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Abstract: Long-standing controversy persists over the presence and role of iron–rich melts in the formation of volcanic rock-hosted iron deposits. Conjugate iron–rich and silica–rich melt inclusions observed in thin-sections are considered as direct evidence for the presence of iron-rich melt, yet unequivocal outcrop-scale evidence of iron-rich melts are still lacking in volcanic rock-hosted iron deposits. Submarine volcanic rock-hosted iron deposits, which are mainly distributed in the western and eastern Tianshan Mountains in Xinjiang, are important resources of iron ores in China, but it remains unclear whether iron-rich melts have played a role in the mineralization of such iron ores. In this study, we observed abundant iron-rich agglomerates in the brecciated andesite lava of the Heijianshan submarine volcanic rock–hosted iron deposit, Eastern Tianshan, China. The iron-rich agglomerates occur as irregular and angular masses filling fractures of the host brecciated andesite lava. They show concentric potassic alteration with silicification or epidotization rims, indicative of their formation after the wall rocks. The iron-rich agglomerates have porphyritic and hyalopilitic textures, and locally display chilled margins in the contact zone with the host rocks. These features cannot be explained by hydrothermal replacement of wall rocks (brecciated andesite lava) which is free of vesicle and amygdale, rather they indicate direct crystallization of the iron-rich agglomerates from iron-rich melts. We propose that the iron-rich agglomerates were formed by open-space filling of volatile-rich iron-rich melt in fractures of the brecciated andesite lava. The iron-rich agglomerates are compositionally similar to the wall-rock brecciated andesite lava, but have much larger variation. Based on mineral assemblages, the iron-rich agglomerates are subdivided into five types, i.e., albite-magnetite type, albite-K-feldspar-magnetite type, K-feldspar–magnetite type, epidote-magnetite type and quartz-magnetite type, representing that products formed at different stages during the evolution of a magmatic-hydrothermal system. The albite-magnetite type represents the earliest crystallization product from a residual iron-rich melt; the albite-K-feldspar-magnetite and K-feldspar–magnetite types show features of magmatic-hydrothermal transition, whereas the epidote-magnetite and quartz-magnetite types represent products of hydrothermal alteration. The occurrence of iron-rich agglomerates provides macroscopic evidence for the presence of iron-rich melts in the mineralization of the Heijianshan iron deposit. It also indicates that iron mineralization of submarine volcanic rock-hosted iron deposits is genetically related to hydrothermal fluids derived from iron-rich melts.

Key words: iron-rich agglomerates, iron-rich melt, volatile, submarine volcanic iron deposit, Heijianshan, Eastern Tianshan

1 Introduction

Volcanic rock–hosted iron deposits are important sources of high–grade iron ores in the world, which can be subdivided into Kiruna type and submarine volcanic rock–hosted type. Kiruna–type iron deposits, also known as magnetite–apatite deposits, are associated with volcanic rocks or sub–volcanic intrusions, with typical examples such as Kiruna in Sweden, El Laco in Chile and porphyrite...
type in the Middle–Lower Yangtze River region of China. Iron deposits of submarine volcanic rock–hosted type are associated with submarine volcanic–sedimentary successions and mainly occur in Western and Eastern Tianshan in China, such as Zhibo, Chagangnuoer, Beizhan and Yamansu. Long–standing controversy persists over the presence/absence of iron–rich melts in the genesis of this type of iron deposits. Some investigators have interpreted these deposits as direct crystallization from an iron–rich melt, with evidence including distinct magnetite volcanic flow structures, vesicles in the magnetite ore veins with chilled margins, degassing tubes similar to textures observed in basaltic flows, and the presence of ‘ore breccia’ (Nyström and Henriquez, 1994; Chen et al., 2010; Mao Jingwen et al., 2012; Tornos et al., 2016; Broughm et al., 2017). However, others have invoked a hydrothermal model in which they propose that the above ore features can be explained by open–space filling of ascending hydrothermal fluids, as evidenced by the pervasive presence of hydrothermal alteration and the low–Ti feature of magnetite (Frotos and Oyarzun, 1975; Gu Lianxing and Ruan Huichu, 1988; Bookstrom, 1995; Sillitoe and Burrows 2002; Dare et al., 2015). Immiscible iron–rich and silica–rich melts have been observed within melt inclusions in the host andesite rocks at El Laco, considered as a direct evidence of the existence of iron–rich melts (Tornos et al., 2016; Velasco et al., 2016). However, unambiguous outcrop–scale evidences of iron–rich melts have not yet been observed in the volcanic rock–hosted iron deposits.

In this study, we investigated the Heijianshan submarine volcanic rock–hosted iron deposit in Eastern Tianshan, China. Abundant iron–rich agglomerates are observed in the brecciated andesite lava of the deposit. A continuous alteration rim is commonly developed in the contact between the iron–rich agglomerates and brecciated andesite lava. Thus, the iron–rich agglomerates represent outcrop–scale evidences of iron–rich melt formed by magma evolution. We report petrographic and mineralogical features of the iron–rich agglomerates as well as their relationship with brecciated andesite lava, aiming to constrain the genesis of iron–rich melt and to explore the relationship between iron enrichment and magma evolution during the submarine volcanic–hosted iron–ore mineralization.

