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Contributed Paper

Microstructures in Pyrope Garnets from Thailand

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ABSTRACT

Garnets associated with ruby-sapphire that are related to basaltic and gabbroic rocks from Trat, Chanthaburi and Si Sa Ket Provinces in eastern and northeastern parts of Thailand have been observed. All crystals are orangey red to brownish red colored, refractive index of 1.75-1.77, specific gravity of 3.498-3.789, and sizes between 0.3-1.5 cm in diameter. The physical properties and chemical compositions are comparable to those reported for the pyrope end-member: $Py_{59-68}Al_{18-26}Gr_{11-13}$ for basalts-related pyrope and $Py_{52-57}Al_{27-31}Gr_{13-14}$ for gabbros-related pyrope. Garnets associated with ruby-sapphire contained several types of inclusions and microstructures. Inclusions are composed of needles, black inclusions, cloud, minute exsolved particles, liquid inclusions and tension discs. Several kinds of microstructural features can be recognized under microscopic examination, including: (1) a high density of fiber-like tubes penetrating from rims to cores of grains, (2) a network of tubes that looks like a bird's nest, and (3) a thread-like line along grain-boundary microcracks of garnet crystals. The chemical analyses of the materials within tubes reveal the clay mineral composition and was formed during alteration processes after garnet host. Kink-bands of a densely formed fibers-like tubes imply that they are the result of the deformation processes. This discovery of the microstructural features in pyrope garnets are unique and are first reported for Thai garnets.

Keywords: garnet, pyrope, microstructures, microstructural features, fiber-like tubes, Thailand

1. INTRODUCTION

Famous and valuable gemstones in Thailand are corundum, and especially ruby and sapphire. The associated minerals with corundum are garnet, zircon, spinel, pyroxene, sanidine and peridot. Most of them were found in alluvial, eluvial and/or residual soil associated with alkaline basaltic flows [1, 2]. In this paper, the studied gems included pyrope garnets were studied from six localities in eastern and northeastern parts of the country. Six study areas are consisted of Ban Nong Bon, Ban Bo Rai, and Ban Bo Phloi in Bo Rai District, Trat Province; Khao Wua - Khao Phloi Waen and Ban Bang Kacha in Tha Mai District, Chanthaburi Province and Phu Fai, Si Sa Ket Province. All samples were collected from alluvial deposits.

The aim of this research is to investigate different kinds of micro-structures occurred in pyrope garnets from Thailand.

1.1 Geology of Study Areas

All pyrope garnets in these six study areas were found in residual soil associated with corundum in basalts (Figure 1). Detailed geologic description of these six locations are grouped into three areas and are described below:

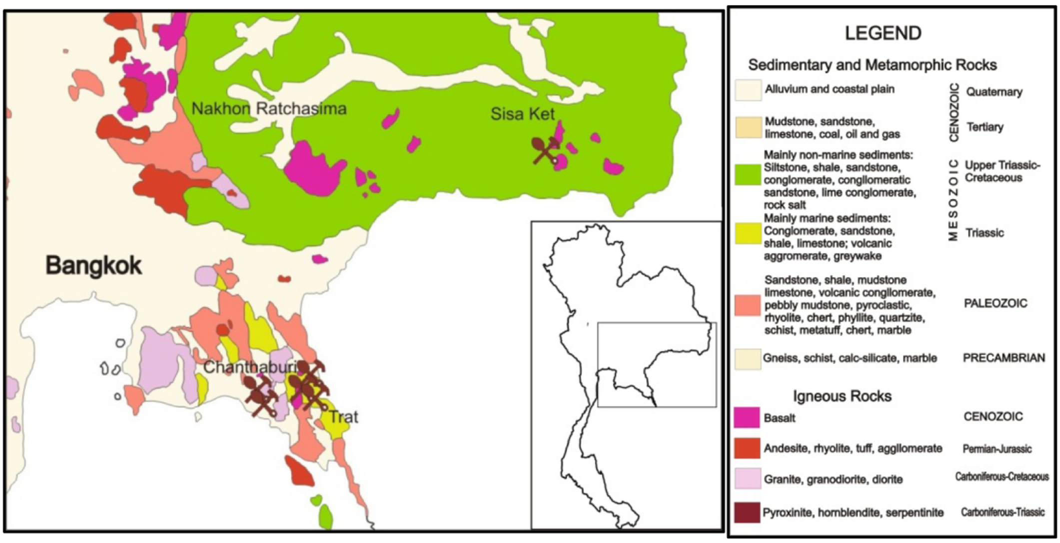

Figure 1. Geologic map showing six sample locations in eastern and northeastern parts of Thailand.

