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Mineral Chemistry, S-Pb-O Isotopes, and S/Se Ratios of the Niubiziliang Ni-(Cu) Sulfide Deposit in North Qaidam Orogenic Belt, NW China: Constraints on the Parental Magma Composition, Evolution, and Sulfur Saturation Mechanism

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Abstract: The Niubiziliang Ni-(Cu) deposit is the first magmatic Ni-Cu sulfide deposit in the North Qaidam Orogenic Belt (NQOB), NW China, and plays a significant role in geological evolution, Ni-Cu mineralization, and exploration in the NQOB. Here, we report on the mineral chemistry, S-Pb-O isotopes, and S/Se ratios of the mafic-ultramafic complex, which provide insights on the parental magma, evolution, and sulfur saturation mechanism. The Niubiziliang mafic-ultramafic intrusion contains four ore blocks and about ten Ni-(Cu) ore/mineralization bodies. Olivines in Niubiziliang belong to the species of chrysolite with Fo values of 88~89, and the pyroxenes are mainly orthopyroxene (En = $79 \sim 82$) and clinopyroxene (En = $44 \sim 40$). The olivines and some pyroxenes likely crystallized in a magma chamber at a depth of 35.45~36.55 km at a high temperature (1289~1369 °C) and pressure (9.38~9.67 kbar), whereas the Niubiziliang complex formed at a moderate depth (8.13~8.70 km) with a temperature and pressure of 1159~1253 °C and 2.15~2.30 kbar, respectively. The parental magma was considered to be high-Mg picritic basalt with MgO and NiO contents of 14.95~16.58% and 0.053~0.068%, respectively, which indicated high-degree partial melting of the depleted mantle. The mantle-derived primary magma underwent significant fractional crystallization and crustal assimilation and contamination, which was strongly supported by S-Pb-O isotope data and S/Se ratios, resulting in sulfur saturation and sulfide immiscibility in the magma. Crustal assimilation and contamination contributed more to sulfur saturation than fractional crystallization.

Keywords: mineral chemistry; S/Se ratios; crustal contamination; Niubiziliang Ni-(Cu) sulfide deposit; NW China

1. Introduction

The magmatic Cu-Ni-PGE sulfide deposits associated with the mafic-ultramafic complex host major Ni, Cu, Co, and PGE resources, and have significant implications for the evolution of the mantle, magmatism, tectonics, and geodynamic evolution [1]. They are generally characterized by large-scale,



high-grade Ni-Cu-PGE; tractability; and a concentrated distribution. Several world-class Cu-Ni-(PGE) deposits, including Sudbury, Noirl'sk, Bushveld, Jinchuan, Voisey's Bay, Duluth, Thompson, Mt. Keith, Perchenga, and Yilgam deposits, host the majority of global Ni and PGE resources [2–5]. Consequently, metallogenic dynamics, genesis, metallogenic mechanisms, and explorations for magmatic Ni-Cu-PGE deposits, especially world-class deposits, have attracted a large number of researchers [2–10]. The parental magma composition, magmatic evolution, and sulfur saturation mechanism have been longstanding concerns for researchers. Naldrett (1995) proposed three key factors for the genesis of world-class Cu-Ni-PGE deposits [3]: (a) The host magma must become saturated in sulfide and segregated immiscible sulfide; (b) these sulfides must react with a sufficient amount of magma to concentrate chalcophile elements to an economic level; and (c) the sulfides must themselves be concentrated in a restricted locality to constitute an ore body. The author also suggested that the segregation of liquid sulfide, coupled with settling of the sulfide to form rich basal accumulations, was not part of the normal cooling and crystallization of mafic-ultramafic magma; that is to say, the fractional crystallization of magma had little effect on the sulfur saturation. Conversely, the mixing of mafic-ultramafic magma with a felsic contaminant could lower the ability of the resulting hybrid to dissolve sulfides, resulting in immiscibility, which plays a major role in sulfide segregation [10].

Niubiziliang is the first known magmatic Cu-Ni sulfide deposit with economic significance in the North Qaidam Orogenic Belt (NQOB). It is located in the Altun region of the northwestern margin of Qaidam Basin and its geotectonic location is the westernmost segment of the NQOB. The Niubiziliang Ni-(Cu) deposit was discovered by the Qinghai Geological Bureau of Nuclear Industry in 2008, during an investigation of the Cu-Co-Ni-Cr drainage anomaly. Several ore-bearing ultramafic intrusions and 12 Ni-(Cu) ore/mineralization bodies were found in 2009~2010 [11,12], in which a massive Cu-Ni ore was found at depth in the No. II ore block, with an average grade of 0.56% and a maximum of 1.57% Ni, which drove further explorations for Cu-Ni sulfide deposits at the time. The discovery of the Niubiziliang Ni-(Cu) deposit broadened the potential for further exploration, and is also significant in terms of the tectonic, magmatic, and dynamic evolution of the northern margin of Qaidam.

Previous studies on the Niubiziliang Ni-(Cu) deposit have mainly focused on the deposit geology, metallogenic age, deposit genesis, metallotectonic background, nature of the magmatic source area, and magmatic evolution [11–16]. Yu et al. (2019) proposed that the Niubiziliang mafic-ultramafic complex was formed during post-orogenic extension in the middle-late Devonian and that the primary magma originated from the partial melting of the asthenosphere mantle that was previously metasomatized by subduction-related fluids [16]. Ling et al. (2014a and 2014b) considered that the primary magma of the Niubiziliang mafic-ultramafic complex was a tholitic basaltic magma with an MgO content of 10.8%, and that a low degree of partial melting in the mantle source led to the loss of PGE from the magma [13,14]. Presently, researchers generally agree that Niubiziliang is a magmatic Cu-Ni sulfide deposit, which formed in a Devonian extensional environment at the northern margin of Qaidam Massif and that fractional crystallization and crustal contamination took place extensively in the ore-forming process. However, the mineralogy and isotope geochemistry of the Niubiziliang mafic-ultramafic complex are relatively poorly understood, so the primary magma composition, magmatic evolution, sulfide saturation mechanism, and their constraints on mineralization also remain poorly understood. One controversy is that although Ling et al. (2014a) [13] estimated the w_{MeO} of the primary magma in the Niubiziliang complex to be 10.8%, the Fo value of olivine used in the calculation was too low. Our paper attempts to determine the parental magma composition, crystallization conditions, magmatic evolution, sulfur saturation mechanism, and their constraints on mineralization through a systematic study of the mineralogy, O-S-Pb isotope geochemistry, and S/Se ratios in this complex, in order to provide new insights into the metallogenesis of the Niubiziliang Ni-(Cu) sulfide deposit.

2. Regional Geology

The Niubiziliang Ni-(Cu) deposit is located in the northwestern margin of Qaidam Massif and the southern slope of the Altun Mountains, and is also the intersection of the Altun Orogenic Belt (AOB) and the NQOB (Figure 1a). The metallogenic belt in which the Niubiziliang Ni-(Cu) deposit is located belongs to the metallogenic belt of Hercynian iron, copper, lead, zinc, rare earth elements, tungsten, and bismuth. The northwestern margin of the Qaidam Basin is located in an area where multiple geological structures are complex, intersecting, and undergoing multiple tectonic overlaying and transformation. This area has experienced multiple tectonic and magmatic activities, from Archean to Cenozoic, and a large number of geological records provide good information for researching this area. The strata in this area are simple, the tectonic framework is clear, and the magmatism of different ages is very intense, especially the strong extensional background, which provide important tectonic preconditions for mafic-ultramafic magmatism and mineralization. However, the activity of the Altun Tagh fault began in the late Triassic [17], which has had a strong controlling effect on the uplift of the northern boundary of the Qinghai-Tibet Plateau. This occurred later than the formation of the Niubiziliang Ni-(Cu) deposit and belonged to a post-metallogenic fault, which had a destructive effect on this deposit. Therefore, the formation of the Hercynian mafic-ultramafic rocks and Cu-Ni deposits in the northwestern margin of Qaindam Massif was not related to the formation and evolution of the AOB, but was related to the NQOB (Figure 1b).



Figure 1. Structural location map (**a**) and geological sketch map (**b**) of the northern margin of Qaidam Basin (modified after Qian et al. (2015) [15]).