2 Geology of the Heijianshan Deposit

The Heijianshan iron deposit, about 160 km southeast of Shanshan County, Xinjiang, is developed in the volcano–sedimentary sequences of the Aqishan–Yamansu back–arc basin (Fig. 1) (Qin Kezhang et al., 2003; Ding Jianhua et al., 2016). The estimated ore reserve is 12.06 Mt with an average grade of 43.32wt% total Fe (XUARGS, 2003).

The exposed strata are composed of Upper Carboniferous Dikaner Formation. The Dikaner Formation is divided into three lithological members from the bottom upwards. The first member is exposed in the northern and eastern part of the deposit and comprises sedimentary tuff, tuff and basalt, the second member is observed in the central and western part of the deposit and comprises tuff, brecciated andesite lava and basalt, and the third member is merely seen in the central and western part of the deposit and comprises andesitic lava. The Heijianshan iron deposit is developed in the second and third lithological member (Fig. 2). Intermediate to felsic intrusive rocks are common in the Heijianshan iron deposit, with quartz syenite porphyry, diorite porphyry and porphyritic diabase dykes occurring in the north, and quartz syenite porphyry, diorite porphyry, quartz diorite porphyry and porphyritic diabase dykes in the south. Faults are developed in the deposit, and the ore body is crosscut by a NW striking

![Fig. 1. Tectonic framework in the Eastern Tianshan orogen and distribution of iron ore deposits in Aqishan–Yamansu back–arc basin (modified from Qin Kezhang et al., 2003).](image-url)
fault with a length of 5.5 km (Fig. 2).

The Heijianshan orebody is commonly stratiform, and is up to 4.4 km long and 2.4 km wide covering an area of 5.4 km² (Fig. 2). The maximum thickness of the orebody is 9.59 m (3.22 m in average). The orebody is characterized by extensive alteration with mineral assemblages dominated by sericite, chlorite, epidote, quartz, carbonate minerals, malachite, and pyrite. Iron ores belong to light-green colored alteration type and are commonly massive, disseminated and stockwork-like. Iron ores comprise varying proportions of magnetite, hematite and alteration minerals (chlorite, quartz, epidote, garnet, calcite, uralite), and locally have subordinate amount of chalcopyrite, pyrrhotite and pyrite.

3 Geology of the Iron-rich Agglomerates

Iron-rich agglomerates occur in brecciated andesite lava. Based on the mineral assemblages, we subdivide the iron-rich agglomerates into five types, including albite–magnetite type (AM), albite–K-feldspar–magnetite type (AKM), K-feldspar–magnetite type (KM), epidote–magnetite type (EM) and quartz–magnetite type (QM).

Geochemical analyses were performed in-situ using Energy Dispersive Spectrometer (EDS) with appropriate beam size. The EDS measurements were carried out using a TM3000 Tabletop SEM (Hitachi) equipped with a Quantax 70 EDS attachment (Bruker) which has proven to give reliable analytical results comparable with those from X-ray fluorescence spectra (XRF) analyses (Li et al., 2015c). EDS results are presented in Table 1.

3.1 Albite–magnetite type (AM)

Three samples (HJS–4, HJS–6, HJS16–18) belong to this type and exhibit porphyritic and amygdaloidal textures. Phenocrysts of the AM are dominated by albite, and groundmass is mainly composed of albite and magnetite. K-feldspar and other minerals are scarce. Compared to the AM, the brecciated andesite lava is also mainly composed of albite and magnetite, but in different proportions.

Iron-rich agglomerates of sample HJS–4 are "brecciated" (Fig. 3a). A continuous alteration rim occurs in its contact with the brecciated andesite lava. The rim is 1–2 cm wide and transitional with the brecciated andesite lava. The iron-rich agglomerates comprise phenocrysts of
Table 1 EDS analyses (wt%) of the iron–rich agglomerates, altered iron–rich agglomerates, wall rocks and altered wall rocks

<table>
<thead>
<tr>
<th>Agglomerate type</th>
<th>Sample</th>
<th>Rock type</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite–magnetite type</td>
<td>HJS16–18</td>
<td>Iron–rich agglomerates</td>
<td>36.32</td>
<td>12.23</td>
<td>40.58</td>
<td>1.61</td>
<td>0.55</td>
<td>6.96</td>
<td>0.54</td>
<td>0.37</td>
<td>99.16</td>
<td></td>
</tr>
<tr>
<td>Albite–magnetite type</td>
<td>HJS16–14</td>
<td>Wall rock</td>
<td>54.16</td>
<td>17.24</td>
<td>6.1</td>
<td>2.98</td>
<td>3.38</td>
<td>1.5</td>
<td>11.23</td>
<td>1.52</td>
<td>1.13</td>
<td>99.61</td>
</tr>
<tr>
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<td>HJS16–5</td>
<td>Iron–rich agglomerates</td>
<td>49.12</td>
<td>16.68</td>
<td>22.19</td>
<td>1.57</td>
<td>0.6</td>
<td>4.68</td>
<td>4.43</td>
<td>0.27</td>
<td>99.54</td>
<td></td>
</tr>
<tr>
<td>Albite–K–feldspar–magnetite type</td>
<td>HJS16–14</td>
<td>Altered iron–rich agglomerates</td>
<td>47</td>
<td>16.07</td>
<td>23.35</td>
<td>4.2</td>
<td>0.27</td>
<td>3.6</td>
<td>4.95</td>
<td>0.08</td>
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<td></td>
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</tbody>
</table>

