Chemical variation in garnets from aplites and pegmatites, peninsular Thailand

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ABSTRACT. Electron microprobe analyses of almandine-spessartine garnets from pegmatites and aplites from the Hub Kapong batholith and Phuket Island in peninsular Thailand show three types of zoning. Garnets from pegmatites show extreme zoning, with Mn-rich cores ($\simeq 80\%$ spessartine) and Mn-poor rims ($\geqslant 40\%$ spessartine), whereas those from aplites are either unzoned (35-40% spessartine) within the limits of detection, or have Mn-enriched rims (cores 45%, rims 55% spessartine). The origin of the three types of zoning is considered to reflect different crystal growth histories in each case. The pegmatitic garnets grew under conditions favourable for the development and preservation of marked concentration gradients—low nucleation density, rapid growth rate and slow cation diffusion rates for the crystal and rapid diffusion rates for the pegmatitic liquid. The aplitic garnets had a more complex growth history, with slower growth rates and faster diffusion rates for the crystal, coupled with slower diffusion rates within the aplite magma, tending to prevent the formation and preservation of concentration gradients. Subsequent resorption of aplitic garnets at lower temperatures gave rise to Mn-rich rims because of the preferential retention of Mn by the garnet; lower cation diffusion rates within the crystal permitted these marginal concentration gradients to be preserved.

THIS paper is intended to be a companion to a previous paper describing the chemical and morphological variation shown by tourmalines from aplites and pegmatites from peninsular Thailand (Manning, 1982). Several, but not all, of the tourmaline-bearing rocks carry accessory garnets, which have now been analysed. In addition to material from the Hub Kapong batholith, samples from Phuket Island have also been examined. Details of the geological setting have already been given (Manning, 1982) and so will not be repeated here.

Garnet is a common accessory mineral within granitic rocks, and within late differentiates (aplites and pegmatites) is often relatively manganese-rich almandine-spessartine solid solution. Although the

origin of granitic garnets is in certain cases controversial, a magmatic origin is acceptable for these Mn-rich garnets (e.g. Miller and Stoddard, 1981). The purpose of this study is to determine the extent of chemical variation within the almandine-spessartine garnets from peninsular Thailand, and to examine how this changes with paragenesis.

Petrography and field relationships. The field relationships and petrography of the bodies sampled in Hub Kapong are described fully by Manning (1982). The same sample numbers are used here. For comparison with analyses of material from Hub Kapong, additional samples from Phuket Island have also been studied. Samples 4036 and 4041 are both from tourmaline pegmatite sheets up to 2-3 m across within porphyritic biotite granite from a road section 3 km east of Ban Pa Tong (locality given in Garson et al., 1975). These pegmatites are similar in mineralogy to those from Ban Nong Sua (samples 4057, 4063; 4061, 4062), Hub Kapong, with skeletal tourmalines; however, cassiterite has not been recorded from these particular samples although similar pegmatites are worked for cassiterite elsewhere on Phuket Island. Sample 4012 is of tourmaline-bearing aplite, from a vein (0.1 m across) cutting non-porphyritic biotite granite which forms a small hill 2 km north-east of Phuket town.

Although from different areas, the garnets show similar variation in morphology. Those from the aplite samples are anhedral, with very irregular margins suggesting a period of reaction with the aplite magma. In contrast, those from the pegmatites can be entirely euhedral (e.g. sample 4059), but more usually present a few straight faces in section, the others being slightly rounded. The garnets from the aplites usually occur as isolated grains up to approximately 1 mm in diameter, whereas those from the pegmatites may reach 5 mm or more in diameter and, in addition to occurring as isolated grains, may form aggregates with skeletal tourmaline grains. Concentric bands of opaque inclusions are present within garnets in sample

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Table I. Average electron microprobe analyses of garnets from aplites and pegmatites, peninsular Thailand. 4012 = aplite, Vijid Silalert, 2 km NW of Phuket town. 4036, 4041, 4059 = pegmatites: 4036 and 4041 from Kathu - Ban Pa Tong road section, Phuket; 4059 from Leu Rot Wong mine, Ban Nong Sua, Hub Kapong. 4063, 4069, 4070, 4071 = aplites, Hub Kapong. 2σ given for atomic proportions. n = no. of analyses. M, N = analyses carried out at Manchester, Nancy respectively; T, R = traverse, random analyses respectively.

