

Article

Chemical Signatures of Ge in Magnetite of Wugang BIF, China

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Abstract: Magnetite is a representative ore mineral found in various deposits. The trace element composition of ore deposits is controlled by several physiochemical factors such as temperature, pressure, and oxygen or sulfur fugacity. The chemical behavior of Germanium (Ge) is distinct in different environments. Consequently, the composition patterns of Ge in magnetite can be used to infer the provenance conditions. This study focuses on the Ge composition in magnetite from the Wugang banded iron formation (BIF) to understand the compositional characteristics of BIF sources and reconstruct of origin of Wugang BIF. The magnetite of the Wugang BIF has a porous texture, indicating high dissolution-reprecipitation processes and easy fluid infiltration, owing to its increased effective permeability. The Ge in the magnetite of the Wugang BIF was incorporated into iron hydroxide from the hydrothermal fluid and seawater during precipitation. The formation period of the Wugang BIF was consistent with significant oxidation events that led to the oxidation of ferrous ions in the Precambrian Ocean. Certain processes promote the chemisorption and coprecipitation of Ge into iron hydroxides or oxides.

Keywords: germanium; hydrothermal fluid; paleo-depositional conditions; banded iron formation



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1. Introduction

The reconstruction of the early earth conditions is essential for understanding the links between ocean chemistry and the evolution of the biosphere and atmosphere [1]. Banded iron formations (BIFs) are Precambrian sedimentary successions defined as laminated chemical sediments containing >15% Fe, with alternating layers of Fe-rich minerals, and chert of various scales [2]. It is well known that anoxic and ferruginous marine conditions occurred in the Archean and Paleoproterozoic eras, and BIFs precipitated until soluble iron was exhausted, causing their cessation [3]. These are the primary products of marine iron oxyhydroxides formed via diagenetic bacterial iron reduction [4]. Therefore, BIFs can be used as essential geological proxies for understanding the tectonic evolution processes, compositions of the early hydrosphere and atmosphere, and biological activities caused by their formation at specific geological times and conditions to understand early earth conditions [5,6].

Previous studies on the reconstruction of early earth conditions have included thermodynamic calculations of phase equilibria to understand the Archean subseafloor basalt-hosted hydrothermal system [7], redox processes in ferruginous anoxic oceanic conditions [1], evidence for ferruginous conditions from geochronological data with mineralogy, sedimentary features, and REE (rare earth element) systematics from a suite of Fe-rich chemical sedimentary rocks [3,8], experiments on the simulation of Precambrian ocean chemistry from marine photoferrotrophs, and marine Fe(III)-reducing bacteria [9].

Recently, numerous studies have focused on the trace element composition of magnetite in BIFs because it can be used as a direct or indirect provenance fingerprint of the

genetic conditions and mineralization styles of ore deposits [10–15]. Magnetite is a representative ore mineral found in BIFs, with a hydrothermal origin and an inverse AB_2O_4 spinel structure [14,16]. Nb^{5+} , Ta^{5+} , Mo^{4+} , W^{4+} , Ti^{4+} , Si^{4+} , Ge^{4+} , Sn^{4+} , V^{3+} , V^{4+} , Cr^{3+} , Al^{3+} , As^{3+} , Ga^{3+} , Mn^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Cu^{2+} , Mg^{2+} , and Ca^{2+} can enter the structure of the magnetite [14]. Specifically, divalent cations such as Mg^{2+} , Fe^{2+} , Ni^{2+} , Mn^{2+} , Co^{2+} , and Zn^{2+} are present at site A, and trivalent cations such as Al^{3+} , Fe^{3+} , Cr^{3+} , V^{3+} , Mn^{3+} , and Ga^{3+} are present at site B. In addition, Ti^{4+} can enter site B by substituting for a divalent cation [17,18]. Magnetite can crystallize in igneous, metamorphic, and sedimentary environments over a wide range of pressures and temperatures [14]. Hydrothermal ore deposits usually contain up to 10 ppm of trace elements, such as Ti, Si, V, Al, Ca, Mg, and Na [19]. Among the trace elements in magnetite, the distribution and chemical behavior of Ge (belonging to subgroup VIA of the periodic table) are closely related to ore-forming fluids, such as hydrothermal fluids, which contribute to the precipitation of magnetite. Ge exists in two oxidation states, Ge^{2+} and Ge^{4+} . Ge^{4+} is more common and stable than Ge^{2+} , and most Ge^{2+} are unstable under atmospheric conditions [20]. Ge^{4+} in silicate minerals can easily substitute Si^{4+} because they have similar geochemical signatures [21]. Ge exhibits different chemical behaviors in various geological environments because it possesses siderophilic, lithophilic, chalcophilic, and organophilic behaviors [21]. Ge is present in minor quantities in silicate minerals and is widely distributed in oxides, hydroxides, hydroxysulfates, and sulfides [20]. As Ge is not confined to specific conditions, it can occur as a minor and trace element in various types of ore deposits [21,22]. The concentration of Ge is largely dependent on the physicochemical parameters of the magnetite formation system, including the primary magma/fluid composition, with subordinate influences of oxygen fugacity, sulfur fugacity, and temperature [22].

