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Garnet-Biotite Chemistry for Thermometry of Staurolite Schist from South of Mashhad, NE Iran

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Abstract

Mashhad Metamorphic Complex (MMC) with metamorphic, granitic intrusions and ophiolite units is situated in the suture zone of Paleotethys in NE Iran. Triassic staurolite-garnet schist of Khalaj represents the highest grade of metamorphism in MMC. In this study EPMA analyses of garnet and biotite used to determine the maximum temperature for regional metamorphism. The pattern of zoning in garnet also used to describe the exhumation history of the area during metamorphic events. Maximum temperature for staurolite garnet schist of MMC calculated with garnet-biotite thermometer is ~618°C. The quantitative analysis of major elements along core to rim profiles obtained for garnet porphyroblast show the presence of growth zoning. Mg and Fe increase slightly outwards, while Mn decreases from core to the rim. Preserved garnet growth zoning in temperature above 600°C, indicates that staurolite-garnet schists of MMC on the margin of Paleotethys in NE Iran were rapidly heated and cooled. However, growth zoning is not well preserved in the rim of garnet grain. It could be an evidence for the presence of later retrograde metamorphic phase which influenced regional metamorphic schists in MMC.

Keywords: Garnet; Thermometry; Paleotethys; Mashhad; Iran

Introduction

Estimates of metamorphic P-T conditions provide fundamental information about tectonic history of exposed crustal sections in orogenic belts. Garnet and biotite are the most useful minerals for thermometry of pelitic metamorphic rocks, because they usually occur in pelitic rocks and are sensitive to temperature changes. Chemical zoning of garnet also has been extensively studied to provide quantitative descriptions of metamorphic system. The study of zoning in metamorphic garnets was initiated from 1970s and synchronous with the development of electron microprobe (e.g., [12,13,18]). Growth zoning in garnet especially in green schist and amphibolite facies is one of the controversial discussion issues in metamorphic petrology, since the distribution of the elements in solid solutions present among the garnet end members is a leading map which records *P-T* variations in prograde metamorphism (e.g. [35, 36]). Distribution of elements such as Mn, Fe, Mg and Ca in garnet porphyroblasts also depends on metamorphic cooling rates. A good

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example is the application of zoning to estimate cooling rates during retrograde diffusion (e.g. [11]).

The Mashhad Metamorphic Complex (MMC) with composite tectonometamorphic history on the margin of NE Iran block comprises metamorphic and igneous rocks. The formation and uplift history of the MMC is not well known. Thermometry and study of the uplift and exhumation process of pelitic metamorphic rocks would aid in understanding the evolution history of the NE Iran. In this paper, using the garnet and biotite chemistry in staurolite garnet schist of Khalaj area, exposed in south of Mashhad, we considered the following questions:

(1) What is the highest temperature recorded in metapelitic rocks? (2) What information concerning the exhumation history may be derived from the zoning of garnet porphyroblasts?

Material and Methods

Regional Geological Setting

Since the work of Alavi [3] in northeast of Iran (Fig 1a) most workers have divided the area into a series of tectonic domains: (1) Kopehdagh zone which is part of Turan plate and consists predominantly epicontinental sedimentary rocks, (2) suture zone with metamorphic, granitic intrusions and ophiolite units, and (3) Binalod zone with Paleozoic to Tertiary rocks forms part of the NE Iran block. The suture zone with NW trend results from collision of Turan plate with NE Iran block and closure of Paleotethys in the late Paleozoic [2,3]. General geology and field relations of these series have been described by many authors [3,4,9,19,27,28,33,37].

Mashhad Metamorphic Complex

Mashhad Metamorphic Complex (MMC) with NW trend situated in suture zone between Turan plate in the north and NE Iran block in the Khorasan province. It is located south of Mashhad city and consists of Permian and Triassic metamorphic rocks, granitic intrusions and ophiolite units. Prior to this study petrography and petrology of many igneous and metamorphic rocks were described by [1,5,6,14,26,29,31].

Permian metamorphic rocks are: (1) metamorphosed ultrabasic and basic rocks consist of metaharzburgite, metalherzolite, serpentinite and metagabbro with minor metabasalt, (2) spilitized metabasalts with pillow structure, (3) crystallized limestone with traces of Permian fossils, (4) metamorphosed sandstone, (5) a complex of phylite, slate, marble schists and metaconglomerate and metatuff. Triassic metamorphic rocks are mainly low to medium grade metapelitic rocks known as Mashhad phylites.

