

## Article

# Origin and Nature of Parental Magma and Sulfide Segregation of the Baixintan Magmatic Ni–Cu Sulfide Deposit, Southern Central Asian Orogenic Belt (CAOB), NW China: Insights from Mineral Chemistry of Chromite and Silicate Minerals

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**Abstract:** The mineral chemistry of chromite and silicate minerals in the Baixintan magmatic Ni–Cu sulfide deposit in the Northern Tianshan, southern Central Asian Orogenic Belt (CAOB) are reported here. Two types of chromite were identified in mafic-ultramafic rocks. Type I chromite occurs as inclusions encased in olivine and has a primary and magmatic origin and homogeneous composition with Cr# values (49–66). It is characterized by high Ti contents (0.33–1.52 wt%) and small quantities of ZnO (0–0.21 wt%), MnO (0.28–0.45 wt%), and NiO (0.06–0.24 wt%) contents. In contrast, type II chromite with interstitial phase and larger compositional variations has significantly higher TiO<sub>2</sub> (up to 6.2 wt%) and FeO<sub>T</sub> contents (up to 69.3 wt%) and slightly lower Al<sub>2</sub>O<sub>3</sub> (minimum 3.0 wt%) and MgO contents (minimum 0.53 wt%). It is considered to crystallize from a more evolved and fractionated melt and suffers from post-magmatic alteration, such as serpentinization and chloritization. The olivine has forsterite values (Fo) varying from 76.8 to 85.6. The parental magma is characterized by high temperature (1389 °C), high pressure (3.8 GPa), and high Mg content (11.4 wt%) with oxidized (FMQ + 1.6) and hydrous nature based on compositions of primary chromite and olivine–chromite pairs. The intrusion originated from high-degree partial melting of depleted mantle that had been modified by crustal components and metasomatized by subduction fluid in a post-orogenic extensional setting. Two stages of sulfide segregation have been recognized. Early segregation led to the depletion of platinum group elements (PGE), and disseminated sulfide mineralization was the product of later segregation. The assimilation of crustal Si and S components played more important roles on sulfide segregation rather than fractional crystallization.

**Keywords:** chromite; mineral chemistry; parental magma; tectonic setting; mantle source; sulfide segregation; Baixintan

## 1. Introduction

Chromite serves as one of the earliest crystallization phases in mafic-ultramafic magma, in which trivalent irons (Cr<sup>3+</sup> and Al<sup>3+</sup>) diffuse at a much lower rate compared with divalent ions (Mg<sup>2+</sup> and Fe<sup>2+</sup>) [1,2]. It has thus been an important petrogenetic indicator in mantle-origin rocks, such as implications for parental magma conditions, mantle source, and tectonic setting [3–9]. On the other hand, post-magmatic hydrothermal alteration, metamorphism, and subsolidus re-equilibration have significant effects on chromite composition [10–14]. Modified chromite has fingerprinted the

alteration processes, while magmatic chromite with primary composition has traced the nature of parental magma. The olivine–chromite pair can also give constraints on equilibrium condition, such as temperature, pressure, and oxygen fugacity [10,15,16]. These conditions are key factors controlling sulfide immiscibility in magmatic sulfide deposits, and chromite composition has been used to understand Ni–Cu–platinum group element (PGE) mineralization in the Jinchuan [17], the Noril'sk–Talnakh [18], and the Sudbury deposits [19] as well as deposits in the southern Central Asian Orogenic Belt (CAOB) [20–22].

Abundant early Permian (275–285 Ma) mafic-ultramafic intrusions associated with Ni–Cu sulfide deposits occur in the Northern Tianshan, southern CAOB [23–25]. These deposits are mainly located in the eastern segment; however, there are some breakthroughs of Ni prospecting in the western segment in the past several years [26–29]. One example is the Baixintan deposit, a medium-sized deposit with  $6.49 \times 10^4$  tons of Ni and  $8.43 \times 10^4$  tons of Cu [30]. Preliminary petrogenetic studies have been conducted in the newly discovered deposit, such as geology, geochronology, geochemistry, and Sr–Nd–Hf–O–S isotopic studies [29,31–33]. The sulfide mineralization has also been discussed, such as sulfur saturation, quantitative modeling of sulfide segregation, and regional Ni–Cu sulfide prospectivity [26,29,32]. These studies are beneficial for understanding petrogenesis and mineralization; however, mineralogical studies, especially detailed chromite study, have not yet been conducted though it is widespread as accessory mineral in ultramafic-mafic rocks.

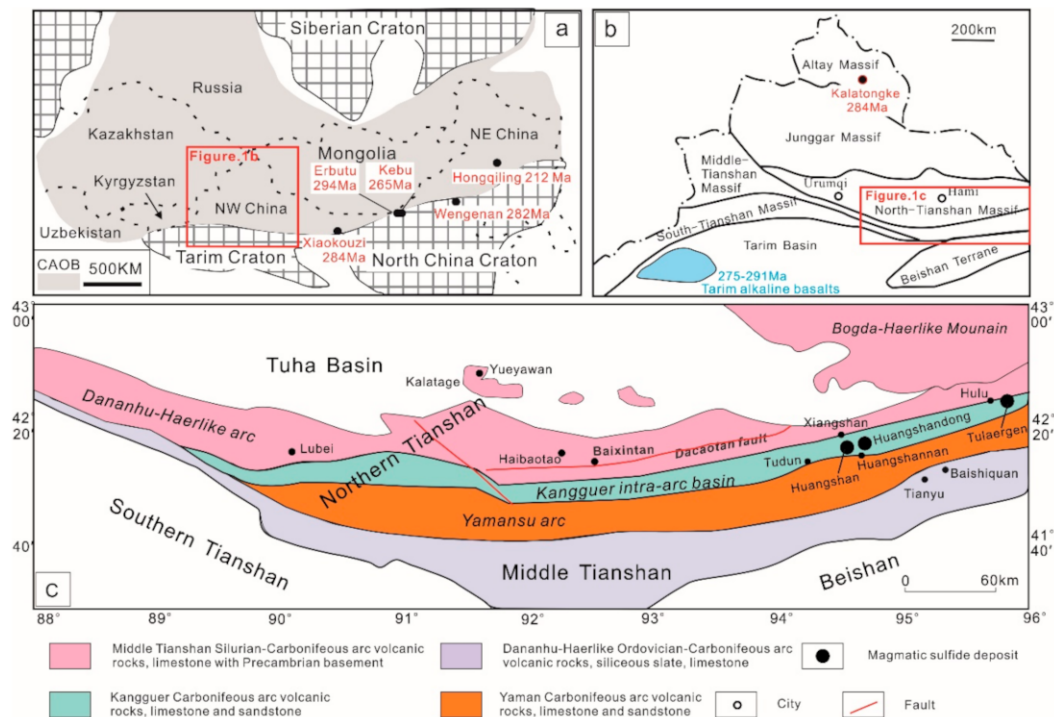
In this paper, systematical mineralogical studies of chromite and silicate minerals are conducted. First, two types of chromite have been identified according to mineral texture and occurrence. Then, parental magma composition and physicochemical conditions, including temperature, pressure, and oxygen fugacity, are estimated based on a new dataset of mineral chemistry. Their implications for tectonic setting and mantle source of mafic-ultramafic rocks are consequently presented. Finally, timescale and trigger factors of sulfide segregation are discussed based on olivine crystallization model and magma evolution.

## 2. Geological Background

### 2.1. Regional Geology

The CAOB, set between the Siberian and the Tarim-North China cratons, is one of the largest Phanerozoic accretionary belts on the globe and hosts numerous polymetallic deposits [34]. It is formed by multiple subduction-accretion of island arcs, oceanic plateaus, seamounts, ophiolites, and microcontinents that occurred from the late Proterozoic to the Mesozoic [35]. A series of Permian mafic-ultramafic rocks and related Ni–Cu deposits are located in the southern margin of the CAOB from NW China to NE China (Figure 1a, [36]). The Northern Tianshan and Beishan orogens are situated northeast to the Tarim craton and represent the southernmost segments of the CAOB in eastern Xinjiang, NW China (Figure 1b). The Northern Tianshan is separated from Tuha Basin to the north and the Middle Tianshan by the Aqikkuduk fault to the south and comprises the Dananhu–Harlike island arc, the Kangguer intra-arc basin, and the Yamansu arc [29,37–39].

The Dananhu–Harlike arc is composed of Ordovician–Carboniferous arc volcanic rocks, siliceous slate, and limestone [29]. Precambrian inherited zircons have been found in volcanic rocks from the Kalatage area [37,39]. The Late Carboniferous pillow basaltic rocks may form in a back-arc tectonic setting [40,41], whereas the Permian bimodal volcanism in the Bogda zone is considered to have formed in a post-collisional extensional environment caused by slab break-off [42,43]. Various types of arc-related ore deposits occur in this area, including the Silurian Huangtan volcanogenic massive sulfide (VMS) Cu–Au deposit, the Silurian Hongshan epithermal deposit, the Middle Devonian Xierqu skarn Fe deposit, the Middle Devonian Yudai porphyry Cu deposit, and the Early Carboniferous Tuwu porphyry Cu deposit [39].

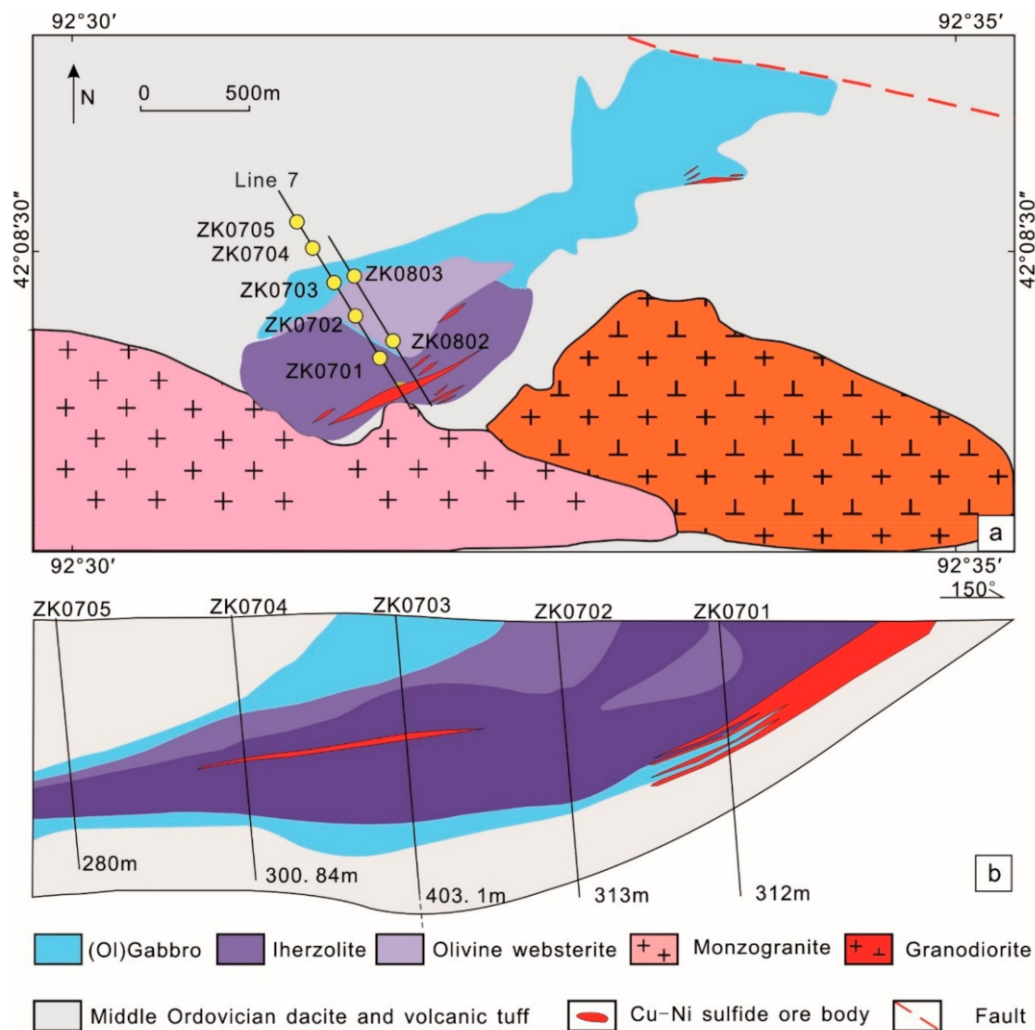


**Figure 1.** (a) Location map of the study area and Ni-bearing mafic-ultramafic intrusions in the south margin of the Central Asian Orogenic Belt (CAOB) (modified after Jahn et al. [34]); (b) schematic division of massifs and the location of the Northern Tianshan, NW China (modified after Ruan et al. [36]); and (c) a regional geological map showing the distribution of early Permian mafic-ultramafic complexes in Northern Tianshan (modified after Deng et al. [29]).