***Chanthaburi areas*:** The region is has been covered with Quaternary basalt. In a survey carried out by Barr and Macdonald [3], the basalt yield K-Ar age of 0.44±0.11 Ma, making it is the youngest rock in the immediate area. The rocks which lie underneath this basalt are of Carboniferous age. They consist of phyllitic shale, shale sandstone, siltstone, and chert [1,4-6]. Basalts are generally strongly alkali and they have low in silica and high in titanium. The basalts are generally fine-grained and olivine-bearing, and, at several places, are characterized by the presence of clinopyroxene megacrysts and mantle-derived spinel lherzolite xenoliths.

***Trat areas*:** The rocks in these areas are of Carboniferous-Permian age [5]. They consist of siltstone, mudstone, tuffaceous sandstone, agglomerate and locally interbedded with conglomerate lenses [4,7]. Basalts in this area are classified as nephelinite and olivine nephelinite [3,8,9].

***Si Sa Ket area*:** Phu Fai hill is situated in the SE quadrant of the Khorat Plateau, near the border between Thailand and Cambodia. The surrounding area of gem deposits is composed of the rock of Khok Kruat and Phu Phan Formations (Cretaceous) and Sao Khua Formations (Jurassic) which are included in the Khorat

Group. Phu Fai hill consists of medium- to coarse-grained rocks of basaltic composition and was described as gabbroic plug [3,10].

1.2 Physical and Optical Properties

A total of 300 pyrope garnets were examined for their physical, optical and gemological properties. The study pyrope garnets from six localities are shown in Figure 2 and the summarized the physical and optical properties are listed in Table 1.

2. METHODS

2.1 Sample Description and Preparation

All pyropes were orangey red to brownish red colored, rough, anhedral crystal, conchoidal fracture, semi-translucent to transparent and sizes between 0.3-1.5 cm in diameter. The samples were cut and polished into two-faced. The stereozoom microscope (up to 75 × magnification) was used to study their external/internal microstructural features using several illumination techniques.

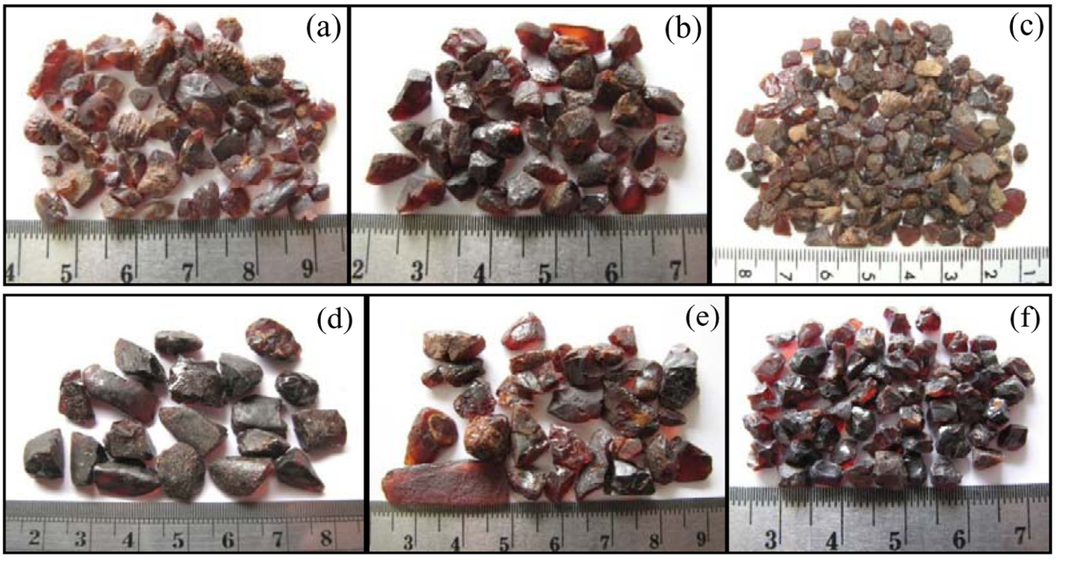

Figure 2a-f. Garnet samples from various Thai gem-fields that are associated with ruby-sapphires: (a) Ban Bo Phloi - BP, (b) Ban Bo Rai - BR, (c) Ban Nong Bon - NB, (d) Ban Bang Kacha - BK, (e) Khao Wua - Khao Phloi Waen - KW, and (f) Phu Fai – PF.