-albite in a groundmass of fine–grained magnetite and albite. A chilled margin composed of fine–grained magnetite is developed (Fig. 3b). The amygdales mostly show round shape and are filled with quartz or carbonate minerals in a lesser amount. According to the EDS results, major oxides of the iron–rich agglomerates are: SiO₂ 64.62wt %, Al₂O₃ 12.20wt %, FeO 12.84wt %, MgO 0.08wt %, CaO 1.32wt %, Na₂O 7.45wt % and K₂O 0.19wt %. The brecciated andesite lava, wall rock of the iron–rich agglomerates, is altered and composed of albite (50vol %), K–feldspar (15vol %), magnetite (10vol %), epidote (10vol %), chlorite (10vol %) and subordinate amount of other minerals (5vol %). It exhibits porphyritic and amygdaloidal textures with an alteration rim (Fig. 3d), and it contains phenocrysts of albite in a groundmass of fine–grained magnetite and albite. In places, albite has been altered to K–feldspar and quartz (Fig. 3e). EDS results of the iron–rich agglomerates reveal a composition made of: SiO₂ 42.31wt %, Al₂O₃ 9.97wt %, FeO 38.93wt %, MgO 1.03wt %, CaO 0.44wt %, Na₂O 6.08wt % and K₂O 0.85wt %. The hosting brecciated andesite lava exhibits hyalopilitic texture and is composed of albite and subordinate amount of K–feldspar, quartz, chlorite, magnetite, titanite and carbonate veinlets. EDS results of brecciated andesite lava: SiO₂ 63.18wt %, Al₂O₃ 15.60wt %, FeO 4.83wt %, MgO 1.51wt %, CaO 3.93wt %, Na₂O 8.06wt % and K₂O 1.13wt %. Alteration rim comprises epidote (60vol %) and quartz (40vol %) (Fig. 3f).

The brecciated andesite lava is mainly composed of lath–shaped albite with subordinate amount of chlorite, epidote, titanite and magnetite (Figs. 3g, 3h). EDS results of the brecciated andesite lava: SiO₂ 60.08wt %, Al₂O₃ 19.46wt %, FeO 5.10wt %, MgO 5.02wt %, CaO 0.28wt %, Na₂O 8.85wt % and K₂O 0.50wt %. Iron–rich agglomerates of sample HJS16–18 are composed of magnetite, albite and minor chlorite (Fig. 3i), and yielded EDS results of SiO₂ 36.32wt %, Al₂O₃ 12.23wt %, FeO 40.58wt %, MgO 1.61wt %, CaO 0.55wt %, Na₂O 6.96wt % and K₂O 0.54wt %. Iron–rich agglomerates formed later than the
wall rock, because the iron–rich agglomerate crosscuts the albite laths of the brecciated andesite lava (Fig. 3h) which has developed a potassic alteration rim.

3.2 Albite–K–feldspar–magnetite type (AKM)

Four samples (HJS16–1, 2, 5 and 14) belong to this type. The AKM exhibits porphyritic and amygdaloidal textures. Phenocrysts of the AM are dominated by K–feldspar or albite altered to K–feldspar. Groundmass is mainly composed of magnetite, albite and K–feldspar.

Iron–rich agglomerates of sample HJS16–1 are scattered in the brecciated andesite lava and are always surrounded by epidote geode (Fig. 4a). They are composed of albite, K–feldspar and magnetite. Amygdales in the iron–rich agglomerates are mostly filled with K–feldspar and occasionally with epidote (Fig. 4b). Quartz amygdales are rare and where present they commonly have potassic alteration rims. Apatite occurs in some iron–rich agglomerates. The EDS result of iron–rich agglomerates is: SiO$_2$ 50.18wt%, Al$_2$O$_3$ 12.29wt%, FeO 23.89wt%, CaO 0.99wt%, Na$_2$O 6.64wt% and K$_2$O 2.29wt%. Brecciated andesite lava has subjected to silicification and potassic alteration, but its hyalopilitic textures are retained, with fine–grained K–feldspar, quartz and minor chlorite occurring interstitially in the lath–shaped albite (Fig. 4c). The EDS result of brecciated andesite lava is: SiO$_2$ 71.78wt%, Al$_2$O$_3$ 15.37wt%, FeO 1.76wt%, MgO 0.99wt%, CaO 0.69wt%, Na$_2$O 5.41wt% and K$_2$O 2.64wt%.

Iron–rich agglomerates of sample HJS16–2 are ‘brecciated’ in the brecciated andesite lava or occur in geodes (Fig. 4d). Chilled margins have been developed at the contact between the iron–rich agglomerates and the brecciated andesite lava (Fig. 4e). Iron–rich agglomerates comprise phenocrysts of albite which have experienced potassic alteration, in a groundmass of fine–grained magnetite, K–feldspar, albite and minor chlorite (Fig. 4f). The amygdales are mostly rounded and filled with quartz.
Fig. 4. Photographs and photomicrographs illustrating the features of the albite–K–feldspar–magnetite type iron–rich agglomerates.