According to petrography and petrology, geographic distribution, topography and shape, granitic intrusions of MMC classified into two phases [29]: older porphyroid granite (G1) which is composed of small and separated bodies and younger leucogranite (G2) with 15 km long and 10 km wide.

The ophiolitic unit is positioned southwest of Mashhad city (Fig. 1b) and presents tectonic contact with metamorphic rocks. Within ultramafic-mafic rocks at Torbar-e-jam to Fariman lineament samples with komatiite nature have been described and mapped suggesting a new petrogenetic model for magmatism in the region (e.g. [32]).

The Study Area

The study area is located between 36° 11′ and 36° 19′ longitudes and 59° 30′ to 59° 36′ eastern latitudes and 5km southwest of Mashhad city (Fig. 1b). The main rocks in the area are metamorphic rocks with metapelitic nature, G1 and G2 granites with pegmatites and aplite veins. Mineralogy of main units of MMC is summarized in Table 1.

Regional metamorphism of flysch type sediments of Triassic age [3], composed of phyllite, mica schist, garnet schist, staurolite-garnet schist, amphibolites, intercalated with crystalline limestone and metasandstone. Metamorphic grade increase from slate in the northeast to staurolite-garnet schist in the southeast close to Khalaj village, with following metamorphic zones:

Biotite zone: This zone is recognized by biotite appearances in the metapelites. Biotite zone contains chlorite+ biotite + muscovite + quartz ± iron oxides ± calcite assemblage.

Garnet zone: Garnet zone exists in the southeast of the MMC with abundant almandine type garnet. Its mineralogy is different from mica schists of biotite zones and stronger schistosity is observed. This zone is recognized by garnet + biotite + muscovite + quartz ± chlorite assemblage. 0.5 to 3 mm euhedral garnet crystals present uniform distribution in the rock.

Staurolite zone: This zone is characterized by staurolite isograd, exposed in Khalaj region with low topography. Staurolite zone is recognized by staurolite schists and staurolite-garnet schists composed of staurolite + biotite + muscovite + quartz ± garnet assemblage and present the highest metamorphic grade in the area.

The samples selected for present study were derived from staurolite-garnet schists of Khalaj area (Kh-62 and

