

Article



Chemical Composition and Genesis Implication of Garnet from the Laoshankou Fe-Cu-Au Deposit, the Northern Margin of East Junggar, NW China

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Abstract: In order to reveal the formation mechanism of different garnets and its implications for the fluid evolution in the Laoshankou Fe-Cu-Au deposit in the northern margin of East Junggar (NW China), three types of garnet have been investigated in detail in this study. (1) Type 1 grossular, formed at Ca-silicate stage (stage I, the pre-mineralization stage), was replaced by Type 2 garnet and magnetite, and displays a compositional range of Grs₄₄₋₅₃Adr₄₄₋₅₃, which has relatively lower total REE (rare earth elements) contents (8.14–32.8 ppm) and markedly depleted LREE (light rare earth elements) with distinctive positive Eu anomaly (1.36–9.61). (2) Type 2 Al-rich andradite, formed at the early sub-stage of amphibole-epidote-magnetite stage (stage II, the main magnetite mineralization stage), can be divided into two sub-types, i.e., Type 2a and Type 2b. Type 2a garnets exhibit polysynthetic twinning and relatively narrow compositional variations of Adr₆₃₋₆₆Grs₃₁₋₃₄ with HREE-(heavy rare-earth elements) enrichment and positive Eu anomalies (3.22–3.69). Type 2b garnets own wide compositional variations of Adr₅₅₋₇₇Grs₂₁₋₄₃ with relatively higher REE contents (49.1–124 ppm), markedly depleted LREE and a distinctive positive Eu anomaly (2.11–4.61). (3) Type 3 andradite (Adr_{>91}) associated with sulfide stage (stage III, the main copper-gold mineralization stage) is different from other types of garnets in Laoshankou, which are characterized by lowest total REE contents (1.66–91.1 ppm), flat HREE patterns, LREE-enrichment and the strongest positive Eu anomalies (3.31-45.48). Incorporation of REE into garnet is largely controlled by external factors, such as fluid chemistry, pH, fO₂ and water-rock ratios as well as its crystal chemistry. Type 1 and 2 garnets mainly follow the creation of X^{2+} (e.g., Ca^{2+}) site vacancy, e.g., $[X^{2+}]_{-3}^{VIII}[]_{+1}^{VIII}[REE^{3+}]_{+2}^{VIII}$. The REE³⁺ substitution mechanism for Type 3 garnet is the Na⁺-REE³⁺ coupled substitutions, e.g., $[X^{2+}]_{-2}^{VIII}[X^+]_{+1}^{VIII}[REE^{3+}]_{+1}^{VIII}$, without the evaluation of the creation of site vacancy. The compositional variations from Type 1 to Type 3 garnet indicate significant differences of fluid compositions and physicochemical conditions, and can be used to trace the fluid-rock interaction and hydrothermal evolution of garnet. Type 1 grossular was formed by magmatic fluid under low water-rock ratios and fO_2 , and neutral pH environment by diffusion metasomatism in a nearly closed system with the preferential incorporation into the grossular of HREE. As the long fluid pore residence and continuing infiltration metasomatism under nearly closed-system conditions, fluids with high water/rock ratios were characterized by increased fO_2 , more active incorporation of Fe³⁺ and REE, and formed Type 2 Al-rich andradite. In contrast, Type 3 garnet formed by oxidizing magmatic fluid under a mildly acidic environment with highest fO_2 and water-rock ratios, and was influenced by externally derived high salinity and Ca-rich fluids in an open system. Thus, the geochemical features of different types and generations of garnets in the Laoshankou deposit can provide important information of fluid evolution, revealing a transition from neutral magmatic fluid to oxidizing magmatic fluid with addition of external non-magmatic Ca-rich fluid from the Ca-silicate stage to the sulfide stage. The above proved the fluid evolution process further indicates that the Laoshankou deposit prefers to be an IOCG-like (iron oxide-copper-gold) deposit rather than a typical skarn deposit.



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). **Keywords:** garnet geochemistry; Fe-Cu-Au deposit; Laoshankou; East Junggar; central Asian orogenic belt (CAOB)

1. Introduction

Garnet is a common rock-forming mineral in igneous-metamorphic rocks [1,2], and a major associated gangue mineral in different types of skarn or associated deposits [3]. Rock-forming garnet in metamorphic and magmatic systems is known to fractionate HREE from LREE and has high Sm/Nd and Lu/Hf ratios, which has been widely applied to estimate the physicochemical conditions of rocks [4–7], and to date the metamorphic/mineralization geochronology [2,8,9]. Hydrothermal garnet in skarn-type or associated deposits can be divided into pyralspite (pyrope, almandine, spessartine) and ugrandite (uvarovite, grossular, andradite) groups [10], and generally is in the grossular-andradite solid solutions [11,12]. The formation of hydrothermal garnet is controlled by the related hydrothermal processes and physicochemical conditions, e.g., fluid–rock interaction, fluid temperature, oxygen fugacity, fluid flow rate, pH, and chemical compositions [12–16], and characterized by concentric oscillatory zoning [17,18]. These features make hydrothermal garnet an ideal mineral for researching ore-forming processes and fluid evolution [7,19–22].

The Central Asian Orogenic Belt (CAOB; Figure 1a; [23]), situated between two major Precambrian cratons (the Siberian to the north and the North China-Tarim to the south), is the largest Paleozoic to Mesozoic accretionary orogeny in the world. The northern margin of the East Junggar terrane (Figure 1b; [24]), as the important metallogenic belt in the CAOB [25], is highly prospective for Paleozoic Fe-Cu-Au mineralization targeting. The Laoshankou Fe-Cu-Au deposit (41 km southwest of Qinghe City, Xinjiang, NW China) is one of the important magnetite deposits in the northern margin of East Junggar (Figure 1c; [26,27]). The previous speculation of various genetic types for the formation of the Laoshankou deposit include submarine volcanic-type [28–30] and skarn-type [31,32]. Recently, based on the microthermometry of fluid inclusions and stable isotopic analyses, an iron-oxide copper gold (IOCG)-like type with skarn alteration was proposed [26]. The confusion of defining genetic types highlights the importance of detailed hydrothermal fluid evolution and mineralization processes. On the basis of megascopic and microscopic texture relationships and mineral assemblages, significant two-stage mineralization existed in the Laoshankou deposit, e.g., Fe and Cu-Au mineralization [26,33]. Garnet in the Laoshankou deposit formed in both two mineralization stages, which show significantly different features [26]. Despite of many previous studies on geological descriptions, the age of the intrusion and mineralization, fluid inclusions and C-H-O-S stable isotopes for the Laoshankou deposit [26,31,32], few studies paid attention to the calc-silicate minerals, such as garnet, and the hydrothermal fluid evolution of pH and oxygen fugacity during the formation of garnets.

In this study, we conducted an integrated study of garnet mineralogy as well as major and trace element compositions of garnet from different stages to discuss (1) trace elements and REE substitution mechanism, (2) change in garnet composition at different stages, and (3) hydrothermal fluid evolution processes of the Fe-Cu-Au deposit.



Figure 1. (a) Simplified tectonic map of the Central Asian Orogenic Belt (CAOB) (modified from [23]). (b) Simplified geologic map of North Xinjiang (modified from [24]). (c) Regional geologic and mineralization map of the SE Chinese Altay and NE East Junggar (modified from [26,27]). Abbreviations (fault): Ar, Armantai; E, Erqis; F, Fuyun; and K, Kelameili. Abbreviations (geological terrane): 1, Norte; 2, Central Altay; 3, Qiongkuer-Abagong; 4, Erqis; 5, Dulate; 6, Yemaquan; and 7, Halike.

2. Regional and Deposit Geology

2.1. Regional Geology

The Chinese Altay and East Junggar located along the boundary between the Siberian and Kazakhstan-Junggar terranes [34], is an important part of the Central Asian Orogenic Belt (CAOB; Figure 1a). The northern margin of the East Junggar terrane is dominated by the Dulate Paleozoic active island-arc belt, which is separated from the Chinese Altay terrane to the north by the Erqis fault (Figure 1b). Major structures in the region comprise mainly NW-trending and NNW-trending fault systems, as represented by the regional Erqis and Fuyun fault zones, respectively (Figure 1c; [26,27]). The Erqis Fault (or Irtysh Fault), striking NW-SE (290°–300°), dipping 75° to the NE, and extending 400 km, is one of the largest trans-current faults of Asia [35,36]. Previous research indicated that the Erqis Fault is a sinistral strike-slip fault, and was initiated from 290 to 275 Ma [36–39]. The Fuyun Fault, which has strikes of 342° (NNW) with dips of approximately 70° to the east, and extends 200 km, crosscuts the Erqis Fault and was considered to be dextral strike-slip fault [40,41].

The lithostratigraphy in the northern margin of East Junggar is mainly composed of the Upper Paleozoic volcanic-sedimentary sequences with minor exposed Upper Ordovician pyroclastic rocks, including shallow marine medium-fine grained sandstone to limestone of the Late Ordovician Jiabosaer Formation, marine pyroclastic and sedimentary rocks of the Early Devonian Tuoranggekuduke Formation, coastal-shallow marine intermediate-basic volcanic rocks of the Middle Devonian Beitashan Formation, shallow marine-paralic continental pyroclastic and volcanic rocks of the Middle Devonian Yundukala Formation, coastal-continental sandstone to limestone of the Late Devonian Kaxiweng Formation, pyroclastic-continental clastic rocks of the Late Devonian-Early Carboniferous Jiangzierkuduke Formation, continental-coastal volcanic-sedimentary rocks of the Early Carboniferous Nanmingshui Formation, multi-cyclic continental-rift bimodal volcanic rocks of the Middle Carboniferous Batamayineishan Formation, and continental pyroclastic rocks of the Permain Zhaheba Formation from the base upward [26,32,42].