(a), Quartz–epidote geode near the iron–rich agglomerates (HJS16–1); (b), Iron–rich agglomerates composed of lath–shaped albite, fine–grained magnetite and quartz amygdale (HJS16–1); (c), Andesite lava showing hyalopilitic structure (HJS16–1); (d), Iron–rich agglomerates in geode (HJS16–2); (e), A chilled margin in the contact between iron–rich agglomerates and brecciated andesite lava (HJS16–2); (f), Amygdale in the iron–rich agglomerates dominated by apatite and quartz (HJS16–2); (g), Brecciated andesite lava showing hyalopilitic structure (HJS16–2); (h, i), Late–stage hematite–quartz–carbonate minerals mineralization (HJS16–2); (j), Iron–rich melt intruded along the fractures in the brecciated andesite lava (HJS16–5); (k), Feldspar in the groundmass growing along the boundary of the phenocryst, showing flow features crystallized from melt (HJS16–5); (l) Chlorite amygdale in the iron–rich agglomerates (HJS16–5); (m, n), Potassic alteration rim of the iron–rich agglomerates (HJS16–14); (o), Iron–rich agglomerates (HJS16–14). (b, e, f, j, k, l, n, o), Plane–polarized light; (c, g, i), Cross–polarized light; (h), Reflected–polarized light; Ab, Albite; Ap, Apatite; BAL, Brecciated andesite lava; Ep, Epidote; Hem, Hematite; IRA, Iron–rich agglomerates; Mag, Magnetite; Qtz, Quartz.
in the cores surrounded by rims composed of chlorite and titanite. The EDS result of iron–rich agglomerates is: SiO$_2$ 43.53wt%, Al$_2$O$_3$ 16.07wt%, FeO 2.98wt%, CaO 5.38wt%, Na$_2$O 1.50wt%, K$_2$O 11.23wt%, TiO$_2$ 1.52wt% and P$_2$O$_5$ 1.13wt%, which is K–P–Ti–richer than other samples.

3.3 K–feldspar–magnetite type (KM)

Two samples (HJS16–4 and 11) belong to this type. The KM exhibits porphyritic and amygdaloidal textures and is mainly composed of magnetite and K–feldspar.

Quartz and epidote are common near or inside the iron–rich agglomerates in sample HJS16–4 and locally occur as geodes (Fig. 5a). Iron–rich agglomerates are mainly composed of K–feldspar and magnetite. Some K–feldspar crystals occur as pseudomorphs after albite. The iron–rich agglomerates are K–rich and are composed of SiO$_2$ 50.91wt%, Al$_2$O$_3$ 16.65wt%, FeO 16.36wt%, MgO 2.62wt%, CaO 0.58wt%, Na$_2$O 0.54wt% and K$_2$O 11.42wt%. The amygdales are composed of chlorite and a trace amount of titanite (Fig. 5b). The geodes are filled with epidote and quartz showing radial growth as well as subordinate amount of chlorite, titanite, magnetite and albite (Fig. 5c). The geodes are Ca–rich and have SiO$_2$ 49.77wt%, Al$_2$O$_3$ 19.12wt%, FeO 9.42wt%, MgO 0.45wt%, CaO 13.19wt%, Na$_2$O 5.48wt% and K$_2$O 0.35wt%.

Iron–rich agglomerates of sample HJS16–11 exhibit angular shape and occur along fractures of the brecciated andesite laves with a sharp boundary. They are composed of K–feldspar and magnetite. The iron–rich agglomerates have suffered alteration inside with quartz or both quartz and epidote (Figs. 5d, 5e). The EDS result of iron–rich agglomerates is: SiO$_2$ 40.17wt%, Al$_2$O$_3$ 14.43wt%, FeO 34.68wt%, MgO 0.55wt%, CaO 1.01wt%, Na$_2$O 2.65wt% and K$_2$O 5.15wt%. Phenocrysts are dominated by K–feldspar. The amygdales are composed of quartz and exhibit oriented textures. Minerals of the iron–rich agglomerates have been altered to quartz, K–feldspar and titanite. A partially altered quartz amygdale is observed (Fig. 5f). The EDS result of the alteration products is: SiO$_2$ 64.02wt%, Al$_2$O$_3$ 17.93wt%, FeO 4.13wt%, MgO 1.83wt%, CaO 2.31wt%, Na$_2$O 5.70wt% and K$_2$O 2.86wt%. Coarse–grained quartz and epidote are common alteration products, some of which are distributed in vesicles and form amygdales, and some fill in geodes and exhibit radial textures (Figs. 5g, 5h, 5i). The surrounding brecciated andesite laves comprises lath–shaped albite, chlorite and minor K–feldspar, magnetite and titanite. Its EDS result is: SiO$_2$ 56.62–57.55wt%, Al$_2$O$_3$ 16.69–18.22wt%, FeO 7.67–8.81wt%, MgO 3.76–6.19wt%, CaO 0.87–2.66wt%, Na$_2$O 6.67–7.03wt%, K$_2$O 1.67–2.66wt% and TiO$_2$ 0.67–1.25wt%.
3.4 Epidote–magnetite type (EM)

Two samples (HJS16–9 and 13) belong to this type. The EM exhibits porphyritic and amygadaloidal textures. It is mainly composed of epidote and magnetite.

