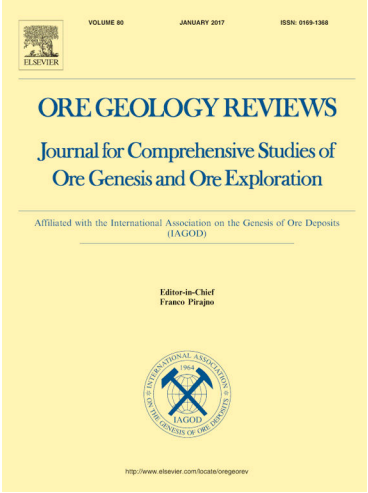
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Title	Phase relations of arsenian pyrite and arsenopyrite
Authors	Stepanov, Aleksandr S.;Large, Ross R.;Kiseeva, Ekaterina S.;Danyushevsky, Leonid V.;Goemann, Karsten;Meffre, Sebastien;Zhukova, Irina;Belousov, Ivan A.
Publication date	2021-06-06
Original Citation	Stepanov, A. S., Large, R. R., Kiseeva, E. S., Danyushevsky, L. V., Goemann, K., Meffre, S., Zhukova, I. and Belousov, I. A. (2021) 'Phase relations of arsenian pyrite and arsenopyrite', Ore Geology Reviews, 136, 104285 (15pp). doi: 10.1016/j.oregeorev.2021.104285
Type of publication	Article (peer-reviewed)
Link to publisher's version	10.1016/j.oregeorev.2021.104285
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Download date	2026-11-05 21:41:51
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Review

Phase relations of arsenian pyrite and arsenopyrite

Aleksandr S. Stepanov, Ross R. Large, Ekaterina S. Kiseeva, Leonid V. Danyushevsky, Karsten Goemann, Sebastien Meffre, Irina Zhukova, Ivan A. Belousov

PII: S0169-1368(21)00311-5
DOI: https://doi.org/10.1016/j.oregeorev.2021.104285
Reference: OREGEO 104285

To appear in: *Ore Geology Reviews*

Received Date: 31 January 2021
Revised Date: 27 May 2021
Accepted Date: 3 June 2021

Please cite this article as: A.S. Stepanov, R.R. Large, E.S. Kiseeva, L.V. Danyushevsky, K. Goemann, S. Meffre, I. Zhukova, I.A. Belousov, Phase relations of arsenian pyrite and arsenopyrite, *Ore Geology Reviews* (2021), doi: https://doi.org/10.1016/j.oregeorev.2021.104285

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Phase relations of arsenian pyrite and arsenopyrite

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Abstract

Arsenian pyrite containing above 1 wt. % As plays a crucial role in deposition and deportment of Au and other chalcophile elements. The importance of arsenian pyrite led to theoretical and experimental studies that examined properties and genesis of the mineral; however, the interpretation of the phase relations between arsenian pyrite and arsenopyrite is conflicting. In this contribution, we present the results of a review of the experimental studies that have investigated the crystallisation of pyrite in As-bearing systems, a summary of As content in pyrite coexisting with arsenopyrite in 37 deposits and the composition of arsenian pyrite in deposits with little or no arsenopyrite. The review demonstrates that the previous experimental studies that attempted to achieve an equilibrium between pyrite and arsenopyrite observed about 1 wt. % As or less in pyrite. The literature survey of the assemblages of pyrite and arsenopyrite shows that pyrite crystallising together with arsenopyrite commonly has a very heterogeneous composition with As content varying from below detection to about 10 wt. % As and no clear discontinuities were observed across this range. In the deposits without arsenopyrite, arsenic content in pyrite can reach 20 wt. % As. We consider three principal scenarios of the relations of arsenian pyrite and arsenopyrite: (A) Pyrite with high As content is stable in equilibrium with arsenopyrite. Low-As pyrite coexisting with arsenopyrite is a product of disequilibrium crystallisation; (B) a scenario of control of As content in pyrite coexisting with arsenopyrite by thermodynamic parameters including temperature, pressure, the activity of components and fluid composition and (C) a scenario where arsenian pyrite is a metastable mineral. The experimental and natural observations are inconsistent with a model of 5–6 wt.% As in pyrite coexisting with arsenopyrite in equilibrium (scenario A). The stability range of the assemblage of pyrite and arsenopyrite constrains the thermodynamic control on the composition of pyrite crystallising in equilibrium with arsenopyrite (scenario B). The scenario of metastable crystallisation of arsenian pyrite (C) proposes formation of the mineral by fast growth from oversaturated fluids with As content controlled by surface adsorption and can explain such features as sector zoning of the mineral and the apparent negative temperature dependence of the solubility.

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45 The data phase relations of arsenian pyrite highlight the need for new experimental studies, and
46 suggest that the scenario of disequilibrium phase relations of arsenian pyrite should be considered
47 for interpretation of natural assemblages.
48

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Contents

On the phase relations of arsenian pyrite and arsenopyrite 1
Abstract 2
1. Introduction 5
2. Samples and methods 6
3. Results 7
3.1 Substitution mechanisms of As in pyrite 7
3.2 Experimental data on As in pyrite 8
3.3 Arsenic concentration in pyrite coexisting with arsenopyrite in sulfidic ores 10
3.4 Arsenic concentrations in arsenian pyrite 12
4. Discussion 13
4.A Scenario A: arsenian pyrite is formed in equilibrium with arsenopyrite 14
4.B Scenario B: Thermodynamic control on equilibrium As content in pyrite 16
4.B.1 The effect of temperature and pressure 17
4.B.2 The effect of grain size 17
4.B.3 The effect of the activity of components 18
4.B.4 The effect of the fluid composition 19
4.B.5 The effect of redox conditions and As substitution mechanism 20
4.C Scenario C: metastability of arsenian pyrite 21
4.C.1 The role of surface process in crystallisation of arsenian pyrite 23
4.C.2 The role of solid state diffusion in pyrite 24
4.C.3 The effect of temperature on the crystallisation of arsenian pyrite 25
4.C.4 The effect of fluid composition on surface-controlled pyrite crystallisation 26
5. Implications 26
6. Conclusions 28
7. Acknowledgements 30
Figures and tables 31
References 40

Journal Pre-proofs

1. Introduction

Pyrite is the most abundant sulfide in the Earth's crust and characterised by wide variations in composition (Abraitis et al., 2004; Deditius et al., 2014; Gregory et al., 2015). One of the most abundant impurities in pyrite is arsenic (As), and pyrite with As content above about 1 wt. % As is commonly referred to as arsenian pyrite (Wells and Mullens, 1973). The recognition of the economic importance of arsenian pyrite came in the 1970s, when studies demonstrated that this mineral could be the principal host for invisible, refractory Au (Wells and Mullens, 1973; Fleet et al., 1988, 1993; Morishita et al., 2018), and As could enhance the uptake of gold and other trace elements into pyrite in hydrothermal ore deposits (Fleet et al., 1988; Huston et al., 1995; Fleet and Mumin, 1997; Reich et al., 2005; Deditius et al., 2014; Peterson and Mavrogenes, 2014; Xing et al., 2019a; Large and Maslennikov, 2020). In addition to its economic importance, arsenian pyrite plays a significant geochemical role, hosting poisonous As that can release into the environment during metamorphism, ore mineral processing and weathering (Large et al., 2007; Pitcairn et al., 2006; Savage et al., 2000).

Despite the economic and geochemical importance of arsenian pyrite, the phase relations of arsenian pyrite in the Fe-As-S system, are still a matter of debate (e. g. Stepanov, 2019; Xing et al., 2019). The experimental studies performed at high temperature reported low As solubility in pyrite (Clark, 1960; Hem and Makovicky, 2004a), whereas lower temperature experiments produced pyrite and marcasite with 2.9–12.6 wt.% As that were interpreted as metastable phases (Fleet and Mumin, 1997). These findings are at odds with the first-principles models proposed that As substituting S can be a stable component in pyrite (Blanchard et al., 2007; Reich and Becker, 2006). Specifically, Reich and Becker (2006) estimated that pyrite with approximately 6 wt.% of As should coexist in equilibrium with arsenopyrite but that pyrite with higher As content is metastable and at lower As content, pyrite should be undersaturated in As. These estimates were used to develop models of

hydrothermal pyrite deposition that also predicted that only pyrite with a narrow range of As concentrations can coexist with arsenopyrite (Vilor et al., 2014; Xing et al., 2019a). These models are at odds with the observations of natural arsenopyrite-pyrite assemblages which can have wide ranges of As concentrations in pyrite from below several hundred ppm to several wt. % (Li et al., 2014; Sung et al., 2009; Wu et al., 2019b). Given the importance of arsenian pyrite, this study reviews the previous studies and discusses different scenarios of the relationship between equilibrium pyrite-arsenopyrite and metastable arsenian pyrite based on the experimental results and natural observations.

2. Samples and methods

As concentrations and substitution mechanisms in pyrite are most commonly analysed by the Electron Probe Microanalyzer (EPMA) and Laser Ablation Inductively Coupled Mass Spectrometry (LA–ICP–MS). Other methods used for the study of As incorporation into the pyrite structure include X-ray absorption spectroscopy (Le Pape et al., 2018; Qian et al., 2013), transmission electron microscopy (Palenik et al., 2004) and secondary ion mass spectrometry (SIMS) (Barker et al., 2009; Chouinard et al., 2005; Morishita et al., 2019). The estimation of the substitution mechanism of As in pyrite requires accurate and precise data on all significant components of pyrite and generally measurements by EPMA equipped with WDS detectors are the most suitable for this purpose, although other methods such as SIMS have been occasionally used to study substitution mechanisms (Chouinard et al., 2005). LA–ICP–MS allows measurement of As concentrations in pyrite over the extensive range of concentrations with low detection limits as long as sufficiently low backgrounds are maintained. However, significant fractionation of S and Fe during ablation of sulfides might hinder the quantification of these elements with the accuracy required for the estimation of substitution mechanisms (Gilbert et al., 2014; Stepanov et al., 2020) and low spatial resolution of LA–ICP–MS precludes observation of small scale variation in As content.