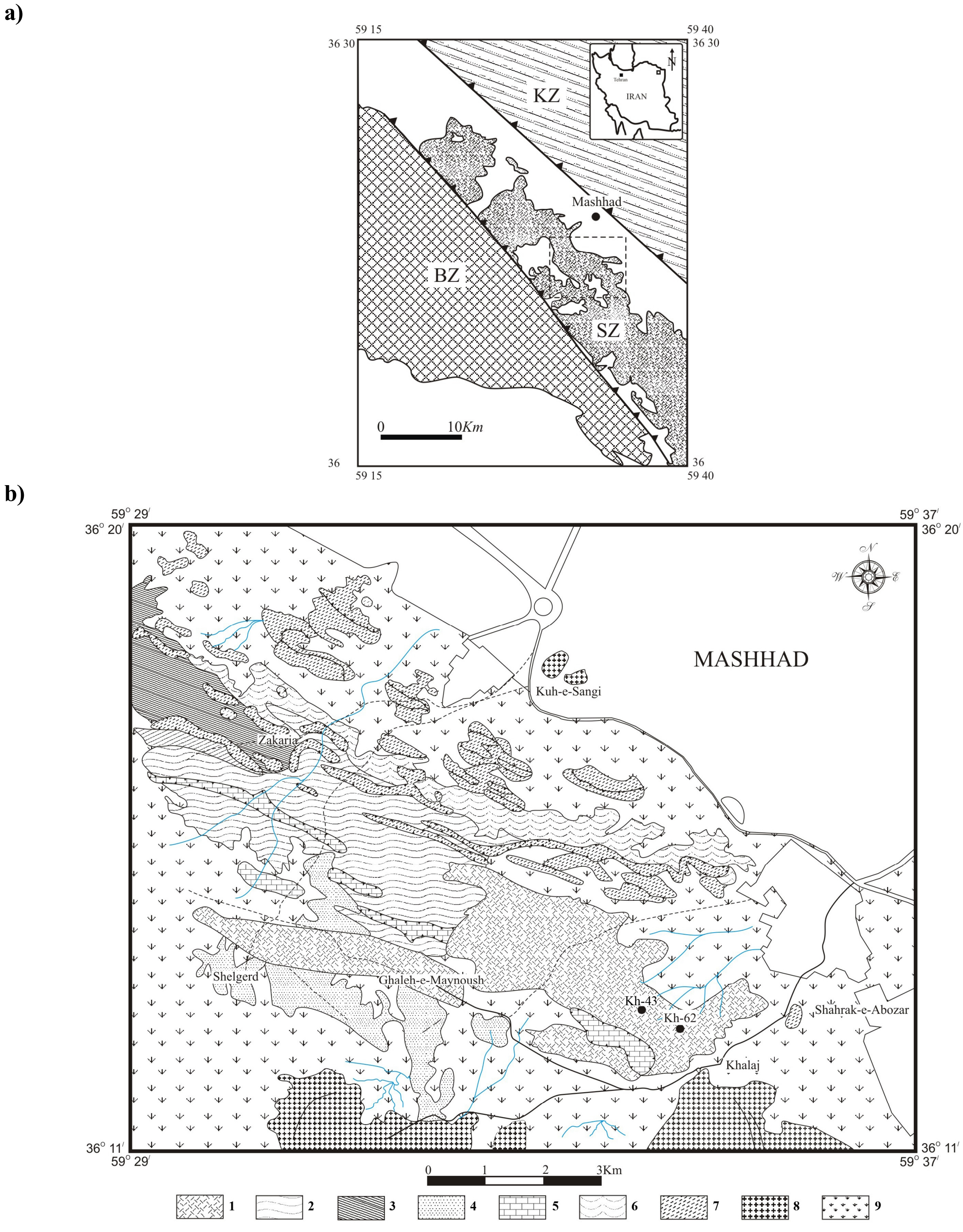

Figure 1. (a) Main tectonic domains in NE Iran (after [3]), KZ: Kopehdagh zone, SZ: Suture zone and BZ: Binalod zone, (b) Geological sketch map of the studied area. Circle showing location of sample (modified after [4]). 1-Staurolite schist, staurolite garnet schist (Permian), 2- Mica schist (Permian), 3- Phyllite, slate (Permian), 4- Quartzite (Permian), 5- Marble (Permian), 6- Association of sedimentary sequence with ultramafic rocks and spilite (Permian), 7- Metamorphosed lherzolite, serpentinite, tuff, lapillitiff, olistolith (Permian), 8- Leucogranite, tourmaline-muscovite granite (Pre-Bajocian), 9- Alluvium (Quaternary).

Table 1. Mineralogy of main rock units in Mashhad Metamorphic Complex

Rock unit	Mineralogy
staurolite-Garnet schist	Garnet + Staurolite + Muscovite + Biotite + Quartz
staurolite schist	Staurolite + Muscovite + Biotite + Quartz
Mica schist	Quartz + Biotite + Muscovite + Chlorite ± Opaque
Phyllite	Quartz + Biotite + Chlorite ± Sericite ± Garnet ± Opaque
Amphibolite	Amphibole ± Plagioclase ± Quartz
Quartzite	Quartz + Muscovite + Chlorite
Marble	Calcite ± Quartz ± Muscovite ± Biotite
Granite G1	Plagioclase + Quartz + Feldspar ± Muscovite
Granite G2	Plagioclase + Quartz + Feldspar + Biotite ± Muscovite ± Tourmaline
Pegmatites-Aplite	Quartz + Feldspar ± Tourmaline ± Muscovite

Kh-43). The regionally metamorphic schists are mainly located in the southern part of the MMC complex (Fig. 1b). In hand specimen, rocks mainly contain staurolite, garnet and mica in a fine-grained matrix. Garnet crystals are uniform in size and distribution. Garnets have euhedral crystal face on some sides, with diameters between 0.5 and 3 mm. Garnet is red to brownish red, and crystals in staurolite - garnet schists have lighter colors than those in garnet schist. In thin section, staurolite - garnet schists show quartz (up to 5%), garnet (up to 3%), staurolite (up to 5%), and biotite (up to 6%) in a very fine-grained matrix (Fig. 2).