		4012			4036		4041	4059	4063		4069		4070	4071	
wt. % oxides	SiO$_2$	29.77	29.13	30.60	29.44	29.07	29.76	29.52	29.71	30.52	29.81	30.77	29.63	29.76	29.95
	Al$_2$O$_3$	34.45	34.17	35.40	34.38	35.48	34.10	34.17	34.42	35.13	34.06	35.22	34.21	34.31	34.56
	TiO$_2$	-	-	0.08[1]	0.19[1]	0.10[1]	-	-	-	0.05[1]	-	0.03[1]	-	-	0.12[1]
	FeO	9.44	8.77	9.18	17.94	15.45	17.54	16.47	21.01	20.71	19.19	18.37	16.60	17.33	15.79
	MnO	26.13	27.60	26.43	17.36	19.68	18.22	19.19	13.79	12.85	16.43	16.99	18.82	18.01	18.74
	MgO	-	-	0.03[2]	0.18[2]	0.07[2]	-	0.19[1]	0.38	0.37	0.22	0.18	0.22[1]	-	0.10[2]
	CaO	0.29	0.32	0.32	0.62	0.67	0.55	0.43	0.55	0.57	0.24	0.27	0.21	0.20	0.28
	Total	100.08	99.99	102.04	100.11	100.52	100.19	99.96	99.85	100.20	99.95	101.85	99.70	99.59	99.54
atomic proportions	Si	5.942	5.854	5.976	5.905	5.988	5.939	5.918	5.935	6.008	5.962	6.008	5.947	5.967	5.983
	Al	4.044	4.040	4.065	4.056	4.060	4.004	4.029	4.046	4.068	4.009	4.046	4.038	4.047	4.061
	Ti	-	-	0.012	0.028	0.014	-	-	-	0.008	-	0.005	-	-	0.018
	Fe	1.574	1.468	1.495	2.998	2.504	2.918	2.752	3.499	3.397	3.200	2.990	2.776	2.896	2.628
	Mn	4.411	4.687	4.360	2.942	3.236	3.073	3.252	2.328	2.136	2.778	2.803	3.193	3.051	3.164
	Mg	-	-	0.009	0.054	0.020	-	0.056	0.115	0.110	0.065	0.054	0.067	-	0.029
	Ca	0.063	0.068	0.066	0.133	0.140	0.118	0.092	0.117	0.120	0.052	0.058	0.045	0.043	0.059
2σ	Si	0.066	0.080	0.086	0.057	0.085	0.045	0.091	0.061	0.056	0.068	0.081	0.058	0.050	0.097
	Al	0.050	0.053	0.088	0.050	0.080	0.036	0.059	0.050	0.075	0.081	0.071	0.034	0.048	0.071
	Ti	-	-	0.015	0.007	0.015	-	-	-	0.015	-	0.012	-	-	0.024
	Fe	0.770	0.609	0.676	0.745	0.676	0.375	1.466	0.243	0.116	0.300	0.329	0.131	0.344	0.375
	Mn	0.819	0.698	0.692	0.738	0.687	0.369	1.540	0.300	0.126	0.172	0.346	0.185	0.327	0.307
	Mg	-	-	0.023	0.012	0.019	-	0.014	0.046	0.031	0.033	0.032	-	-	0.045
	Ca	0.024	0.023	0.029	0.036	0.041	0.032	0.035	0.024	0.051	0.024	0.057	0.034	0.016	0.046
	Alm	26.03	23.59	25.21	48.93	42.44	47.77	44.73	57.75	58.94	52.50	50.64	45.65	48.35	44.69
	Spess	72.93	75.32	73.52	48.02	54.85	50.30	52.86	38.42	37.06	45.58	47.47	52.51	50.93	53.81
	Pyr	-	-	0.15	0.34	0.34	-	0.91	1.90	1.91	1.07	0.91	1.10	-	0.49
	Gross	1.04	1.09	1.11	2.17	2.37	1.93	1.50	1.93	2.08	0.85	0.98	0.74	0.72	1.00
	n	20	12	24	32	56	22	27	20	26	18	26	9	20	16
		M/R	M/T	N/T	M/R	N/T	M/T	M/T	M/R	N/T	M/T	N/T	M/R	M/R	N/T
				[1] n=13	[1] n=9	[1] n=44		[1] n=9		[1] n=14		[1] n=11	[1] n=3		[1] n=12
				[2] n=12	[2] n=10	[2] n=47									[2] n=15