Journal Pre-proofs

Most of the data used in this study was gathered from the scientific literature but four samples of ores with pyrite and arsenopyrite assemblages from Western Australia are reported for illustration purposes. The four samples have been selected from our collection of ores from >35 Au deposits of Western Australia (Belousov et al., 2016) and are characterised by BSE images and EPMA. The detailed description of these deposits has been provided by Belousov et al. (2016). For these samples BSE images and concentrations of Fe, S, and As were determined by point analyses on a Cameca SX100 EPMA at 20kV accelerating voltage and 20 nA probe current, using a focussed beam and the Probe Software Inc. for EPMA software package. Counting times on wavelength-dispersive spectrometry detector (WDS) for all elements were 60 seconds each for both peak and total background. Fe and S were measured using Kα line calibrated on PPP-1 pyrite standard (S. E. Gilbert et al., 2014). Arsenic was measured on Lα line and calibrated on GaAs Astimex standard.

3. Results

3.1 Substitution mechanisms of As in pyrite

Pyrite could incorporate As in a variety of substitution mechanisms (Deditius et al., 2014, 2008; Qian et al., 2013). The most widespread substitution mechanism in pyrite is S $\Leftrightarrow$ As or $Fe(S, As)_2$ (Fleet and Mumin, 1997). Another substitution type Fe $\Leftrightarrow$ As or $(Fe, As)S_2$ has been observed in the Yanacocha deposit and in synthetic pyrite (Deditius et al., 2008; Le Pape et al., 2018; Qian et al., 2013). The presence of trace element nanoparticles (Deditius et al., 2011) and nanoscale "liquid" inclusions of As–Fe–S has been reported in pyrite from some deposits (Deditius et al., 2009). Coupled substitutions $(Fe,As_{0.5}Ag_{0.5})S_2$ and $(Fe,As_{0.5}Cu_{0.5})S_2$ have been observed in the Pascua epithermal deposit (Chouinard et al., 2005). Pyrite with the substitution $Fe(S,As)_2$ is formed at reduced conditions such as orogenic gold deposits hosted by sediments, whereas substitution (Fe,

Journal Pre-proofs

As)S_2 was observed at the oxidised conditions in epithermal deposits (Deditius et al., 2008; Kusebauch et al., 2018a; Qian et al., 2013).

3.2 Experimental data on As in pyrite

The synthesis of pyrite in As-bearing systems has been achieved by different experimental techniques (Table 1). The duration of the experiments varied from several hours to about a year. Some studies attempted to achieve equilibrium and employed such techniques as long experimental runs with additional rounds of regrinding and annealing, and the addition of fluxes to increase reaction rates (Barton, 1969; Clark, 1960; Hem and Makovicky, 2004a; Kretschmar and Scott, 1976). Other studies aimed to reproduce the natural hydrothermal processes and performed experiments over shorter periods (Fleet and Mumin, 1997; Kusebauch et al., 2018a; Qian et al., 2011).

Clark (1960) performed experiments on pyrite in evacuated silica glass tubes at 500–600°C and estimated that at 600°C, pyrite coexisting with pyrrhotite and the sulfur-arsenic liquid contained just under 0.53 wt.% As (Fig. 1a). The dissolution of As in pyrite was proposed based on the decreasing pyrrhotite content in the assemblage. One of the principal features of the system discovered by Clark (1960) was a reaction of pyrite and arsenopyrite producing pyrrhotite (Fig. 2). The temperature of this reaction was closely bracketed at 491±12°C (Fig. 2) by using long high-temperature runs and a magnet for identification of the first appearance of pyrrhotite (Barton, 1969). These and additional experiments in the Fe-As-S system allowed Barton (1969) to propose the first thermodynamic model of the system.

Arsenopyrite, a principal mineral in As-bearing assemblages, often described by the formula FeAsS, but it has variable contents of As and S and hence should be described as Fe(As, $S)_2$ or FeAs(As, S). The dependence of the arsenopyrite composition on various parameters has been studied by Kretschmar and Scott (1976) who used two types of experiments: dry experiments with only Fe-S-As phases present and experiments with the addition of mixtures of halides with low melting

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temperatures that increased the reactions' speed. The later study by Sharp et al. (1985) considered the effect of pressure on arsenopyrite phase relations. These studies have not reported compositions of pyrite in experimental products, possibly due to the heterogeneity of this mineral. The experiments in the Ni-Co-Fe-As-S system at 500°C produced Ni and Co-bearing pyrite with 1.1±0.7 wt.% As in equilibrium with monosulfide solid solution and arsenopyrite characterised by $Fe(S,As)_2$ substitution (Fig. 3a) (Hem and Makovicky, 2004a). These experiments involved several cycles of annealing for 3–4 months, regrinding and repeated annealing. The total duration of the experiments was close to a year, and they represent the best data currently available on the composition of pyrite coexisting with arsenopyrite at conditions close to equilibrium.

To reproduce crystallisation of sulfides in magmatic systems and to produce larger pyrite crystals, Cafagna and Jugo (2016) synthesised pyrite by multistep cooling of mixtures of Fe-sulfides with chalcophile elements including As (Table 1). The main crystallisation stage at 650°C was followed by quenching. The synthesised pyrite contained As-rich inclusions and in some experiments coexisted with As-rich sulfide melt with about 7.4 wt.% As. Pyrite which crystallised at these conditions contained 260–400 ppm As.

Another type of experimental studies aimed to reproduce the conditions of arsenian pyrite growth in hydrothermal deposits (Table 1). Arsenian pyrite and marcasite were synthesised by Fleet and Mumin (1997) at temperatures of 310–405°C. The arsenic content of minerals varied from 2.9 to 7.7 wt.% As in arsenian pyrite and 10–12.5 wt.% As in marcasite synthesised at 310°C. Marcasite with 16.5 wt.% As was observed in an experiment at an unspecified temperature. The compositions of pyrite corresponded to $Fe(S, As)_2$ substitution (Fig. 3a). Using the reaction of S- and As-rich fluids with magnetite at 120–220°C, Qian et al., (2013) produced pyrite with $(Fe, As)S_2$ substitution and As contents from <0.03 to 23.8 wt.%. In the experiments where the source of As was more reduced arsenopyrite or lollingite, the As content in pyrite was lower than in experiments where As was sourced from realgar and compounds with oxidised As, such as As_2O_3 and $Na_2HAsO_4*7H_2O$.

Journal Pre-proofs

Kusebauch et al. (2018) performed experiments on the replacement of siderite by pyrite from As-bearing fluids that produced a wide range of pyrite compositions with up to 7 wt. % As and showed systematic variation in As content of pyrite with changes in compositions of starting solutions.

3.3 Arsenic concentration in pyrite coexisting with arsenopyrite in sulfidic ores

Assemblages of pyrite and arsenopyrite are widespread in ore deposits and in unmineralised metamorphic rocks (Tomkins et al., 2007). A systematic literature-based data compilation of pyrite composition from arsenopyrite-bearing samples from 37 ore deposits (Table 2) show that this assemblage is common in orogenic gold type, but is sometimes reported in epithermal, gold skarn, Carlin-type and volcanic-hosted massive deposits (Fig. 1b). The ores of WA deposits commonly show evidence of simultaneous crystallisation of pyrite and arsenopyrite (Fig. 3, 4, Table 2, Supplementary Table S1). For example, the ore from the Meekatharra Prohibition deposit contains arsenopyrite both as small inclusions in the zoned pyrite crystals and coarse grains in the silicate and carbonate matrix (Fig. 4). The highest As content of 3.2% occurs in irregular inner zones (Supplementary Table S1), whereas zones containing <260 ppm As occur in direct arsenopyrite crystals (Fig. 4a). The samples of ores from Youanmi and Lancefield deposits are composed of massive fine-grained pyrite intergrown with crystals of arsenopyrite which crystallised together (Fig. 4c–d). While As content in pyrite was variable from <260 pm to 2200 ppm, in the immediate vicinity of arsenopyrite As content reached very low values down to the limit of detection (Fig. 4c–d). A sample from the Paddington deposit is composed of a quartz vein with large (2–3 mm) crystals of pyrite and arsenopyrite that have no immediate contact. The cores of pyrite contain inclusions of pyrrhotite and have negligible As contents (5–35 ppm As by LA-ICP-MS; Belousov et al., 2016). In contrast, the inner rim zones of the pyrites have 1–1.3 wt.% As, followed by the rims with 0.2–0.5 wt.% As (Fig. 4b).

The deposits with pyrite-arsenopyrite assemblages described in the literature similarly contained multiple generations of pyrite, sometimes several stages of arsenopyrite crystallisation and

abundant evidence of the simultaneous crystallisation of the two minerals. While in some deposits the arsenopyrite formed late in the history of the ores (e. g. Boiron et al., 1989), in others the pre-ore stage pyrites, sometimes of sedimentary origin, with low to moderate As concentrations were followed by the stages of co-crystallisation of arsenian pyrite and arsenopyrite (Hou et al., 2016; Large et al., 2007; Li et al., 2014; Zhang et al., 2017). In the epithermal Patricia deposit in Chile pyrite and arsenopyrite crystallised prior and after the main stage of sulfide deposition (Chinchilla et al., 2016) whereas in Kuh-Pang deposit in Iran, pyrite and arsenopyrite crystallisation preceded the deposition of copper sulfides (Rajabpour et al., 2017). In the Gutaishan deposit, China Li et al. (2019) documented crystallisation of arsenopyrite with pyrite during several stages with an increasing abundance of arsenopyrite. The ores from Fairview and Sheba mines in South Africa contained both coarse arsenopyrite and arsenopyrite inclusions in pyrite (Agangi et al., 2014).

The survey of the literature indicates that almost universally pyrite shows heterogeneity in As content that is well outside of the analytical uncertainty. For example, in over 50% of the deposits the difference between the maximum and minimum As content of pyrite coexisting with arsenopyrite is larger than a factor of 10 (Table 2). These observations are consistent with the previous detailed studies of pyrite in ore deposits that demonstrated that the distribution of pyrite compositions could be multimodal and multiple complex correlations of elements commonly occur (Cook and Chryssoulis, 1990; Morey et al., 2008; Sykora et al., 2018; Winderbaum et al., 2012). Arsenic variations in pyrite may occur on submicron to nano-scale levels (Peterson and Mavrogenes, 2014; Wu et al., 2019b). For multimodal populations, the average values could be unrepresentative and arithmetic mean, geometric means and median could differ significantly while the standard deviation could be an inadequate measure of the dispersion. The great diversity in the pyrite compositions reported in different studies complicates the comparison of the observations. Therefore, in order to better show the compositional variations reported by different studies, we chose to report the highest, lowest and the average As content of pyrite coexisting with arsenopyrite in Figure 1b and Table 2. The pyrite compositions reported in many papers are not suitable for

252 proper evaluation of the mechanism of substitution of As in pyrite (e. g. incomplete analysis,
253 insufficient precision on Fe and S concentrations,). However, where the substitution mechanism was
254 investigated, the $Fe(S, As)_2$ substitution was observed (Agangi et al., 2014; Li et al., 2014; Zacharias et
255 al., 2004). Overall, a broad trend of As content increasing with decreasing temperature is apparent in
256 the dataset and also apparent in the experimental data. A somewhat similar trend has been
257 observed by (Deditius et al., 2014) in the dataset of average As concentrations in pyrite from various
258 deposits.