Pressure shadow is observed around garnet crystals, provided suitable space for growing mica. Garnet and staurolite porphyroblasts are synkinematic and mica rinds in matrix around porphyroblasts. Garnet grains are notably poor in inclusions.

Mineral analyses were collected using Cameca X100 electron microprobe at Iran Mineral Processing Research Center.

For garnet porphyroblasts, major element profiles were acquired at operating conditions of 15kV accelerating voltage and 10 nA beam current. Along a linear traverse from core to rim of the crystals (Fig. 3), 12 (sample Kh-62) and 10 (Kh-43) analyses with the equal interval were obtained for Mn, Fe, Mg, Al, Ca, and Ti. The cores to rim results are summarized in Table 2. All iron was assumed to be Fe^{2+} on recalculation.

The quantitative analyses of selected biotites from were performed with a 15 kV accelerating voltage, a 15nA beam current and a 2-5 μm beam size. The counting time at each peak was 20-30 s.

Biotites are rather homogeneous and their compositions are uniform throughout the sample. However, rims of several (usually 2, sometimes 3 or 5) biotites were measured. All measured rims of biotites are in contact with garnet, which is an important requirement for application of thermobarometry. Representative analytical data are listed in Table 3.

Result and Discussion

Pattern and Origin of Zoning

The quantitative analysis of elements along core to rim profiles obtained for garnet in both samples (Kh-62, Kh-43) (Fig. 4), show relatively homogeneous or weakly zoned core for Ca, Mn and Mg. Up to point 7 in sample Kh-62 and point 6 in sample Kh-43, Fe is the element which shows limited oscillatory changes (Fig. 4). Toward the rim, the garnet crystall gives way to pronounced zoning in Fe, Mg and Mn. Fe and Mg have been increased from point 7 towards the rim while Mn and Ca have been decreased. Near the rim, Fe, Mg, Ca and Mn reveal a sudden change. In the case of Mg, Fe and Ca the changes are not followed the general pattern and are reverse. However, Mn shows a normal decrease from core to rim. There is no detectable Si and Al zoning (Fig. 4). Chemical trend of changes in garnet composition from core to rim on Mn, Mg and Fe ternary diagram, (Fig. 5) shows linear chemical changes from core to rim for analyzed garnet grains.

Main types of zoning patterns in metamorphic rocks were discovered from microprobe analysis of zoned garnet grains at the beginning of 60^{th} (e.g. [7,23,24]). Garnets with growth zoning have Mn rich cores, and Fe and Mg contents are greatest at the rim [8,24,25,38,40]. In contrast, in diffusion zoning the relatively homogeneous or weakly zoned core of garnet gives way to pronounced zoning in Fe, Mg and Mn near the rim, and the sense of zoning of Mg and Mn is the reverse of that in growth zoning [15,17,38].

