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Iron isotope fractionation during skarn-type alteration: Implications for metal source in the Han-Xing iron skarn deposit

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ABSTRACT

The Han-Xing iron mineralization in the central North China Craton is a typical Fe skarn deposit associated with altered diorites. Here we report the Fe isotopic compositions of whole rocks and mineral separates from this deposit with a view to evaluate the Fe isotope fractionation during the formation of Fe skarn deposit, and to constrain the metal source. The Fe isotopes show a large variation both in whole rocks and mineral separates. Altered diorites show a wide range in δ^{56}Fe values (−0.07‰ to +0.21‰ relative to the Fe isotope standard IRMM-014) which positively correlate with their TFe_2O_3/TiO_2 ratios (Fe_2O_3 and FeO calculated as TFe_2O_3). The positive correlation indicates that heavy Fe isotopes were preferentially leached from diorites during the skarn-type alteration. Among the metallic minerals, pyrite and pyrrhotite are isotopically heavier (+0.12‰ to +0.48‰) than the magnetite (+0.07‰ to +0.21‰). Fe isotope fractionation between mineral pairs demonstrates that magnetite did not attain Fe isotopic equilibrium with pyrite and pyrrhotite, whereas pyrite and pyrrhotite might have attained isotopic equilibrium. Petrological observations and major element data also suggest that iron was leached from the diorites during the skarn-type alteration. If the leached iron provides the main Fe budget of the Han-Xing Fe skarn deposit, magnetite in ores would be isotopically heavier than the unaltered diorite. However, our results are in contrast with the magnetite being isotopically lighter than the unaltered diorite. This suggests that the major Fe source of the Han-Xing Fe skarn deposit is not from the leaching of diorites, and might be from magmatic fluid which is isotopically lighter than the silicate melt. Our data demonstrate that Fe isotopes can be used as important tracers in deciphering the metal source of Fe skarn deposits.

1. Introduction

Tracing the source of metals is a key issue in investigations related to the genesis of ore deposits. Light stable isotopes such as H, C, O, N, and S have been used to trace the origin of metal deposits (e.g., Jia and Kerrich, 1999; Ohmoto, 1972; Rye, 1966; Sheppard et al., 1971; Taylor, 1974). However, these elements are not metallogenic elements themselves and have different isotopic signatures under different tectonic settings (Hedenquist and Lowenstern, 1994), which makes it difficult to decipher the metal source. For example, the hydrogen and oxygen isotopic compositions of hydrothermal minerals from Cu porphyry deposit often show a mixed feature of magmatic and meteoric water, whereas sulfur isotope records the isotopic composition of mantle sulfur. Thus none of these proxies provide direct information on the source of copper. Therefore, metal stable isotopes (e.g., Fe, Mg, Cu, Zn, Cr and Mo) have emerged as more precise tracers. As an important rock-forming and metallogenic element, iron occurs in either reduced ferrous iron or oxidized ferric iron in nature. The differences in the behavior of iron with different redox states and significant isotopic variations make Fe isotope useful for tracing the iron geochemical cycle (Beard and Johnson, 2004).

The application of Fe isotopes to trace metal source is still debated, due to lack of precise information on the Fe isotope fractionation during metallogenic processes. In a study of the Grasberg Cu–Au porphyry deposit, Graham et al. (2004) found that Fe isotopic compositions of pyrite and chalcopyrite from the Grasberg Igneous Complex and the skarn overlapped, based on which they invoked a genetic relationship. However, this conclusion can be debated since Fe isotopes can fractionate during many processes (e.g., Bullen et al., 2001; Icopini et al., 2004; Skulan et al., 2002; Teng et al., 2008; Cheng et al., 2015). Markl et al. (2006) suggested that Fe isotopes are not suitable to derive information on metal sources as the isotopic composition is strongly dependent on the characteristic of fluid and precipitation history. However, in another case, Wang et al. (2011) studied the Fe isotopic fractionation of the metallogenic processes in the Xinqiao Cu–S–Fe–Au deposit and excluded the sedimentary strata as the iron source.

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As the largest skarn deposit type on the globe, Fe skarn deposits occur in different times and geological settings (Meinert et al., 2005). In China, Fe skarn deposits constitute the dominant source of high-grade iron ores (Zhang et al., 2014a). The various models proposed for the metal sources of Fe skarn deposits can be grouped into three: 1) recycling of pre-existing ore deposits (e.g., Johnson et al., 1990; Wang et al., 1981); 2) alteration of associated igneous rocks (e.g., Feng, 1998; Zheng et al., 2007); and 3) products of magmatic hydrothermal system (e.g., Shimazaki, 1980). Apart from a few examples for skarn formation through the recycling of pre-existing ore deposits, most researchers favor the second and third models above (e.g., Hedenquist and Lowenstern, 1994; Jin et al., 2015; Xie et al., 2015; Zhang et al., 2014b). In this paper, we report Fe isotopic compositions of altered diorites, limestone and metallic minerals from the Han-Xing Fe skarn deposit as well as the major element compositions of altered diorites, in an attempt to evaluate the behavior of elemental iron and iron isotopes during the formation of Fe skarn deposit, as well as to constrain the Fe source. Our results demonstrate that heavy Fe isotopes were preferentially leached from the diorites during the skarn-type alteration and the main Fe budget was derived from magmatic fluid.

