Wüstite in a hydrothermal silver-lead-zinc vein, Lucky Friday mine, Coeur d'Alene mining district, U.S.A.

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ABSTRACT

The Coeur d'Alene mining district of northern Idaho is one of the major Ag-Pb-Zn producers in the world; it contains Ag-Pb-Zn replacement veins in clastic burial metamorphic rocks of the Middle Proterozoic Belt Supergroup. Electron microprobe analyses and Raman spectroscopy of samples from the Gold Hunter vein of the Lucky Friday mine revealed the presence of the rare iron oxide wüstite $(Fe_{1-x}O)$ coexisting with stable magnetite. An assemblage of galena, pyrite, and siderite is associated with the two iron oxides although these minerals do not share phase boundaries with wüstite and their coexistence is, therefore, thermodynamically precluded.

Wüstite is stable under high-temperature conditions (above 570 °C at 1 bar). Increasing pressure can lower this temperature significantly. However, the veins in the Coeur d'Alene district formed well outside the wüstite stability field and represent a low-temperature (250–350 °C), low-pressure (1–3 kbars), and low- f_{O_2} environment. To form wüstite at temperatures around 250–350 °C a pressure increase of at least 70 kbars would be required. This corresponds to burial of around 250 km, which is geologically unrealistic. Similarly, to form wüstite, the temperature must have exceeded 570 °C, which exceeds the maximum temperatures of vein formation by at least 200 °C. A temperature increase of that scale is not reflected in the mineral assemblage of the veins or the host rocks, which both contain siderite. We conclude that wüstite formed as a metastable phase at 250–350 °C and pressures below 100 bars because of the low- f_{O_2} conditions in the Coeur d'Alene district.

Keywords: Coeur d'Alene district, Belt Supergroup, Lucky Friday, Gold Hunter, Ag-Pb-Zn veins, magnetite, wüstite

INTRODUCTION

The Coeur d'Alene mining district of northern Idaho is one of the most important Pb, Zn, and Ag mining districts in the world. It contains mainly narrow veins in sub-greenschist to greenschist facies burial metamorphic rocks of the Middle Proterozoic Belt Supergroup that have been classified as Ag-Pb-Zn replacement veins in clastic metasedimentary terranes (e.g., Beaudoin and Sangster 1992; Landis and Hofstra 1991). Many studies have thoroughly investigated the mineralogy and vein formation conditions in the Coeur d'Alene district (e.g., Beaudoin and Sangster 1992; Fryklund 1964; Landis and Hofstra 1991; Leach et al. 1988; Sack and Lichtner 2009). Siderite (FeCO₃) is a prominent gangue mineral in mineralized veins. Iron oxides like hematite (Fe₂O₃) and magnetite (Fe₃O₄) have been recognized as common constituents of the host rocks and rare constituents of some veins since the early works of Fryklund (1964). However, wüstite has not been previously reported in the district. Here we present the results of petrographic examination, electron microprobe analyses, and Raman spectroscopy that document the presence of metastable wüstite in the Gold Hunter Ag-Pb-Zn vein of the Coeur d'Alene mining district.

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WÜSTITE

The rare cubic iron oxide wüstite, Fe_{1-x}O, is named after the German metallurgist Friedrich Wüst (1860-1938). It is a member of the periclase group and typically forms as an alteration product of other iron-bearing minerals at high temperatures in a highly reducing environment (e.g., Anthony et al. 1997). At low pressures, it is never stoichiometric and contains Fe³⁺ and, depending on temperature and f_{02} , some vacancies (e.g., Lindsley 1976; Wriedt 1991). The highly defective, nonstoichiometric NaCl-type structure of wüstite (Wyckoff and Crittenden 1925) extends from nearly stoichiometric FeO to $Fe_{0.88}O$ at 1000 °C (Andersson and Sletnes 1977). The low- f_{O_2} and high-temperature conditions that are required to form wüstite, combined with its preference to react to silicates under all but the most silica-undersaturated environments, account for its rarity in crustal rocks (Lindsley 1991). The literature reports values for the temperature of the eutectoid equilibrium for wüstite-α-Fe-magnetite from 518 to 620 °C, but most direct measurements appear to be close to 570 °C (Wriedt 1991 and references therein). Figure 1 shows that wüstite is unstable under atmospheric conditions at temperatures below 570 °C and decomposes to magnetite and α -Fe (Hentschel 1970; Yin et al. 2007). Once formed, residual wüstite can persist as a metastable

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phase in coexistence with a stable phase like magnetite below 570 °C (Flaschen and Osborn 1957; Hoffmann 1959). As an iron phase, wüstite is often overlooked because of its close resemblance to magnetite (Wells 1954).