259

260 *3.4 Arsenic concentrations in arsenian pyrite*

261 As a mineral, arsenian pyrite is commonly observed in deposits without or with very little
262 arsenopyrite (Simon et al., 1999a). Such assemblages could represent As-undersaturated systems (e.
263 g. Xing et al., 2019) and therefore, we compare here As content in pyrite from these type of ores. For
264 this purpose, we used the list of deposits by Deditius et al. (2014) which, in most cases, did not
265 contain significant amounts of arsenopyrite and plotted the data as the maximum As content versus
266 the temperature of mineralisation (Fig. 1c).

267 Arsenian pyrite has been reported from several deposit types including orogenic gold, VHMS, Carlin-
268 type, epithermal and deposits with transitional characteristics (Supplementary Table S2). Pyrite
269 commonly has a highly heterogeneous As distribution with oscillatory and sector zoning (Fig. 5). In
270 orogenic type deposits the As content in pyrite can reach 7.6 wt. % As, similar to the values we
271 found in orogenic gold deposits with arsenopyrite (Table 2). Arsenian pyrite occurs in epithermal
272 type deposits where it forms at temperatures 150–305°C (Table 2). The As content in pyrite in
273 epithermal deposits is highly variable and can reach up to 9.4 wt. %. The pyrites with highest As
274 concentrations reaching 10–20 wt. % occur in Carlin-type gold deposits formed at temperatures
275 close to 200°C (Barker et al., 2009; Gopon et al., 2019; Reich et al., 2005; Simon et al., 1999b). The

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potential of the presence of micro inclusions of arsenopyrite in pyrite analyses with extremely high As concentrations should not be overlooked, substitution $Fe(S, As)_2$ is characteristic for Carlin-type deposits (Deditius et al., 2014; Reich et al., 2005).

4. Discussion

Reich and Becker (2006) predicted a bell-shaped solvus between pyrite-arsenopyrite and estimated a slight decrease of As from about 6 wt. % As in pyrite in equilibrium with arsenopyrite at 450°C (Fig. 1a) to about 5 wt. % As at 200°C. Below these values, the solid solution should be undersaturated and above, the solid solution was interpreted to be metastable. Based on the diagram by Reich and Becker (2006), subsequent studies have developed thermodynamic models for hydrothermal As-bearing systems that predicted that pyrite with <5 wt. % As cannot be in equilibrium with arsenopyrite (Vilor et al., 2014; Xing et al., 2019a).

Judging by the experimental data and studies of natural sulfidic ores summarised above, we conclude that these models fail to reproduce the following key observations:

- Experiments estimated that, in pyrite in equilibrium with arsenopyrite, arsenic solubility in pyrite is about or below 1 wt. % (Fig. 1a), especially the results by Hem and Makovicky (2004).
- Pyrite occurring with arsenopyrite in nature has widely variable As content (Fig. 1b) with the maximum As content reaching 6–10 wt.% As. However, in the majority of cases, arsenic content is significantly lower than these values and the lowest reported As content in pyrite coexisting with arsenopyrite for all the compiled ore deposits is <3 wt. % (Fig. 1, Table 2).
- Arsenopyrite can coexist at distances of several microns or in direct contact with pyrite containing >400 ppm As (Fig. 4).

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- In deposits where arsenopyrite is absent, the highest As contents of 10–20 wt. % As have been reported, whereas in arsenopyrite-bearing assemblages, arsenic content in pyrite is <10 wt. % (Fig. 1c).
- A negative temperature dependence of As content in pyrite is apparent in the experimental data and natural occurrences of pyrite (Fig. 1).

Several scenarios of the phase relationship between pyrite and arsenopyrite are proposed (Fig. 6):

- Scenario A) Pyrite with high As content is stable in equilibrium with arsenopyrite. Low-As pyrite coexisting with arsenopyrite is a product of disequilibrium crystallisation.
- Scenario B) As content in pyrite coexisting with arsenopyrite in equilibrium depends on the thermodynamic conditions (p, T, fO_2, fluid composition).
- Scenario C) Arsenian pyrite (i. e. pyrite with high As) is formed by disequilibrium crystallisation and could represent a metastable phase.

In the following sections we compare these scenarios with the observations and investigate their implications.

4.A Scenario A: arsenian pyrite is formed in equilibrium with arsenopyrite

Vilor et al. (2014) and Xing et al. (2019) have developed models of the behaviour of the arsenian pyrite in hydrothermal systems by fitting the thermodynamic parameters to data of Reich and Becker (2006). Unfortunately, the predictions of these models are in disagreement with the widespread coexistence in nature of arsenopyrite and pyrite with As content much lower than 5–6 wt.% (Fig. 1b) and the experimental studies that attempted to attain equilibrium (Fig. 1a). Moreover, our review and study of natural samples from various sulfide deposits (Table 2) failed to find a single example of an assemblage of arsenopyrite and homogeneous pyrite with 5–6 wt.% As that is predicted in this scenario.

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Xing et al. (2019b) proposed that coexistence of low-As pyrite with arsenopyrite could be explained by disequilibrium crystallisation of the minerals, although they did not specify details. One such mechanism could be the crystallisation of arsenopyrite and low-As pyrite from separate batches of fluids with different As content, however, it contradicts the numerous observations of simultaneous crystallisation of arsenopyrite with low-As pyrite (e. g. Agangi et al., 2014; Fig. 4c, d). In this scenario, fluids entering rocks that contain arsenopyrite and pyrite should be able to dissolve arsenopyrite and produce pyrite with increasing As content, which is not supported by the observations. Another disequilibrium pathway could require crystallisation of low-As pyrite from solutions with high As content. This mechanism does not seem geologically likely as the formation of an oversaturated solid solution is much more common than undersaturated solid solutions (e. g. Watson, 1996).

If the assemblage of low-As pyrite and arsenopyrite occurs at disequilibrium, as proposed by Xing et al. (2019b), then the metamorphism or recrystallisation of these mineral assemblages should result in the evolution of the system to equilibrium compositions: that is to the dissolution of arsenopyrite in pyrite, the diffusion of As into pyrite and the development of As-rich haloes around arsenopyrite inclusions in pyrite. Such textures have not been documented in the literature. On the contrary, in Meekatharra Prohibition arsenopyrite inclusions are associated with pyrite with very low As content (Fig. 4a). Moreover the textures of replacement of arsenian pyrite by aggregates of pyrite and arsenopyrite have been reported at Bogosu-Prestea mining district of the Ashanti Gold Belt, Ghana (Mumin et al., 1994), Sunrise Dam in WA (Sung et al., 2009), and Zhuangzi deposit in China (Li et al., 2018).

The textures of pyrite and arsenopyrite from sulphide deposits of Western Australia provide additional evidence against scenario A (Fig. 4). For example, pyrite from Paddington deposit shows zonation from the very low As content in core, to mantle of arsenian pyrite with highest As (1.3–1.5 wt. % As) and then to rim with approximately 0.2 wt. % As. The core could be interpreted as formed before the introduction of high-As fluid to the system but the mantle and rim formed before or

347 together with arsenopyrite and no zone recorded the values of 5-6 wt. % As predicted by the models
348 (e. g. Xing et al., 2019). In many deposits with the pyrite and arsenopyrite assemblage, all analysed
349 pyrites had As contents significantly lower than 6 wt. % (Fig. 1b), for example 50% of deposits in
350 Table 2 have all reported As concentrations <3 wt.% As and all analyses from 4 deposits from
351 Western Australia is <1.6 wt. % (Fig. 4). The only way to reconcile such assemblages with the phase
352 diagram of Xing et al., (2019) is to assume the complete absence of equilibrium in these occurrences,
353 hence rendering the diagram inapplicable to the natural systems.

354 *4.B Scenario B: Thermodynamic control on equilibrium As content in*
355 *pyrite*

356 The critical question for this scenario of the thermodynamic control of equilibrium As solubility in
357 arsenian pyrite (Fig. 6b) is in the specific parameters that affect the stability of arsenian pyrite in
358 nature. In general, the main parameters that could affect the behaviour of a thermodynamic system
359 include temperature, pressure, the activities of components, the presence of fluid and fluid
360 composition parameters such as pH and redox conditions. Additional factors, such as mineral grain
361 size and substitution mechanism also could play a role. To account for the effect of each
362 thermodynamic parameter, experimental studies are required that investigate one parameter at a
363 time and thoroughly demonstrate equilibrium between pyrite and arsenopyrite. Unfortunately, to
364 the authors' knowledge, such data do not exist at the time of writing. The lack of equilibrium
365 experimental data is exacerbated by lack of well documented examples of assemblages of arsenian
366 pyrite and arsenopyrite that can be demonstrated to represent equilibrium assemblages.
367 Nevertheless, in the discussion below, we will attempt to summarise the results of basic
368 thermodynamic considerations with the observations from this contribution and the studies
369 available in the literature to delineate some principal limitations on this scenario.

Journal Pre-proofs

4.B.1 The effect of temperature and pressure

Temperature has the strongest effect on solubility and stability of components. Compounds with limited mutual solubility form a bell-shaped solvus with decreasing solubility at lower temperatures (Massalski, 1989). The compilations of As content in pyrite coexisting with arsenopyrite (Fig. 1b) and arsenian pyrite (Fig. 1c) show a conspicuous pattern of increasing As content with decreasing temperature, opposite to what is expected from a solvus. The experimental data suggest that at 500–600°C, arsenic solubility in pyrite is 0.5–1.1 wt. % (Clark, 1960; Hem and Makovicky, 2004b), however there are no data on equilibrium As solubility in pyrite at lower temperatures. Nevertheless, since the compilation of natural pyrite-arsenopyrite pairs which formed between 200 and 300°C have variable As content down to very low concentrations (Fig. 1b), there is no evidence that at some temperatures pyrite coexisting with arsenopyrite in equilibrium has high As content.