Table 1. The physical and optical properties of Thai garnet from six localities.

Sample Locations		Color	Refractive Index	Specific Gravity	Transparency
Trat	Ban Bo Phloi (BP)	brownish red	1.75-1.77	3.579-3.756	semi TL – TL
Trat	Ban Bo Rai (BR)	brownish red	1.75-1.77	3.676-3.771	TL – semi TP
Trat	Ban Nong Bon (NB)	brownish red	1.75-1.77	3.498-3.696	semi TL – TL
Chanthaburi	Ban Bang Khacha (BK)	brownish red	1.75-1.77	3.654-3.769	TL – semi TP
Chanthaburi	KhaoWua (KW)	brownish red	1.75-1.77	3.698-3.789	TL – semi TP
Si Sa Ket	Phu Fai (PF)	brownish red	1.75-1.77	3.549-3.768	TL – semi TP

Note: TL = translucent, TP = transparent.

2.2 Chemical Analyses

For chemical analyses, we chose 18 garnet samples from six locations, using the CAMECA SX-50 electron microprobe at Department of Earth Sciences, Uppsala University, Sweden. 10-15 spots were analyzed on each crystal using a beam current of 15 nA and an acceleration voltage of 20 kV. Mg, Al, Fe, and Cr were analyzed using the standards: MgO, Al_2O_3, Fe_2O_3 and Cr_2O_3; wollastonite was used for Ca and Si; and $MnTiO_3$ was used for Ti and Mn. The crystallochemical formulas were calculated from the garnet composition. Details of garnet samples and their chemical compositions are presented in Table 2.

Microstructural features study was performed by using Hitachi S4300 FE-SEM electron microprobe that was equipped with an energy-dispersive X-ray spectrometry unit (SEM-EDS) at Swedish Museum of Natural History, Sweden. Samples were cracked and chose only pieces containing microstructural features. They were coated with carbon film by an evaporation technique to prevent charging during an electron bombardment. Condition for analyses was 15 kV of the accelerating voltage.

3. Results

The microscopic examinations were carried out with Nikon stereozoom SMZ-U. The most typical inclusions observed in these pyrope garnets are needles, liquid inclusions,cloud,black inclusions, minute exsolved particles and tension discs (Figure 3).

Several kinds of microstructural features can be recognized under microscopic examination, including: (1) a high density of fiber-like tubes penetrating from rims to cores of grains, (2) a network of tubes looking like a bird's nest, and (3) a thread-like line along grain-boundary microcracks of garnet crystals.

Figure 4 provides several examples of microstructural features in studied pyrope garnets. Figure 4 e.g., sample NB 67 and NB 87 show grain-boundary microcracks in pyrope garnet which, in some directions, looked like a bird's nest. They were short/long thin liked hollow tubes that put out branches. Figure 4 (NB 67) shows the penetrations of microfractures starting from rims to cores of grains. It is also found that the microfractures occur entirely the whole grain (Figure 4, NB 17). The above-mentioned hollow tubes were 2.5 - 20 μm thick and could be up to 1 mm long. The hollow tubes looked golden or orangey-red colored. The deformed microstructures of parallel fiber-like tubes have been observed and are characterized by kink-bands (Figure 4, BR 20 and BR 80). Kink-bands are mostly found at rim of garnet crystals.

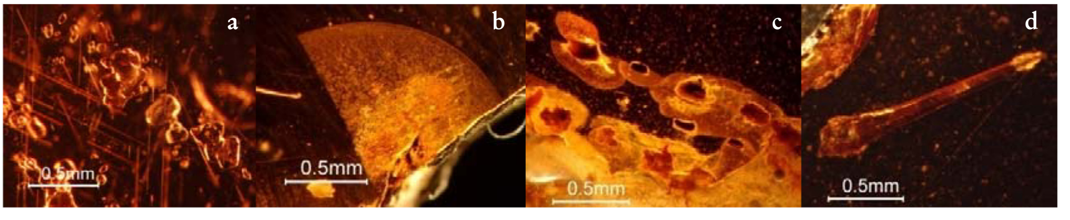

Figure 3. Showing typical inclusions in Thai pyrope garnets: (a) needles and crystals (BK 05), (b) liquid inclusion (KW 51), (c) tension discs (NB 25) and (d) hollow tube (KW 34) (darkfilled illumination).