FIGURE 1. Phase diagram for the join Fe-O at 1 bar (redrawn from Darken and Gurry 1945; Hoffmann 1959; Lindsley 1976, 1991).

GEOLOGICAL BACKGROUND

The Coeur d'Alene mining district is located in northern Idaho and comprises mainly Ag-Pb-Zn veins in clastic greenschist facies burial metamorphic rocks of the Lower Belt and Ravalli Group (e.g., Beaudoin and Sangster 1992). The ore bodies are spatially associated with the Lewis and Clark line, a 50 to 100 km wide and 200 to 250 km long zone of WNW trending structures including the regionally important Osburn and Placer Creek faults (e.g., Hobbs et al. 1965) (Fig. 2). Igneous rocks of the area include Cretaceous monzonite stocks and related dikes, as well as lamprophyre and diabase dikes of probable Tertiary age, which are oriented along these northeast-striking fractures (Fryklund 1964). Folding and metamorphism in the area have been ascribed to the Kootenay orogeny (~850 Ma) (Harrison 1974). The mineral belts shown in Figure 2 represent structural features that consist of productive and non-productive veins that formed along fracture systems or shear zones (Fryklund 1964).

Although vein formation in the Coeur d'Alene district is mainly structurally controlled, stratigraphy plays a fundamental role in determining where veins produce ore (Bennett 1984; Mauk and White 2004). The Ag-Pb-Zn veins formed under relatively low-temperature and low-pressure conditions of 250–350 °C and 1–3 kbars (e.g., Landis and Hofstra 1991; Leach et al. 1988). Oxygen isotope analyses (Nadoll et al. 2009), petrologic examination, and a recent study on aqueous solution-mineral equilibria for fahlore-bearing assemblages (Sack and Lichtner 2009) confirm these vein formation temperatures, which correspond to peak metamorphic conditions in the area (Doughty and Chamberlain 1996). The findings by Sack and Lichtner (2009) also place further constraints on the prevailing f_{02} conditions of the Gold Hunter vein system. They estimate a f_{02} value of 8.5×10^{-31} bars at 300 °C for the Gold Hunter vein based on fluid compositions.



FIGURE 2. Location of the Coeur d'Alene district and the map area inset. The map shows the location of the Lucky Friday and Gold Hunter mines and the two major structural features, the Osburn and the Placer Creek faults. Also shown are the major intrusions of this area, the Late Cretaceous Gem stocks. The Gem-Gold Hunter and Golconda-Lucky Friday mineral belts are part of a system of well-defined parallel to sub-parallel mineral belts in the Coeur d'Alene district (e.g., Fryklund 1964).

The steeply dipping veins consist mainly of galena and sphalerite with associated minor pyrite, chalcopyrite, and a complex suite of pyrrhotite, arsenopyrite, and other sulfides, including tetrahedrite (e.g., Beaudoin and Sangster 1992; Fryklund 1964). Siderite and quartz are the most abundant gangue minerals, but calcite, ankerite, and dolomite are also common in the Coeur d'Alene district (e.g., Beaudoin and Sangster 1992; Fryklund 1964). Magnetite commonly is present as disseminated porphyroblasts in the burial metamorphic host rocks or as an alteration mineral in thin halos that envelop many Ag-bearing veins in the Coeur d'Alene district (White 1998).

The Lucky Friday vein is hosted by the Revett Formation, which also hosts several other deposits in the Coeur d'Alene district (Mauk and White 2004). The vein strikes northeast nearly parallel to the strata and dips steeply to the south. The Gold Hunter vein, adjacent to the Lucky Friday vein, contains several high-grade silver-bearing veins that are hosted by the St. Regis Formation (Fig. 2). The Lucky Friday and Gold Hunter vein mineralogy is similar to other deposits in the Coeur d'Alene district. The veins occur in fine-grained quartzite and very finegrained siltite-argillites with locally extensive siderite alteration. The siderite alteration ranges from disseminated spots to massive flooding and veins containing sulfide mineralization.

