Geochronology, Geochemistry and Sr-Nd-Pb-Hf Isotopes of No. I Complex from the Shitoukengde Ni–Cu Sulfide Deposit in the Eastern Kunlun Orogen, Western China: Implications for the Magmatic Source, Geodynamic Setting and Genesis

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Abstract: The Shitoukengde Ni-Cu deposit, located in the Eastern Kunlun Orogen, comprises three mafic-ultramafic complexes, with the No. I complex hosting six Ni-Cu orebodies found recently. The deposit is hosted in the small ultramafic bodies intruding Proterozoic metamorphic rocks. Complexes at Shitoukengde contain all kinds of mafic-ultramafic rocks, and olivine websterite and pyroxene peridotite are the most important Ni-Cu-hosted rocks. Zircon U-Pb dating suggests that the Shitoukengde Ni-Cu deposit formed in late Silurian (426–422 Ma), and their zircons have $\varepsilon_{\rm Hf}(t)$ values of -9.4 to 5.9 with the older T_{DM1} ages (0.80–1.42 Ga). Mafic-ultramafic rocks from the No. I complex show the similar rare earth and trace element patterns, which are enriched in light rare earth elements and large ion lithophile elements (e.g., K, Rb, Th) and depleted in heavy rare earth elements and high field strength elements (e.g., Ta, Nb, Zr, Ti). Sulfides from the deposit have the slightly higher δ^{34} S values of 1.9–4.3‰ than the mantle $(0 \pm 2\%)$. The major and trace element characteristics, and Sr-Nd-Pb and Hf, S isotopes indicate that their parental magmas originated from a metasomatised, asthenospheric mantle source which had previously been modified by subduction-related fluids, and experienced significant crustal contamination both in the magma chamber and during ascent triggering S oversaturation by addition of S and Si, that resulted in the deposition and enrichment of sulfides. Combined with the tectonic evolution, we suggest that the Shitoukengde Ni-Cu deposit formed in the post-collisional, extensional regime related to the subducted oceanic slab break-off after the Wanbaogou oceanic basalt plateau collaged northward to the Qaidam Block in late Silurian.

Key words: Sr-Nd-Pb-Hf isotopes, crustal contamination, oceanic slab break-off, post-collisional extension, Shitoukengde Ni-Cu deposit, Eastern Kunlun Orogen

1 Introduction

Many magmatic Ni–Cu sulfide deposits associated with small-scale (~1 km²) ultramafic intrusion in orogenic belt have been discovered in Xinjiang Province (Huangshan, Wang Chongyi et al., 1986; Huangshandong, Ni Zhiyao, 1991; Kelatongke, Zhang Zhaochong et al., 2003; Zhang et al., 2009a; Tulaergen, Sun He et al., 2006; Jiao Jiangang et al., 2012; Fu Piaoer et al., 2012; Huangshannan, Zhao Yun et al., 2016), Qinghai Province (Xiarihamu; Li Shijin et al., 2012; Wang Guan et al., 2014a; Peng et al., 2016)

and Jilin Province (Hongqiling; Lu Linsu et al., 2012; Wei et al., 2013) of China, and they have been the focus of several studies in recent years. Such deposits typically form from pulses of magma injection and are extensively mineralized. Tang Zhongli et al. (1991) suggested that several such small intrusions combine to form large deposits, and tectonic models have been proposed for the formation of magmatic Ni–Cu sulfide deposits in China (Tang Zhongli et al., 1991, 2006, 2007).

The Eastern Kunlun Orogen (EKO) hosts abundant mafic–ultramafic complexes, containing Ni, Cu, and Co economic mineralization, and Silurian-Devonian has been

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the most significant Ni-Cu metallogenic period, including the Shitoukengde (424 Ma; Zhou Wei et al., 2015), Maxingdawannan, Binggounan, Akechukesai, and Langmuri ore spots/deposits, particularly the recently discovered Xiariham large-scale Ni-Cu deposit (394-439 Ma; Wang Guan et al., 2014a; Jiang Changyi et al., 2015; Li et al., 2015; Peng et al., 2016; Song et al., 2016). Increased Ni-Cu exploration in the EKO, stream sediment surveys in Shitoukengde area performed by the Sichuan Bureau of Geology and Mineral Exploration in 2013, led to the discovery of Ni-Cu-hosted complexes of the Shitoukengde, with initial grades of 903 t Cu, 68,943 t Ni, and 3309 t Co recently. Drilling programs conducted 2014-2015 intersected six Ni-Cu-bearing during orebodies that have yet to be thoroughly studied (Zhou Wei et al., 2015, 2016) owing to its new discovery. Although the Silurian-Devonian Ni-Cu metallogenic events have been thoroughly studied on ore-forming time, genesis, magmatic source and evolution (Li Shijin et al., 2012; Wang Guan et al., 2014a; Jiang Changyi et al., 2015; Li et al., 2015; Zhou Wei et al., 2015, 2016; Peng et al., 2016; Song et al., 2016), there is still a debate on the geodynamic setting. Same researchers considered that Xiarihamu complexes formed in the island-arc background related to the subduction of Proto-Thetys Oceanic plate (Jiang Changyi et al., 2015; Li et al., 2015), while others suggested the post-collisional, extensional setting after Proto-Thetys Ocean closed (Li Shijin et al., 2012; Wang Guan et al., 2014a; Peng et al., 2016). This study presents the results of zircon U-Pb dating and Hf isotopes as well as whole-rock geochemical, Sr-Nd-Pb and sulfide S isotopic analyses of the Shitoukengde Ni-Cu deposit to discusses the timing of mafic-ultramafic magmatism, magmatic sources, ore genesis, tectonic setting and geodynamic process.

2 Regional Geological Setting

The Eastern Kunlun Orogen is located in the western segment of the Central Orogenic Belt in mainland China (Fig. 1a), which is bordered by the Qaidam Block (QDB) to the north and the Bayan Har-Songanganzi Terrane (BHSG) to the south. The Eastern Kunlun metallogenic belt trends E–W and is ~1500 km long and 50–200 km wide. Its northern and southern parts differ significantly in terms of basement and geological characteristics, and they are separated by the Middle Kunlun Fault. Sun Fengyue et al. (2009) considered the EKO to be a continental marginal orogen resulted from the Wanbaogou oceanic basalt plateau (OBP), as a "soft basement", collaged northward to the Qaidam Block, and records multiple stages of orogeny. Several belts are divided by the E-W-

trending regional faults from north to south: the Caledonian back-arc rift belt of north Eastern Kunlun (CBNK), the basement uplifting and granite belt of middle Eastern Kunlun (BGMK), the composite collage belt of south Eastern Kunlun (CCSK), the Anyemaqen Suture Belt (ASB) and the Northern Bayan Har Orogen (NBHO) (Sun Fengyue et al., 2009; Fig. 1b). The CBNK and BGMK, located north of the Middle Kunlun Fault, have a crystalline basement composed of the Paleoproterozoic Jinshuikou Group, whereas the CCSK is a complex comprising a Meso–Neoproterozoic oceanic basalt plateau and a continental collage belt.

The Shitoukengde Ni-Cu deposit, located in the town of Zongjia, Dunlan County, Qinghai Province, China (96°07' 04"-96°14'31"E, 35°54'21"-35°58'18"N), formed in the BGMK, near the Middle Kunlun Fault (Fig. 1c). The regional strata are dominated by Proterozoic, Triassic, minor Jurassic, and Tertiary sedimentary rocks (Fig. 1c), and they are mainly biotite-plagioclase gneisses, dolomite quartz schists, and diopside marbles of Paleoproterozoic Jinshuikou Group, as well as intermediate volcanics, carbonates, and sandstones of Meso-Neoproterozoic Wanbaogou Group. The widespread magmatic suite comprises Cu-Ni-bearing Silurian-Devonian maficultramafic intrusions, and abundant Triassic granites. The study area is crossed by the E-W-trending North Kunlun, Middle Kunlun, and South Kunlun regional faults. In addition, several secondary NW-WNW-trending faults associated with sinistral rotation and compressive shearing have controlled the locations of Triassic hydrothermal vein deposits in the area.

3 Geological Setting of the Shitoukengde Deposit

The country rocks of Shitoukengde deposit are mainly Paleoproterozoic Jinshuikou Group and Meso-Neoproterozoic Wanbaogou Group metamorphic rocks. The Jinshuikou Group, comprising amphibole-plagioclase and biotite-plagioclase gneisses, diopside marble, and quartzite, hosts the No. I and II complexes. However, the No. III complex intrudes the Meso-Neoproterozoic Wanbaogou Group, including carbonatite with minor tuffaceous slate and limestone in the southern part of the deposit. Minor volcanic and clastic rocks of the Late Triassic Babaoshan Formation, and Quaternary sediments occur locally. The N-S-trending Haideguole-Laren and Wenlengsi-Dawagie faults, forming part of the Middle Kunlun structure, cross-cut the Shitoukengde deposit, together with NW-SE- and NE-SW-trending secondary faults. Mineralized mafic-ultramafic intrusives of the Laren Complex and intermediate-acidic plutons are

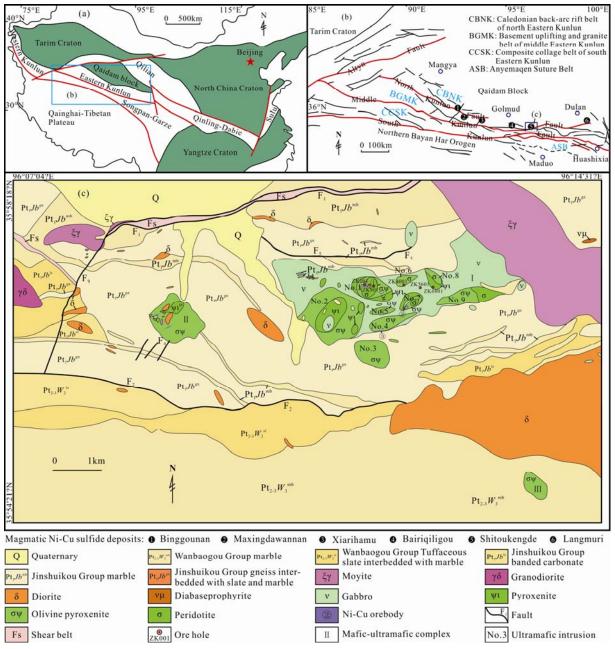


Fig. 1. Geological map showing (a, b) the regional structure of the eastern Kunlun Orogenic Belt, and (c) geology of the Shitoukengde Cu–Ni deposit (modified from Zhou et al., 2016).

oriented E–W in the study area (Fig. 1c). Meanwhile, there are some moyite, granodiorite, diorite, quartz diorite and diabase prophyrite present in the eastern of Shitoukengde (Fig. 1c).