The strata in the study area mainly include Paleoproterozoic Jinshuikou Group, Jurassic Dameigou Formation, Neogene Youshashan Formation, and Quaternary sediment strata. The Jinshuikou Group

is the main stratum in the study area, which can be divided into gneiss formation and marble formation. The Jinshuiou Group in the Niubiziiliang Ni-(Cu) mining area is mainly gneiss formation with NW-SE strike, and the lithology is dominated by Biotite plagiogneiss with some sericite-quartz schist, muscovite-bearing quartzite, and tremolite-bearing marble. The Altun south margin fault, north Qaidam margin fault, and Hongsanhan-Niubiziliang fault formed the regional structural framework of the northwestern margin of Qaidam Massif. At the same time, many ductile shear zones, folds, and joints were formed, which had an important influence on the tectonism and magmatism in this area. The faults can be divided into four groups according to the strike, including a nearly SE direction, NE-SW direction, NW-SE direction, and NS direction. The NE-SW faults are related to the formation of the AOB, while the NW-SE faults are likely related to the formation and evolution of the NQOB. The magmatic rocks in this area are widely distributed, large in scale, and mainly intrusive rocks, with poor volcanic rocks. The intrusive rocks were developed from ultrabasic to acidic with many types of rocks and were mainly formed in the Luliang, Jinning, Hercynian, and Indosinian periods, among which Hercynian and Indosinian acid intrusive rocks represent the most developed. Basic-ultrabasic rocks, including Niubiziliang, Yanchangbeishan, Qaidam gate, western Qaidam gate, and western Qingxinjie Mt. rocks, have mainly been produced as complex or vein-like forms, and are distributed sporadically (Figure 1b). The Cu-Ni mineralization in the study area is almost entirely related to the mafic-ultramafic complex. The most Hercynian diorites, granites, and other intrusive rocks intruded at the strong extensional background after the closure of the northern margin of the Qaidam Massif Ocean (NMQMO), which is consistent with that of the mafic-ultramafic rocks in Niubiziliang [18,19].

3. Deposit Geology

3.1. Mining Area Geology

The strata in the Niubiziliang Ni-(Cu) mining area are dominated by the Paleoproterozoic Jinshuikou Group and Quaternary sedimentary successions (Figure 2). The Jinshuiokou Group is a set of gneiss with intense migmatitization, mainly including biotite plagiogneiss, amphibolite gneiss, and tremolite marble [11]. The Quaternary sediments are mainly composed of sand, gravel, and sand oil.

The faults in the Niubiziliang mining area were all formed during the post-mineralization stage and some of them had a destructive effect on the deposit. According to the orientation, they can be divided into two groups, as follows: The NE–SW and NW–SE trending fault systems. Among these, the F_1 fault has the largest scale and almost runs through the whole mining area. This fault strikes the NE and dips to the NW, whereas the middle of F_1 dips to the SE. This gives the interpretation that the F_1 is a sinistral translational fault with normal fault characteristics [20]. It divides the original ore-hosted ultramafic intrusion into the No. II and III ore blocks (Figure 2). The eastern part of F_1 is covered by the Quaternary sediments, forming a large gully. The normal fault effect of F_1 relatively lowers the No. II ore block in the hanging wall and raises the No. III ore block in the footwall. Due to this, under the same denudation conditions after mineralization, the ore-hosted ultramafic intrusion in the No. III ore block was exposed on the surface and the bottom ore body in the No. II ore block was preserved.

The Niubiziliang mafic-ultramafic complex, which formed in the Devonian period (367 Ma [13], 388~402 Ma [15], and 373~389 Ma [16]), is the metallogenic intrusion of the Niubiziliang Ni-(Cu) sulfide deposit. The rocks from the period tite facies to the gabbro facies are well-developed in this mafic-ultramafic complex, and the harzburgite is the most important ore-hosting rock. Devonian magmatic rocks, mainly including diorite and granite, are the products of magmatic activities after mineralization and have a great influence on the preservation of the deposit [19,21]. Dark inclusions are common in the diorite, the condensation edge of which develops crystalline rings. The monzonitic



granite is widely exposed in the central and northeastern part of the mining area and intruded into the mafic-ultramafic complex, having a very destructive effect on the No. I ore block.

Figure 2. Geological map of the Niubiziliang Ni-(Cu) deposit (modified after Zhao et al. (2012a) [11]).

3.2. Mafic-Ultramafic Intrusions

The Niubiziliang Ni-(Cu) deposit can be divided into four ore blocks according to the location of ultramafic intrusion (Figures 2 and 3), among which the Ni-(Cu) ore bodies are mainly hosted in the No. II and III ultramafic intrusions [20]. Gabbros in this deposit are widely distributed, forming the main part of the complex, and the ultramafic intrusions output in stocks into the gabbro or Jinshuikou Group gneiss. The exposed areas of ultramafic intrusions in the four ore blocks are different and the overall areas are small, mostly ranging between 0.08 and 0.12 km². There are a few banded cumulate gabbros in the No. I ore block and the No. IV ore block is composed of widely distributed gabbros and three small separated outcrops of ultramafic rocks. The ore-hosting ultramafic intrusions in No. II and III ore blocks originally belonged to the same intrusion, which was divided into two isolated intrusions by the F₁ fault. The ultramafic rocks in No. I and IV ore blocks are mainly pyroxenite, websterite, and olivine pyroxenite, whereas the ultramafic rocks in the No. II and III ore blocks are dominated by harzburgite and lherzolite (Figure 3).



Figure 3. Representative field photographs of the Niubiziliang mafic-ultramafic complex. (a) Banded gabbro from the No. I ore block; (b) Ore-bearing ultramafic intrusion from the No. II ore block; (c) Ore-bearing ultramafic intrusion from the No. III ore block; (d) Ultramafic intrusion from the No. IV ore block.

The Niubiziliang ore-forming pluton is a complex which was formed by the multiple emplacement of mafic-ultramafic magmas in the Devonian period [16], and was then intruded by post-metallogenic diorite and granite as dyke or stock. It is inferred that there are two possible shapes of the deep ultramafic intrusion based on a large number of drill holes and magnetic data, as follows: (a) Intruding the gabbros as stock, such as the No. I and IV ore blocks. The ultramafic intrusion in the No. IV ore block is a semi-steep lopolith in space, and the ultramafic rocks on the surface are the outcrops of the lopolith edge. The second is (b) intruding the gabbros or gneiss as a steeply dipping and gentle-lateral-trending apophysis, such as the No. II and III ore blocks. They are controlled by the NW trending fault with striking NW and dipping SW (Figure 4). The shape of the ultramafic intrusion has a strong effect on the location of the ore body. The steeply dipping apophysis usually forms the hanging orebody, while the semi-steep lopolith tends to form the bottom ore body.

600m

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inshuikou Group neiss Diorite

Fracture zone

afic rocks includin rgite, lherzolite

Figure 4. The line 3 section of the No. II ore block in the Niubiziliang Ni-(Cu) deposit (modified after Zhao et al. (2012a) [11]).

3.3. Ni-(Cu) Ore Body and Mineralization

3.3.1. Characteristics of Ni-(Cu) Ore Body

The mineralization in the four ore blocks is quite different. In general, the gabbro is rarely mineralized, with starspot pyrite occurring locally, whereas the ultramafic rocks mainly include starspot, disseminated, sideronitic, and crumby/massive sulfides. Most ultramafic intrusions contain starspot and disseminated sulfides, but their grades of Cu, Ni, and Co are generally low, with no economic value. The amount of sulfide is closely related to the content of olivine, for example, the harzburgite and lherzolite in the No. II and III ore blocks contain more sulfides than pyroxenite and websterite in the No. I and IV ore blocks. The ore body is usually formed by ultramafic rocks with sideronitic or crumby/massive sulfides, with a generally high grade of Cu, Ni, and Co. About 10 ore bodies (including concealed ore bodies) are defined in the No. II and III ore blocks at present, and their characteristics are listed in Table 1. However, there are no ore bodies in the No. I and IV ore blocks, in which ultramafic rocks only contain starspot or disseminated sulfides.

Five ore/mineralization Ni-(Cu) bodies can be found in the No. II ore block, including one Ni-Cu industrial ore body (G-M1), two low-grade ore bodies (D-M1 and D-M2), and two mineralization bodies (M3 and M4). The M1~M3 ore bodies occur in the cracked harzburgite and lherzolite in the

 F_3 fracture zone dipping to S at 72°, in which the hanging wall is ore-bearing harzburgite and the footwall is Jinshuikou Group gneiss (Figure 4). The other five ore/mineralization bodies have the same ore rock, sulfide assemblage, and texture. They are a group of ore bodies of the same type, and their ore rocks are all harzburgite and lherzolite. The G-M1 ore body contains massive ores, whereas the others mainly contain disseminated sulfides. Prryhotite, pentlandite, and chalcopyrite are the main sulfides of the ore bodies, and the more sulfides, the higher the ore grade.

Seven Ni-(Cu) ore/mineralization bodies have been found in the No. III ore block, all of which are concealed ore bodies, including two industrial ore bodies (M7 and G-M10), four low-grade ore bodies (M6, M8, M9, and D-M10), and one mineralization body (M5). The rock core of ZKIII-0801 and ZKIII-1601 in the G-M1 ore body contains many massive ores and has a high content of sulfides, with a maximum value of about 80%.