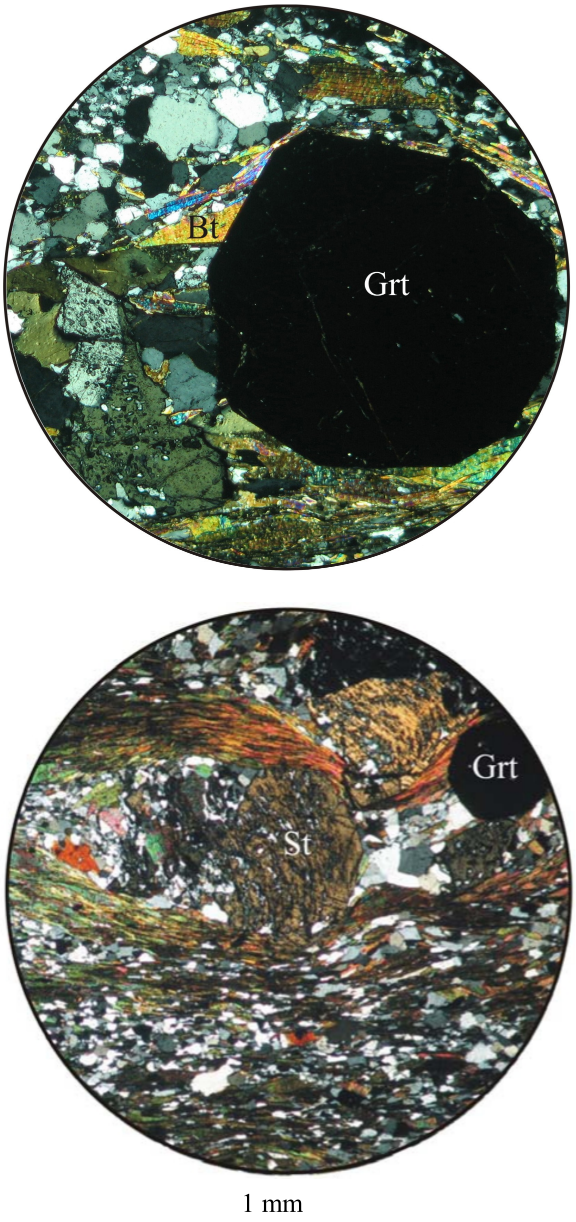

Figure 2. Staurolite garnet schists of Khalaj in MMC (a: sample Kh-62, XPL and b: sample Kh-43, XPL). Grt = garnet, Bt = biotite.

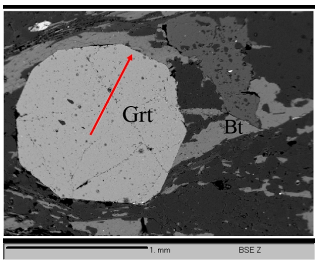

Figure 3. BSE image analyzed sample (Kh- 62). Grt = garnet, Bt = biotite.

General gradual decrease in Mn and increase in Fe and Mg from the core to the rim of the garnet porphyroblasts (Fig. 4) and trend of changes in Mn, Mg and Fe ternary diagram, (Fig. 5) are indicative of continuous growth zoning. Such a growth zoning has been reported for garnets in some amphibolite facies rocks (e. g. [39, 40]). However, growth zoning is not well preserved in the rim of garnet from staurolite-garnet schists of MMC. It could be an evidence for the presence of limited retrograde diffusion.

Carlson [10] reviewed evidences in metamorphic rocks for partial chemical disequilibrium and suggested that even though Fe and Mg might equilibrate at cm scale under lower greenschist facies conditions, Mn might not equilibrate at that scale until upper greenschist facies conditions were reached, Ca and some trivalent cations might not equilibrate until the middle amphibolite facies. Sudden reverse changes for Fe and Mg and normal change for Mn in the rim of the studied garnet crystals are in line with such a suggestion. Masoudi et al. [30], by study of almandine garnet from metamorphosed Al-Fe rich rocks from Dehsalm metamorphic complex in east of Iran, concluded that Ca distribution is not concentric and it is difficult to offer an conclusion for behavior of Ca based on a single traverse in garnet.

Garnet-Biotite Thermometry

Garnet and biotite are commonly co-existing minerals in pelitic metamorphic rocks, so they are usually used for thermometry [20-22]. Ferry and Spear [16] introduced an equation of state for thermometry, based on Fe and Mg substitution in garnet and biotite. In order to calculate the maximum temperature for metamorphism, chemistry of the core was used in the case of garnet. Temperature for garnet-biotite assemblages calculated based on Ferry and Spear [16] for sample Kh-62 following the equation: $LnK_D = (-2109/T) + 0.782$. K_D is calculated based on $(Mg/Fe)_{grt}$ / $(Mg/Fe)_{Bt}$ ratio in analyzed sample. Maximum temperature for staurolite-garnet schist of MMC is 618°C.

Exhumation History of MMD

Well-preserved growth zoning in the garnet is not very common in higher amphibolite facies rocks. In prograde metamorphism, garnets begin to homogenize above 600°C, depending on the duration of high temperature conditions and the grain size [34]. Garnet - biotite thermometry shows that the garnet in studied sample has been formed above 600°C and the presence