The Shitoukengde deposit contains three maficultramafic complexes that intruded the Proterozoic strata, and the No. I complex is the main host of the Ni-Cu mineralization (Fig. 1c). Economic Ni–Cu sulfide ores have also been discovered in the No. I complex, where evidence of strong mineralization has been obtained from trench and drill-core samples collected during recent prospecting work. As the two other complexes do not show any significant mineralization, so mainly complex I is discussed here. The No. I mafic-ultramafic complex, the largest complex in this deposit, is located in the northeast part of the ore district, strikes approximately E-W, and is elongate. It is 3.8-4.6 km long and 0.6-1.2 km wide with an exposed area about 5.2 km². A few marble xenoliths were residual in No. I complex. This complex is composed gabbro. gabbronorite. websterite, mainly of orthopyroxenite, lherzolite, peridotite, pyroxene peridotite and olivine websterite, and olivine websterite and pyroxene peridotite are the most important Ni-Cu-hosted rocks. Field relationships show that the gabbro emplaced

earliest and is most extensive, followed by the pyroxenite and peridotite. Many small ultramafic intrusions, hosted the most significant Ni-Cu mineralization, intruded the older gabbroic and metamorphic rocks (Fig. 1c). In this study, we have further subdivided the No. I complex into nine stocks, namely No. 1–No. 9 in Figure 1b.

Six Ni-Cu-bearing orebodies have been identified in the No. I complex (No. 1)-6), of which No. 1) and No. 4) are the largest). The No. (1) orebody consists of mediumto coarse-grained pyroxenites and olivine websterite comprising disseminated, conglomeration and massive sulfide ores. It is 235 m long, 20-30 m wide, strikes at 075° and dips at 80° to the NW (Fig. 2). Annabergites are commonly observed on the weathered surfaces of this ore body, and assemblage of pentlandite, pyrrhotine and chalcopyrite is hosted in fresh ores. A total of 21 samples were collected and analyzed from the TC004 and TC005, averaging 1.27% Ni over 28.34 m. A total of 22 samples were collected and analyzed from BT0201, averaging 1.09% Ni over 30.81 m. Meanwhile, the No. (4) ore body is concealed Ni-Cu orebody, containing medium-grained pyroxenites and medium- to fine-grained olivine pyroxenites with disseminated, conglomeration and massive sulfide ores. Boreholes ZK4001 and ZK5601 contain 0.2%-0.6% Ni over 120.75 m, and borehole ZK6801 contains 0.2%-0.41% Ni over 50.97 m (Fig. 2).

No. 2 orebody: a Ni-Cu orebody, about 2.7 m wide,

strikes at 10° - 30° and dips at 50° - 75° to the SE. Mediumgrained olivine pyroxenolite is the Ni-Cu-hosted rock with the average grade of Ni 0.37%.

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No. ③ orebody: a Ni-Cu orebody, about 2.0 m wide, strikes near E-W, inclination and dip are not clear. Medium-grained olivine pyroxenolite is the Ni-Cu-hosted rock with the average grade of Ni 0.22%.

No. (5) orebody: a concealed Ni-Cu orebody, about 4.5 m wide. Medium- to fine-grained olivine pyroxenolite is the Ni-Cu-hosted rock with the grade of Ni 0.20%-0.63%.

No. (6) orebody: a concealed Ni-Cu orebody, about 6.0 m wide. Medium- to fine-grained olivine pyroxenolite and peridotite are the Ni-Cu-hosted rock with the grade of Ni 0.20%-0.37%.

In general, the deposit has a weakly post-magmatic hydrothermal alteration with a few serpentines, tremolites and chlorites. Sulfides in the deposit contain the primary magmaitc sulfide, including pentlandite, pyrrhotite, chalcopyrite with minor chronmite and magnenite (Fig. 3), and hydrothermal-related sulfide, such as pyrite, violarite, and bornite. Meanwhile, many oxide minerals, such as annabergite, malachite and limonite, occur on the weathered surface. Pentlandite, pyrrhotite, and chalcopyrite are intergrown, and skeletal pentlandite grains are developed at the margins of pyrrhotite grains (Fig. 3). The sulfides are typically idiomorphichypidiomorphic and are not equigranular, showing

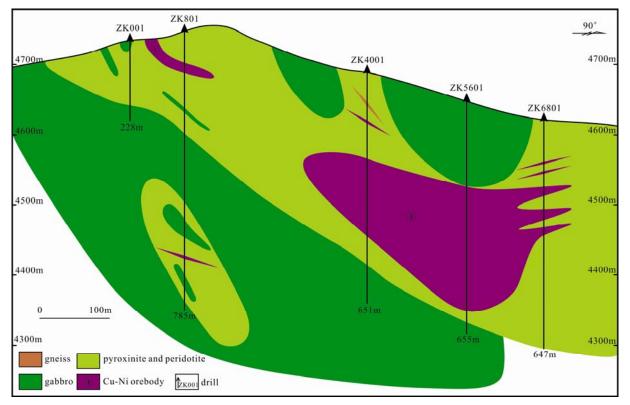


Fig. 2. Cross-section of the No. I mafic–ultramafic complex of the Shitoukengde Ni-Cu deposit showing the location and depth of boreholes ZK001, ZK801, ZK4001, ZK5601, and ZK6801.

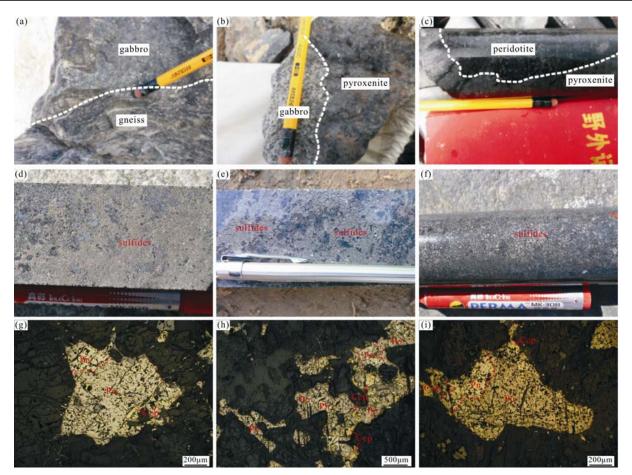


Fig. 3. Field photographs of mafic-ultramafic rocks (a, b, c), Ni-Cu ores (d, e, f) and photomicrographs of sulfides from No. I mafic-ultramafic complex at Shitoukengde (g, h, i; plane polarized light).

(a), Gabbro intruded gneiss (after Zhou et al., 2016); (b), The sharp contact between gabbro and pyroxenite (after Zhou et al., 2016); (c), The sharp contact between peridotite and pyroxenite (after Zhou et al., 2016); (d), (e), The massive Ni-Cu ores; f-Ni-Cu ores with sideronitic texture; (g), (h), (i), Primary pentlandites, chalcopyrites and pyrrhotites in Ni-Cu ores under the microscope. Pn: pentlandite; Ccp: chalcopyrite; Po: pyrrohotite.

metasomatic and sideronitic textures (Fig. 3). The ore is disseminated, showing stellate and mottled structures.

4 Sample Descriptions and Analytical Techniques

4.1 Sample descriptions

The No. I complex of the Shitoukengde deposit was sampled due to its size, extensive mineralization, and succession of mafic–ultramafic rocks, including gabbro (Fig. 4a), olivine websterite (Fig. 4b–c), websterite (Fig. 4d), pyroxenite allivalite (Fig. 4e), orthopyroxenite (Fig. 4f), olivine pyroxenite, pyroxene peridotite, olivine gabbro, and gabbronorite. Samples of olivine websterite (14STKD-ZK001-N1) and gabbro (14STKD-ZK001-N2), were selected to analyse for zircon U-Pb geochronology and Hf isotopes, whole-rock geochemistry and Sr-Nd-Pb isotopes.

The gabbro is gray in color and composed of mediumgrained idiomorphic–subhedral, is massive, and mainly contain plagioclase ($\sim 60\%$), orthopyroxene ($\sim 5\%$), clinopyroxene (\sim 38%), olivine (\sim 5%), and sulfides (\sim 2%; Fig. 4a). The plagioclase grains are euhedral and clintheriform, measuring 3.5–5.0 mm in length and showing polysynthetic twinning under cross-polarized light. Pyroxenes are subhedral and 1.5–2.0 mm long.

The olivine websterite is gray–black in color, mediumto fine-grained, massive, and contains clinopyroxene (\sim 30%), orthopyroxene (\sim 55%), olivine (\sim 10%), and minor sulfides (\sim 5%; Fig. 4b–c). The pyroxenes are subhedral and weakly altered, measuring 2.0–2.5 mm. Olivine grains are subhedral, 1.5–2.0 mm in size, and have been serpentinized.

4.2 Analytical methods

4.2.1 Zircon U-Pb dating

Zircons were separated from whole-rock samples using the conventional heavy liquid and magnetic techniques, and then by handpicking under a binocular microscope, at the Langfang Regional Geological Survey, Hebei Province, China. The handpicked zircons were examined under transmitted and reflected light with an optical

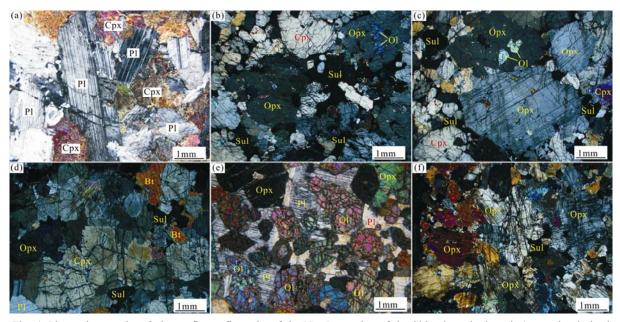


Fig. 4. Photomicrographs of ultramafic-mafic rocks of the No. I complex of the Shitoukengde deposit (crossed-polarized light).

