Geochronology and geochemistry of submarine volcanic rocks in the Yamansu iron deposit, Eastern Tianshan Mountains, NW China: Constraints on the metallogenesis

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A B S T R A C T

The Yamansu skarn iron deposit is hosted in Early Carboniferous submarine lava flow and volcaniclastic rocks of the Yamansu Formation in Eastern Tianshan Mountains, NW China. The lava flows are predominantly basaltic, with minor andesites. Laser ablation inductively coupled plasma mass spectrometry (LA−ICP−MS) U−Pb zircon dating of the basalts and skarns yields almost coeval ages of 324.4 ± 0.94 and 323.47 ± 0.95 Ma, respectively. The basalts contain clinopyroxene and plagioclase phenocrysts with a considerable amount of Fe−Ti oxide minerals in the groundmass as interstitial phases, probably suggesting that olivine−clinopyroxene−plagioclase fractionation within the magma chamber. Geochemically, the basalts are characterized by slight variations in SiO2 (42.90−46.61 wt.%) and Al2O3 (14.71−19.93 wt.%), total Fe2O3 (8.14−12.60 wt.%) and MgO (4.96−8.52 wt.%). They possess flat to light rare earth element (REE)-depleted patterns and display variable degrees of depletions in high field-strength elements (HFSE), suggesting a transitional feature between MORB and arc volcanic rocks, and indicating a back-arc tectonic setting. Furthermore, the geochemical signature also suggests that the volcanic rocks of Yamansu Formation were produced by partial melting of the spinel-facies, asthenospheric mantle peridotite which had been metasomatized by slab-derived fluids. The broadly overlapping ages of the basalts and skarn mineralization suggest that the skarn formation in the Yamansu deposit is related to subaqueous volcanism. In combination with the available information including fluid inclusions and stable isotope data, we infer that the hydrothermal fluids that generated the skarns could be a mixture of evolved magma-derived fluids and convecting sea water driven by the heat from the shallow active magma chamber. The Yamansu basalts provided the source of iron for the skarn mineralization. We envisage the submarine volcanism, skarn alteration and iron mineralization in the Yamansu iron deposit as a continuous process, different from either conventional intrusion-related skarn type or submarine volcanic exhalation sedimentation type.

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1. Introduction

Dill (2010) classified iron ores into four types: magmatic, structure-related, sedimentary and metamorphic. The magmatic iron deposits are further divided into five subgroups: 1) Fe−Ti−V deposits related to mafic intrusions; 2) apatite-bearing Fe oxide deposits (Kiruna-type); 3) apatite-bearing Fe oxide deposits related to alkaline igneous rocks; 4) volcanic-hosted Fe (unmetamorphosed) deposits; and 5) contact metamorphic Fe deposits (Fe skarn). Most of the major high-grade iron ores of the world are predominantly sourced from sedimentary and metamorphic iron deposits (Clout and Simonson, 2005). In contrast, skarn type deposits constitute the most important source for high-grade iron ores in China (Zhao et al., 2004), together with some Kiruna-type and submarine volcanic-hosted iron ore deposits.

The metallogenesis of submarine volcanic-hosted iron ore deposits is poorly understood (Dill et al., 2008). Most of these deposits in China are commonly characterized by extensive skarn alteration, such as the Mengku in Altai (Xu et al., 2010); Beizhan and Chaqangnuoer in western Tianshan (Hong et al., 2012; Zhang et al., 2012); and Dahongshan in southern Yangtze craton (Zhao and Zhou, 2011). However, these skarns lack any clear spatial link with intrusive rocks and are therefore distinct from the conventional types (e.g., Finaudi et al., 1981), leading to debates on the genesis of these deposits over decades (e.g., Jiang and Wang, 2005). Some authors suggest that the skarns could be genetically related to a buried intrusion (Mao et al., 2005), whereas others consider them to be related to coeval submarine volcanism (Jiang, 1983). Accordingly, these deposits have been classified into two contrasting types: intrusion-related skarn deposit (e.g., Mao et al., 2005; Pirajno, 2010; Yang et al., 2010) and submarine volcanic exhalation sedimentation type (e.g., Jiang, 1983).

The Yamansu iron deposit in Eastern Tianshan Mountains (Pirajno, 2010) is a typical example for the latter type of deposit. The iron
mineralization in the Yamansu deposit is stratabound, with thickness varying from 100 to 130 m, and spatially related to the garnet-dominant skarns (Mao et al., 2005). In this paper, we report zircon LA–ICP-MS ages for both volcanic rocks and garnet skarn, with a view evaluating their genetic linkage. From bulk-rock geochemistry and Sr–Nd isotopic compositions of the ore-hosting volcanic rocks, we discuss the petrogenesis and geodynamic setting of the iron deposit.

2. Geological setting

2.1. Regional geology

The Tianshan orogenic collage extends for about 2400 km—from the Aral Sea eastwards through Uzbekistan, Tajikistan, and Kyrgyzstan, to Xinjiang in China and is an important component of the Central Asian Orogenic Belt (CAOB; De Grave et al., 2012; Dong et al., 2011; Kröner et al., 2011, 2013; Lei et al., 2011; Long et al., 2012; Rojas-Agramonte et al., 2011; Windley et al., 2007; Wong et al., 2010; Xiao et al., 2004a,b, 2010, 2013; Yang et al., 2012). The Paleozoic tectonic evolution history of the Eastern Tianshan remains controversial. Some researchers have suggested that the Eastern Tianshan resulted from the southward subduction of the Junggar Ocean along the Dananhu–Tousuquan belt (Ma et al., 1993; Qin, 2000; Zhang et al., 2004), whereas others consider a northward subduction of the south Tianshan Ocean (Wang et al., 2006b). The main structures of the Eastern Tianshan consist of a series of approximately east–west-trending faults, including the regional-scale Kalamai, Kanggur, Aqishan–Yamansu, Weiya, Aqikkudug and Kumishi faults (Fig. 1).