3.3.2. Sulfides and Ni-(Cu) Mineralization

Pyrrhotite, pentlandite, chalcopyrite, and pyrite are the main sulfides of the Niubiziliang Ni-(Cu) deposit, with minor amounts of violarite, bornite, magnetite, and ilmenite (Figure 5), and there are a few supergene minerals (e.g., malachite, annabergite, and limonite) in the surface. They are often disseminated, while sideronitic and massive sulfides occur locally. Pentlandite usually occurs in the inner or outer margin of pyrrhotite in the form of xenomorphic aggregates, showing a typical exsolution texture and sulfide assemblage in the magmatic Ni-Cu sulfide deposit.

Pyrite is the most widely distributed sulfide in Niubiziliang, with a variable content of 5~20%. It generally has a xenomorphic-hypautomorphic granularity, is vein-like, and is crumby in shape, with a size of 0.05~2.50 mm (Figure 5a). The vein-like pyrites formed in the late stage often cut the early rocks and sulfides.

The pyrrhotite is distributed between the gangue minerals in the form of a xenomorphic or irregular granularity, with a size of 0.02~1.00 mm. It generally coexists with pentlandite and chalcopyrite, and the contact boundary between them is smooth and straight, showing a common symbiotic texture (Figure 5b–d).

Ore Block	Ore Body		Type of Ore Body	Length (m) Thicknes	Thickness (m)	s (m) Occurrence	Mineralization	Ore Grade		
OIC DIOCK							Characteristics	Ni(%)	Cu(%)	Co(%)
Ore block II	M1 G-M1		High-grade industrial ore body	200	1.22~22.6	174°∠72°	It contains massive ores, which mainly includes pyrrhotite, chalcopyrite, and pentlandite with many hydrothermal pyrites as well, and the hosted rocks are mainly harzburgite and lherzaolite.	Max 1.57, average 0.50	Max 0.79, average 0.29	Max 0.079, average 0.030
		D-M1	Low-grade ore body	100	1.18			0.21~0.36, average 0.24	0.19~0.26	0.015~0.029
-	M2		Low-grade ore body	80	1.50	194°∠67°		0.20~0.30, average 0.23	0.11~0.12	0.023~0.025
	M3		Mineralization body		0.92			Average 0.21	Average 0.12	Average 0.016
_		M4	Concealed mineralization body		0.93		The ore-hosted rocks are mainly harzburgite lberzolite	Max 0.33, average 0.29	0.07~0.22	0.014~0.0.019
- Ore block III -	M5		Concealed mineralization body		0.89		and olivine pyroxenite with the major disseminated sulfides	Average 0.32	Average 0.30	Average 0.017
	M6		Concealed ore body	240	0.68~2.15		and locally crumb, sideronitic	Max 0.39, average 0.29	0.06~0.20	0.012~0.018
	M7		Concealed industrial ore body	320	0.39~2.58		amounts pyrrhotites, chalcopyrites, pentlandites and	Max 0.48, average 0.32	0.10~0.36	0.015~0.023
	M8		Concealed ore body	80	0.75~1.16		pyrites, and the higher contents	Max 0.31, average 0.26	0.07~0.14	0.016~0.019
	M9		Concealed ore body	80	6.90		of suinde, the higher ore grade.	Max 0.28, average 0.23	Max 0.32, average 0.22	Max 0.018, average 0.016
	M10	G-M10	Concealed industrial ore body	80	2.33			Max 1.06, average 0.69	0.03~0.36	0.011~0.057
		D-M10	Concealed ore body	80	6.89			Max 0.65, average 0.25	0.04~0.37	0.01~0.032



Figure 5. Representative microphotographs showing the sulfides assemblage and their paragenetic relationship in the Niubiziliang Ni-(Cu) deposit. (a) Ccp+Qz assemblage in the G-M1 ore body; (b) Ccp+Po+Pn assemblage with Mt in the G-M1 ore body; (c) Pn+Po+Ccp assemblage with Mt in the G-M10 ore body; (d) Po+Pn+Ccp assemblage with Mt in the M7 ore body. Ccp, chalcopyrite; Qz, quartz; Pn, pentlandite; Po, pyrrhotite; Mt, magnetite; Py, pyrite.

Pentlandite is the most important Ni-bearing mineral in Niubiziliang and provides the majority of Ni resources. It usually occurs in the inner or outer margin of pyrrhotite in the form of xenomorphic-hypidiomorphic aggregates with a minor hypidiomorphic granularity in gangue minerals, with a size of about 0.1~0.5 mm (Figure 5b–d).

Chalcopyrite in Niubiziliang mainly occurs in the following two forms: (a) Coexisting with pyrite (Figure 5a), and (b) coexisting with pentlandite and pyrrhotite (Figure 5b–d). The former chalcopyrite is mainly hosted in the GM-1 Ni-Cu ore body in disseminated, crumby, or massive forms, whereas the latter is mainly distributed in the remaining Ni-(Cu) ore/mineralization bodies in dissemination, dropwise, or veinlet forms.

The original sulfide ore is the most important ore in the Niubiziliang Ni-(Cu) deposit, with a few oxidized ores. It is generally composed of pyrite, pyrrhotite, chalcopyrite, and pentlandite, and can be divided into disseminated (<20% sulfides), sideronitic (20~40% sulfides), vein-like (10~30% sulfides), crumby (40~60% sulfides), and massive (>60% sulfides) types. The ore texture is mainly a xenomorphic granular texture, xenomorphic intersertal texture, and sideronitic texture, and the disseminated structure, vein structure, and massive structure are the main ore structures in the Niubiziliang deposit. In fact, the formation of different types of ore is closely related to the magma exhibiting variable sulfide melting.

A disseminated ore is usually composed of <20% sulfides, being the main type of ore in Niubiziliang. The sulfides in the disseminated ore are mainly pyrrhotite, pentlandite, and chalcopyrite, with a few pyrites and magnetites (Figure 5c), in which pyrrhotite, pentlandite, and chalcopyrite often coexist.

A disseminated ore becomes a sideronitic ore when the sulfide content reaches 20~40% and sulfides are often filled between the silicate minerals in the form of a xenomorphic assemblage. The sideronitic ore mainly occurs in the M10 Ni-(Cu) ore body, which means that its Ni grade is higher than that of other ore/mineralization bodies.

A crumby and massive ore usually contains >60% sulfides and is mainly hosted in the GM-1 Ni-Cu ore body, which provides the majority of Ni resources of Niubiziliang, with the highest grade of Ni of 1.57%. The GM-1 Ni-Cu ore body contains many pyrites, in addition to the Po + Pn + Ccp assemblage, and chalcopyite is often associated with pyrite (Figure 5a), which is quite different from other ore/mineralization bodies.

3.4. Samples and Petrography

The Niubiziliang mafic-ultramafic complex can be divided into mafic to ultramafic rocks, and is comprised of peridotites, pyroxenites, and gabbros. The gabbro is widely distributed, constituting the main part of the complex, and is then intruded by the peridotite, pyroxenite, and post-mineralization diorite and granite. The probable emplaced sequence of the mafic-ultramafic rocks is gabbro—pyroxenite—peridotite, according to a large number of rock core data. Harzburgite is the most important ore-hosted rock, while the mineralization of gabbro is weak, with a few pyrites occurring locally. The mafic-ultramafic rocks in Niubiziliang mainly contain harzburgite, olivine pyroxenite, lherzolite, olivine websterite, hornblende lherzolite, pyroxenite, websterite, olivine gabbro, melagabbro, bojite, and gabbro (Figure 6).



Figure 6. Representative microphotographs of mafic-ultramafic rocks in the Niubiziliang Ni-(Cu) deposit. (a) Gabbro; (b) Melagabbro; (c) Websterite with sulfides; (d) Olivine pyroxenite; (e) Harzburgite with serpentinization; (f) Harzburgite with sulfides and serpentinization, talcitization. Pl, plagioclase; Cpx, clinopyroxene; Ol, olivine; Opx, orthopyroxene; Sep, serpentine; Hb, hornblende; Sul, sulfide; Tr, tremolite; Px, pyroxene.

The gabbro is gray in color, has a gabbro texture, and is massive, and mainly contains clinopyroxene (40%), plagioclase (55%), and hornblende (5%) (Figure 6a). The plagioclase is euhedral clintheriform, measuring 1.0~1.5 mm, with a weak alteration. The pyroxene is mainly filled between the plagioclases in the form of a xenomorphic-hypidiomorphic granularity, with a size of about 1.0 mm. In addition, there are a few banded gabbros in the No. I ore block, and the pyroxenes and plagiaclases occur in band and alternation, which indicates the in situ fractional crystallization and cumulation of mafic minerals in the diagenic process.

