

Article

Magnetite Geochemistry of the Jinchuan Ni-Cu-PGE Deposit, NW China: Implication for Its Ore-Forming Processes

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Abstract: The Jinchuan Ni-Cu-PGE deposit is the single largest magmatic Ni-sulfide deposit in the world, with three different hypotheses on its ore-forming processes (e.g., in-situ sulfide segregation of sulfide-bearing magma, deep segregation with multiple injections of magma, and hydrothermal superimposition) mainly based on study of whole-rock geochemistry and isotopes (e.g., S-Sr-Nd-Hf). In this study, we mainly concentrated on magnetite textural and geochemical characteristics from different sulfide ores to clarify the genetic types and geochemical difference of the Jinchuan magnetite, and to explore a new credible ore-forming process by magnetite formation process when combined with detailed deposit geology. Three types of magnetite from massive and disseminated sulfide ores were observed by different textural analysis, and they were shown to have different genetic types (mainly in geochemistry) and trace elemental features. Type I magnetite is subhedral to anhedral from massive Ni- (or Fe-) and Cu-rich sulfide ores, with apparent magmatic origin, whereas Type II (dendritic or laminar crystals) and III magnetite (granular crystals as disseminated structures) from disseminated Cu-rich sulfide ores may have precipitated from late stage of melts evolved from a primitive Fe-rich and sulfide-bearing system with magmatic origin, but their geochemistry being typical of hydrothermal magnetite, videlicet, depletions of Ti (< 20 ppm), Al (< 51 ppm), Zr (0.01–0.57 ppm), Hf (0.03–0.06 ppm), Nb (0.01–0.14 ppm), and Ta (0.01–0.21 ppm). Such different types of magnetite can be clearly distinguished from concentrations and ratios of their trace elements, such as Ti, V, Co, Ni, Zn, Zr, Sn, Ga, and Ni/Cr. Those different types of Jinchuan magnetite crystallized from (evolved) sulfide-bearing systems and their geochemistries in trace elements are controlled mainly by evolution of ore-related systems and geochemical parameters (e.g., T and fO_2), with the former playing a predominant role. Combining the previous literature with this study, we propose that the Jinchuan deposit formed by multiple pluses of sulfide-bearing magma during fractional crystallization, with the emplacing of more fractionated and sulfide-bearing magma during sulfide segregation playing a predominant role. During this multiple emplacement and evolving of sulfide-bearing systems, Type I magmatic magnetite crystallized from primitive and evolved Fe-rich MSS (monosulfide solid solution), while Type II and III magnetite crystallized from evolved Fe-rich MSS to Cu-rich ISS (intermediate solid solution) during sulfide fractionation, with those Type II and III magnetite having much higher Cu contents compared with that of Type I magnetite.

Keywords: magnetite geochemistry; LA-ICP-MS; Jinchuan Ni-Cu-PGE deposit; ore-forming processes; NW China



1. Introduction

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Magnetite (Fe²⁺Fe³⁺₂O₄), as one of most common oxide minerals of the spinel group, forms in a variety of rocks, including igneous, sedimentary, and metamorphic rocks as an accessary mineral, and mineral deposits (e.g., magmatic Ni-Cu and Fe-Ti-V oxide deposits, porphyry, skarn, and iron oxide-copper-gold (IOCG) deposits, and banded iron formation (BIF)) [1–5] as an important ore mineral, with its forming temperatures varying from high magmatic to low hydrothermal temperature [6]. It commonly contains many trace elements, such as Si, Al, Ti, Ca, Mn, Mg, V, Cr, Co, Ni, Zn, Ga, Ge, Y, Zr, Hf, Nb, Mo, and Ta [2,3,5], that can substitute Fe²⁺ and Fe³⁺ in magnetite under many parameters of the similarity of the ionic radii and the valence of the cations, magma/fluid compositions, temperature, and oxygen fugacity [1,2,7–10]. Such trace element geochemistry of magnetite can be used as clues in deposits to provide information on origin, features, and processes for ore-forming fluids or systems [11–21], ore deposit provenance [2,3,9,11,15,16,20–22], and mineral exploration [12,19,23].

The Jinchuan Ni-Cu-PGE deposit (500 Mt @ 1.1% Ni and 0.7% Cu) [24] is one of the three largest magmatic Ni-sulfide deposits followed by Sudbury and Noril'sk and the largest single magmatic Ni-sulfide deposit in the world [25–27]. In the last two decades, many studies have concentrated mainly on the Jinchuan deposit, such as host intrusions and mineral geochemistry [25,26,28–38]. But the genesis of the Jinchuan Ni-Cu-PGE deposit is still controversial, with three predominant contributions of the in-situ sulfide segregation of sulfide-bearing magma, deep segregation with multiple injections of magma, and hydrothermal superimposition [24,32]. Hence, a study on the ore-forming processes for the Jinchuan Ni-Cu-PGE deposit may be highly meaningful. Actually, in magmatic Ni-Cu-PGE deposits, magnetite can not only crystallize from early Fe-rich monosulfide solid solution (MSS) at high temperatures (1180–940 °C) [39], but also from the residual sulfide liquid together with Cu-rich intermediate solid solution (ISS) at lower temperatures (940–800 °C) [40,41]. The Jinchuan deposit has different textural types of magnetite in various sulfide ores, including massive Cu- and Ni-rich sulfide ores and disseminated sulfide (mainly by chalcopyrite) ores. Such different types of Jinchuan magnetite are closely related with sulfides (e.g., chalcopyrite, pyrrhotite, and pentlandite), which can be used as indicators to explore ore-forming magma [6,12,19,42] and even processes.

Therefore, in this paper, we present a comprehensive overview of the cognition and data from former published papers, as well as the ore deposit geology and magnetite geochemistry constrained by trace elements from different magnetite textural types in various sulfide ores of the Jinchuan Ni-Cu-PGE deposit in NW China to clarify magnetite genesis, discuss the controlling factors of magnetite compositions, and explore the ore-forming processes.

2. Geological Background

The Jinchuan Ni-Cu-PGE sulfide deposit is located in the Longshoushan Terrane, which is widely believed to be part of the North China Craton (Figure 1a) [26,43,44]. The NW-striking Longshoushan Terrane is bounded by the thrust faults from the Chaoshui Depression Belt to the north and the Qilianshan Orogentic Belt to the south (Figure 1b). This terrane is mainly composed of Proterozoic metamorphic basement of the Longshoushan Group and covers of Mesoproterozoic and Neoproterozoic metasedimentary rocks [32]. The Proterozoic Longshoushan Group can be further divided into the Baijiazuizi and Tamazigou Formations by different rock types, with the former consisting of migmatite, gneiss, and marble, while the latter is comprised of schist and banded marble [45]. Many intrusions with compositions varying from ultramafic through mafic to felsic are documented in the Longshoushan Terrane. In the Longshoushan Terrane, the mafic-ultramafic intrusions are abundant with small exposed areas and some of them are associated with magmatic Ni-Cu deposits, such as the well-known Jinchuan Ni-Cu-PGE deposit (Figure 1b). The available published works showed that such mafic-ultramafic intrusions may emplace at two episodes, videlicet (*viz.*), ~830 Ma and ~420 Ma [25,45,46]. The granitic intrusions are widely distributed not only in the Longshoushan Terrane, but also in the adjacent belts (Figure 1b), e.g., the Qilianshan Orogenitic Belt, with published zircon U-Pb ages in 512–383 Ma that

can be divided into three groups, i.e., 512–460 Ma, 440–420 Ma, and <420 Ma, with corresponding tectonic settings of arc, syn-collision, and post-collision ([25] and references therein).