The Wugang BIF consists of early Neoproterozoic basement rock. U–Pb age dating of Wugang BIF detrital zircons indicates an age of 2.60–2.45 Ga, and it was formed in the near-shore continental shelf or back-arc basin geological environment. The geochemical data of the Eu and Ce anomalies and the occurrence of carbonate minerals provide evidence of the superior-type BIF affinity of the Wugang BIF. In addition, Fe mainly originates from seawater and hydrothermal fluids, with river flux and minor continental detrital materials [23]. Although several studies have been conducted, the timing of precipitation, related tectonic evolutionary processes, and the chemical signatures of hydrothermal and seawater are poorly understood [23]. Therefore, we focused on the composition of magnetite from the Wugang BIF, especially the concentration of Ge, to provide further information on the compositional signatures of the hydrothermal fluid and seawater. Complementing the results of previous studies, this study provides insights into the reconstruction of the origin of Wugang BIF based on newly acquired geochemical data.

2. Geological Setting and Methods

2.1. Geological Setting and Samples

The North China Craton (NCC) is the oldest craton in the world and the largest craton and has experienced several geological events, including the removal of deep cratonic mantle roots, multiple episodes of continental crust growth, and precipitation of mineral resources [23–25]. The NCC is composed of the eastern and western blocks of the Trans-North China Orogen (TNCO) based on lithology, structure, metamorphic grade, and geochronological data [26,27]. The TNCO is a Paleoproterozoic subduction–collision belt, and Neoproterozoic terranes are distributed in the southern areas, including the Dengfeng, Zhongtiao, and Taihua complexes [26–28]. The Taihua Complex consists mainly of early Precambrian medium- to high-grade metamorphic rocks, tonalite–trondhjemite–granodiorite (TTG) gneisses, amphibolites, migmatites, and spracrustal rocks. The Huashan, Xiaoshan, Luoning, Lushan, and Wugang terranes are distributed from northwest to southeast (Figure 1a) [23,29]. The Wugang BIF is hosted in the Wugang block, which is located in the easternmost part of the Taihua complex in the southern part of the NCC, and is considered a representative iron ore in the Central Plain [23]. The Taihua complex is divided

into the Paleoproterozoic upper Taihua unit (metapelitic gneisses, marbles, quartzites, and banded iron formations) and the Neoarchean lower Taihua unit (TTG gneisses and amphibolites) [29]. Two major iron ores, the Tieshanmiao-type iron ore and the Zhaoanzhuang-type magmatic-origin iron ore, are distributed in the Taihua complex (Figure 1b). These two Fe deposits have contrasting geochemical and mineralogical signatures. The Zhaoanzhuang-type magmatic-origin iron ore is spatially and temporally related to ultramafic rocks of magmatic origin [30]. The Tieshanmiao-type Fe deposits are included in the BIF and display general geochemical signatures of other BIFs, including low concentrations of Al_2O_3 and TiO_2 , and REE + Y patterns [23,31,32]. Macroscopic and microscopic analyses revealed that the iron ore from the Wugang BIF exhibited a layered or massive texture (Figure 2). The banding texture consisted of alternating magnetite–pyroxene-rich and quartz-rich bands at various scales. The massive texture was composed of pyroxene and magnetite.