Melagabbro is grayish-black in color, has a gabbro texture, and is massive, and mainly contains pyroxene (70%), plagioclase (25%), and hornblende (5%) (Figure 6b). The pyroxene is mainly clinopyroxene (80%) and xenomorphic-hypidiomorphic granular in shape, with a size of 0.50~2.0 mm. The plagiaclase is often filled between the pyroxene in the form of a xenomorphic-hypidiomorphic granularity, with a size of 0.2~3.0 mm. The plagioclase is euhedral clintheriform, measuring 1.0~1.5 mm, with weak alteration.

The websterite is black in color, has a stacking texture, and is massive, and is mainly composed of orthopyroxene (50%), clinopyroxene (35%), olivine (8%), plagiaclase (5%), and opaque mineral (2%) (Figure 6c). The orthopyroxene (70%) and clinopyroxene are usually xenomorphic-hypidiomorphic granular in shape, with a size of 0.5~1.5 mm, and enclose the olivine. The olivine is rotund in shape and 0.3~1.0 mm in size, with cleavage and high protuberance.

The olivine pyroxenite is black in color, has a granular texture, and is massive, and is mainly composed of pyroxene (50%), olivine (40%), hornblende (5%), and plagioclase (5%) (Figure 6d). The pyroxenes are mainly composed of orthopyroxene (70%) and clinopyroxene (30%), and they have a xenomorphic-hypidiomorphic granularity, with a size of 0.5~1.5 mm. The olivine is rotund in shape and 0.3~1.0 mm in size, with cleavage and high protuberance, and has been serpentinized and talcolized. The hornblende is brownish in color, 0.5~2.0 mm in size, and filled between the pyroxene and olivine grains in the form of xenomorphic granularity.

The harzburgite is black in color, granular, and massive, and is mainly composed of olivine (60%), orthopyroxene (30%), clinopyroxene (5%), and opaque mineral (5%), with strong alteration (Figure 6e,f). The olivine is rotund in shape and 1~2 mm in size, with cleavage and high protuberance, and has been serpentinized and talcolized. The orthopyroxene has a xenomorphic-hypidiomorphic granularity, with a size of 1.5~3.0 mm, and most of it is altered into tremolite and talc. The opaque minerals are mainly pyrrhotite, chalcopyrite, and pentlandite.

4. Analytical Methods

4.1. Electron Microprobe Analysis

A total of eight samples (e.g., harzburgite, websterite, olivine pyroxenite, olivine gabbro, gabbro, and bojite) were selected to conduct the electron microprobe analysis for the main silicate minerals in this study. Eight polished thin sections were analyzed on a JEOL JXA8230 electron probe microanalyzer at the MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences. The operating conditions were executed with an accelerating voltage of 20 kV and a beam current of 20 nA, with a 5 μ m diameter beam size. The spectral lines, standards, and count times that were used and averages of detection limits are listed in Supplementary Materials Table S1, and the EMPA data of olivines, pyroxenes, plagioclases, and hornblendes presented in this paper are all shown in Tables S2–S5.

4.2. Sulfide S-Pb Isotope Analysis

A total of twelve sulfides (i.e., pyrite, pentlandite, and pyrrhotite) were selected from the massive and disseminated ores in the No. II and III ore blocks for S and Pb isotope analyses, and were tested at the Beijing Research Institute of Uranium Geology. A Finnigan MAT 251 mass spectrometer was utilized to analyze the S isotopic compositions and the uncertainty was $\pm 0.2\%$ for $\delta^{34}S_{V-CDT}$. The reported data are relative to Vienna Canon Diablo Troilite (V-CDT) sulfide. As for the Pb-isotopic compositions of sulfides, 50 mg of powder was dissolved in a mixed solution of hydrofluoric and perchloric acid, followed by elution through anion exchange resin, in order to separate Pb. The Pb isotopic compositions were measured on an ISOPROBE-T Thermal Ionization Mass Spectrometer with the NBS SRM 981 standard. The precisions for $^{204}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios were better than 0.005, and the results are listed in Tables 2 and 3.

Sample	Rock Type	Mineralization	Testting Sulfide	δ ³⁴ S(‰)	Reference
	I I a unita unita		Dentlen dite	1 5	
NBZL-11-ZK0801-B1	Harzburgite	Massive ore	Pentlandite	-1.5	
NBZL-II-ZK0801-B11	Lherzolite	Massive ore	Pentlandite	-0.8	
NET III TKOMI POO	Olivine pyrovenite	Discominated and	Pyrrhotite	3.9	This paper
NDZL-III-ZK0001-D20	Onvine pyroxenne	Disseminated ofe	Pyrite	1.4	
NIDZI III ZKOOOI DOI	TAT-1 t:t-	Discontinuitad	Pentlandite	3.7	
NDZL-111-ZK0801-D21	Websterite Disseminated ore		Pyrrhotite	0.7	
NBZL-III-ZK0801-B22	Olivine pyroxenite	Disseminated ore	Pyrrhotite	7.4	
NS-1			Pyrite	-1.4	
NS-2			Pyrite	-1.8	
NS-3			Pyrite	-0.1	
NS-4			Pyrite	-2.8	Ling 2014 [22]
NS-5			Pyrite	-8.4	Ling, 2014 [22]
In-situ 1			Cu-Ni sulfide	9.47	
In-situ 2			Cu-Ni sulfide	6.79	
In-situ 3			Cu-Ni sulfide	0.32	

Table 2. The sulfur isotopes of sulfides from the Niubiziliang mafic-ultramafic complex.

Table 3. The lead isotopes of sulfides from the Niubiziliang mafic-ultramafic complex.

Sample NBZL-II-ZK0801-B11		NBZL-III-ZK0801-B20		NBZL-III-ZK0801-B21	NBZL-III-ZK0801-B22	
Rock Type Harzburgite		Olivine pyroxenite		Websterite	Olivine pyroxenite	
Testing Sulfide	Pentlandite	Pyrrhotite	Pyrite	Pyrrhotite	Pentlandite	
²⁰⁶ Pb/ ²⁰⁴ Pb	21.359	18.153	18.334	17.958	19.574	
²⁰⁷ Pb/ ²⁰⁴ Pb	16.161	15.604	15.655	15.549	15.819	
²⁰⁸ Pb/ ²⁰⁴ Pb	42.379	38.265	38.610	38.363	40.108	
²⁰⁶ Pb/ ²⁰⁷ Pb	1.3216	1.1634	1.1711	1.1549	1.2374	
t(Ma)	-1000	357.8	289.5	432.3	-402.6	
μ	10.65	9.50	9.58	9.42	9.79	
ω	42.73	37.27	38.17	38.29	38.88	
Th/U	3.88	3.80	3.86	3.93	3.84	
V1	250.93	67.09	80.21	64.39	149.05	
V2	180.90	54.51	60.83	42.44	109.59	
$\triangle \alpha$	265.24	75.32	86.05	63.77	159.5	
$\triangle \beta$	55.72	19.34	22.67	15.74	33.38	
$ riangle \gamma$	149.34	37.76	47.12	40.42	87.75	

4.3. Whole-Rock O Isotope Analysis

Four mafic-ultramafic rock samples (i.e., harzburgite and gabbro) were obtained from the No. II and III ore blocks to conduct the O isotopic analysis, and were tested at the Beijing Research Institute of Uranium Geology. The whole-rock samples were reacted with pure bromine pentafluoride at 500~680 °C for 14 h, in order to release the O₂ and impurity under a vacuum condition of 10^{-3} Pa in the sample preparation unit. After this, the impurity components, such as SiF₄ and BrF₃, were separated using the freezing method, the pure O₂ was reacted with graphite at a constant temperature under the condition of 700 °C, and a platinum catalyst was employed to produce CO₂. CO₂ was collected by using the freezing method, and the O isotopic composition of the whole-rock samples was analyzed by MAT253 gas isotopic mass spectrometry. The measurement results are defined as SMOW and marked as $\delta^{18}O_{V-SMOW}$, and the analysis accuracy is better than $\pm 0.2\%$. The reference standard for an oxygen isotope is GBW-04409 and GBW-04410 of quartz, of which $\delta^{18}O$ is 11.11 $\pm 0.06\%$ and $-1.75 \pm 0.08\%$, respectively, and the results are listed in Table 4.

Sample	Rock Type	Mineralization	δ ¹⁸ O _{V-SMOW} (‰)	Reference
NBZL-II-DB-B8	Harzburgite	Disseminated sulfides	7.4	
NBZL-II-DB-B9	Harzburgite	Disseminated sulfides	8.1	This name
NBZL-III-DB-B8	Gabbro	Starspot pyrite locally	6.7	rins paper
NBZL-III-DB-B9	Gabbro	Starspot pyrite locally	7.1	
401-I-G4-2	Harzburgite	Disseminated sulfides	6.6	
401-I-G5	Harzburgite	Disseminated sulfides	5.1	
II 5-14	Gabbro	Starspot pyrite locally	6.8	Ling, 2014 [22]
II 5-15	Gabbro	Starspot pyrite locally	7.8	
II 6-5	Olivine-pyroxene hornblendite	Disseminated sulfides	6.5	

Table 4. The whole-rock oxygen isotopes of the Niubiziliang mafic-ultramafic complex.