In addition to widespread intermediate-mafic volcanic eruptions, more than 30 mafic-ultramafic intrusions have been identified along the east-trending Kangguer–Huangshan deep fault [26,28,44]. Available age data show that they were emplaced in early Permian with a major peak at approximately 280 Ma due to the interaction between the metasomatized lithospheric mantle and the ascending asthenospheric mantle, as a result of slab break-off or an upwelling mantle plume [23,24,43,45–48]. A few intrusions are known to host magmatic Ni–Cu sulfide deposits, such as evidenced by the Huangshan, Huangshandong, Tulaergen, and the newly found Yueyawan deposits. Most of them are located to the eastern segment of Northern Tianshan, and the Ni mineralization belt was previously considered not to extend to the western segment. However, the recent Ni prospecting breakthroughs in the Baixintan and Lubei mafic-ultramafic intrusions have extended the metallogenic belt to the west for 180 km (Figure 1c) [26,28,29].

## 2.2. Deposit Geology

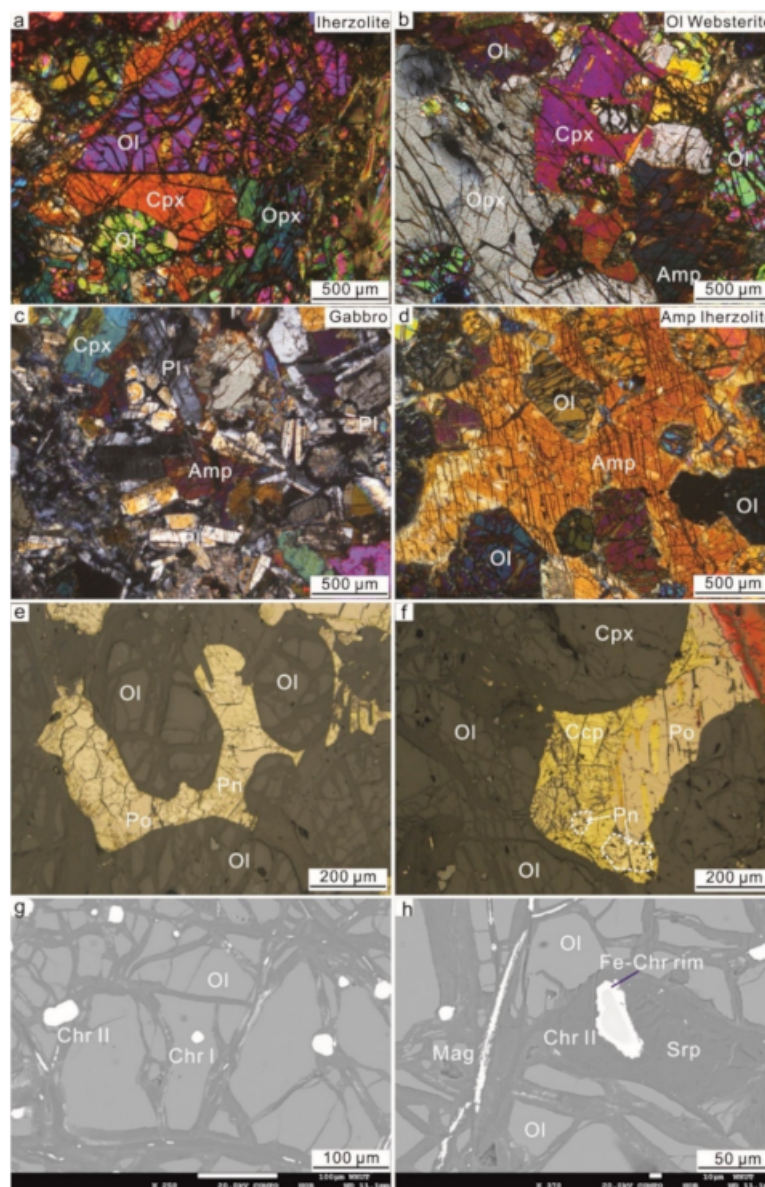
The Baixintan complex occurs along the secondary Dacatou fault and has an exposed area of 5 km<sup>2</sup>. It extends to depths of more than 400 m with a flat funnel shape. The immediate country rocks are middle Ordovician dacite, basaltic andesite, volcanic tuff, and sandstone clastic rocks, and later monzogranite and granodiorite are situated in the south. The complex generally consists of olivine gabbro, olivine websterite, and lherzolite. The olivine gabbro occurs in the north, and mineralized lherzolite appears in the southwestern region. The olivine websterite is found between lherzolite and olivine gabbro. The lherzolite and olivine websterite are enveloped by olivine gabbro in the cross section (Figure 2b).



**Figure 2.** (a) Simplified geological map and (b) section of line 7 of the Baixintan deposit, showing the distribution of mafic and ultramafic rocks and sulfide mineralization.

The Iherzolite is dark black and composed of olivine (50–60%); pyroxene (25–30%); amphibole (10–15%); and a little bit of plagioclase, chromite, and phlogopite (Figure 3a,d). The olivine websterite is grey black and contains pyroxene (50–70%) olivine (20%), plagioclase (5–10%), and accessory amphibole and chromite (Figure 3b). Significant alteration has been identified in these ultramafic rocks, including serpentinization, iddingsitization, chloritization, and talcization. The olivine in ultramafic rocks are 0.2–3 mm, idiomorphic, and surrounded by clinopyroxene and serpentine. The gabbro and olivine gabbro exhibit a mosaic texture and predominantly consist of plagioclase (approximately 50%), pyroxene (approximately 40%), and occasional olivine (5–10%) (Figure 3c).

The ore bodies occur as lenticles and funnels at depths of 0–200 m (Figure 2b). The sulfide mineralization appears mainly at the bottom of Iherzolite with Ni content ranging from 0.27 wt% to 5.45 wt% (average 0.41 wt%) and Cu content ranging from 0.24 wt% to 1.54 wt% (average 0.60 wt%), respectively. They are dominantly disseminated sulfide, and vein-type sulfide is also recently discovered at these depths. Sulfide minerals, including chalcopyrite, pyrrhotite, pentlandite, pyrite, minor bornite, and violarite, occur as interstitial phases between olivine grains (Figure 3e,f).



**Figure 3.** Photomicrographs of mafic-ultramafic rocks showing the occurrence of silicate minerals, sulfide, and chromite: (a) Iherzolite, rounded olivine encased in clinopyroxene; (b) olivine websterite; (c) gabbro, with slight alteration of silicate minerals; (d) amphibole Iherzolite, widespread amphibole enveloping olivine grains and exhibiting two groups of complete cleavage; (e,f) interstitial sulfide of pentlandite, pyrrhotite, and chalcopyrite occurring between silicate minerals; and (g) two types of chromite. Type I chromite occurs as inclusions enclosed in olivine (Chr I). Type II chromite occurs as interstitial phase in serpentine (Chr II). (h) A few type II chromites display zonation with bright rims. Ol: olivine, Cpx: clinopyroxene, Opx: orthopyroxene, Amp: amphibole, Pl: plagioclase, Po: pyrrhotite, Pn: pentlandite, Ccp: chalcopyrite, Chr: chromite, Srp: serpentine, and Mag: magnetite.

### 3. Mineral Occurrence

Chromite, usually the first phase to crystallize from mafic-ultramafic magmas, occurs as an accessory mineral in the Baixintan complex and is more common in ultramafic rocks than in mafic rocks. It has sizes ranging from 20 to 200 µm. Two types of chromite have been identified based on their morphology and occurrence. The first type occurs as euhedral-subhedral inclusions in olivine and pyroxene and has straight borders and a bright white color (Figure 3g). The second type is more common and refers to anhedral or irregular interstitial grain surrounded by alteration minerals, such as

serpentine and chlorite (Figure 3h). They usually have rough boundaries produced by later dissolution and alteration. Some of them have bright rims in BSE images.

The olivine dominantly occurs as cumulate grains in lherzolite or is occasionally enclosed by pyroxene and amphibole. The cumulate grains have larger size (0.3–3 mm) and are more fragmented. The enclosed ones are round and fresh with small size (0.2–0.5 mm). Pentlandite and pyrrhotite are found filled among olivine grains in lherzolite. The orthopyroxene mainly occurs as short columnar and granular in olivine websterite and lherzolite, while clinopyroxene is common in various rock types. Alteration minerals are generally found surrounding pyroxene, such as urallite, chlorite, and talc. Plagioclase is characterized by short columnar, perfect cleavage, and polysynthetic twin. Amphibole is common in various rock types and is characterized by urallitization and talcization. Hydrous minerals, including amphibole and phlogopite are widely found in the intrusion.

#### 4. Materials and Methods

Thirty samples of lherzolite, websterite, olivine gabbro, and gabbro were collected from drill cores in profile 7 (Figure 2) and outcrops for petrographic observations and mineral composition analysis. Chromite and silicate minerals, including olivine, pyroxene, plagioclase, and amphibole, in different rock types have been analyzed. The thin sections were carefully observed by transmitted and reflected optical microscopy as well as by environmental scanning electron microscope (ESEM) under backscattered electron (BSE) mode prior to quantitative electron probe microanalysis (EPMA). The latter were performed using a Cameca SX 50 electron microprobe instrument at Wuhan Sample Solution Analytical Technology Co., Ltd., China and the Materials Research and Testing Center, Wuhan University of Technology.

The standards used for EPMA of chromite were spinel for Mg and Al, diopside for Si, ilmenite for Ti, chromite for Cr and Fe, manganese oxide for Mn, niccolite (NiAs) for Ni, sphalerite for Zn, albite for Na, and phlogopite for K. Peak and background counting times were set at 30 and 15 s, respectively. The beam diameter was 3–5  $\mu\text{m}$ , and spot mode was used for tiny particles or minerals with rough surfaces. The experimental conditions were 20 kV of accelerating voltage and 10 nA of beam current. Detection limit was 0.1 wt%. Iron was determined as total iron ( $\text{FeO}_t$ ), and  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were calculated by assuming an  $\text{R}^{2+}\text{R}^{3+}_2\text{O}_4$  formula and by balancing  $\text{RO}:\text{R}_2\text{O}_3 = 1$  for chromite [49].