The effect of pressure is typically small on sulfide equilibria because they have high densities and low compressibility (Barton, 1974). Chalcophile element partitioning into sulphides is also considered relatively independent of pressure (Barton, 1974; Kiseeva and Wood, 2013; Tomkins et al., 2007), in particular at relatively small pressure intervals. The majority of deposits summarised in Table 2 formed at upper crustal conditions at relatively low-pressure and a major role for pressure in stabilisation of arsenian pyrite is unlikely.

4.B.2 The effect of grain size

Grain size could be another parameter affecting the stability of pyrite and As content. Fine-grained aggregates have higher total energy than coarse-grained crystals due to a contribution of surface energy. Arsenian pyrite could occur both in fine-grained aggregates and as coarse crystals (Fig. 5). Deditius et al. (2008) observed that arsenian pyrite forming micro-size grains (<1 micron) is composed of nanoparticulate aggregates of single crystals of arsenian pyrite and reported an increase of As content in smaller nanocrystals of pyrite with (Fe, As)S_2 substitution from Yanacocha deposit. A correlation with highest Au concentrations (up to about 900 ppm Au) in aggregates of

smallest pyrite grains was observed by Simon et al. (1999) in a Carlin-type deposit. Qian et al. (2013) synthesised texturally similar nano-crystalline pyrite in experiments on replacement of magnetite. In contrast, euhedral pyrite produced by the hydrothermal replacement of carbonates, had higher As content than fine-grained framboidal and porous pyrite (Kusebauch et al., 2018b). Overall, while the grain size commonly shows correlations with pyrite composition in many environments, it does not seem to be the primary factor controlling As content, since both coarse crystalline pyrite and fine-grained pyrite with high As concentrations are commonly observed (Deditius et al., 2008; Peterson and Mavrogenes, 2014; Sykora et al., 2018).

4.B.3 The effect of the activity of components

The stability and composition of arsenian pyrite as a phase in the Fe-As-S system can be affected by the activities of the components such as As and S (aS$_2$ for sulfur activity and aAs for As activity). The effect of the activity of the components on the stability of phases in the system Fe-As-S was evaluated by Barton (1969) who demonstrated that at constant P and T, the phase rule predicted that the assemblage of pyrite with arsenopyrite occurs on a line in aS$_2$–aAs space. The assemblages of the three phases define nonvariant points, and the line of coexisting pyrite and arsenopyrite is limited by the point pyrite coexisting with arsenopyrite and pyrrhotite at lower S and As activity, and pyrite and arsenopyrite coexisting with sulfur-arsenic liquidat higher S and As activity (Fig. 7). When pyrite is in equilibrium with arsenopyrite, then the activity of arsenic is proportional to the activity of sulfur (Fig. 7b). The composition of pyrite in the buffered assemblage of pyrrhotite, pyrite and arsenopyrite in the system containing Co and Ni was reported by Hem and Makovicky (2004a), however, no experimental or natural data are available on the composition of pyrite in equilibrium assemblages with higher aS$_2$/aAs such as assemblages with sulfur-arsenic liquid. Considering that pyrite with arsenopyrite is stable over less than one order of magnitude of S and As activity at any given temperature (Fig. 7), it is unlikely that the increase of S and As activities alone could control the composition of pyrite with As concentration varying by over three orders of magnitude.

4.B.4 The effect of the fluid composition

The composition of fluids can have a profound effect on the solubility of minerals and hence control their transporting ability. The effects of the pH and H_2S activity on the solubility of arsenopyrite in a fluid have been studied by experiments where the attainment of equilibrium has been demonstrated by saturation and dissolution experiments (Perfetti et al., 2008; Pokrovski et al., 2002). Among the experiments on arsenian pyrite available so far, those that attempted to achieve equilibrium have been performed only in dry systems. The fluid-bearing experiments of Fleet and Mumin, (1997) produced arsenian pyrite that was interpreted as a metastable product in addition to the observed metastable arsenian marcasite. Other hydrothermal experiments produced highly zoned, often fine-grained pyrite aggregates that also likely represent metastable products where composition was controlled by the reaction path (Kusebauch et al., 2018a; Qian et al., 2013). In the absence the equilibrium hydrothermal experiments with arsenian pyrite we consider the natural samples observations and the thermodynamic constraints on the system.

Stepanov (2019) criticised the model by Xing et al. (2019) because it failed to reproduce some of the key experimental observations of the system. One such disagreement is that maximum temperature of stability of the assemblage of pyrite and arsenopyrite is 491°C (Fig. 2 and Fig. 7) (Kretschmar and Scott, 1976) which increases by 14°C per kbar with pressure (Sharp et al., 1985). The calculations of Xing et al. (2019a) estimated the highest temperature of the assemblage pyrite-arsenopyrite was at about 580°C and 2 kbar, about 60°C higher than estimates from dry experiments. Xing et al. (2019b) explained this discrepancy by the dissolution of significant amounts of Fe and S by the hydrous fluid. They proposed that the limits of thermal stability of assemblages of arsenopyrite and pyrite established in dry systems did not apply to water-bearing systems. However, since all minerals in Fe-As-S system are anhydrous, the presence of H_2O cannot have a direct effect on the stability and composition of the minerals. When additional components are present in the system, then the stability field of some minerals could diminish due to their solubility in the fluid. For example, As-S

445 melt/liquid that is present in the dry Fe-As-S system is unlikely to occur in hydrous systems.
446 However, the presence of water in the system cannot increase the maximum stability temperature
447 of an assemblage of anhydrous minerals such as pyrite and arsenopyrite (Barton, 1974; Tomkins et
448 al., 2007).

449 The role of a fluid in mineral-mineral equilibria can be demonstrated on the simpler phase relations
450 of pyrite and pyrrhotite. Pyrrhotite has a variable composition $Fe_{(1-x)}S$ depending on temperature and
451 fS_2 (Toulmin and Barton, 1964). The composition of pyrrhotite coexisting with pyrite at any given
452 temperature and pressure is independent of the presence of fluid and fluid composition (Kishima,
453 1989; line of coexisting pyrite and pyrrhotite at Fig. 7a). Similarly, the effect of fluid composition on
454 composition of pyrite in equilibrium with arsenopyrite could be only indirect, for example, by
455 affecting the activity of S/As in the system. Notwithstanding the arguments presented above, the
456 effect of fluid on the phase relations between pyrite and arsenopyrite requires further studies at
457 clearly defined equilibrium and disequilibrium conditions.

458 **4.B.5 The effect of redox conditions and As substitution mechanism**

459 Redox state is an essential parameter during crystallisation of As-bearing pyrite because As occurring
460 as $As^{+3}(OH)_3$ in solutions (Perfetti et al., 2008; Pokrovski et al., 1996) changes to As^{-1} or As^{+2} in pyrite
461 depending on the mechanism of As substitution in pyrite (Qian et al., 2013). Of the two main
462 substitution types, the $Fe(S,As)_2$ substitution is by far the most common in pyrite coexisting with
463 arsenopyrite in hydrothermal ore deposits (Section 2.3, Fig. 3). Because in pyrite with $Fe(S,As)_2$
464 substitution As is in the same state As^{-1} as in arsenopyrite $Fe(S,As)_2$ the exchange of As between
465 minerals can occur without redox reactions and hence the As content in $Fe(S,As)_2$ pyrite could be
466 independent of the redox conditions. This point was inadvertently illustrated by the model of Xing et
467 al. (2019a) that showed that at oxidised and reduced conditions the As content of pyrite coexisting
468 with arsenopyrite remained the same. For example, they estimated that irrespective of redox
469 conditions at approximately 180°C, the As content in pyrite coexisting with arsenopyrite is 5 wt. %

and at (yellow vertical lines in the field of pyrite and arsenopyrite at Figs. 2C and D in Xing et al. (2019a)). While the exact values of As concentrations are in disagreement with the experimental and natural data (Fig. 1), the modelling by (Xing et al., 2019a) suggests that redox conditions have no effect on As solubility in pyrite with $Fe(S,As)_2$ type substitution.

The pyrite with $(Fe,As)S_2$ substitution has been observed in Yanacocha deposit (Deditius et al., 2008) and was synthesised in experiments by (Qian et al., 2013). In Yanacocha deposit $(Fe,As)S_2$ pyrite formed under rapid local changes in temperature and/or the chemical composition of the mineralising fluids at non-equilibrium conditions (Deditius et al., 2008). The wide range of As contents, intensive zonation and the fine-grained textures suggest that this type also formed by disequilibrium crystallisation. As there is no evidence of equilibrium in assemblages with this type of pyrite, probably the pyrite with $(Fe,As)S_2$ substitution is always a product of reaction path dependent disequilibrium crystallisation (Qian et al., 2013; Xing et al., 2019a).

4.C Scenario C: metastability of arsenian pyrite

The growth of a mineral from a hydrothermal solution occurs by the absorption of atoms to the surface of the crystal. It commonly results in disequilibrium compositions of minerals because the energy of atoms in the crystal volume (that define the energy of a thermodynamic substance) is generally different from the energy of atoms on the surface of a crystal (Watson, 1996): "*…crystal is growing, any trace elements bound in the surface layer may be buried and trapped in the newly-formed lattice, resulting in lattice concentrations that deviate substantially from those predicted by equilibrium partitioning between the crystal and its growth medium*". The disequilibrium composition of the surface followed by burial by the new layers and then intracrystalline diffusion is necessary for homogenisation of the mineral composition and equilibration with the fluid and surrounding crystals. Therefore, the phenomena controlling the mineral growth in the fluid (diffusion in fluid, development of the boundary layer), on the surface (nucleation and adsorption)

Journal Pre-proofs

and inside the crystal (intracrystalline diffusion or lack of thereof) can lead to deviations of the mineral composition from equilibrium.