(a), Gabbro; (b), (c), Olivine websterite; (d), Websterite; (e), Pyroxenite troctolite; (f), Orthopyroxenite. Pl: plagioclase; Cpx: clinopyroxene; Opx: orthopyroxene; Ol: olivine; Bt: biotite; Sul: sulfide.

microscope. To reveal their internal structures, cathodoluminescence (CL) images were obtained using a JEOL scanning electron microscope housed at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, China. The testing method, testing process and data processing are introduced in reference of Tang et al. (2015) and the data are shown in Table 1.

4.2.2 Whole-rock geochemistry analysis

For geochemical analysis, whole-rock samples, after the removal of altered surfaces, were crushed in an agate mill to ~200 mesh. X-ray fluorescence (XRF; PW1401/10) using fused-glass disks and ICP-MS (Agilent 7500a with a shield torch) were used to measure the major and trace elements compositions, respectively, at the Testing Center of Jilin University, after acid digestion of samples in Teflon bombs. The analytical results for the BHVO-1 (basalt), BCR-2 (basalt), and AGV-1 (andesite) standards indicate that the analytical precision for major elements is better than 5%, and for trace elements, generally better than 5% when the content >10ppm, and better than 10% when <10ppm. The analytical results of major and trace elements are listed in Table 2.

4.2.3 Hf isotope analysis

In situ zircon Hf isotope analyses were carried out using a NewWave UP213 laser-ablation microprobe, attached to a Neptune multi-collector ICP - MS at the Institute of Mineral Resources, Chinese Academy of Geological Sciences. Instrumental conditions and data acquisition techniques have been comprehensively described by Wu et al. (2006). Lu-Hf isotopic measurements were made on the same zircon grains previously analyzed for U-Pb with ablation pits 55 μ m in diameter, repetition rates of 8–10 Hz, laser beam energy density of 10 J/cm², and an ablation time of 26s. The testing method, testing process and data processing are introduced in reference of Guo et al. (2012) and the data are shown in Table 3.

4.2.4 Whole-rock Sr-Nd-Pb isotope analysis

Whole-rock Sr-Nd-Pb isotope analysis were carried out at Analytical Laboratory of the Beijing Research Institute of Uranium Geology, China, by using an ISOPROBE-T thermal ionization mass spectrometer. Sample powders were dissolved in HF + HNO₃ + HClO₄ mixture. Digested samples were dried and redissolved in 6 mol/L NHCl, dried again and redissolved in 0.5 mol/L NHCl (for Sr and Nd separation) or 0.5 mol/L NHBr (for Pb separation). Sr and Nd fractions were separated following standard chromatographic techniques using AG50x8 and PTFE-HDEHP resins with HCl as eluent, while Pb fraction was separated using strong alkali anion exchange resin with HBr and HCl as eluents. Measured Nd isotopic compositions were corrected for instrumental mass bias using a ⁸⁶Sr/⁸⁸Sr and ¹⁴⁶Nd/¹⁴⁴Nd values of 0.1194 and 0.7219. Analysis of the Nd standard JNdi-1 gave a ¹⁴³Nd/¹⁴⁴Nd value of 0.512109±3. For convenience, 143 Nd/ 144 Nd ratios are expressed as ε Nd (Jacobsen and Wasserburg, 1980). A factor of 1‰ per mass unit for

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38U	1σ	0.0006	0.0007	0.0006	0.0008	0.000	0.0007	CT00.0	0.0006	0.0010	0.0006	0.0005	0.0005	0.0008	0.0005	0.0000	0.0005	0.0010	0.0006	0.0008	0.0005	0.0009	0.0019	0.0015	0.0017	0.0020	0.0023	0.0074	0.0017	0.0020	0.0018	0.0032	0.0018	0.0024	0.0031	0.0034	0.0029	0.0031	0.0070	00000
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35U	lσ	0.0091	0.0068	0.0087	0.0083	0.0118	0.0110	0.0081	0.0085	0.0120	0.0085	0.0074	0.0075	0.0081	0.0072	0.0086	0 0069	0.0102	0.0092	0.0107	0.0101	0.0160	0.020/	0.0424	0.0460	0.0481	0.0437	0.0400	0.0414	0.0505	0.0451	0.0440 0.0647	0.0702	0.0643	0.0937	0.0899	0.0844	0.1196	0.1465	0,000
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²⁰⁷ Pb/ ²⁰⁶ Pb	Ratio	0.0565														2020 0						0.0588						0.0751				0.0/00					0.0900		0.1083	0 1514
Th/IT	0/11	0.04														00.0						0.10						0.78				0.52					0.51			
Ω.	ppm	19606		16576	8677	77001										01701						2779						1501		523		0/8 431					1528 446			101
Th	ppm	841 1														1 188	1383		_		1427	272	240 870	142	230	148	210	416 / 61	647	235	430	291 224	368	1468	700	386	773 380	31	670	100
Pb	pp m dd	1297														1/01					_	244						205 548				508 218			1054	672	1213	501 615		200
Analweie en ote		14STKD-ZK001-N1-01 1														481KD-ZK001-N1-16			_			[4STKD-ZK001-N2-0]						1451KD-ZK001-N2-08 14STKD-ZK001-N2-09				48TKD-ZK001-N2-13					[4STKD-ZK001-N2-19] [4STKD-ZK001-N2-20			ACTURING TOTAL