Figure 1. (a) The location of the Jinchuan Ni-Cu-PGE deposit in China (modified after [32]). (b) Simplified geological map of the Longshoushan Terrane (modified after [35]). Abbreviations: CAOB, Central Asian Orogenic Belt; CC, Cathaysia Craton; COB, Central Orogenic Belt; NCC, North China Craton; TAC, Tarim Craton; TIC, Tibet Craton; YC, Yangtze Craton.

The Jinchuan ultramafic intrusion emplaced in the Proterozoic marble and gneiss and is ~6500 m long and 20–300 m wide, with a downward extension reaching at least 1000 m below the surface [25,32]. The current Jinchuan ultramafic intrusion has an area of 1.34 km² and is a SE-trending lens-shaped dyke that is subparallel to the regional structural lineament [25,32]. Based on structural reconstruction, it has been widely accepted that the original geometry of the Jinchuan intrusion was a sub-horizontal sheet formed at a depth between 4 km and 9 km, which was subsequently rotated to a near-vertical shape [30,31]. The Jinchuan intrusion is divided into four segments by a series of faults (Figure 2): Segment III at the north west end, Segment I in the north west, Segment II in the central part, and Segment IV in the south east end, with Segment I being separated from Segment II by an EW-trending strike-slip fault (e.g., F₁₆₋₁; Figure 2). The detailed description of each segment for the Jinchuan deposit can be found in Jiao et al. (2018) [32].

The rock types of the Jinchuan intrusion are represented by dunite, lherzolite, olivine websterite, and minor plagioclase lherzolite and troctolite [44], with lherzolite being the predominant rock type (Figure 2). Spatially, lherzolite is found in the central part, with a small amount of olivine websterite along with plagioclase lherzolite occurring in the margins of the intrusion.



Figure 2. Geological map of the Jinchuan Ni-Cu-PGE deposit (modified after [35] and references therein).

In the Jinchuan deposit, the structures of sulfide ores include disseminated, net-textured, and massive (Figure 3a–d). The detailed description of sulfide ores can be found in Jiao et al. (2018) [32]. In this study, we present a simplified and comprehensive introduction of sulfide ores. The disseminated sulfide ores are observed in Segments I, II, and IV, and are mainly associated with lherzolite, dunite, and olivine websterite, with major minerals of pyrrotite, pentlandite, and chalcopyrite, with minor pyrite and occasional chromite [25,32]. The net-textured sulfide ores mainly observed in the lower part of the intrusion in Segments I and II are commonly related with dunite and iherzlite, whereas the massive sulfide ores mainly occur in the bottom of Segment II and the nearby surrounding rocks, with the both two types of ores having similar sulfide mineral assemblages to the disseminated sulfide ores of pyrrhotite, pentlandite, and chalcopyrite [25,32]. At Jinchuan, the major sulfide minerals are pyrrhotite, pentlandite, and chalcopyrite, while commonly observed oxide minerals include Cr-spinel and/or magnetite. The Jinchuan deposit has also undergone post-magmatic hydrothermal overprinting events, with hydrothermal/alteration minerals of serpentine, chlorite, tremolite, actinolite, and magnetite [25].



Figure 3. The main types of sulfide ores and different magnetite types in various sulfide ores of the Jinchuan Ni-Cu-PGE deposit: (a) Disseminated sulfide ore, (b) net-textured sulfide ore, (c) massive Cu-rich sulfide ore, (d) massive Ni-rich (or Fe-rich) sulfide ore, (e,f) Type I magnetite in massive Ni-and Cu-rich sulfide ores, and (g,h) Type I and III magnetite in disseminated Cu-rich sulfide ores. Abbreviations: Ccp, chalcopyrite; Mag, magnetite; Pn, pentlandite; Po, pyrrhotite; Py, pyrite.

3. Analytical Method

3.1. Back-Scattered Electron (BSE)

Before magnetite geochemistry analysis, some representative magnetite samples were selected to clarify the texture relationships and homogeneous features in magnetite grains by BSE imaging work. BSE imaging with a Field Emission Gun Scanning Electron Microscope (FEG-SEM) was performed using a JXA-8100 electron microprobe at the Key Laboratory of Western China's Mineral Resources and Geological Engineering, Ministry of Education, Chang'an University, with an acceleration voltage of 15 kV and a beam current of 20 nA.

3.2. LA-ICP-MS

Element analyses of magnetite in thin sections were conducted by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) at Nanjing FocuMS Technology Co. Ltd (Nanjing, China). Teledyne Cetac Technologies Analyte Excite laser-ablation system (Bozeman, MT, USA) and Agilent Technologies 7700× quadrupole ICP-MS (Hachioji, Tokyo, Japan) were combined for the experiments. The 193 nm ArF excimer laser, homogenized by a set of beam delivery systems, was focused on magnetite surface with fluence of 3.59 J/cm². Ablation protocol employed a spot diameter of 40 µm at 6 Hz repetition rate for 40 s (equating to 280 pulses). Helium was applied as carrier gas to efficiently transport aerosol to ICP-MS. Element contents were calibrated against multiple reference materials as external standards (including BIR-1G, BHVO-2G, BCR-2G, and GSE-1G) using ⁵⁷Fe as the internal standard. SRM 612 and 610 glasses were for tuning the instrument, and QC CGSG-1 and QC CGSG-2 were used as quantity control of the time-dependent calibration for sensitivity drift as unknown samples. Raw data reduction was performed off-line by ICPMSDataCal software (version 10, China University of Geosciences, Wuhan, China) using 100% normalization strategy (100 wt.%) for a given anhydrous mineral [47]. Of the determined elements in magnetite, S, Si, Na, K, Ca, and Cu were monitored to exclude the analyses from impure magnetite and inclusions of silicate and/or sulfide minerals. Furthermore, screen signals during off-line data processing were also carefully examined to exclude impure magnetite or silicate/sulfide inclusions. The Fe²⁺/ Σ Fe ratio of 0.33 as an average reference value was used for data reduction based on magnetite compositions obtained by Chen et al. (2015) [13].

4. Results

Six representative magnetite samples from different Ni- (or Fe-) and Cu-rich sulfide ores in the Jinchuan deposit were analyzed for magnetite chemistry by LA-ICP-MS to examine magnetite compositions. Of those samples, two and one of them were from massive Ni- (or Fe-) and Cu-rich sulfide ores, respectively, while three of them were from disseminated Cu-rich sulfide ores, with details in Table 1. The LA-ICP-MS analytical results are listed in Table 2 and Supplementary Materials after examination, excluding the unbelievable data affected by other mineral inclusions or disturbed screen signals, and are illustrated in Figures 4–8.

Sample Number	Location	Magnetite Types	Hosted Ores	Comments
Ni2	Drill core ZK4503, 1294 m in depth, No. 2 orebody, Segment II	Type I-A	Massive Ni-rich sulfide ore	Magnetite is commonly subhedral to anhedral granular with different
Cu3	No. 15 exploration line, No. 24 orebody, Segment I	Type I-A	Massive Ni-rich sulfide ore	pyrite and pentlandite.
Cu1	No. 10 exploration line, No. 1 orebody, Segment II	Type I-B	Massive Cu-rich sulfide ore	Magnetite is commonly subhedral to anhedral granular with different sizes, and is intergrown with chalcopyrite, pyrrhotite, and minor pentlandite.
Cu9	No. 6 exploration line, No. 24 orebody, Segment I	Type II	Disseminated Cu-rich sulfide ore	Magnetite is euhedral to subhedral as dendritic or laminar crystals, with the former being majority, coexisting with pentlandite and minor chalcopyrite. This type of magnetite has different sizes that commonly infilled pentlandite along its cleavages, indicating this type of magnetite silightly postdated pentlandite.
Cu4	No. 16 exploration line, No. 24 orebody, Segment I	Type III	Disseminated Cu-rich sulfide ore	Magnetite is fine-grained and euhedral to anhedral with disseminated structures, akin to metasomatic textures replacing
Cu14	No. 7 exploration line, No. 24 orebody, Segment I	Type III	Disseminated Cu-rich sulfide ore	chalcopyrite, probably showing magnetite having a relatively later crystallization phase than chalcopyrite.