Table 2. Quantitative core to rim results of EMPA analyses. a) along traverse marked by white line on Figure 2 in sample Kh-62, and b) sample Kh-43

	a) Analyzed point (Kh-62)											
Element (Wt%)	*1 (core)*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12 (rim)*
Mg	3.47	3.52.	3.5	3.47	3.47	3.5	3.5	3.52	3.5	4.14	4.17	3.92
Fe	32.64	32.39	32.87	32.63	32.64	32.17	32.17	33.8	33.57	33.79	34.03	33.33
Al	13.89	14.08	13.99	13.89	14.58	13.99	13.99	14.08	13.99	13.79	13.99	13.73
Ca	1.39	1.41	1.4	1.39	1.39	1.4	1.4	0.7	0.7	0.69	0.69	5.88
Mn	5.56	5.63	5.59	5.59	5.59	5.59	5.59	4.93	4.9	4.83	4.17	2.61
Si	43.06	42.96	42.66	43.06	42.36	43.36	43.36	42.96	43.36	42.76	43.06	40.52
Xalm	0.76	0.75	0.76	0.76	0.76	0.75	0.75	0.79	0.79	0.78	0.79	0.73
Xpyr	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.1	0.1	0.09
Xalm/Xalm+Xpyr	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.91	0.91	0.87	0.89	0.85

	b) Analyzed point (Kh-43)									
Element (Wt%)	*1 (core)*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10 (rim)*
Mg	3.43	3.51	3.51	3.45	3.45	3.50	3.50	4.17	4.21	3.90
Fe	32.53	32.4	32.73	32.65	32.67	32.17	33.81	33.80	34.10	33.35
Al	13.89	14.01	13.94	13.92	14.53	14.01	14.11	13.71	13.95	13.70
Ca	1.39	1.39	1.38	1.38	1.38	1.04	0.71	0.63	0.68	6.12
Mn	5.63	5.85	5.85	6.01	6.01	6.01	5.01	4.89	4.20	2.58
Si	43.17	43.01	42.56	42.94	42.43	43.43	43.3	42.83	43.1	40.52
Xalm	0.76	0.75	0.75	0.75	0.75	0.75	0.78	0.78	0.79	0.72
Xpyr	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.95	0.10	0.08
Xalm/Xalm+Xpyr	0.90	0.90	0.90	0.90	0.90	0.90	0.91	0.45	0.89	0.90

Table 3. Representative analyses of biotite from staurolite garnet schists of Khalaj area

Element (Wt%)	**Analyzedpoint (Kh-62 sample)**				**Analyzedpoint (Kh-43 sample)**	
	1	*2*	*3*	*4*	*1*	*2*
Si	42.12	42.14	41.84	41.84	34.3	38.41
Ti	1.43	1.43	1.42	1.42	1.16	1.32
Al	13.57	13.57	13.48	13.48	22.10	25.16
Fe	15.15	15.13	15.6	15.60	17.44	18.54
Mg	19.86	19.86	19.84	19.84	12.21	13.91
Na	0.71	0.71	0.71	0.71	1.16	3.02
K	7.14	7.14	7.09	7.09	11.63	1.32
Mn	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.00	0.00	0.00	0.00	0.00	0.00

of growth zoning indicates that duration of high temperature has not been long enough to homogenize the growth pattern.

In the other hand, very slow cooling of a rock, after crystallization of final mineral assemblages, may allow significant diffusion to occur. In the literature, a cooling rate of 1-10°C/Ma is estimated for such a slow cooling and formation of retrograde diffusion in garnet grains [15,38]. Retrograde diffusion was only limited to the rim of the studied garnet, suggesting, rapid cooling soon after peak metamorphism with the cooling rate of higher than introduced for slow cooling rate. Such a rapid cooling could be observed during rapid uplift and unroofing of the metamorphic terrains [11]. However, growth zoning is not well preserved in the rim of garnet grain. It could be an evidence for the presence of later retrograde metamorphic phase which influenced regional metamorphic schists in MMC. Such a possibility remains to be tested with further dating in MMD.