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14STKD-ZK0 01-Y2-7 52.15 0.29 17.00 4.89	$\begin{array}{c} 10.09\\ 9.82\\ 2.56\\ 0.87\\ 0.87\\ 3.50\\ 3.50\\ 3.50\\ 3.50\\ 3.50\\ 3.50\\ 3.50\\ 1.81\\ 1.81\\ 1.13\\ 1.13\\ 1.12$	$\begin{array}{c} 0.23\\ 0.70\\ 0.70\\ 0.10\\$	13.4 2.23 36.6 36.6 3.73 16.4 10.4 0.31 0.31 0.31 0.31 0.31 0.31 0.31 0.31
14STKD-ZK0 14STKDZ0 1297	$\begin{array}{c} 9.95\\ 10.71\\ 0.546\\ 0.54\\ 0.05\\ 3.07\\ 3.07\\ 3.07\\ 3.07\\ 3.07\\ 3.10\\ 0.79\\ 0.79\\ 0.79\\ 1.26\\ 1.26\\ 1.26\\ 1.26\\ 1.26\end{array}$	$\begin{array}{c} 0.28\\ 0.31\\ 0.12\\$	13.0 2.34 5.13 5.13 6.13 6.13 0.79 0.79 0.26 0.26 0.26 0.142 0.03
114STKD-ZK(01-Y2-5 50.43 0.29 18.52 4.66	9.26 10.88 0.45 0.45 99.56 3.83 3.80 3.80 3.83 3.80 1.14 1.17 0.87 1.24 1.14 1.14	$\begin{array}{c} 0.24\\ 0.74\\ 0.74\\ 0.70\\ 0.70\\ 0.70\\ 0.70\\ 0.70\\ 0.70\\ 0.70\\ 0.74\\ 0.70\\ 0.70\\ 0.74\\ 0.70\\ 0.70\\ 0.74\\ 0.70\\ 0.70\\ 0.70\\ 0.74\\ 0.70\\$	$\begin{array}{c} 14.5\\ 14.5\\ 2.15\\ 4.19\\ 16.4\\ 16.4\\ 17.7\\ 0.93\\ 0.31\\ 0.22\\ 0.22\\ 0.22\\ 0.22\\ 0.02\end{array}$
14STKD-ZK0 01-Y2-4 Gabbro 51.94 0.31 12.56 6.36	15,42 7.77 1.57 1.57 1.57 1.57 3.11 3.11 2.24 2.01 2.01 2.01 1.22 0.01 2.01 1.22 0.73 0.74 0.73 0.73 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.7	0.30 0.72 0.72 0.72 0.72 0.72 0.72 1.23 1.07 1.25 1.23 1.23 1.25 1.25 2.33 7.1.2 2.65 2.95 2.95 2.95 2.95 2.95 2.95 2.95 2.9	$\begin{array}{c} 10.8\\ 2.75\\ 6.8.3\\ 6.40\\ 1.02\\ 1.02\\ 1.02\\ 1.02\\ 0.30$
14STKD-ZK0 01-Y2-3 52.01 0.42 16.81 4.45	$\begin{array}{c} 8.3\\ 8.3\\ 13.96\\ 2.40\\ 0.03\\ 2.85\\ 2.85\\ 2.85\\ 2.85\\ 10.16\\ 1.61\\ 1.61\\ 1.61\\ 2.24\\ 2.24\\ 2.24\end{array}$	0.48 0.130 0.16 0.17 0.18 0.18 0.18 2.56 1.62 2.58 2.66 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.6 1.52 3.76 3.76 3.76 3.76 3.76 3.76 3.76 3.76	$\begin{array}{c} 13.8\\ 15.4\\ 15.4\\ 15.4\\ 15.5\\ 1.48\\ 1.38\\ 1.38\\ 1.38\\ 1.38\\ 1.38\\ 1.38\\ 1.38\\ 1.38\\ 1.38\\ 1.38\\ 1.38\\ 1.48\\ 0.62\\ 1.38\\ 1.48\\ 0.62\\ 1.38\\ 1.48\\$
4STKD-ZK0 01-Y2-2 51.14 0.31 15.79 5.83 5.83	11.44 9.54 2.01 3.58 3.58 3.19 0.73 0.73 0.73 0.73 1.11 1.12 1.23	0.27 0.73 0.73 0.10 0.10 0.10 0.10 0.10 1.88 1.88 1.12 1.42 1.42 1.42 1.42 1.42 1.42 1.42	1255 2.47 5.55 6.55 0.74 0.23 0.23 0.23 0.23 0.05
4STKD-ZK01 01-Y2-1 51.92 0.29 16.92 5.06	10.55 9.92 9.92 9.92 9.96 9.76 9.76 8.1 8.1 8.1 1.12 0.78 0.78 1.12 1.12 1.12 1.12 1.12 1.12 1.12 1.1	$\begin{array}{c} 0.27\\ 0.73\\ 0.73\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.10\\ 0.23\\ 0.10\\ 0.10\\ 0.23\\ 0.10\\$	13.2 2.33 37.4 3.7.4 3.93 3.93 3.93 3.93 1.2.8 1.2.8 0.88 0.23 0.23 0.23 0.23 0.23 0.23 0.23 0.23 0.23 0.23 0.23 0.23 0.23 0.23 0.23 0.23 0.23 0.23 0.24 0.23 0.24 0.23 0.23 0.23 0.24 0.23 0.23 0.24 0.23 0.24 0.23 0.24 0.23 0.24 0.23 0.24 0.23 0.24 0.23 0.24 0.23 0.24 0.23 0.24 0.23 0.24 0.23 0.24 0.23 0.24 0.23 0.24 0.24 0.23 0.24
Samples 145TKD-ZK0 16.92	33.60 0.98 0.13 0.16 0.16 0.16 0.95 82 82 82 82 82 82 0.95 0.95 0.91 0.91 0.91 0.76 0.91 0.76 0.91 0.76 0.91 0.76 0.91 0.76 0.91 0.76 0.95 0.95 0.95 0.95 0.95 0.95 0.95 0.95	0.18 0.51 0.58 0.08 0.07 0.07 1.44 1.3 1.59 1.59 1.59 1.59 1.59 1.59 1.52 1.52 1.59 1.52 1.53 1.52 1.52 1.53 1.52 1.53 1.52 1.53 1.53 1.53 1.53 1.53 1.53 1.53 1.53	5.60 3.34 6.03 6.03 1.6.8 5.59 0.89 0.23 0.23 0.23 0.23 0.23 0.03
87KD-ZK01 01-Y1-6 37.19 0.42 2.10 13.77	$\begin{array}{c} 33.83\\ 1.37\\ 0.11\\ 0.18\\ 0.18\\ 0.05\\ 10.66\\ 1.07\\ 1.07\\ 1.07\\ 1.07\\ 1.07\\ 1.07\\ 2.38\\ 0.05\\ 0.87\\ 0.67\\ 0.67\\ 0.13\end{array}$	0.16 0.47 0.47 0.47 0.44 0.44 1.4.2 1.4.2 1.26 1.26 1.26 1.26 1.26 1.26 1.26 1.	5.05 5.05 6.0.8 5.05 5.05 6.0.8 17.9 1.06 0.61 0.61 0.78 0.78 0.78 0.43
457KD-ZK01- 01-Y1-5 40.56 0.21 4.28 13.10 13.10	29.54 2.44 0.441 0.46 0.03 8.61 99.80 99.80 0.33 8.2 1.56 1.56 1.56 0.54 0.54 0.54 0.54 0.54 0.54 0.54 0.55 0.54 0.55 0.54 0.54	0.13 0.13 0.06 0.05 0.05 0.05 0.05 0.05 0.05 0.05	3.65 3.65 3.51 3.64 3.64 12.3 0.72
(0 14STKD-ZK0 12 01-Y1-4 01vine websterite 36.49 0.19 2.24 13.39	34.65 0.80 0.12 0.12 0.12 0.12 0.12 0.12 0.12 0.03 0.03 0.32 0.03	0.26 0.78 0.78 0.78 0.69 0.69 1.53 1.21 1.21 1.21 1.23 1.23 1.23 1.23 1.2	4.52 8.79 8.77 8.77 6.40 6.40 1.12 1.16 0.145 0.745 0.745 0.745 0.14
STKD-ZK0 14 01-Y1-3 01v 38.67 0.20 2.77 11.87 11.87	33.34 0.78 0.78 0.64 0.65 9.64 11.21 0.05 3.08 1.52 0.67 0.67 0.74 0.53 0.53 0.53 0.53 0.53 0.53	0.13 0.37 0.36 0.36 0.36 0.36 0.36 0.36 0.37 1.32 1.32 1.32 1.32 1.32 1.32 1.32 1.32	3.34 3.58 3.58 3.58 3.15 11.0 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.73 0.74 0.03 0.03
STKD-ZK0 14 01-Y1-2 37.92 0.24 3.20 12.97	32.90 1.97 0.23 0.29 0.04 9.95 9.95 0.07 0.04 0.17 0.55 0.17 0.77 0.53 0.17 0.53 0.17 0.53 0.12 0.53 0.12	0.13 0.39 0.39 0.36 0.37 1.15 1.05 1.15 1.15 1.15 1.15 1.15 1.15	5.44 3.40 3.40 1.65 1.65 0.62 0.24 0.24 0.24 0.03
STKD-ZK0 145 01-Y1-1 42.80 0.18 4.09 12.10	30.18 2.94 0.38 0.62 0.62 0.63 0.65 0.65 0.85 0.85 0.85 0.96 0.15 0.15 0.15	0.19 0.53 0.08 0.07 0.07 0.07 1.1.50 1.1.50 1.1.50 1.1.50 1.1.50 1.1.50 1.1.50 1.1.50 1.1.50 1.1.50 1.1.50 1.1.50 1.1.50 1.50	$\begin{array}{c} 4.63\\ 3.24\\ 3.24\\ 1.3.2\\ 1.3.2\\ 1.5.4\\ 1.5.4\\ 0.86\\ 0.17\\ 0.17\\ 0.18\\ 0.18\\ 0.18\end{array}$
Samples 144 Rocks Rocks SiO ₂ TiO ₂ Al ₂ O ₃ TFe ₂ O ₃	$\begin{array}{c} MgO\\ CaO\\ CaO\\ K_{2}O\\ K_{2}O\\ K_{2}O\\ K_{2}O\\ Co\\ LOI\\ LOI\\ LOI\\ La\\ Mg^{\#}_{2}\\ Mg^{H}_{2}O\\ Sm\\ Pr\\ Pr\\ Pr\\ Sm\\ Dy\\ Dy\\ Dy\\ Dy\\ Dy\\ Dy\\ Dy\\ Dy\\ Dy\\ Dy$	Ho Er Tm Tm Tm Fr Fu Cu Cu Cu Cu Cu Cu Cu Cu Cu Cu Cu Cu Cu	⊂∄¤??≭%&666

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Table 3 Zircon Lu-Hf isotopi	c compositions	of olivine websterite in	n the No.	I mafic-ultramafic complex

Table 5 Zh con Eu-III isotopic compositions of onvine websterite in the No. 1 manc-ulti amanc complex													
Sample	t(Ma)	¹⁷⁶ Yb ^{/177} Hf	2σ	¹⁷⁶ Lu/ ¹⁷⁷ Hf	2σ	¹⁷⁶ Hf/ ¹⁷⁷ Hf	2σ	$\epsilon_{\rm Hf}(0)$	$\epsilon_{\rm Hf}(\underline{t})$	2σ	$T_{\rm DM1}$	$T_{\rm DM2}$	$f_{\rm Lu/Hf}$
14STKD-ZK001-N1-01	422	0.048031	0.000781	0.001500	0.000036	0.282256	0.000019	-18.2	-9.4	0.7	1424	1999	-0.95
14STKD-ZK001-N1-02	424	0.013577	0.000206	0.000480	0.000003	0.282364	0.000017	-14.4	-5.2	0.6	1237	1740	-0.99
14STKD-ZK001-N1-03	422	0.015653	0.000204	0.000558	0.000006	0.282356	0.000017	-14.7	-5.6	0.6	1250	1759	-0.98
14STKD-ZK001-N1-04	423	0.012135	0.000228	0.000427	0.000004	0.282397	0.000014	-13.3	-4.1	0.5	1190	1666	-0.99
14STKD-ZK001-N1-05	422	0.038116	0.000607	0.001297	0.000021	0.282367	0.000017	-14.3	-5.4	0.6	1260	1748	-0.96
14STKD-ZK001-N1-06	421	0.042006	0.001068	0.001393	0.000027	0.282316	0.000028	-16.1	-7.3	1.0	1335	1864	-0.96
14STKD-ZK001-N1-07	422	0.016699	0.000198	0.000614	0.000004	0.282411	0.000016	-12.8	-3.7	0.6	1177	1639	-0.98
14STKD-ZK001-N1-08	422	0.016749	0.000240	0.000607	0.000005	0.282322	0.000017	-15.9	-6.8	0.6	1300	1837	-0.98
14STKD-ZK001-N1-09	422	0.030016	0.000579	0.000987	0.000022	0.282684	0.000030	-3.1	5.9	1.1	804	1031	-0.97
14STKD-ZK001-N1-10	422	0.015420	0.000101	0.000522	0.000001	0.282305	0.000021	-16.5	-7.4	0.7	1320	1873	-0.98
14STKD-ZK001-N1-11	423	0.030995	0.000213	0.001037	0.000017	0.282374	0.000020	-14.1	-5.0	0.7	1241	1727	-0.97
14STKD-ZK001-N1-12	423	0.015620	0.000177	0.000567	0.000004	0.282381	0.000015	-13.8	-4.7	0.5	1216	1704	-0.98
14STKD-ZK001-N1-13	422	0.013280	0.000113	0.000467	0.000006	0.282394	0.000014	-13.4	-4.2	0.5	1195	1674	-0.99
14STKD-ZK001-N1-14	422	0.020707	0.001315	0.000693	0.000035	0.282353	0.000019	-14.8	-5.7	0.7	1259	1768	-0.98
14STKD-ZK001-N1-15	422	0.030700	0.000610	0.001021	0.000019	0.282332	0.000021	-15.6	-6.6	0.7	1300	1822	-0.97
14STKD-ZK001-N1-16	421	0.011849	0.000089	0.000424	0.000004	0.282417	0.000014	-12.6	-3.4	0.5	1162	1622	-0.99

instrumental mass fractionation was applied to the Pb analyses, using NBS 981 as reference material. Measurement of the common-lead standard NBS 981 gave average values of 208 Pb/ 206 Pb = 2.164940 ± 15, 207 Pb/ 206 Pb = 0.914338 ± 7 and 204 Pb/ 206 Pb = 0.0591107 ± 2, with uncertainties of <0.1% at the 95% confidence level.