Several hypotheses have been proposed for the source of mineralizing fluids responsible for Ag-Pb-Zn mineralization in the Coeur d'Alene district. However, recent research that is largely based on stable isotope and fluid inclusion work seems to favor a complex metamorphic-hydrothermal system with mineralizing fluids that were derived from the Belt Supergroup by metamorphic devolatilization processes (Eaton et al. 1995; Fleck et al. 2002; Hofstra et al. 1985; Leach et al. 1998; Rosenberg and Larson 2000). Low-Ag (Zn-rich or Pb-rich) Coeur d'Alene veins are Proterozoic in age, whereas others contain Proterozoic galena and Late Cretaceous to Early Tertiary Ag-rich tetrahedrite and siderite (Leach et al. 1988, 1998; Rosenberg and Larson 2000).

EXPERIMENTAL METHODS

We collected host rock, wall rock, and vein samples from a Gold Hunter drill core (Gold Hunter 61-05, interval 391.5 ft, E 591790 N 5258215). Magnetic separation was used to split the crushed samples into magnetite and gangue separates. Magnetite grains were then mounted in epoxy resin and polished for microprobe analysis. Thin sections were prepared for petrographic work.

The magnetite-magnetite/wüstite grains were analyzed for major and trace elements with electron microprobe at the University of Auckland using a 15 kV standard energy dispersive signal (EDS) with a 800 pA beam current and a 2 μ m beam size and at the University of Michigan using a 20 kV wavelength dispersive signal (WDS) with a 20 nA beam current and a <1 μ m beam size. Results were accepted only if the compound wt% total was between 98.5 and 101.5%. The Fe²/Fe³⁺ content in Fe_{1-x}O and Fe₃O₄ was determined based on stoichiometry and charge balance.

Raman spectra were recorded on a Renishaw 1000 Raman Imaging Microscope consisting of a single grating spectrograph, a Leitz microscope and an air-cooled CCD array detector. The excitation source was a Renishaw solid-state diode laser emitting a line in the near-infrared region at -785 nm with a grating of 1200 lines/ mm. An incident laser power of 0.26 mW was used to avoid laser-induced thermal degradation; this was reduced to 26 μ W at the sample. The resolution was 4 cm⁻¹, the entrance slit width was 50 μ m, and a 100× objective was used, which focused the beam to a size of 1–2 μ m at the sample surface. The spectra were recorded and analyzed using the Grams32 spectroscopic software; the integration time was 10 s and 20 accumulations were co-added for each spectrum.

RESULTS

The wüstite was found in a siderite vein with associated sulfide mineralization at the Gold Hunter 4900 level (Fig. 3a). Massive siderite is the most abundant gangue mineral, but calcite is also present (Figs. 3a). The main sulfide phase is galena, which is accompanied by pyrite ($<50 \mu$ m) and minor subhedral to euhedral magnetite ($<100 \mu$ m) (Figs. 3b and 3c). Petrographic examinations of siderite-magnetite contacts display no signs of disequilibrium. In contrast, siderite shows signs of replacement by sulfides, in particular galena.

The wüstite grain was identified in an epoxy mounted magnetic separate. Hence, magnetite is the only associated mineral where direct phase relationships can be observed. The wüstite is distinguished from magnetite under the microscope by its slightly higher reflectivity. The phase boundary between wüstite



FIGURE 3. (a) Gold Hunter Ag-Pb-Zn vein with associated siderite and calcite (b, petrographic photomicrograph and c, polished section in reflected light). Mineral assemblage of the Gold Hunter vein, comprised of siderite, galena, pyrite, and minor magnetite.



FIGURE 4. (a) Contrast enhanced image of the magnetitewüstite compound grain showing the position of the electron microprobe line scan. (b) Plot of the corresponding electron microprobe line scan for MnO (\times 50) and FeO/Fe₃O₄.