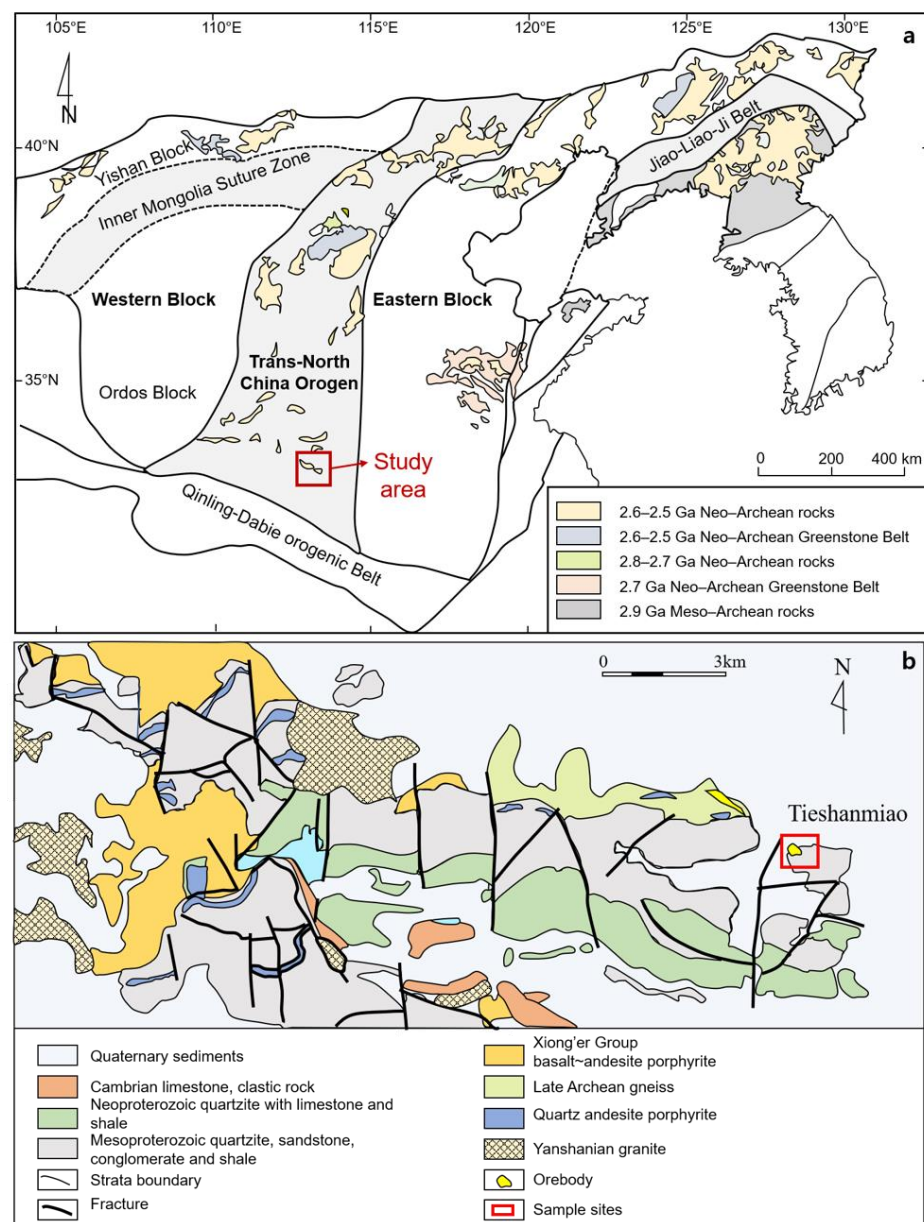


Figure 1. (a) Map of the North China Craton with the location of the study area, modified after [27]; (b) Simplified geological map of the sampling area [29].