Iron–rich agglomerates of sample HJS16–14 show rims that have suffered epidotization, and the host brecciated andesite lava exhibits potassic alteration (Fig. 6a). However, chilled margins of the iron–rich agglomerates are characterized by magnetite and lath–shaped albite replaced by K–feldspar (Fig. 6b). The iron–rich agglomerates are composed of fine–grained magnetite, K–feldspar and minor lath–shaped albite. The amygdales are dominated by chlorite (Fig. 6c). The EDS result of iron–rich agglomerates is: SiO$_2$ 45.47 wt%, Al$_2$O$_3$ 15.61 wt%, FeO 23.59 wt%, MgO 0.34 wt%, CaO 1.06 wt%, Na$_2$O 4.60 wt% and K$_2$O 8.20 wt%. Rims of the iron–rich agglomerates are mainly composed of magnetite, epidote and albite, and its EDS result is: SiO$_2$ 28.81 wt%, Al$_2$O$_3$ 12.51 wt%, FeO 44.60 wt%, MgO 0.32 wt%, CaO 7.61 wt%, Na$_2$O 3.72 wt% and K$_2$O 0.68 wt%. The brecciated andesite lava comprises lath–shaped albite, intergranular anhedral K–feldspar and chlorite as well as subordinate amount of magnetite and titanite. The EDS result of the brecciated andesite lava is: SiO$_2$ 68.42 wt%, Al$_2$O$_3$ 17.37 wt%, FeO 1.67 wt%, MgO 1.30 wt%, CaO 0.49 wt%, Na$_2$O 6.69 wt% and K$_2$O 3.53 wt%. The brecciated andesite lava surrounding iron–rich agglomerates has suffered potassic alteration and comprises mainly of K–feldspar, albite and chlorite with a trace amount of titanite. Its EDS result is: SiO$_2$ 57.97–60.51 wt%, Al$_2$O$_3$ 18.77–19.09 wt%, FeO 3.14–5.68 wt%, MgO 3.14–3.75 wt%, CaO 0.19–1.14 wt%, Na$_2$O 1.15–5.50 wt%, K$_2$O 5.71–13.53 wt% and TiO$_2$ 0.58–1.13 wt%.

Iron–rich agglomerates of sample HJS16–14 are composed of magnetite and K–feldspar with minor albite. The amygdales in this sample are dominated by K–
feldspar (Fig. 6d). The EDS result is: SiO$_2$ 38.75wt%, Al$_2$O$_3$ 11.18wt%, FeO 41.41wt%, MgO 0.37wt%, CaO 0.22wt%, Na$_2$O 3.07wt% and K$_2$O 4.26wt%. Iron–rich agglomerates that suffered epidotization still retain hyalopilitic texture, but the K–feldspar and albite have been completely replaced by epidote and quartz (Fig. 6e). Apatite and specularite platelets coexist with epidote and quartz (Fig. 6f). The EDS result of this type of iron–rich agglomerates is: SiO$_2$ 46.55wt%, Al$_2$O$_3$ 7.25wt%, FeO 26.55wt%, MgO 0.45wt%, CaO 13.94wt%, Na$_2$O 0.01wt%, K$_2$O 0.21wt%, TiO$_2$ 1.26wt% and P$_2$O$_5$ 3.07wt%, suggesting that the wall–rock alteration is a process of bringing in Ca and P but taking out of Na and K.

### 3.5 Quartz–magnetite type (QM)

Two samples (HJS16–3 and 13) belong to this type. The QM has suffered from silicification and comprises magnetite and quartz, but the hyalopilitic structure retained.

Five members are identified in samples of this type, from the center of the iron–rich agglomerates to the host brecciated andesite lava, including: inner core of the iron–rich agglomerates, amygdale–rich mantle of the iron–rich agglomerates, chilled margin, altered brecciated andesite lava, unaltered brecciated andesite lava (Figs. 7a, 7b).

The amygdale–rich mantle accounts for a major part of the iron–rich agglomerates and comprises magnetite, K–feldspar, albite and quartz. The amygdales are irregular–shaped and dominated by K–feldspar (Fig. 7c). The EDS result of the amygdale–rich mantle is SiO$_2$ 35.84wt%, Al$_2$O$_3$ 6.54wt%, FeO 49.42wt%, MgO 0.03wt%, CaO 1.40wt%, Na$_2$O 2.95wt% and K$_2$O 2.73wt%.

The chilled margin is composed of magnetite, albite, K–feldspar altered from albite and exhibits hyalopilitic structure (Fig. 7d). The EDS result of the chilled margin is: SiO$_2$ 53.36wt%, Al$_2$O$_3$ 16.06wt%, FeO 17.59wt%, MgO 0.13wt%, CaO 0.90wt%, Na$_2$O 7.87wt% and K$_2$O 3.15wt%.

The inner core is composed of fine–grained magnetite, K–feldspar, carbonate minerals, quartz and titanite (Fig. 7e). Albite and hyalopilitic texture are not observed. The EDS result of the inner core is: SiO$_2$ 52.95wt%, Al$_2$O$_3$ 11.31wt%, FeO 22.66wt%, MgO 1.13wt%, CaO 2.54wt%, Na$_2$O 0.65wt%, K$_2$O 6.79wt% and TiO$_2$ 1.36wt%.