5. Results

5.1. Mineral Chemistry

5.1.1. Olivine

The olivine Fo values of the Niubiziliang complex are 88~89, all of which belong to chrysolite Table S2). They are slightly lower than the olivine Fo values of mantle peridotite (Fo = 90.8 [23]) and island arc calc-alkaline basalt (mostly more than 90), and similar to the typical magmatic Cu-Ni sulfide deposits in China, such as Xiarihamu (Fo = 82~88 [24]), Hongqiling (Fo = 83~87 [25]), and Jinchuan (Fo = 84~84; [26]) deposits, but higher than the Fo values (79~84) obtained by Ling et al. (2014a) [3].

5.1.2. Pyroxene

Pyroxene mainly includes orthopyroxene and clinopyroxene (Table S3). The orthopyroxene is mainly distributed in the ultramafic rocks, being an important and symbol mineral of the ore-hosting ultramafic rocks. The En value of the orthopyroxene in Niubiziliang is 79~82, which belongs to clinoenstatite (Figure 7a), and is close to that of Xiarihamu (En = 78~86 [24]).



Figure 7. Wo-En-Fs diagram of pyroxenes (**a**) modified after Morimoto (1988) [27]); Al₂O₃-Na₂O-TiO₂ diagram of pyroxenes (**b**) modified after Qiu and Liao (1996) [28]); Au-Ab-Or diagram of plagioclases (**c**) modified after Parsons (2010) [29]), in the Niubiziliang mafic-ultramafic complex.

The clinopyroxene mainly occurs in gabbro, bojite, and other mafic rocks often coexisting with hornblende, and the websterite and olivine pyroxenite also contain some clinopyroxenes. The clinopyroxenes mainly fall into the augite and diopside in the Wo-En-Fs diagram (Figure 7a) and fall into the tholeiite in the Al₂O₃-Na₂O-TiO₂ diagram (Figure 7b).

5.1.3. Plagioclase

Plagioclase is widely distributed in all kinds of mafic-ultramafic rocks, and mainly falls into the labradorite, with some falling into bytownite and oligoclase, in the An-Ab-Or diagram (Figure 7c and Table S4). The An values for plagiaclase in ultramafic rocks are usually large, and are dominated by

bytownite and labradorite. However, the An values for plagioclase in gabbro vary greatly, and are mainly concentrated at 50~60 (labradorite), with the minority being as low as 10~14 (oligoclase). The An values for plagioclase in ultramafic rocks are generally higher than those of mafic rocks, indicating that the An values of plagioclase are closely related to the degree of basicity of rocks.

5.1.4. Hornblende

The hornblende in the Niubiziliang complex mainly belongs to calcareous hornblende (Table S5). In the classification diagram of Leake et al. (1997) [30], the hornblende of olivine pyroxenite was pargasite, whereas the hornblende of basic rocks (e.g., gabbro, bojite, and melagabbro) was pargasite and tremolite (Figure 8). Hornblendes in olivine pyroxenite all have a mantle origin, while hornblendes from the basic rocks mainly have a crust origin, with some mantle origin, in the diagrams of Al₂O₃-TiO₂ and Si-Al atoms (Figure 9). This could indicate that crustal contamination and the ultrabasic magma and mantle-origin hornblende evolved to the basic magma and crust-origin hornblende due to the addition of crustal felsic components.



Figure 8. Classification diagram of calcium hornblende family in the Niubiziliang mafic-ultramafic complex (modified after Leake et al. (1997) [30]).



Figure 9. Al₂O₃-TiO₂ (**a**) and Si-Al atoms (**b**) diagrams of calcium hornblendes showing the mantle and crust origins, respectively, in the Niubiziliang mafic-ultramafic complex (modified after Jiang and An (1984) [31]).

5.2. S-Pb Isotopes of Sulfide

5.2.1. S Isotopes

The δ^{34} S value of the fifteen sulfides in Niubiziliang is $-8.4 \sim 9.47\%$, with a wide range of variation (Table 2), among which eight samples are $-1.8 \sim 1.4\%$, and thus close to that of the upper mantle (0 ± 2‰ [32]). However, the δ^{34} S values of the remaining seven samples are $-8.4 \sim -2.8\%$ and $3.7 \sim 9.47\%$, which are significantly different from that of the upper mantle.

5.2.2. Pb Isotopes

The values of ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb of the five sulfides are 17.958~21.359, 15.549~16.161, and 38.265~42.379, respectively (Table 3), with a wide range of variation. The discriminant diagrams show that the Pb in Niubiziliang is mainly derived from the orogenic belt, with some upper crust Pb (Figure 10). The Pb isotope of pentlandite in the No. II ore block (falling outside of Figure 10) is quite different from that of the sulfides in the No. III ore block and is abnormal Pb, which could be related to the later hydrothermal activities.



Figure 10. Diagrams of lead isotope of sulfides showing a mixing lead with majority coming from the orogen in the Niubiziliang Ni-(Cu) deposit (modified after Zartman and Doe (1981) [33]). 1, mantle; 2, upper crust; 3, magmatism in subduction zone; 3b, sedimentation in subduction zone; 4, chemically deposition; 5, submarine hot-water; 6, mesometamorphism; 7, hypometamorphism in lower crust; 8, orogen; 9, ancient shale in upper crust; 10, retrometamorphism. (**a**) Coming from the orogen and upper crust; (**b**) Coming from the orogen; (**c**) Coming from the orogen.

5.3. Whole-Rock O Isotopes and S/Se Ratios

5.3.1. O Isotopes

The δ^{18} O value of the four samples employed in this study is 6.7~8.1‰, with a wide range of variation (Table 4), which is close to the data obtained by Ling et al. (2014) [13] (δ^{18} O = 5.1~7.8‰). Therefore, all of the samples have higher values than the δ^{18} O value of the mantle, except for one sample, which is close to the mantle.

5.3.2. S/Se Ratios

The S/Se value of five samples from the Niubiziliang complex is 1864~5890, most of which are higher than that of the mantle (Table 5). One sample is in the mantle region, another is in the S loss region, and those remaining are in the S addition region (Figure 11).

Fable 5. Concentrations of S, Se, and Te from the Niubizilian	g mafic-ul [.]	tramafic com	plex.
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Sample	Rock Type	S(ppm)	Se(ppm)	Te(ppm)	S/Se
NBZL-II-ZK0302-B15	Harzburgite	1845	0.36	0.06	5185
NBZL-II-DB-B14	Gabbro	615	0.33	0.04	1864
NBZL-III-ZK0801-B20	Olivine pyroxenite	1640	0.31	0.04	5230
NBZL-III-ZK0801-B21	Websterite	4100	1.04	0.06	3927
NBZL-III-ZK0801-B22	Olivine pyroxenite	2665	0.45	0.05	5890



Figure 11. Contamination diagram of S-Se showing an extra sulfur adding to the magma in the Niubiziliang Ni-(Cu) deposit (modified after Smith et al. (2016) [34]).

6. Discussion

6.1. Parental Magma

Previous studies have shown that the distribution coefficient of Mg-Fe between peridotite and melt was a relatively stable value, that is, $Kd_{Ol-Melt} = (TFeO/MgO)_{Ol}/(TFeO/MgO_{mag}) = 0.3~0.33$ [35,36]. The MgO/TFeO value of the melt coexisting with olivine in this study was obtained by using the above formula, resulting in a value of 1.37~1.51 (choosing Fo_{max} = 89 for olivine), which was lower than that of the whole-rock geochemistry (MgO/TFeO = 2.36~2.98); selecting the whole-rock geochemistry data from Yu et al. (2019) [16] in the Niubiziliang complex. Therefore, the analyzed results in this study could not represent the coexisting melt components, and there were excess olivines adding to the pre-emplaced magma, implying that the pre-emplaced magma is a derivative magma that has undergone deep olivine crystallization by the parental magma. Meanwhile, the NiO content of olivine (0.10~0.23%) in this study was significantly lower than that of olivine ($\approx 0.4\%$ [24]) crystallized from the primitive basaltic magma, which equilibrated with pyrolite. This indicates that the magma of the Niubiziliang complex is derivative magma from which the parental magma underwent differentiation and resulted in strong NiO depletion. Additionally, all of the samples are located below the curve representing the parental magma composition in the MgO-Fo-FeO^T diagram (Figure 12), which also indicates the addition of extra olivine.