From SEM images (Figure 5) some fibrous tubes showed the hexagon shape and inside the tube had other materials. Three spots per samples: garnet, surface tubes and materials inside tubes, were analyzed using EDS and summarized in Table 3. The results from SEM-EDS showed high value of FeO content at the surface tube 44.8 - 86.1 wt% and materials in the tubes had high value of Al_2O_3 and SiO_2 but low MgO, TiO_2, MnO and FeO.

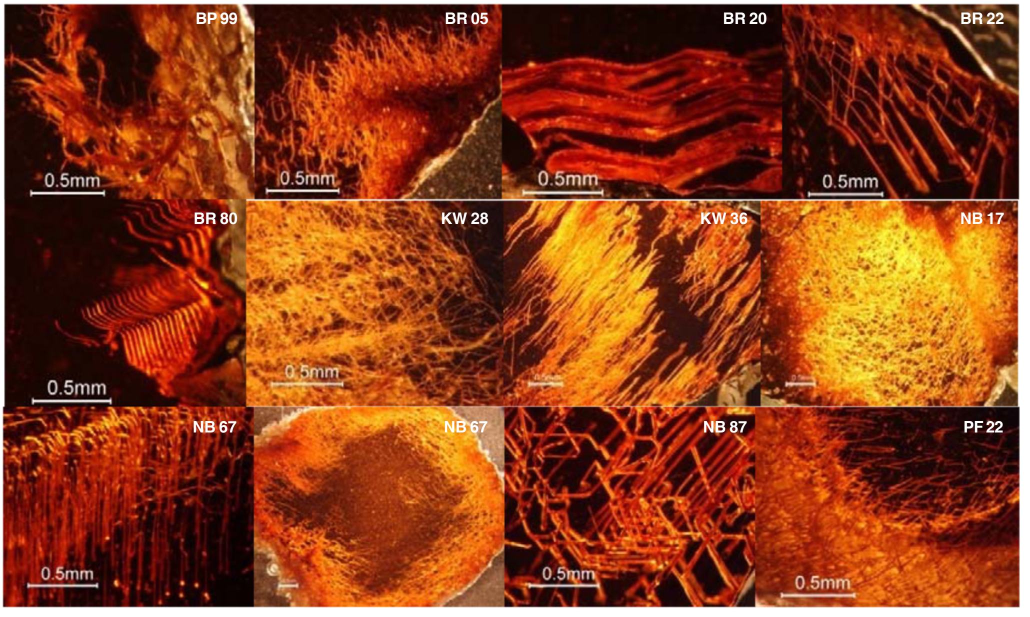

Figure 4. Showing many kinds of microstructural features in Thai pyrope garnets from six localities (darkfilled illumination).

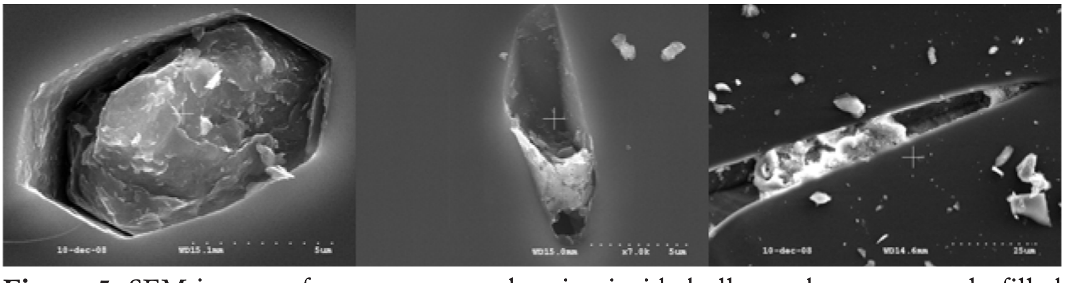

Figure 5. SEM images of pyrope garnet showing inside hollow tubes were partly filled by some materials (a-c).