Two stages of Paleozoic magmatism at 390–370 Ma and 320–270 Ma have been conformed in the northern margin of East Junggar terrane [43–46]. The 390–370 Ma I-type calc-alkaline intrusions were closely related to a series of bipolar subductions [47–49] and have been recently documented to form during basin inversion in a volcanic arc setting [26,50,51]. Coeval mineralization dominated by the arc-related Fe-Cu (-Au) and porphyry copper deposits generally occurred in the northern margin of East Junggar. The 330–280 Ma A-type alkaline intrusions were interpreted to have formed in a postcollision/intraplate extension setting [50,52], and genetically linked to deposits such as the Suoerkuduke skarn Cu-Mo deposit, the Xilekuduke porphyry Cu-Mo deposit and Aketasi hydrothermal-vein Au deposit.

2.2. Deposit Geology

The Laoshankou Fe-Cu-Au deposit has an estimated metal reserve of 3.26 Mt Fe at 33.5–36.42%, 9.8 kt Cu at 0.19–0.41%, and 0.14 t Au at 0.49–1.31 g/t [29,53]. The orebodies are hosted in the Middle Devonian Beitashan Formation (380.5 \pm 2.0 Ma; [54]) that contains mainly basaltic/and esitic breccias and tuffs intercalated with fossiliferous limestone (Figure 2b). The basaltic breccias are mainly located in the footwall of the orebody, while the andesitic breccias are located in the hanging-wall of the orebody (Figure 3). Monzodiorite and diorite porphyry have close temporal and spatial relationship with Fe-Cu-Au mineralization in the Laoshankou deposit, with zircon U-Pb ages of 379.2 \pm 4.4 Ma and 379.7 \pm 3.0 Ma, respectively [45,55], which usually crosscut the earlier Beitashan volcanic rocks. There are two large NW-trending faults in the deposit, i.e., the Fuyun Fault in the north (dips at 60°–70°) and the Shanqian Fault in the south (dips at ~70°, subparallel to Fuyun Fault) (Figure 2a; [29]). A series of subsidiary E-W-striking faults (i.e., F3, F4, F5 and F6) are present between Fuyun and Shanqian faults, and divided the ore district into a number of rhombic sectors.

Two ore zones have been delineated at Laoshankou, including the upper ore zone dominated by magnetite orebodies with minor Cu-Au mineralization, and the lower ore zone containing mainly Cu-Au orebodies (Figure 3) [29,31]. Ore minerals mainly include magnetite, chalcopyrite, and pyrite, with minor chalcocite and hematite, while gangue minerals include garnet, diopside, epidote, chlorite, hornblende, actinolite, plagioclase, K-feldspar, quartz, and calcite, with rare apatite and sphene. Based on the mineral assemblages and ore textures, the ores in magnetite orebodies are mainly massive and banded magnetite-epidote-sulfide, whilst the Cu-Au orebodies are mainly characterized by massive and disseminated chalcopyrite [26].



Figure 2. Structural map (**a**) and geologic map (**b**) of the Laoshankou deposit (modified from [29] and Xinjiang Geological Survey, unpublished). Abbreviations: F1, Fuyun Fault; F2, Shanqian Fault; F3, F4, F5, F6, unnamed secondary faults. Sample locations: 1, LS-024-2, LS-024-3; 2, No. 5 pit, LS-006; 3, Stock heap, LS-026, LS14-012-5, LS14-012-6, LS14-012-7; 4, TS-001, TS-001-7.



Figure 3. Cross section along the No. 0 prospecting line in the Laoshankou Fe-Cu-Au deposit (modified from Xinjiang Geological Survey, unpublished).

Pervasive pre-mineralization Na-Ca silicate alteration were preserved at the Laoshank ou deposit, and two-stage mineralization of Fe and Cu-Au were precipitated in a multiphase paragenetic sequence. Three hypogene hydrothermal alteration and mineralization stages (Figure 4; [26]) include the Ca-silicate alteration (Stage I), amphibole-epidote-

magnetite alteration/mineralization (Stage II) and pyrite-chalcopyrite mineralization (Stage III). The Ca-silicate alteration (Stage I) is recorded mainly by garnet with lesser amounts of pyroxene/diopside and scapolite in the wall rocks adjacent to orebodies. The amphibole/actinolite-epidote-magnetite alteration/mineralization (Stage II) is the main mineralization stage characterized by abundant magnetite, amphibole/actinolite, epidote with minor prior garnet. Abundant sulfide minerals are present in the pyrite-chalcopyrite mineralization (Stage III) with two major mineral associations, i.e., pyrite-epidote-quartz-garnet and chalcopyrite-amphibole/actinolite-chlorite/ripidolite-pycnochlorite (-garnet). Garnets formed in all three stages.

Ca-silicate alteration	Amphibole-Epidote-Magnetite alteration/mineralization	Pyrite-Chalcopyrite mineralization	Minerals
Stage I	Stage II	Stage III	
	?		Garnet Amphibole ? Magnetite Epidote Pyrite Hematite
			 Quartz Chalcopyrite Gold Chlorite Calcite



3. Samples and Analytical Methods

Sampled garnet in this study were collected from different stages of the Laoshankou Fe-Cu-Au deposit, which including TS-001, TS-001-7, LS-006, LS-024-2, LS-024-3, LS-026, LS14-012-5, LS14-012-6, and LS14-012-7. The detailed location can be seen in Figure 2 and Table 1.

Table 1. Descriptions of sampled garnets from the Laoshankou deposit.

Sample No.	Location	Description of Characteristics	Garnet Types
LS-024	N46°28'14.82"; E90°6'3.98"	Banded skarnization in volcanic rocks	Type 1 and Type 2a
LS-024-2	N46°28'14.82"; E90°6'3.99"	Banded skarnization in volcanic rocks	Type 1 and Type 2a
LS-024-3	N46°28'14.82"; E90°6'3.100"	Banded skarnization in volcanic rocks	Type 1 and Type 2a
TS-001	N46°27′7.62″; E90°7′24.36″	Garnet vein in volcanic rocks	Type 2b
TS-001-7	N46°27′7.62″; E90°7′24.37″	Garnet vein in volcanic rocks	Type 2b
LS-026-4	Stock heap	Massive magnetite ore with related epidote and disseminated pyrite	Type 2b
LS-006-4	No.5 pit	Massive magnetite ore with taxitic pyrite	Type 3
LS14-012-5	Stock heap	Garnet in massive chalcopyrite ore	Type 3
LS14-012-6	Stock heap	Garnet in massive chalcopyrite ore	Type 3
LS14-012-7	Stock heap	Garnet in massive chalcopyrite ore	Type 3

3.1. Electron Microprobe Analysis

Quantitative mineral analyses for garnet in situ major elements geochemistry and back-scattered electron (BSE) images were performed using a JEOL JXA-8100 at the Key Laboratory of Mineral and Metallogenic, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS), Guangzhou, China. The analytical parameters used an accelerating voltage of 15 kV, a beam current of 20 nA, and 1 μ m beam diameter. Natural minerals and metals were used as standards. Analysis data were treated with the conventional ZAF program, and the number of ions of garnet spots were calculated on 12 oxygens and with Fe²⁺/Fe³⁺ calculated assuming full site occupancy [56]. The major element analyses of garnet by EMPA and the calculated number of ions for garnet are listed in Table 2.

3.2. LA-ICP-MS Analysis

Trace elements of garnet were conducted with a pulsed RESOlution M-50 Laser Ablation system (Resonetics, USA) coupled with an Agilent 7500a ICP-MS at the Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS), Guangzhou, China. Detailed operating conditions for the LA-ICP-MS instrument and data reduction have been described by Liu et al. (2008) [57]. Helium was applied as a carrier gas and argon as a makeup gas mixed with the carrier gas via a T-connector before entering the ICP. Each analysis includes a background acquisition of approximately 20 s for a gas blank, followed by 40 s data acquisition from the sample. Laser spots were 40 µm in diameter with successive pulses at 4 Hz. The external standards were BCR-2G and SRM612, analyzed twice every five to six sample analyses to correct the time-dependent drift of sensitivity and mass discrimination as quality control. Offline data reduction was performed with ICPMSDataCal v.10 [57], including selection and integration of background and analysis signals, time drift correction, and quantitative calibration. Trace elements and EPMA measurements were made in the same place in the minerals. For most trace elements (> 0.5 ppm), the accuracy is better than 5% of relative deviation with precision of 10%. All the analyses of garnet samples and standards are provided in Table 3.

Table 2. EPMA analysis results (wt.%) of garnets from the Laoshankou deposit.