Concluding Remarks

Staurolite garnet schist of Khalaj represents the

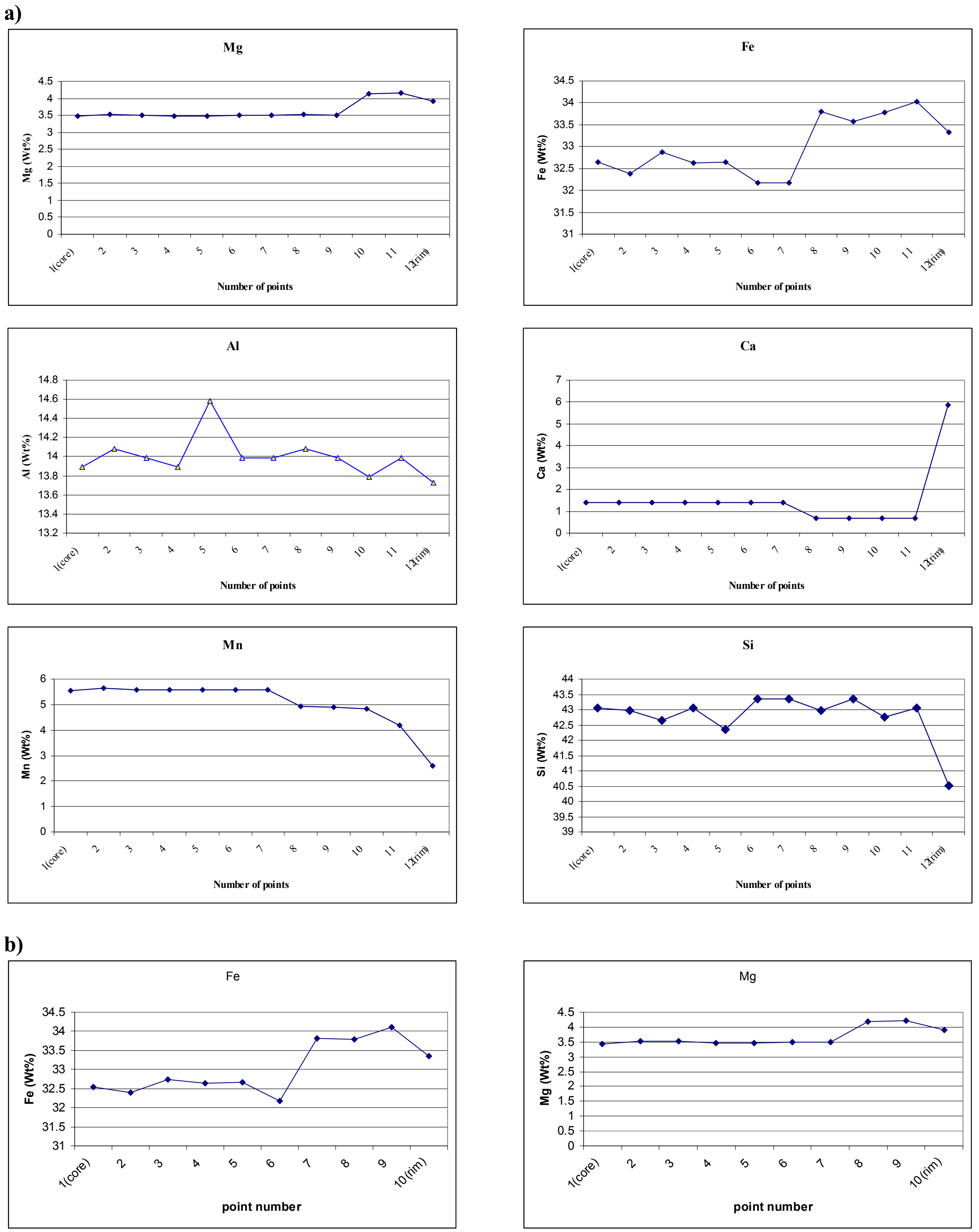

Figure 4. Major element profiles of core to rim of analysis along linear traverse with equal interval in garnet. a) sample Kh-62 and, b) sample Kh-43.

b)