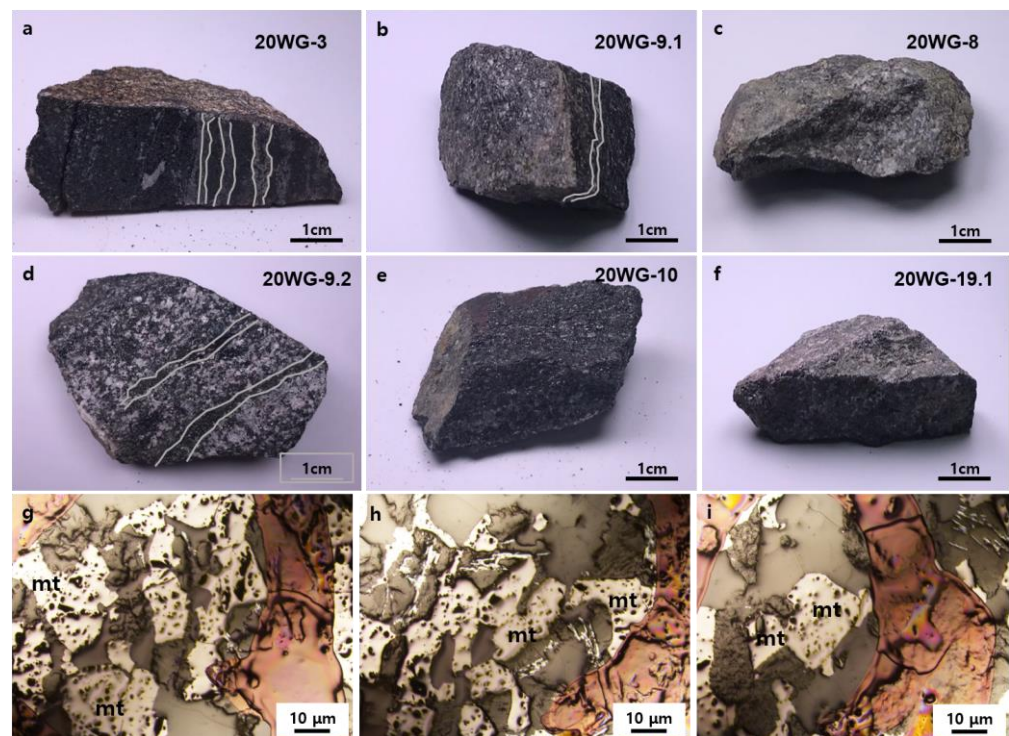


Figure 2. Petrographic features of iron ores from Wugang BIF. (a–f) Macroscopic aspect of iron ores and (g–i) microscopic aspect of magnetite, mt—magnetite. Iron ore has both a distinctive layer texture and a massive texture. Coarse-grained subhedral magnetite-associated quartz is also observed.

2.2. Analytical Methods

Laser ablation inductively coupled mass spectrometry (LA-ICP-MS) analyses were applied to evaluate trace elements used as petrogenetic indicators [12,14,33]. LA-ICP-MS is a rapid and precise method with a spatial resolution of <0.1 mm and a sub-ppm detection limit [22]. Many previous studies have focused on trace elements in ore minerals using in situ LA-ICP-MS analyses [34–38].

Concentrations of major element oxides (FeO, MnO, Cr₂O₃, MgO, SiO₂, K₂O, CaO, TiO₂, Na₂O, and Al₂O₃) (Table 1) and trace elements (Mg²⁴⁺, Al²⁷⁺, Si²⁹⁺, Ca⁴³⁺, Sc⁴⁵⁺, Ti⁴⁸⁺, V⁵¹⁺, Cr⁵³⁺, Mn⁵⁵⁺, Co⁵⁹⁺, Ni⁶⁰⁺, Cu⁶³⁺, Zn⁶⁶⁺, Ga⁶⁹⁺, Ge⁷³⁺, Y⁸⁹⁺, Zr⁹⁰⁺, Nb⁹³⁺, Mo⁹⁵⁺, Hf¹⁷⁸⁺, W¹⁸²⁺, and Pb²⁰⁸⁺) (Table 2) were analyzed using field-emission electron probe microanalyzer (FE-EPMA; JEOL JXA-8530F, JEOL) and quadrupole inductively coupled plasma mass spectrometry (iCapQ ICP-MS, Thermo Fisher Scientific, Waltham, MA, USA) equipped with femtosecond laser ablation systems (J200 LA model, Applied Spectra Inc., West Sacramento, CA, USA), respectively, at the Core Research Facility of the Pusan National University (Busan, Republic of Korea). The samples were analyzed at a pulse repetition rate of 10 Hz, and a pulse width of 480 fs for trace element analysis. An ablated spot size of 70 μm with a laser energy density of approximately 100 μJ cm^{−2}, for approximately 15 s, was used on the sample. NIST 610 glass was used as an external standard for the calculation of elemental concentrations in magnetite. Data reduction was performed using the trace element data reduction scheme of IOLITE4 software. Analyzed data are presented by Supplementary Tables S1 and S2.

Table 1. Major element abundance of magnetite from Wugang BIF (n = 64, wt. %).

	FeO ^T	MnO	Cr ₂ O ₃	MgO	SiO ₂	K ₂ O	CaO	TiO ₂	Na ₂ O	Al ₂ O ₃	Total
Min	89.2	-	-	-	-	-	-	-	-	-	89.6
Max	94.2	0.2	0.1	0.1	0.3	0.2	-	0.1	0.4	0.1	94.5
Median	92.2	0.1	-	-	-	-	-	-	-	-	-
Standard deviation	1.0	-	-	-	-	-	-	-	-	-	-

Table 2. Trace element abundance of magnetite from Wugang BIF (n = 140, ppm).