Samples	Spot No.	Types	Description	SiO ₂	TiO ₂	Al ₂ O ₃	FeO ^T	MnO	MgO	CaO	Na ₂ O	Cr ₂ O ₃	Total	Si	Al ^{iv}	Al ^{vi}
LS-024	LS-024-GRT1	Type 2a	slightly bright gray	36.27	0.30	6.13	18.70	0.79	0.11	33.17	0.01	b.d.l.	95.49	3.06	b.d.l.	0.64
LS-024	LS-024-GRT3	Ťype 1	dark gray	36.78	1.50	9.97	12.99	0.92	0.13	34.13	0.02	0.14	96.59	3.01	b.d.l.	0.99
LS-024	LS-024-GRT5	Type 2a	slightly bright gray	36.31	0.62	6.18	18.79	0.74	0.06	33.61	0.01	0.02	96.35	3.04	b.d.l.	0.64
LS-024	LS-024-GRT6	Ťype 1	dark gray	36.90	0.87	9.68	14.34	0.99	0.16	33.64	b.d.l.	0.003	96.57	3.03	b.d.l.	0.97
LS-024-2	LS-024-2-1GRT	Type 1	dark gray	37.53	1.42	10.75	16.26	0.91	0.18	34.50	0.07	0.003	101.62	2.94	0.06	0.97
LS-024-2	LS-024-2-2GRT	Type 2a	slightly bright gray	36.66	0.79	6.38	22.48	0.84	0.12	34.08	0.02	0.02	101.39	2.95	0.05	0.58
LS-024-2	LS-024-2-3GRT	Type 1	dark gray	37.38	0.23	10.73	17.20	0.87	0.10	34.28	0.02	0.37	101.18	2.95	0.05	0.99
LS-024-2	LS-024-2-4GRT	Type 2a	slightly bright gray	36.77	0.69	6.60	22.62	0.96	0.13	33.59	0.01	0.08	101.45	2.96	0.04	0.61
LS-024-2	LS-024-2-5GRT	Type 1	dark gray	37.30	0.07	9.13	19.33	0.85	0.04	34.06	0.05	0.20	101.03	2.97	0.03	0.87
LS-024-3	LS-024-3-1	Type 2a	slightly bright gray	36.65	0.53	6.79	20.87	0.95	0.33	34.89	b.d.l.	b.d.l.	101.00	2.94	0.06	0.62
LS-024-3	LS-024-3-3	Type 1	dark gray	36.85	1.35	10.71	14.69	1.06	0.20	36.05	0.06	0.02	100.99	2.91	0.09	0.94
LS-024-3	LS-024-3-5	Type 1	dark gray	37.13	1.18	10.90	14.98	0.91	0.16	35.41	0.001	0.01	100.67	2.93	0.07	0.98
LS-024-3	LS-024-3-8	Type 2a	slightly bright gray	36.85	0.48	6.82	21.19	0.96	0.29	34.25	0.01	b.d.l.	100.86	2.96	0.04	0.64
TS-001	TS-001-10	Type 2b	bright gray	36.08	0.49	5.41	22.61	1.04	b.d.l.	33.29	b.d.l.	b.d.l.	98.92	2.98	0.02	0.54
TS-001	TS-001-11	Type 2b	slightly bright gray	36.62	0.16	6.93	19.67	0.34	0.18	35.43	b.d.l.	b.d.l.	99.34	2.98	0.02	0.67
TS-001	TS-001-20	Type 2b	slightly bright gray	36.29	0.78	5.78	21.77	0.89	0.25	34.07	0.05	0.01	99.88	2.96	0.04	0.54
TS-001	TS-001-GRT3	Type 2b	slightly bright gray	35.51	0.10	8.06	16.72	0.65	0.07	34.16	0.05	0.02	95.33	2.99	0.01	0.82
TS-001	TS-001-GRT4	Type 2b	bright gray	35.05	0.43	4.49	20.38	0.84	0.07	32.89	0.02	0.02	94.17	3.03	b.d.l.	0.48
TS-001-7	TS-001-7-1GRT	Type 2b	bright gray	36.28	0.52	5.32	24.55	1.25	0.09	31.95	0.002	b.d.l.	99.94	2.98	0.02	0.52
TS-001-7	TS-001-7-2GRT	Type 2b	slightly bright gray	35.85	0.44	5.36	24.00	0.85	0.09	33.38	0.01	0.01	99.99	2.94	0.06	0.49
TS-001-7	TS-001-7-3GRT	Type 2b	bright gray	36.13	0.15	4.26	25.62	0.86	0.08	33.04	0.004	b.d.l.	100.16	2.97	0.03	0.41
TS-001-7	TS-001-7-4GRT	Type 2b	slightly bright gray	36.08	0.49	5.49	23.91	0.79	0.10	33.21	0.01	0.003	100.10	2.96	0.04	0.51
TS-001-7	TS-001-7-5GRT	Type 2b	slightly bright gray	36.08	0.73	6.06	23.10	1.04	0.09	32.99	0.03	0.01	100.18	2.95	0.05	0.56
TS-001-7	TS-001-7-6GRT	Type 2b	bright gray	35.95	0.55	5.42	23.94	0.97	0.09	33.11	b.d.l.	0.001	100.06	2.95	0.05	0.50
LS-026-4	LS-026-4-G-2	Type 2b	bright gray	36.20	0.34	4.74	22.59	0.42	0.04	34.18	0.02	b.d.l.	98.53	3.00	b.d.l.	0.49
LS-006-4	LS-006-4-G-1	Type 3	homogeneity	36.59	0.50	2.06	26.78	0.26	0.13	33.79	0.02	b.d.l.	100.14	3.02	b.d.l.	0.21
LS14-012-5	LS14-012-5-GRT1	Type 3	homogeneity	35.69	b.d.l.	0.01	29.74	0.48	0.004	33.25	b.d.l.	0.01	99.18	3.02	b.d.l.	0.001
LS14-012-5	LS14-012-5-GRT2	Type 3	homogeneity	35.79	b.d.l.	0.26	29.33	0.43	b.d.l.	33.40	0.02	0.02	99.25	3.02	b.d.l.	0.03
LS14-012-5	LS14-012-5-GRT3	Type 3	homogeneity	36.20	b.d.l.	0.16	29.36	0.36	b.d.l.	33.74	b.d.l.	b.d.l.	99.82	3.03	b.d.l.	0.02
LS14-012-5	LS14-012-5-GRT-1	Type 3	homogeneity	34.68	b.d.l.	0.09	28.94	0.43	0.01	33.28	0.01	b.d.l.	97.44	2.99	0.01	b.d.l.
LS14-012-5	LS14-012-5-GRT-2	Type 3	homogeneity	34.83	b.d.l.	0.02	28.61	0.38	0.02	33.28	0.003	b.d.l.	97.14	3.00	b.d.l.	0.002
LS14-012-5	LS14-012-5-GRT-3	Type 3	homogeneity	34.46	b.d.l.	0.01	28.94	0.39	b.d.l.	33.53	b.d.l.	0.01	97.33	2.97	0.001	b.d.l.
LS14-012-6	LS14-012-6-GRT1	Type 3	homogeneity	35.92	0.01	1.45	27.89	0.39	0.02	33.72	0.02	0.001	99.41	3.01	b.d.l.	0.15
LS14-012-6	LS14-012-6-GRT2	Type 3	homogeneity	35.59	b.d.l.	0.50	29.09	0.37	b.d.l.	33.33	0.01	b.d.l.	98.89	3.01	b.d.l.	0.05
LS14-012-6	LS14-012-6-GRT3	Type 3	homogeneity	35.67	b.d.l.	0.37	29.64	0.46	b.d.l.	33.65	0.02	0.03	99.82	2.99	0.01	0.03
LS14-012-6	LS14-012-6-GRT-1	Type 3	homogeneity	34.10	b.d.l.	0.16	28.87	0.41	b.d.l.	33.13	0.02	0.01	96.69	2.96	0.02	b.d.l.
LS14-012-7	LS14-012-7-GRT-1	Type 3	homogeneity	34.55	b.d.l.	0.004	28.99	0.38	0.01	33.28	0.02	0.02	97.26	2.98	0.0004	b.d.l.

9 of 25

Table 2. Cont.