Table 1.	Sample o	description	of analyzed	different	magnetite	types in	the Jinchuan	Ni-Cu-PGE deposit.	

Flements	Detection Limit	Magnetite	Iagnetite from Massive Ni-rich Sulfide Ores (Type I-A, $n = 28$)			Magnetite from Massive Cu-Rich Sulfide Ores (Type I-B, $n = 24$)					
Liements	2 0000000 20000	Min	Max	Mean	Stdev	п	Min	Max	Mean	Stdev	n
²⁴ Mg	2.35	61.4	388	239	94	27	854	1158	1014	68.0	24
²⁷ Al	2.45	6.16	940	114	221	28	79.9	438	333	69.6	24
⁴⁷ Ti	1.79	6.87	120	60.1	34.4	27	2249	4855	3441	518	24
^{51}V	0.17	116	3859	653	698	28	360	658	493	58.1	24
⁵² Cr	5.78	19.2	66,596	20,778	25,171	28	7.01	86.8	22.0	19.1	22
⁵⁵ Mn	1.20	1115	4560	2157	1188	28	9127	11239	10529	610	24
⁵⁹ Co	0.18	42.1	72.6	52.6	7.63	28	20.3	96.4	53.9	22.9	24
⁶⁰ Ni	0.70	1247	2137	1687	166	28	854	1432	1255	111	24
⁶³ Cu	1.10	2.78	2.78	2.78	0.00	1	1.13	9.48	3.52	2.64	8
⁶⁶ Zn	1.44	13.0	85.6	39.0	19.7	28	165	2417	1101	480	24
⁷¹ Ga	0.09	3.48	24.8	9.78	4.30	28	10.1	13.0	11.5	0.68	24
⁷² Ge	2.92	3.11	8.24	5.92	1.28	28	2.98	8.70	6.51	1.32	24
⁹⁰ Zr	0.01	0.01	7.17	0.71	1.47	24	1.31	28.4	11.5	7.06	24
⁹³ Nb	0.01	0.01	5.88	1.10	1.90	17	2.01	12.7	6.96	2.62	24
⁹⁵ Mo	0.06	0.07	0.13	0.09	0.02	12	0.29	1.37	0.86	0.29	24
¹¹⁸ Sn	1.93	2.23	9.39	5.06	1.62	24	23.5	62.6	49.9	7.48	24
¹⁷⁸ Hf	0.02	0.03	0.15	0.06	0.05	4	0.04	0.33	0.14	0.07	23
¹⁸¹ Ta	0.00	0.00	0.06	0.02	0.02	10	0.07	0.23	0.17	0.04	24
10			Magnetite from Disseminated Cu-rich Sulfide Ores (Type II, <i>n</i> = 13)				Magnetite from Disseminated Cu-rich Sulfide Ores (Type III, $n = 23$)				
Elamanta	Detection Limit	Magnetite f	rom Dissemina	ted Cu-rich S	ulfide Ores (Ty	pe II, <i>n</i> = 13)	Magnetite f	rom Dissemina	ted Cu-rich Su	lfide Ores (Typ	e III, n = 23)
Elements	Detection Limit	Magnetite fr Min	rom Dissemina Max	ited Cu-rich S Mean	ulfide Ores (Ty Stdev	pe II, <i>n</i> = 13) <i>n</i>	Magnetite f	rom Dissemina Max	ited Cu-rich Su Mean	lfide Ores (Typ Stdev	e III, $n = 23$) n
Elements	Detection Limit	Magnetite fr Min 25.8	rom Dissemina Max 1428	ited Cu-rich S Mean 351	ulfide Ores (Ty Stdev 435	pe II, <i>n</i> = 13) <i>n</i> 8	Magnetite fr Min 2.42	rom Dissemina Max 3326	ited Cu-rich Su Mean 1105	lfide Ores (Typ Stdev 880	e III, n = 23) n 21
Elements ²⁴ Mg ²⁷ Al	Detection Limit 2.35 2.45	Magnetite fr Min 25.8 2.95	rom Dissemina Max 1428 50.6	tted Cu-rich S Mean 351 22.5	ulfide Ores (Ty Stdev 435 15.4	pe II , <i>n</i> = 13) <i>n</i> 8 6	Magnetite fr Min 2.42 2.49	rom Dissemina Max 3326 23.9	nted Cu-rich Su Mean 1105 7.71	lfide Ores (Typ Stdev 880 5.93	e III, n = 23) n 21 10
Elements	Detection Limit 2.35 2.45 1.79	Magnetite fr Min 25.8 2.95 2.37	rom Dissemina Max 1428 50.6 19.7	tted Cu-rich S Mean 351 22.5 9.40	ulfide Ores (Ty Stdev 435 15.4 7.29	pe II , <i>n</i> = 13) <i>n</i> 8 6 4	Magnetite fr Min 2.42 2.49 1.52	rom Dissemina Max 3326 23.9 9.32	tted Cu-rich Su Mean 1105 7.71 3.76	lfide Ores (Typ Stdev 880 5.93 2.58	e III, n = 23) n 21 10 6
Elements	Detection Limit 2.35 2.45 1.79 0.17	Magnetite fr Min 25.8 2.95 2.37 0.21	rom Dissemina Max 1428 50.6 19.7 0.34	tted Cu-rich S Mean 351 22.5 9.40 0.30	ulfide Ores (Ty Stdev 435 15.4 7.29 0.06	pe II , <i>n</i> = 13) <i>n</i> 8 6 4 3	Magnetite f Min 2.42 2.49 1.52 0.22	rom Dissemina Max 3326 23.9 9.32 5.79	tted Cu-rich Su Mean 1105 7.71 3.76 2.98	lfide Ores (Typ Stdev 880 5.93 2.58 2.54	e III, $n = 23$) n 21 10 6 4
Elements	2.35 2.45 1.79 0.17 5.78	Magnetite fr Min 25.8 2.95 2.37 0.21 8.63	rom Dissemina Max 1428 50.6 19.7 0.34 154	tted Cu-rich S Mean 351 22.5 9.40 0.30 63.3	ulfide Ores (Ty Stdev 435 15.4 7.29 0.06 46.9	pe II, n = 13) n 8 6 4 3 12	Magnetite fr Min 2.42 2.49 1.52 0.22 7.84	rom Dissemina Max 3326 23.9 9.32 5.79 354	tted Cu-rich Su Mean 1105 7.71 3.76 2.98 93.3	Ifide Ores (Typ Stdev 880 5.93 2.58 2.54 88.6	e III, n = 23) n 21 10 6 4 21
Elements	2.35 2.45 1.79 0.17 5.78 1.20	Magnetite fr Min 25.8 2.95 2.37 0.21 8.63 1623	rom Dissemina Max 1428 50.6 19.7 0.34 154 3333	tted Cu-rich S Mean 351 22.5 9.40 0.30 63.3 2333	ulfide Ores (Ty Stdev 435 15.4 7.29 0.06 46.9 473	pe II, n = 13) n 8 6 4 3 12 13	Magnetite fr Min 2.42 2.49 1.52 0.22 7.84 913	rom Dissemina Max 3326 23.9 9.32 5.79 354 6344	tted Cu-rich Su Mean 1105 7.71 3.76 2.98 93.3 3454	Ifide Ores (Typ Stdev 880 5.93 2.58 2.54 88.6 1785	e III, n = 23) n 21 10 6 4 21 23
Elements	2.35 2.45 1.79 0.17 5.78 1.20 0.18	Magnetite fr Min 25.8 2.95 2.37 0.21 8.63 1623 0.38	rom Dissemina Max 1428 50.6 19.7 0.34 154 3333 11.5	tted Cu-rich S Mean 351 22.5 9.40 0.30 63.3 2333 2.59	ulfide Ores (Ty) Stdev 435 15.4 7.29 0.06 46.9 473 2.89	pe II, n = 13) n 8 6 4 3 12 13 12	Magnetite fr Min 2.42 2.49 1.52 0.22 7.84 913 0.39	rom Dissemina Max 3326 23.9 9.32 5.79 354 6344 12.1	tted Cu-rich Su Mean 1105 7.71 3.76 2.98 93.3 3454 4.97	Ifide Ores (Typ Stdev 880 5.93 2.58 2.54 88.6 1785 2.72	e III, n = 23) n 21 10 6 4 21 23 21