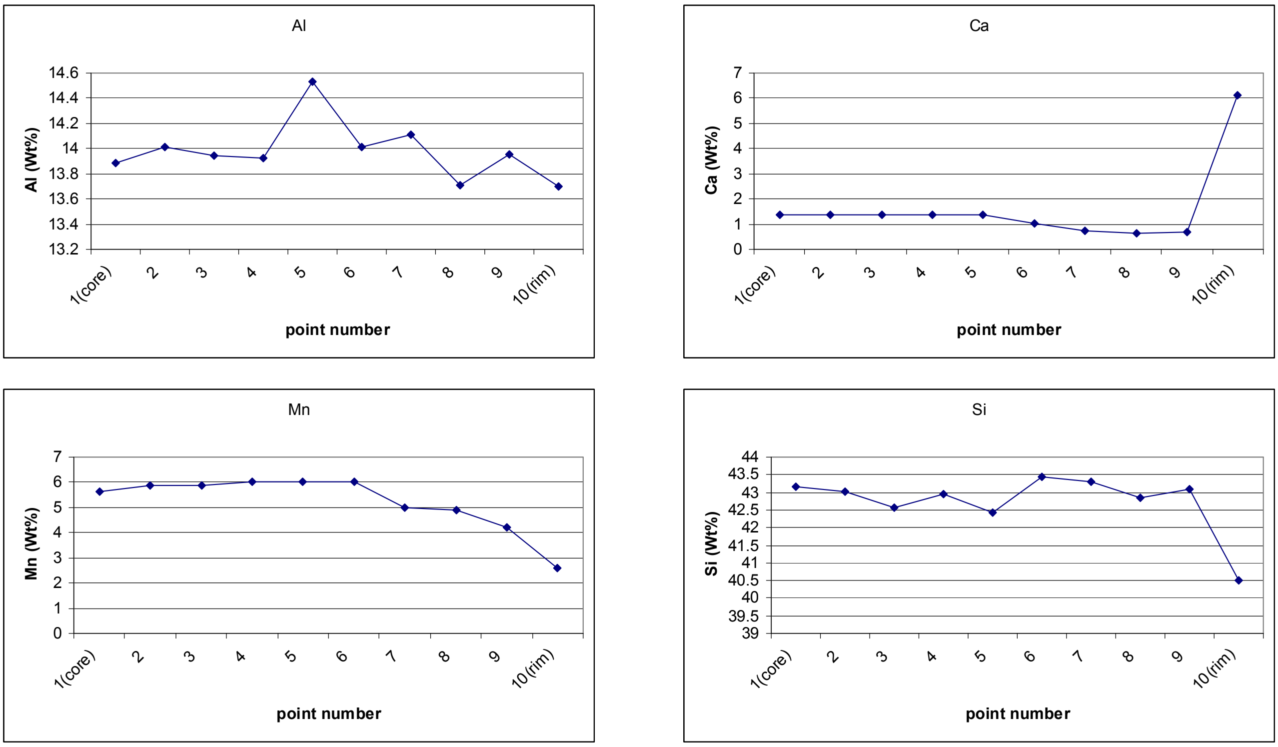

Figure 4. Continued.

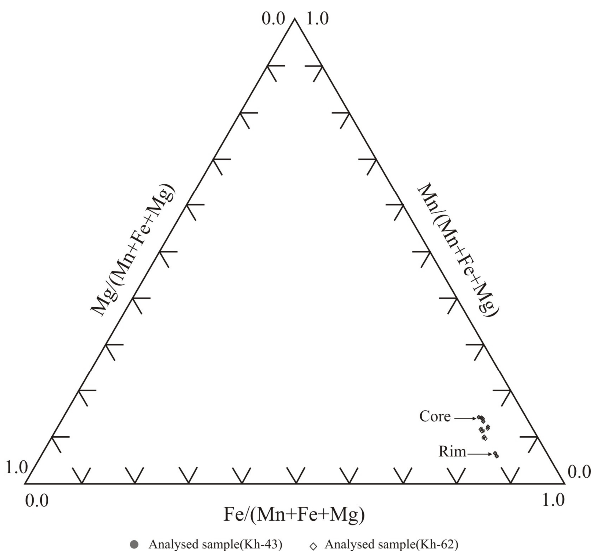

Figure 5. Linear trends in core to rim chemical composition of garnet on Mn-Mg-Fe ternary diagram.

highest grade of metamorphism in MMC. Based on garnet-biotite thermometry, maximum temperature of 618°C calculated for regional metamorphism in the MMC. Presence of growth zoning in garnet provides information about tectonic history of metamorphism. Mg and Fe in garnet increase slightly outwards, while Mn decreases from the core to the rim. Preserved garnet growth zoning indicates that staurolite- garnet schists of MMC on margin of Paleotethys in NE Iran were rapidly heated and cooled during rapid uplift and unroofing. The presence of subsequent diffusional modification in the rim of garnet porphyroblast implies that later retrograde metamorphic events affected the staurolite-garnet schists.

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