Samples	Spot No.	Types	Description	Ti	Cr	Fe ³⁺	Fe ²⁺	Mn	Mg	Ca	Alm	Adr	Grs	Prp	Sps	Uv
LS-024	LS-024-GRT1	Type 2a	slightly bright gray	0.02	b.d.l.	1.09	0.23	0.06	0.01	3.00	0.00	64.09	33.12	0.56	2.23	0.00
LS-024	LS-024-GRT3	Ťype 1	dark gray	0.09	0.01	0.77	0.12	0.06	0.02	2.99	0.00	44.22	52.21	0.60	2.45	0.52
LS-024	LS-024-GRT5	Type 2a	slightly bright gray	0.04	0.001	1.09	0.23	0.05	0.01	3.01	0.00	63.99	33.58	0.29	2.05	0.09
LS-024	LS-024-GRT6	Type 1	dark gray	0.05	0.0002	0.81	0.17	0.07	0.02	2.96	0.00	46.52	50.10	0.75	2.62	0.01
LS-024-2	LS-024-2-1GRT	Type 1	dark gray	0.08	0.0002	0.81	0.26	0.06	0.02	2.90	0.00	44.87	52.14	0.76	2.22	0.01
LS-024-2	LS-024-2-2GRT	Type 2a	slightly bright gray	0.05	0.001	1.16	0.36	0.06	0.01	2.94	0.00	65.60	31.62	0.53	2.17	0.08
LS-024-2	LS-024-2-3GRT	Ťype 1	dark gray	0.01	0.02	0.84	0.30	0.06	0.01	2.90	0.00	44.95	51.30	0.42	2.10	1.24
LS-024-2	LS-024-2-4GRT	Type 2a	slightly bright gray	0.04	0.01	1.14	0.38	0.07	0.01	2.89	0.00	64.34	32.33	0.57	2.47	0.29
LS-024-2	LS-024-2-5GRT	Type 1	dark gray	0.004	0.01	0.95	0.34	0.06	0.005	2.91	0.00	52.24	44.80	0.18	2.09	0.68
LS-024-3	LS-024-3-1	Type 2a	slightly bright gray	0.03	b.d.l.	1.14	0.26	0.06	0.04	3.00	0.00	63.99	32.12	1.48	2.42	0.00
LS-024-3	LS-024-3-3	Type 1	dark gray	0.08	0.001	0.84	0.13	0.07	0.02	3.05	0.00	45.76	50.77	0.85	2.56	0.05
LS-024-3	LS-024-3-5	Type 1	dark gray	0.07	0.0003	0.81	0.18	0.06	0.02	3.00	0.00	44.48	52.61	0.68	2.21	0.02
LS-024-3	LS-024-3-8	Type 2a	slightly bright gray	0.03	b.d.l.	1.12	0.30	0.07	0.03	2.95	0.00	63.48	32.75	1.30	2.47	0.00
TS-001	TS-001-10	Type 2b	bright gray	0.03	b.d.l.	1.21	0.35	0.07	b.d.l.	2.95	0.00	69.65	27.55	0.00	2.80	0.00
TS-001	TS-001-11	Type 2b	slightly bright gray	0.01	b.d.l.	1.12	0.22	0.02	0.02	3.09	0.00	62.69	35.59	0.83	0.89	0.00
TS-001	TS-001-20	Type 2b	slightly bright gray	0.05	0.001	1.19	0.30	0.06	0.03	2.98	0.00	68.11	28.35	1.16	2.36	0.03
TS-001	TS-001-GRT3	Type 2b	slightly bright gray	0.01	0.001	1.00	0.18	0.05	0.01	3.08	0.00	55.47	42.42	0.32	1.72	0.07
TS-001	TS-001-GRT4	Type 2b	bright gray	0.03	0.001	1.23	0.24	0.06	0.01	3.04	0.00	72.86	24.27	0.37	2.42	0.08
TS-001-7	TS-001-7-1GRT	Type 2b	bright gray	0.03	b.d.l.	1.22	0.47	0.09	0.01	2.81	0.00	70.32	25.94	0.40	3.33	0.00
TS-001-7	TS-001-7-2GRT	Type 2b	slightly bright gray	0.03	0.001	1.25	0.40	0.06	0.01	2.94	0.00	70.65	26.64	0.43	2.23	0.05
TS-001-7	TS-001-7-3GRT	Type 2b	bright gray	0.01	b.d.l.	1.33	0.44	0.06	0.01	2.91	0.00	76.22	21.10	0.40	2.29	0.00
TS-001-7	TS-001-7-4GRT	Type 2b	slightly bright gray	0.03	0.0002	1.23	0.41	0.05	0.01	2.91	0.00	69.87	27.57	0.47	2.08	0.01
TS-001-7	TS-001-7-5GRT	Type 2b	slightly bright gray	0.04	0.001	1.18	0.40	0.07	0.01	2.89	0.00	66.83	29.97	0.42	2.73	0.05
TS-001-7	TS-001-7-6GRT	Type 2b	bright gray	0.03	0.0001	1.24	0.41	0.07	0.01	2.91	0.00	70.22	26.78	0.44	2.56	0.00
LS-026-4	LS-026-4-G-2	Type 2b	bright gray	0.02	b.d.l.	1.25	0.31	0.03	0.01	3.04	0.00	73.04	25.61	0.21	1.14	0.00
LS-006-4	LS-006-4-G-1	Type 3	homogeneity	0.03	b.d.l.	1.45	0.40	0.02	0.02	2.99	0.00	87.83	10.79	0.64	0.74	0.00
LS14-012-5	LS14-012-5-GRT1	Type 3	homogeneity	b.d.l.	0.0005	1.64	0.46	0.03	0.001	3.01	0.00	99.90	0.00	0.02	0.05	0.03
LS14-012-5	LS14-012-5-GRT2	Type 3	homogeneity	b.d.l.	0.001	1.62	0.45	0.03	b.d.l.	3.02	0.00	98.32	0.36	0.00	1.23	0.09
LS14-012-5	LS14-012-5-GRT3	Type 3	homogeneity	b.d.l.	b.d.l.	1.62	0.44	0.03	b.d.l.	3.03	0.00	99.02	0.00	0.00	0.98	0.00
LS14-012-5	LS14-012-5-GRT-1	Type 3	homogeneity	b.d.l.	b.d.l.	1.66	0.42	0.03	0.001	3.07	0.00	99.46	0.00	0.03	0.51	0.00
LS14-012-5	LS14-012-5-GRT-2	Type 3	homogeneity	b.d.l.	b.d.l.	1.65	0.41	0.03	0.002	3.07	0.00	99.91	0.00	0.09	0.00	0.00
LS14-012-5	LS14-012-5-GRT-3	Type 3	homogeneity	b.d.l.	0.0004	1.68	0.41	0.03	b.d.l.	3.10	0.00	99.91	0.00	0.00	0.07	0.02
LS14-012-6	LS14-012-6-GRT1	Type 3	homogeneity	0.001	0.0001	1.53	0.42	0.03	0.002	3.02	0.00	91.47	7.36	0.07	1.09	0.00
LS14-012-6	LS14-012-6-GRT2	Type 3	homogeneity	b.d.l.	b.d.l.	1.61	0.45	0.03	b.d.l.	3.02	0.00	96.98	1.95	0.00	1.07	0.00
LS14-012-6	LS14-012-6-GRT3	Type 3	homogeneity	b.d.l.	0.002	1.63	0.45	0.03	b.d.l.	3.03	0.00	97.70	0.90	0.00	1.29	0.11
LS14-012-6	LS14-012-6-GRT-1	Type 3	homogeneity	b.d.l.	0.001	1.67	0.43	0.03	b.d.l.	3.08	0.00	99.01	0.00	0.00	0.94	0.05
LS14-012-7	LS14-012-7-GRT-1	Type 3	homogeneity	b.d.l.	0.001	1.67	0.42	0.03	0.001	3.08	0.00	99.91	0.00	0.02	0.00	0.07

Note: number of cations on the basis of 12O.

Table 3. LA-ICP-MS major and trace elements data (wt. % and ppm) of garnets from the Laoshankou deposit.