Elements	2.35 2.45 1.79 0.17 5.78 1.20 0.18 0.70	Magnetite fr Min 25.8 2.95 2.37 0.21 8.63 1623 0.38 13.8	rom Dissemina Max 1428 50.6 19.7 0.34 154 3333 11.5 309	tted Cu-rich S Mean 351 22.5 9.40 0.30 63.3 2333 2.59 67.2	ulfide Ores (Ty) Stdev 435 15.4 7.29 0.06 46.9 473 2.89 88.7	pe II, n = 13) n 8 6 4 3 12 13 12 9	Magnetite fr Min 2.42 2.49 1.52 0.22 7.84 913 0.39 13.4	rom Dissemina Max 3326 23.9 9.32 5.79 354 6344 12.1 423	tted Cu-rich Su Mean 1105 7.71 3.76 2.98 93.3 3454 4.97 137	Ifide Ores (Typ Stdev 880 5.93 2.58 2.54 88.6 1785 2.72 109	e III, n = 23) n 21 10 6 4 21 23 21 17
Elements 24Mg 27Al 47Ti ⁵¹ V ⁵² Cr ⁵⁵ Mn ⁵⁹ Co ⁶⁰ Ni ⁶³ Cu	2.35 2.45 1.79 0.17 5.78 1.20 0.18 0.70 1.10	Magnetite fr Min 25.8 2.95 2.37 0.21 8.63 1623 0.38 13.8 1.33	rom Dissemina Max 1428 50.6 19.7 0.34 154 3333 11.5 309 24.7	tted Cu-rich S Mean 351 22.5 9.40 0.30 63.3 2333 2.59 67.2 10.9	ulfide Ores (Ty) Stdev 435 15.4 7.29 0.06 46.9 473 2.89 88.7 9.42	pe II, n = 13) n 8 6 4 3 12 13 12 9 4	Magnetite fr Min 2.42 2.49 1.52 0.22 7.84 913 0.39 13.4 3.50	rom Dissemina Max 3326 23.9 9.32 5.79 354 6344 12.1 423 184	tted Cu-rich Su Mean 1105 7.71 3.76 2.98 93.3 3454 4.97 137 68.5	Ifide Ores (Typ Stdev 880 5.93 2.58 2.54 88.6 1785 2.72 109 60.6	e III, n = 23) n 21 10 6 4 21 23 21 17 11
Elements 24Mg 27Al 47Ti 51V 52Cr 55Mn 59Co 60Ni 63Cu 66Zn	2.35 2.45 1.79 0.17 5.78 1.20 0.18 0.70 1.10 1.44	Magnetite fr Min 25.8 2.95 2.37 0.21 8.63 1623 0.38 13.8 1.33 1.83	rom Dissemina Max 1428 50.6 19.7 0.34 154 3333 11.5 309 24.7 32.3	tted Cu-rich S Mean 351 22.5 9.40 0.30 63.3 2333 2.59 67.2 10.9 8.00	ulfide Ores (Ty) Stdev 435 15.4 7.29 0.06 46.9 473 2.89 88.7 9.42 8.71	pe II, n = 13) n 8 6 4 3 12 13 12 9 4 12	Magnetite fr Min 2.42 2.49 1.52 0.22 7.84 913 0.39 13.4 3.50 1.70	rom Dissemina Max 3326 23.9 9.32 5.79 354 6344 12.1 423 184 247	tted Cu-rich Su Mean 1105 7.71 3.76 2.98 93.3 3454 4.97 137 68.5 30.2	Stdev 880 5.93 2.58 2.54 88.6 1785 2.72 109 60.6 61.9	e III, n = 23) n 21 10 6 4 21 23 21 17 11 18
Elements 24Mg 27Al 47Ti ⁵¹ V ⁵² Cr ⁵⁵ Mn ⁵⁹ Co ⁶⁰ Ni ⁶³ Cu ⁶⁶ Zn ⁷¹ Ga	2.35 2.45 1.79 0.17 5.78 1.20 0.18 0.70 1.10 1.44 0.09	Magnetite fr Min 25.8 2.95 2.37 0.21 8.63 1623 0.38 13.8 1.33 1.83 0.09	rom Dissemina Max 1428 50.6 19.7 0.34 154 3333 11.5 309 24.7 32.3 0.17	tted Cu-rich S Mean 351 22.5 9.40 0.30 63.3 2333 2.59 67.2 10.9 8.00 0.12	ulfide Ores (Ty) Stdev 435 15.4 7.29 0.06 46.9 473 2.89 88.7 9.42 8.71 0.03	pe II, n = 13) n 8 6 4 3 12 13 12 9 4 12 7	Magnetite fr Min 2.42 2.49 1.52 0.22 7.84 913 0.39 13.4 3.50 1.70 0.12	rom Dissemina Max 3326 23.9 9.32 5.79 354 6344 12.1 423 184 247 0.39	tted Cu-rich Su Mean 1105 7.71 3.76 2.98 93.3 3454 4.97 137 68.5 30.2 0.23	Stdev 880 5.93 2.58 2.54 88.6 1785 2.72 109 60.6 61.9 0.10	e III, n = 23) n 21 10 6 4 21 23 21 17 11 18 6
Elements 24Mg 27Al 47Ti 51V 52Cr 55Mn 59Co 60Ni 63Cu 66Zn 71Ga 72Ge	Detection Limit 2.35 2.45 1.79 0.17 5.78 1.20 0.18 0.70 1.10 1.44 0.09 2.92	Magnetite fr Min 25.8 2.95 2.37 0.21 8.63 1623 0.38 13.8 1.33 1.83 0.09 3.84	rom Dissemina Max 1428 50.6 19.7 0.34 154 3333 11.5 309 24.7 32.3 0.17 7.15	tted Cu-rich S Mean 351 22.5 9.40 0.30 63.3 2333 2.59 67.2 10.9 8.00 0.12 5.47	ulfide Ores (Ty) Stdev 435 15.4 7.29 0.06 46.9 473 2.89 88.7 9.42 8.71 0.03 1.01	pe II, n = 13) n 8 6 4 3 12 13 12 9 4 12 7 12	Magnetite fr Min 2.42 2.49 1.52 0.22 7.84 913 0.39 13.4 3.50 1.70 0.12 3.35	rom Dissemina Max 3326 23.9 9.32 5.79 354 6344 12.1 423 184 247 0.39 7.98	tted Cu-rich Su Mean 1105 7.71 3.76 2.98 93.3 3454 4.97 137 68.5 30.2 0.23 6.29	Stdev 880 5.93 2.58 2.54 88.6 1785 2.72 109 60.6 61.9 0.10 1.09	e III, n = 23) n 21 10 6 4 21 23 21 17 11 18 6 22
Elements 24 Mg 27 Al 47 Ti 51 V 52 Cr 55 Mn 59 Co 60 Ni 63 Cu 66 Zn 71 Ga 72 Ge 90 Zr	Detection Limit 2.35 2.45 1.79 0.17 5.78 1.20 0.18 0.70 1.10 1.44 0.09 2.92 0.01	Magnetite fr Min 25.8 2.95 2.37 0.21 8.63 1623 0.38 13.8 1.33 1.83 0.09 3.84 0.01	rom Dissemina Max 1428 50.6 19.7 0.34 154 3333 11.5 309 24.7 32.3 0.17 7.15 0.03	tted Cu-rich S Mean 351 22.5 9.40 0.30 63.3 2333 2.59 67.2 10.9 8.00 0.12 5.47 0.02	ulfide Ores (Ty) Stdev 435 15.4 7.29 0.06 46.9 473 2.89 88.7 9.42 8.71 0.03 1.01 0.01	pe II, n = 13) n 8 6 4 3 12 13 12 9 4 12 7 12 6	Magnetite fr Min 2.42 2.49 1.52 0.22 7.84 913 0.39 13.4 3.50 1.70 0.12 3.35 0.02	rom Dissemina Max 3326 23.9 9.32 5.79 354 6344 12.1 423 184 247 0.39 7.98 0.57	tted Cu-rich Su Mean 1105 7.71 3.76 2.98 93.3 3454 4.97 137 68.5 30.2 0.23 6.29 0.12	Ifide Ores (Typ) Stdev 880 5.93 2.58 2.54 88.6 1785 2.72 109 60.6 61.9 0.10 1.09 0.17	e III, n = 23) n 21 10 6 4 21 23 21 17 11 18 6 22 8