	Ge	Ti	V	Mg	Al	Cr	Mn	Co	Zn	Ga	Ni
Min	3.3	40	2.5	17	78	0.4	244	0.4	6.8	0.5	<0.01
Max	11	262	17	953	1764	405	4205	22	119	6.5	22
Median	4.7	54	3.9	135	341	4.5	622	1.2	43	0.8	4.0
Standard deviation	1.0	46	3.1	240	356	32	594	5.1	25	1.2	3.9

3. Results and Discussion

3.1. Geochemical Properties of Ge in Magnetite in Various Ore Deposits

Ge is used as a direct or indirect geochemical factor to evaluate the genetic condition of ore deposits because its concentration and chemical behavior are controlled by hydrothermal fluids, partition coefficients, and physicochemical conditions, such as temperature, and oxygen and sulfur fugacity [14,39]. Meng, Hu, Huang and Gao [22] summarized the concentration and chemical behavior of Ge in magnetite from the Fe–Ti–(V) oxide deposit in the Emeishan large igneous province of SW China containing Taihe, Baima, Hongge, Panzhihua, and Anyi intrusions with Fe–Ti–P deposits [39]; Bushveld complex of South Africa, Sept-Iles intrusive Suite of Canada, and St. Charles de Bourget of Canada; Ni–Cu–platinum-group elements (PGE) deposits of the Sudbury igneous complex in Canada [40]; Voisey’s Bay anorthosite complex in Canada [41]; Noril’sk–Talanakh intrusion in Siberia [42]; Huangshandong intrusion in China [43,44]; Sokoman iron formation in the Labrador Trough of Canada [11]; Skarn Fe deposits of the Nanling Range, South China [38]; in Tongling, Eastern China [45]; and Vegas Peledas of Argentina [39]; IOCG deposits in the Kangdian metallogenic province of SW China [46,47]; igneous derived hydrothermal Fe deposits of the Cihai Fe deposit in the Beishan terrane of NW China [48]; and Heifengshan, Shuangfengshan, and Shaquanzi Fe deposits in the Eastern Tianshan Orogenic Belt of NW China [49]. These studies provided information on the chemical behavior of Ge in each ore deposit. In the case of Fe–Ti–P deposits, the concentration of Ge in magnetite varies from 0.69 to 26.6 ppm, and its wide range is indicative of different degrees of magmatic evolution [39,50]. High Ge content magnetite is enriched in Zn and Ga and depleted in Cr, Co, and Ni [39]. In Ni–Cu–PGE deposits, magnetite occurs as an accessory mineral with a concentration of 0.15–1.27 ppm of Ge with an average of 0.74 ppm [33]. The geochemical affinity of Ge is similar to those of Cr, Ti, V, Al, Mn, and Ga and is compatible with iron oxide in sulfide melts [33]. The concentration of these lithophilic elements in iron oxide gradually decreases during the continuous crystallization of iron oxide from the sulfide liquid [33]. Chung et al. [11] investigated three types of magnetite (primary, altered, and volcanic breccia) in the Sokoman Iron Formation in the Labrador Trough of Canada, to compare trace element composition trends. The three types of magnetite exhibited different trends in trace element composition. The primary, altered, and volcanic breccia magnetites contain Ge concentrations of 13–39 ppm (average 23 ppm), 3.8–110 ppm (average 25 ppm), and 12.1–247 ppm (average 59 ppm), respectively [11]. The trace element composition of primary magnetite is homogeneous, whereas that of altered magnetite varies widely, indicating the role of exhalative volcanic processes and hydrothermal fluids in modifying the trace element composition of magnetite [11,22]. The magnetite in the Fe–Ti–(V) oxide ore deposits exhibited extensive trellis or sandwich exsolution lamellae of ilmenite and spinel, and had variable trace element concentrations owing to their crystallography (such as the affinity of the ionic

radius and the overall charge balance), oxygen fugacity, magma composition, and coexisting minerals [50]. Liu, Zhou, Chen, Gao, and Huang [50] investigated the relationship between the oxygen fugacity and concentration of Ge using quartz–ulvöspinel–ilmenite–fayalite (QUILF) equilibrium modeling. They concluded that the Panzhihua and Baima intrusions crystallized under high oxygen and possessed a slightly higher concentration of Ge compared to other intrusions in the Emeishan large igneous province, indicating that Ge can easily enter the magnetite structure at higher oxygen fugacities.