	wt.% wt.% ppm ppm ppm ppm ppm ppm ppm ppm
LS-024 LS-024-GRT1 Type 2a LS-024-GRT1 36.2 0.39 8.89 19.5 0.95 0.11 34.4 0.005	b.d.l. 0.01 7.90 676 79.7 0.62 0.28 b.d.l. 3.59 14.1
LS-024 LS-024-GRT2 Type 1 LS-024-3-3 36.7 1.96 9.84 17.4 0.90 0.20 35.7 0.01	0.001 0.01 10.6 1138 44.5 0.76 0.77 1.52 2.77 21.6
LS-024 LS-024-GRT3 Type 1 LS-024-GRT3 36.7 1.88 10.7 15.3 1.13 0.27 35.1 0.02	0.02 0.01 33.4 1531 726 0.78 0.85 7.17 5.17 11.3
LS-024 LS-024-GRT4 Type 1 LS-024-3-5 36.7 0.72 8.64 19.0 0.88 0.12 34.8 0.01	0.003 0.01 23.7 714 55.7 0.47 0.46 88.5 3.11 14.7
LS-024 LS-024-GRT5 Type 2a LS-024-GRT5 36.3 0.76 7.82 20.5 0.83 0.10 34.0 0.004	0.0005 0.01 4.37 518 10.6 1.59 42.5 414 51.5 18.3
LS-024 LS-024-GRT6 Type 1 LS-024-GRT6 36.8 0.91 9.88 17.5 1.12 0.13 34.3 0.01	0.001 0.01 3.61 412 41.1 0.49 0.50 77.1 2.21 10.8
TS-001 TS-001-GRT1 Type 2b TS-001-10 36.0 0.50 5.77 23.6 1.10 0.10 34.0 0.003	b.d.l. 0.01 8.60 414 12.2 1.65 0.97 b.d.l. 3.71 11.4
TS-001 TS-001-GRT2 Type 2b TS-001-11 36.0 0.93 5.66 23.5 1.04 0.12 34.1 0.01	0.004 0.01 27.8 813 18.1 1.61 1.53 1.57 7.45 11.4
15-001 15-001-GR13 1ype 2b 15-001-GR13 36.0 0.49 7.64 20.4 1.03 0.12 33.5 0.01	0.001 0.01 6.73 312 1.93 1.44 1.05 b.d.l. 2.85 11.4
15-001 15-001-GR14 1ype 2b 15-001-GR14 36.0 0.54 5.89 23.2 1.12 0.11 33.0 0.01	0.003 0.01 6.67 440 23.5 1.77 1.25 3.72 4.45 12.7
15-001 15-001-GR15 199E2D 15-001-20 36.5 0.65 5.34 20.8 0.85 1.94 30.4 0.02	0.01 0.01 21.0 325 4.97 33.8 16.4 121 37.2 12.3
LS14-012-5 LS14-012-5K11 1/pe 5 LS14-012-5K1-1 55.7 0.001 0.14 50.0 0.45 0.02 54.0 0.002 154.0 0.002 154.0 0.002 154.0 0.002 0.04 30.7 0.46 0.02 35.7 0.002	b.d. 0.01 0.74 12.5 0.d. 0.25 0.00 1.11 1.51 4.50
LS14-012-5 LS14-012-GR12 Type 5 LS14-012-5-GR12 30.1 0.0005 0.04 50.7 0.40 0.02 5.57 0.002	bdl 001 0.77 896 bdl 0.22 1.19 bdl 0.12 2.30
LS14-012-6 LS14-012-GRT3 1/pc-5 LS14-012-6-GRT-1 355 0.005 0.57 0.04 0.46 0.01 0.07 337 0.003	bdl 001 064 145 bdl 051 074 bdl 325 125
L514-012-7 L514-012-GRT5 Type 3 L514-012-7-GRT-1 35.6 0.0001 0.06 30.2 0.46 0.03 34.5 0.004	0,0005 0,01 1,01 22.4 1,65 0,27 0,92 9,34 3,06 6,56
Calibrated EPMA Ge As Rb Sr Y Zr Nb Sn	Cs Ba La Ce Pr Nd Sm Eu Gd Tb
Samples Spot No. Types Spot no. ppm ppm ppm ppm ppm ppm ppm ppm ppm	ppm
LS-024 LS-024-GRT1 Type 2a LS-024-GRT1 4.09 11.7 0.09 0.95 23.2 17.0 0.24 6.65	b.d.l. 1.16 b.d.l. 0.28 0.16 3.06 5.74 6.59 6.79 0.90
LS-024 LS-024-GRT2 Type 1 LS-024-3-3 5.04 13.6 b.d.l. 0.48 20.0 32.8 3.41 4.56	0.03 0.35 b.d.l. 0.16 0.12 2.29 4.47 8.32 7.55 1.09
LS-024 LS-024-GRT3 Type 1 LS-024-GRT3 3.70 11.2 0.14 0.99 27.9 47.2 2.15 1.17	b.d.l. 1.56 0.04 0.10 0.02 0.35 0.42 0.36 1.32 0.40
LS-024 LS-024-GRT4 Type 1 LS-024-3-5 3.98 13.7 0.12 1.16 18.2 26.2 0.42 4.59	0.06 1.36 0.03 0.12 0.04 0.88 1.41 3.41 2.66 0.46
LS-024 LS-024-GRT5 1ype 2a LS-024-GRT5 3.99 47.1 b.d.l. 0.92 11.7 19.3 0.26 6.14	b.d.l. 0.31 0.37 0.99 0.23 4.05 5.40 6.80 5.79 0.59
L5-024 L5-024-GK16 IPpe1 L5-024-GK16 3.70 14.0 0.07 0.55 10.0 21.0 2.55 4.96	b.d.l. 0.32 0.03 0.04 0.02 0.13 0.19 1.90 1.14 0.25
15-001 15-001-GR11 19/P2-20 15-001-10 11.6 15.6 0.0.1. 0.25 51.0 76.7 0.00 11.2 T\$C011 T\$C011 CPT2 Time 1b T\$C0111 102 185 0.24 140 011 121 0.01 742	0.01. 0.01. 0.15 2.79 1.34 14.5 0.50 0.00 0.00 0.95 0.02 0.80 0.18 2.70 1.27 18.2 18.2 14.7 25.1 2.25
15-001 15-001-0012 170-20 15-001-11 15-2 16-5 0.50 1.49 51.1 151 0.51 7.42 T\$-001 T\$-001-007 T\$-001-007 861 189 0.06 0.49 31.2 51.3 1.36 5.67	0.25 0.09 0.10 2.79 1.27 10.2 10.2 14.7 2.51 $5.550.04$ bdl 0.11 1.88 0.84 10.2 61.2 7.62 6.86 1.00
TS-001 TS-001-GRT4 Type 2b TS-001-GRT4 10.9 238 0.17 0.81 285 76.9 1.07 9.29	bdl 049 019 227 103 133 7.37 9.04 8.01 0.91
T\$-001 T\$-001-GRT5 Type 2b T\$-001-20 6.07 29.9 0.10 3.19 18.0 141 0.47 8.57	b.d.l. 9.68 0.36 7.11 1.28 14.0 5.84 7.99 4.44 0.46
LS14-012-5 LS14-012-GRT1 Type 3 LS14-012-5-GRT-1 1.08 1810 b.d.l. 1.01 0.51 b.d.l. b.d.l. 8.63	b.d.l. b.d.l. 1.55 0.80 0.06 0.21 0.09 0.23 b.d.l. 0.01
LS14-012-5 LS14-012-GRT2 Type 3 LS14-012-5-GRT-2 1.06 1462 b.d.l. 1.02 0.36 b.d.l. b.d.l. 5.48	0.07 b.d.l. 0.63 0.41 0.05 0.22 0.04 0.21 b.d.l. 0.01
LS14-012-5 LS14-012-GRT3 Type 3 LS14-012-5-GRT-3 b.d.l. 2016 b.d.l. 0.95 0.66 b.d.l. b.d.l. 4.67	b.d.l. b.d.l. 0.61 0.57 0.04 0.31 0.12 0.32 0.06 0.01
LS14-012-6RT4 Type 3 LS14-012-6-GRT-1 1.17 3245 b.d.l. 0.72 0.62 0.05 0.05 14.1	b.d.l. b.d.l. 2.95 4.37 0.37 0.96 0.13 2.25 0.17 0.03
L514-012-7 L514-012-GRT5 Type 3 L514-012-GRT-1 1.33 2332 b.d.l. 0.80 37.1 b.d.l. b.d.l. 2.35	b.d.l. b.d.l. 20.0 28.0 2.88 14.2 4.05 5.46 6.26 0.83
Samples Spot No. Types Calibrated Dy Ho Er Tm Yb Lu Hf Ta	Au Bi Th U ∑REE ∑LREE/ (La/Yb) _N δEu δCe
Егих Spot No. ррш ррш ррш ррш ррш ррш ррш	ррш ррш ррш ррш _пкее
LS-024 LS-024-GRT1 Type 2a LS-024-GRT1 5.16 0.85 1.92 0.23 1.45 0.22 0.38 0.04	0.01 b.d.l. 0.07 1.38 33.4 0.90 b.d.l. 3.22 b.d.l.
LS-024 LS-024-GRT2 Type 1 LS-024-3-3 5.04 0.72 1.64 0.18 1.09 0.11 0.62 0.12	b.d.l. b.d.l. 0.89 9.32 32.8 0.88 b.d.l. 4.35 b.d.l.
LS-024 LS-024-GRT3 Type 1 LS-024-GRT3 3.72 0.97 3.44 0.62 4.13 0.61 1.30 0.06	0.01 b.d.l. 0.09 0.41 16.5 0.09 0.01 1.36 0.85
L5-024 L5-024-GR14 Type 1 L5-024-3-5 3.40 0.70 1.72 0.26 1.56 0.21 0.58 0.02	b.d.l. b.d.l. 0.16 2.23 16.8 0.54 0.02 5.29 0.65
LS-024 LS-024-GR15 Iype 2a LS-024-GR15 2.41 0.46 1.08 0.15 0.73 0.13 0.33 0.03	b.d.l. b.d.l. 0.09 2.64 29.2 1.57 0.37 3.69 0.82
LS-024 LS-024-GR16 IPpe1 LS-024-GR16 1.94 0.38 1.09 0.14 0.76 0.12 0.48 0.15 TS-001 TS-001 CDT1 Two-1b TS-00110 570 1.06 2.04 0.46 2.76 0.41 1.74 0.06	b.d.l. b.d.l. 0.05 2.07 8.14 0.40 0.02 9.61 0.46
157001 $157001-5001$ $1ype 20$ $157001-10$ 577 1.00 2.59 0.40 2.76 0.41 1.74 0.00 $1%$ $1%$	bdl 0.03 0.21 3.00 34.0 1.01 0.04 3.3% 0.62 bdl 0.03 0.35 2.82 124 0.81 0.02 2.11 0.44
TS-001 TS-001-CRT2 Type 20 TS-001-11 10.7 5.54 0.57 1.24 7.50 1.11 4.54 0.25 TS-001 TS-001-CRT3 Type 2b TS-001-CRT3 6.34 1.13 3.21 0.43 3.00 0.37 1.39 0.15	bdl bdl 0.32 497 401 120 0.03 358 0.66
TS-001 TS-001-CRT4 Type 2b TS-001-CRT4 560 108 2.95 0.42 2.80 0.35 1.73 0.00	0.03 0.04 0.28 4.89 55.3 1.50 0.05 3.58 0.64
TS-001 TS-001-CRT5 Type 2b TS-001-20 3.29 0.63 1.68 0.25 0.72 2.00 0.57 4.42 0.07	bdl 0.03 0.47 5.58 49.6 2.82 0.13 4.61 1.55
L514012-5 L514012-GRT1 Type 3 L514012-5GRT-1 0.07 b.dl. 0.03 b.dl. 0.04 0.01 b.dl. b.dl.	0.02 0.09 b.d. 0.10 3.10 17.9 26.7 b.d. 0.37
LS14-012-5 LS14-012-GRT2 Type 3 LS14-012-5-GRT-2 0.05 0.01 0.04 b.d.l b.d.l b.d.l b.d.l b.d.l b.d.l	0.02 0.09 b.d.l. 0.01 1.66 13.7 b.d.l. b.d.l. 0.42
LS14-012-5 LS14-012-GRT3 Type 3 LS14-012-5-GRT-3 0.09 0.02 0.06 b.d.l. 0.04 0.01 b.d.l. b.d.l.	b.d.l. 0.07 b.d.l. 0.02 2.26 6.91 11.0 10.6 0.62
LS14-012-6 LS14-012-GRT4 Type 3 LS14-012-6-GRT-1 0.10 0.02 0.05 0.01 0.03 b.d.l. b.d.l. b.d.l.	b.d.l. 0.12 b.d.l. 1.77 11.4 26.5 61.9 45.5 0.87
LS14-012-7 LS14-012-GRT5 Type 3 LS14-012-7-GRT-1 4.97 0.88 1.98 0.21 1.23 0.14 0.004 b.d.l.	0.01 0.10 0.01 0.23 91.1 4.53 11.6 3.31 0.80

4. Results

4.1. Garnet Petrography

Based on geology, transmitted-reflected light microscopy, BSE and EPMA studies, garnets from the Laoshankou deposit can be divided into three types with changes in color. There is no obvious contact interface between the different garnets. (1) Type 1, the brown garnet in stage I occurs in the volcanic wall rocks (Figure 5a,b) with allotriomorphic texture (Figure 6a–c), which is optically dark and homogeneous in BSE images (Figure 6c). Type 1 garnet is generally replaced by the subsequent Type 2 garnet, magnetite, epidote, albite, and calcite (Figures 5b and 6a,b) with preservation of their original textures. (2) Type 2, the dark red garnet in the early sub-stage of stage II forms adjacent to the orebody (Figure 5c) or cross-cuts the diorite porphyrite near the orebody (Figure 5d) with fine-grained texture (Figure 6d-f), which coexists with K-feldspar and is replaced by subsequent epidote, calcite and chlorite (Figure 6d,e). Two forms of Type 2 garnet occur, the Type 2a garnet is irregular and replaces the Type 1 garnet (Figure 6c), while the Type 2b has unobvious oscillatory zoning on the scale of an individual crystal (Figure 6f). (3) Type 3, garnet is yellow-green and coexists with sulfides, quartz, amphibole and chlorite (Figure 5e,f) with obvious coarsegrained texture (1–5 mm; Figure 6g–i) at pyrite-chalcopyrite stage. The back-scattered electron images and reflected light images show that the Type 3 garnet is homogeneous without zones (Figure 6i).