5 Results

5.1 LA-ICP-MS U-Pb zircon dating

Zircons from the olivine websterite sample (14STKD-

ZK001-N1) are 80–120 μ m long, charcoal, mostly wide stubby columnar, and show no oscillatory zoning (Fig. 5). The internal parts of the grains are texturally homogeneous, and there is no inherited cores (Fig. 5) and yielding Th/U values of 0.04–0.14 (Table 1), indicative of a basic magmatic origin. The U–Pb ages of 22 zircons are concordant, ranging from 421 ± 3 Ma to 424 ± 4 Ma with a weighted mean age of 422.1 ± 1.5 Ma (MSWD = 0.04; Fig. 6a), representing the timing of mineralization in the deposit.

Zircons separated from the gabbro sample (14STKD-

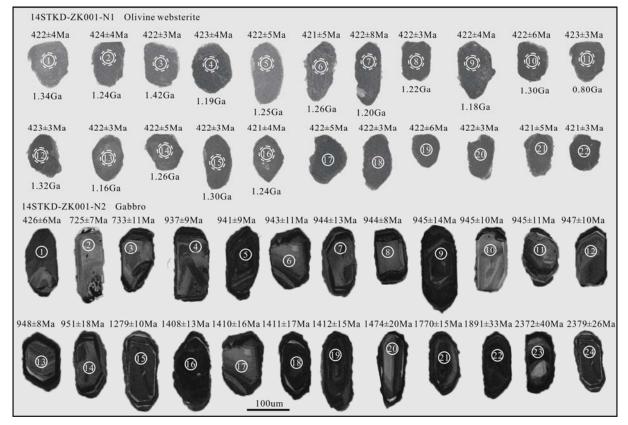


Fig. 5. Cathodoluminescence (CL) images of representative zircons of mafic-ultramafic rocks in the No. I complex selected for U-Pb isotopic analysis.

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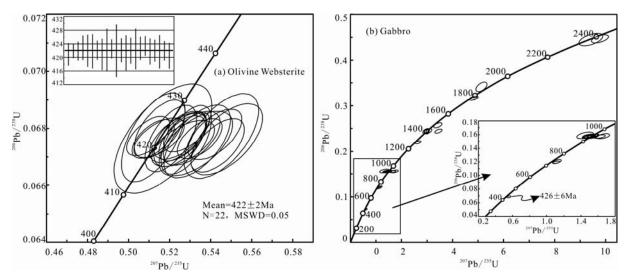


Fig. 6. U–Pb isotope concordia diagrams for analyzed zircons from (a) olivine websterite (insets show weighted mean age diagrams) and (b) gabbro.

Table 4 Whole-rock Sr-Nd	isotopic composi	tions of the No. I	mafic-ultramafic complex

Samples	Rocks	T (Ma)	Rb (ppm)	Sr (ppm)	⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr	2s	(⁸⁷ Sr/ ⁸⁶ Sr) _i	$\frac{\varepsilon_{\mathrm{Sr}}}{(t)}$	Sm (ppm)	Nd (ppm)	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	2s	(¹⁴³ Nd/ ¹⁴⁴ Nd) _i	$\frac{\varepsilon_{\rm Nd}}{(t)}$
14STKD- ZK001-B1	Olivine websterite	422	13.1	39.7	0.955822	0.719708	0.000020	0.713960	141.4	0.96	2.69	0.215730	0.512182	0.000008	0.511586	-9.93
14STKD- ZK001-B2	Olivine websterite	422	7.09	25.4	0.808069	0.713567	0.000009	0.708710	66.9	0.74	1.91	0.234213	0.512374	0.000009	0.511727	-7.17
14STKD- ZK001-B3	Gabbro	426	37.4	393	0.275565	0.716145	0.000013	0.714470	148.8	1.14	3.25	0.212038	0.512180	0.000010	0.511589	-9.77
14STKD- ZK001-B4	Gabbro	426	60.6	355	0.494535	0.721042	0.000012	0.718040	199.5	1.10	3.28	0.202733	0.512311	0.000010	0.511745	-6.72
14STKD- ZK001-B5	Gabbro	426	15.4	443	0.100649	0.714896	0.000013	0.714290	146.2	2.00	6.39	0.189204	0.512268	0.000008	0.511740	-6.82

Table 5 Whole-rock Pb isotopic compositions of the No. I mafic-ultramafic complex

	1								1					
Samples	Rocks	T (Ma)	U (ppm)	Th (ppm)	Pb (ppm)	²⁰⁶ Pb/ ²⁰⁴ Pb	2s	²⁰⁷ Pb/ ²⁰⁴ Pb	2s	²⁰⁸ Pb/ ²⁰⁴ Pb	2s	(²⁰⁶ Pb/ ²⁰⁴ Pb) _i	(²⁰⁷ Pb/ ²⁰⁴ Pb) _i	(²⁰⁸ Pb/ ²⁰⁴ Pb) _i
14STKD-ZK001-B1	Olivine websterite	0.18	1.65	4.60	422	18.342	0.003	15.625	0.003	38.303	0.007	18.174	15.616	37.808
14STKD-ZK001-B2	Olivine websterite	0.03	1.43	2.14	422	18.342	0.005	15.613	0.004	38.195	0.010	18.282	15.610	37.274
14STKD-ZK001-B3	Gabbro	0.04	1.80	8.61	426	18.226	0.003	15.607	0.002	38.169	0.007	18.206	15.606	37.879
14STKD-ZK001-B4	Gabbro	0.05	1.65	6.57	426	18.541	0.004	15.633	0.003	38.639	0.010	18.508	15.631	38.286
14STKD-ZK001-B5	Gabbro	0.62	3.47	7.35	426	18.435	0.003	15.404	0.003	38.463	0.006	18.070	15.384	37.805

Table 6 S isotopic compositions of sulfides from Shitoukengde Ni-Cu deposit

· · ·	5	*		
Samples	Rocks	Tested minerals	δ^{34} S (‰)	References
STKD2015-II-TC01-B1	Gabbro-type disseminated ore	Pyrrhotine	3.1	
STKD2015-II-TC01-S2	Gabbro-type disseminated ore	Pyrrhotine	3.2	This paper
STKD2015-TC005-B1	Pyroxenite-type disseminated ore	Pyrrhotine	2.6	This paper
STKD2015-TC005-S1	Pyroxenite-type disseminated ore	Pyrrhotine	2.6	
S-22	Gabbro-type disseminated ore	-	2.1	
S-33	Gabbro-type disseminated ore	-	1.9	
002-6	Pyroxenite-type disseminated ore	-	2.3	
002-8	Pyroxenite-type disseminated ore	-	2.5	Zhou, 2016
S-18	Peridotite-type disseminated ore	-	3.2	
4001-5	Peridotite-type disseminated ore	-	4.3	
4001-6	Peridotite-type disseminated ore	-	3.8	

ZK001-N2) are 100–150 μ m long, stubby columnar (Fig. 5), show obvious oscillatory zoning and rhythmically zoned textures (except the first zircon), which are different to the zircons from basic intrusions. Only one crystallization age of 426±6 Ma was obtained from this sample, representing the crystallization age of gabbro (Fig. 6b). However, inherited zircons from this sample yield

values concentrate at 940–950 Ma (Fig. 6b), in response to the Neoproterozoic magmatic event (Jin Lijie et al., 2015; Wang Guan et al., 2016).

Thus, we suggest that Shitoukengde Ni-Cu sulfide deposit formed in late Silurian (426–422 Ma), which was supported by the gabbro U-Pb age of 424 Ma (Zhou Wei et al., 2015), and they are the same to other magmatic Ni-

Cu sulfide deposits, such as Xiarihamu (394–439 Ma; Li Shijin et al., 2012; Wang Guan et al., 2014a; Jiang Changyi et al., 2015; Li et al., 2015; Peng et al., 2016; Song et al., 2016).

5.2 Geochemical characteristics 5.2.1 Major elements

The elivine websterite

The olivine websterites contain 36.41-42.80wt% SiO₂ (averaging 38.58wt%), 11.87-14.44wt% TFe₂O₃ (averaging 13.09wt%), 0.78-2.94wt% CaO (averaging 1.61wt%), 29.54-34.65wt% MgO (averaging 32.58wt%), and Na₂O+K₂O contents of 0.23-1.00wt% (averaging 0.55wt%). These samples have Mg[#] = 82-85 {Mg[#] = $100 \times Mg^{2+}/(Mg^{2+}+TFe^{2+})$ } and m/f values {m/f = $Mg^{2+}/(TFe^{2+}+Mn^{2+})$ } of 4.40-5.51.

The gabbros contain 50.43-52.21 wt% SiO₂ (averaging 51.69 wt%), 4.45-6.36 wt% TFe₂O₃ (averaging 5.14 wt%), 7.77-13.96 wt% CaO (averaging 10.72 wt%), 8.33-15.42 wt% MgO (averaging 10.72 wt%), and Na₂O+K₂O contents of 2.82-3.50 wt% (averaging 3.17 wt%). They have Mg[#] = 79-83 and m/f values of 3.59-4.67.

The rocks of complex No. I are low in SiO₂, TiO₂, and $(Na_2O + K_2O)$, and high in MgO and Mg[#]. They have m/f

values of 3.59–5.51 (averaging 4.44), suggests that the mafic–ultramafic complex makes it a potential source of Cu–Ni mineralization (Wu Liren, 1963). The olivine websterite spot in the ultramafic cumulate (Fig. 7a) and Tholeiitic series (Fig. 7b), while the gabbros belong to the calc-alkaline series (Fig. 7).