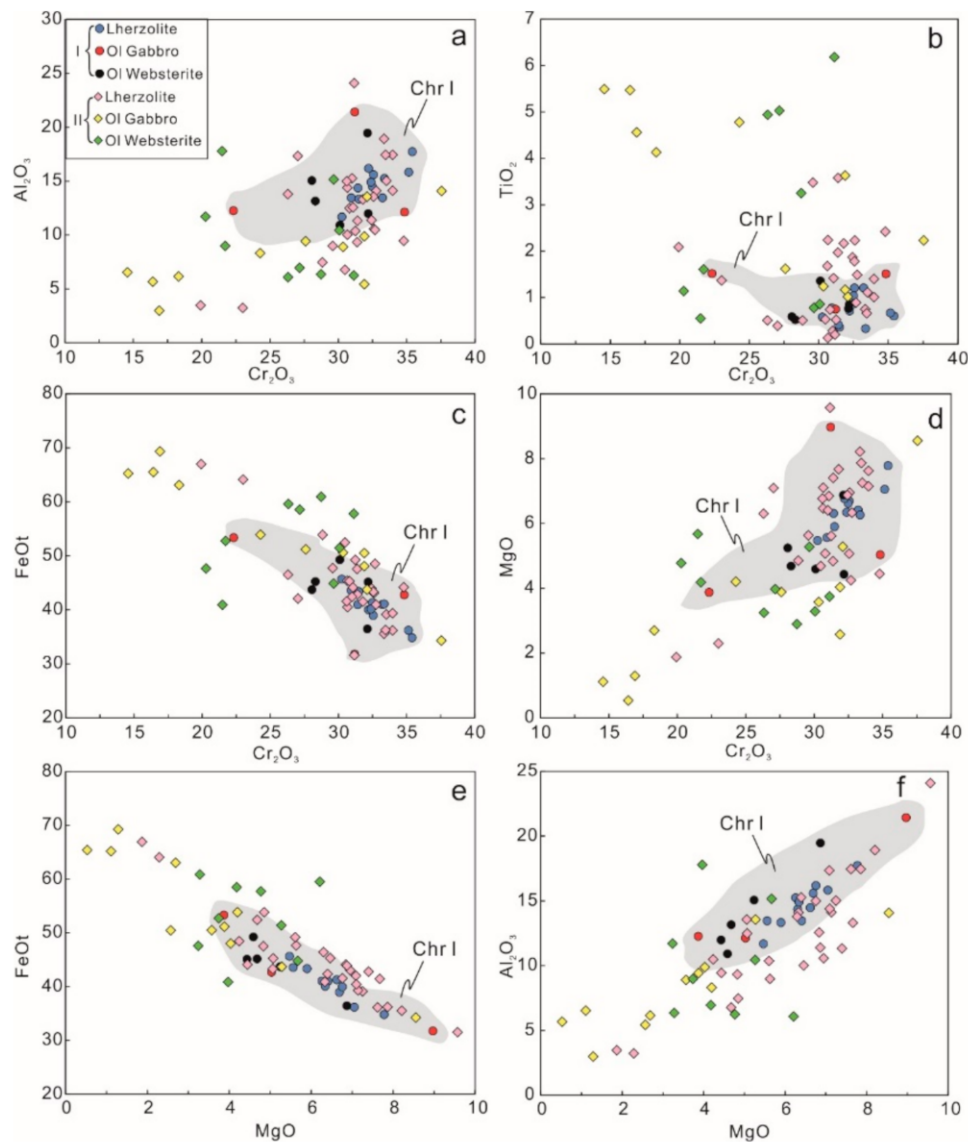
The same experimental conditions were applied to silicate minerals. Most olivine and pyroxene were altered, and thus, only fresh grains with crystal integrity were selected for analyses. The standards used were olivine for Mg and Si, garnet for Al, diopside for Ca, omphacite for Na, ilmenite for Ti, chromite for Cr, fayalite for Fe, niccolite (NiAs) for Ni, sphalerite for Zn, phlogopite for K, and manganese oxide for Mn.

#### 5. Results

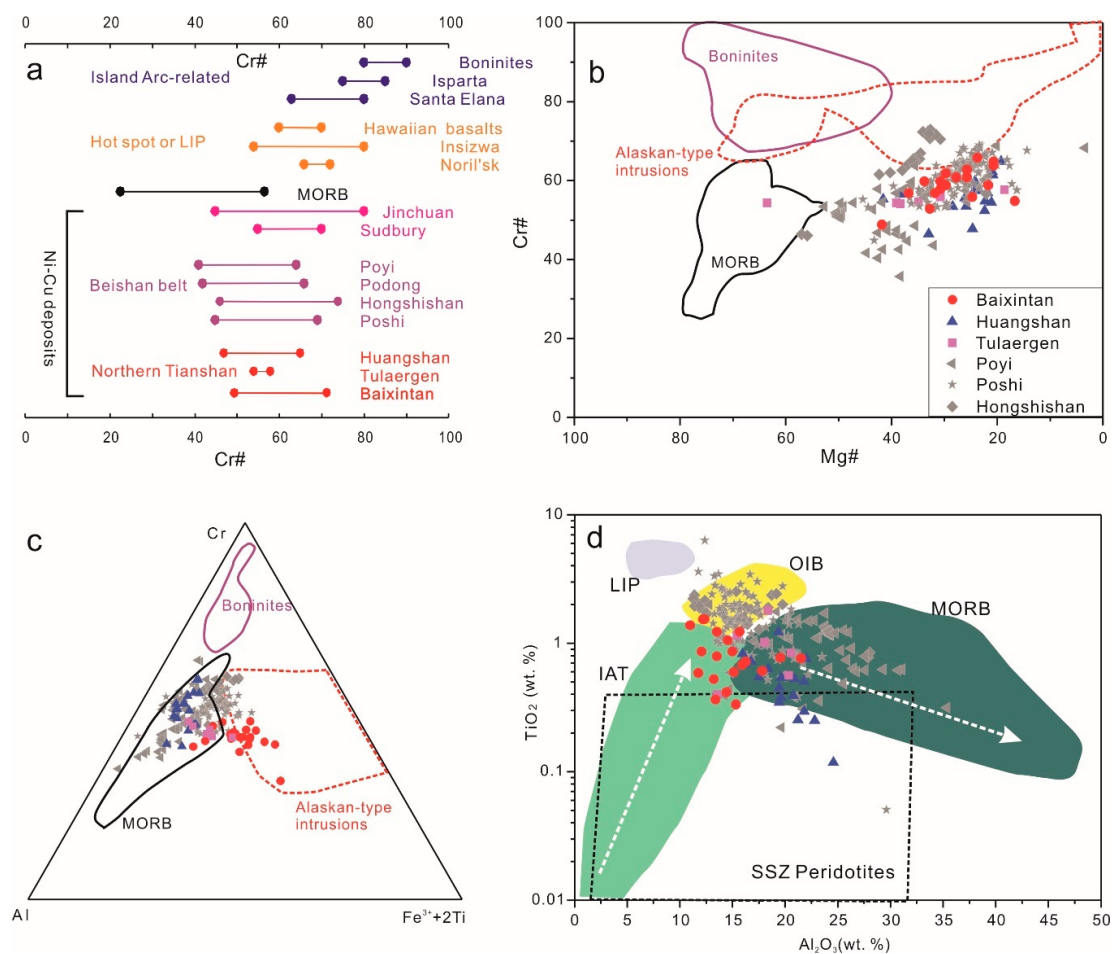
##### 5.1. Chromite

Type 1 chromite, enclosed within olivine, exhibits compositional variations with 3.9–9.0 wt% MgO, 22.3–35.4 wt %  $\text{Cr}_2\text{O}_3$ , and 10.9–21.4 wt%  $\text{Al}_2\text{O}_3$  (Figure 4 and Table S1). The stoichiometric FeO and  $\text{Fe}_2\text{O}_3$  contents are 20.7–27.5 wt% and 12.3–28.8 wt%, respectively. The chromite is characterized by high Ti contents (0.33–1.52 wt%) and small quantities of ZnO (0–0.21 wt%), MnO (0.28–0.45 wt%), and NiO (0.06–0.24 wt%) contents (Table S1). The MgO contents display positive relationships with  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  contents and a negative relationship with  $\text{FeO}_t$  contents (Figure 4d–f). Generally, chromite in lherzolite, representing the earliest chromite, has slightly higher MgO and  $\text{Cr}_2\text{O}_3$  contents and lower  $\text{FeO}_t$  and  $\text{TiO}_2$  contents than that in other rocks. Chromite in olivine gabbro is more scattered than that in lherzolite and websterite, which may be because it consists of different stages of chromite. The calculated Cr# values ( $(100\text{Cr}/(\text{Cr} + \text{Al}))$ , molar) thus range from 49 to 66. The Mg# values ( $(100\text{Mg}/(\text{Mg} + \text{Fe}^{2+}))$ , molar) range from 20 to 44 (Figure 5a,b). In contrast, type II chromite (Chr II) has more dispersed compositions and is characterized by significantly high  $\text{TiO}_2$  content (up to 6.2 wt%)

and FeOt content (up to 69.3 wt%) and slightly low  $\text{Al}_2\text{O}_3$  content (minimum 3.0 wt%) and MgO content (minimum 0.53 wt%) (Figure 4). Chr II in olivine gabbro has larger compositional variations than that in lherzolite and olivine websterite, which is similar to type I chromite. Particularly, a few type II chromites in olivine gabbro have the lowest  $\text{Cr}_2\text{O}_3$  content (<20 wt%). The Cr# and Mg# ranges are 46–83 and 3–46, respectively (Table S1). As a whole, all the chromites constitute positive relationships between MgO and  $\text{Al}_2\text{O}_3$  and between MgO and  $\text{Cr}_2\text{O}_3$  (Figure 4d,f), and negative relationships between FeOt and  $\text{Cr}_2\text{O}_3$  and between FeOt and MgO (Figure 4c,e). Chr I represents the primary chromite and thus can give constraints to the nature of parental magma.



**Figure 4.** Major oxide variations for two types of chromite and different rocks in the Baixintan mafic-ultramafic intrusion (wt%): the shadow area is roughly defined by primary type I chromite (Chr I, circles). (a) Plot of  $\text{Al}_2\text{O}_3$ – $\text{Cr}_2\text{O}_3$ ; (b) Plot of  $\text{TiO}_2$ – $\text{Cr}_2\text{O}_3$ ; (c) Plot of  $\text{FeOt}$ – $\text{Cr}_2\text{O}_3$ ; (d) Plot of  $\text{MgO}$ – $\text{Cr}_2\text{O}_3$ ; (e) Plot of  $\text{FeOt}$ – $\text{MgO}$ ; (f) Plot of  $\text{Al}_2\text{O}_3$ – $\text{MgO}$ .



**Figure 5.** Chromite composition in the Baixintan (only Chr I) and other mafic-ultramafic intrusions in the Northern Tianshan and Beishan: (a) the Cr# range in island arc-related intrusions, hot spots or LIP, and Ni-Cu deposits; (b) a diagram of Cr#-Mg#, fields for boninites, and the middle ocean ridge basalt (MORB) from Barnes and Roeder [50], and Alaskan-type intrusions from Zhou et al. [19]; (c) a Cr-Al-(Fe<sup>3+</sup> + 2Ti) ternary diagram, with the references of fields the same as in (b); and (d) a plot of Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> constraining tectonic setting. The chromite compositional fields for MORB, ocean island basalt (OIB), island-arc tholeiite (IAT), supra-subduction zone (SSZ), and large igneous provinces (LIP) are from Kamenetsky et al. [8]. Data of the other intrusions in Northern Tianshan and Beishan are from references [20,51,52].

The chromite compositional comparison between the Baixintan and other mafic-ultramafic intrusions is illustrated in Figure 5. Only Chr I was used for comparison since it represents the primary chromite while Chr II crystallized from a more evolved and fractionated melt (see the discussion in Section 6.1). The Baixintan chromite as well as the chromite in the Northern Tianshan and Beishan display similar Cr# values to the middle ocean ridge basalt (MORB), which is slightly lower than that in island arc-related intrusions, boninites, hot spot, and large igneous provinces (LIPs), while their Mg values are slightly higher than MORB (Figure 5a,b). The Baixintan chromite is characterized by higher Fe<sup>3+</sup> than others and some plot in the fields of Alaskan-type intrusions and island-arc tholeiite (Figure 5c,d).