The magnetite in this study contained concentrations of 3.3–11.2 ppm of Ge (average 5.1 ppm), 40.1–261.5 ppm of Ti (average 80.6 ppm), 2.5–17.2 ppm of V (average 5.3 ppm), 17.0–952.5 ppm of Mg (average 211.7 ppm), and 77.7–1763.8 ppm of Al (average 404.5 ppm) (Table 2, Figure 3). Magnetites from the Wugang BIF have enriched concentrations of Ge with values higher than those of the bulk continental crust [51]. In the Ti + V and Al + Mn discrimination diagrams [12], the trace element compositions of magnetite plot slightly outside the BIF field owing to lower Ti + V and Al + Mn values, which reflect the complex genetic conditions of the Wugang BIF (Figure 4). The dissolution–reprecipitation processes (DRP) process can be deduced using the textural and compositional data of magnetite, which is evidence of the hydrothermal origin of magnetite. Magnetite affected by DRP has distinct textural features of secondary magnetite intergrown with relict primary magnetite, and this secondary magnetite exhibits a porosity-rich texture [52]. The magnetite in the Wugang BIF had low Al and Si contents with abundant porosity, and it can be assumed that geological events and subordinate variations in oxygen and sulfur fugacity in the fluid caused the DRP in magnetite in the Wugang BIF. The porous texture might be related to volume loss and lead to easy fluid infiltration owing to an increase in the effective permeability; therefore, magnetite dissolution occurs [52].

The narrow ranges of trace elements with respect to the composition of Ge in magnetite, as shown in Figure 3, are indicative of an original fluid source of the Wugang BIF. The partition coefficients of trace elements are primarily controlled by temperature [53], with increasing and decreasing trends in trace-element concentrations [14]. In addition, the concentration of Ge in water positively correlates with temperature [54]. However, there is still no clear evidence of a relationship between the Ge concentration in magnetite and the crystallization temperature [22]. The Ge in magnetite was positively correlated with Cr, Ni, Zn, Al, Ti, Mg, Ga, and V and slightly negatively correlated with Co (Figure 4). The chemical behavior of Ge was assumed to be similar to those of Cr, Ni, Zn, Al, Ti, Mg, Ga, and V. In addition, the positive correlations between these trace elements and Ge indicated the compatibility of Ge with magnetite [33]. In conclusion, the textural, compositional, and geochemical data for magnetite from the Wugang BIF confirm its hydrothermal origin and indicate the compositional signatures of the original hydrothermal fluids.

3.2. Controlling Factor of Ge in Magnetite in the Hydrothermal System

The Wugang BIF is appropriate for reconstructing its origin because (1) the alternating banding texture (Figure 2a,b,d) indicated that the Wugang BIF precipitated under stable depositional conditions [23]; (2) the preserved fine-grained magnetite (euhedral to subhedral) indicates the preservation of the original signatures [11]; and (3) the relatively narrow range of trace element composition of magnetite can provide insights into the original signature of magnetite-precipitation conditions. Non-altered magnetite and altered magnetite show different compositional trends, with the former having a homogenous compositional trend and the latter having a wide variation [11]. Therefore, according to the relict banding texture, euhedral to subhedral magnetite, and homogenous magnetite trace element composition, the Wugang BIF and magnetite can be used as proxies for paleo-depositional reconstruction, even though they have experienced post-depositional metamorphism and deformation.