Elements 24Mg 27Al 47Ti 51V 52Cr 55Mn 59Co 60Ni 63Cu 66Zn 71Ga 72Ge 90Zr 93Nb	Detection Limit 2.35 2.45 1.79 0.17 5.78 1.20 0.18 0.70 1.10 1.44 0.09 2.92 0.01	Magnetite fr Min 25.8 2.95 2.37 0.21 8.63 1623 0.38 13.8 1.33 1.83 0.09 3.84 0.01	rom Dissemina Max 1428 50.6 19.7 0.34 154 3333 11.5 309 24.7 32.3 0.17 7.15 0.03 0.04	tted Cu-rich S Mean 351 22.5 9.40 0.30 63.3 2333 2.59 67.2 10.9 8.00 0.12 5.47 0.02 0.02	ulfide Ores (Ty) Stdev 435 15.4 7.29 0.06 46.9 473 2.89 88.7 9.42 8.71 0.03 1.01 0.01 0.01	pe II , <i>n</i> = 13) <i>n</i> 8 6 4 3 12 13 12 9 4 12 7 12 6 7	Magnetite fr Min 2.42 2.49 1.52 0.22 7.84 913 0.39 13.4 3.50 1.70 0.12 3.35 0.02 0.01	rom Dissemina Max 3326 23.9 9.32 5.79 354 6344 12.1 423 184 247 0.39 7.98 0.57 0.14	tted Cu-rich Su Mean 1105 7.71 3.76 2.98 93.3 3454 4.97 137 68.5 30.2 0.23 6.29 0.12 0.04	Ifide Ores (Typ) Stdev 880 5.93 2.58 2.54 88.6 1785 2.72 109 60.6 61.9 0.10 1.09 0.17 0.04	e III, n = 23) n 21 10 6 4 21 23 21 17 11 18 6 22 8 14
Elements 24Mg 27Al 47Ti 51V 52Cr 55Mn 59Co 60Ni 63Cu 66Zn 71Ga 72Ge 90Zr 93Nb 95Mo	Detection Limit 2.35 2.45 1.79 0.17 5.78 1.20 0.18 0.70 1.10 1.44 0.09 2.92 0.01 0.01 0.06	Magnetite fr Min 25.8 2.95 2.37 0.21 8.63 1623 0.38 1.33 1.83 0.09 3.84 0.01 0.01 0.01 0.09	rom Dissemina Max 1428 50.6 19.7 0.34 154 3333 11.5 309 24.7 32.3 0.17 7.15 0.03 0.04 0.26	tted Cu-rich S Mean 351 22.5 9.40 0.30 63.3 2333 2.59 67.2 10.9 8.00 0.12 5.47 0.02 0.02 0.02 0.15	ulfide Ores (Ty) Stdev 435 15.4 7.29 0.06 46.9 473 2.89 88.7 9.42 8.71 0.03 1.01 0.01 0.01 0.01 0.08	pe II, n = 13) n 8 6 4 3 12 13 12 9 4 12 7 12 6 7 3	Magnetite fr Min 2.42 2.49 1.52 0.22 7.84 913 0.39 13.4 3.50 1.70 0.12 3.35 0.02 0.01 0.07	rom Dissemina Max 3326 23.9 9.32 5.79 354 6344 12.1 423 184 247 0.39 7.98 0.57 0.14 1.12	tted Cu-rich Su Mean 1105 7.71 3.76 2.98 93.3 3454 4.97 137 68.5 30.2 0.23 6.29 0.12 0.04 0.27	Ifide Ores (Typ) Stdev 880 5.93 2.58 2.54 88.6 1785 2.72 109 60.6 61.9 0.10 1.09 0.17 0.04 0.35	e III, n = 23) n 21 10 6 4 21 23 21 17 11 18 6 22 8 14 7
Elements 24Mg 27Al 47Ti 51V 52Cr 55Mn 59Co 60Ni 63Cu 66Zn 71Ga 72Ge 90Zr 93Nb 95Mo 118Sn	Detection Limit 2.35 2.45 1.79 0.17 5.78 1.20 0.18 0.70 1.10 1.44 0.09 2.92 0.01 0.01 0.06 1.93	Magnetite fr Min 25.8 2.95 2.37 0.21 8.63 1623 0.38 1.33 1.83 0.09 3.84 0.01 0.01 0.01 0.09 2.02	rom Dissemina Max 1428 50.6 19.7 0.34 154 3333 11.5 309 24.7 32.3 0.17 7.15 0.03 0.04 0.26 3.43	tted Cu-rich S Mean 351 22.5 9.40 0.30 63.3 2333 2.59 67.2 10.9 8.00 0.12 5.47 0.02 0.02 0.02 0.15 2.65	ulfide Ores (Ty) Stdev 435 15.4 7.29 0.06 46.9 473 2.89 88.7 9.42 8.71 0.03 1.01 0.01 0.01 0.01 0.01 0.08 0.49	pe II, n = 13) n 8 6 4 3 12 13 12 9 4 12 7 12 6 7 3 6	Magnetite fr Min 2.42 2.49 1.52 0.22 7.84 913 0.39 13.4 3.50 1.70 0.12 3.35 0.02 0.01 0.07 2.16	rom Dissemina Max 3326 23.9 9.32 5.79 354 6344 12.1 423 184 247 0.39 7.98 0.57 0.14 1.12 9.25	tted Cu-rich Su Mean 1105 7.71 3.76 2.98 93.3 3454 4.97 137 68.5 30.2 0.23 6.29 0.12 0.04 0.27 4.42	Ifide Ores (Typ) Stdev 880 5.93 2.58 2.54 88.6 1785 2.72 109 60.6 61.9 0.10 1.09 0.17 0.04 0.35 1.65	e III, n = 23) n 21 10 6 4 21 23 21 17 11 18 6 22 8 14 7 22
Elements 24Mg 27Al 47Ti 51V 52Cr 55Mn 59Co 60Ni 63Cu 66Zn 71Ga 72Ge 90Zr 93Nb 95Mo 118Sn 178Hf	Detection Limit 2.35 2.45 1.79 0.17 5.78 1.20 0.18 0.70 1.10 1.44 0.09 2.92 0.01 0.06 1.93 0.02	Magnetite fr Min 25.8 2.95 2.37 0.21 8.63 1623 0.38 13.8 1.33 1.83 0.09 3.84 0.01 0.09 2.02 0.03	rom Dissemina Max 1428 50.6 19.7 0.34 154 3333 11.5 309 24.7 32.3 0.17 7.15 0.03 0.04 0.26 3.43 0.03	tted Cu-rich S Mean 351 22.5 9.40 0.30 63.3 2333 2.59 67.2 10.9 8.00 0.12 5.47 0.02 0.02 0.02 0.15 2.65 0.03	ulfide Ores (Ty) Stdev 435 15.4 7.29 0.06 46.9 473 2.89 88.7 9.42 8.71 0.03 1.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.02 0.08 0.49 0.00	pe II, n = 13) n 8 6 4 3 12 13 12 9 4 12 7 12 6 7 3 6 1	Magnetite fr Min 2.42 2.49 1.52 0.22 7.84 913 0.39 13.4 3.50 1.70 0.12 3.35 0.02 0.01 0.07 2.16 0.03	rom Dissemina Max 3326 23.9 9.32 5.79 354 6344 12.1 423 184 247 0.39 7.98 0.57 0.14 1.12 9.25 0.06	tted Cu-rich Su Mean 1105 7.71 3.76 2.98 93.3 3454 4.97 137 68.5 30.2 0.23 6.29 0.12 0.04 0.27 4.42 0.05	Ifide Ores (Typ) Stdev 880 5.93 2.58 2.54 88.6 1785 2.72 109 60.6 61.9 0.10 1.09 0.17 0.04 0.35 1.65 0.01	e III, n = 23) n 21 10 6 4 21 23 21 17 11 18 6 22 8 14 7 22 3