## 5.2. Silicate Minerals

The olivine in lherzolite has the highest MgO content (41.5–46.0 wt%) compared to that in olivine websterite (38.0–44.4 wt%) and in olivine gabbro (39.2–41.7 wt%). The calculated Fo values of the whole olivine ( $Fo = 100 \times \text{MgO}/(\text{MgO} + \text{FeO})$ , molar ratio) ranges from 76.8 to 85.6. Olivine in lherzolite

has higher Fo values (Fo = 80.9–85.6) than that in olivine websterite (Fo = 76.8–83.4) and olivine gabbro (Fo = 78.7–82.4). The Ni contents in olivine from the lherzolite have a wider range (1149–2837 ppm) than that from olivine websterite (864–1807 ppm) and olivine gabbro (629–1336 ppm). The olivine in all these samples are characterized by low MnO and CaO contents, which vary from 0.17 wt% to 0.36 wt% and from 0.02 wt% to 0.22 wt%, respectively (Table S2, Supplementary Material).

Pyroxene is characterized by tholeiite to calc-alkaline series. Orthopyroxene is classified as enstatite with Mg# = 85.0. Clinopyroxene is more common than orthopyroxene and is classified as augite and diopside. Clinopyroxene in lherzolite displays high Mg# = 86.5 and Wo = 43.7. Its compositional variation seems to be more related to a rift cumulated trend and is different from that of typical Alaskan-type complexes (Figure S1 and Table S3).

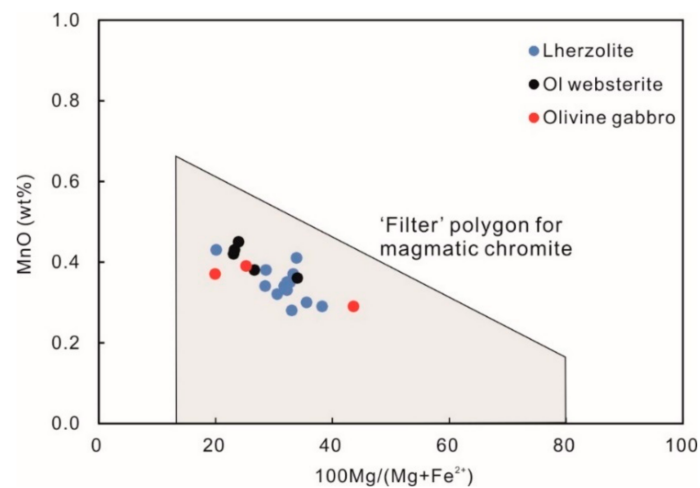
The anorthite proportions of plagioclase (An numbers) are from 67.4 to 80.8 for lherzolite, from 72.5 to 82.5 for olivine gabbro, and from 69.1 to 86.1 for gabbro. Except for a few grains of labradorite, all plagioclases are classified as bytownite (Figure S2 and Table S4).

The amphiboles in lherzolite and olivine gabbro are classified as pargasite and endenite, respectively, while that in websterite has larger compositional variations. Amphibole in lherzolite and websterite has higher Mg# ( $\text{Mg\#}/(\text{Mg\#} + \text{Fe}^{2+})$ ) than that in olivine gabbro. They almost all have a mantle origin and similar compositions with other amphibole in ultramafic rocks (Figure S3 and Table S5).

## 6. Discussion

### 6.1. Primary and Magmatic Chromite

Chromite is sensitive to hydrothermal alteration and prograde metamorphism, which may modify its composition [50,53,54]. Type I chromite mainly occurs as inclusions in olivine and, rarely, in silicate interspaces. They were crystallized earlier and captured by olivine crystals, which had avoided reaction with interstitial evolving liquid. It is noteworthy that magmatic type I chromites are outside any specific field of MORB, IAT, and Alaskan-type intrusions. This may be caused by a possible Fe–Mg subsolidus exchange equilibrium, in which process  $\text{Fe}^{2+}$  could incorporate into chromite crystals as an isomorphism of Mg, resulting in lower Mg# values than MORB (Figure 5b). The incorporation of  $\text{Fe}^{3+}$  and loss of Al lead to some samples plotting in the Alaskan-type intrusions and IAT (Figure 5c,d). Despite compositional changes, the extent of modification could be evaluated by Mg# ratios and MnO content. Significant subsolidus exchange between chromite and olivine commonly gives rise to low Mg# ratios (<15) and high MnO content (up to 2 wt%) because  $\text{Fe}^{2+}$  and Mn could replace Mg during subsolidus exchange [55–57]. Type I chromite has Mg# ranging from 20 to 44 and low MnO content (0.28–0.45 wt%) and plots the “filter polygon” for magmatic chromite (Figure 6) [55,58]. The subsolidus exchange may have an effect on type I chromite composition but at a much slower rate. Type I chromite can thus represent magmatic chromite, while type II chromite cannot be treated as primary chromite due to its interstitial phase and large compositional variations. It is considered to crystallize from a more evolved and fractionated melt [20,58]. Some samples have low MgO,  $\text{Al}_2\text{O}_3$ , and  $\text{Cr}_2\text{O}_3$  contents and high FeO and  $\text{TiO}_2$  contents, indicating far greater modification than type I chromite (Figure 4). Particularly, Fe-rich chromite rims in zoned chromite formed during serpentinization and chloritization [14,20,54,59]. The loss of Al, Mg, and Cr may be caused by chloritization, which involved the reaction of chromite, olivine, and magnetite to produce Fe-rich chromite rim and chlorite [20].



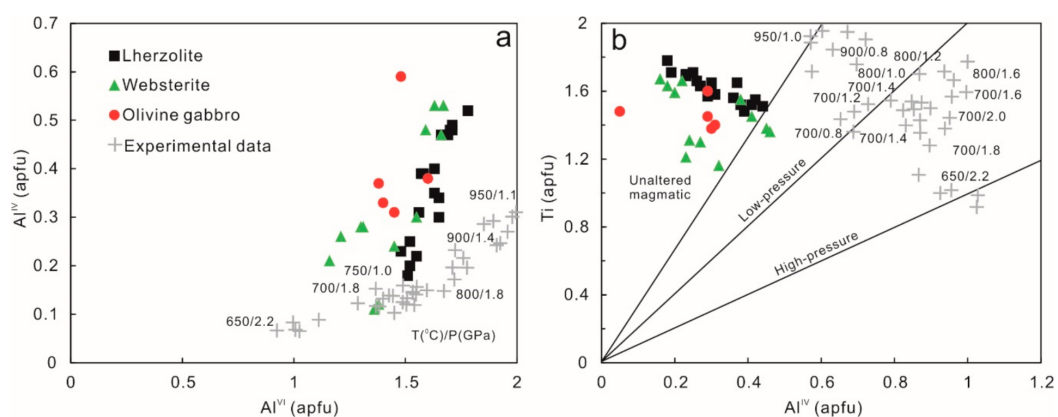
**Figure 6.** Mg# vs. MnO diagram for type I chromite: the “filter polygon” is from Evans and Evans [55].

## 6.2. Nature of Parental Magma

### 6.2.1. Temperature and Pressure

The chromite and olivine compositions can give constraints on the nature of parental magma, such as crystallization temperature and pressure, oxygen fugacity, and compositions [7,9,22,60]. As mentioned above, type I chromite with primary and magmatic origin and olivine with the highest Fo value (Fo = 85.6), are appropriate to calculate magma composition and physicochemical condition. The crystallization temperature of chromite is calculated to be 1389 °C using the thermometer proposed by Fabriès [60]:  $T (^{\circ}\text{C}) = (4250 * \text{Cr\#} + 1343)/(\ln K_d + 1.825\text{Cr\#} + 0.571) - 273$ , where  $\ln K_d = 0.34 + 1.06(\text{Cr\#})^2$ . The pressure is estimated as 3.8 GPa by the empirical formula:  $P(\text{GPa}) = 0.187 + 2.79(X_{\text{Spl}}^{\text{Cr}} + X_{\text{Spl}}^{\text{Fe}^{3+}})$ , where  $X_{\text{Spl}}$  is the mole fraction in chromite [61].

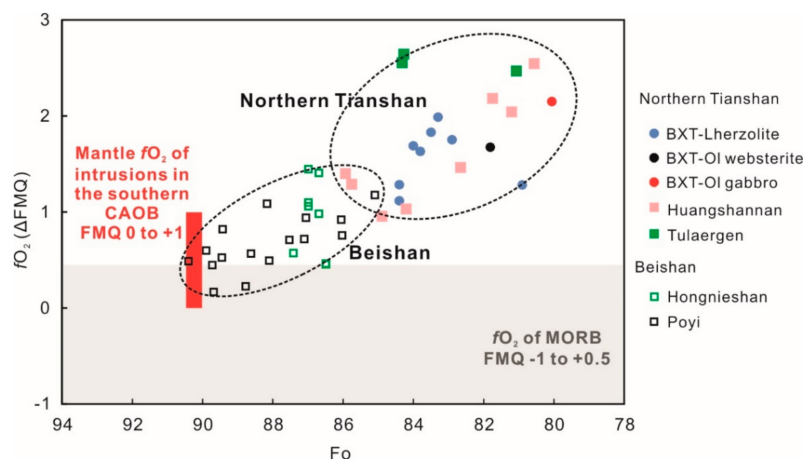
The crystallization temperature and pressure of olivine, pyroxene, and amphibole are also respectively estimated. The initial crystallization temperature of olivine with the highest Mg# value is estimated to be 1309 °C using the empirical formula:  $T (^{\circ}\text{C}) = 1066 + 12.067\text{Mg\#} + 312.3(\text{Mg\#})^2$  [62]. The clinopyroxene has a temperature of 1206 °C and a pressure of 0.62 GPa using the thermobarometer proposed by Thompson [63]. Amphibole in the Baixintan intrusion characterizes low pressure ( $\leq 0.8$  GPa) and relatively high temperature ( $\geq 950$  °C, Figure 7), with the reference of experimentally synthesized amphibole in various temperature–pressure conditions [64].



**Figure 7.** Diagrams of  $\text{Al}^{\text{VI}}\text{-Al}^{\text{IV}}$  (a) and  $\text{Al}^{\text{IV}}\text{-Ti}$  (b) of amphibole in the Baixintan deposit: grey cross symbols are the experimental result of T–P conditions for various compositions of synthesized amphibole [64]. Note: The grey cross symbols are the experimental result of T–P conditions for various compositions of synthesized amphibole.

### 6.2.2. Oxygen Fugacity

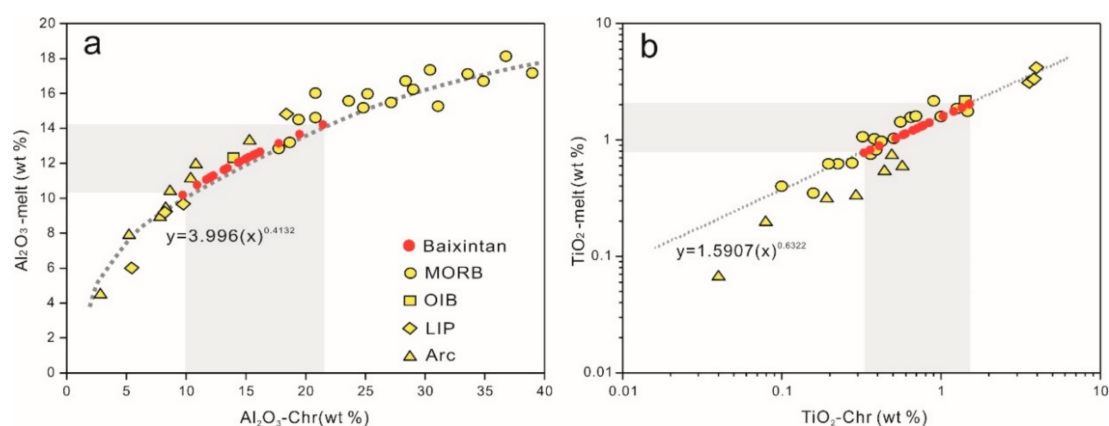
The magma oxygen fugacity corresponding to the olivine–chromite pairs is calculated as FMQ + 1.1 to FMQ + 2.1, with an average of FMQ + 1.6, using the method proposed by Ballhaus et al. [15] (Table S1). The oxygen fugacity exhibits a generally elevated trend with fractionation of magmas. Specifically, the olivine has relatively higher oxygen fugacity (FMQ + 2.1) than lherzolite (FMQ + 1.5) and olivine websterite (FMQ + 1.7). The result is similar to the other mafic-ultramafic intrusions in Northern Tianshan, such as the Tulaergen and Huangshandong intrusions, and higher than those in the Beishan area, for which the parental magma commonly have higher MgO content (Figure 8).