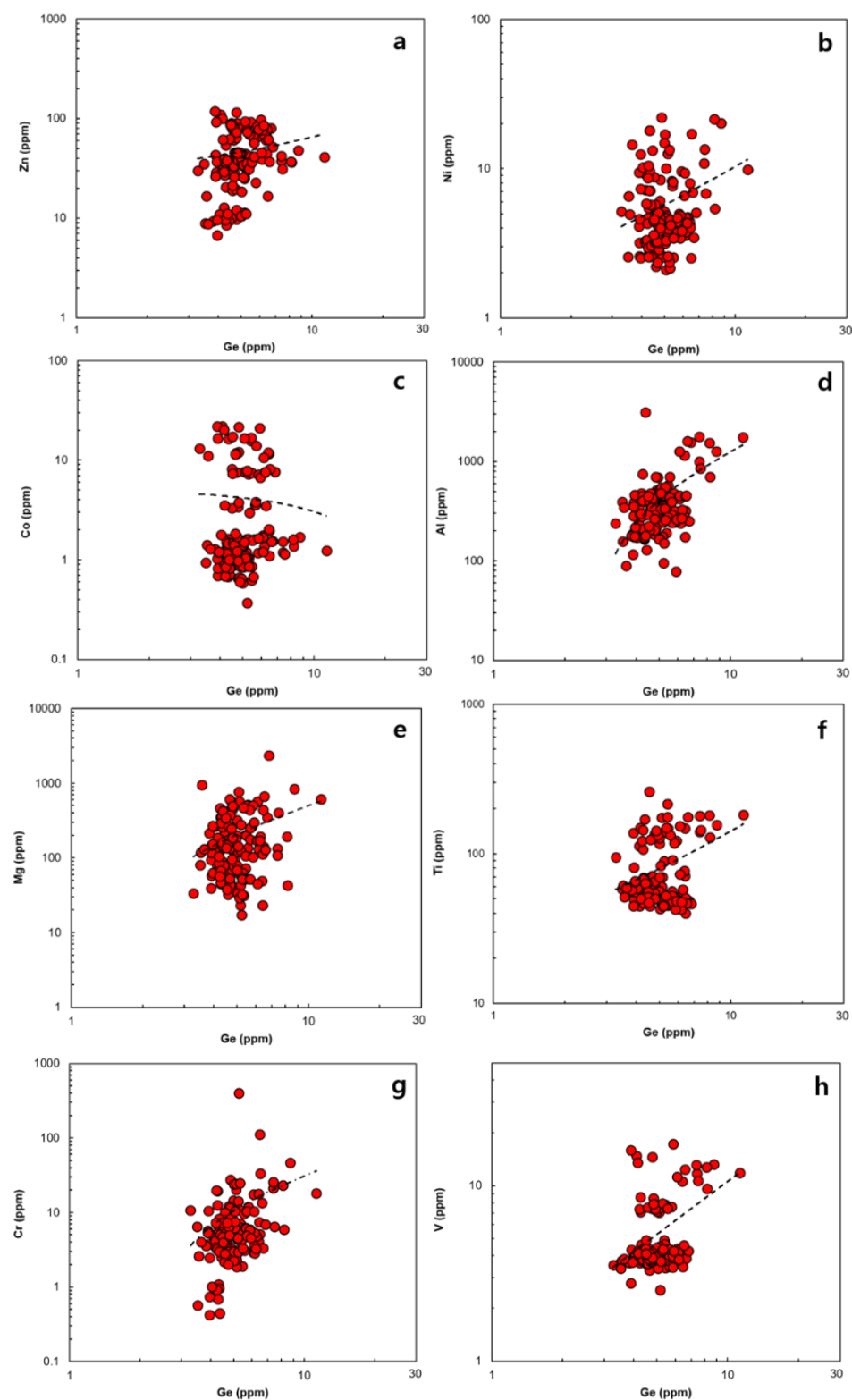


Figure 3. Plots of Ge versus selected trace elements of (a) Zn, (b) Ni, (c) Co, (d) Al, (e) Mg, (f) Ti, (g) Cr, and (h) V of magnetite from Wugang BIF (red dot). The chemical behavior and correlation are given by the dashed line. The Ge concentration of magnetite from the Wugang BIF was not high and can be considered its chemical signature.