As the models of equilibrium relations between arsenian pyrite and arsenopyrite cannot describe the observed phase relations, there is a need for an additional mechanism. One of the possible explanations is metastability, i.e. the existence of phases stable outside the conditions of thermodynamic stability or phases without stability fields (Brazhkin, 2006). Metastable phases are commonly described in chemistry and metallurgy. In fact, the majority of organic compounds and useful alloys are metastable relative to simpler and more thermodynamically stable compounds (Turnbull 1981; Brazhkin 2006). Metastability is also widespread in the mineral world (e. g. Korsakov et al. 2010; Starr and Pattison 2019). The interpretation that arsenian pyrite could be a metastable/disequilibrium phase has been proposed in several studies (Ballantyne and Moore, 1988; Fleet et al., 1993; Fleet and Mumin, 1997; Reich and Becker, 2006; Sykora et al., 2018), though was not favoured by recent models (Xing et al., 2019b). Scenario C of widespread metastability/disequilibrium between arsenian pyrite and arsenopyrite (Fig. 7) could offer solutions to some conundrums of the system but also triggers new questions.

4.C.1 The role of surface process in crystallisation of arsenian pyrite

The characteristic features of absorption-controlled growth are sector and oscillatory zoning (Reeder and Paquette, 1989; Shtukenberg et al., 2009; Watson, 1996), which are common in pyrite (Chouinard et al., 2005; Fleet et al., 1988; Peterson and Mavrogenes, 2014; Sykora et al., 2018). Sector zoning (Fig. 5) is a specific indicator of disequilibrium partitioning during growth because it could only develop when growth of different facies produces different mineral compositions, whereas the equilibrium growth of the mineral should result in a homogeneous composition (Watson, 1996). Oscillatory zoning could form due to different processes, which include changes in the chemistry of fluids, variations in growth rate and growth controlled by the diffusion from the solution and commonly indicates disequilibrium crystallisation processes (Tiller and Ahn, 1980;

519 Watson, 1996). Therefore, the common presence of intense zonation in arsenian pyrite is an
520 evidence for the disequilibrium conditions during crystallization of arsenian pyrite.

521 Gold is an important impurity in pyrite commonly correlating with As contents in the mineral
522 (Deditius et al., 2014; Kusebauch et al., 2019; Large and Maslennikov, 2020; Reich et al., 2005; Simon
523 et al., 1999a). In the low-As systems pyrite can have relatively low partitioning coefficients for Au
524 (Pokrovski et al., 2019) and can be associated with Te (Large and Maslennikov, 2020). The processes
525 proposed as responsible for high contents of gold in arsenian pyrite include:

526 • chemisorption (Fleet and Mumin, 1997);
527 • localisation of highly reducing conditions at the surface of arsenic-rich minerals during
528 dissolution (Pokrovski et al., 2019, 2002);
529 • electrochemical accumulation of gold on charged p-type pyrite surfaces (Möller and Kersten,
530 1994);
531 • formation of particles which are stable only on a pyrite substrate (non-autonomous nano-
532 particles; Tauson et al., 2014, 2010);
533 • coupled As-Au partitioning into pyrite in As-bearing systems (Kusebauch et al., 2019) and
534 chemisorption in As-free systems (Pokrovski et al., 2019).

535 The majority of these mechanisms emphasise the important role of adsorption in the formation
536 of high-Au and high-As pyrite and these processes inherently tend to result in the
537 heterogeneous composition of the mineral unless it is homogenised by diffusion (Watson, 2004).
538 High concentrations of Au are typically observed in pyrite with As content above 1 wt. % As
539 (Reich et al., 2005), that falls in the range of metastable pyrite compositions proposed in this
540 study (Fig. 8). Therefore, the future studies investigating the mechanisms of Au concentration in
541 pyrite should investigate the role of metastability in pyrite-arsenopyrite system.

Journal Pre-proofs

4.C.2 The role of solid state diffusion in pyrite

After entrapment, the composition of a mineral that is in equilibrium with surrounding phases can be achieved by solid state diffusional exchange and recrystallisation. Therefore, intracrystalline diffusion in pyrite and arsenopyrite are the principal parameters that govern the attainment of equilibrium between the minerals in nature and experiments. Unfortunately, there are no estimates of the diffusion rates in arsenopyrite and information on diffusion rates in pyrite is very limited: Brenan et al., (2000) measured the diffusion of Os and Watson et al. (2009) estimated the diffusion rate of sulfur isotopes. All available experimental estimates suggest extremely slow diffusion in pyrite. Additional constraints on the diffusion rate in pyrite are the observations that pyrite in natural rocks typically has strong and sharp compositional zonation (Fig. 4, 5) also suggesting very slow diffusion rates in the mineral (Peterson and Mavrogenes, 2014; Sykora et al., 2018).

The common preservation of the growth zonation in pyrite coupled with the very slow diffusion suggests that arsenian pyrite could be considered as a metastable phase defined as **"**…*a nonequilibrium state of a substance whose properties change reversibly over a period of the experiment or observation"* (Brazhkin, 2006). Low diffusion rate prevents the mineral from irreversible changes such as homogenization that are necessary for achieving an equilibrium composition.

4.C.3 The effect of temperature on the crystallisation of arsenian pyrite

Temperature affects the disequilibrium uptake of trace elements in multiple ways (Watson, 2004, 1996). The increase of temperature increases diffusion in the growth medium (fluid) and hence decreases the development of the boundary layer during crystal growth. Temperature also increases the rate of intracrystalline diffusion in the mineral and hence can facilitate the attainment of equilibrium. The negative slope of maximum As concentrations with temperature (Fig. 1 and 8) is in

Journal Pre-proofs

agreement with the model of Watson (1996) that proposed that with an increase in temperature, the efficiency of entrapment of trace elements decreases. However, the relative role of the increase of diffusion in the fluid and the crystal and changes in fluid composition with the temperature needs to be established by further studies.

The rate of mineral growth could be another important parameter likely affecting the incorporation of impurities, such as As into pyrite. It has been proposed that a lower rate of mineral growth can result in crystallisation of pyrite with lower contents of trace elements other than Ni, Co, Se, and Te that are isomorphic with either Fe or S (Abraitis et al., 2004; Sykora et al., 2018). High growth rate results in disequilibrium adsorption of atoms to the mineral surface and also covering by the new layers, hence preventing from reaching equilibrium. In the case study of Lihir gold deposit, PNG, Sykora et al. (2018) proposed that at the high temperature of porphyry stage, growth rate was lower resulting in the low content of trace elements, whereas at the low temperatures of the epithermal stage the growth rate was higher producing pyrite with high contents of trace elements including As. The crystal growth rate is closely related to the fluid (over-) saturation and cooling rate that likely were different between the two stages of ore genesis in Lihir deposit. Overall, with decreasing temperature there is a multitude of factors that favour the development of surface-controlled crystal growth that results in crystallization of arsenian pyrite.

4.C.4 The effect of fluid composition on surface-controlled pyrite crystallisation

The scenario of metastable crystallisation of arsenian pyrite does not exclude the effect of the thermodynamic parameters such as fluid composition on pyrite crystallisation as it could play an essential role during disequilibrium crystallisation as well. Pyrite growth from oversaturated solutions, commonly occurs by the reaction of S-rich fluid with Fe bearing minerals (Fleet and Mumin, 1997; Kusebauch et al., 2018b; Qian et al., 2013). In natural fluids at equilibrium, arsenic mainly occurs as $As(OH)_3$ (Perfetti et al., 2008; Pokrovski et al., 1996, 2002). Hydrothermal

Journal Pre-proofs

591 replacement experiments (Kusebauch et al., 2018b) demonstrated that As partitioning coefficients
592 between pyrite and fluid decrease with As content in the fluid, whereas equilibrium partitioning is
593 expected to be independent of the concentration (e. g. Barton, 1974). The experiments by Qian et al.
594 (2013) demonstrated that fluids that sourced As from such minerals as arsenopyrite and lollingite
595 precipitated pyrite with considerably lower As content (maximum 0.6 wt. % As) than pyrite formed
596 from the fluids that dissolved As from such substances as As_2O_3 (up to 23.8 wt. % As as $(Fe, As)S_2$
597 solid solution). This evidence of the dependence of pyrite composition from As sources might
598 suggest that sorption properties of pyrite could be different in fluids with different compositions,
599 however further studies are needed to understand the relative role of equilibrium and the
600 disequilibrium processes and different fluid compositional parameters on the composition of
601 arsenian pyrite.

602 # 5. Implications

603 In this contribution we suggest that high-As pyrite could be a metastable phase at much lower As
604 concentrations than previously thought. The potential metastability of high-As pyrite has significant
605 implications for the interpretation of this mineral's behaviour during metamorphism of sediments
606 and ore deposits. Pyrite is the major host of chalcophile elements in sediments and low grade
607 metamorphic rocks (Gregory et al., 2015). Fluids forming orogenic gold deposits are produced by the
608 dehydration of sediments during metamorphism (Evans et al., 2006; Phillips and Powell, 2010;
609 Stepanov, 2021; Tomkins, 2010), and the most likely source of Au and As in fluids is sedimentary
610 pyrite in black shales (Pitcairn et al., 2006, 2010, 2014; Large et al., 2007, 2012, 2011; Tomkins, 2010;
611 Thomas et al., 2011). The decomposition of pyrite to pyrrhotite was proposed as the main
612 mechanism controlling the release of Au and As to the metamorphic fluid(s) (Pitcairn et al., 2010;
613 Large et al., 2011; Thomas et al., 2011). The recrystallization of high-As and high-Au sedimentary
614 pyrite during the metamorphic devolatilization can be one of the mechanisms of generation of Au-
615 rich fluids during low grade metamorphism. The recrystallization of metastable arsenian pyrite could

Journal Pre-proofs

616 explain the survival of metamorphic pyrite to higher temperature conditions than the "window" of
617 generation of Au-bearing fluids that is observed in some zoned metamorphic complexes (Ferry,
618 1981; Pitcairn et al., 2015).

619 The metastability of high-As pyrite has implications for interpretation of sulfide assemblages. The
620 geothermometry of sulfide assemblages is known to be problematic, especially for pyrite (Barton,
621 1974). To date there is no reliable method to determine the temperature of pyrite formation from
622 its composition, although attempts have been made to use the partitioning of sulfur isotopes
623 between individual growth sectors of pyrite (van Hinsberg et al., 2010). Also, many sulfide minerals
624 show little variation in partitioning of trace elements with temperature (George et al., 2016). The
625 metastability of arsenian pyrite might offer an explanation for the consistent difficulty in
626 development of reliable geothermometers for pyrite.