**Figure 8.** The estimated oxygen fugacity verse Fo value for the Baixintan and other magmatic sulfide Ni–Cu deposits in the Northern Tianshan and Beishan. Data sources: MORB [65], the mantle  $fO_2$  of intrusions in the southern CAOB [22], Huangshannan and Tulaergen [22], Poyi [21], and Hongnieshan (unpublished data). MORB: middle ocean ridge basalt.

### 6.2.3. Compositions

The mafic-ultramafic rocks are classified as subalkaline and tholeiite series [29,33]. The MgO content of parental magma can be quantitatively estimated as follows:  $wMgO = 0.561Kd * Fo / (1 - Fo) * wFeO$ , where  $Kd = (Fe/Mg)_{Ol} / (Fe/Mg)_{melt} = 0.3$  [56] and  $wFeO$  is the FeO content of the cumulative lherzolite (unpublished data). The olivine with the highest Fo number (Fo = 85.6) should be used in the calculations [66], and the result is thus calculated to be 11.4 wt% MgO and 11.4 wt% FeO. The MgO content is similar to that of other intrusions in the Northern Tianshan, such as the Tulaergen (12.5 wt% MgO [67]), the Huangshandong (11.7 wt% MgO [44]), and the Hulu (11.0 wt% MgO [68]). For comparison, the parental magma in the Northern Tianshan is lower than that in the Beishan (14.5–15.1 wt% MgO [36]). The linear relationship between the  $Al_2O_3$  and  $TiO_2$  contents of chromite and the melt from which it crystallized provides an effective tool to estimate the  $Al_2O_3$  and  $TiO_2$  content of parental magma [8,9]:  $Al_2O_{3-melt} = 3.996 * (Al_2O_{3-Chr})^{0.4132}$  and  $TiO_{2-melt} = 1.5907 * (TiO_2)^{0.6322}$ . The conjectured melt is characterized by 10.7–14.2 wt%  $Al_2O_3$  (average 12.1 wt%) and 0.8–2.1 wt%  $TiO_2$  (average 1.4 wt%) (Figure 9). The high  $TiO_2$  content is also recognized in the Beishan intrusions, southern CAOB [20,51]. In addition, the hydrous nature of parental magma is indicated by the presence of unaltered magmatic amphibole and phlogopite (Figures 3d and 7b).



**Figure 9.** Estimated composition of the parental melt in equilibrium with chromite from the Baixintan complex: (a) plot of  $\text{Al}_2\text{O}_3$ -melt– $\text{Al}_2\text{O}_3$ -Chr and (b) plot of  $\text{TiO}_2$ -melt– $\text{TiO}_2$ -Chr. The ordinate is the calculated compositions of parental magma. The abscissa is the compositions of chromite. The regression lines and data of MORB, OIB, LIP, and Arc are derived from Kamenetsky et al. [8] and Rollinson [9]. Only primary type I chromite is used in calculations. MORB: middle ocean ridge basalt, OIB: ocean island basalt, IAT: island-arc tholeiite, and LIP: large igneous provinces.

In summary, the parental magma of the Baixintan intrusions is characterized by high temperature (1389 °C), high pressure (3.8 GPa), and high Mg content (11.4 MgO wt%) with oxidized (FMQ + 1.6) and hydrous nature.

### 6.3. Origin of the Complex

#### 6.3.1. Tectonic Setting

The tectonic setting of early Permian mantle-origin rocks in the Northern Tianshan has been a disputed topic. Some research considered that they are the Alaskan-type complexes emplaced in an island-arc environment because of widespread hydrous minerals with no alteration origin and island-arc signature of trace elements [69,70]. However, the presence of orthopyroxene in these complexes in the Northern Tianshan, which is extremely scarce in the Ural-Alaskan-type intrusions [71–73], argues against the Alaskan-type origin. Furthermore, a post-orogenic extensional setting has gained growing recognition in the past several years due to increasing studies of geochronology and metallogeny. The Paleo-Asian ocean subducted southward until later Carboniferous (310 Ma) [74–76], which predates the early Permian mafic-ultramafic complexes (275–285 Ma) in the Northern Tianshan. The arc-related deposits in this area, such as porphyry-type and VMS deposits in this area, mainly formed from Silurian to Carboniferous rather than in Permian [37,39]. Our mineralogical studies in the Baixintan intrusions also give new constraints on the origin and support the post-orogenic extensional setting.

The Cr# of Baixintan chromite (49–66) as well as chromite in other early Permian intrusions in the northern Tianshan and Beishan are significantly lower than that in island arc-related rocks (Cr# 75–90, Figure 5a). Chromite from island-arc tholeiite (IAT) is characterized by low Al content and significant positive relationship between Al and Ti content [8], whereas chromite in early Permian intrusions in Northern Tianshan and Beishan displays a negative relationship and relatively high Al content. Their compositions are mainly plotted in the mid-ocean ridge basalt (MORB) and ocean island basalt (OIB) area rather than in the IAT area (Figure 5d). Clinopyroxene in this area is mainly augite and exhibits a rift cumulate trend, while clinopyroxene in the Alaskan-type complexes is mainly diopside and exhibit an arc cumulate trend (Figure S1). In addition, a non-arc setting is also indicated by plagioclase composition. Plagioclase from early Permian mafic-ultramafic rocks in Northern Tianshan and Beishan has higher CaO and  $\text{Al}_2\text{O}_3$  contents and lower  $\text{SiO}_2$  and alkaline content than that from typical Alaskan-type intrusions (Figure S4).

### 6.3.2. Mantle Source

A depleted mantle source modified by a subducted slab has been indicated by Hf-Sr-Nd-O isotope and trace element geochemistry. Our oxygen fugacity calculation provides new evidence to support the conclusion. The parental magma in the Northern Tianshan is relatively oxidized because its  $fO_2$  value is clearly higher than those of MORBs (FMQ – 1 to FMQ + 0.5 [77]) and the mantle  $fO_2$  of intrusions in the southern CAOB (FMQ – 1 to FMQ + 0.5 [22]), implying incorporation of minor slab-derived oxidized components into the mantle source. The extent of oxidized component involvement in the Northern Tianshan is slightly higher than that in the Beishan (Figure 8). A few chromite samples exhibit subduction signatures, such as plotting in the field of Alaskan-type intrusions and IAT (Figure 5c,d). Chen et al. [28] used the silicate-liquid model pMELTS to simulate magmatic evolution of the adjacent Lubei intrusion, and the result showed that the mantle was hydrous (approximately 0.29 wt %  $H_2O$ ). The hydrous nature may be ascribed to the mantle source having been metasomatized by subduction fluid. The partial melting degree can be estimated by the composition of primary chromite enclosed within olivine according to the formula:  $F = 10 * \ln(Cr\#) + 24$  [5]. The result ranges from 17.0% to 18.9% with average 18.3% and shows a high degree of partial melting.

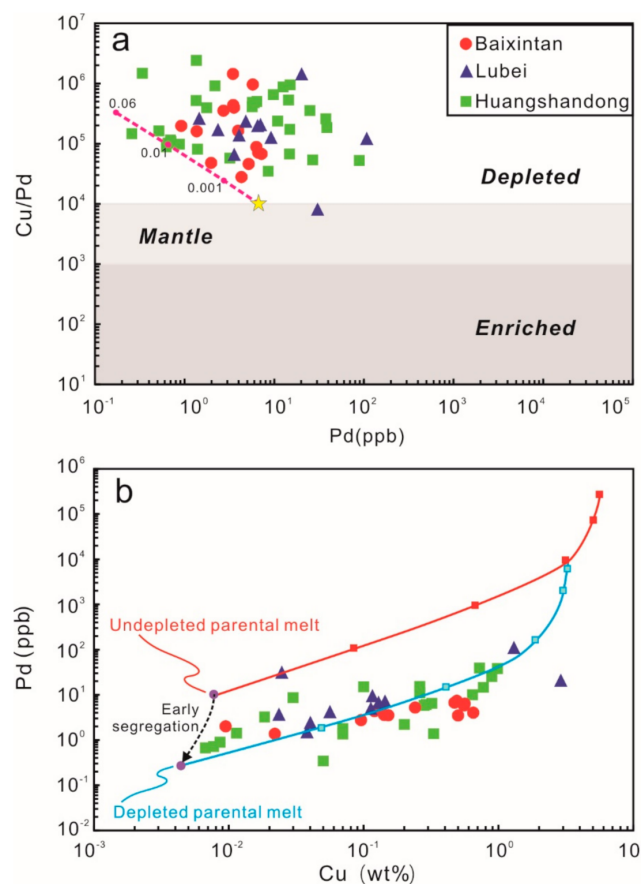
To sum up, the mafic-ultramafic rocks originated from high-degree partial melting of depleted mantle that had been modified by crustal components and metasomatized by subduction fluid in a post-orogenic extensional setting.

### 6.4. Implications for Sulfide Segregation

#### 6.4.1. Early Segregation

High Mg tholeiite magma caused by high-degree mantle partial melting is enriched in the chalcophile element, especially Ni, Cu, and PGE [78,79]. The Baixintan intrusion has a high partial melting degree (18.3%), which is sufficient to eliminate sulfide retention in the mantle source [79]. Besides, the oxidized nature (FMQ + 1.6, Figure 8) could significantly increase the sulfur solubility [22,80]. The parental magma should be enriched in Ni, Cu, and PGE, which are positive factors to form magmatic Ni–Cu–PGE sulfide deposits. However, the mineralization mainly occurs as a disseminated sulfide with a relatively low Ni–Cu tenor, and the PGE is depleted in the sulfide ore [26,29]. Similar PGE depletion had also been confirmed in other Ni–Cu deposits in the Northern Tianshan with a high degree of partial melting and oxidized parental magma (Table S6), and it was considered to be caused by early sulfide segregation at depths.