 TABLE 1.
 Electron microprobe results for wüstite, coexisting magnetite, and siderite

Element wt%	Fe ²⁺	Fe ³⁺	Ti	Al	Mn	Mg	Ca	Cr	Ni	0	Total
LOD* EPMA UoM	-	-	0.03	0.05	0.03	0.02	0.03	0.03	-	-	-
LOD* EPMA UoA	-	-	0.05	0.05	0.06	0.11	0.03	0.03	0.04	-	-
513 wüstite	76.98	-	0.1	-	0.81	-	-	0.07	0.13	22.45	99.5
515 wüstite	75.64	0.04	-	-	1.15	-	-	-	0.09	21.98	98.99
516 wüstite	75.92	-	-	-	0.95	-	0.03	0.08	0.21	22.18	99.38
517 wüstite	75.62	-	-	0.13	0.84	-	-	0.03	0.24	21.96	98.57
518 wüstite	75.76	-	-	-	0.89	-	0.03	0.03	0.23	22.04	98.68
519 wüstite	75.63	0.53	-	-	0.83	-	-	0.03	0.09	21.92	99.1
521 wüstite	76.04	-	-	0.07	1.06	-	-	0.09	0.1	22.14	98.99
522 wüstite	75.83	0.18	-	-	1.29	-	-	0.03	-	22.06	99.28
210/9 wüstite	76.17	-	-	0.32	0.99	-	-	-	-	22.2	99.07
210/10 wüstite	76.52	-	-	0.32	0.92	-	-	-	-	22.3	99.43
512 magnetite	23.87	47.79	-	0.08	0.43	-	0.04	-	-	20.8	99.8
524 magnetite	24.41	47.66	0.07	-	0.54	-	-	0.05	0.13	21.15	100.88
525 magnetite	24.18	48.11	-	-	0.49	-	0.03	-	0.13	21.01	100.7
528 magnetite	23.69	48.8	-	0.05	0.57	-	-	-	0.14	21.1	101.36
529 magnetite	23.54	48.28	-	-	0.45	-	-	-	0.31	20.65	100.07
210/1 magnetite	23.42	48.65	-	0.06	0.4	-	-	-	-	20.82	100.34
210/2 magnetite	23.61	48.44	-	0.35	0.4	-	-	-	-	21.05	100.77
210/3 magnetite	23.18	48.86	-	-	0.42	-	-	-	-	20.52	99.7
210/4 magnetite	23.43	48.55	-	0.13	0.39	-	-	-	-	20.84	100.3
210/5 magnetite	23.65	49.01	-	0.12	0.42	-	-	-	-	21.04	101.26
3667 siderite	40.01	-	-	-	4.92	0.42	0.17	-	-	13.37	95.18
3668 siderite	37.68	-	-	-	4.83	1.22	0.65	-	-	13.2	94.16
3669 siderite	38.71	-	-	-	4.65	1.3	0.39	-	-	13.37	95.52
3670 siderite	37.12	-	-	-	4.45	2.37	0.6	-	-	13.63	96.04
3671 siderite	37.61	-	-	-	5.24	1.34	0.66	-	-	13.67	95.29
3672 siderite	37.08	-	-	-	5.03	1.47	0.65	-	-	13.54	94.16
3673 siderite	38.73	-	-	-	4.67	1.68	0.38	-	-	13.34	96.89
3675 siderite	38.08	-	-	-	4.75	1.5	0.36	-	-	13.73	95.01
3676 siderite	38.55	-	-	-	4.74	1.6	0.35	-	-	13.36	96.3
3677 siderite	38.62	-	-	-	4.62	1.63	0.4	-	-	13.79	96.44
median wüstite	75.87	0.18	0.1	0.22	0.94	-	0.03	0.03	0.13	22.1	99.08
median magnetite	23.63	48.5	0.07	0.1	0.42	-	0.04	0.05	0.14	20.92	100.52
median siderite	38.31	-	-	-	4.74	1.48	0.4	-	-	13.46	95.41

Notes: Values are given in wt%. The respective detection limits (LOD) for the University of Auckland and University of Michigan electron microprobe are shown in the first two rows. Blank spaces represent values below the respective LOD. The Fe^{2+}/Fe^{3+} content in $Fe_{1-x}O$ and Fe_3O_4 was determined based on stoichiometry and charge balance.

* The limit of detection (LOD) is equivalent to three times the standard deviation.

and magnetite is irregular (Fig. 4). The area left of the wüstite in Figure 4 does not represent a third phase. It is merely cut at an angle to the polished mount surface. grain consists of magnetite and wüstite (Fig. 4; Table 1). The calculated element wt% values are listed in Table 1. Based on 10 spot analyses, wüstite has the following formula, Fe_{0.98}Mn_{0.01}O. Negligible contents of Si, Ti, Al, Ca, Cr, and Ni are also present.