627 The pyrite geochemistry has been used for numerous geochemical problems, including the use of
628 the systematic variations in Au concentrations in sedimentary pyrite for estimation of Au content in
629 ocean water though time (Large et al., 2015a), tracing of biologically important nutrient elements
630 during history of the ocean (Large et al., 2015b), the usage of geochemistry of pyrite as a pathfinder
631 for ore mineralisation (Large et al., 2017); and as a recorder of the geochemistry of ore-forming
632 fluids (Tardani et al., 2017). These applications do not require the equilibrium partitioning of trace
633 elements between pyrite and fluid. As long as pyrite preserves composition from the growth event
634 and provided that suitable partition coefficients have been estimated, the compositions of pyrite can
635 be a sensitive indicator of the composition of the solutions that produced this mineral.

636

637 # 6. Conclusions

638 In this study, we have reviewed the compositions of experimentally produced and naturally
639 coexisting pyrite and arsenopyrite and elaborate on the phase relations of arsenian pyrite

Journal Pre-proofs

and arsenopyrite. While our study highlights the need for new experimental and theoretical data on the system, the following observations are pertinent from this review:

- The experimental studies that attempted to achieve equilibrium show the coexistence of arsenopyrite and pyrite with ≤1wt. % As.
- The published data from natural samples demonstrate highly heterogenous pyrite in terms of As concentrations and the widespread occurrence of low-As (e. g. <3 wt. % As) pyrite coexisting with arsenopyrite.
- In assemblages without arsenopyrite, the As content in pyrite can attain higher concentrations than in arsenopyrite-bearing assemblages.
- We discussed three possible scenarios that could potentially explain the conundrums of the system, including (A) equilibrium crystallisation between only high-As pyrite (5–6 wt. % As) and arsenopyrite; (B) strong dependence of As content in pyrite on thermodynamic parameters (e. g. temperature, fluid presence and composition) and (C) equilibrium of low-As pyrite (< 1 wt. % As) with arsenopyrite and metastable crystallisation of arsenian pyrite.
- Scenario A of stable coexistence of arsenian pyrite and arsenopyrite fails to explain multiple observations in experiments and natural samples.
- Scenario B of the considerable variation of pyrite composition in equilibrium with arsenopyrite is constrained by the limits of the stability of the assemblage of pyrite and arsenopyrite.
- Scenario C of the metastability of arsenian pyrite allows explanation of multiple observations including the widespread heterogeneity of arsenian pyrite, textures of decomposition and the surface control on mineral chemistry.
- The highest As content in arsenian pyrite is found in arsenopyrite-free environments in Carlin-type deposits.
- Experimental constraints such as As partitioning coefficients between pyrite and fluid estimated by Kusebauch et al., (2018) and arsenopyrite solubility (Perfetti et al., 2008;

Journal Pre-proofs

Pokrovski et al., 2002) are independent of the interpretations of the phase relation of arsenian pyrite and arsenopyrite, however, the possibility of the extensive metastability should be considered in the planning of the future experimental studies as was done by Pokrovski et al. (2002).

- This study represents a reconnaissance attempt of delineation of metastability in the system pyrite-arsenopyrite. A number of recent studies investigated the crystallisation at conditions typical for hydrothermal ore deposits, however, experimental data in the high-temperature range of conditions are limited: the principal study by Clark (1960) was conducted almost 60 years ago and since has not been reproduced. Additional experimental and natural studies will be required to obtain better constraints on phase relations in the critically important systems involving pyrite and arsenopyrite.

7. Acknowledgements

We thank the Geological Survey of Western Australia for providing samples used in this study. Vadim Brazhkin provided valuable insights into the definition and thermodynamics of metastable phases. Two anonymous reviewers are thanked for constructive reviews, and Arthur Deditius, Christof Kusebauch and Gleb Pokrovski are acknowledged for insightful discussions. This study was supported by the National Natural Science Foundation of China (No. 42073058 and No. 42073036). The work of Kate Kiseeva in Oxford University was financially supported by NERC grant NE/L010828/1.

Journal Pre-proofs

Figures and tables

Figure 1. The compilation on As content in pyrite versus temperature. a) Data from experimental studies. The solubility of As in pyrite in equilibrium with arsenopyrite calculated by Reich and Becker, (2006) is shown by dashed line. b) As content in pyrite coexisting with arsenopyrite from different types of ore deposits. The data sources are listed in Table 2 and the number of deposits in each category is provided as N. c) Maximum As concentrations in pyrite from various ore deposits compiled by Deditius et al. (2014) and typically in assemblages without arsenopyrite. The references are provided in Supplementary Table S2.

Figure 2. Simplified sections through dry Fe-As-S system (Clark, 1960; Kretschmar and Scott, 1976). At low temperatures (a) pyrite could coexist with a variety of hgh-As phases though these assemblages rarely occur in nature. The temperature range between 281 and 491°C (b) represent typical conditions of the assemblage of pyrite and arsenopyrite. The principal reaction occurs at 491°C above which (c) assemblage of pyrite and arsenopyrite is no longer possible. Asp – arsenopyrite, Py – pyrite, Po – pyrrhotite, Lo – lollingite, $(S, As)_L$ – sulfur –arsenic liquid/melt, Orp– orpiment and Rl–realgar.

Figure 3. Arsenic substitution types in pyrite. (a) Pyrite from experimental studies that shows both $(Fe, As)S_2$ and $Fe(S, As)_2$ type substitution mechanisms; (b) pyrite from the ores with pyrite and arsenopyrite assemblage that exclusively show $Fe(S, As)_2$ substitution mechanism though significant data scutter is apparent; (c) the analyses of pyrite from Western Australian deposits with pyrite and arsenopyrite assemblage showing a tight trend consistent with $Fe(S, As)_2$ mechanism.

Journal Pre-proofs

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711 Figure 4. BSE images of pyrite from deposits in Western Australia with assemblage of pyrite and
712 arsenopyrite with As concentration in representative zones of pyrite obtained by EPMA. The image
713 collection was optimized for visualisation of pyrite zonation and the matrix assemblages of silicates
714 and carbonates are not resolved in the black background of the images due to low BSE signal of
715 these minerals. Brightness of pyrite grains reflects variations in As content. Note low concentrations
716 of As in pyrite coexisting with arsenopyrite and at distances of 10s to100s micron.

717

718 Figure 5. Reflected light images of sector and oscillatory zoning in pyrite from Lihir gold deposit,
719 Papua New Guinea etched with NaClO. The details on the deposit are provided in Sykora et al. (2018)
720 and etching technique was described by Peterson and Mavrogenes (2014). The bands of darker
721 brown colour correspond to higher As content in pyrite (Peterson and Mavrogenes 2014). The sector
722 and oscillatory zoning visible in Lihir pyrite are typical products of surface-controlled disequilibrium
723 growth (Watson, 1996). a) A pyrite crystal with intense sector and oscillatory zoning that shows
724 transition from original octahedral morphology to cubic crystal shape. b) A pyrite crystal with large
725 euhedral core composed of pyrite low trace element content and without, visible zonation,
726 surrounded by a rim with fine oscillatory zoning and sector zoning; c) a polycrystalline, possibly
727 botryoidal aggregate of pyrite with oscillatory zoning.

728

729 Figure 6. A schematic plot of principal scenarios of the phase relation between arsenian pyrite and
730 arsenopyrite. See discussion in the text.

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732 Figure 7. a) Simplified sulfur activity (*a*S2) versus temperature diagram (Kretschmar and Scott, 1976;
733 Tomkins et al., 2006) that shows the fields of the coexisting pyrite and arsenopyrite and pyrrhotite
734 and arsenopyrite. b) Sulfur activity versus arsenic activity (*a*As) diagrams relevant for stability of
735 arsenopyrite and pyrite (Barton, 1969). The thickened line shows coexistence of pyrite with
736 arsenopyrite. Abbreviations are the same as in Fig. 2.

737

738 Figure 8. A subset of the FeS_2–$FeAs_2$ phase diagram with the fields of pyrite composition delineated
739 based on the data from Fig. 1. The compositional range of arsenopyrite is shown after Kretschmar
740 and Scott (1976). The line X–X represents potential solubility of As in pyrite in equilibrium with
741 arsenopyrite, line Y–Y shows maximum As content in pyrite coexisting with arsenopyrite and Z–Z is
742 maximum As in arsenian pyrite.

Journal Pre-proofs

743 Table 1. A summary of conditions of the experimental studies performed in As-bearing systems with
744 pyrite.

Reference	Temperature	System/components	Duration
Clark (1960)	400–750°C	Fe-As-S	5–304 days
Barton (1969)	281–825°C	Fe-As-S	21–338 days
Kretschmar and Scott (1976)	300–680°C	• Fe-As-S • Eutectic halides (flux)	4–187 days
Hem and Makovicky, (2004a, 2004b)	500–650°C	• Fe–Co–Ni–As–S • LiCl–KCl flux	3 times 3–4 months with regrounding
Tauson (1999)	500°C	• Greenockite • Pyrite • H_2O solution NH4Cl, Au, As	Not reported
Cafagna and Jugo, (2016b)	• Fused at 1200°C (then cooling at 60°C/h), • 750°C (then cooling at 0.5°C/h) • Annealing at 650°C • quench	• Natural sulfides (pyrrhotite, chalcopyrite, pentlandite) • elemental S • Metalloids and PGE	About 200 hours
Fleet and Mumin, (1997)	310–605°C	• Fe-As-S • H_2O • NaCl and KCl (flux)	5–57 days

Journal Pre-proofs

Qian et al. (2013)	125–220°C	• Magnetite • Thioacetamide • Buffer solutions • Various As substance	31 days
Kusebauch et al. (2018a)	200°C	• Siderite or black shale containing siderite • Pyrite seeds • Thioacetamide • H_2O solution with S and As	22–332 hours
Pokrovski et al. (2002)	300–450°C	• Arsenopyrite • +/- H_3AsO_3 • +/-HCl/NaOH solutions • +/- Py–Po–Mt buffer	1–125 days

745

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747 Table 2. A summary of compositions of pyrite coexisting with arsenopyrite in various deposits from a

748 literature survey.