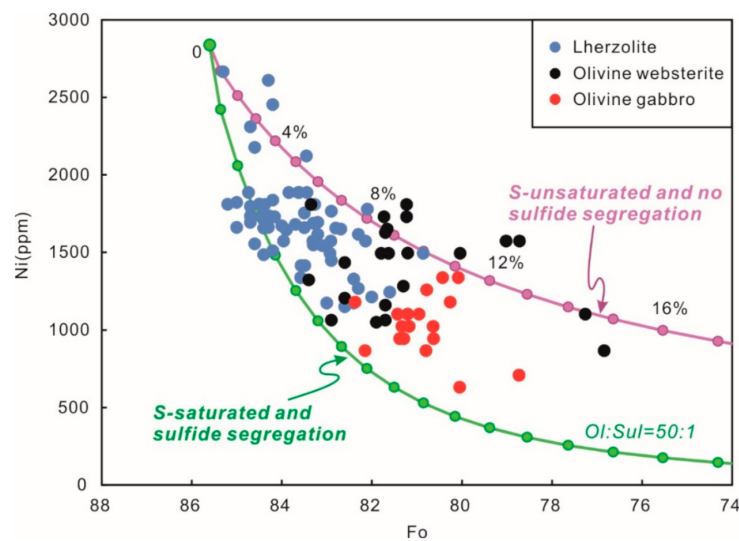
Early segregation could remove a majority of PGE because of their higher partition coefficients between sulfide and silicate ( $10^3$  and  $10^5$ ) than that for Ni (300–1000) and Cu ( $10^2$ – $10^3$ ) [81]. A slightly negative relationship between Cu/Pd and Pd is illustrated by the Baixintan deposits as well as the adjacent Lubei and Huangshandong deposits (Figure 10a), and this may be the effect of early segregation, since the Cu/Pd ratio could increase rapidly when Pd is strongly partitioned into a sulfide liquid during early segregation [82]. The evolution of sulfides formed by early segregation and by PGE-depleted melt is also depicted by the plot of Pd vs. Cu (Figure 10b). Lightfoot et al. [83] illustrated that an assumed initial PGE-undepleted melt of approximately 80 ppm Cu and approximately 10 ppb Pd produced PGE- and Cu-rich sulfide ores (red line). Conversely, sulfides that precipitated from a PGE-depleted melt (approximately 45 ppm Cu and approximately 0.278 ppb Pd) after early segregation would be Cu-rich but PGE-poor (blue trend line). Almost all the sulfide ores plot along the blue trend line, suggesting that they formed from a PGE-depleted melt due to early segregation (Figure 10b). Moreover, the 100% sulfide calculation of PGE in the Baixintan and Lubei deposits suggests that the primary magma underwent 0.007% early sulfide removal at depth and lost much chalcophile content. Then, the sulfide was segregated from PGE-depleted parental magma in a shallow chamber under R factors ( $R$  = silicate/sulfide, mass ratio) of 100 to 800 [29]. Though trigger factors need further study, the early segregation has been widely recognized in the Northern Tianshan [26,29,44,84].



**Figure 10.** Platinum group element (PGE) contents and ratio sulfide ores in the Baixintan and other magmatic sulfide Ni–Cu deposits in the Northern Tianshan, indicating early segregation and PGE-depleted parental magma (after Barnes et al. [82]): (a) plot of Cu/Pd vs. Pd (after Lightfoot et al. [83]). The numbers are sulfide percentages removed from the initial magma system. The yellow star represents the composition of the primitive mantle. (b) Pd vs. Cu. Data sources: Baixintan [26,29], Lubei [29], and Huangshandong [44].

#### 6.4.2. Later Segregation

The later segregation is represented by disseminated sulfide occurring as the interstitial phase between olivine grains (Figure 3e,f), which indicates that sulfide segregation is posterior to olivine crystallization. The Fo–Ni variation during olivine crystallization has been modelled in the Baixintan deposit (Figure 11 and Table S7). As a whole, the Ni content decreased as olivine crystallization. A few olivine samples in lherzolite have high Ni contents (approximately 2500 ppm) and plot along with the S-unsaturated curve, indicating that no sulfide segregation had occurred in the initial crystallization, while most olivine samples plot below the S-unsaturated line, especially for that in mineralized lherzolite and olivine websterite. The calculated result shows that the Ni depletion begun after about 3% olivine crystallization; then, the Ni content significantly dropped to approximately 1900 ppm, and the missing Ni was partitioned into segregated sulfide, which was evidently indicative of later segregation.



**Figure 11.** Model of olivine crystallization showing the variations of Ni content and Fo value in the Baixintan deposit: the detailed modelling principle and process can be seen in Table S7.

#### 6.4.3. Segregation Factors

Limited fractional crystallization could not induce S-oversaturation and sulfide segregation. Factors controlling sulfur content at sulfide saturation (SCSS) mainly consist of temperature, pressure, and magma composition without considering crustal assimilation [85]:

$$\ln(\text{SCSS}) = -1.76 - 0.474(10^4/T) - 0.021P + 5.559X_{\text{FeO}} + 2.565X_{\text{TiO}_2} + 2.709X_{\text{CaO}} - 3.192X_{\text{SiO}_2} + 3.049X_{\text{H}_2\text{O}} \quad (1)$$

The pressure and temperature are almost unchanged during initial limited crystallization and have opposite effects on SCSS. During fractional crystallization from chromite (1389 °C and 3.8 GPa) to amphibole (950 °C and 0.8 GPa), the T–P conditions decreased together, and their contributions on SCSS counteracted each other by the following partial differential equations:

$$\partial(\ln(\text{SCSS}))/\partial(P) = -0.021 \quad (2)$$

$$\partial(\ln(\text{SCSS}))/\partial(T) = 4740 * T^{-2} \quad (3)$$

About 3% olivine crystallization would consume FeO and SiO<sub>2</sub> content (Table S7); similarly, their influences on SCSS also offset each other. Therefore, limited and simple fractional crystallization would not trigger sulfur oversaturation.

The contamination of crustal Si and S components are more important factors for sulfide segregation rather than fractional crystallization. The assimilation had been indicated by trace elements and Hf–O–Sr–Nd isotopic compositions [26,29,30,33]. In addition, the lower Ordovician volcanics are potential source of external S since a series of Cu-polymetallic deposits developed in volcanics, such as the Huangtupo and Huangtan VMS deposits, the Hongshan epithermal deposit, and the Heicaotan volcanic hydrothermal deposit [39]. Though the sulfide in the Baixintan deposit is near zero ( $\delta^{34}\text{S} = -0.7$  to  $+1.1$ ) [22], the sulfide in volcanic strata also displayed a mantle signature and the possibility of incorporation of external S could not be excluded. Furthermore, assimilation of the Si component from southern granitoid is also a positive factor for S oversaturation. The fact is different from Ni deposits in the Beishan, for which immediate country rocks consist marble, and the contamination of CaO would hinder S oversaturation [25]. In addition, the relatively higher oxygen fugacity in Northern Tianshan can dissolve more sulfide than the Beishan (Figure 8). They may be key reasons that the Ni mineralization in Beishan is poorer than that in Northern Tianshan.

## 7. Conclusions

The mineralogical studies of chromite and silicate minerals in the Baixintan magmatic Ni deposit in Northern Tianshan (southern CAOB) have given us the following conclusions:

- (1) Two types of chromite were identified in mafic-ultramafic rocks. Type I chromite occurs as inclusions enclosed in olivine and has a primary and magmatic origin. Type II chromite with an interstitial phase crystallized from a more evolved melt and suffered from post-magmatic alteration.
- (2) The parental magma is characterized by high temperature (1389 °C), high pressure (3.8 Gpa), and high Mg content (11.4 MgO wt%) with oxidized (FMQ + 1.6) and hydrous nature.
- (3) The mafic-ultramafic rocks originated from high-degree partial melting of a depleted mantle that had been modified by crustal components and metasomatized by subduction fluid in a post-orogenic extensional setting.
- (4) Two stages of sulfide segregation have been recognized. The assimilation of crustal Si and S components played more important roles on sulfide segregation rather than fractional crystallization.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2075-163X/10/12/1050/s1>. Figure S1: The composition of pyroxene in the Baixintan deposit: (a) the classification of pyroxene, (b) the plot of Ti vs. (Ca + Na) of clinopyroxene, (c) the plot of Ti vs. total Al of clinopyroxene, and (d) the plot of Al<sub>2</sub> vs. TiO<sub>2</sub> of clinopyroxene. The shadowed area is from Su [24]. Di—Diopside, He—Hedenbergite, Au—Augite, Pi—Pigeonite, ClEn—Clinoenstatite, and ClFs—Clinoferrosilite, Figure S2: Plagioclase classification in the Baixintan deposit, Figure S3: Composition and classification of amphibole in the Baixintan deposit: (a) diagram of Si–Mg/(Mg + Fe<sup>2+</sup>) and (b) diagram of Si–(Na + K). (c) The amphibole has a mantle origin. (d) The amphibole is consistent with that in ultramafic rocks, Figure S4: Plagioclase composition compared with that of arc-related intrusions, modified from Ruan [86], (a) Plot of CaO–SiO<sub>2</sub>; (b) Plot of (Na<sub>2</sub>O+K<sub>2</sub>O)–Al<sub>2</sub>O<sub>3</sub>. Table S1: Chromite compositions, Table S2: Olivine compositions, Table S3: Pyroxene compositions, Table S4: Plagioclase compositions, Table S5: Amphibole compositions, Table S6: PGE compositions in the Baixintan, Lubei, and Huangshandong Ni–Cu deposits, Table S7: Olivine crystallization simulation.

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## References

1. Dharma Rao, C.V.; Santosh, M.; Sajeew, K.; Windley, B.F. Chromite–Silicate Chemistry of the Neoarchean Sittampundi Complex, Southern India: Implications for Subduction-Related Arc Magmatism. *Precambrian Res.* **2013**, *227*, 259–275. [CrossRef]
2. Baumgartner, R.J.; Zaccarini, F.; Garuti, G.; Thalhhammer, O.A.R. Mineralogical and Geochemical Investigation of Layered Chromitites From the Bracco–Gabbro Complex, Ligurian Ophiolite, Italy. *Contrib. Mineral. Petrol.* **2013**, *165*, 477–493. [CrossRef]
3. Irvine, T.N. Chromian Spinel as a Petrogenetic Indicator. Part I Theory. *Can. J. Earth Sci.* **1965**, *2*, 648–672. [CrossRef]
4. Irvine, T.N. Chromian Spinel as a Petrogenetic Indicator. Part II Petrological Applications. *Can. J. Earth Sci.* **1967**, *4*, 71–103. [CrossRef]
5. Dick, H.J.B.; Bullen, T. Chromian Spinel as a Petrogenetic Indicator in Abyssal and Alpine-Type Peridotites and Spatially Associated Lavas. *Contrib. Mineral. Petrol.* **1984**, *86*, 54–76. [CrossRef]
6. Allan, J.F.; Sack, R.O.; Batiza, R. Cr-Rich Spinel as Petrogenetic Indicators; MORB-type Lavas from the Lamont Seamount Chain, Eastern Pacific. *Am. Mineral.* **1988**, *73*, 741–753.