4059—these are far too small to identify, but demonstrate that the grains are indeed euhedral.

Chemical variation. Electron microprobe analyses were carried out using the Cambridge Geoscan III with Link Systems energy dispersive system at Manchester University and the Cameca Camebax wavelength dispersive system at the University of Nancy I. No detectable difference between analyses using the two instruments was found, apart from lower detection limits (e.g. for Ti and Mg) as would be expected with the wavelength dispersive system. The analyses obtained are summarized in Table I. 2σ variation is given in each case as an indication of the considerable variation in Fe and Mn contents in particular, as shown by certain samples (e.g. 4059). Overall, the garnets examined are essentially almandine-spessartine solid solutions, with less than 2–3 % grossular and pyrope combined. All the samples show a slight excess in Al and a slight deficiency in Si compared with the theoretical values, 4 and 6 respectively. In order to examine closely the variation in spessartine-almandine substitution, a number of traverses were carried out and are summarized in fig. 1. Error bars in these figures were estimated using precision limits given by Dunham and Wilkinson (1978). The traverses for pegmatitic garnets (4036, 4041, 4059) show considerable enrichment in spessartine in the cores (up to 80 % spessartine in sample 4059) in comparison with the rims. That for aplitic garnet 4012 again shows considerable Mn enrichment in the core (with over 80 % spessartine) compared with
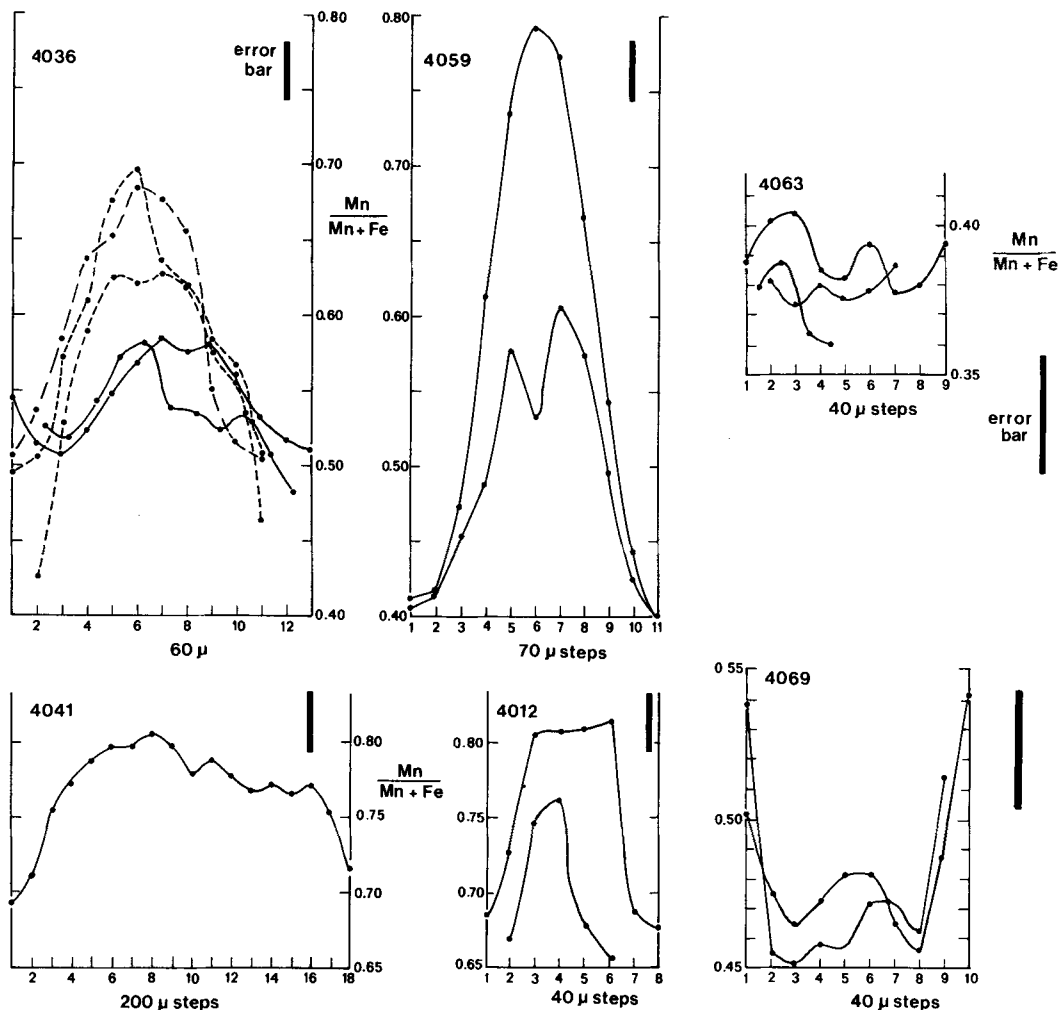
FIG. 1. Profiles showing Mn–Fe zoning within garnets from pegmatites (4036, 4041, and 4059) and aplites (4012, 4063, 4069) from peninsular Thailand. Specimen numbers as in Table I.