The Eastern Tianshan is bound to the north by the Turpan–Hami (commonly abbreviated as Tuha) basin, which is a part of the Junggar block, and to the south by the Aqikuduke–Shaquanzi Fault, which separates this northern belt of the Tianshan from the Middle Tianshan (or Central Tianshan). The Eastern Tianshan mainly consists of three tectonic units: Bogeda–Haerlike Belt in the north, Juelluotage Belt in the center and Middle Tianshan Microblock in the south (Fig. 1; Xu et al., 2009). The Bogeda–Haerlike Belt is made up of well developed Ordovician-Carboniferous volcanic rocks, granites and mafic–ultramafic complexes (BGMRXUAR, 1993; Gu et al., 2001; Li et al., 2006). The Middle Tianshan microblock is composed of Precambrian crystalline basement (BGMRXUAR, 1993; Qin et al., 2002, 2006b). The Juelluotage Belt is characterized by Middle Paleozoic volcanic and sedimentary rocks, including subaerial volcanics, sandstones and pelitic slates with inter-layered limestones, mudstones, siltstones and conglomerates (BGMRXUAR, 1993). This belt can be further subdivided, from north to south, into the Wutongwozi–Xiaorequanzi belt, Dananhu–Tousuquan belt, Kanggur–Huangshan ductile shear zone and Yamansu belt (Fig. 1; Qin et al., 2002). The Dananhu–Tousuquan belt is made up of Devonian to Carboniferous volcanic and intrusive rocks, and several porphyry copper deposits (e.g. Tuwu and Yandong) occur in this belt (Fig. 1. Gu et al., 2001; Li et al., 2006). The high-Mg andesites, adakite and Nb-rich basalts recognized in this belt have led to the interpretation of an arc setting (Wang et al., 2006b). The Wutongwozi–Xiaorequanzi belt and Kanggur–Huangshan ductile shear zone are characterized by Carboniferous sedimentary rocks, and the latter hosts Cu–Ni deposits associated with mafic complexes (e.g. Huangshan and Xiangshan) as well as porphyry deposits (e.g. Sanchakou Cu–Mo and Baishan Mo–Re), located between the Kanggur and Aqishan–Yamansu faults (Fig. 1). The Yamansu belt lies between the Aqishan–Yamansu fault, which marks the southern boundary of the Kanggur–Huangshan ductile shear zone, and the Aqikkudug fault (Fig. 1). The exposed rocks comprises a ~5 km thick succession of Mississippian bimodal volcanic rocks of the Yamansu Formation, Pennsylvanian flysch of the Shaquanzi Formation, and clastic rocks; andesitic tuff, and intercalated carbonate rocks of the Tugutublak Formation and overlying Permian marine and terrestrial clastic rocks, which are intercalated with bimodal volcanic rocks and carbonate rocks. Extensive Carboniferous–Permian magmatism resulted in the emplacement of high-Na, relatively...
oxidized, sub-alkaline magmas (Qin et al., 2002, 2003). Although many workers proposed that the volcanic rocks in the Yamansu formation were generated in a back-arc basin setting (Li et al., 2002; Xiao et al., 2004a,b) the tectonic regime of the belt is still debated. Several high-grade iron ore deposits such as the Yamansu, Kumutag, Bailingshan and Hongyuntan, have been recognized in these volcanic rocks (Fig. 1).

2.2. Deposit geology

2.2.1. Stratigraphy and igneous rocks

The Yamansu iron deposit occurs about 80 km south of Hami City (Fig. 1). Regionally, the exposed strata consist of Lower Carboniferous Yamansu Formation, Upper Carboniferous Shaquanzi Formation, and Lower Permian Aqikebulake Formation. Around the Yamansu open pit, the Yamansu Formation comprises intermediate-mafic lava and pyroclastic rocks, limestone and minor felsic rocks. The Shaquanzi Formation mainly comprises flesch, and is overlain by the Lower Permian marine and terrestrial clastic rocks, which are intercalated with bimodal volcanic rocks and carbonate rocks. A number of faults have been recognized surrounding the deposit, and they include five NNE to ENE-trending faults (Fig. 2).

The lava flows are predominantly basaltic with minor andesite in the Yamansu deposit. The basaltic and andesitic lavas display a gradational contact, and the two rock types cannot be easily distinguished in hand specimen. These flows are generally several meters thick, rarely up to 100 m. The lava flows are interbedded within pyroclastic rocks. The basalts are dark gray to dark green, and are locally amygdaloidal with calcite, chalcedony and chlorite. These rocks show typical porphyritic texture (Fig. 3a), and contain phenocrysts of partially to completely altered plagioclase (~40%), amphibole, pyroxene altered to chlorite (~30%), and minor biotite. The groundmass is fine grained, with interstitial or intergranular texture, and consists predominantly of plagioclase and augite with minor accessory anhedral iron oxides, apatite, biotite and hornblende. The andesites possess a mineral assemblage and textural features similar to those of the basalts, but with considerably lower contents of clinopyroxene.

No intrusions have been identified at the Yamansu deposit, except for the subvolcanic pyroxene–diorite porphyry exposed about 500 m southwest of the orebodies (Fig. 2a). However, a gravity survey suggests that some buried intrusive rocks might be present at depth (Mao et al., 2005). Several ancient volcanic edifices were recognized adjacent to the deposit on the basis of remote sensing and facies analysis of the
volcano-sedimentary rocks. The Yamansu volcanic lavas are considered to be located within or adjacent to a volcanic centre (BGMRXUAR, 2010).