7. Arai, S. Characterization of Spinel Peridotites by Olivine-Spinel Compositional Relationships: Review and Interpretation. *Chem. Geol.* **1994**, *113*, 191–204. [[CrossRef](#)]
8. Kamenetsky, V.S. Factors Controlling Chemistry of Magmatic Spinel: An Empirical Study of Associated Olivine, Cr-Spinel and Melt Inclusions from Primitive Rocks. *J. Petrol.* **2001**, *42*, 655–671. [[CrossRef](#)]
9. Rollinson, H. The Geochemistry of Mantle Chromitites From the Northern Part of the Oman Ophiolite: Inferred Parental Melt Compositions. *Contrib. Mineral. Petrol.* **2008**, *156*, 273–288. [[CrossRef](#)]
10. Lehmann, J. Diffusion Between Olivine and Spinel: Application to Geothermometry. *Earth Planet. Sci. Lett.* **1983**, *64*, 123–138. [[CrossRef](#)]
11. Liermann, H.P.; Ganguly, J.  $\text{Fe}^{2+}$ -Mg Fractionation Between Orthopyroxene and Spinel: Experimental Calibration in the System  $\text{FeO-MgO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-SiO}_2$ , and Applications. *Contrib. Mineral. Petrol.* **2007**, *154*, 491. [[CrossRef](#)]
12. Melluso, L.; de Gennaro, R.; Rocco, I. Compositional Variations of Chromiferous Spinel in Mg-rich Rocks of the Deccan Traps, India. *J. Earth Syst. Sci.* **2010**, *119*, 343–363. [[CrossRef](#)]
13. Merlini, A.; Grieco, G.; Diella, V. Ferritchromite and Chromian-Chlorite Formation in Melange-Hosted Kalkan Chromitite (Southern Urals, Russia). *Am. Mineral.* **2009**, *94*, 1459–1467. [[CrossRef](#)]
14. Kumar, S.P.; Shaikh, A.M.; Patel, S.C.; Sheikh, J.M.; Behera, D.; Pruseth, K.L.; Ravi, S.; Tappe, S. Multi-Stage Magmatic History of Olivine-Leucite Lamproite Dykes From Banganapalle, Dharwar Craton, India: Evidence From Compositional Zoning of Spinel. *Mineral. Petrol.* **2020**. [[CrossRef](#)]
15. Ballhaus, C.; Berry, R.F.; Green, D.H. High Pressure Experimental Calibration of the Olivine-Orthopyroxene-Spinel Oxygen Geobarometer: Implications for the Oxidation of the Mantle. *Contrib. Mineral. Petrol.* **1991**, *107*, 27–40. [[CrossRef](#)]
16. Wan, Z.H.; Coogan, L.A.; Canil, D. Experimental Calibration of Aluminum Partitioning Between Olivine and Spinel as a Geothermometer. *Am. Mineral.* **2008**, *93*, 1142–1147. [[CrossRef](#)]
17. Barnes, S.J.; Tang, Z.L. Chrome Spinels from the Jinchuan Ni-Cu Sulfide Deposit, Gansu Province, People's Republic of China. *Econ. Geol.* **1999**, *94*, 343–356. [[CrossRef](#)]
18. Ryabov, V.V.; Shevko, A.Y.; Gora, M.P. *Trap Magmatism and Ore Formation in the Siberian Noril'sk Region; Modern Approaches in Solid Earth Sciences*; Springer: Dordrecht, The Netherlands, 2014; pp. 223–230.
19. Zhou, M.; Lightfoot, P.C.; Keays, R.R.; Moore, M.L.; Morrison, G.G. Petrogenetic Significance of Chromian Spinels From the Sudbury Igneous Complex, Ontario, Canada. *Can. J. Earth Sci.* **1997**, *34*, 1405. [[CrossRef](#)]
20. Ruan, B.; Yu, Y.; Lv, X.; Feng, J.; Wei, W.; Wu, C.; Wang, H. Occurrence and Mineral Chemistry of Chromite and Related Silicates From the Hongshishan Mafic-Ultramafic Complex, NW China with Petrogenetic Implications. *Mineral. Petrol.* **2017**, *111*, 693–708. [[CrossRef](#)]
21. Cao, Y.; Wang, C.Y.; Wei, B. Magma Oxygen Fugacity of Permian to Triassic Ni-Cu Sulfide-Bearing Mafic-Ultramafic Intrusions in the Central Asian Orogenic Belt, North China. *J. Asian Earth Sci.* **2019**, *173*, 250–262. [[CrossRef](#)]
22. Cao, Y.; Wang, Y.C.; Wei, B. Magma Oxygen Fugacity of Mafic-Ultramafic Intrusions in Convergent Margin Settings: Insights for the Role of Magma Oxidation States on Magmatic Ni-Cu Sulfide Mineralization. *Am. Mineral.* **2020**. [[CrossRef](#)]
23. Qin, K.; Su, B.; Sakyi, P.A.; Tang, D.; Li, X.; Sun, H.; Xiao, Q.; Liu, P. SIMS Zircon U-Pb Geochronology and Sr-Nd Isotopes of Ni-Cu-Bearing Mafic-Ultramafic Intrusions in Eastern Tianshan and Beishan in Correlation with Flood Basalts in Tarim Basin (NW China): Constraints On a Ca. 280 Ma Mantle Plume. *Am. J. Sci.* **2011**, *311*, 237–260. [[CrossRef](#)]
24. Su, B. *Mafic-Ultramafic Intrusions in Beishan and Eastern Tianshan at Southern CAOB: Petrogenesis, Mineralization and Tectonic Implication*; Springer: Berlin/Heidelberg, Germany, 2014; pp. 1–310.
25. Li, W.; Wang, Y.; Qian, B.; Liu, Y.; Han, Y. Discussion on the Formation of Magmatic Cu-Ni-Co Sulfide Deposits in Margin of Tarim Block. *Earth Sci. Front.* **2020**, *27*, 276–293.
26. Feng, Y.; Qian, Z.; Duan, J.; Xu, G.; Ren, M.; Jiang, C. Geochronological and Geochemical Study of the Baixintan Magmatic Ni-Cu Sulphide Deposit: New Implications for the Exploration Potential in the Western Part of the East Tianshan Nickel Belt (NW China). *Ore Geol. Rev.* **2018**, *95*, 366–381. [[CrossRef](#)]
27. Sun, Y.; Wang, J.; Lv, X.; Yu, M.; Long, L. Geochronology, Petrogenesis and Tectonic Implications of the Newly Discovered Cu-Ni Sulfide-Mineralized Yueyawan Gabbroic Complex, Kalatag District, Northwestern Eastern Tianshan, NW China. *Ore Geol. Rev.* **2019**, *109*, 598–614. [[CrossRef](#)]

28. Chen, B.; Yu, J.; Liu, S.; Tian, J. Formation of the Lubei Magmatic Ni–Cu Deposit in a Post-Subduction Setting in East Tianshan, North West China. *Ore Geol. Rev.* **2019**, *104*, 356–372. [[CrossRef](#)]
29. Deng, Y.; Yuan, F.; Hollings, P.; Song, X.; Zhou, T.; Fu, B.; Denyszyn, S.; Zhao, B. Magma Generation and Sulfide Saturation of Permian Mafic-Ultramafic Intrusions From the Western Part of the Northern Tianshan in NW China: Implications for Ni–Cu Mineralization. *Miner. Depos.* **2020**, *55*, 515–534. [[CrossRef](#)]
30. Ren, M. Study on Petrography, Mineralogy and Genesis of Baixintan Cu–Ni Sulfide Deposits in Xinjiang. Master Thesis, Chang'an University, Xi'an, China, 2017.
31. Li, X.; Wang, D.; Zhao, S. The Discovery of Baixintan Magmatic Ni–Cu Sulfide Deposits in Hami Area, Xinjiang. *Xinjiang Geol.* **2014**, *32*, 466–469.
32. Wang, Y.L.; Zhang, Z.W.; You, M.X.; Xin, L.I.; Kan, L.I.; Wang, B.L. Chronological and Geochemical Characteristics of the Baixintan Ni–Cu Deposit in Eastern Tianshan Mountains, Xinjiang, and their Implications for Ni–Cu Mineralization. *Geol. China* **2015**, *42*, 452–467.
33. Zhao, B.; Deng, Y.; Zhou, T.; Yuan, F.; Zhang, D.; Deng, G.; Li, W.; Li, Y. Petrogenesis of the Baixintan Ni–Cu Sulfide-Bearing Mafic-Ultramafic Intrusion, East Tianshan: Evidence From Geochronology, Petrogeochemistry and Sr–Nd Isotope. *Acta Petrol. Sin.* **2018**, *34*, 2733–2753.
34. Jahn, B.; Windley, B.; Natal'in, B.; Dobretsov, N. Phanerozoic Continental Growth in Central Asia. *J. Asian Earth Sci.* **2004**, *23*, 599–603. [[CrossRef](#)]
35. Goldfarb, R.J.; Taylor, R.D.; Collins, G.S.; Goryachev, N.A.; Orlandini, O.F. Phanerozoic Continental Growth and Gold Metallogeny of Asia. *Gondwana Res.* **2014**, *25*, 48–102. [[CrossRef](#)]
36. Ruan, B.; Yu, Y.; Lv, X.; Wu, C.; Liu, X. Sulfide Segregation Mechanism of Magmatic Ni Mineralization in Western Beishan Region, Xinjiang, NW China: Case Study of the Hongshishan Mafic–Ultramafic Complex. *Ore Geol. Rev.* **2020**, *122*, 103503. [[CrossRef](#)]
37. Sun, B.; Ruan, B.; Lv, X.; Tuohan, B.; Ratchford, M.E. Geochronology and Geochemistry of the Igneous Rocks and Ore-Forming Age in the Huangtan AuCu Deposit in the Kalatag District, Eastern Tianshan, NW China: Implications for Petrogenesis, Geodynamic Setting, and Mineralization. *Lithos* **2020**, *368–369*, 105594. [[CrossRef](#)]
38. Xiao, W.J.; Windley, B.F.; Allen, M.B.; Han, C.M. Paleozoic Multiple Accretionary and Collisional Tectonics of the Chinese Tianshan Orogenic Collage. *Gondwana Res.* **2013**, *23*, 1316–1341. [[CrossRef](#)]
39. Deng, X.; Wang, J.; Pirajno, F.; Mao, Q.; Long, L. A Review of Cu-dominant Mineral Systems in the Kalatag District, East Tianshan, China. *Ore Geol. Rev.* **2020**, *117*, 103284. [[CrossRef](#)]
40. Xie, W.; Luo, Z.Y.; Xu, Y.G.; Chen, Y.B.; Ma, Q. Petrogenesis and Geochemistry of the Late Carboniferous Rear-Arc (Or Back-Arc) Pillow Basaltic Lava in the Bogda Mountains, Chinese North Tianshan. *Lithos* **2016**, *244*, 30–42. [[CrossRef](#)]
41. Xie, W.; Xu, Y.; Chen, Y.; Luo, Z.; Hong, L.; Ma, L.; Liu, H. High-Alumina Basalts From the Bogda Mountains Suggest an Arc Setting for Chinese Northern Tianshan During the Late Carboniferous. *Lithos* **2016**, *256*, 165–181. [[CrossRef](#)]
42. Shu, L.; Wang, B.; Zhu, W.; Guo, Z.; Charvet, J.; Zhang, Y. Timing of Initiation of Extension in the Tianshan, Based On Structural, Geochemical and Geochronological Analyses of Bimodal Volcanism and Olistostrome in the Bogda Shan (NW China). *Int. J. Earth Sci.* **2011**, *100*, 1647–1663. [[CrossRef](#)]
43. Song, X.; Chen, L.; Deng, Y.; Xie, W. Syncollisional Tholeiitic Magmatism Induced by Asthenosphere Upwelling Owing to Slab Detachment at the Southern Margin of the Central Asian Orogenic Belt. *J. Geol. Soc.* **2013**, *170*, 941–950. [[CrossRef](#)]
44. Mao, Y.; Qin, K.; Li, C.; Tang, D. A Modified Genetic Model for the Huangshandong Magmatic Sulfide Deposit in the Central Asian Orogenic Belt, Xinjiang, Western China. *Miner. Depos.* **2015**, *50*, 65–82. [[CrossRef](#)]
45. Zhou, M.; Michael Leshner, C.; Yang, Z.; Li, J.; Sun, M. Geochemistry and Petrogenesis of 270 Ma Ni–Cu–(PGE) Sulfide-Bearing Mafic Intrusions in the Huangshan District, Eastern Xinjiang, Northwest China: Implications for the Tectonic Evolution of the Central Asian Orogenic Belt. *Chem. Geol.* **2004**, *209*, 233–257. [[CrossRef](#)]
46. Pirajno, F.; Mao, J.; Zhang, Z.; Zhang, Z.; Chai, F. The Association of Mafic–Ultramafic Intrusions and A-type Magmatism in the Tian Shan and Altay Orogens, NW China: Implications for Geodynamic Evolution and Potential for the Discovery of New Ore Deposits. *J. Asian Earth Sci.* **2008**, *32*, 165–183. [[CrossRef](#)]
47. Zhang, C.; Xu, Y.; Li, Z.; Wang, H.; Ye, H. Diverse Permian Magmatism in the Tarim Block, NW China: Genetically Linked to the Permian Tarim Mantle Plume? *Lithos* **2010**, *119*, 537–552. [[CrossRef](#)]