the rims. The range in spessartine contents for all these samples lies between 40% and 85%. In contrast, the garnets from other aplites (4063, 4069, and 4071 which is similar to 4069) show very much less variation, which is itself irregular, and probably within analytical error. The only significant variation which was found in some cases (4069, 4071) was Mn enrichment in the rims. The range in spessartine content shown by the aplitic garnets (45%–55% spessartine) lies close to the lower limit of the much greater range shown by the pegmatitic garnets.

Discussion. Several recent papers have discussed the origin of Mn-rich garnets with granitic rocks (e.g. Miller and Stoddard, 1981 (and subsequent

discussion); Clemens and Wall, 1981) and earlier papers have considered the origin of Mn-rich cores in both igneous and metamorphic garnets, which have been known since electron microprobe traverses of garnets were first carried out (e.g. Atherton, 1968; Bizouard *et al.*, 1970). Experimental studies of garnet stability (Green, 1977; Weisbrod, 1974; Clemens and Wall, 1981) have shown quite clearly that Mn-rich Fe–Mn garnets may be stable within a granitic melt at pressures below 5 kbar, and, with ever increasing Mn contents, may be stable at lower pressures (down to below 1 kbar at 750 °C; Weisbrod, 1974). Consequently, it is quite clear from experimental evidence that Mn-rich garnets may crystallize directly from granitic

magmas and pegmatitic liquids under conditions believed to obtain at a late magmatic stage.