2.2.2. Orebodies

The Yamansu iron deposit contains a reserve of 32 Mt with an average grade of 51% Fe (Mao et al., 2005). Eighteen orebodies have been recognized in the deposit and occur as EW-trending stratiform, banded podiform to lenticular bodies (Fig. 2). Nos. 1, 2, 4, 7 and 8 orebodies are the largest, and Nos. 1 and 2 orebodies are the most economic. No. 1 orebody is >940 m long, and dips southwards with the dip angle of 43° at surface (980 m above sea level) to 72° at 420 m above sea level. The average width of the No. 1 orebody is 8.6 m. The No. 2 orebody strikes ~1300 m discontinuously, dip southwards at 59° and is 7–17 m wide. Country rocks to orebodies are mainly mafic lavas and pyroclastic rocks intercalated with limestone of Yamansu Formation (Fig. 3c). The orebodies are mostly conformable with their country rocks (Fig. 2b).

Based on mineral assemblages, three types of ores have been identified: garnet–magnetite, garnet–magnetite–pyrite and magnetite–pyrite (BGMRXUAR, 2010). Field evidence and petrographic observation indicate four stages of mineralization: (1) prograde stage: garnet + albite + apatite, (2) retrograde stage: magnetite + epidote + chlorite + quartz + amphibole + apatite, (3) sulfide stage: pyrite + chalcopyrite + pyrrhotite + chlorite + quartz + calcite + galena + sphalerite, and (4) supergene stage: hematite + malachite + siderite + quartz + calcite (BGMRXUAR, 2010). Magnetite is the predominant ore mineral which occurs together with minor hematite, pyrite and chalcopyrite. The gangue minerals consist of garnet, hornblende, biotite, chlorite, epidote, quartz, calcite and other calc-silicate minerals (Mao et al., 2005). Ore textures include massive, banded, disseminated and irregular.

The sulfide stage is dominated by pyrite, chalcopyrite and pyrrhotite. Pyrite occurs as cubes in massive veins (<5 mm) or as isolated grains with amphibole and plagioclase, which often display cavities and embayed margins. Calcite and minor quartz are the main gangue minerals in this stage. They usually cut the earlier formed minerals like garnet and amphibole as veins or stockworks. Hematite, siderite and malachite are restricted to the supergene stage.

2.2.3. Skarns

Skarn is ubiquitous and intensively developed in the Yamansu deposit, with a strike length of ~1000 m, a depth in excess of 600 m and an average width of 120 m as demarcated from surface mapping and diamond drilling (Fig. 2). The skarn shows a distinct boundary with the country rocks (Fig. 3d). The dominant skarn minerals are garnet with subordinate amphibole, epidote, chlorite, pyroxene, albite, as
well as magnetite, pyrite, chloropyrite and pyrrhotite. Relics of garnet and epidote can be observed in massive ores (Fig. 3e). The prograde stage is characterized by formation of a large amount of garnet (grossularite–andradite; Fig. 3f). In contrast, pyroxene is very limited (<5%) and typically occurs as random pods (Ding, 1990). The retrograde stage is characterized by hydrous alteration, and dominated by epidote, and minor amphibole and chlorite (Fig. 3b), which replace the prograde minerals to variable degrees. The epidote is closely associated with the magnetite (BGMRXUAR, 2010). The amphibole veins commonly cut across garnets, indicating that amphibole formed later than garnet (Fig. 3f). During the late retrograde stage, a large quantity of magnetite, and epidote, amphibole, chlorite and garnet formed. Epidote is the most common mineral in the strongly retrograde altered rocks. Field relations and petrographic studies on the mineral paragenesis reveal that the skarn at Yamansu is similar to other conventional iron-bearing skarn deposits (Einaudi et al., 1981; Meinert, 1992).

3. Analytical methods

3.1. Zircon U–Pb dating and Lu–Hf isotopes

Zircons were separated from one ~20 kg basalt sample (YMS-44) and ~30 kg mineralized garnet skarn sample (YMS-45) by conventional heavy liquid and magnetic techniques, and then handpicked under a binocular microscope. Zircon grains were mounted on adhesive tape then enclosed in epoxy resin and polished to about half of their diameter. In order to observe textures of the polished zircons, CL imaging was carried out using a Hitachi S3000-N scanning electron microscope (SEM) with Mono CL3 Cathodoluminescence System for high resolution imaging and spectroscopy at the Institute of Geology, Chinese Academy of Geological Sciences (CAGS). Zircon U–Pb dating was performed by Finnigan Neptune multi-collector ICP-MS with a Newwave UP213 laser-ablation system at the Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing. Helium was used as the carrier gas to enhance the transport efficiency of the ablated material. The analyses were conducted with a beam diameter of 25 μm with a 10 Hz repetition rate and a laser power of 2.5 J/cm² (Hou et al., 2009). The isotope ratios were measured using a 204Pb monitored by 204Hg. The isotope ratios were measured using a 204Pb monitored by 204Hg; the 206Pb/204Pb were calculated using the ICPMSDataCal 4.3 program (Liu et al., 2008). The common-Pb was not corrected because of the high 206Pb/204Pb ratios (>1000). Data with abnormally high 204Pb contents were deleted. The zircon Plesovice is dated as unknown samples and yielded weighted mean 206Pb/238U age of 337 ± 2 Ma (2SD, n = 12), which is in good agreement with the recommended 206Pb/238U age of 337.13 ± 0.37 Ma (2SD) (Sláma et al., 2008). The age calculation and plotting of concordia diagrams were performed using Isoplot/Ex 3.0 (Ludwig, 2003).

The zircon Hf analytical procedures followed those described in K.J. Hou et al. (2007). All analyses were performed using a Neptune MC–ICP-MS located at CAGS. This mass spectrometer is equipped with double-focusing multi-collectors. A Geolas 200M laser ablation system (Microlas, Göttingen, Germany) was used equipped with an ArF excimer 193 nm laser. In this study, a 40 μm laser spot size was selected during the ablation with a repetition rate of 8 Hz. Measured 176Hf/177Hf ratios were not corrected for isobaric interference of 176Lu on 176Hf due to the extremely low 176Lu/177Hf in zircon (normally ~0.002). 176Lu/177Hf = 0.002655 was used for elemental fractionation correction. Isobaric interference of 176Yb on 176Hf was corrected using the mean fractionation index proposed by Liu et al. (2005). The applied value of 176Yb/177Yb is 0.5886 (Vervoort et al., 2004). A 176Hf/177Hf ratio of 0.282007 ± 7 (2σ, n = 36) was obtained for zircon GJ1, which is identical to values obtained by the solution method (K.J. Hou et al., 2007). Analytical data of this study were corrected using a 176Hf/177Hf ratio of 0.281994 ± 15 of zircon GJ1 (mean square weighted deviation = 2.2, n = 12).