Table 2. Summary of LA-ICP-MS results for representative trace elements (in ppm) of different magnetite types in the Jinchuan Ni-Cu-PGE deposit.

10,00

1,0

(a)





100,00

1,00

Ъ 10,00

Figure 4. Binary diagrams of (a) Ni vs. Co, (b) Ti vs. Co, (c) Zr vs. Co, (d) Co vs. Zn, (e) Ti vs. Zn, (f) Zr vs. Zn, (g) Co vs. Ga, (h) Sn vs. Ga, and (i) Ni/Cr vs. Ga for the Jinchuan different types of magnetite in massive and disseminated sulfide ores.



Figure 5. Multielement variation diagrams for different types of magnetite in the Jinchuan Ni-Cu-PGE deposit. Normalized to bulk continental crust values are from [48]. Note: The selected elements in this figure were sequenced by their increasing compatibility into magnetite using the compilation of experimental and empirical partition coefficients between magnetite and silicate magmas. More details can be found in [2] and references therein.



Figure 6. Diagrams showing hydrothermal-like affinity for the Jinchuan Type II and III magnetite in disseminated Cu-rich sulfide ores. (**a**–**d**) Type II magnetite infilled pentlandite along its cleavage. (**e**) Type III magnetite wrapped or replaced chalcopyrite. (**f**) Ti vs. Ni/Cr diagram (modified from [2]) showing magmatic and hydrothermal origin for magnetite. Hydrothermal magnetite data from porphyry (e.g., Yuleken), skarn (e.g., Tengtie, Tieshan, Baijian, and Fushan), and IOCG deposits (e.g., Lala) are from [13,15,20,49–51]. Note that the limited data for Type III and unpresented Type II magnetite with hydrothermal magnetite affinity in Figure 6f is due to the exclusion of some unbelievable Ni/Cr ratios and low detection limit of Ti in their geochemical data, with detailed geochemical data in Supplementary Materials. Abbreviations: Ccp, chalcopyrite; Mag, magnetite; Pn, pentlandite; Po, pyrrhotite; Py, pyrite.



Figure 7. Binary diagrams of (**a**) Ti vs. Ni, (**b**) V vs. Ni, (**c**) Ti vs. Ga, (**d**) Ti vs. V, (**e**) V vs. Zn, and (**f**) V vs. Co for the Jinchuan different types of magnetite in massive and disseminated sulfide ores. Note that the limited data for Type II and III magnetite in this figure is same as Figure 6.



Figure 8. Plots of (**a**) V vs. Cr and (**b**) Ni vs. Cr for the Jinchuan different types of magnetite in massive and disseminated sulfide ores. Fields of primitive Fe-rich MSS, evolved Fe-rich MSS, and Cu-rich ISS areas are from [6]. The evolution trends of Talnakh and Voisey's Bay are from [12]. Hydrothermal magnetite data from porphyry, skarn, and IOCG deposits and references are same as Figure 6.

4.1. Petrography

Magnetite in massive and disseminated Ni- and Cu-rich sulfide ores (Figure 3a,c,d) has three different textures, including (1) granular crystals in massive ores (Type I) that can be further divided into subtypes according to being in different Ni-rich (Type I-A; Figure 3e) and Cu-rich sulfide ores (Type I-B; Figure 3f), respectively; (2) dendritic or laminar crystals in disseminated Cu-rich sulfide ores (Type II; Figure 3g); and (3) granular crystals as disseminated structures in disseminated Cu-rich sulfide ores (Type III; Figure 3h).

4.2. Magnetite Geochemistry

Type I magnetite generally have high Co (20.3–96.4 ppm), Ni (854–2137 ppm), Ti (6.87–4855 ppm, except one abnormal high value of 6165 ppm), Zr (0.01–28.4 ppm), Zn (13.0–2417 ppm), Ga (3.48–24.8 ppm), Sn (2.23–62.6 ppm), and Ni/Cr contents/ratios (0.03–177), with Type I-A magnetite having lower former mentioned trace elements when compared with Type I-B magnetite (Figure 4; Table 2 and Supplementary Materials). On the bulk continental crust normalized diagram, Type I-A and I-B magnetite are enriched in Ge, Sn, Mn, Co, V, and Ni, and depleted in Si, Ca, Al, Mg, Cu, and high field strength elements (HFSE; e.g., Y, P, Zr, Hf, and Ta), with the former having enrichment of Zn (Figure 5a,b).

Type II and III magnetite have narrower ranges of trace elements concentrations than Type I magnetite. Type II magnetite commonly have variable and low Co (0.38–11.5 ppm), Ni (13.8–309 ppm), Ti (2.37–19.7 ppm), Zr (0.01–0.03 ppm), Zn (1.83–32.3 ppm), Ga (0.09–0.17 ppm), Sn (2.02–3.43 ppm), and Ni/Cr contents/ratios (0.46–4.40; Figure 4; Table 2 and Supplementary Materials). Those Type II magnetite grains have enrichment of Ge, Sn, and Mn, and depletion of HFSE (e.g., Y, P, Zr, Hf, Ta, and Nb), and Si, Al, Mg, W, Mo, Ga, Ti, Zn, Co, V, and Cr on the bulk continental crust normalized diagram (Figure 5c). However, Type III magnetite have Co contents of 0.39–12.1 ppm, Ni contents of 13.4–423 ppm, Ti contents of 1.52–9.32 ppm, Zr contents of 0.02–0.57 ppm, Zn contents of 1.70–247 ppm, Ga contents of 0.12–0.39 ppm, Sn contents of 2.16–9.25 ppm, and Ni/Cr ratios of 0.05–23.9 (Figure 4; Table 2 and Supplementary Materials). They have similar enrichment and depletion characters with Type II magnetite on the bulk continental crust normalized diagram (Figure 5d).