5.2.2 Trace elements

The ultramafic–mafic rocks in the No. I complex contain low total rare-earth-element contents (SREE = 9.29-33.60 ppm). These samples show the flat, overall similar normalized trace element patterns, and they are slightly enriched in light rare earth element (LREE) and depleted in heavy rare earth element (HREE) (Fig. 8a), with (La/Yb)_N, (La/Sm)_N, and (Gd/Yb)_N values of 1.88–3.88, 1.07-1.88, and 1.15-1.62, respectively. These results indicate enrichment in light rare earth elements relative to the middle and heavy rare earth elements but only very weak fractionation of the middle and heavy rare earth elements (Fig. 8a). In addition, these rocks are characterized by the positive Eu anomalies (Eu/Eu^{*} = 1.24–2.29).

On the primitive-mantle-normalized spidergrams (Fig.

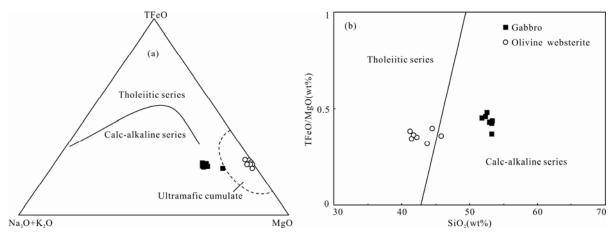


Fig. 7. TFeO-(Na₂O+K₂O)-MgO and SiO₂ vs. TFeO/MgO diagrams of the mafic-ultramafic rocks in No. I complex.

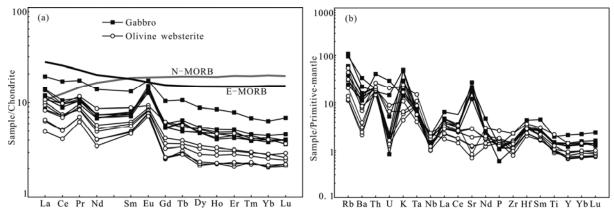


Fig. 8. Trace element characteristics of ultramafic-mafic rocks of the No. I complex showing (a) chondrite-normalized REE patterns, and (b) primitive-mantle-normalized trace element abundances.

8b), the trace element abundances of these samples are similar, and they are relatively enriched in large ion lithophile elements (LILE; e.g., K, Rb, Th) and depleted in high field strength elements (HFSE; e.g., Nb, Ta, Zr, Ti).

5.3 Hf isotopes of zircon

16 zircons of olivine websterite in No. I maficultramafic complex have ¹⁷⁶Hf/¹⁷⁷Hf ratios between 0.282256 and 0.282684, and in response to $\varepsilon_{\rm Hf}(t)$ values of -9.4 to 5.9, and their T_{DM1} ages fall between 0.80 Ga and 1.42 Ga (Table 2; Fig. 9). The crystallization ages of mafic -ultramafic rocks would be approximative to the T_{DM1} ages of zircons, if their primary magmas were derived from uncontaminative depleted mantle (Wu Fuyuan et al., 2007). However, the T_{DM1} ages of olivine websterite were beyond the crystallization age (zircon U-Pb age 422 Ma), suggesting they deriving from the enriched lithospheric mantle or contamination of the crust material in the magmatic source (Wu Fuyuan et al., 2007).

5.4 Whole-rock Sr-Nd-Pb isotopes

The olivine websterite and gabbro samples in this paper have the similar Sr and Nd isotopic compositions $\{\varepsilon_{Nd}(t)=$ -9.93 - 6.72 $({}^{87}\text{Sr}/{}^{86}\text{Sr})_{I}$ = 0.708710 - 0.718040suggesting the same magmatic source. These rocks have small negative $\varepsilon_{\rm Nd}(t)$ values and $({}^{87}{\rm Sr}/{}^{86}{\rm Sr})_{\rm i}$ values that are higher than those of MORB (Sauders et al., 1988) with the characteristics of enriched mantle source. They are dispersed and all plot between the DMM (depleted MORB mantle) and EMII (II-type enriched mantle) in the diagram of $\varepsilon_{Nd}(t)$ vs. (⁸⁷Sr/⁸⁶Sr)_i (Fig. 10a), approaching to Xiarihamu Sr-Nd isotopics (Peng et al., 2016), which show the evidence for evolution to an EMII end-member composition (Yang Xin et al., 2016).

The mafic-ultramafic rocks in the No. I complex have the $({}^{206}Pb/{}^{204}Pb)_{i}=18.176-18.508$, $({}^{207}Pb/{}^{204}Pb)_{i}=15.384-$

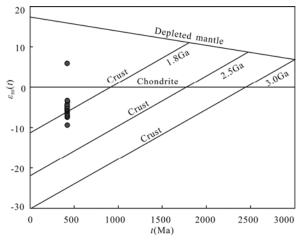


Fig. 9. Zircon Hf isotopic compositions of olivine websterite in the No. I mafic-ultramafic complex.

15.631, and $(^{208}\text{Pb}/^{204}\text{Pb})_{I} = 37.281-38.290$. These samples plot in close to EMII on the diagrams of $(^{206}\text{Pb}/^{204}\text{Pb})_{i}$ vs. $\varepsilon_{\text{Nd}}(t)$ and $(^{207}\text{Pb}/^{204}\text{Pb})_{i}$ (Fig. 10b–c) and they mainly fall in MORB on the diagram of $(^{206}\text{Pb}/^{204}\text{Pb})_{i}$ vs. $(^{208}\text{Pb}/^{204}\text{Pb})_{i}$ (Fig. 10d), which indicates that their were probably derived from enriched mantle or contaminated greatly by the enriched component.

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6 Discussion

6.1 Magmatic sources

The similar major and trace element characteristics, and Sr, Nd and Pb isotopes of the mafic-ultramafic rocks in No. I complex suggest that they were originated from a common source. Meanwhile, these rocks show the flat and similar chondrite-normalized REE patterns, and the olivine websterites contain the low SiO₂ (36.41–42.80 %), CaO (0.78-2.94 %), Na₂O (0.05-0.41 %), K₂O (0.12-0.64 %) and TiO₂ (0.18–0.42 %) concentrations, and the low SLREE (7.07–15.5 ppm), indicate that their primary magmas were derived from partial melting of depleted mantle and less possibly the enriched mantle (Fig. 8a; Sun and McDonough, 1989; Huang Qiangtai et al., 2015). What is more, this also supported by the positive $\varepsilon_{\text{Hf}}(t)$ value ($\varepsilon_{\text{Hf}}(t)=5.9$) of olivine websterite zircons. The Hf model ages of zircons may reflect the time at which they separated from depleted mantle, if the parental magma of the zircons came directly from unmodified depleted mantle. In such a case, the crystallization ages of the zircons should be roughly the same as the Hf model ages of the zircons (Wu Fuyuan et al., 2007). Thus, the zircons of olivine websterite at Shitoukengde have Hf model ages $(T_{DM1} = 0.80-1.42 \text{ Ga})$ that are considerably older than their crystallization ages (426-422 Ma) implies that their magmatic source had been contaminated greatly by the enriched component.

It is inevitable that mantle-derived magma will experience assimilation-contamination during ascent (Peng et al., 2016) for the continental mafic-ultramafic complexes. One of the most significant evidences of this for the No. I complex is the numerous xenoliths of Paleoproterozoic Jinshuikou Group gneiss (Fig. 3a). Meanwhile, a great number of Precambrian captured zircons with the U-Pb ages peak of 940-950 Ma were obtained from the gabbros (Fig. 6a). The mafic-ultramafic rocks display the different chondrite-normalized REE patterns to those of N-MORB sourced from asthenospheric mantle (Fig. 8a) and are characterized by the enrichment in LREE and LILE (e.g., K, Rb, Th), and depletion in HREE and HFSE (e.g., Nb, Ta, P, Ti), and the gabbros have Sr of 255-570 ppm, indicate that their primary magmags had experienced some enrichment.

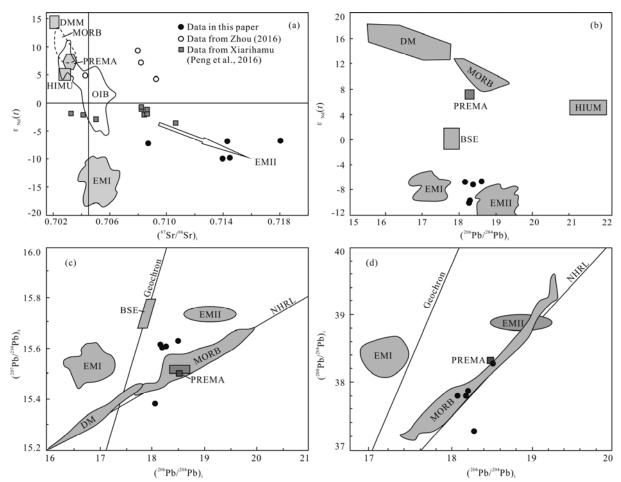


Fig. 10. Diagrams of $({}^{87}\text{Sr}/{}^{86}\text{Sr})_i$ vs. $\varepsilon_{Nd}(t)$, $({}^{206}\text{Pb}/{}^{204}\text{Pb})_i$ vs. $\varepsilon_{Nd}(t)$, $({}^{206}\text{Pb}/{}^{204}\text{Pb})_i$ vs. $({}^{207}\text{Pb}/{}^{204}\text{Pb})_i$ and $({}^{206}\text{Pb}/{}^{204}\text{Pb})_i$ vs. $({}^{208}\text{Pb}/{}^{204}\text{Pb})_i$ of the mafic–ultramafic rocks in the No. I complex.

These samples show a trend toward the EMII end member, which are similar to the Xiarihamu (Peng et al., 2016), and form an array between the DMM and EMII end members (Fig. 10). The EMI end member appears to be less possibly because they plot in the right of Geochron (Fig. 10c–d) for the EMI mantle enriching non-radioactive Sr, Nd and Pb isotopes and originating from lithospheric mantle under the continents (Hart, 1988; Menzies, 1989; Xia Zhaode et al., 2017). Therefore, we suggest that the primary magma of the Shitoukengde No. I maficultramafic complex originated from asthenospheric mantle that experienced contamination of EMII component during ascent.