A possible control over the appearance of Mn-rich garnet may be the Mn content of the parental magma (Miller and Stoddard, 1981). The range of rock types examined in this study is limited to very late-stage differentiates of the granite batholiths of Hub Kapong and Phuket, and so it is not possible to examine fully the degree of Mn enrichment with differentiation. In general, the field relationships and tourmaline chemical variation suggest that the aplites may represent earlier differentiates than the pegmatites (Manning, 1982); the overall higher Mn contents of the pegmatitic garnets is consistent with this. However, the only other significant ferromagnesian mineral present, which is also the only other major Mn-bearing phase, is tourmaline, and the analyses previously published (Manning, 1982) show no significant variation in the tourmaline $Mn/(Mn + Fe + Mg)$ ratio with paragenesis. Thus the tourmalines do not indicate Mn enrichment during the transition from the aplite to the pegmatite stages. On the other hand, whole-rock analyses are available for the aplites and the biotite granites host to the aplites and pegmatites (Manning and Suensilpong, in preparation); the molar $Mn/(Fe + Mg + Mn)$ ratio varies from approximately 0.01–0.03 for the biotite granites and 0.03 to 0.19 for the aplites. This indicates relative enrichment of the aplite magma in Mn although absolute MnO contents are similar to those of the biotite granite (< 0.05 wt. % MnO in all cases), because the aplites are very poor in Fe and Mg. Consequently, the crystallization of the Mn-rich garnets within the pegmatites and aplites may indeed be due to the observed late-stage relative enrichment in Mn within the aplites and pegmatites compared with the earlier biotite granites. In this case, the lack of variation in the $Mn/(Mn + Fe + Mg)$ ratio shown by tourmaline may reflect low values for K_D ($K_D = X_{Mn,crystal}/X_{Mn,melt\ or\ vapour}$) for tourmaline. In addition, the absence of biotite and the presence of primary muscovite in the garnet-bearing aplites and pegmatites under consideration is consistent with the crystallization of garnet + muscovite rather than biotite in Mn-rich peraluminous liquids, as proposed by Miller and Stoddard (1981).

The observed concentration profiles require further consideration. Previous descriptions of Mn-rich garnets from late-stage granitic rocks have recorded each of the three types of zoning encountered in the present study: Mn-rich cores (Bizouard et al., 1970); Mn-rich rims (Kistler et al., 1981) and unzoned (Miller and Stoddard, 1981). Other reports of Mn-rich garnets from aplites and pegmatites do not describe zoning (e.g. Hall, 1965; Paraskevopoulos et al., 1972) possibly because any

zoning was not detected with the analytical methods used. The origin of each of these styles of zoning will be considered in turn. First of all, Mn-rich cores to garnets in general are well known, and their origin is discussed at length by Atherton (1968). Atherton considers that the Mn concentration profiles may be essentially controlled by strong partitioning of Mn in favour of the garnet during growth, provided that: there is negligible diffusion involving Mn within the crystal; there is complete diffusion within the medium of growth (i.e. it maintains a constant composition); and the distribution coefficient ($K_D = X_{Mn,garnet}/X_{Mn,melt\ or\ vapour}$) does not change during crystal growth. In effect, with $K_D > 1$, the garnet will act as a sink for Mn, which will become depleted within the growth medium. This model will be directly applicable to the pegmatitic garnets with Mn-rich cores, especially in view of their conditions of growth. The differences in crystal growth kinetics within a pegmatitic liquid (see note 1) or a silicate melt have already been discussed with respect to the tourmalines from Hub Kapong (Manning, 1982). The major features of growth within a pegmatitic liquid are considered to be: low crystal nucleation rates; rapid crystal growth rates; and rapid diffusion rates within the liquid. All of these are essentially consequences of the lower viscosity and disrupted structure (with respect to silicate polyanions) of the pegmatitic liquid compared with a granitic melt (viscosity of pegmatitic liquid = 10^{-3}–10^{-4} poise, cf. 10^6–10^7 poise for hydrous granite magmas; Jahns and Burnham, 1969). Furthermore, diffusion of cations, in particular Fe–Mn interdiffusion, in garnets is slow compared with many other silicate minerals (Freer, 1981) and is considered by some authors (e.g. Yardley, 1977) to be negligible below about 600–700 °C. The pegmatites are the latest differentiates of the composite batholiths of Phuket and Hub Kapong, and so it is quite reasonable to suppose that they crystallized at or below the lower limit of this temperature range. Thus, assuming that K_D is in fact constant, the other major requirement for growth of strongly zoned crystals (negligible cation diffusion within the crystal) is also satisfied.