5. Discussion

5.1. Genesis of Magnetite

In the Jinchuan Ni-Cu-PGE deposit, Type I magnetite is commonly subhedral to anhedral and is intergrown with pyrrhotite, chalcopyrite, and minor pyrite and pentlandite, showing early crystallization phase and probably crystallized from primitive Fe-rich liquids (Figure 3e–f) [6]. Type II magnetite is euhedral to subhedral, coexisting with pentlandite and minor chalcopyrite, and commonly presented in the intervals of pentlandite along its cleavages infilling the latter, indicating this type of magnetite slightly postdated pentlandite and probably crystallized from evolved Fe-rich liquids (Figures 3g and 6a–d) [6]. Type III magnetite is fine-grained and euhedral to anhedral, with disseminated structures to wrap chalcopyrite comparable to metasomatic textures in hydrothermal deposits (e.g., skarn and porphyry deposits). Type III magnetite also has a later crystallization phase than chalcopyrite (Figures 3h and 6e). By inference of microstructures of magnetite, we can preliminarily conclude that Type I magnetite is magmatic, whereas Type II and III magnetite crystallized from late stage of melts with magmatic origin which is also comparable to hydrothermal magnetite in their geochemistry, e.g., Ti vs. Ni/Cr diagram (Figure 6f).

However, at Jinchuan, Type I magnetite have high Cr (7.01–66,596 ppm), Co (20.3–96.4 ppm), Ni (854–2137 ppm), and Ti contents (6.87–4855 ppm), suggesting that those magnetite crystallized from sulfide liquids with mafic magma affinity. However, Type II and III magnetite have depletions of Ti (<20 ppm), Al (<51 ppm), Zr (0.01–0.57 ppm), Hf (0.03–0.06 ppm), Nb (0.01–0.14 ppm), and Ta (0.01–0.21 ppm), suggesting that those types of magnetite have hydrothermal magnetite affinities in their geochemistry [2,3,5,9,50]. Considering the mineral paragenesis that Type II and III

magnetite formed slightly later than pentlandite and chalcopyrite in disseminated Cu-rich sulfide ores (Figure 6a-e) and their geochemical characteristics, we prefer to suggest that those two types of magnetite crystallized from late stage of melts or probably from evolved Fe-rich MSS to Cu-rich ISS during sulfide fractionation. Their magnetite origin is classified into being magmatic, but simply geochemically similar to hydrothermal magnetite because of the former geochemical similarities between the Jinchuan Type II and III magnetite and hydrothermal magnetite. Such hydrothermal-like origin in geochemistry for Type II and III magnetite at Jinchuan may be comparable to magnetite crystallized from magmatic-hydrothermal fluids or systems of hydrothermal deposits, such as porphyry (e.g., Yuleken deposit) [49], skarn (e.g., Tengtie, Tieshan, Baijian, and Fushan deposits) [15,20,51], and IOCG deposits (e.g., Lala deposit) [13], in Ni/Cr ratios (Figure 6f). Type II and III magnetite at the Jinchuan Ni-Cu-PGE deposit crystallized from evolved primitive Fe-rich liquids have apparent similar geochemical features with hydrothermal magnetite from hydrothermal deposits or systems. However, it is worth noting that Type II and III magnetite did crystallize from late stage of melts in a magmatic Ni-Cu-PGE system with magmatic origin, but simply having hydrothermal magnetite affinities in their geochemistry. The term "hydrothermal-like magnetite affinities in their geochemistry" used in this study can well-represent such special origin for Type II and III magnetite in the Jinchuan Ni-Cu-PGE deposit. Therefore, we can conclude that Type I magnetite from massive sulfide ores is magmatic origin, whereas Type II and III magnetite from disseminated sulfide ores have hydrothermal-like magnetite affinities in their geochemistry.

5.2. Factors Controlling Magnetite Compositions

Magnetite with different genetic types commonly contains distinct contents of trace elements which are controlled by different factors. For example, the geochemistry of magmatic magnetite is primarily controlled by magma compositions, temperature (T), pressure (P), cooling rate, oxygen and/or sulfur fugacity (fO_2 and/or fS_2), and silica activity, whereas the geochemistry of hydrothermal magnetite is mainly controlled by fluid and host rock compositions, coexisting minerals, T, P, and fO_2 ([21] and references therein).

The Jinchuan magnetite has magmatic origin (discussed in the above section), but Type II and III magnetite also have hydrothermal-like magnetite affinities in their geochemistry. Therefore, these different types of magnetite may be controlled by various factors as mentioned above. It is widely recognized that there are multiple primary magmas for the Jinchuan magmatic Ni-Cu-PGE deposit from a complicated magma plumbing system with fractional crystallization (including sulfide segregation) and crustal contamination, during ascent or in staging chambers [25,35]. Therefore, we prefer to propose that the Jinchuan magnetite with different "origin" (the latter two types of magnetite at Jinchuan have obvious hydrothermal-like magnetite affinities in geochemistry, hence, we used a different origin to differentiate the genetic type of the Jinchuan magnetite, viz., the difference of geochemical characteristics in the Jinchuan magnetite) were probably sourced from the same primary magma and can be considered as a whole to preliminary discuss controlling factors (illustrated in detail in the following part) in their geochemistry. However, those Jinchuan magnetite grains are homogeneous under their BSE images (e.g., Type II magnetite; Figure 6a–d), we suggest that the magnetite geochemistry constrained by LA-ICP-MS is from the same magnetite generation in each type of magnetite, different from magnetite of hydrothermal deposits commonly with inhomogeneous character that is influenced by hydrothermal alteration or dissolution and reprecipitation processes with several generations (e.g., skarn deposits) [20,52].

5.2.1. Factor I: Magma Compositions

Magma compositions dominantly control magnetite geochemistry, which can be reflected by different contents of trace elements. Moreover, minerals co-precipitated with magnetite may also affect concentrations of some trace elements within the magnetite due to different partition coefficients [2,9]. In the Jinchuan Ni-Cu-PGE deposit, Type I magmatic magnetite is commonly intergrown with pyrrhotite, chalcopyrite, and minor pyrite and pentlandite (Figure 3e–f), and chalcophile elements

(e.g., Co, Ni, Cu, and Zn) are partitioned preferentially into such coexisting sulfides compared to magnetite [2]. The higher Co, Ni, and Zn contents of Type I magmatic magnetite in massive sulfide ores (Figures 4 and 7; Supplementary Materials) can be explained by two possibilities: (1) Precipitation of sulfides in massive Cu- and Ni-rich sulfide ores did not significantly affect contents of Co, Ni, and Zn in magnetite, or (2) these elements were saturated and rich in the magma or ore-related systems during the early mineralization stage, with the latter likely being much more reasonable.