3.2. Mineral chemistry

Microprobe analyses of garnets in skarn were performed by wavelength dispersive analysis (WDS) using standard procedures on the JXA-8200 electron microprobe at Washington University in St. Louis (MO, USA), using “Probe for Windows” for data reduction (see http://www.probesoftware.com/). Electron microprobe analyses were performed on clinopyroxene, plagioclase and magnetite, and the measured data were corrected using CITZAF after Armstrong (1985). Oxide and silicate standards were used for calibration (e.g., Amelia albite for Na, Si; microcline for K; Gates wollastonite for Ca; Alaska Anorthite for Al; synthetic fayalite for Fe; synthetic forsterite for Mg; synthetic TiO2 for Ti; synthetic Mn-olivine for Mn; synthetic Cr2O3 for Cr).

3.3. Major and trace elements

After screening under the microscope, relatively fresh samples of the basaltics were selected and sawed into slabs and the central parts were used for whole-rock analyses. Specimens were crushed in a steel mortar and ground in a steel mill to powders of ~200 mesh. Major elements were acquired through the analysis of fusion glass disks using a scanning wavelength dispersion X-ray fluorescence (XRF) spectrometer at the Key Laboratory of Orogenic Belts and Crustal Evolution, Ministry of Education, School of Earth and Space Sciences, Peking University. The analytical uncertainties are less than 1%, estimated from repeated analyses of two standards (andesite GSR-2 and basalt GSR-3). Loss on ignition was determined gravimetrically after heating the samples at 980 °C for 30 min.

Trace elements were determined by solution ICP-MS performed at the ICP-MS Laboratory at the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing. After complete dissolution, powders (~40 mg) were dissolved in distilled HF + HClO4 in 15 ml Savillex Teflon screw-cap breakers. Precision for most elements was typically better than 5% RSD (relative standard deviation), and the measured values for Zr, Hf, Nb and Ta were within 10% of the certified values. Two standards (granite GSR-1, basalt GSR-3) were used to monitor the analytical quality.

3.4. Sr–Nd isotopes

Relatively fresh samples of basaltic lava were chosen for Sr–Nd isotope analyses. Rb–Sr and Sm–Nd isotopic compositions were obtained using a Finnigan Triton Tl mass spectrometer at the Department of Earth Sciences, Nanjing University. Sr and Nd isotopic ratios were normalized against 86Sr/88Sr = 0.1194 and 146Nd/144Nd = 0.7219, respectively. 87Sr/86Sr for the NIST987 Sr standard was 0.710268 ± 0.000007 (2σ standard deviation, n = 8), and 143Nd/144Nd for the La Jolla Nd standard was 0.511842 ± 0.000006 (2σ standard deviation, n = 6). Total blanks were 100 pg for Sr and 80 pg for Nd, and negligible for the determination of isotopic compositions.

4. Results

4.1. Zircon U–Pb dating and Hf isotope

Zircon grains separated from the basalt (sample YMS-44) are generally transparent, euhedral, and prismatic, with clear oscillatory zoning (Fig. 4a) and high Th/U values (1.03–2.48, Table 1), typical of igneous zircons (Corfu et al., 2003). The measured U–Pb isotopic ratios are...
presented in Table 1. A group of seven zircon grains defines a concordia age of 324.4 ± 0.94 Ma (95% confidence level, MSWD of 1.7; Fig. 4a), interpreted as the crystallization age for the basalts of Yamansu Formation.

Compared with the zircon grains in the basalts, those from the skarn (sample YMS-45) are much darker, lack any obvious oscillatory zoning (Fig. 4b), and show lower Th/U values (0.85–1.27; Table 1). These features indicate zircon precipitation from hydrothermal fluids similar to those reported by Hu et al. (2004) from a quartz vein in the Rushan lode gold deposit in the Jiaodong Peninsula, Eastern China. Five zircon grains yield ages between 322.6 to 324.7 Ma, with a mean weighted age of 323.47 ± 0.95 Ma and MSWD of 0.68 (Fig. 4b), coeval with the basalts. Since most of the zircons from the basalts were damaged during age determinations, Lu–Hf analyses are given only for two grains, which show εHf(t) range of +10.13 to +13.51. Five zircons from the mineralized skarn define a relatively wide εHf(t) range of −1.26 to +8.40, significantly lower than those for basalts (see Table 2).

4.2. Garnet compositions

Electron microprobe analyses show that all garnets in the Yamansu deposit are calcium-rich in composition (Table 3). End-member calculations show that the garnet is mainly andradite and grossular (>90%; Fig. 5) with a compositional range of And_{2.65-97.16}Groz_{0.00-42.23}(Spe + Alm)_{1.09-5.08}Pyr_{0.05-0.76}. Zoned garnets are characterized by a relatively Fe-rich core and Al-rich rim. On ternary plots of garnet compositions from major skarn types (Fig. 5), our data plot within the fields defined by conventional iron skarn (Meinert, 1992) and iron skarn related to submarine volcanic rocks in China (Hong et al., 2012; Xu et al., 2010), but are markedly different from those associated with VMS deposits, which are typically dominated by Mn- and Fe-rich spessartine and almandine, such as the Sawusi Pb–Zn–Fe oxide deposit in Chinese Altai (Liu et al., 2012) and the Aguilar Pb–Zn–Ag deposit in Argentina (Gemmell et al., 1992) which are typically dominated by Mn- and Fe-rich spessartine and almandine (Fig. 5).