Unaltered brecciated andesite lava exhibits hyalopillic texture and comprises albite and minor magnetite and chlorite. Altered brecciated andesite lava has experienced potassic alteration and silicification and comprises K–feldspar, albite and minor magnetite, quartz and chlorite (Fig. 7f). Its EDS result is SiO$_2$ 72.37wt%, Al$_2$O$_3$ 10.00wt%, FeO 4.17wt%, MgO 1.25wt%, CaO 3.43wt%, Na$_2$O 1.78wt% and K$_2$O 5.77wt%.

Apart from epidotization, iron–rich agglomerates of the strongly altered sample HJS16–14 also show replacement of albite by quartz (Figs. 7g, 7h). Where the alteration is extremely strong, the original magmatic texture is no
longer retained. Besides magnetite, the iron–rich agglomerates also comprise coarse–grained epidote and quartz of hydrothermal origin (Fig. 7i).

4 Discussions

4.1 Temporal relationship between the iron–rich agglomerates and the brecciated andesite lava

Potassic alteration, silicification and epidotization are commonly observed in the brecciated andesite lava that hosts the iron–rich agglomerates (Figs. 3a, 3d, 4a, 4d, 5a, 5d, 6a, 7a and 7b). Ring–shaped alteration has developed surrounding the iron–rich agglomerates, indicating a close relationship between them. It is unlikely that the alteration has been generated by xenolith capturing. Instead, the iron–rich agglomerates formed later than the host brecciated andesite lava. Particularly, we observed that some iron–rich agglomerates are irregularly distributed in fractures of the brecciated andesite lava (Figs. 4j and 5e), and the boundary of the iron–rich agglomerates crosscut the lath–shaped feldspar of the brecciated andesite lava (Figs. 3g and 3h), suggesting that the ‘brecciated’ distribution is actually the result of fracture filling.

4.2 Evidence for the presence of iron–rich melts

There are two possible origins for the iron–rich agglomerates: (1) amygdales formed by hydrothermal replacement and open–space filling, and (2) crystallization directly from iron–rich melts. Hydrothermal origin can be excluded based on the following lines of evidence: (1) Iron-rich agglomerates locally display sharp and angular boundaries, in contrast with the rounded or sub-rounded amygdales; (2) Amygdales are generally thought to have formed by filling of gas-bubble vesicles with secondary minerals such as carbonate, zeolite and quartz. However, iron–rich agglomerates comprise feldspar and magnetite,
exhibit hyalopilitic, amygdaloidal and pumice textures (Figs. 3b, 3e, 4b, 4e, 4f, 4i, 4l, 5b, 5e, 5f, 6c, 7c, 7d), show chilled margins in contact with the brecciated andesite lava (Figs. 3b, 4e, 6b), and have lath–shaped feldspar surrounding phenocrysts (Fig. 4k), which indicate typical volcanic features formed by crystallization of intermediate–mafic magma; (3) The iron–rich agglomerates exhibit obvious porphyritic, hyalopilitic and amygdaloidal textures (Figs. 3c, 4c and 4g), indicating direct crystallization from iron–rich melts, and these textures cannot be formed by hydrothermal replacement of the wall rocks (brecciated andesite lava) which are free of vesicles and amygdales. Thus, the iron–rich agglomerates were probably crystallized directly from iron–rich melts and deposited in the fractures of the brecciated andesite lava. The features above provide robust outcrop–scale evidence for the presence of iron–rich melts.

### 4.3 Origin of the iron–rich melts

Both liquid immiscibility and fractional crystallization from late–stage residual magma have been proposed for the formation mechanism of iron–rich melts. Liquid immiscibility results in conjugate iron–rich and silica–rich melts. The difference between them is obvious, but the crystallized rocks of each melt are relatively stable (Philpotts, 1982; Naslund, 1983; Veksler, 2009). No Si–rich rocks or melt inclusions are observed in the Heijianshan iron deposit. Instead, mineral assemblages of the crystallized rocks from late–stage residual magma are similar to those crystallized from the common parental magma, but show greater variations in mineral proportion (Jang et al., 2001; Duchesne et al., 2006). The iron–rich agglomerates have similar mineral assemblages to the hosting brecciated andesite lava, both contain magnetite with various contents. As shown in Fig. 8, chemical compositions of the brecciated andesite lava and the five types of iron–rich agglomerates exhibit well–defined linear trends, showing enrichment of Fe with decreasing Si and Al. Thus, the iron–rich agglomerates can be explained as late–stage residual magma during fractional crystallization of the parental magma. High solubility of volatile contents in iron–rich melts impede the crystallization of iron–rich agglomerates, as a result the agglomerates show features of fracture filling in the earlier crystallized brecciated andesite lava. No iron–rich veins are observed in the fractures of the brecciated andesite lava. The potassic alteration, silicification and epidotization have developed around or inside the iron–rich agglomerates. No alteration veins composed of K–feldspar, quartz and epidote are observed in the fractures. These features suggest that the hydrothermal alteration was synchronous with volcanic activity and occurred before complete solidification of the brecciated andesite lava.