Figure 5. Photographs of garnet varieties from the Laoshankou deposit. (**a**) brown garnet in the volcanic wall rocks; (**b**) brown garnet replaced by subsequent epidote and albite; (**c**) dark red garnet adjacent to the orebody; (**d**) dark red garnet cross-cuts the diorite porphyrite near the orebody; (**e**) yellow-green garnet coexists with sulfides; (**f**) yellow-green garnet coexists with sulfides, quartz, amphibole and chlorite. Abbreviations: Ab, albite; Amp, amphibole; Ccp, chalcopyrite; Chl, chlorite; Ep, epidote; Grt, garnet; Mag, magnetite; Py, pyrite; Qz, quartz.

4.2. Major Elements of Garnet by EMPA

Electron microprobe analyses show that the andradite content increases steadily for garnets from stage I to stage III in the Laoshankou deposit, ranging in composition from $Adr_{44}Grs_{53}$ to almost pure andradite Adr_{100} (Figure 7) with almandine, spessartine, pyrope and uvarovite collectively less than 5% (Table 2). The textural and optical characteristics of different types of garnets show a clear correspondence with major element compositions (Figure 8). Type 1 garnet has poor compositional zoning and mainly contain SiO₂ (36.78–37.53 wt.%), CaO (33.64–36.05 wt.%), Al₂O₃ (9.13–10.90 wt.%), and FeO^T (12.99–19.33 wt.%) with a small amount of TiO₂ (0.07–1.50 wt.%), MnO (0.85–1.06 wt.%), and MgO (0.04–0.20 wt.%), yielding an end-member formula of Grs_{44–53}Adr_{44–53}Sps_{2–3}Uv $_{0-2}Prp_{0-1}$, which is more enriched in grossularite (Figure 7). Compared with Type 1 garnet, the Type 2 garnets have higher concentrations of FeO^{T} , but lower concentrations of Al_2O_3 (Figure 8a,b), which are all located in the Al-rich andradite field (Figure 7). Type 2a garnet is xenomorphic granular and has poor compositional zoning, yielding an end-member formula of $\text{Adr}_{63-66}\text{Grs}_{31-34}\text{Sps}_{2-3}\text{Prp}_{0-2}\text{Uv}_{0-1}$. The concentrations of SiO_2 , CaO, Al_2O_3 , and FeO^{T} are 36.27-36.85 wt.%, 33.17-34.89 wt.%, 6.13-6.82 wt.% and 18.70-22.62 wt.%, respectively. The Type 2b has unobvious oscillatory zoning and fine-grained texture (Figures 6f and 8c) with stable SiO_2 , CaO, Al_2O_3 , and FeO^{T} concentrations (Figure 8c,d). The SiO_2 , CaO, Al_2O_3 , and FeO^{T} concentrations (Figure 8c,d). The SiO_2 , CaO, Al_2O_3 , and FeO^{T} concentrations of Type 2b garnet are 35.05-36.62 wt.%, 31.95-35.43 wt.%, 4.26-8.06 wt.% and 16.72-25.62 wt.%, yielding an end member formula of $\text{Adr}_{55-77}\text{Grs}_{21-43}\text{Sps}_{0-4}\text{Prp}_{0-2}\text{Uv}_{0-1}$. In comparison, the Type 3 garnet contains the highest concentrations of FeO^{T} (27.89–29.74 wt.%) and lowest concentrations of Al_2O_3 (0-1.45 wt.%), which are plot in the andradite component (Figure 7), yielding an end member formula of $\text{Adr}_{91-100}\text{Grs}_{0-8}\text{Sps}_{0-2}\text{Prp}_{0-1}\text{Uv}_{0-1}$.



Figure 6. Transmitted-reflected light photomicrographs and BSE images of garnets from the Laoshankou deposit. (**a**,**b**) Type 1 brown garnet is corroded by subsequent Type 2a garnet, epidote and calcite; (**c**) Type 1 and Type 2a garnets with different BSE extinction; (**d**,**e**) Type 2 dark red garnet coexists with K-feldspar and is cut by subsequent epidote, calcite and chlorite; (**f**) unobvious oscillatory zoning in fine-grained Type 2b garnet; (**g**) Type 3 yellow-green garnet with obvious coarse-grained texture; (**h**) yellow-green garnet coexists with chalcopyrite, quartz, amphibole and chlorite; (**i**) homogeneous Type 3 garnet crystal. Abbreviations: Amp, amphibole; Cal, calcite; Ccp, chalcopyrite; Chl, chlorite; Ep, epidote; Grt, garnet; Kfs, K-feldspar; Mag, magnetite; Py, pyrite.







Figure 8. Back-scattered scanning electron microscope images (**a**,**c**) and major elements compositional variations (**b**,**d**) for Type 1 and Type 2 garnet crystals.

4.3. Trace and Rare Earth Elements of Garnet by LA-ICP-MS 4.3.1. Trace Elements

Different garnets collected from the Laoshankou deposit have varying trace element contents (Figure 9). The Type 1 garnet has the highest Sc (3.61–33.4 ppm), Ti (4333–11,778 ppm), V (412–1531 ppm), Ga (10.8–21.6 ppm), Nb (0.42–3.41 ppm) and Th (0.03–0.89 ppm) contents. The Type 2 garnets (Type 2a and Type 2b) have the highest Co (0.62–53.8 ppm) and Zn (2.85– 51.5 ppm) contents. The difference of Type 3 garnet is the most obvious. The Type 3 garnet has the lowest Sc (0.64–1.01 ppm), Ti (0.77–32.6 ppm), V (3.61–145 ppm), Cu (1.11–9.34 ppm), Co (0.22–0.51 ppm), Zn (0.92–3.25 ppm), Ga (2.44–12.5 ppm), Nb (0.05 ppm), Hf (0.004 ppm) and Th (0.01 ppm), and the highest As (1462–3245 ppm) content.



Figure 9. Box-plots of trace elements in different garnets from the Laoshankou deposit.

The normalized multi-element diagram shows that all garnets in Laoshankou are generally depleted in large ion lithophile elements (LILEs, e.g., Rb, Sr, and Ba) relative to the average primitive mantle [59]. However, high field strength elements (HFSE) show a more consistent variation with major element geochemistry and petrographic observations. Both Type 1 and Type 2 garnets have higher U, Th, Hf, Y, and Ti, compared to the average primitive mantle (Figure 10). In contrast, Th, Nb, Hf, Y, and Ti compositions of Type 3 garnet are lower than the average primitive mantle (Figure 10).



Figure 10. Primitive mantle-normalized multi-element diagram of garnets from the Laoshankou deposit. Normalization values are from [59].

4.3.2. Rare Earth Elements

Chondrite-normalized REE patterns of different types of garnets show distinct differences. Both Type 1 and Type 2 garnets are strongly depleted in LREEs, and have distinctly low Σ LREE/ Σ HREE and (La/Yb)_N ratios, as well as positive Eu anomalies (Figure 11a,b). Σ LREE/ Σ HREE ratios (0.09–0.88) and Σ REE contents (8.14–32.8 ppm) of Type 1 garnet are lower than these (0.81–2.82; 29.2–124 ppm) of Type 2 garnet (Figure 11a,b). Type 3 garnet has a flat to moderately downward sloping (LREE relatively enriched and HREE-depleted) trend with obviously positive Eu anomalies (Figure 11c). Compared to Type 1 and Type 2 garnets, the andradite Type 3 garnet is characterized by the highest (La/Yb)_N ratios (11.0–61.9) and positive Eu anomalies (Figure 11d and Table 2).



Figure 11. Chondrite-normalized REE patterns of different garnets from the Laoshankou deposit. (**a**) Type 1 garnet; (**b**) Type 2a and Type 2b garnets; (**c**) Type 3 garnet; (**d**) incorporation of different types of garnet. Normalization values are from [59].