4.3. Geochemical variations of volcanic rocks

The major elements of the samples are recalculated on a volatile free basis, because some of the samples show loss on ignition up to 4.88 wt.%, possibly due to post-magmatic alteration (Fyfe, 1976; Melson et al., 1968). According to their degree of alteration, the basalts can be classified into two types: basalts and epidote-alteration basalts. The basalts are characterized by a slight variation in SiO₂.
Sr isotopic compositions of the Yamansu basalts exhibit positive εNd(t) values reaching up to +5.1 (Table 5), indicating that the effects of seawater alteration and metamorphism on the Nd isotopic system are minimal.

5. Discussion

5.1. Alteration effects

Because the Yamansu volcanic rocks were formed during the late Palaeozoic (~320 Ma) and have undergone greenschist facies metamorphism, it is necessary to assess the alteration and metamorphic effects before we employ the geochemical features as a tracer. Previous studies have shown that the concentrations of some trace elements such as REE and HFSE in igneous rocks are not generally affected during seawater alteration (e.g., Beswick, 1982), implying that their original trace element signature is still preserved. However, some mobile elements such as Ba, Rb, Sr and U show variable concentrations, implying that their original concentrations were likely altered by sea-floor metamorphism. Some major elements such as Ti and P are not readily affected by hydrothermal alteration (e.g., Zhou, 1999), whereas K and Na are typically mobile (Beswick, 1982), implying that their original concentrations were likely modified by alteration effects. Thus, these mobile elements will not be utilized in the discussions below.

Previous studies have also shown that only severe seawater alteration can affect the 143Nd/144Nd ratios of oceanic rocks because seawater is exceedingly low in Nd and Sm (4 × 10^{-6} and 8 × 10^{-7} ppm, respectively; Mahoney et al., 1998). Severe alteration will also significantly decrease 143Nd/144Nd and Sm/Nd ratios (e.g., Dupre and Mahoney, 1992; Dosso et al., 1993, and references therein). The REE-depleted patterns (La/SmN = 0.27–0.59) with only minor or no negative Eu anomalies, features that are identical to those of mid-ocean ridge basalts (MORB; Fig. 6a). Furthermore, the basalt samples generally possess higher concentrations of large ion lithophile elements (LILE), such as Th (0.15–0.19 ppm), relative to high field strength elements (HFSE), Nb, Zr and Hf depletion is also displayed in the absence of any obvious Ta anomaly (Fig. 6b).

The depletion to slight enrichment in LREE, flat HREE patterns and negative Nb anomaly of the Yamansu basalts are similar to those of back-arc basin basalts (BABB) in the Mariana Trough (Gribble et al., 1996, 1998), Manus BABB in Papua New Guinea (Sinton et al., 2003) and Kuerti BABB in Chinese Altai (Xu et al., 2003) (Fig. 6). In contrast, the geochemical features of the Yamansu basalts are markedly different from typical submarine volcanic rocks associated with iron deposits in the Western Tianshan, e.g., Chagangnuoer and Zhibo, which display LREE + LILE enrichment and HFSE depletion, and have been correlated to island volcanic arc environment (Jiang et al., 2012). In addition, our Zircon Hf isotopic compositions of Yamansu basalts and skarns.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Isotopic ratios</th>
<th>Apparent ages (Ma)</th>
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<tr>
<td></td>
<td>207Pb/206Pb</td>
<td>1σ</td>
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<tr>
<td>YMS-44</td>
<td>1 0.0546</td>
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<td>6</td>
<td>0.0528</td>
</tr>
<tr>
<td>YMS-44</td>
<td>7</td>
<td>0.0560</td>
</tr>
</tbody>
</table>

207Pb/235U calculated using 207Pb/206Pb(238U/206Pb × 1/137.88). Rho is the error correlation defined as err207Pb/235U/err207Pb/206U.

Table 2

Zircon Hf isotopic compositions of Yamansu basalts and skarns.

<table>
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<tr>
<th>No.</th>
<th>Age (Ma)</th>
<th>176Yb/177Hf</th>
<th>177Hf/176Hf</th>
<th>εHf(t)</th>
<th>εHf(t)</th>
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<tr>
<td>YMS44-3</td>
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<td>0.002737</td>
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<td>0.002050</td>
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<td>YMS44-6</td>
<td>323.0</td>
<td>0.056111</td>
<td>0.001730</td>
<td>2.82546</td>
<td>0.00024</td>
</tr>
<tr>
<td>YMS44-7</td>
<td>323.4</td>
<td>0.064892</td>
<td>0.001509</td>
<td>2.82430</td>
<td>0.00023</td>
</tr>
</tbody>
</table>
suggested Mg# ≥ 67 and FeOt/MgO ratios < 1.1, whereas Tatsumi and Eggins (1995) have documented Mg# > 70 and FeOt/MgO ratios < 1 for primary basaltic magmas. Moreover, primary magmas are characterized by 250–300 ppm Ni, 500–600 ppm Cr and 27–80 ppm Co contents (Frey et al., 1978; Perfit et al., 1980; Wilkinson and Le Maitre, 1987). Hence, the Mg# range between 45 and 62 for the Yamansu basalts, together with low Cr (44.54–71.91 ppm), Co (4.79–24.92 ppm) and Ni (17.32–34.83 ppm) indicate that the basalts of the Yamansu Formation are evolved.

