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Contributed Paper

The Oscillatory Zoning in Grandite Garnet from Khao Phu Kha, Lop Buri, Central Thailand

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ABSTRACT

Oscillatory zoning in skarn garnet from Khao Phu Kha area, Lop Buri, Central Thailand, preserves a record of the temporal evolution of contact metasomatism. Garnets with oscillatory zoning are small (0.5-3 mm in diameter) euhedral crystals. They contain mm-scale oscillatory zoning of varying grossular-andradite composition (mole % number of andradite = 45.35 to 98.32). The zoning indicates that garnet was developed during early metasomatism involving diorite intrusion and Permian limestone. During this metasomatic event, Al, Fe, and Si in the fluid reacted with Ca in the carbonate rocks to form grandite garnet. The zoned data were collected by electron microprobe and back-scattered electron images. Detailed electron microprobe line profile and small-area compositional maps of zoned garnet favours crystal growth process for the zoning formation. The grandite garnet displays Fe-rich core with oscillatory zoning at rim. The zoning at the edge is relatively high in Al while Fe content decreases toward the rim. A change in fluid composition during growth may cause the garnet to stop growing temporarily or keep growing but at a much slower rate allowing the Al to precipitate rather than Fe. The fluctuation of the fluid composition could be internally and/or externally controlled.

Keywords : oscillatory zoning, grandite garnet, skarn.

1. INTRODUCTION

Oscillatory zoning in minerals is a common phenomenon [1], and has been reported from a variety of geological environments. Chemical zoning is defined by the spatial variation in the composition of a mineral. Many metamorphic minerals display chemical zoning to one degree or another. One of the most obvious examples in petrology is garnet, which is nearly ubiquitously zoned in the major cations: Fe, Mg, Mn, Ca and Al. The study of zoned crystals has long been an active area of research in petrology since the advent of the electron microprobe in the 1960's, which permitted rapid micro-chemical analysis with spatial resolution on the order of 1 μm. In addition to major element zoning, it is now known that metamorphic minerals such as garnet are also zoned in trace element abundances and oxygen isotope [2,3]. Calcic garnets of hydrothermal and skarn deposits frequently possess compositional zoning. The zoning can be gradational or oscillatory with sharp boundaries. Oscillatory compositional zoning in these garnets is often correlated with isotropic and birefringent regions. In some grossular-andradite series garnet, the zoning correlates with variation in Al / Fe^{3+} with the Al-rich zones being isotropic [4] while in others the isotropic zone are Fe^{3+} rich[5].

The Khao Phu Kha area is in the northern part of Lop Buri Province, central Thailand, approximately 200 km north of Bangkok (Figure 1). This area is located at a contact zone between Permo-Triassic diorite intrusion and Permian carbonate rocks. The intrusion had thermally metamorphosed the host rock into marble and skarn rock. Calcic garnet belonging to grossularite-andradite (grandite) series occurs in the skarn rock. Grandite garnets show oscillatory zoning and dodecahedral twin. Optical microscopy, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were used to describe in detail the relationships of the mineral textures and their chemical composition. The main purpose of this study is to present the detailed result of mineral chemistry and to examine how this changes with paragenesis.

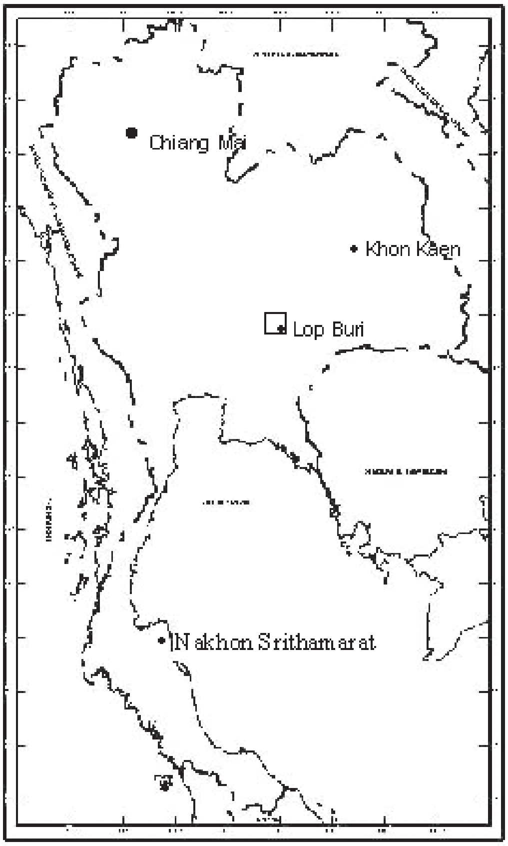

Figure 1. Location map of the study area.