4. DISCUSSION AND CONCLUSION

Pyrope-rich garnets from six localities in eastern and northeastern parts of Thailand are related to gems corundum especially ruby, yellow and green sapphires. Pyrope can be divided into two groups: (1) pyrope garnets that are related to basaltic rocks in Chanthaburi and Trat Provinces and (2) pyrope garnets that are related to gabbroic rocks in Si Sa Ket Province. Their end-member of pyropes which are related to basalts and gabbros are $Py_{59-68}Al_{18-26}Gr_{11-13}$ and $Py_{52-57}Al_{27-31}Gr_{13-14}$, respectively.

The grain-boundary microcrack, as shown in Figure 4 (NB 67 and NB 87), which it looked like a bird's nest or branches in some directions. These microstructural

Table 2. Chemical analyses and their end-members.

	wt% oxide									% end-members						
Sample	**MgO**	**Al_2O_3**	**SiO_2**	**CaO**	**TiO_2**	**Cr_2O_3**	**MnO**	**Fe_2O_3**	**H_2O**	**Pyr**	**Alm**	**Sps**	**Uva**	**Gro**	**And**	**Total**
BP	17.82	22.80	40.68	5.04	0.47	0.00	0.35	12.45	0.00	64.76	21.38	0.71	0.00	12.21	0.95	100.01
BR	16.61	22.64	41.03	5.08	0.46	0.00	0.34	13.29	0.00	60.23	25.92	0.68	0.00	12.79	0.38	100.00
NB	18.01	22.94	41.27	5.14	0.50	0.01	0.31	12.03	0.00	64.43	21.71	0.64	0.00	12.55	0.67	100.00
BK	17.27	22.78	41.16	5.05	0.47	0.00	0.34	13.31	0.00	61.97	24.30	0.69	0.00	12.40	0.64	100.00
KW	19.06	22.91	41.23	4.83	0.42	0.07	0.30	11.05	0.00	68.25	18.69	0.64	0.00	11.60	0.83	100.01
PF	15.65	22.62	40.34	5.52	0.44	0.00	0.36	14.86	0.00	57.34	27.33	0.77	0.00	13.69	0.87	100.00

Sample	Color	Formula Proportions
Ban Bo Phloi (BP)	brownish red	$(Mg_{3.78}Fe^{2+}_{1.33}Ca_{0.79}Mn_{0.04})_{5.93}(Al_{3.89}Fe^{3+}_{0.21})_{4.10}(Si_{5.90}Ti_{0.05})_{5.95}O_{24}$
Ban Bo Rai (BR)	brownish red	$(Mg_{3.65}Fe^{2+}_{1.49}Ca_{0.80}Mn_{0.04})_{5.98}(Al_{3.90}Fe^{3+}_{0.12})_{4.02}(Si_{5.96}Ti_{0.05})_{6.01}O_{24}$
Ban Nong Bon (NB)	brownish red	$(Mg_{3.87}Fe^{2+}_{1.26}Ca_{0.80}Mn_{0.04})_{5.97}(Al_{3.87}Fe^{3+}_{0.21})_{4.08}(Si_{5.91}Ti_{0.05})_{5.96}O_{24}$
Ban Bang Kacha (BK)	brownish red	$(Mg_{3.80}Fe^{2+}_{1.38}Ca_{0.77}Mn_{0.04})_{5.99}(Al_{3.88}Fe^{3+}_{0.15})_{4.03}(Si_{5.94}Ti_{0.05})_{5.99}O_{24}$
KhaoWua (KW)	brownish red	$(Mg_{3.93}Fe^{2+}_{1.29}Ca_{0.75}Mn_{0.04})_{6.01}(Al_{3.87}Fe^{3+}_{0.12})_{3.99}(Si_{5.96}Ti_{0.05})_{6.01}O_{24}$
Phu Fai (PF)	brownish red	$(Mg_{3.33}Fe^{2+}_{1.71}Ca_{0.88}Mn_{0.04})_{5.96}(Al_{3.89}Fe^{3+}_{0.17})_{4.06}(Si_{5.92}Ti_{0.05})_{5.97}O_{24}$

Note: Pyr = pyrope, Alm = almandine, Sps = spessartine, Uva = uvarovite, Gro =grossular, And = andradite

Table 3. Chemical analyses of garnet, surface tubes and materials in tubes.