In the Yamansu deposit, the basalts contain clinopyroxene and plagioclase phenocrysts with Fe–Ti oxide minerals in the groundmass as interstitial phases (Fig. 3a). Furthermore, SiO2, Al2O3 and total Fe2O3 show a weak negative correlation with MgO, whereas TiO2 remains constant with decreasing MgO (Fig. 8a). However, the enrichment of the LILEs (e.g. Th), relative depletion of the anatexial Nd isotopic composition similar to present day MORB. The positive εNd(t) values (Table 5), the depleted LREE patterns and MORB-like signatures for most of the samples indicate that these rocks originated by partial melting of an asthenospheric mantle source and MORB-like signatures for most of the samples indicate that these rocks originated by partial melting of an asthenospheric mantle source

5.3. Nature of the mantle source

Generally, magmas originating from the asthenospheric mantle are characterized by depletion in incompatible elements and high εNd(t) values (Saunders et al., 1992). This is the case for the most of Yamansu basalts. The positive εNd(t) (Table 5), the depleted LREE patterns and MORB-like signatures for most of the samples indicate that these rocks originated by partial melting of an asthenospheric mantle source with a depleted Nd isotopic composition similar to present day MORB. However, the enrichment of the LILEs (e.g. Th), relative depletion of
the high-field strength elements (HFSEs) (Nb and Ti), and the HREE (Yb) are characteristic features of magmas generated in supra-subduction zone settings (e.g., Wilson, 1989). The basalt sample YMS-29 shows a variable enrichment in LREE (Fig. 6) with (La/Yb)N ratio of 2.62, and (Tb/Yb)N value of 0.70 (Yang et al., 2007). Hence, nearly-flat to slightly fractionated chondrite-normalized HREE patterns, and the relatively high HREE and Y contents (Yb: 1.28 ppm, Lu: 0.19 ppm, Y: 7.84 ppm) for Yamansu basalts suggest absence of garnet control during melting. The heavy REE contents of primary magmas are mainly controlled by mantle composition and degree of partial melting and they have been widely used to determine the origin of magmas (e.g., Green, 2006; Gurenko and Chaussidon, 1995; Johnson, 1998; Münker, 2000). The REE are moderately incompatible during melting of mantle peridotite (Johnson, 1998), and thus, their concentrations and ratios are not greatly affected by mantle depletion and fluid influx (Münker, 2000; Pearce, 1995). In general, the heavy REE (e.g. Yb and Y) are preferentially retained by garnet during melting (c.f. Zhang et al., 2008), and thus, low La/Yb ratios reflect a melting regime dominated by relatively large melt fraction and/or spinel as the predominant residual phase, whereas high La/Yb ratios are indicative of smaller melt fractions and/or garnet control (Yang et al., 2007). Hence, nearly-flat to slightly fractionated chondrite-normalized HREE patterns, and the relatively high HREE and Y contents (Yb: 1.28–1.57 ppm, Lu: 0.19–0.25 ppm, 2–12 times the chondritic values; Y: 7.84–13.99 ppm) for Yamansu basalts suggest absence of garnet in the residue (c.f. Maheo et al., 2009; Wilson, 1989). This inference is further supported by the results obtained from the mantle melting modeling for the Yamansu basalts using La/Sm versus Tb/Yb ratios. All the basalt samples plot within the field of spinel peridotite (Fig. 9c), suggesting that the Yamansu basalts were produced by partial melting of the spinel-facies, asthenospheric mantle peridotite which was affected by slab-derived materials at depths of ~60–70 km (McKenzie and Bickle, 1989; Sun and McDonough, 1989).

The whole-rock REE contents of primary magmas are mainly controlled by mantle composition and degree of partial melting and they have been widely used to determine the origin of magmas (e.g., Green, 2006; Gurenko and Chaussidon, 1995; Johnson, 1998; Münker, 2000). The REE are moderately incompatible during melting of mantle peridotite (Johnson, 1998), and thus, their concentrations and ratios are not greatly affected by mantle depletion and fluid influx (Münker, 2000; Pearce, 1995). In general, the heavy REE (e.g. Yb and Y) are preferentially retained by garnet during melting (c.f. Zhang et al., 2008), and thus, low La/Yb ratios reflect a melting regime dominated by relatively large melt fraction and/or spinel as the predominant residual phase, whereas high La/Yb ratios are indicative of smaller melt fractions and/or garnet control (Yang et al., 2007). Hence, nearly-flat to slightly fractionated chondrite-normalized HREE patterns, and the relatively high HREE and Y contents (Yb: 1.28–1.57 ppm, Lu: 0.19–0.25 ppm, 2–12 times the chondritic values; Y: 7.84–13.99 ppm) for Yamansu basalts suggest absence of garnet in the residue (c.f. Maheo et al., 2009; Wilson, 1989). This inference is further supported by the results obtained from the mantle melting modeling for the Yamansu basalts using La/Sm versus Tb/Yb ratios. All the basalt samples plot within the field of spinel peridotite (Fig. 9c), suggesting that the Yamansu basalts were produced by partial melting of the spinel-facies, asthenospheric mantle peridotite which was affected by slab-derived materials at depths of ~60–70 km (McKenzie and Bickle, 1989).

Table 4

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>YMS25</th>
<th>YMS26</th>
<th>YMS27</th>
<th>YMS28</th>
<th>YMS29</th>
<th>YMS30</th>
</tr>
</thead>
<tbody>
<tr>
<td>46.61</td>
<td>45.06</td>
<td>45.71</td>
<td>44.01</td>
<td>42.90</td>
<td>46.36</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.78</td>
<td>0.75</td>
<td>0.74</td>
<td>0.82</td>
<td>0.82</td>
<td>0.81</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>17.13</td>
<td>17.53</td>
<td>14.71</td>
<td>16.77</td>
<td>16.75</td>
<td>19.93</td>
</tr>
<tr>
<td>TFeO₃</td>
<td>8.97</td>
<td>11.83</td>
<td>10.20</td>
<td>12.66</td>
<td>9.36</td>
<td>8.14</td>
</tr>
<tr>
<td>CaO</td>
<td>6.93</td>
<td>11.45</td>
<td>11.90</td>
<td>10.25</td>
<td>15.13</td>
<td>7.21</td>
</tr>
<tr>
<td>MgO</td>
<td>8.52</td>
<td>4.96</td>
<td>7.82</td>
<td>6.95</td>
<td>7.46</td>
<td>6.33</td>
</tr>
<tr>
<td>MnO</td>
<td>0.97</td>
<td>0.72</td>
<td>0.60</td>
<td>0.65</td>
<td>0.35</td>
<td>0.88</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.93</td>
<td>1.01</td>
<td>2.83</td>
<td>0.07</td>
<td>0.06</td>
<td>3.59</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.79</td>
<td>3.04</td>
<td>1.34</td>
<td>3.33</td>
<td>2.06</td>
<td>2.15</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.11</td>
<td>0.08</td>
<td>0.12</td>
<td>0.12</td>
<td>0.12</td>
<td>0.10</td>
</tr>
<tr>
<td>LOI</td>
<td>4.04</td>
<td>3.30</td>
<td>3.85</td>
<td>4.25</td>
<td>4.88</td>
<td>3.97</td>
</tr>
<tr>
<td>Total</td>
<td>99.77</td>
<td>99.73</td>
<td>99.82</td>
<td>99.88</td>
<td>99.89</td>
<td>99.69</td>
</tr>
</tbody>
</table>