2. MATERIALS AND METHODS

Garnet samples were prepared as polished thin-section approximately 0.3 mm thick, then examined optically under a petrographic microscope to define and photograph all patterns of zonation. All the polished samples were carbon-coated for electron microprobe investigation at the Department of Mineralogy, the Natural History Museum, London.

Electron microprobe imaging and quantitative analyses were performed using a Cameca SX-50 electron microprobe. Imaging of polished thin-section involved mapping with back-scattered electron and in one case with element X-rays. Quantitative analyses use natural and synthetic crystal as standards. Operating conditions were 15 keV accelerating voltage with a beam current of 20 nA. Garnet formulae were calculated on the basis of 12 cations following the method of Deer [6]. The Fe^{2+} and Fe^{3+} values were recalculated from total FeO following Droop[7].

A Jeol 7900 scanning electron microscope with EDS attachment was employed for back-scattering electron image. Operating parameter were 15 keV accelerating voltage with counting time of 40 seconds. This instrument was calibrated using recognized international natural mineral and synthetic crystal standards.

3. RESULT AND DISCUSSION

The garnet frequently displays dodecahedral twinning and is commonly anisotropic. Figure 2 displays back-scattered electron image (BSE) of euhedral garnet that has a fairly homogeneous core surrounded by a striking oscillatory zonation, with sharp boundaries between layers of different composition. In the BSE image, brighter area has higher average atomic mass and correlate to greater andradite content. An iron Ka X-ray map (Figure 3) was made on garnet from the same sample. This image reveals zoning that is concentric and generally parallel to the crystal faces alternating between grossular-rich (reddish brown) and andradite-rich (yellow), with andradite zones comprising the majority of the garnet.

Analytical profile (Figure 4), obtained from 20 spot analyses by electron microprobe from core to rim, reveals major and minor element zoning that is correlated to the colour zoning in the BSE image. Data are presented in Table 1. Composition variation of the garnet can be roughly described as a binary mixture of grossular ($Ca_3Al_2Si_3O_{12}$) and andradite ($Ca_3Fe_2Si_3O_{12}$) with minor composition of spessartine ($Mn_3Al_2Si_3O_{12}$). They range in composition from Al_2O_3 = 0.08 to 12.41 wt%, FeO = 13.32 to 28.03 wt%, and MnO = 0.21 to 0.61 wt% respectively. The major chemical variation along the analyzed section is an inverse relation between Al_2O_3 and FeO. MnO shows minor symmetrical increases with Al_2O_3 (Figure 5). The garnet crystal shows symmetrical but complex profile with large variation in Al_2O_3, FeO and MnO from core to rim. At the inner, less developed zone with FeO concentration of approximately 27%, there is only a slight variation in Al_2O_3 and MnO values with an equivalent minor increase in the Al_2O_3 values. At the outer and better defined zone, FeO content decreases to low value (approximately 17% FeO) which corresponds to sharp increases in Al_2O_3 and MnO profiles. Towards the crystal margin, FeO content increases to normal value (27% FeO) with Al_2O_3 and MnO decrease to low value until MnO content reaches 0.2%. After that, FeO decreases to lowest value (13% FeO) then increases again to approximately 24% FeO at the crystal rim whereas Al_2O_3 and MnO increase to higher values (12% Al_2O_3 and 0.6% MnO) then decrease to low values again at the crystal rim. Two oscillatory zonings can be observed which correspond to sharp colour zoning in BSE image. Figure 6 shows oscillatory behaviour initially changed between a composition close to mole % end member of andradite = 45.35 to 98.32 and mole % end member of grossular = 0.98 to 53.73. The thickness of the zones varies from a few mm to a few mm. An increase of grossular garnet corresponds to decrease of FeO and increase of Al_2O_3 as shown in Figure 4.