Figure 12. MgO-Fo-FeO diagram of harzburgite showing an excess of olivine adding to the magma in the Niubiziliang Ni-(Cu) deposit (modified after Zhang and Wang (2003) [37]). The MgO value in abscissa takes the mean value of MgO content in the whole-rock geochemistry of the corresponding sample and assumes the distribution coefficient of 0.3.

Therefore, the MgO content of parental magma was estimated to be 16.58% by using the formula of $w_{MgO} = [0.56095 \times \text{Kd} \times \text{Fo}/(1 - \text{Fo})] \times w_{\text{TFeO}}$ (Kd = 0.3, FeO^T = 12.18%, Fo = 89; [35]). Meanwhile,

the MgO and FeO^T contents of the parental magma could also be estimated to be 14.9% and 13.43%, respectively, by using the extrapolation method of MgO-FeO^T (Figure 13a). Therefore, we believe that the MgO content of the parental magma is about 14.95~16.58%, which is higher than the value (MgO = 10.8%) estimated previously by Ling et al. (2014a) [13], and the corresponding FeO^T content is about 13.43~14.89%. The difference mainly reflects the different Fo value of olivine in the samples used in the calculations. The Fo value of olivine in harzburgite samples chosen by Ling et al. (2014a) [13] was 84, which was five lower than in the samples used in this study. It resulted in a low MgO content, a large error in the composition of the parental magma, and a low degree of partial melting of the mantle. The MgO content of parental magma in Niubiziliang is significantly higher than that of Jinchuan (12.6% [38]) and Xiarihamu (12.48% [24] and 12.74% [39]), and the NiO content in it could be estimated to be 0.053~0.068% by using the discrimination diagram of MgO-NiO (Figure 13b). Meanwhile, the Mg[#] value of parental magma was calculated to be 71 by the formula of Mg[#] = 1/(1 + (1 - Fo)/(Kd × Fo)) (Kd = 0.3, Fo = 89), which is close to the Mg[#] value of primary basaltic magma. Therefore, the parental magma of the Niubiziliang complex is considered to be high-Mg picritic basalt, which also suggests high-degree melting of depleted mantle ($\varepsilon_{Hf(t)} = 4.2~10.9$ [16]).



Figure 13. MgO-FeO^T diagrams of extrapolation method for primary magma estimation (**a**) modified after Tao et al. (2002) [40]); MgO-NiO diagram of magma composition in equilibrium with mantle peridotite during fractional crystallization of primary magma (**b**) modified after Sato (1977) [41]), in the Niubiziliang Ni-(Cu) deposit.

6.2. Estimation of Mineral Crystallization Conditions

6.2.1. Olivine

The crystallization temperature of olivine is generally calculated by the geological thermometer formula of $T(^{\circ}C) = 1056.6 + 17.3 \times MgO \pm 26$ [42], where the MgO, here, presents its content in parental magma. Therefore, the crystallization temperature of olivine in Niubiziliang was calculated to be 1289~1369 °C by the geological thermometer formula above. Meanwhile, the CaO content of olivine was low (0~0.35%), indicating a high crystallization pressure [43], that it had crystallized in the magma chamber, and that olivine is frequently surrounded by pyroxene in a round shape to form a poikilitic texture.

6.2.2. Pyroxene

Since orthopyroxene and clinopyroxene widely existed in the Niubiziliang mafic-ultramafic complex, two-pyroxene thermobarometry proposed by Putirka (2008) [44] was very appropriate for estimating their crystallization temperature and pressure. Firstly, we used the T-independent equation of P(kbar) = $-279.8 + 293X_{opx_{Al(VI)}} + 455X_{opx_{Na}} + 299X_{opx_{Cr}} + 519X_{opx_{Fm2}}Si_{2}O_6 - 563X_{opx_{En}} + 371X_{opx_{Di}} + 372\alpha_{opx_{En}} + 1.19/K_f$ to obtain the crystallization pressure of ortho- and clinopyroxene for the two groups, as follows: $1.76\sim2.89$ kbar (average 2.30 kbar) and $9.38\sim9.67$ kbar. The $K_f = X_{opx_{Ca}}/(1 - X_{cpx_{Ca}})$ is as in Mercier et al. (1984) [45]; Fm_2Si_2O_6^{opx} = EnFs^{opx}, X_{opx_{En}} = (X_{opx_{Em}}Si_{2}O_6)(X_{opx_{Mg}}/[X_{opx_{Mg}}])

+ X_{opx_{Mn}} + X_{opx_{Fe}]), X_{opx_{Di}} = (X_{opx_{CaFm}²Si₂O₆)(X_{opx_{Mg}}/[X_{opx_{Mg}} + X_{opx_{Mn}} + X_{opx_{Fe}]); $\alpha_{opx_{En}}$ = (0.5X_{opx_{Mg}}/(X_{opx_{Ca} + 0.5X_{opx_{Mg}} + 0.5X_{opx_{Mg}} + 0.5X_{opx_{Mg}} + X_{opx_{Mn}} + X_{opx_{Na}})) × (0.5X_{opx_{Mg}}/(0.5X_{opx_{Fe}²⁺ + X_{opx_{Fe}³⁺ + X_{opx_{Al}(VI)} + X_{opx_{Ti}} + X_{opx_{Cr}} + 0.5X_{opx_{Mg}})), and here, X_{opx_{Fe}²⁺ = X_{opx_{Fe}} - X_{opx_{Fe}³⁺, where Fe³⁺ was calculated as in Papike et al. (1974) [46], i.e., Fe³⁺ = Al^{IV} + Na - Al^{VI} - Cr - 2Ti. Secondly, their corresponding crystallization depth was calculated to be 6.65~10.92 km (average 8.7 km) and 35.45~36.55 km using the equation d(km) = 100 × P(kbar)/(ρ g), where ρ is 2.7 g/cm³ for the average basement of Jinshuikou Group gneiss. In addition, the Al^{IV}/(Al^{IV} + Al^{VI}) value of clinopyroxene was 0.32~0.78, with an average of 0.56, indicating the relatively low crystallization pressure [47]. This further suggested that clinopyroxene likely crystallized after the magma intruded the existing space and its fractional crystallization was not remarkable. Therefore, we suggest that 6.65~10.92 km could be the invaded depth of the Niubiziliang mafic-ultramafic complex, while 34.45~36.55 km likely presents the depth of the magma chamber. Finally, we calculated the crystallization temperatures of ortho- and clinopyrexene to be 1185~1335 °C, with an average of 1253 °C, by using the thermometer of 10⁴/T(°C) = 11.2 - 1.96ln (X_{cpx_{Enfs}/X_{opx_{Enfs}) - 3.3X_{cpx_{Ca}} - 25.8X_{cpx_{CrCaTs} + 33.2X_{opx_{Mn}} - 23.6X_{opx_{Na}} - 2.08X_{opx_{En}} - 8.33X_{cpx_{Di}} - 0.05P(kbar) [44], which is slightly lower than that of olivine.}}}}}}}}}}}

6.2.3. Hornblende

The thermometer of $T(^{\circ}C) = -151.487 \times Si^* + 2041$ proposed by Ridolfi et al. (2009) [37] is one of the most widely used and precise thermometers for estimating the crystallization temperature of hornblende. Here, $Si^* = Si + Al^{IV}/15 - 2Ti - Al/2 + Ti/1.8 + Fe^{3+}/9 + Fe^{2+}/3.3 + Mg/26 + Ca_B/5 + Na_B/1.3 - Na_A/15 + K_A/2.3$, where cations in this thermometer are calculated using 23 standard oxygen atoms. The crystallization temperature of hornblende, except for tremolite, in Niubiziliang was calculated to be 1098~1234 °C, with an average of 1159 °C. Secondly, we used the calcareous amphibole formula of P(kbar) = 19.209 × $e^{1.438Al(Tot)}/100$ [48], where Al(Tot) = Al^{IV} + Al^{VI}, to estimate the crystallization pressure of hornblende, except for tremolite, resulting in a value of 1.68~2.77 kbar, with an average of 2.15 kbar. Moreover, we also calculated the crystallization depth by applying the physical equation for the gravitational pressure of d(km) = $100 \times P(kbar)/(\rho g)$, where ρ is 2.7 g/cm³ for the average basement of Jinshuikou Group gneiss. Therefore, it could be estimated that the crystallization depth of hornblende in the Niubiziliang complex is about 6.35~10.47 km, with an average of 8.13 km.

According to the crystallization temperature mentioned above, the crystallization sequence of silicate minerals in Niubiziliang is as follows: Olivine→orthopyroxene→clinopyroxene-(plagioclase)→hornblende. This is consistent with the observation results under the microscope, and reflects the mineral crystallization at different temperatures, pressures, and depths. Olivines and some orthopyroxenes first crystallized in the magma chamber at a depth of 35.45~36.55 km, with a pressure and temperature of 9.38~9.67 kbar and 1289~1369 °C, respectively, and they are the optimum mineral for restoring the parental magma. However, most of the silicate minerals crystallized in the existing space at a depth of 8.13~8.70 km, with a pressure and temperature of 2.15~2.30 kbar and 1159~1253 °C, respectively. Finally, the Niubiziliang complex and different kinds of mafic-ultramafic rocks formed through magmatic crystallization and crustal contamination.