5. Discussion

5.1. Garnet Substitution Mechanisms

The general formula of garnet is $X_3Y_2Z_3O_{12}$, where X site is divalent cations (Ca, Mg, Mn, or Fe²⁺) in eight-fold coordination, Y site is trivalent cations (Fe³⁺, Al, and Cr) in octahedral coordination, and Z site is mainly Si in tetrahedral coordination [12]. Based on the ionic radii and garnet crystal radii for elements relevant in garnet chemistry, the only possible incorporation of U, REE³⁺, and yttrium is substitution of X site divalent cations (such as Ca²⁺) in dodecahedral site [11,12,60]. For Eu²⁺, the substitution is isovalent and does not imply any charge imbalance by replacing the X²⁺ site. However, the U, REE³⁺, and yttrium have different charge from the X²⁺ site [12]. The charge imbalance of substitution, like substitution of a trivalent cation (e.g., Fe³⁺ or Al³⁺) into the Z (Si) site $[X^{2+}]_{-1}^{VIII} [REE^{3+}]_{+1}^{VIII} [Si^{4+}]_{-1}^{IV} [Z^{3+}]_{+1}^{IV}$ (yttrium aluminum garnet-YAG; [61]), $[X^{2+}]_{-2}^{VIII} [X^{+}]_{+1}^{VIII} [REE^{3+}]_{+1}^{VIII}$ (X⁺ is essentially Na⁺; [62]), and substitution of divalent cations (e.g., Mg²⁺; Fe²⁺) into the Y site $[X^{2+}]_{-1}^{VIII} [REE^{3+}]_{+1}^{VIII} [P^{3+}]_{+1}^{VII} [REE^{3+}]_{+1}^{VIII} [P^{3+}]_{+1}^{VIII} [P^{2+}]_{+1}^{VII} (menzerite-type; [10,60]); or (2) the creation of a vacancy, like <math>[X^{2+}]_{-3}^{VIII} [V^{1II} [REE^{3+}]_{+2}^{VIII} [63].$ The positive ΣREE^{3+} vs. Fe³⁺ (Figure 12a), and negative ΣREE^{3+} vs. total Al

The positive $\sum REE^{3+}$ vs. Fe³⁺ (Figure 12a), and negative $\sum REE^{3+}$ vs. total Al (Figure 12b) correlations of Type 1 and 2 garnets in Laoshankou are not in favors of a YAG-type scheme. Furthermore, the Type 2 Al-rich andradite has higher $\sum REE$ than the Type 1 grossular, which is also not consistent with the YAG-type equation. Therefore, the YAG-type is not the REE substitution mechanism for Type 1 and 2 garnets. This is completely different to most garnets from global skarn deposits [7]. Neither the total Al or Fe³⁺ contents correlate with the REE³⁺ contents (Figure 12a,b) in the Type 3 garnet, suggesting that the YAG-type is not the substitution mechanism for Type 3 garnets, either. All garnets in the Laoshankou deposit do not show obvious negative $\sum REE^{3+}$ vs. Fe²⁺ (Figure 12c), and positive $\sum REE^{3+}$ vs. Mg (Figure 13a) correlations, implying that the incorporation of REEs of all garnets in Laoshankou is also not favorable to the menzerite-type substitution mechanism [10,60].



Figure 12. Plots of $\sum \text{REE}^{3+}$ with (a) Fe³⁺, (b) total Al, (c) Fe²⁺ and (d) Fe³⁺/Fe^T (a.p.f.u., in atoms per formula unit) for garnets in the Laoshankou deposit.



Figure 13. Plots of $\sum \text{REE}^{3+}$ with (a) Mg, (b) Na, (c) Ca, (d) Y, and (e) U (ppm) for garnets in the Laoshankou deposit.

Therefore, the REE³⁺ incorporation into garnets in Laoshankou possibly followed the Na substitution $([X^{2+}]_{-2}^{VIII}[X^+]_{+1}^{VIII}[REE^{3+}]_{+1}^{VIII})$ and the creation of vacancies in the Ca site $([X^{2+}]_{-3}^{VIII}]_{+1}^{VIII}[REE^{3+}]_{+2}^{VIII}$; [64,65]). Owing to the low REE contents in all garnets from Laoshankou, the mere presence of Na in the garnet structure is in itself a proof of the intervention of the corresponding Na substitution scheme, even the Na contents of all Laoshankou garnets are far below those of Na-bearing garnet (up to 0.30% Na₂O; [62]). However, the Na contents do not display a liner relationship with the REE³⁺ contents for Type 1 and 2 garnets (Figure 13b), indicating that REEs in Laoshankou Type 1 and 2 garnets did not undergo Na⁺-REE³⁺ coupled substitutions, but possible the creation of X²⁺ (e.g., Ca) site vacancy. Type 3 garnet in Laoshankou show different REE correlations from those of Type 1 and 2 garnets, which may imply a different substitution mechanism for Type

3 garnet. A positive correlation between Na and REE³⁺ implies that the key substitution mechanism for Type 3 garnet may be the Na cooperating substitution mechanism. However, the mechanisms involving the creation of structural vacancies are difficult to evaluate [66] for Type 3 garnets in Laoshankou.

In spite of the above controlled condition of crystal chemistry (e.g., coupled substitution mechanism), previous studies proved that incorporation of REEs into garnet can also be largely controlled by external factors, such as fluid chemistry, physicochemical parameters (e.g., pH, fO_2), and water-rock ratios [2,7,12,17,67]. Yttrium, Ca, U and REE³⁺ in garnets from the Laoshankou deposit do not display obvious linear relationships (Figure 13c–e), indicated that incorporation of trace elements and REEs into the Laoshankou garnets can be also strongly governed by fluid-rock chemistry and physicochemical parameters.

5.2. Physicochemical Conditions of Fluids

5.2.1. Oxygen Fugacity (fO_2)

Uranium as the redox-sensitive element can occurs in different valence stages (U⁴⁺ and U⁶⁺), which is significantly affected by fO_2 [68], making U to be an effective tool to estimate fO_2 of hydrothermal fluids. As the ionic radius of U⁴⁺ is more comparable to that of Ca than U⁶⁺, U⁴⁺ is more likely to substitute Ca²⁺ [12,68–70], meaning the higher U contents of garnet may indicate the lower fO_2 of hydrothermal fluids. Type 1 and Type 2 garnets have higher U contents (0.41–9.32 ppm) than these of Type 3 garnet (0.01–1.77 ppm), which partly indicate that Type 3 garnet formed under higher fO_2 . However, any conceivable substitution scheme (such as $[Ca^{2+}]_{-3}^{VIII}[]_{+2}^{VIII}[U^{6+}]_{+1}^{VIII}$) and increase of U solubility (caused by increasing fO_2 of the fluid system; [69]) may also cause these changes in U content, more evidence is discussed below.

In addition to the influence of U content, previous studies suggested that increased fO_2 of fluid favors radite precipitation [14,71], as the activity of Fe³⁺ with respect to Al³⁺ increased. The electrovalence of iron is sensitive to oxygen fugacity. Ferrous and the Fe^{2+} bearing minerals tend to be composed in a reduced condition, and the ferrous minerals could be converted to ferric minerals (such as Fe³⁺-bearing and radite and magnetite) if the reduced condition changed to oxidized, and vice versa [12,72]. The end member formula of $Adr_{91-100}Grs_{0-8}Sps_{0-2}Prp_{0-1}Uv_{0-1}$ for Type 3 garnet (Figure 7) indicated the highest fO_2 condition, which may explain the significant differences from typical skarn Fe-Cu deposit, e.g., the existence of magnetite at sulfide stage (stage III) of the Laoshankou deposit [26]. However, a variation in the relative content of andradite and grossular can also be due to the alumina activity of the fluid, or reaction with epidote and other alumina-bearing minerals. Fortunately, variation in the Fe^{3+/}Fe^T ratios could be explained in terms of variations in fO_2 . The relationships between the Fe^{3+/}Fe^T ratios and the \sum REE (Figure 12d) shows the high fO_2 for Type 3 garnet in stage III. Moreover, the clear drop in V content from stage II magnetite to stage III magnetite at Laoshankou also suggests that the oxygen fugacity at stage III increased [73]. As oxygen fugacity increased, the partition coefficient of V in magnetite decreased [74].

The ephemeral presence of hematite (change to mushketovite; [26,73]) at early amphi bole-epidote-magnetite stage (stage II) records the increased fO_2 from stage I to stage II (Figure 4). The compositional variation from Type 1 grossular to Type 2 Al-rich andradite (Figure 7) partly indicates the slight increase of fO_2 from Type 1 to Type 2 garnet. However, the minimal variation of Fe^{3+/}Fe^T ratios between Type 1 and 2 garnets (Figure 12d) indicates that the change of fO_2 from stage I to stage II is indistinctive, which may explain the rapid transformation from hematite to mushketovite in stage II [26,73].

5.2.2. pH, Temperature and Salinity

Previous studies demonstrate that the pH of hydrothermal fluid can significantly affect the REE fractionation [2,75], for example, the fluids are commonly LREE-enriched and HREE-depleted with positive Eu anomalies under mildly acidic condition [75], whereas HREE-enriched and LREE-depleted with negative or no Eu anomalies in the nearly neutral condition [67,69,70]. Divalent Eu should predominate in skarn system at temperatures above 250 °C [76]. Especially, under mildly acidic conditions, the REE patterns are significantly controlled by the presence of Cl⁻⁻, which can enhance the stability of soluble Eu²⁺ (the dominant species being EuCl₄²⁻) with respect to REE³⁺ and favor the transportation of Eu²⁺ in hydrothermal fluid, forming distinctly positive Eu anomalies [12,77,78]. In Laoshankou, the isotopic thermometer and fluid inclusion microthermometry showed that all garnets formed at relative higher temperatures (> 250 °C with pressure of 0–3 kbar) [26], meaning Eu mainly occurred as Eu²⁺ in the hydrothermal fluid during the formation of different types of garnets. Type 1 and 2 garnets in Laoshankou show LREE-depletion, HREE-enrichment, and a relatively weak positive Eu anomaly (Figure 11a,b), implying that they crystallized from a nearly neutral fluid. In contrast, the Type 3 garnet shows LREE-enriched, HREE-depleted, and a pronounced positive Eu anomaly (Figure 11c), indicating that Type 3 garnet formed in a mildly acidic and Cl⁻-rich fluid.

Garnet at relatively high temperatures is stable and less likely to leak fluids, which favors the preservation of primary inclusions trapped in garnet crystal [70]. Fluid inclusions in Type 1 garnet have a high homogenization temperature (Th) of >300 °C, low eutectic temperatures (TFM) of -46 to -33 °C and high salinity of 18–24 wt.%, with pressures of 2.5–3.4 kbar [26], indicating a high temperature, medium-high-salinity, and Mg/Fe-rich magmatic fluid in stage I. In contrast, fluid inclusions in Type 3 garnet at stage III have two significant groups: medium-temperature (200 to 413 °C), low-salinity (6–12 wt.%), Na-dominated (TFM = -28 to -20 °C) fluids and medium-temperature (200 to 280 °C), medium-high-salinity (14–24 wt.%), Ca-rich fluids (TFM = -48 to -38 °C) [26]. The presence of low-temperature secondary fluid inclusions (110–150 °C) in Type 3 garnet [26] may indicate an addition of external fluids and an open system in stage III.