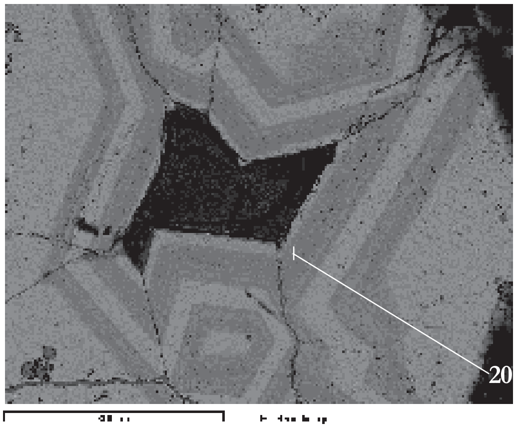

Figure 2. Back-scattered electron image (BSE) of euhedral garnet that has fairly homogeneous core surrounded by a striking oscillatory zonation, with sharp boundaries between layers of different composition. White line indicates line profile analysis from rim (1) to core (20).

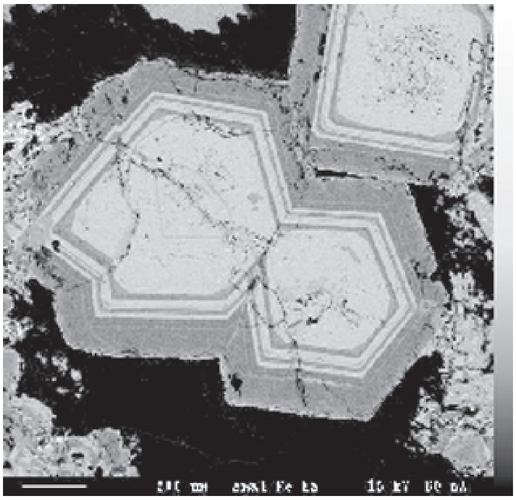

Figure 3. Iron Kα X-ray map of oscillatory zoning in garnet. This image reveals zoning that is concentric and generally parallel to the crystal faces alternating between grossular-rich (reddish brown) and andradite-rich (yellow).

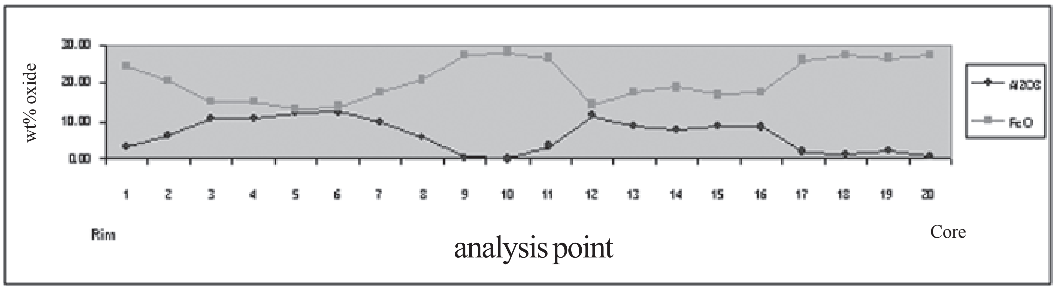

Figure 4. Analytical profile obtained from 20 spot analyses by electron microprobe from rim to core (cf. Fig. 2), reveals major element zoning that is correlated to the chemical zoning in the BSE image.

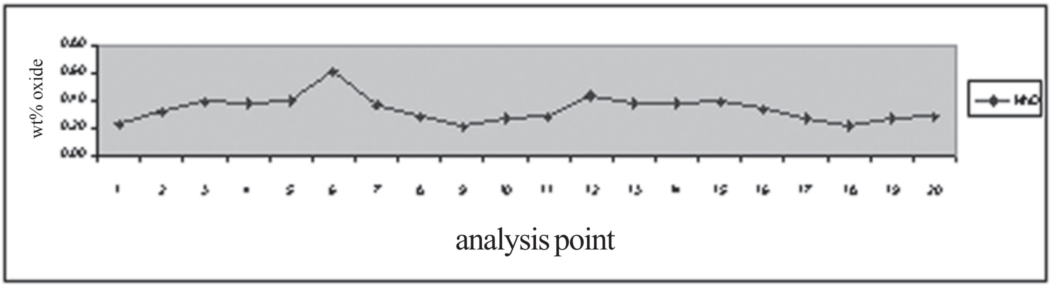

Figure 5. Analytical profile of MnO that corresponds with Al_2O_3.