Electron microprobe results suggest that the composite

In comparison, the calculated formula for the associated magnetite is $Fe_{0.98}^{2+}Fe_{1.99}^{3+}Mn_{0.02}Ni_{0.01}O_4$ with negligible amounts of Ti, Al, Ca, and Cr. Apart from an indicative difference in calculated Fe^{2+}/Fe^{3+} concentrations, the trace element data show that Mn concentrations, although low, are higher (by a factor of two) in wüstite than in the associated magnetite. The measured Mn concentration in magnetite corresponds to average Mn contents found in magnetite grains from the Belt Supergroup (Nadoll et al. 2007). Coexisting siderite is composed of 38.04 wt% Fe plus minor amounts of Mn, Mg, and Ca.

Raman spectroscopy confirms the electron microprobe results and clearly identifies wüstite and magnetite. The two oxide phases in the compound grain have characteristic Raman spectra (Fig. 5). Magnetite displays a distinctive peak at Raman wave number 667 cm⁻¹ (Oh et al. 1998) and wüstite shows a comparatively low-intensity peak at wave number ~650 cm⁻¹ (Ovsyannikov et al. 2010; Faria et al. 1997; Raman 2006).

DISCUSSION

Upon leaving the wüstite stability field, wüstite decomposes to magnetite and native iron following Equation 1. The decomposition of wüstite comprises different stages, and Hentschel (1970) proposed that stoichiometric FeO is an intermediate metastable phase during this process. Other workers also report that metastable wüstite undergoes a transformation from non-



FIGURE 5. Recorded Raman spectra for wüstite and magnetite with indicative peaks at Raman wavenumber 650 and 667 cm⁻¹, respectively.



FIGURE 6. Schematic phase diagram for the system Fe-O-S in $f_{0_2} f_{s_2}$ space (redrawn after Hall 1986). Although the values for f_{0_2} and f_{s_2} vary greatly with temperature, the geometry of the diagram changes little, and pyrite and wüstite will not share a phase boundary under any conditions.



FIGURE 7. Temperature- f_{O_2} diagram showing the siderite (FeCO₃) stability field for 1 and 100 atm (redrawn after Thomas-Keprta 2009). Note that the presence of Mg, Ca, and Mn can increase the stability of siderite to higher temperature- f_{O_2} conditions (e.g., Deer et al. 1997). The blue shaded area represents the Gold Hunter vein formation conditions as estimated by Sack and Lichtner (2009).

stoichiometric Fe_{1-x} to nearly stoichiometric FeO during decomposition (e.g., Shen et al. 1983; Stølen et al. 1995).

$$4\text{FeO} \leftrightarrow \text{Fe}_3\text{O}_4 + \text{Fe}^0 \tag{1}$$

The veins in the Coeur d'Alene district formed under conditions that preclude the existence of stable wüstite. Coexisting phases like siderite, pyrite, and other sulfides do not share phase boundaries with wüstite (Figs. 6 and 7). However, the textures in our samples suggest that the minerals, including magnetite, seem to be widely in equilibrium apart from minor siderite replacement by galena. There are two potential pathways in which wüstite may form in this environment. These are discussed herein with their thermodynamic implications and possible geologic settings.

Pathway 1

Wüstite can form directly as one of the first phases from hightemperature (>570 °C) and low- f_{02} hydrothermal fluids. Wüstite forms only at temperatures above 570 °C, and siderite is unstable above 363 ± 10 °C at 500 bars (French 1971). As siderite is a common, widespread, and stable mineral in the Coeur d'Alene district, the hydrothermal fluids could not have been heated enough to enter the wüstite stability field.

Ramdohr (1980) wrote in his fundamental work on ore minerals that the stability field for wüstite in the system Fe-O is such that formation of wüstite is very unlikely under common geologic conditions, and even if P-T- f_{02} conditions were suitable to form wüstite, it would later be decomposed. Indeed, the temperature and pressure conditions in the Coeur d'Alene district (250–350 °C and 1–3 kbars) (e.g., Landis and Hofstra 1991; Leach et al. 1988) rule out the presence of wüstite as a stable mineral phase. In terrestrial rocks, wüstite is usually restricted to high temperatures, but can be preserved below 570 °C as residual metastable wüstite that coexists with stable magnetite (e.g., Hoffmann 1959). Increasing pressure can lower this temperature significantly (Haavik et al. 2000; Shen et al. 1983). However, to form wüstite at temperatures around 250–350 °C, a pressure increase of at least 70 kbars would be required. This corresponds to burial of around 250 km, which is geologically unrealistic.