Sc content in the basalt samples is between 0.364 and 0.75 ppm, respectively, where our samples plot above the MORB-OIB array (Pearce and Peate, 1995), clearly indicating a subduction component in their source areas because fluid/melt released from a subducted slab is known to result in high Th and low Nb in the upper mantle wedge (Pearce et al., 1995).
Although the tectonic regime of the Yamansu belt has been widely discussed in previous works, debate surrounds the tectonic setting for the Lower Carboniferous Yamansu Formation (Li et al., 2002; Xiao et al., 2004a,b). Specifically, the bimodal signature of the volcanic rocks of the Yamansu Formation and their exceptional thickness (~5 km), led to the suggestion by Li et al. (2002) that they represent volcanism in a rift zone. An island arc model has also been proposed (Xiao et al., 2004a,b).

Back-arc basin basalts (BABB) are generated by decompression melting with eruption along spreading ridges in a manner indistinguishable from that of true MORB and in most compositional aspects are similar to MORB (Klein and Langmuir, 1987). At the same time, a subduction component is also clearly involved (Gribble et al., 1996, 1998; Hawkins and Kerrich, 2000). Such a compositional feature is generally acknowledged to be unique to BABB (Hollings and Kerrich, 2000).

The Yamansu lavas show positive εNd(t) values (+1.4 to +5.1), zircon εNd(t) values (+10.13 to +13.51) and variable depletion of LREE, reflecting that the mantle source is moderately depleted, and this inference is consistent with other geochemical features, most of the samples plotting subparallel to the MORB trend in trace element diagrams, and possessing flat HREE patterns (Fig. 6). However, the εNd(t) values (+1.4 to +5.1) of the Yamansu basalts are obviously lower than the typical MORB values (εNd(t) = +10; Dosso et al., 1993; Mahoney et al., 1992, and references therein). Together with the significantly negative Nb anomalies displayed by our samples, we infer the possible involvement of slab-derived materials. Consequently, the Yamansu basalts have both arc-like and MORB-like geochemical affinities, which are typical features of BABB. Such an inference is supported by the results obtained from the tectono-magmatic discrimination diagrams (Fig. 10a–d) that clearly exhibit transitional features between island arc and mid-ocean ridge basalts.

Mafic rocks with a high Nd isotopic signature occur in some forearc regions where they are commonly associated with boninitic and intermediate to felsic volcanic rocks such as in the Izu–Bonin forearc (Taylor et al., 1992), Acoje block in the Zambales ophiolites (Evans et al., 1991; Hawkins and Evans, 1983) and in the Trinity ophiolites (Wallin and Metcalfe, 1998). Although most of the Yamansu basalts are highly depleted in light REE and have an elevated Nd isotopic ratio, no boninitic and high-Mg andesite rocks have been found within the suite. However, Mississippian high-Mg andesites, adakite and Nb-rich basalts have been recognized in the Dananhu zone. A ni- slan model has also been proposed (Xiao et al., 2004a,b), specifically acknowledging that the mantle source is moderately depleted, and this inference is consistent with other geochemical features, most of the samples plotting subparallel to the MORB trend in trace element diagrams, and possessing flat HREE patterns (Fig. 6). However, the εNd(t) values (+1.4 to +5.1) of the Yamansu basalts are obviously lower than the typical MORB values (εNd(t) = +10; Dosso et al., 1993; Mahoney et al., 1992, and references therein). Together with the significantly negative Nb anomalies displayed by our samples, we infer the possible involvement of slab-derived materials. Consequently, the Yamansu basalts have both arc-like and MORB-like geochemical affinities, which are typical features of BABB. Such an inference is supported by the results obtained from the tectono-magmatic discrimination diagrams (Fig. 10a–d) that clearly exhibit transitional features between island arc and mid-ocean ridge basalts.
Junggar Ocean margin in the Eastern Tianshan. The Junggar Ocean is believed to have existed to the north of Eastern Tianshan during the Palaeozoic (c.f. Xiao et al., 2004a,b). Because it is located to the north of the Yamansu back-arc basin, we infer that an island arc (Dananhu–Tousuquan)–backarc basin (Yamansu) system was formed in response to the southward subduction of the Junggar ocean rather than the northward subduction of the south Tianshan ocean.

5.5. Genesis of skarn

The skarn mineralization in the Yamansu iron deposit does not exhibit a clear spatial link with any intrusions, but occurs stratabound within
the intermediate-basic volcanic lava and clastic rocks. These features are comparable with both volcanic exhalation–sedimentation deposits and skarn deposits. Therefore, a volcanic exhalation–sedimentation model has been proposed to explain the origin of the Yamansu skarn and related iron oxide deposit. According to the volcanic exhalation–sedimentation model, the skarn formation occurs by reaction between hydrothermal fluids and submarine seafloor rocks (volcanic rocks and limestone). Stratiform skarns have been proposed and described by many researchers. The garnets at Yamansu are Ca-rich and Fe-rich spessartine and almandine, consistent with enrichment of Fe and Mn, such as the Fe–Mn crust on the seafloor.