Crustal contamination and hybridization typically causes an elevated SiO₂, K₂O, Rb, Ba, Th, Zr, Hf, Ta/Nb, Zr/Hf, ⁸⁷Sr/⁸⁶Sr, and ²⁰⁷Pb/²⁰⁴Pb (Zhao et al., 2007; Mir et al., 2011), a decrease in P₂O₅, TiO₂, Ti/Yb, Ce/Pb, and ¹⁴³Nd/¹⁴⁴Nd (Barker et al., 1997; Macdonald et al., 2001; Wang Guan et al., 2014a), and triggers the saturation of S in the magma (Zhang et al., 2009b). Thus, it can be identified by the covariant relationships between ratios of elements with similar distribution coefficients that are not

affected by fractional crystallization or the degree of partial melting (Mecdonald et al., 2001; Jiao Jiangang et al., 2012; Wang Guan et al., 2014a; Qian Xin et al., 2016), such as Ce/Yb, La/Yb, Th/Yb, Zr/Yb, Nb/Ta and Zr/Nb. The mafic-ultramafic rocks in No. I complex show positive correlations for Ce/Yb vs. La/Yb and Th/Yb vs. Zr/Yb (Fig. 11a-b). Meanwhile, diagram of (Th/Nb)_N vs. $(Sm/Yb)_N$ (Fig. 11c) shows the crustal contamination trend for these samples as well (Qian Xin et al., 2016). Furthermore, the Ti/Cr ratios of Shitoukengde No. I complex (0.45-4.42, averaging 2.18) are greater than those of the mantle (0.32; Taylor et al., 1985), whereas the continental crust is 29.19 (Taylor et al., 1985), and their Ce/Pb ratios (0.55–1.75, averaging 1.01) are smaller then those of the continental crust (<15; Furman et al., 2004) and the mantle $(25 \pm 5;$ Furman et al., 2004), suggesting the significant crustal contamination. These samples plot near the average values of the middle crust on the diagram of (Th/Yb)_N vs. (Ta/Th)_N (Fig. 12a) and plot between the average values of the lower and upper crust on the diagram of (La/Nb)_N vs. (Th/Ta)_N (Fig. 12b), which suggests that the materials responsible for contamination

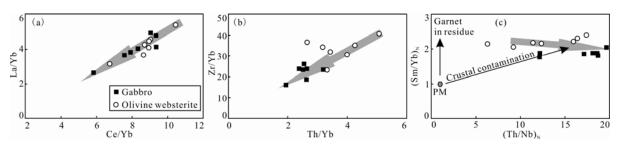


Fig. 11. Ce/Yb vs. La/Yb (a), Th/Yb vs. Zr/Yb (b) and $(La/Nb)_N$ vs. $(Th/Ta)_N$ (c) diagrams of the mafic-ultramatic rocks in the No. I complex.

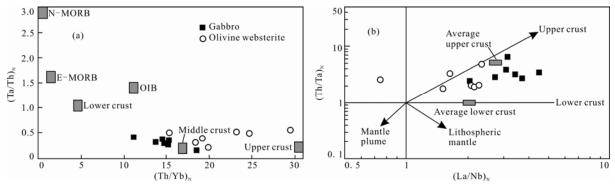


Fig. 12. $(Th/Yb)_N$ vs. $(Ta/Th)_N$ (a) and $(La/Nb)_N$ vs. $(Th/Ta)_N$ (b) diagrams of the mafic-ultramafic rocks in the No. I complex.

mainly originated from the middle crust. The similar phenomena also took place in other complexes associated with magmatic sulfide deposits, such as Voisey's Bay in Canada (Li et al., 2000), Jinchuan in Gansu Province of China (Li and Ripley, 2011), and Xiarihamu in Qinghai Province of China (Wang Guan et al., 2014a; Peng et al., 2016).

The mafic-ultramafic rocks in No. I complex show the geochemistry of enrichments of LREE and LILE (e.g., Rb, Th, K), depletions of HREE and HFSE (e.g., Nb, Ta, Ti, and Zr), and relatively high Th/Yb values (1.40–4.41), and typical arc-like geochemical features (Deng Yufeng et al., 2011), indicate that the source of the magma was affected by subduction-related fluids or melts (Pearce and Peate,1995; Zhao Yun et al., 2016). On the diagram of Nb/Yb vs. Th/Yb (Fig. 13a), these samples plot in the volcanic arc array, reflecting the influence of subduction components. In addition, their Nb/Tb (2.0–7.0) and Zr/Hf

(14.1-32.8) values are significantly lower than those of primitive mantle (17.8 and 37, respectively; McDonough and Sun, 1995) and crust (11 and 33 respectively; Taylor and Mclennan, 1985), which, together with the relationships between Th/Nb-Ba/Th and Th/Zr-Nb/Zr (Fig. 13b-c), suggest that the mantle was metasomatized by fluids derived from dehydration of a subducted plate. The above characteristics indicate that a great amount of fluid was injected into the magmatic mantle source (Woodhead et al., 2001; Hanyu et al., 2006; Li Zhuang et al., 2016). Previous studiers have shown that the geochemical composition of mantle magmatic sources in subduction environments was affected by the interaction between mantle peridotite and fluids or melts released during the alteration of oceanic crust, or subduction zone sediments (Hanyu et al., 2006; Tian et al., 2011). As a result, rutile, ilmenite, sphene, and other titanium-bearing minerals have a wide range of Nb, Ta, and Ti distribution

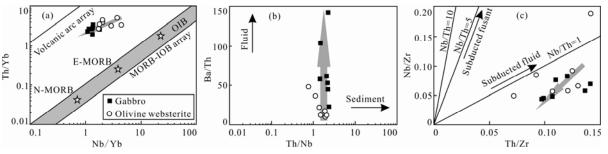


Fig. 13. Nb/Yb vs. Th/Yb (a) and Th/Nb vs. Ba/Th (b) and Th/Zr vs. Nb/Zr (c) diagrams of the mafic-ultramafic rocks in the No. I complex.

coefficients, and fluids derived from the dehydration of oceanic crust are relatively enriched in LILE and depleted in HFSE. These fluids interact with mantle material, enriching it in LILE and further depleting it in HFSE (Stolz et al., 1996; Wang Guan et al., 2014a). In conclusion, we consider that the primary magmas associated with the Shitoukengde magmatic sulfide deposit were originated from a metasomatised, asthenospheric mantle source which had previously been modified by subduction-related fluids.

6.2 Tectonic setting

The Shitoukengde Ni-Cu deposit is located in the basement uplifting and granite belt of middle of Eastern Kunlun, being one part of the Proto-Tethys Ocean tectonic domain. A large igneous province named Wanbaogou OBP (Sun Fengyue et al., 2009) formed on the Pre-Proto Tethys Ocean Mesoproterozoic-early in late Neoproterozoic (Sun Fengyue et al., 2009; Jin Lijie et al., 2015). Like the Ontong Java OBP on the western Pacific, which is the greatest large igneous province in the world recently, Wanbaogou OBP have great thickness of 25-35 km. So it is difficult to subduct beneath the continental crust unlike other normal oceanic plate. Many researches suggest that the Proto-Tethys Ocean opened and expanded due to the rifting and prolonged break-up of Rodinia supercontinent at about 860-570 Ma (Li et al., 2008; Lu Songnian, 2001). Subsequently, the southern margin of Qaidam Block translated from passive continental margin into active continental margin resulting in the trench-arcbasin system in early Caledonian, and the present North Kunlun terranes was the back-arc rift belt at Caledonian. Meanwhile, the Wanbaogou OBP moved toward the Qaidam Block.

A series of ophiolitic melange which distributed along the Middle Kunlun Fault were interpreted as the relic of Proto-Tethys Ocean closure, many mafic rocks of which formed at 522-509 Ma (Yang et al. 1996; Feng Jianyun et al., 2010). With subduction northward of the Proto-Tethys Ocean, a series of arc igneous rocks formed in the southern margin of Qaidam Block. The Kekesha quartz diorite from eastern of BGMK yields an emplaced age of 515 ± 4 Ma and it was regarded as the subduction product of the Proto-Tethys Oceanic plate in early stage (Zhang Yafeng et al., 2010). Zheng Yong et al. (2016) obtained the zircon U-Pb age of Bashikangkuole gabbro which was located in the Qiman Tagh area of 501 ± 1 Ma and suggested it formed in the back-arc basin setting. Volcanic -magma arc belt including different kinds of basic-acid magmatic rocks related to the early Paleozoic subduction of oceanic crust formed in Qiman Tagh area, such as the Yaziquan gabbro and diorite (480 ± 3 Ma; Cui Meihui et al., 2011), Kuangou-Xiaolangyashan basalt and rhyolite $(440 \pm 2 \text{ Ma} \text{ and } 450 \pm 1.2 \text{ Ma}; Wang Bingzhang et al., 2012)$ and Bashierxi granite $(458 \pm 9 \text{ Ma}; \text{Gao Xiaofeng et al., 2010})$. Consequently, the Baiganhu flysch basin formed due to the back-arc extension in Silurian (Li Guochen et al., 2012). Moreover, gabbro from Qingshuiquan area ($452 \pm 5 \text{ Ma}; \text{Sang Jizhen et al., 2016}$), meta-lava near Dulan County ($448 \pm 4 \text{ Ma};$ Chen Nengsong et al., 2002) and granodiorite from Gouli area ($454 \pm 2 \text{ Ma};$ Chen Jiajie et al., 2016) were the responsive product of the subduction northward of the Proto-Tethys Oceanic plate in the eastern part.