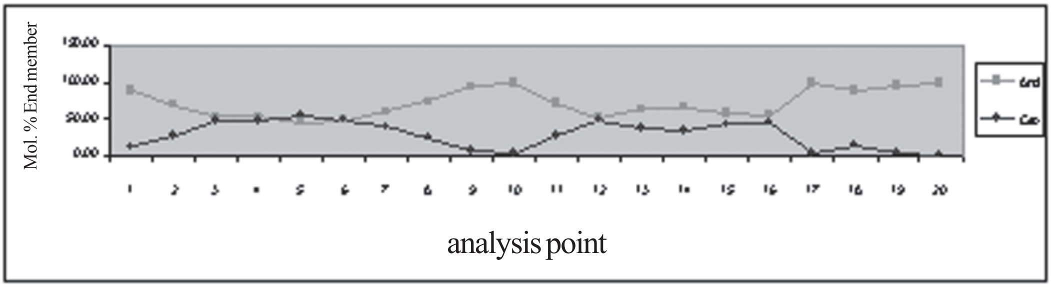

Figure 6. Oscillatory behaviour initially changed between a composition close to mole % end member of andradite and grossular.

Table 1. Variations of the chemical composition (wt%) from rim to core in the oscillatory zoning garnet.

Point	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
SiO2	35.26	36.57	37.22	36.74	37.14	34.15	35.65	36.23	34.46	35.50	32.76	36.62	35.94	36.28	36.14	36.14	34.27	33.67	33.49	35.63
TiO2	0.03	0.01	0.00	0.00	0.01	0.00	0.00	0.02	0.02	0.00	0.03	0.06	0.00	0.00	0.04	0.01	0.00	0.01	0.01	0.02
Al2O3	3.04	6.26	10.73	10.59	11.97	12.41	9.48	5.84	0.56	0.08	3.51	11.22	8.61	7.55	8.91	8.42	1.80	1.24	2.33	0.66
Cr2O3	0.01	0.01	0.02	0.00	0.01	0.08	0.03	0.06	0.00	0.03	0.00	0.03	0.00	0.00	0.04	0.04	0.27	0.00	0.03	0.01
FeO	24.77	20.57	15.30	15.25	13.32	13.70	17.34	20.96	27.82	28.03	26.98	14.61	17.61	19.00	17.25	17.60	26.17	27.63	26.83	27.77
MnO	0.23	0.32	0.40	0.39	0.41	0.61	0.36	0.29	0.21	0.27	0.28	0.44	0.39	0.38	0.39	0.35	0.27	0.22	0.27	0.28
MgO	0.23	0.00	0.01	0.01	0.00	0.03	0.00	0.00	0.00	0.01	0.03	0.00	0.02	0.00	0.01	0.00	0.02	0.04	0.03	0.02
CaO	33.84	34.60	35.49	35.63	35.57	34.53	34.51	34.89	33.27	33.56	32.36	35.74	35.25	34.86	35.35	35.37	34.01	33.03	32.66	33.64
Na2O	0.02	0.00	0.02	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.05	0.00	0.01	0.01	0.04	0.04	0.00	0.02	0.03	0.01
K2O	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.03	0.00	0.02	0.01	0.00	0.00	0.01	0.00	0.01	0.02	0.00	0.00	0.00
NiO	0.00	0.00	0.01	0.00	0.00	0.00	0.02	0.09	0.00	0.03	0.03	0.07	0.01	0.03	0.00	0.00	0.08	0.05	0.04	0.09
Total	97.43	98.35	99.21	98.63	98.44	95.53	97.41	98.39	96.34	97.52	96.03	98.79	97.83	98.11	98.18	97.97	96.90	95.91	95.73	98.13
								Mol. Percent end-members												
Pyrope	0.05	0.00	0.05	0.03	0.00	0.12	0.01	0.00	0.00	0.03	0.09	0.00	0.09	0.00	0.02	0.01	0.09	0.10	0.14	0.09
Almandine	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Spessartine	0.52	0.73	0.88	0.85	0.90	1.38	0.86	0.64	0.34	0.42	0.46	0.96	0.86	0.86	0.68	0.60	0.62	0.36	0.65	0.64
Andradite	87.94	71.02	51.65	52.53	45.35	48.53	59.54	73.58	93.21	98.32	72.56	50.24	62.13	66.15	55.82	54.45	96.59	86.83	95.73	98.20
Uvaninite	0.04	0.02	0.07	0.00	0.02	0.25	0.10	0.19	0.00	0.25	0.00	0.10	0.01	0.00	0.09	0.10	0.00	0.02	0.12	0.03
Grossular	11.34	28.22	47.25	46.50	53.73	49.65	39.53	25.59	6.46	0.98	26.89	48.70	36.88	32.97	43.38	44.85	2.68	12.70	3.20	0.97