Having suggested that conditions may have been ideal for the growth of strongly zoned garnet crystals within the pegmatites, the other types of zoning shown by the aplitic garnets can be discussed comparatively. It should be noted that the aplitic garnets are in general anhedral corroded grains, and so may have a relatively long history of growth and dissolution within the aplite magma prior to complete consolidation. In addition, as the aplites are earlier differentiates than the pegmatites, the growth history for the garnets may have

involved higher temperatures, within or above the range of 600–700 °C suggested by Yardley (1977). Furthermore, the viscosity of the aplite magma is relatively high (diffusion rates are correspondingly slow) and garnet nucleation rates were evidently relatively high (many small crystals). Taken together, all these factors indicate that the requirements for growth of strongly zoned crystals (and preservation of zoning) were less likely to have obtained for the aplitic garnets than for the pegmatitic garnets. This may account for their relatively homogenous compositions.

The aplite garnets for sample 4012 show strong zoning similar to garnets from the pegmatites. These crystals may have undergone a growth history intermediate between the other aplite garnets and the pegmatite garnets—they may have grown at lower temperatures (too low for cation diffusion within the crystal to reduce concentration gradients) and may in addition have grown from a magma more enriched in volatiles (hence more depolymerized and less viscous and so with higher diffusion rates).

The third style of zoning encountered in this study is that where the garnets show Mn enrichment in the rims. This feature has been observed previously (e.g. Grant and Weiblen, 1971) and is believed to be due to preferential retention of Mn within the garnet during resorption. Although this process has mainly been discussed in the context of solid-state reaction during retrograde metamorphism, it may equally take place during crystal-melt reequilibration. For those aplitic garnets with homogenous cores and relatively Mn-rich rims (e.g. 4069), the growth history may have involved a stage at sufficiently high temperatures that cation diffusion within the crystal prevented the formation of concentration gradients, followed by resorption with preferential retention of Mn by the garnet at lower temperatures, with cation diffusion rates sufficiently low that the concentration gradients near the rims formed and were preserved.

Conclusions. The major conclusion to be drawn from this study is once again to demonstrate how conditions of growth appear to affect the chemical variation shown by certain minerals. As for the tourmalines from Hub Kapong (Manning, 1982) the garnets from minor intrusions from both the Hub Kapong and Phuket batholiths show characteristic zoning (Mn–Fe) depending on their paragenesis. Those from pegmatites appear to have grown in conditions ideal for the formation and preservation of strongly zoned crystals: low nucleation density, rapid growth rate and slow cation diffusion rates for the crystal, rapid diffusion rates for the medium of growth and K_D for Mn greater than one. In

contrast, the garnets from the aplites may have had a more complex growth history, involving higher nucleation density, slower growth rates for the crystal and slower diffusion rates for the magma, and perhaps most importantly, higher cation diffusion rates for the crystal which prevented the initial formation and later preservation of concentration gradients. Finally, some of the aplite garnets suffered resorption at temperatures low enough that diffusion rates within the crystal were sufficiently low for the preservation of marginal Mn enrichment arising from preferential retention of Mn within the crystal.

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APPENDIX

Terminology. Throughout this paper the term pegmatitic liquid has been used to avoid the possibility of misconceptions arising from the alternative terms, pegmatitic melt or pegmatitic fluid. Černý (1982) has recently summarized theories of pegmatite genesis, and concludes that the parent medium from which the crystalline assemblage developed is in general more likely to be an aluminosilicate melt than an aqueous fluid. However, the physical properties of the parent medium were evidently very different from those of a 'normal' silicate magma. In particular, the difference in diffusion rates and viscosities of magmatic and pegmatitic liquids is believed to arise from volatile enrichment and consequent depolymerization of the melt. It is considered that residual granite pegmatites, such as those discussed here, crystallized from liquids which were essentially a limiting case of a depolymerized aluminosilicate melt, in which the proportion of polymeric aluminosilicate species is minimal, and the proportion of water very high. Such a liquid, a 'water–silicate mixture', would represent a link between magmatic (i.e. melt dominated) and hydrothermal (i.e. aqueous solution (fluid) dominated) processes.