6.3. Magmatic Evolution

6.3.1. Fractional Crystallization

Fractional crystallization is a geological process that occurs extensively in the process of mafic-ultramafic diagenesis and mineralization, and mainly takes place in the early stage of magmatic crystallization. Niubiziliang is a representative mafic-ultramafic complex with multiple invasions by magma in NQOB. It has complete lithofacies, diverse rock types, clear lithofacies boundaries, and a high degree of differentiation. Cumulates such as peridotite, pyroxenite, and anorthosite are all formed by the strong fractional crystallization of primitive basaltic magma in the magma chamber. Meanwhile, some banded gabbros in the No. I ore block (Figure 3a) indicate the local and relatively weak fractional

crystallization of magma after invasion. The olivine-encircled texture and interstitial texture were developed in the Niubiziliang complex, which showed that the residual magma between olivine grains formed clinopyroxene to enclose olivine or filled spaces between olivine grains. This is the crystallized result of olivine, which crystallized in the magma chamber at 35.45~36.55 km, and residual magma in the existing space at 8.13~8.70 km.

At the same time, the geochemistry of mafic-ultramafic rocks also shows the significant fractional crystallization in the diagenetic process. The Mg[#] value of ultramafic rocks in Niubiziliang is 81~84 [16], which is higher than that of primary basaltic magma (68~73 [49,50]), suggesting that fractional crystallization occurred at an early stage. Meanwhile, the NiO content of olivine (0.10~0.23%) is significantly lower than that of olivine crystallized by primitive basaltic magma, which is balanced with pyrolite ($\approx 0.4\%$), also supporting magma differentiation and leading to a strong deficit of Ni in the parental magma. SiO₂ correlates negatively with MgO (Figure 14a), and Ni, Co, and Cr show positive correlations with MgO (Figure 14d-f), indicative of the crystallization of olivine, and the strong negative correlation between Al₂O₃, CaO, and MgO reflects the fractional crystallization of plagioclase or clinopyroxene (Figure 14b,c). If the magma has a significant fractional crystallization of clinopyroxene, in general, the CaO/Al₂O₃ value and Mg[#] value show a positive correlation, while the CaO content and CaO/Al₂O₃ value in the magma also decrease accordingly [51]. However, these characteristics are not clear in the Niubiziliang mafic-ultramafic rocks (Figure 14g,h), indicating that the fractional crystallization of clinopyroxene did not dominate the magma evolution. Despite this, the fractional crystallization of clinopyroxene in gabbro is quite obvious, similar to what occurs for olivine and orthopyroxene in ultramafic rocks during magma evolution (Figure 14i). Simkin et al. (1970) [43] suggested that the CaO content typically increased at a faster cooling rate and low pressures during olivine crystallization. However, the low CaO content of olivine (<0.35%) in Niubiziliang suggests a slow rate and high-pressure (about 9.38~9.67 kbar) conditions [52], which is consistent with what was concluded due to the wide variation of the Fo value and Mg[#] of olivine. This further suggests that the magma chamber is deep (about 35.45~36.55 km) and sufficiently differentiates, which is favorable for mineralization.



Figure 14. Geochemical diagrams of the mafic-ultramafic rocks in the Niubiziliang Ni-(Cu) deposit. (a) The negative correlation between MgO and SiO₂; (b) The negative correlation between MgO and Al₂O₃;

- (c) The negative correlation between MgO and CaO; (d) The positive correlation between MgO and Ni;
- (e) The positive correlation between MgO and Co; (f) The positive correlation between MgO and Cr;
- (g) The discrete relationship between $Mg^{\#}$ and CaO/Al_2O_3 ; (h) The discrete relationship between CaO
- and CaO/Al₂O₃; (i) The crystallizations of clinopyroxene and orthopyroxene.

6.3.2. Crustal Assimilation and Contamination

Crustal assimilation and contamination and fractional crystallization typically occur simultaneously during the evolution and emplacement of magma [53], and the crustal assimilation and contamination, which often occur during the formation of a large-scale Ni-Cu deposit, are considered to be some of the key factors in the formation of a magmatic Ni-Cu sulfur deposit (Voisey's Bay [4], Jinchuan [5], Noril'sk [9], and Xiarihamu [54]). First of all, the presence of many xenoliths in the Niubiziliang complex indicates that crustal contamination inevitably occurs during the emplacement of magma. Then, the crustal contamination is not only manifested in the geology, but also usually gives several geochemical fingerprints, such as an increase of SiO₂, K₂O, Rb, Ba, Th, Zr, S, ⁸⁷Sr/⁸⁶Sr, ²⁰⁷Pb/²⁰⁴Pb, δ^{18} O, S/Se, and ¹⁸⁷Os/¹⁸⁸Os, and a decrease of P₂O₅, TiO₂, Ti/Yb, Ce/Pb, and ¹⁴³Nd/¹⁴⁴Nd in magma [55]. The sulfur solubility in magma decreases rapidly with an increase of, for example, SiO₂, CaO, and K₂O contents, which plays a significant role in the sulfur saturation.

The mantle and crust have quite different values of δ^{34} S, δ^{18} O, S/Se, 207 Pb/ 204 Pb, 208 Pb/ 204 Pb, $^{187}Os/^{188}Os$, γ_{Os} , $(^{87}Sr/^{86}Sr)_i$, and $\epsilon_{Nd}(t)$, and therefore, they can be effectively used to judge the crustal assimilation and contamination of magma [56,57]. It is generally believed that the metallogenic materials (e.g., S, Pb, Cu, Ni, Co, O, and Se) of magmatic Ni-Cu sulfide deposits are mostly from the mantle, but they change significantly with great variation if contaminated with crustal compositions. Firstly, the S/Se value of the mantle is about 2850~4350, whereas that of the crust is about 3500~10,000, with a varied δ^{34} S value of $\langle -40 \rangle \rangle 30\%$ [58]. Yamamoto (1976) [59] suggested that the increase of the S/Se value was the result of the assimilation of crustal sulfur, while the decrease was likely related to the desulfurization of hydrothermal fluids. The S/Se value of the Niubiziliang mafic-ultramafic rocks is 1864~5890 (Table 5), among which three samples are notably higher than that of the mantle and fall into the S additional area (Figure 11). Secondly, the δ^{34} S value of the mantle is generally within ±2‰, while δ^{34} S values with a wide range of variation are generally considered to be associated with metamorphism and deposition [21]. The sulfide δ^{34} S value in Niubiziliang is $-8.4 \sim 9.47\%$, with a significantly wide range of variation (Table 2), which indicates a mixture of sulfur with different origins. It is reasonable to attribute the δ^{34} S values of $-1.8 \sim 1.4\%$ to a mantle origin, but not the δ^{34} S values of $-8.4 \sim -2.8\%$ and 3.7~9.47‰. They are significantly different to that of the upper mantle and are considered to be the result of the sulfur having assimilated from the Paleoproterozoic Jinshuikou Group in NQOB. Thirdly, the sulfides in Niubiziliang have a great variability in terms of the Pb isotopic compositions (Table 3), and their values of ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb are 15.549~16.161 and 38.265~42.379, respectively, both of which are higher than that of the mantle (Table 3). Their discriminant diagrams of ²⁰⁶Pb/²⁰⁴Pb vs. 207 Pb/ 204 Pb, 206 Pb/ 204 Pb vs. 208 Pb/ 204 Pb, and $\Delta\beta$ vs. $\Delta\alpha$ show that they were mainly derived from the orogenic belt, with some upper crust Pb (Figure 10), which also provides strong support for crustal contamination. Last but not least, the whole-rock δ^{18} O value of mantle-derived magma is usually modest, at 6.0‰, even with the influence of mantle heterogeneity or magmatic crystallization. It is generally believed that there are two mechanisms for increasing the value of δ^{18} O in mantle-derived magmatic hydrothermal alteration and crustal contamination. The δ^{18} O value of mafic-ultramatic rocks in Niubiziliang is 6.5~8.1‰ (except for one sample of 5.1‰), with a wide range of variation (Table 4), all of which are higher than that of the mantle. Therefore, it is more likely that the high δ^{18} O values of mafic-ultramafic rocks are the result of contamination with the Jinshuikou Group metamorphic rocks, considering that there is no notable hydrothermal alteration in Niubiziliang. In conclusion, they all give strong evidence of crustal assimilation and contamination resulting in greatly elevated S/Se, δ^{34} S, 207 Pb/ 204 Pb, 208 Pb/ 204 Pb, and δ^{18} O values, with a wide range of variation, and play an important role in the sulfur saturation of parental magma in Niubiziliang. Moreover, hornblendes in Niubiziliang have mantle and crust origins, which could indicate crustal contamination, and the ultrabasic magma

and mantle-origin hornblende evolved to the basic magma and crust-origin hornblende due to the addition of crustal felsic components.