Deep intrusion-related fluids can travel some distance from their source to interact with appropriate country rocks to generate skarns. The garnets at Yamansu are Ca-rich and Fe-rich spessartine and almandine, consistent with enrichment of Fe and Mn, such as the Fe–Mn crust on the seafloor.

5.6. Iron mineralization

Previous fluid inclusion studies had yielded formation temperatures of around 340–330 °C for magnetite and 220–150 °C for pyrite, with salinities between 12.9 and 2.7 wt.% NaCl equiv., indicating...
hydrothermal fluids (Mao et al., 2005). Experimental studies suggest that the solubility of Fe in solutions is dependent on the activity of NaCl (Bell and Simon, 2011); when the content of cations in solutions reaches about 30 wt.%, the solubility of Fe could be up to 8 wt.% (Kwak et al., 1986). The moderate to high salinity of Fe-bearing fluids favors transportation of Fe as a chloride complex (Bell and Simon, 2011). Since the skarn at Yamansu was probably formed by interaction between hydrothermal fluids and Ca-rich volcanic rocks and/or carbonates as stated above, the iron ores possibly have a similar origin. The common occurrence of Cl-rich hornblende and other hydrous minerals such as apatite, epidote and chlorite in the skarn and iron ores indicates aqueous chloride solutions as carriers of dissolved Fe (Bell and Simon, 2011).

The geochemical data presented in this study favor a mantle source for the submarine volcanic rocks of Yamansu Formation, metasomatized by subduction-related fluids. Thus, a relatively higher content of volatiles would be expected in the mantle-derived magma (e.g. Johnson et al., 2009). In addition, the fractional crystallization of anhydrous minerals such as olivine, clinopyroxene and plagioclase is also capable of enhancing the volatile content of the residual magma. This is consistent with the presence of some igneous hydrous minerals (hornblende and biotite) which occur as interstitial phases in the basalts. The volatile- and chlorine-rich magmatic fluids favor the formation of hydrothermal fluids by exsolution or degassing during the late magmatic stage (e.g. Halter and Webster, 2004; Webster et al., 1999) especially when the magma is emplaced at shallow depth under the seafloor (e.g. Woods and Pyle, 1997). Moreover, the δ18O values of magnetites in this deposit range from 5.3‰ to 12.8‰ (Mao et al., 2005 and references therein), suggesting that the magma-derived fluids mixed with meteoric water, probably seawater. Given the submarine environment, it can be inferred that the hydrothermal fluids could have been derived from a mixture of evolved magmas and seawater heated by the shallow magma chamber beneath the Yamansu deposit.

With respect to the iron source, it is difficult to explain the carbonate rocks as the potential source, because they have very low iron contents. The mafic volcanic rocks of the Yamansu formation are relatively enriched in iron (Table 4). This is substantiated by the tholeiitic evolution trend (Fig. 7b) which elevates the iron concentration in the residual magma (Osborn, 1959). Therefore, the volcanic rocks are the potential candidate for the source of most of the iron in the Yamansu deposit. However, the negative correlation between total Fe2O3 and loss-on-ignition (LOI) of our samples (Fig. 11) indicates post-magmatic hydrothermal removal of iron in the basalts rather than enrichment of iron. Since the major iron mineralization is closely related to the formation of epidote in wall rocks, it is very likely that leaching of erupted basalts could account for the enrichment iron in the ores. Considering that most of the ore bodies show stratabound affinity and the volcanic exhalation–sedimentation had been excluded, a fluid source at depth is considered to be most reasonable. Moreover, such a distal expression model is also consistent with the compositional zoning of garnet from skarn environments, where garnet growth, i.e. Fe-rich core and Al-rich margin (Table 3), reflects the interplay of heating and fluid infiltration (e.g., Jamtveit, 1997). The garnet composition changes during the passage of the ascending fluids and alteration front, and the zonation patterns therefore differ with proximity to the fluid source (Meinert et al., 2005), and the Fe decrease on the garnet rim probably corresponds to the onset of the iron oxide mineralization (e.g., Chiaradia, 2003).

Based on the above discussion, and considering the extensive occurrence of faults in these deposits, a convection cell driven by temperature gradients established by the active magma chamber can be envisaged. Circulation of ore-forming fluids is accommodated by the faulting of the submarine rocks of Yamansu Formation and the resulting enhanced
CaCl₂ and CO₂, some of which may descend with the return flow, magnetite is precipitated and the solutions become enriched in retrograde alteration stage, in concomitance with the formation of epiformed skarns between volcanic rocks and limestone. The erupted basaltic lava by volcanic rocks and limestone.

Although some CaCl₂ in the return flow could be removed by precipitation of Ca-bearing minerals, such as plagioclase or calcite, dilution by the sea water is also possible in an open circulation cell, which could account for the formation of more dispersed and low abundance skarn minerals in the submarine rocks of Yamansu Formation, i.e. volcanic rocks and limestone. This hypothesis requires the presence of a “magma chamber” that gave rise to both the submarine volcanism and the ore-forming fluids, as separate events.

6. Conclusions

The LA-ICP-MS zircon U–Pb age data obtained in this study show that the Yamansu volcanic rocks and skarns in the Eastern Tianshan of NW China are broadly coeval, yielding ages of 324.4 ± 0.94 and 323.47 ± 0.95 Ma, respectively. The Yamansu basalts possess a geochemically transitional character between MORB and IAB, suggesting that they were possibly generated in an oceanic back-arc basin tectonic setting related to the southward subduction of the Junggar oceanic crust beneath the Eastern Tianshan region. Furthermore, they were probably derived from a spinel-facies ashenphoritic mantele source which had been metasomatized by subduction-related materials. The skarns and iron ores were formed by interaction between fluids which were derived from a deep seated active magma chamber with the involvement of seawater and submarine rocks of Yamansu Formation, represented by volcanic rocks and limestone.

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