2. Geological setting

2.1. Regional geology

The NCC is a collage of Archean microcontinents which were assembled into major crustal blocks at the end of Archean followed by rifting-subduction-accretion collision that culminated by end Paleoproterozoic, building the fundamental cratonic architecture (Santosh et al., 2015; Yang and Santosh, 2015; Yang et al., 2015; Zhai and Santosh, 2011; Zhai, 2014; Zhao and Zhai, 2013), The Han-Xing iron district is located in the central part of the NCC (Fig. 1A). The basement rocks in this region are mainly composed of tonalite-trondhjemite-granodiorite (TTG) gneisses and amphibolites, the protoliths which formed during Meso–Neoarchean and were metamorphosed during late Paleoproterozoic coeval with the final cratonization of the NCC (Zhai and Santosh, 2011). Regionally, the sedimentary rocks in this area are dominated by Cambrian–Ordovician carbonates in the western part and Carboniferous–Permian clastic rocks in the eastern part (Fig. 1B). Mesozoic magmatic rocks intruded into the Precambrian basement as well as the sedimentary cover. Previous studies proposed that the source magmas of these intermediate intrusive rocks with zircon SHRIMP U-Pb ages of 126–138 Ma were generated by crust-mantle interaction (Chen et al., 2008).

2.2. Ore geology

The samples for this study were collected from the Wu'an iron cluster region which is composed of several iron deposits, about 10 km away from the Wu'an County, Hebei Province (Fig. 1B). The dominant basement rocks in this region belong to the Archean Zanhuang Complex, intruded by the Mesozoic intermediate plutons of monzonite, monzodiorite, diorite, and quartz–diorite. The major sedimentary unit associated with the deposit is the Middle Ordovician Majiagou limestone.

The main ore-controlling structure is a set of NNE extensional faults. Most of the Fe deposits formed around the Wu'an fault basin (Li, 1986) (Fig. 1 B). Ore bodies occur as complex lenses with serrated and interspersed features typically at the contact zone of the dioritic plutons and the Majiagou limestone. The well developed alteration zone between the dioritic plutons and limestone can be further divided into five zones as: altered diorite, endoskarn, magnetite ore, exoskarn and marmorized limestone zone. In general, the endoskarn shows a wider

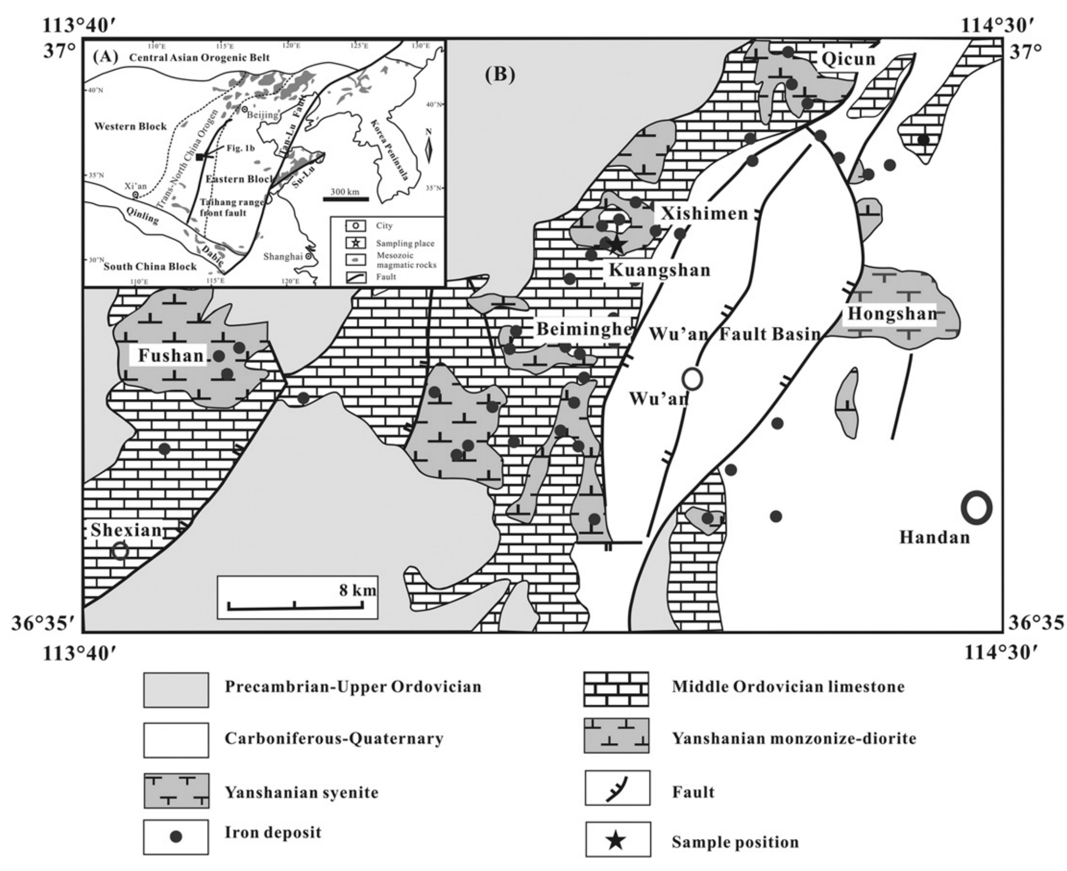

Fig. 1. (A) Simplified geological map showing major tectonic subdivisions of the North China Craton (NCC) with an emphasis on the distribution of Mesozoic magmatic rocks (after Zhao et al., 2005; Qian and Hermann, 2010). (B) Local geological map of the Wu'an iron deposit (modified from Shen et al., 2013).