Magnetite from the Kangdian IOCG deposits in SW China have higher Ni contents than magnetite from the Tengtie skarn Fe deposit, likely because the ore-forming fluids for the Kangdian IOCG deposits had much more mafic precursor than that of the Tengtie skarn Fe deposit in the Nanling Range of the Cathaysia Block, SW China [13]. The decreasing trend of Ni contents from Type I through Type II to Type III magnetite at Jinchuan (Figure 7a,b) may indicate that: (1) The magma had much more mafic precursor during Type I magmatic magnetite formation, and (2) the magma evolved during the formation of the Jinchuan magnetite (e.g., from the magmatic to hydrothermal-like magnetite affinities in their geochemistry, the associated magma evolved during fractional crystallization and sulfide segregation). However, Type I magnetite have relatively higher Cr, Ni, and V concentrations than Type II and III magnetite, and Type I magnetite grains plot in the fields of primitive and/or evolved Fe-rich MSS (Figure 8). Type II and III magnetite grains plot in the vicinity of fields of evolved Fe-rich MSS and Cu-rich ISS (Figure 8) and have higher Cu concentrations than Type I magnetite (Table 2). The decreasing Cr, Ni, and V concentrations from Type I to Type II or even Type III magnetite at Jinchuan may indicate the compositions of parental magma (or melts) changed or evolved, which is similar to other magmatic Ni-Cu-PGE deposits worldwide constrained by magnetite geochemical data (e.g., Sudbury in Canada, Voisey's Bay in Canada, and Talnakh in Russia) [6,12]. Such transition for the nature of magma also indicates that the parental magma/melts evolved during ascent accompanied by sulfide segregation and crustal contamination, or another staging sulfide-rich magma chamber participated into the former existed magma system to form the Jinchuan Ni-Cu-PGE deposit [25,26,35]. It is worth pointing out that the evolved Fe-rich MSS at Jinchuan Ni-Cu-PGE deposit may be comparable to magmatic-hydrothermal fluids in compositions of porphyry, skarn, and IOCG deposits that evolved from intermediate to felsic magma, and magnetite (or even other minerals) formed by such systems (Figure 8b; e.g., evolved Fe-rich MSS of magmatic Ni-Cu deposits and magmatic-hydrothermal fluids of porphyry, skarn, and IOCG deposits) can have different origins in their geochemistry, e.g., magnetite in this study and in albitized granitic plutons in the Handan-Xingtai skarn iron district, North China Craton [20]. Therefore, we can conclude that the compositions and nature of magma control the origin (mainly chemical characteristics, such as magmatic vs. hydrothermal-like) and trace element concentrations (e.g., Cr, Co, Ni, Cu, and Zn) of the Jinchuan magnetite.

5.2.2. Factor II: Temperature and fO_2

The effects of T and fO_2 on the trace element geochemistry of magmatic and hydrothermal magnetite are not well-constrained [9,13,21,53,54], yet for the Jinchuan magnetite.

Titanium in Fe oxides is regarded to be positively correlated with temperature [5,6,13,21]. The Type I magnetite have higher contents of Ti than Type II and III magnetite at Jinchuan (Figure 7a,c–d), which indicates that Type I magnetite from massive sulfide ores formed at relatively higher temperature than Type II and III magnetite from disseminated sulfide ores, *viz.*, the temperature of magma or ore-related systems decreased during forming different sulfide ores or minerals by fractional crystallization in the Jinchuan Ni-Cu-PGE deposit. The similar decreasing trend of Ni contents in the Jinchuan magnetite (Figure 7a,b) may result from the evolution of primary magma during ascent with fractional crystallization. This process may also indicate the decreasing temperature of parental magma contributed to fractional crystallization of pre-crystalized minerals and magma evolution to form the Jinchuan different types of magnetite, *viz.*, Type I, II, and III magnetite.

Vanadium in magnetite can be used to trace the melt/liquid evolution and identify magma replenishment and mixing ([21] and references therein). Published papers [9,54–56] showed that only V³⁺ can be easily incorporated into the magnetite crystal lattice, and the concentration of V³⁺ in magnetite has a negative correlation with fO_2 . The decreasing contents of V from Type I (mean 653 ppm and 493 ppm for Type I-A and I-B magnetite) through Type II (mean 0.30 ppm) to Type III magnetite (mean 2.98 ppm) at Jinchuan (Figure 7b,d–f; Table 2) suggests that the latter Type II and III hydrothermal-like magnetite formed at higher fO_2 . Such condition is consistent with the fact that the formation of sulfide minerals (e.g., pyrrhotite, chalcopyrite, pentlandite, and pyrite) consumed sulfur and lead to increasing of fO_2 in evolved magma or ore-related systems, which may partly prove that a relatively higher fO_2 condition existed during Type II and III magnetite formation in disseminated sulfide ores.

In summary, we can conclude that the Jinchuan magnetite crystallized from (evolved) Ni-Cu-rich liquids and the magnetite geochemistries in trace elements are controlled mainly by evolution of ore-related systems and geochemical parameters (e.g., T and fO_2), with the former probably playing a predominant role.

5.3. Implications for Ore-Forming Processes

Based on available data, Duan et al. (2016) [25] proposed an ore deposit model that the Jinchuan deposit formed by multiple pluses of sulfide-bearing magma during fractional crystallization, with the emplacing of more fractionated and sulfide-bearing magma during sulfide segregation playing a predominant role (Figure 9). As previously discussed in this study, the geochemistry of Jinchuan magnetite is mainly controlled by magma compositions and evolution and geochemical parameters (e.g., T and fO_2 ; Figures 7 and 8). The formation processes of magnetite can also be used to illustrate the detailed ore-forming processes for the Jinchuan deposit. When the primary sulfide-bearing magma was triggered from mantle source, it may have evolved and accompanied with crustal contamination and fractional crystallization (e.g., olivine crystallization and sulfide segregation) during ascent to initiate to form the Jinchuan deposit (Figure 9a) [25,32]. During this process, the Type I magmatic magnetite with high Cr contents (> 20,000 ppm) crystallized from the system with affinity of primitive Fe-rich MSS, similar to the Whistle and Murray deposits of Canada [6]. With the emplacing of new surge of magma (Figure 9b), more Type I magmatic magnetite, having relatively low Cr concentrations (<1000 ppm), crystallized from evolved Fe-rich MSS. During the multiple pluses of new surge of magma emplacing, more fractionated and sulfide-bearing magma participated into the ore-forming systems (Figure 9c). Such systems consumed amount of elements (e.g., Fe, S, Cu, Co, and Ni) during the crystallization of earlier formed sulfides, including pyrrhotite, pentlandite, and chalcopyrite, as well as Type I magnetite, resulting in high fO_2 for the ore-forming systems, which were comparable to transition from evolved Fe-rich MSS to Cu-rich ISS, with Type II and III hydrothermal-like magnetite formed slightly later than pentlandite and chalcopyrite. During the formation of Type II and III hydrothermal-like magnetite, Cu from the evolved systems was incorporated into magnetite crystals to substitute Fe²⁺ and/or Fe³⁺, leading to much higher Cu contents in Type II and III magnetite than Type I magmatic magnetite (Table 2), which may have been controlled by decreasing T, increasing fO_2 , and the evolved surge of fractionated and sulfide-bearing magma. Such phenomenon that Type II and III magnetite have relatively high Cu contents indicates that Cu was saturated during magma to form disseminated sulfide ores and Type II and III magnetite.



Figure 9. Schematic diagrams illustration ore-forming processes of the Jinchuan Ni-Cu-PGE deposit (modified after [25]). (a) Emplacement of Fe-, Cr-, and sulfide-bearing magma forming the Jinchuan deposit, with Type I magnetite (Cr > 20,000 ppm) crystallized from the primary Fe-rich MSS. (b) New surge of magma participated into the ore-forming system, with Type I magnetite (Cr < 1000 ppm) crystallized from the new system that is comparable to the evolved Fe-rich MSS. (c) Emplacement of more fractionated, sulfide-bearing magma participated into the ore-forming system, and Type II and III magnetite formed from the evolved Fe-rich MSS to Cu-rich ISS.

6. Conclusions

(1) Three types of magnetite by textural analysis were observed from the Jinchuan massive and disseminated sulfide ores, with Type I magnetite being magmatic origin, and Type II and III magnetite having hydrothermal-like magnetite affinities in their geochemistry.

(2) The Jinchuan magnetite can be distinguished by many trace elements (e.g., Ti, V, Co, Ni, Zn, and Ga), and their geochemistries are controlled mainly by the evolution of ore-related systems and geochemical parameters (e.g., T and fO_2), with the former playing a predominant role.

(3) Type I magmatic magnetite crystallized from primitive and evolved Fe-rich MSS, whereas Type II and III hydrothermal-like magnetite crystallized from evolved Fe-rich MSS to Cu-rich ISS.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/9/10/593/s1, Supplementary data of the full LA-ICP-MS analytical results (in ppm) for the Jinchuan different types of magnetite is given in the Excel file of Supplementary material.

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