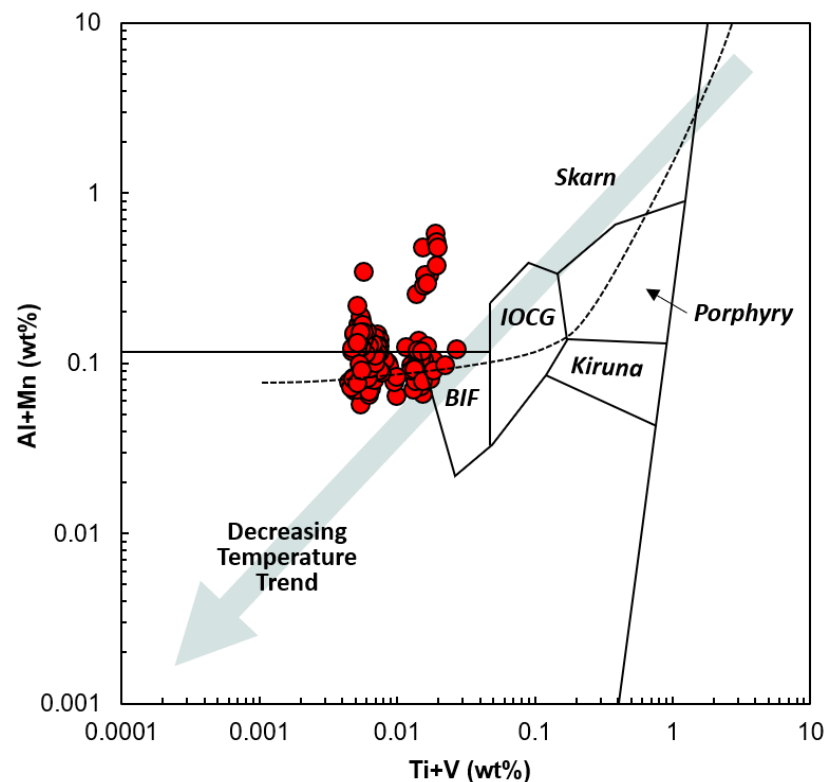


Figure 4. Plots of Ti + V versus Al + Mn of magnetite from Wugang BIF [12]. The decreasing temperature trend is indicative of the estimated formation temperature of each ore deposit. Ti + V and Al + Mn concentrations of magnetite are proportional to temperature [14]. The magnetite composition is plotted inside and outside the BIF field due to the complex genetic conditions of the Wugang BIF. The symbol is same as Figure 3.

The primary sources of iron in the BIFs were hydrothermal fluid and seawater, and magnetite in the BIFs was shown to be of hydrothermal origin [14]. BIFs are mainly composed of oxide, silicate, carbonate, and sulfide sedimentary facies [5,6]. Among these, the oxide facies contained higher concentrations of Ge than the other facies [55]. The (ferro-) ferric oxyhydroxides, including ferrihydrite ($\text{Fe}(\text{OH})_3$), greenalite ($(\text{Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$), siderite (FeCO_3), and amorphous silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) are the precursor mineral phases of magnetite. Ge is incorporated into (ferro) ferric oxyhydroxide during its precipitation from aqueous solutions [20]. The concentrations of Ge in the magnetites in BIFs are relatively higher than those in other ore deposits and are 10–100 times higher than those in the bulk continental crust [22,51]. It is generally accepted that the absorption of Ge in BIFs results from its incorporation into iron hydroxides during precipitation from aqueous solutions [20]. Ge in hydrothermal fluids is mainly controlled by two sources: (a) concentrated in evolved magmatic-hydrothermal fluids through fractional crystallization, or (b) country rock through migrating fluids. Therefore, the concentration of Ge in magnetite is essentially controlled by the composition of the hydrothermal fluids and the degree of the fluid-rock reaction [54].

Ge enrichment processes are closely linked to Earth's evolutionary processes [21]. The great oxidation event (GOE) at 2.3 to 2.4 Ga has led to an increase in $f\text{O}_2$ and influenced the Fe oxidation process (ferrous iron to ferric iron) [5]. Fe^{3+} hydroxide was formed, and the chemisorptive concentration of Ge is promoted [21]. Ge has a high affinity for iron hydroxides or oxides and can coprecipitate into iron hydroxides or oxides through sorption processes at $\text{pH} > 6$ [21,56]. In addition, the “missing Ge sink” in the ocean was due to the sequestration of Ge into authigenic Fe-oxyhydroxides in marine sediments [57], which might be one of the reasons for the absorption of Ge in the magnetite in the Wugang BIF. Considering the environmental conditions of the Precambrian (during the Neoproterozoic–Paleoproterozoic) and

the genetic processes of the Wugang BIF, it can be assumed that the magnetite of the Wugang BIF preserved its original precipitation signatures.

4. Conclusions

This study focused on the concentration of Ge in magnetite from the Wugang BIF. The textural, compositional, and geochemical features of magnetite indicate depositional conditions that were prevalent during the formation of the Wugang BIF. The Ge composition of magnetite has a relatively narrow range and has a similar chemical behavior to Zn, Ni, Al, Mg, Ti, Cr, and V. Combined with the results of previous studies; this study showed the Wugang BIF precipitated under Ge-rich near-shore continental shelf or back-arc basin conditions. Therefore, it is assumed that the contributing hydrothermal fluids and seawater are also enriched in Ge. The depositional timing of the Wugang BIF is consistent with that of the GOE. The subsequent chemical processes occurring in the Paleo-ocean were influenced by an increase in fO_2 , which led to the formation of Fe^{3+} hydroxide. Ge is absorbed by Fe hydroxides or oxides owing to its high affinity. The magnetite can be used as a proxy for the depositional condition of the Wugang BIF.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app13148246/s1>, Table S1: Major elemental compositions (in wt.%) of magnetite in the Wugang BIF; Table S2: Trace elemental compositions (in ppm) of magnetite in the Wugang BIF.

Author Contributions: I.M. designed the study and wrote the manuscript; I.M. and J.J. performed sample analysis; L.L. and X.Y. contributed to sample acquisition; Y.J.S. and Y.H. supported analysis and manuscript writing. All authors have read and agreed to the published version of the manuscript.

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