Mo Xuanxue et al., (2007) considered the Ar-Ar age (445 Ma) of glaucophane schist from Tumuleke, Qiman Tagh area, as the beginning of collision. Meanwhile, Wang Xiaoxia et al. (2012) and Wang Tao et al. (2016) suggested that the Wanbaogou rapakivi granite (441 ± 5) Ma) and Wulonggou granite $(438 \pm 3 \text{ Ma})$ formed in the syn-collisional/conversion of syn-collision and postcollision setting. A series of granites in Baiganhu Wu-Sn orefield (430-414 Ma; Gao Yongbao and Li Wenyuan, 2011; Li Guochen et al., 2012; Wang Zengzhen et al., 2014; Zhou Jianhou et al., 2015; Zheng Zhen et al., 2016), including a strongly peraluminous S-type granite, a high-K calc-alkaline I-type granite and a post-orogenic A₂-type granite, were considered forming in the tectonic setting of post-collision and within-plate. The late Ordovician lava located near Dulan County vielded a ⁴⁰Ar-³⁹Ar plateau age of hornblende with metamorphic origin of 427 ± 4 Ma and represent the metamorphic peak timing of orogenic process (Chen Nengsong et al., 2002). Gao Xiaofeng et al. (2010) obtained the Bashierxi K-feldspar granite with characteristics of A-type granite zircon U-Pb age of 432 ± 1 Ma and suggested that it was the product of the postcollision extensional setting. What's more, Ayak monzonitic granite in Qiman Tagh Mountain (420 ± 4 Ma; Hao Jie et al., 2003) and Houtougou monzogranite in Wulonggou area (Yan Wei et al., 2016) contained the characteristics of typical post-orogenic granite and was considered forming in the post-collision extensional setting. Coexistence of mafic-ultramfic rocks and granites implies that the tectonic regime of Eastern Kunlun Orogen had significantly shifted from syn-collisional extrusion turning into post-collisional extension setting with the intense crust-mantle interaction (Wang Guan et al., 2014a). Last but not least, the large-scale magmatic Ni-(Cu) sulfide deposit associated with the mafic-ultramafic intrusions (394-439 Ma; Li Shijin et al., 2012; Wang Guan et al., 2014a; Jiang Changyi et al., 2015; Li et al., 2015; Peng et al., 2016; Song et al., 2016) was the most significant support for intense extensional setting with the typical post-orogenic A2-type granite in Xiarihamu area

forming at 391 ± 1 Ma (Wang Guan et al., 2014b). Collectively, these geological evidences indicate that Proto-Tethys Ocean has close before ~445 Ma and then got into the syn-collisional stage (445–438 Ma), and after a post-collision extensional stage.

Zircons selected from the olivine websterite in No. I complex show the characteristics of zircons from basic intrusion, which U-Pb age were obtained by 422 Ma, indicates that Shitoukengde Ni-Cu deposit formed in late Silurian, approximate to the Xiarihamu Ni-(Cu) deposit (394-439 Ma; Li Shijin et al., 2012; Wang Guan et al., 2014a; Jiang Changvi et al., 2015; Li et al., 2015; Peng et al., 2016; Song et al., 2016). This suggests that the strong mafic-ultramafic magma activities associated with Ni-Cu mineralization took place at late Caledonian-early Hercymian epoch in the Eastern Kunlun Orogen, and to be the most significant ore-forming event of magmatic sulfide deposits in this area recently. Many researchers (Aldanmaz et al., 2000; Wang et al., 2004) considered that magmas formed in a post-collisional extensional setting may have geochemical signatures of an island arc or active continental margin. Thus, the source region can retain the characteristics of previously subducted oceanic crust, such as a strong enrichment in LILE (e.g., Rb, Ba, Th, U, and K) and depletions in HFSE (e.g., Nb, Ta, P, and Ti). In conclusion, the Shitoukengde mafic-ultramafic complexes probably formed in a post-collisional and extensional regime, the same as to the Xiarihamu Ni-(Cu) deposit.

6.3 Constraints on ore genesis

Magmatic Cu-Ni-(PGE) sulfide deposit is closely related to the coexistent mafic-ultramafic complex frequently and the mineralization was generally hosted in the ultramafic rocks. Sulfide liquids are enriched in chalcophile elements that become differentiated due to gravitational sinking, leading to sulfide enrichment and mineralization. The forming of large-scale magmatic sulfide deposit was often constrained by the following factors (Naldrett, 1999): a) enough ore-forming material (e.g., Ni, Cu, and PGE); b) attainment of sulphur saturation in magmas; c) plenitudinous reaction between the liquated sulphur and magmas in order to extract abundant Ni; d) accumulation in particular position for sulfides, otherwise low possibility for giant and rich deposit, or even non-ore. Tang Zhongli et al. (1991, 2006) suggested that the liquation and preenrichment of sulfide chiefly finished in the chamber and during ascent, and then these sulfides emplaced to the existent place. The chemical activity and solubility of sulphur, geochemistry of metallogenic element are the most obvious and direct indexes for the study of magmatic sulfide deposit. Because the most important factor for sulfide deposition is the attainment of S saturation in magmas (Brugmann et al., 1993; Mavrogenes and O'Neill, 1999). A negative correlation exists between solubility and magma pressure: S tends to become unsaturated as magma pressure decreases during ascent (Peng et al., 2016). Without external influences, magmatic sulfur cannot generate the saturation which is required to form large-scale deposit (Naldrett, 2004). Assimilation, contamination (especially the felsic contamination) and carbonaceous from country rock, resulting in addition of S and Si, are the key factors for the S saturation in magmas, particularly the intense contamination of crustal material approved by numbers of isotopes, rare earth elements and trace elements (Naldrett, 1999). The δ^{34} S values of sulfides from No. I complex have a small range of 1.9-4.3 ‰ that slightly greater than mantle δ^{34} S values (0±2‰; Ripley and Li, 2007), suggesting that magmas that fed the Shitoukengde intrusions assimilated crust-derived S, which was responsible for generating S saturation.

As mentioned above, the mafic-ultramafic rocks from No. I complex have the geochemical signatures of an island arc or active continental margin, such as a enrichment in LREE and LILE (e.g., Rb, Ba, Th, U, and K), depletion in HREE and HFSE (e.g., Nb, Ta, P, and Ti), and its magmatic source was depleted mantle source reformed by subducted fluids. However, complexes in Shitoukengde have great differences to Alaskan-type intrusion on geology, mineralogy, petrology and chemistry. The parental magma of typical Alaskan-type intrusion are generally characterized by CO₂, H₂O-rich fluid, high CaO content and high CaO/Al₂O₃ values (Green et al., 2004; Tian et al., 2011), and the rockforming minerals mainly are olivine, clinopyroxene and hornblende with minor plagioclase and orthopyroxene, and rocks mainly are dunite, clinopyroxene peridotite, clinopyroxenite and hornblendite (Himmelberg and Loney, 1995; Tian et al., 2011), and the content of magnetite reach 10%-20% commonly (Gu Lianxing et al., 1994). However, the complex in Shitoukengde mainly comprise olivine, orthopyroxene, clinopyroxene and plagioclase on minerals, peridotite, harzburgite, websterite, orthopyroxenite and gabbro on rocks with little magnetite. Thus, we suggest that Shitoukengde is a magmatic Ni-Cu sulfide deposit formed in a postcollisional and extensional regime. Because magmas formed in a post-collisional extensional setting may have geochemical signatures of an island arc or active continental margin (Aldanmaz et al., 2000; Wang et al., 2004).

During subduction northward of the Proto-Tethys Oceanic plate in Early Paleozoic, the subcontinental lithospheric mantle was metasomatic by fluids derived from dehydration of the subducted oceanic crust resulting in forming enriched lithospheric mantle. Meanwhile, the Wanbaogou OBP moved toward the Qaidam Block. Then (445–438 Ma) the Wanbaogou OBP, as a "soft basement", collaged to the southern margin of Qaidam Block resulting in the closure of Proto-Tethys Ocean. The subduction of the superficial oceanic crust was impeded due to its great thickness (25-35 km), whereas the oceanic crust in deep still keep downgoing. Thus, the subducted oceanic crust certainly break-out due to the asymmetrical pulling force and slab window formed. The suboceanic asthenospheric mantle passed through the slab window and upwelled, which led to partial decompression melting, and the primitive magmas were contaminated with some enriched lithospheric mantle during ascent that formed in the early subduction stage. The fractional crystallization and contamination of generous crustal material in the magma chamber resulted in S saturation and sulfide liquation, and the parental magmas liquated into ore-free magma, orebearing magma, ore-rich magma and ore magma. These differentiated magmas pulsatorily emplaced to the crust due to their buoyance, and eventually formed the maficultramafic complexes and Ni-Cu deposit (Fig. 14).

7 Conclusions

(1) The Shitoukengde magmatic Ni-Cu sulfide deposit formed in the late Silurian (426–422 Ma) post-collisional, extensional regime related to the subducted oceanic slab break-off after the Wanbaogou oceanic basalt plateau collaged northward to the Qaidam Block.

(2) The primary magmas were originated from a metasomatised, asthenospheric mantle source which had previously been modified by subduction-related fluids, and experienced significant crustal contamination both in the magma chamber and during ascent triggering S oversaturation by addition of S and Si, that resulted in the deposition and enrichment of sulfides.

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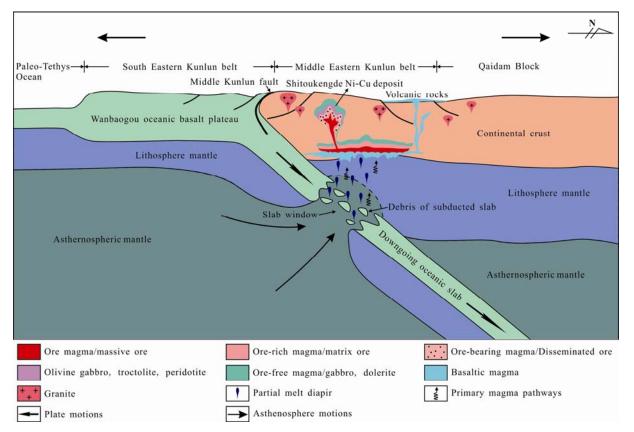


Fig. 14. Diagrammatic sketch of geodynamic process forming the Shitoukengde Ni-Cu deposit in Silurian-Devonian, Eastern Kunlun Orogen (modified from Li Shijin et al., 2012; Barnes et al., 2017).

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