However, according to Ling et al. (2014b) [14], the ($^{187}Os/^{188}Os$)_i values of six sulfides were 0.2750~1.0397, with an average of 0.5448, which was notably higher than that of the mantle-associated Kambalda Ni deposit (0.10889 ± 0.00035, [60]), and also higher than that of the crustal contamination-associated Jinchuan (0.279 ± 0.018 [61]) and Huangshandong Ni-Cu deposits (0.25 ± 0.04 [62]). At the same time, the corresponding γ_{Os} values of sulfides are 56~338, which also provide evidence of crustal contamination, because the more crustal contamination there is, the greater the positive γ_{Os} value [62]. In addition, the Niubiziliang complex has higher ($^{87}Sr/^{86}Sr$)_i values (0.704575~0.705090 [13]) than that of DMM (depleted MORB mantle) and MORB, and they fall into the area between DMM and EMII, which also indicates crustal contamination [3,6,11].

6.4. Sulfur Saturation Mechanism

Many investigations have indicated that sulfide liquation led to a sharp loss of Ni content in magma under sulfur saturation, and thus the olivine also showed a loss of Ni [3,9]. In other words, the Ni content of olivine was significantly controlled by sulfide liquation, and the Ni deficit in olivine was determined by the volume ratio of olivine to sulfide, in magma. Therefore, a sharp decrease of the Ni content in olivine was considered to be a symbol of deep sulfide liquation, and the greater the Ni deficit, the more complete the sulfide liquation and the more favorable the conditions for mineralization. The Ni content of olivine in Niubiziliang mafic-ultramafic rocks was 0.08~0.18%, which was lower than the normal content of olivine by 0.25%, indicating that, in the magma, sulfide liquation had occurred before olivine crystallization, leading to a loss of Ni content in olivine. Stanley and Karleen (1978) [63] believed that the Ni of olivine crystallized in S unsaturated magma was positively correlated with MgO; on the contrary, it represented that the S of magma had reached saturation. However, the projection points of olivine exhibit a great dispersion and no linear relationship in the Ni-MgO diagram (Figure 15a). At the same time, all of the samples fall in the region of sulfide liquation in the Fo-NiO diagram (Figure 15b) and both indicate that sulfide liquation occurred in the magma when the olivine crystallized, leading to the NiO deficit in the olivine.



Figure 15. Diagrams of olivine. (**a**) Ni-MgO showing the discrete relationship between Ni and MgO; (**b**) Fo-NiO showing the sulfide liquation.

The factors affecting the sulfur solubility in magma mainly include the temperature, pressure, oxygen fugacity, sulfur fugacity, and FeO content [2,64], among which the solubility of sulfur in magma is negatively correlated with the pressure, but positively correlated with the temperature [8,65,66]. However, the temperature has little influence on the sulfur solubility compared with the pressure; that is, even if the sulfur in the mantle source is saturated, it remains unsaturated after invading the crust [3]. Therefore, the sulfur in magma tends to be unsaturated, with a decrease of pressure during the rising process of magma, and sulfur in magma has difficulty reaching saturation and forming an Ni-Cu deposit if there is no interference from external factors. A key factor in the formation of magmatic

sulfide deposits is the saturation of sulfur in magma, causing immiscibility between the silicate magma and sulfides, and enrichment in chalcophile elements in the sulfide melt [3]. Sulfur saturation in magma can generally be achieved by any combination of the following processes: (a) Rapid cooling, such as the sulfides at the bottom of the Bushveld complex [67]; (b) magma mixing, such as the Merensky Reef in Bushveld [68]; (c) fractional crystallization, such as the sulfides in chromitites in Bushveld, and the Hongqiling, Huangshan, and Kalatongke deposits [6]; (d) the addition of external sulfur, such as the Voisey's Bay, Duluth, Tianyu, and Baishiquan deposits [7]; and (e) the addition of crustal compositions, such as the Noril'sk, Huangshannan, and Kalatongke deposits [9]. It should be pointed out that the addition of external sulfur and crustal compositions are attributed to the crustal assimilation and contamination, which play a key role in Ni-Cu sulfide deposit formation and often occur during the formation of large-super large Ni-Cu deposits (Voisey's Bay [4], Jinchuan [5], Noril'sk [9], and Xiarihamu [54]).

There could be one or several sulfur saturation mechanisms for the Niubiziliang Ni-Cu deposit. First of all, the low CaO content of olivine (<0.01%) and sufficient differentiation of lithofacies suggest that the magma is crystallizing at a slow rate and higher pressures. In other words, the rate of magma temperature decline is low, which suggests that the rapid cooling of the magma has a limited role in S saturation. Secondly, there is no magmatic inclusion of other constituents found in the Niubiziliang mafic-ultramafic complex, which implies a low probability of magma mixing for S saturation. Thirdly, as previously mentioned, the complete lithofacies of complex and discrimination diagrams suggest the intense fractional crystallization of magma. They lead to the crystallization of large amounts of mafites (e.g., ilmenite, magnetite, olivine, and pyroxene), which alters the magma composition, in particular, rapidly bringing down the FeO content, resulting in a decrease in the sulfur solubility. Therefore, fractional crystallization is considered to be one of the factors in S saturation in the Niubiziliang Ni-Cu deposit. Last but not least, the crustal assimilation and contamination in Niubiziliang determine the S saturation in at least three ways, as follows: (a) Absorbing the sulfur in Jinshuikou Group and increasing the S concentration in magma supported by the S/Se and δ^{34} S values; (b) altering the composition of magma and decreasing the solubility of sulfur in magma, such as the increase of SiO_2 , K_2O_1 , Al_2O_3 , and CaO content; and (c) enhancing the f_{O2} of magma, resulting in a decrease of the sulfur solubility supported by the δ^{18} O values. Therefore, we conclude that the fractional crystallization of magma and crustal assimilation and contamination are the main mechanisms of sulfur saturation in the parental magma of the Niubiziliang Ni-Cu deposit. However, the effect of crustal assimilation and contamination on sulfur saturation is much greater than that of fractional crystallization.

As the primary magma evolved, the fractional crystallization of olivine and pyroxene, together with crustal assimilation and contamination, caused sulfur saturation and strong sulfide immiscibility. Therefore, the parental magma differentiated into a series of magma with various sulfide melting in the magma chamber at a depth of 35.45~36.55 km, including barren, ore-bearing, ore-rich, and ore magma. Then, these magmas were emplaced in multiple stages under the geo-background of continuous extension during the middle-late Devonian in NQOB, and the Niubiziliang mafic-ultramafic complex with Ni-Cu mineralization finally formed in the existing space at a depth of 8.13~8.70 km.

7. Conclusions

(1) The parental magma of the Niubiziliang complex is considered to be high-Mg picritic basalt, with MgO and NiO contents of 14.95~16.58% and 0.053~0.068%, respectively, indicating a high degree of partial melting of the depleted mantle.

(2) The Niubiziliang complex formed at a moderate depth (8.13~8.70 km) with the temperature and pressure of 1159~1253 °C and 2.15~2.30 kbar, respectively, and the crystallization sequence of the main silicate minerals is olivine \rightarrow pyroxene-(plagioclase) \rightarrow hornblende, which is consistent with the observation made under the microscope. However, the olivines and some pyroxenes likely crystallized in the magma chamber at a depth of 35.45~36.55 km, with a high temperature (1289~1369 °C) and pressure (9.38~9.67 kbar).

(3) The primary magma of Niubiziliang underwent significant fractional crystallization and crustal assimilation and contamination, which resulted in sulfur saturation and sulfide immiscibility in the magma. However, the contribution of crustal assimilation and contamination to sulfur saturation is much greater than that of fractional crystallization.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/10/10/837/s1, Table S1: The spectral lines, standards and count times that were used and average of detection limits of electron microprobe analysis, Table S2: Electron microprobe analyses (wt%) of olivine from the Niubiziliang mafic-ultramafic complex, Table S3: Electron microprobe analyses (wt%) of plagioclase from the Niubiziliang mafic-ultramafic complex, Table S4: Electron microprobe analyses (wt%) of plagioclase from the Niubiziliang mafic-ultramafic complex, Table S5: Electron microprobe analyses (wt%) of hornblende from the Niubiziliang mafic-ultramafic complex, Table S5: Electron microprobe analyses (wt%) of hornblende from the Niubiziliang mafic-ultramafic complex.

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