### 4.4 Magmatic–hydrothermal evolution of the iron–rich agglomerates

The Heijianshan iron deposit is hosted in andesite–dacite lava which comprises feldspar and minor magnetite,
titanite and chlorite. The iron–rich agglomerates have similar mineral assemblages with the host andesite–dacite lava, but contain more magnetite. The iron–rich agglomerates exhibit amygdaloidal textures, suggesting that the iron–rich melts were rich in volatiles. However, the host rocks are devoid of vesicles and amygdales, indicating a volatile–poor feature. The five types of iron–rich agglomerates have probably recorded the different evolutionary stages of a magmatic–hydrothermal system. The albite–magnetite type probably represents the earliest crystalized product from residual iron–rich melt, because: (1) the albite–magnetite type exhibits hyalopilitic texture and is composed of lath–shaped albite and fine–grained magnetite, typical of magmatic origin; (2) no albite is observed in amygdales in the albite–magnetite type; and (3) no albitization is observed in the contact between the iron–rich agglomerates and host brecciated andesite lava. The albite–K–feldspar–magnetite type and K–feldspar–magnetite type show features of magmatic–hydrothermal transition. The magnetite is distributed in spaces between the K–feldspar and albite laths, and together they display a hyalopilitic texture, suggesting a magmatic origin. Potassic alteration rims of the host brecciated andesite lava and amygdales in the iron–rich agglomerates filled with K–feldspar also indicate that K–feldspar can be formed in the hydrothermal stage. The compositions of the albite–K–feldspar–magnetite type are related to the extent of replacement of albite by K–feldspar. The K–feldspar–magnetite type was formed when the albite was completely replaced by K–feldspar. The epidote–magnetite type and quartz–magnetite type represent products at the hydrothermal stage. Magmatic textures such as hyalopilitic texture can only be retained in weakly altered rocks. Magnetite minerals in these two types are coarser–grained than those of the other three types (Fig. 9). In addition to forming alteration rims surrounding the iron–rich agglomerates, quartz and epidote of these two types are more likely to occur as coarse–grained aggregates formed by hydrothermal filling in the vesicles and geodes near the iron–rich agglomerates. Quartz and epidote can coexist in geodes, and exhibit zoning patterns (HJS16–7, 8): quartz is more concentrated closer to the center, whereas fine-grained epidote dominates towards the contact with the wall rocks.

The EDS results of the brecciated andesite lava show features of alkali–rich and intermediate volcanic lava. The agglomerates are also alkali–rich and show varied EDS results. The well–developed alteration indicates that the iron–rich melts represent a system composed of iron oxides, silicates (e.g. albite) and volatiles. Hydrothermal fluids derived from late–stage residual melts are rich in volatiles and Ca–K–Si contents (Figs. 8a, 8c), and tend to induce hydrothermal filling and replacement, eventually resulting in characteristic hydrothermal alteration of epidotization, potassic alteration and silicification.

An integrated magmatic–hydrothermal model has been proposed recently to interpret the coexistence of iron–rich melt and widespread hydrothermal alteration in typical

![Photomicrographs of iron oxides of different types of iron–rich agglomerates.](image-url)
Kiruna-type iron deposits (Zhou et al., 2013; Li Yanhe et al., 2014; Knipping et al., 2015; Tornos et al., 2016). Knipping et al. (2015) proposed a magmatic-hydrothermal model of efficient flotation of magmatic magnetite suspension which involves concentration of magnetite by the preferred wetting of magnetite followed by buoyant segregation of the early-formed magmatic magnetite–bubble pairs. Tornos et al. (2016) considered that crystallization of iron–rich melts was accompanied by the exsolution of large amounts of vapor and a small volume of a hydrosaline melt which resulted in alkali-calcic alteration of the host andesite and steam–heated alteration zone at the top of the El Laco system.

Based on the features of the iron–rich melts, and inspired by the model proposed by Knipping et al. (2015), we propose a formation mechanism for the iron–rich agglomerates of the Heijingshan iron deposit as follows:

1) and (2) In hydrous and oxidized andesitic magmas, fluid bubbles exclusively attach to early crystallized magnetite microcrystals (first liquidus phase), and then the bubble–magnetite pairs rise due to buoyancy force (Figs. 10a, 10b) (Knipping et al., 2015).

3) The bubble–magnetite pairs gradually grow and join together with some enclosed andesitic magma to form aggregates during ascent. Iron–rich melts are formed as a rising suspension in andesitic magma (Fig. 10c). Ca, H₂O, and volatiles (e.g., F, Cl, P) strongly fractionate into the iron–rich melts (Lester et al., 2013). The iron–rich melts have similar chemical compositions with andesitic magma, but contain more magnetite and volatiles.

4) The andesitic magma ascends to the surface, and then quickly experiences solidification, crystallization and cracking to form brecciated andesite lava. High contents of volatiles retard the crystallization of iron–rich melts and lower the crystallization temperature (Toplis et al., 1994; Li Houmin et al., 2014; Li et al., 2015c). Eventually, the iron–rich melts crystallize in fractures of the host brecciated andesite lava with release of gas to form vesicular and amygdaloid iron–rich agglomerates (Fig. 10d).

5) The volatile–rich components released from iron–rich melts are rich in Ca, K and Si. They fill in vesicles and fractures to form geodes or amygdales which are dominated by quartz, epidote or K–feldspar. They result in hydrothermal alteration of the host brecciated andesite lava and form silicification, epidotization and potassium alteration rims. They also result in auto–metamorphism of the iron–rich agglomerates and form K–feldspar–epidote–quartz–rich types (Fig. 10e).