5.3. Constraints on Garnet Formation and Fluid Evolution

Trace elements in garnets, especially REEs, can be used to trace the fluid-rock interaction and hydrothermal evolution of garnet [16,68,79,80]. Normalized trace elements and REE patterns for different types of garnets in Laoshankou show distinct differences (Figures 10 and 11), which indicate that the compositions of the fluid undergo an obvious change during the formation from Type 1 and 2 garnets to Type 3 garnet. The \sum REE contents increase from Type 1 grossular to Type 2 Al-rich andradite, but obviously decrease in Type 3 and radite (Figure 12). Previous studies suggested that the low \sum REE contents in garnet may be accommodated by the loss of REE or dilution of relatively immobile REE or mineral/mineral REE partitioning [7,16]. In stage III, REE-bearing minerals as apatite and sphene are not common, even epidote (a REE-bearing mineral) forms as veins coexisting with quartz and calcite [26]. REE decreasing in Type 3 garnet via this method cannot be explained. Loss of REE caused by mixing with a fluid with lower REE content maybe the best way to account for the low REE pattern in skarn garnet, rather than dilution of REE in the hydrothermal system [17]. Long fluid residence or high water/rock ratios (such as intense infiltration metasomatism) can significantly change the REE contents [75,81]. So, the significant decrease of REE concentrations from Type 1 and 2 garnets to Type 3 garnet must be related to different hydrothermal fluid compositions and metamorphic processes.

Most previous studies have shown that magmatic hydrothermal fluids have in general very low REE contents ($\Sigma REE = 10-100$ ppm; [82]) and are LREE-enriched and HREE-depleted with a general positive but variable Eu anomaly [11,83], which contrast with the REE patterns of Type 1 grossular and Type 2 Al-rich andradite. However, for the magmatic fluid, HREE were preferentially incorporated into grossular [7,12], which can result Type 1 grossular in Laoshankou having a low REE concentration (mainly 1–100 ppm), but enrichment in HREE (Figure 11a). The positive correlation between Y and total REE indicates that grossular crystallized at equilibrium in a nearly closed system by diffusive metasomatism (Figure 14; [16]). Diffusive metasomatism means solute diffusion in a stagnant fluid system, which does not involve fluid movement permeating the rocks, but needs long pore fluid residence under nearly closed-system conditions [84]. Fluids

produced by diffusive metasomatism have near neutral pH [7], which is consistent with the pH for Type 1 garnet. So, we infer that the Type 1 grossular formed by magma-derived fluids under relatively low water-rock ratios in a nearly closed system through a process of diffusion metasomatism (Figure 15). Previous studies about fluid inclusions and stable isotopes ($\delta^{18}O_{water}$ values of 9.2‰–9.7‰) by Liang et al. (2019) [26] also indicated the addition of high temperature, medium-high-salinity, and Mg/Fe-rich magmatic fluid, which may exsolve from the diorite porphyry.



Figure 14. Scatter diagrams of yttrium (Y) versus the total REEs for garnets in the Laoshankou deposit (modified after [16]).



Figure 15. The growth sequence of different generation garnets from various mineralization stages in the Laoshankou deposit.

The REE pattern in Type 2 garnet is similar to that of Type 1, but there are changes of \sum REE contents. During the formation of Type 2 garnet in the early sub-stage of amphibole-epidote-magnetite, the neutral and Cl⁻-poor fluid has slightly increased *f*O₂ and more active Fe³⁺, which resulted in high Fe content in fluid and formed magnetite and the Al-rich Type 2 andradite replacing the Type 1 grossular. With an increase of iron-rich mineral compositions, the skarn-related fluid system changes from more diffusive (reaction skarn) metasomatism to more advective (infiltration) metasomatism [3,85]. Advective (infiltration) metasomatism will require the fluid flow. The similar Y and total REEs relationship, and REE pattern between Type 2 and Type 1 garnets show that Al-rich andradite also formed in a relatively Cl⁻-poor fluid system under nearly closed conditions. However, the medium-salinity (~16 wt.%), and more Mg/Fe-rich features of fluid inclusions and higher $\delta^{18}O_{water}$

values (9.6‰–10.7‰) in stage II [26] indicate the influence of ¹⁸O-rich wall-rocks (the Beitashan Formation). So, for the same magmatic fluid, an increase in water/rock ratios, continuing infiltration metasomatism and increasing of fO_2 promoted incorporation of REE into the Type 2 Al-rich andradite, resulting the increasing \sum REE contents from Type 1 grossular to Type 2 Al-rich andradite (Figure 15).

For the Type 3 and radite at the sulfide stage, the fluid system has changed to mildly acidic fluid. As discussed above, Eu mainly occurred as Eu²⁺ in the fluid of Laoshankou. The increasingly positive Eu anomalies in Type 3 garnet from stage III show high W/Rratios and enrichment in Eu²⁺ in the sulfide-related ore-forming hydrothermal fluid, which also contained abundant Cl^{-} and metallic elements. That is consistent with the high salinity (CaCl₂-NaCl system, 14–24 wt.%) of fluid inclusions in stage III [26]. The highest fO_2 , obvious decrease in \sum REE contents and enrichment in LREE for Type 3 garnet indicated a significant different fluid from Type 1 and 2 garnets. The trace element contents (U, Sc, Ti, V, Co, Ga, As, Hf, Th, Zn, and Au) also indicate differences in fluid composition between Type 1, Type 2 and Type 3 garnets. The REE pattern of LREE-enriched and HREEdepleted with pronounced positive Eu anomalies in Type 3 garnet perfectly matches the characteristics of oxidizing magmatic fluid [11,69,70,82,83]. However, previous studies of fluid inclusions and stable isotopes [26] proved a Ca-rich basin brine. The highest Ca content and salinity (CaCl₂-NaCl system) also suggest the influence of Ca-rich fluid in stage III. The significant changes in fluid properties, increase of secondary fluid inclusions in Type 3 garnet crystal and lack of correlation between Y and the total REEs all indicate an open system (Figure 14) and significant influence of externally derived fluids with lower REE content. That was referred to as advective metasomatism [12,86], matching with the presence of non-magmatic external fluid by previous studies [26] (Figure 15). So, the type 3 garnet may be issued from the oxidizing magmatic fluid with addition of Ca-rich basin brine. The lowest contents of Co, Ni, Cu, and Zn in Type 3 garnet (Figure 9) may be caused by the continuous and massive sulfide crystallization.

Hence, a mixing process of different fluids is suggested in the Type 1, Type 2, and Type 3 garnets from different stages of Laoshankou deposit. The high-temperature, mediumhigh-salinity, and Mg/Fe-rich neutral magmatic fluid is dominated in stages I and the early substage of stage II with a control by increase of water/rock ratios and fO_2 . Furthermore, such fluids would have been replaced by oxidizing magmatic fluid with addition of highsalinity, Ca-rich basin brine in stage III, forming Type 3 garnet. Fluids in sulfide stage (stage III) as well as the product of magnetite are much different from a typical skarn Fe-Cu deposit, but have similarities with IOCG-type deposits (especially Central Andes and East Tianshan), which partly proves the particularity of Fe-Cu-Au deposits in the northern margin of East Junggar (such as Laoshankou).

6. Conclusions

The major findings of this study can be summarized as follows:

(1) Three types of garnets can be divided in the Laoshankou deposit: Type 1 grossular at Ca-silicate stage (stage I), yielding an end-member formula of $Grr_{44-53}Adr_{44-53}Sps_{2-3}Uv_{0-2}Prp_{0-1}$; Type 2 Al-rich andradite at magnetite stage (stage II), Type 2a yielding Adr_{63-66} $Grs_{31-34}Sps_{2-3}Prp_{0-2}Uv_{0-1}$, Type 2b yielding $Adr_{55-77}Grs_{21-43}Sps_{0-4}Prp_{0-2}Uv_{0-1}$; Type 3 andradite at sulfide stage (stage III), yielding $Adr_{91-100}Grs_{0-8}Sps_{0-2}Prp_{0-1}Uv_{0-1}$.

(2) The incorporation of REEs of Type 1 and 2 garnets favor the creation of X^{2+} (e.g., Ca) site vacancy, e.g., $[X^{2+}]_{-3}^{VIII}[]_{+1}^{VIII}[REE^{3+}]_{+2}^{VIII}$, while Type 3 mainly favors Na substitutions, e.g., $[X^{2+}]_{-2}^{VIII}[X^{+}]_{+1}^{VIII}[REE^{3+}]_{+1}^{VIII}$.

(3) Type 1 and 2 garnets show higher total REE contents, LREE-depletion, HREEenrichment, and positive Eu anomaly, while Type 3 garnet shows lower total REE contents, LREE-enriched, HREE-depleted, and strongly positive and variable Eu anomaly.

(4) Type 1 grossular formed by magmatic fluid under low fO_2 and nearly neutral environment by diffusive metasomatism in a nearly closed system. Fluids forming Type 2 Al-rich andradite are neutral and Cl⁻-poor with increased fO_2 , water–rock ratios, and more

active incorporation of Fe³⁺ and REE, caused by long fluid pore residence and continuing infiltration metasomatism. Type 3 andradite formed by oxidizing magmatic fluid and external high-salinity and Ca-rich basin brine with highest fO_2 in a mildly acidic open system, which is very different from typical skarn Fe-Cu deposit.

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