48. Song, X.; Xie, W.; Deng, Y.; Crawford, A.J.; Zheng, W.; Zhou, G.; Deng, G.; Cheng, S.; Li, J. Slab Break-Off and the Formation of Permian Mafic–Ultramafic Intrusions in Southern Margin of Central Asian Orogenic Belt, Xinjiang, NW China. *Lithos* **2011**, *127*, 128–143. [\[CrossRef\]](#)
49. Droop, G. A General Equation for Estimating Fe<sup>3+</sup> Concentrations in Ferromagnesian Silicates and Oxides from Microprobe Analyses, Using Stoichiometric Criteria. *Mineral. Mag.* **1987**, *51*, 431–435. [\[CrossRef\]](#)
50. Barnes, S.J.; Roeder, P.L. The Range of Spinel Compositions in Terrestrial Mafic and Ultramafic Rocks. *J. Petrol.* **2001**, *42*, 2279–2301. [\[CrossRef\]](#)
51. Wu, J.; Lv, X.; Feng, J.; Wang, H.; Deng, G.; Liu, Y.; Yin, X.; Zhang, W.; Liu, W. Mineralogical Characteristics of Chromite from the Poyi Mafic-Ultramafic Intrusion in Beishan, Xinjiang, and its Geological Significance. *Geotecton. Metallog.* **2018**, *42*, 348–364.
52. Yu, Y. Mineral Chemistry of Chromite and Solid Inclusions in the Beishan and Eastern Tianshan Area, NW China with Petrological and Mineralization Significance. Master Thesis, China University of Geosciences (Wuhan), Wuhan, China, 2017.
53. Barnes, S.J. Chromite in Komatiites. II. Modification During Greenschist to Mid-Amphibolite Facies Metamorphism. *J. Petrol.* **2000**, *41*, 387–409. [\[CrossRef\]](#)
54. Gervilla, F.; Padron-Navarta, J.A.; Kerestedjian, T.; Sergeeva, I.; Gonzalez-Jimenez, J.M.; Fanlo, I. Formation of Ferrian Chromite in Podiform Chromitites From the Golyamo Kamenyane Serpentinite, Eastern Rhodopes, SE Bulgaria: A Two-Stage Process. *Contrib. Mineral. Petrol.* **2012**, *164*, 643–657. [\[CrossRef\]](#)
55. Evans, B.W.; Frost, B.R. Chrome-Spinel in Progressive Metamorphism—A Preliminary Analysis. *Geochim. Cosmochim. Acta* **1975**, *39*, 959–972. [\[CrossRef\]](#)
56. Roeder, P.L.; Emslie, R.F. Olivine-Liquid Equilibrium. *Contrib. Mineral. Petrol.* **1970**, *29*, 275–289. [\[CrossRef\]](#)
57. Scowen, P.A.H.; Roeder, P.L.; Helz, R.T. Reequilibration of Chromite within Kilauea Iki Lava Lake, Hawaii. *Contrib. Mineral. Petrol.* **1991**, *107*, 8–20. [\[CrossRef\]](#)
58. Mekhonoshin, A.S.; Kolotilina, T.B.; Doroshkov, A.A.; Pikiner, E.E. Compositional Variations of Cr-Spinel in High-Mg Intrusions of the Primorsky Ridge (Western Baikal Region, Russia). *Minerals* **2020**, *10*, 608. [\[CrossRef\]](#)
59. Barra, F.; Gervilla, F.; Hernandez, E.; Reich, M.; Padron-Navarta, J.A.; Gonzalez-Jimenez, J.M. Alteration Patterns of Chromian Spinel from La Cabana Peridotite, South-Central Chile. *Mineral. Petrol.* **2014**, *108*, 819–836. [\[CrossRef\]](#)
60. Fabriès, J. Spinel-Olivine Geothermometry in Peridotites from Ultramafic Complexes. *Contrib. Mineral. Petrol.* **1979**, *69*, 329–336. [\[CrossRef\]](#)
61. O'Neill, H.S.C.; Wall, V.J. The Olivine—Orthopyroxene—Spinel Oxygen Geobarometer, the Nickel Precipitation Curve, and the Oxygen Fugacity of the Earth's Upper Mantle. *J. Petrol.* **1987**, *28*, 1169–1191. [\[CrossRef\]](#)
62. Weaver, J.S.; Langmuir, C.H. Calculation of Phase Equilibrium in Mineral-Melt Systems. *Comput. Geosci.* **1990**, *16*, 1–19. [\[CrossRef\]](#)
63. Thompson, R.N. Some High-Pressure Pyroxenes. *Mineral. Mag.* **1974**, *39*, 768–787. [\[CrossRef\]](#)
64. Ernst, W.G.; Liu, J. Experimental Phase-Equilibrium Study of Al- and Ti-contents of Calcic Amphibole in MORB—A Semiquantitative Thermobarometer. *Am. Mineral.* **1998**, *83*, 952–969. [\[CrossRef\]](#)
65. Cottrell, E.; Kelley, K.A. The Oxidation State of Fe in MORB Glasses and the Oxygen Fugacity of the Upper Mantle. *Earth Planet. Sci. Lett.* **2011**, *305*, 270–282. [\[CrossRef\]](#)
66. Li, C.; Ripley, E.M.; Naldrett, A.J. Compositional Variations of Olivine and Sulfur Isotopes in the Noril'sk and Talnakh Intrusions, Siberia: Implications for Ore-Forming Processes in Dynamic Magma Conduits. *Econ. Geol.* **2003**, *98*, 69–86. [\[CrossRef\]](#)
67. Sun, H. Ore-Forming Mechanism in Conduit System and Ore-Bearing Property Evaluation for Mafic-Ultramafic Complex in Eastern Tianshan, Xinjiang. Ph.D. Thesis, University of Chinese Academy of Sciences, Beijing, China, 2009.
68. Tang, D.; Qin, K.; Su, B.; Sakyi, P.A.; Mao, Y.; Xue, S. Petrogenesis and Mineralization of the Hulu Ni-Cu Sulphide Deposit in Xinjiang, NW China: Constraints From Sr-Nd Isotopic and PGE Compositions. *Int. Geol. Rev.* **2014**, *56*, 711–733. [\[CrossRef\]](#)
69. Ao, S.J.; Xiao, W.J.; Han, C.M.; Mao, Q.G.; Zhang, J.E. Geochronology and Geochemistry of Early Permian Mafic-Ultramafic Complexes in the Beishan Area, Xinjiang, NW China: Implications for Late Paleozoic Tectonic Evolution of the Southern Altai. *Gondwana Res.* **2010**, *18*, 466–478. [\[CrossRef\]](#)

70. Han, C.; Xiao, W.; Zhao, G.; Ao, S.; Zhang, J.; Qu, W.; Du, A. In-Situ U–Pb, Hf and Re–Os Isotopic Analyses of the Xiangshan Ni–Cu–Co Deposit in Eastern Tianshan (Xinjiang), Central Asia Orogenic Belt: Constraints on the Timing and Genesis of the Mineralization. *Lithos* **2010**, *120*, 547–562. [\[CrossRef\]](#)
71. Johan, Z. Platinum-Group Minerals from Placers Related to the Nizhni Tagil (Middle Urals, Russia) Uralian-Alaskan-type Ultramafic Complex: Ore-Mineralogy and Study of Silicate Inclusions in (Pt, Fe) Alloys. *Mineral. Petrol.* **2006**, *87*, 1–30. [\[CrossRef\]](#)
72. Krause, J.; Brüggmann, G.E.; Pushkarev, E.V. Accessory and Rock Forming Minerals Monitoring the Evolution of Zoned Mafic–Ultramafic Complexes in the Central Ural Mountains. *Lithos* **2007**, *95*, 19–42. [\[CrossRef\]](#)
73. Cui, M.; Bai, Y.; Luo, Y.; Su, B.; Xiao, Y.; Wang, J.; Pan, Q.; Gao, D. Characteristics, Petrogenesis and Metallogenesis of Alaskan-type Complexes. *Miner. Depos.* **2020**, *39*, 397–418.
74. Mao, J.W.; Pirajno, F.; Zhang, Z.H.; Chai, F.M.; Wu, H.; Chen, S.P.; Cheng, L.S.; Yang, J.M.; Zhang, C.Q. A Review of the Cu–Ni Sulphide Deposits in the Chinese Tianshan and Altay Orogens (Xinjiang Autonomous Region, NW China): Principal Characteristics and Ore-Forming Processes. *J. Asian Earth Sci.* **2008**, *32*, 184–203. [\[CrossRef\]](#)
75. Pirajno, F.; Seltmann, R.; Yang, Y. A Review of Mineral Systems and Associated Tectonic Settings of Northern Xinjiang, NW China. *Geosci. Front.* **2011**, *2*, 157–185. [\[CrossRef\]](#)
76. Xue, S.; Li, C.; Qin, K.; Tang, D. A Non-Plume Model for the Permian Protracted (266–286Ma) Basaltic Magmatism in the Beishan–Tianshan Region, Xinjiang, Western China. *Lithos* **2016**, *256–257*, 243–249. [\[CrossRef\]](#)
77. Wood, B.J.; Bryndzia, L.T.; Johnson, K.E. Mantle Oxidation State and its Relationship to Tectonic Environment and Fluid Speciation. *Science* **1990**, *248*, 337–345. [\[CrossRef\]](#) [\[PubMed\]](#)
78. Naldrett, A.J. From the Mantle to the Bank: The Life of a Ni–Cu–(PGE) Sulfide Deposit. *S. Afr. J. Geol.* **2010**, *113*, 1–32. [\[CrossRef\]](#)
79. Barnes, S.J.; Mungall, J.E.; Maier, W.D. Platinum Group Elements in Mantle Melts and Mantle Samples. *Lithos* **2015**, *232*, 395–417. [\[CrossRef\]](#)
80. Bai, Z.; Zhong, H.; Zhu, W. Redox State of Mantle-Derived Magma and Constraints on the Genesis of Magmatic Deposits. *Acta Petrol. Sin.* **2019**, *35*, 204–214.
81. Barnes, S.; Makovicky, E.; Makovicky, M.; Rose-Hansen, J.; Karup-Moller, S. Partition Coefficients for Ni, Cu, Pd, Pt, Rh, and Ir Between Monosulfide Solid Solution and Sulfide Liquid and the Formation of Compositionally Zoned Ni–Cu Sulfide Bodies by Fractional Crystallization of Sulfide Liquid. *Can. J. Earth Sci.* **1997**, *34*, 366–374. [\[CrossRef\]](#)
82. Barnes, S.J.; Couture, J.F.; Sawyer, E.W.; Bouchaib, C. Nickel–Copper Occurrences in the Belleterre-Angliers Belt of the Pontiac Subprovince and the Use of Cu–Pd Ratios in Interpreting Platinum-Group Element Distributions. *Econ. Geol.* **1993**, *88*, 1402–1418. [\[CrossRef\]](#)
83. Lightfoot, P.C.; Keays, R.R.; Evans-Lamswood, D.; Wheeler, R. S Saturation History of Nain Plutonic Suite Mafic Intrusions: Origin of the Voisey’s Bay Ni–Cu–Co Sulfide Deposit, Labrador, Canada. *Miner. Depos.* **2012**, *47*, 23–50. [\[CrossRef\]](#)
84. Wang, Y.; Lv, X.; Liu, Y. Petrogenesis and Ni–Cu–Co Sulfide Formation of Mafic Enclaves in Tulaergen Mafic-Ultramafic Intrusive Rocks, Eastern Tianshan, Northwest China: Implications for Liquid Immiscibility and Hydrothermal Remobilization of Platinum-Group Elements. *Econ. Geol.* **2018**, *113*, 1795–1816.
85. Li, C.S.; Ripley, E.M. Sulfur Contents at Sulfide-Liquid or Anhydrite Saturation in Silicate Melts: Empirical Equations and Example Applications. *Econ. Geol.* **2009**, *104*, 405–412. [\[CrossRef\]](#)
86. Ruan, B. Diagenesis and Mineralization of the Hongshishan Mafic-Ultramafic Rock Belt, Western Beishan, Xinjiang. PhD. Thesis, China University of Geosciences, Wuhan, China, 2017.

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