Oxide (wt%)	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_3	K_2O	CaO	TiO_2	Cr_2O_3	MnO	FeO	Total
Garnet (avr.) surface tubes	0.20	18.57	23.04	41.62	bdl	bdl	4.16	0.59	0.00	0.47	11.36	100.00
BR - I1	0.69	6.07	5.24	9.62	bdl	0.08	6.19	1.27	bdl	3.39	67.45	100.00
	0.08	6.86	9.61	20.81	0.71	0.61	12.66	1.75	bdl	1.90	44.99	100.00
	bdl	12.16	13.16	19.58	0.88	bdl	5.37	1.58	bdl	2.51	44.77	100.00
BR - I2	bdl	3.21	7.64	11.43	bdl	0.17	10.28	2.39	bdl	1.94	62.93	100.00
BR - I3	bdl	3.38	2.85	4.58	1.34	bdl	1.19	0.13	bdl	0.39	86.14	100.00
	bdl	6.14	3.79	6.80	0.50	bdl	0.75	0.25	bdl	bdl	81.78	100.00
KW - I3	0.31	6.62	15.22	17.17	bdl	0.90	3.37	bdl	bdl	1.88	54.52	100.00
PF -I1 Materials in tube	bdl	19.94	9.06	6.21	1.21	bdl	1.21	0.51	bdl	0.94	60.91	100.00
BR - I1	0.07	0.25	40.82	55.86	0.09	0.31	0.27	0.28	bdl	0.02	2.05	100.00
BR - I2	bdl	2.49	35.36	50.93	0.88	0.31	0.89	1.22	bdl	0.24	7.69	100.00
BR - I3	0.03	3.73	32.17	47.30	bdl	0.14	1.70	2.89	bdl	bdl	12.03	100.00
KW - I3	0.75	3.73	28.12	54.64	0.39	2.77	1.47	0.55	bdl	0.08	7.50	100.00
PF - I1	0.83	2.00	28.29	54.38	0.74	3.46	0.75	2.03	bdl	0.07	7.45	100.00

Note: bdl = below detection limit

features are similar to those features that were found in spessartine and hessonite garnet [11,12]. Gübelin and Koivula [11,12] suggested that this feature is thread-like line, which proved that it consisted of calcite marking the rims of the grains within the mosaic patterns.

The material inside tubes in Thai pyrope garnets found microcrystalline clay minerals (kaolinite?), which were identified by SEM-EDS (Figure 5d). Chemical compositions at the tube surface had quite high FeO content (up to 86 wt%), that made the tubes looked golden or orangey red colored.

Lepot *et al.* [13] had studied garnet-filled trails associated with carbonaceous matter. Their garnet inclusions looked like some of our fibrous materials filled microstructures. They suggested that the several abiotic processes form filamentous structure in the presence of carbonaceous compounds, once is from ambient inclusion trails (AIT). Knoll and Barghoorn [14] suggested that AIT was formed during burial of the rocks by the movement of a crystal in a crystalline silica matrix during pressure-solution processes, which might be driven by the thermal decomposition of the organics into gases.

Ivarsson *et al*. [15] suggested that fibrous features that formed along these pyrope garnets may be due to biological activities or biologically-assisted leaching processes, due to 1) the channels have started from the surface and progressed inward into the crystals, 2) the structures look very similar to "fungi roots" in the way they branches off and are sometimes interconnected, 3) the channels showed a curvature that is at least unusual for exsolved mineral inclusions, and 4) fibrous features occurred in samples with different compositions and different deposits, so they did not appear to some very unusual original rock.

In this study, several kinds of microstructural features in garnet crystals can be recognized including: (1) a high density of fiber-like tubes penetrations from rims to cores of grains, (2) a networks of tubes look like a bird's nest, and (3) thread-like line along grain-boundary microcracks.

The microstructural features may occur after pyrope garnet crystallization, microfractured and microcracked by pressure-temperature during derivation from upper mantle. Microstructural features in pyrope garnet might have absorbed ambient solution that contained high Al, Si and Fe. The solutions in tubes were recrystallized to clay minerals and some solutions were percolating out before being sealed. The clay minerals have been formed as alteration processes from garnet host. The microstructural features are associated with microfractures and grain-boundary microcracks and thus could have grown from an outer surface which is vulnerable to dissolution by percolating fluids.

Kink-bands of a high density of fibers-like tubes in pyrope garnet imply that they are the result of deformation processes.

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