Locality	Type	As wt. % Max–Min	Average wt. %	Pyrite type coexisting with arsenopyrite	T°C	Reference
Paddington, WA, Australia	Orogenic (Precambrian)	0.2–0.44		Rim Py		This study, Belousov et al. (2016)
Meekatharra Prohibition, WA, Australia	Orogenic (Precambrian)	<0.03–1.6				This study, Belousov et al. (2016)
Lancefield, WA, Australia	Orogenic (Precambrian)	<0.03–0.9			280±30	This study, Belousov et al. (2016), Salier et al. (2005)
Youanmi, WA, Australia	Orogenic (Precambrian)	<0.03–0.09				This study, Belousov et al. (2016)
Sheba and Fairview gold Mines, South Africa	Orogenic (Precambrian)	0.17–0.21	0.19	Py 62_11 Stage 1	300–420	Agangi et al., (2014)
Tanami gold province, NT, Australia	Orogenic (Precambrian)	0.2–0.4				Cook et al. (2013)
Babaikundi area, India	Orogenic (Precambrian)	0.01–1.85				Jha et al. (2015)

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Pampe deposit, Ghana	Orogenic (Precambrian)	0.09–0.65		Py from V2 vein set		Salvi et al. (2016)
Sunrise Dam, WA, Australia	Orogenic (Precambrian)	0.02–5.7			280–320	Sung et al. (2009), Salier et al. (2005)
Daqiao deposit, China	Orogenic	0.01–0.8		Py4-py		Wu et al. (2019)
Zhengchong, China	Orogenic	1–4.2		PyII-1, PyII-2		Shao et al. (2018)
Yangshan gold belt, Qinling, China	Orogenic/epizonal	0.68–10.7		Py2 main ore stage		Li et al., (2014)
	Orogenic/epizonal	0.02–3.59		Py3 late ore stage		
Buracão Area, Brazil	Orogenic	0.16–1.11		Py from veins	260–450	Pires et al., (2019)
Bake deposit, China	Orogenic	0.02–1		P0		Liu et al. (2018)
Um Garayat deposit, Egypt	Orogenic	0.08–0.36		Blocky pyrite	340–360	Zoheir et al. (2019)
Gutaishan deposit, China	Orogenic	0.16–1.9		Py2a,2b,3a		Li et al. (2019)
Suzdal, Kazakhstan	Orogenic	0.2–4.31			300–380	Kovalev et al. (2011, 2009)
Maureen deposit Queensland, Australia	Orogenic	2.3–7.7	4.9		250–300	Hurtig et al. (2014)
Sawayaerdun, Xinjiang, China	Orogenic	0.03–8	1.74	Py1 and Py2	220–270	Zhang et al. (2017)

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Wangu gold deposit, Hunan, China	Orogenic/ intracontinental reactivation	2.0–5.93	3.3		245–387	Deng et al. (2017)
Bhukia-Jagpura gold prospect, India	Metamorphosed orogenic?	0.014–0.021		Py IV with Po	Peak 530–550	Deol et al. (2012)
Homestake, USA	Orogenic (metamorphosed)	0.001–0.3		Py2	500°±50	Steadman and Large (2016)
Rosebery Deposit, Tasmania, Australia	VMS	0.04–0.58	0.18		250–300	Smith and Huston (1992)
Kuh-Pang deposit, Iran	VMS	0.01–4.18	1.76		250–370	Rajabpour et al. (2017)
Brunswick No. 12 deposit, Canada	VMS	0.02–1.05	0.21		350–450ºC	McClenaghan et al. (2009)
Ming Mine, Newfoundland, Canada	VMS	1.07–8.24	2.9	Up Plunge Pyrite	250–300	Brueckner et al. (2014)
Chouichia and Ain el Bey, Tunisia	Epithermal?	2.5–9.3	5.0	Py Stage 2	200–300	Slim-Shimi et al. (1996)
Vorontsovskoe, Urals, Russia	Epithermal/skarn	0.09–0.36	0.22	A3 type Py	310–400	Murzin et al. (2017)
Patricia deposit, Chile	Epithermal	0.83 – 2.7	1.76	Pre-ore (Py1)	210–250	Chinchilla et al. (2016)
		0.12–1.85		Post-ore (Py3)	180–240	
Huijiabao Trend, China	Carlin	0.48–9.83	4.2	Py3, Py4	210±20	Hou et al. (2016)

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West Banshee, USA	Carlin		3.0	Stage 3		Barker et al. (2009)
Jinlongshan, China	Carlin	<0.02–7.27		Py1–Py2		Zhang et al. (2014)
Zhuangzi deposit, China	Unclear	0.17–3.92	1.8	Py1	289–375	Li et al. (2018)
		<0.02–0.2	0.1	Py2	289–375	
Gutaishan, China	Unclear	0.03–1.93	0.6	Py2	200–320	Li et al. (2019)
		0.12–1.85	0.98	Py3	175–215	
Lianhuashan ore field, China	Unclear	0.001–6.5	1	Py2	~ 200	Hu et al. (2018)
Marche-Combrailles Shear Zone, France	Unclear	2–4	3.25	Pyrite IV	240±30	Boiron et al. (1989)
Roudny deposit, Bohemian Massif, Czech Republic	Unclear	0.02–4.66		pyrite-2		Zacharias et al. (2004)
Zaozigou deposit, China	Unclear	0.5–4	2.2		148–304	Tang et al. (2019)
El Sid Gold Mine, Egypt	Unclear	0.072 – 0.2	0.072			El-Bouseily et al. (1985)