Pathway 2

Alternatively, wüstite may have formed as a metastable phase under the low- f_{02} , low- $aSiO_2$ conditions in the hydrothermal Coeur d'Alene veins. Reactions such as Equations 2 and 3 could facilitate the formation of metastable wüstite with coexisting magnetite (e.g., Dubrawski 1991; Ellwood et al. 1986; Gallagher and Warne 1981; Seguin 1966). However, the decomposition of siderite is temperature, f_{02} , and pressure dependent (e.g., Yui 1966; Frost 1979) and the presence of cations such as Mn extend the siderite stability field to higher temperatures and f_{0_2} conditions (e.g., Deer et al. 1997; Gallagher and Warne 1981). Based on fluid compositions, Sack and Lichtner (2009) estimated a f_{O_2} value of 8.5 \cdot 10⁻³¹ bars at 300 °C for the Gold Hunter vein. Under these conditions siderite decomposition to metastable wüstite could only take place at pressures below 100 bars (Fig. 7). At higher pressures siderite is stable under the prevailing temperature and f_{02} conditions (e.g., French 1971; Koziol 2004; Thomas-Keprta et al. 2009; Yui 1966). Widespread decarbonation was not observed in our petrographic examinations. However, sulfide replacement is locally evident and decarbonation could potentially occur on a small scale.

$$Fe(Mn)CO_3 \leftrightarrow Fe(Mn)O + CO_2$$
(2)

$$3Fe(Mn)CO_3 \leftrightarrow Fe_3(Mn)O_4 + CO + 2CO_2$$
 (3)

Oxidation of wüstite to magnetite (Eq. 4) is another possible mechanism to produce metastable wüstite in coexistence with magnetite (e.g., Gallagher and Warne 1981).

$$3Fe(Mn)O + CO_2 \leftrightarrow Fe_3(Mn)O_4 + CO$$
 (4)

Wüstite is usually non-stoichiometric (Fe_{1-x}O) and contains vacancies (e.g., Lindsley 1976; Wriedt 1991), but a metastable wüstite formed under the abovementioned conditions could be nearly stoichiometric (e.g., Hentschel 1970; Shen et al. 1983). The higher Mn content of the residual metastable wüstite compared to coexisting magnetite is in agreement with observations made by other authors (e.g., Buessem and Butler 1963). Ilmenite (FeTiO₃) is usually also enriched in Mn compared to coexisting magnetite (Rumble 1973, 1976). Mayer and Smeltzer (1972) described the non-stoichiometry of wüstite as a function of the Mn content as manganous oxide and wüstite form a solid solution. Furthermore, Sano et al. (1997) and de Medeiros et al. (2004) observed that Mn can stabilize the crystal structure of wüstite.

The formation of metastable wüstite under experimental conditions has been described by several authors. For example, Romanov and Checherskaya (1972) detail the formation of metastable wüstite below 560 °C as the product of hematite reduction. The formation of active (indicating a more unstable form) metastable wüstite at 300 °C as a product of the decomposition reaction of CO₂ to carbon has been demonstrated by Kodama et al. (1992). However, the formation of metastable wüstite that is not the product of decomposition processes initiated under experimental conditions represents a new finding. Baturin and Dubinchuk (1984) describe wüstite in manganese nodules from the Pacific Ocean. With temperatures below 10 °C and pressures below 0.5 kbars (corresponding to 3000 to 4000 m water depth), thermodynamic conditions on the ocean floor are even further away from the wüstite stability field than the hydrothermal Coeur d'Alene veins. They propose that wüstite formed through diagenetic transformation of principal ore minerals, possibly facilitated by bacteria (Baturin and Dubinchuk 1984).

Wüstite in the Gold Hunter siderite vein of the Lucky Friday mine represents the first reported occurrence of wüstite in a low-temperature, low-pressure hydrothermal environment like the Coeur d'Alene district. Several scenarios can be invoked to explain the presence of wüstite in this environment, but the formation of wüstite as a metastable phase during decarbonation reactions of siderite seems to be the most plausible explanation for the formation of this rare mineral under these thermodynamic conditions. Perhaps metastable wüstite forms in other low-temperature, low- f_{02} settings; it could be readily overlooked because of its resemblance to magnetite.

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