### 4.5 Implications for the origin of volcanic rock–hosted iron deposits

The iron–rich agglomerates have FeO contents in the range of 12.84–49.42 wt% (29.92 wt% in average), most of which can reach industrial grades. Thus, emplacement of iron–rich melts can possibly form iron orebodies in case of
reaching a certain size in favorable structures.

However, iron orebodies that retain the characteristics of iron–rich melts are scarce because of the auto–metamorphism induced by large amounts of volatiles from iron–rich melts and the superposition of other hydrothermal fluids associated with volcanic activity. There are plenty of voids in the iron oxides (magnetite or hematite) in the massive iron ores of the El Laco iron deposit. The voids exhibit irregular and angular boundary, but not round boundary, and has residual filling of apatite, quartz and fluorite. It indicates that the voids are not vesicles, but represent residual intergranular interspaces after leaching of some other minerals in the magnetite grains. The iron–rich melts are not composed of pure iron oxides, as also confirmed by experiments (Tollari et al., 2008; Hou et al., 2017). Considering the pervasive alteration in El laco deposit, we consider that the initial crystallization of iron–rich melts forms disseminated iron orebodies, and is then quickly replaced by alkali–rich hydrothermal fluids. This process of leaching impurities from disseminated iron orebodies eventually leads to the formation of porous high–grade iron ores and calc–alkaline and alkaline alteration with characteristic minerals such as scapolite, diopside and anhydrite. Typical examples are the iron oxide–apatite deposits in the Middle–Lower Yangtze River metallogenic belt of China which commonly show alteration zoning, with an upper light–colored zone of silicification, kaolinization and pyritization, a middle dark-colored zone of diopsidization, actinolitization and epidotization, and a lower light–colored zone of extensive albitionization (Yu et al., 2011).

Abundant submarine volcanic rock–hosted iron deposits are hosted in Carboniferous submarine volcanic–sedimentary rocks of the Western and Eastern Tianshan Mountains in Xinjiang, China. The volcanic rocks are characterized by tholeiitic to calc–alkaline basalt–basaltic andesite–andesite–dacite–rhyolite association with arc–related magmatism (Xia et al., 2004; Zhu et al., 2005; Xu Yang et al., 2017). The arc magma is H2O–rich and oxidized, and is favorable for iron mineralization. Iron orebodies occur as stratiform, stratiform–like to lenticular shapes and are mostly conformable with the wall rocks. Wall–rock alteration related to iron mineralization is widespread. The diagenetic and alteration ages are indistinguishable, e.g., volcanic activity at 348–334Ma and alteration at 335Ma of the Yamansu iron deposit in Eastern Tianshan (Luo Ting et al., 2012; Li Houmin et al., 2014), and volcanic activity at 321–314Ma and alteration at 317Ma at Chagangnuoer iron deposit at Western Tianshan (Wang Bangyao and Jiang Changyi, 2011; Hong Wei et al., 2012; Li et al., 2015a; Zhang et al., 2015). This indicates a close relationship between the volcanic and hydrothermal activities (Feng Jing et al., 2009; Yang Fuquan et al., 2011; Zhang Zuoheng et al., 2012; Hou et al., 2014; Li et al., 2015b; Zhang Zhaochong et al., 2016; Zhu Yongfeng et al., 2016). As a result of strong replacement of hydrothermal fluids, most iron deposits merely show hydrothermal features, and it is difficult to observe magmatic textures in orebodies and ores (Jiang et al., 2017; Ding Jianhua et al., 2017; Zhao Liandang et al., 2017; Zhao et al., 2017). However, Skarnization, silicification and epidotization are main types of wall–rock alteration in iron deposits of Eastern Tianshan. The alteration involves bringing in Ca, Fe while taking out of Na and K. For example, the unaltered wall–rock sample has EDS result of SiO2 65.83wt%, Al2O3 15.22wt%, FeO 5.21wt%, MgO 1.61wt%, CaO 0.85wt%, Na2O 6.65wt% and K2O 1.80wt%, which is changed to SiO2 55.90wt%, Al2O3 12.33wt%, FeO 14.52wt%, MgO 0.71wt%, CaO 13.94wt%, Na2O 0.16wt% and K2O 0.02wt% after having experienced silicification and epidotization. In summary, magmatic–hydrothermal fluids associated with iron–rich melts played an important role in the process of iron mineralization.

5 Conclusions

(1) The iron–rich agglomerates were formed by open–space filling of volatile–rich iron–rich melts in fractures of the brecciated andesite lava.

(2) Different types of iron–rich agglomerates are considered as products at different stages of a magmatic–hydrothermal system. The albite–magnetite type represents the earliest crystalized product from residual iron–rich melts. The albite–K–feldspar–magnetite type and K–feldspar–magnetite type show features of magmatic–hydrothermal transition. The epidote–magnetite type and quartz–magnetite type represent products at hydrothermal stage.

(3) Iron–rich melts and the volatiles it carried played an important role in the formation of submarine volcanic rock–hosted iron deposits.

Acknowledgements

This study was financially supported by the Geological Survey Program of China (grants No. K1410 and DD20160346) and the National Natural Foundation of China (grants No. 41672078 and 41402067). We thank Zi JW and two anonymous reviewers for their constructive suggestions.

Manuscript received Feb. 15, 2017
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