The origin of zoning in garnet is still controversial. Spear [8] proposed two major causes of chemical zoning in garnet. First, growth zoning occurs as new shells of different composition are added onto a growing crystal. The compositional differences in the shell arise because of changing external conditions such as changing P-T conditions, or a change in the local bulk composition of the rock. Second, diffusion zoning is a modification of a pre-existing garnet composition by the process of volume diffusion. As with growth zoning, the driving force for diffusion zoning is typically a change in external conditions, but, in contrast to growth zoning, diffusion zoning requires no growth or consumption of the crystal. Moreover, with growth zoning there is no post-growth modification of the garnet composition whereas with diffusion zoning, modification may occur during and following growth. Oscillatory zoning in garnet contains potentially valuable information about crystal growth process as well as changes of the environment in which the crystal grows.

The grandite garnets from Khao Phu Kha area have characteristics diagnostic of the crystal growth process. Most of the garnets form small euhedral crystals and dodecahedral twins. The euhedral garnets are clustered together and grew with euhedral faces toward the interior of the cavity. The spaces around the euhedral faces of the garnet crystal are now totally filled with quartz and calcite. Grandite garnet normally displays oscillatory zonation pattern. A characteristic feature of all these zonation profiles is the abrupt change in chemistry from one intracrystal layer to another. The sharp contacts have been taken as an indication of rapid crystal growth or rapid changes in the composition of the hydrothermal solution. Oscillatory zoning in the grandite garnet most commonly results from variation in Al and Fe^{3+} contents but the distribution of trace elements (for instance Ti, As, Mn) can also be inhomogeneous [9]. The oscillatory fluctuations in grossular-andradite component suggest that variation in Al and Fe^{3+} controlled the zoning. The grandite garnets from Khao Phu Kha area are low in Mn and Ti. Field and microscopic investigations demonstrate that there is a progressive change in the mineral assemblage and in mineral composition from diorite to garnet skarn. The grandite garnets were formed from Si, Al and Fe derived from the diorite and Ca released by consumption of the limestone. The presence of grandite garnet together with quartz, calcite and minor feldspar indicates the reaction:

$CaAl_2Si_2O_8 + 2\ CaCO_3 + SiO_2 =$
$Ca_3Al_2Si_3O_{12} + 2\ CO_2$
(Anorthite) (Calcite) (Quartz) (Grossular)

The central idea behind growth zonation of garnet is that the composition of material supplied to the garnet rim change with time as the garnet grows. This new material is incorporated into the garnet and a shell of a new composition is produced. As long as diffusion is sufficiently slow, the composition of these shells will not change and the zoning profile will faithfully record the composition of the rim of the garnet at the time it was growing. Oscillatory zoning in garnet has been widely reported [4,5,9-13] Several models have been proposed to explain such zoning. Attempts to explain complex mineral zoning pattern commonly have been based on two different assumptions: (1) the zonation is a result of internal crystal growth process such as by self-organization [14-19], or (2) the zonation mainly reflects changes in the external geological environment during crystal growth such as a variable mass flux through an open system or fluctuation in variables such as temperature and pressure [9,14,20].

Detailed chemical analyses of the oscillatory zoning in grandite garnet from Khao Phu Kha area show a fluctuation in chemical composition. The grandite garnets normally displayed Fe-rich core with oscillatory zoning at rim. The zoning at the edge is relatively high in Al while Fe content decreases toward the rim. A change in fluid composition during the garnet growth may cause the garnet to stop growing temporarily or keep growing but at a much slower rate allowing the Al to precipitate rather than Fe. The fluctuation of the fluid composition could be internally and/or externally controlled.

Detailed study of oscillatory zoning in grandite garnet from Khao Phu Kha area suggests that the garnet developed during early metasomatism involving diorite intrusion and the Permian limestone. During this metasomatic event, Al, Fe and Si in the fluid reacted with Ca in the carbonate rocks to form grandite garnet. Oscillatory zoning in the garnet probably reflects an oscillatory change in the fluid composition which may be internally and/or externally controlled.

4. CONCLUSION

4.1 The grandite garnet displays Fe-rich core with oscillatory zoning at rim. The zoning at the edge is relatively high in Al while Fe content decreases toward the rim.

4.2 A change in fluid composition during growth may cause the garnet to stop growing temporarily or keep growing but at a much slower rate allowing the Al to precipitate rather than Fe.

4.3 The fluctuation of the fluid composition could be internally and/or externally controlled.

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