the diadochies in the core occur with increase in ionic radius, which results in a strong enhancement of the cell edge values therein. Zoning being strong and sharp, diffractions from powdered individual crystals appear clearly split at higher angles.

In our case the refractive index is not indicative of zoning, its overall constancy being possibly accounted for by the balancing effects of the low Mg enrichment in the rims of a higher Ca and Mn proxying for Fe^{2+} in the cores, since the Mg diadochy is much more effective in lowering the refractive index of almandine than Ca and Mn.

As regards the partitioning of elements between chlorite and garnet, the only minerals of these chlorite schists, calcium, manganese and total iron are highly enriched in garnet, whereas magnesium is impoverished. It must be borne in mind, however, that, on the ground of microprobe data, even within the limits of qualitative comparisons, the amount by which Ca and Mn decrease in individual crystals from the core toward the rims is higher than when passing from the same rims to the surrounding chlorite flakes.

On the whole then it obviously follows that, as warned by Harte & Henley (1966), the interpretation of bulk chemical composition in reference to metamorphic grades must be approached with caution, especially when a sharp compositional variation occurs, as in this case.

Acknowledgments

The authors are very grateful to Prof. E. A. Vincent for the kind hospitality to G. V. in the Dept. of Geology and Mineralogy, University of Oxford, and to Dr. B. Atkins, of the same Dept., who performed the microprobe analyses. They thank also very warmly Dr. L. G. Berry, Queen's University, Kingston, Prof. P. Gallitelli, University of Bologna and Prof. M. Deriu, University of Parma, for critically reading the manuscript and for useful suggestions, as well as Miss G. Chiavarini for her help in *x*-ray investigations. Financial support was by Consiglio Nazionale delle Ricerche, Rome, Italy (Contratto di ricerca N. 69/00414/1151463).

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Manuscript received September 1970, emended January 1971.