749

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Journal Pre-proofs

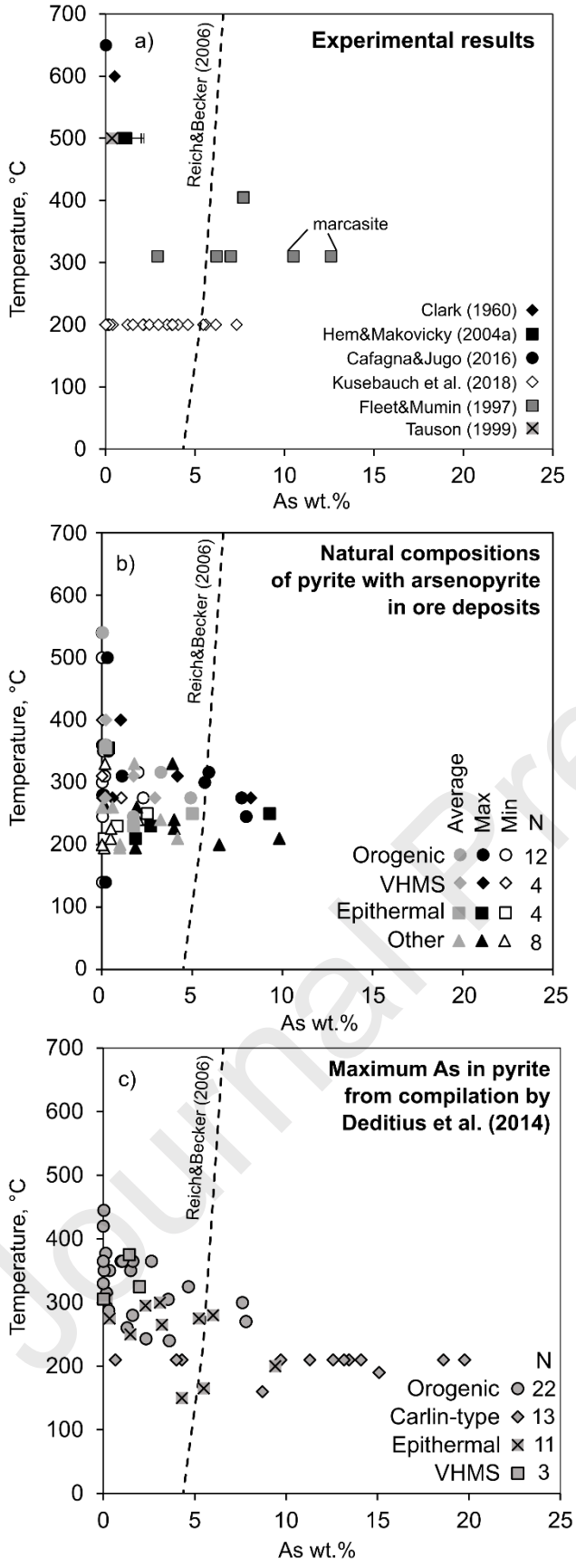


Figure 1

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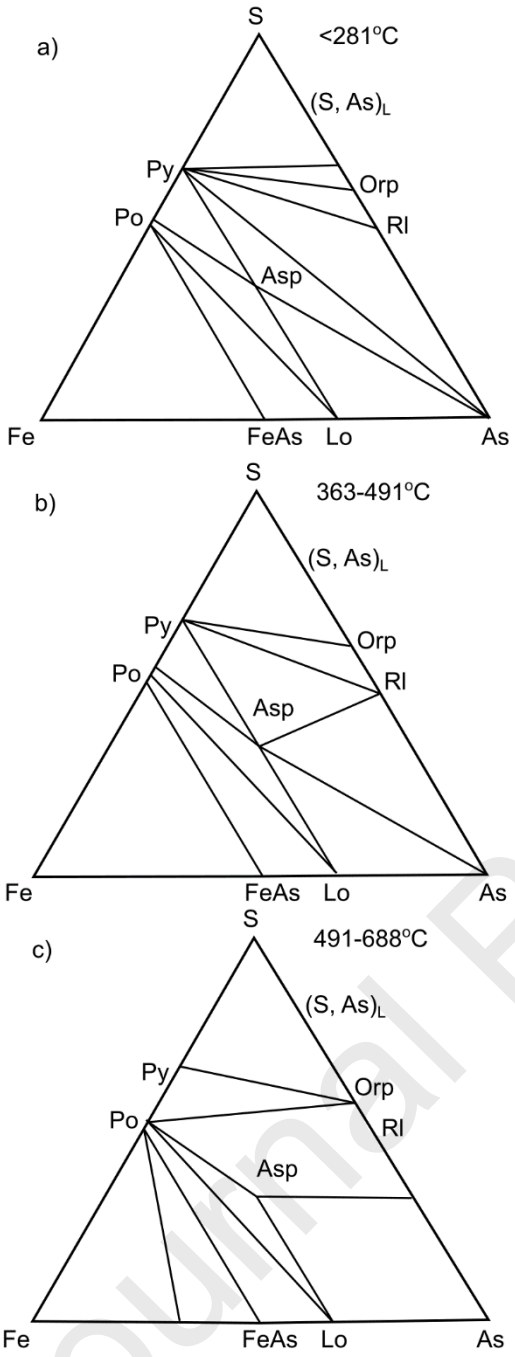
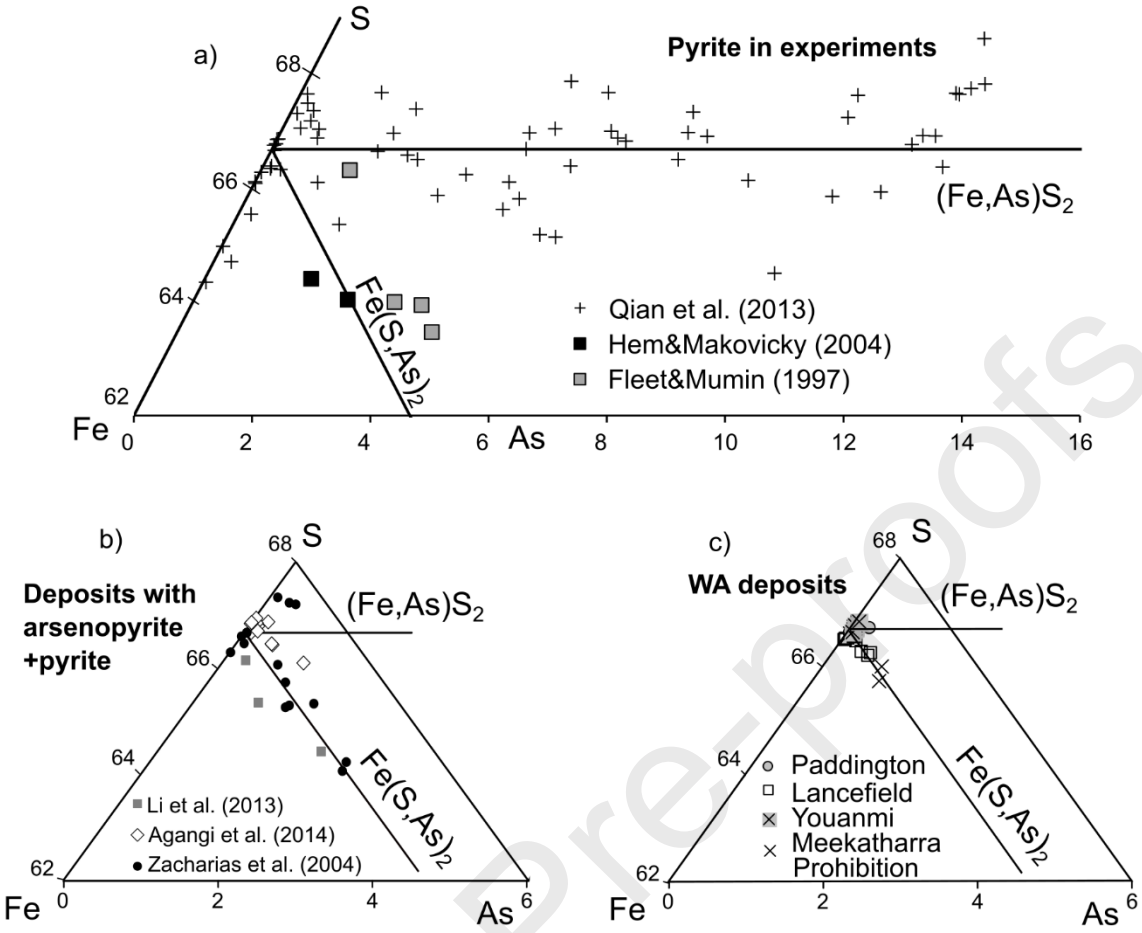


Figure 2

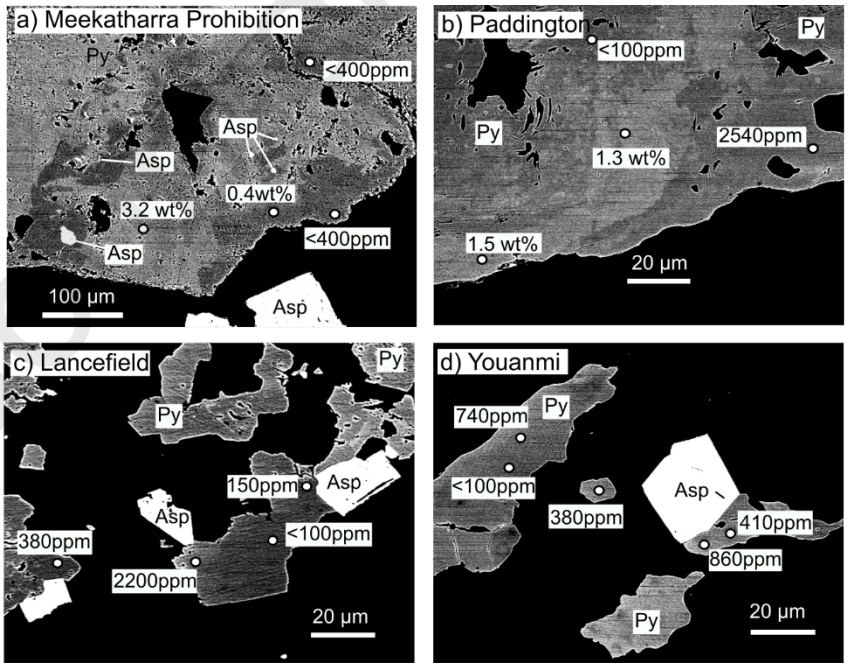
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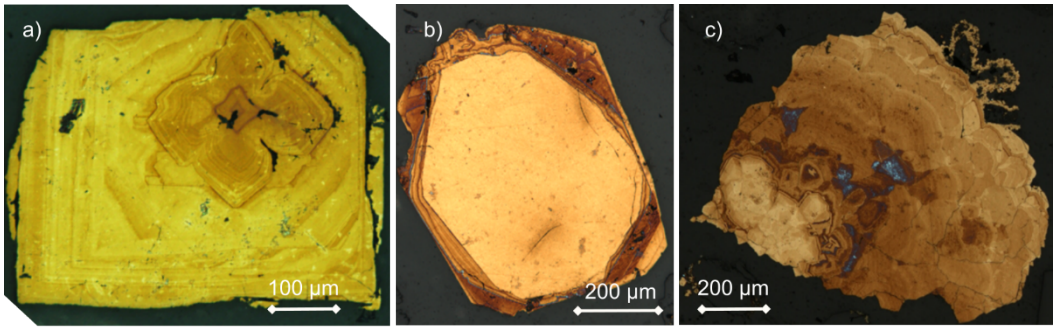
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Figure 3

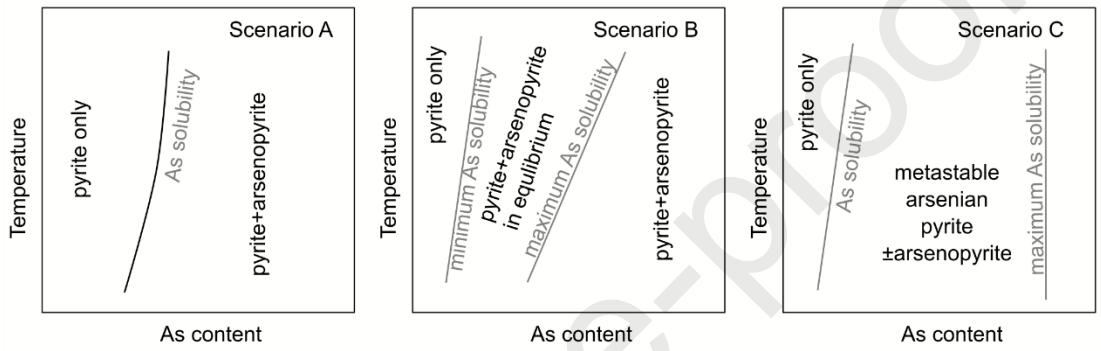


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Figure 4



1190 Figure 5



1191 Figure 6

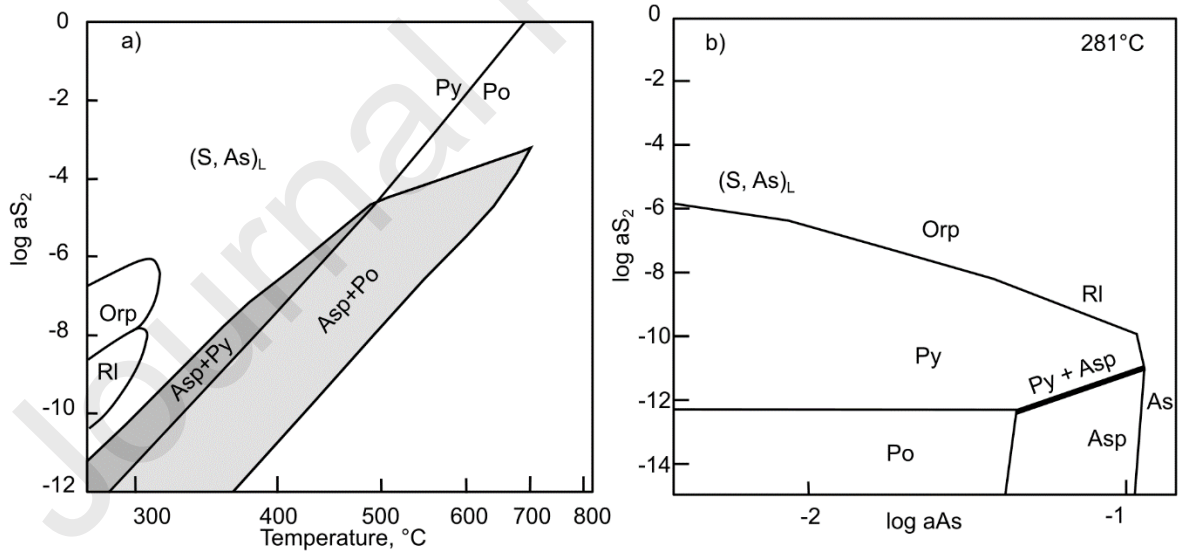


Figure 7

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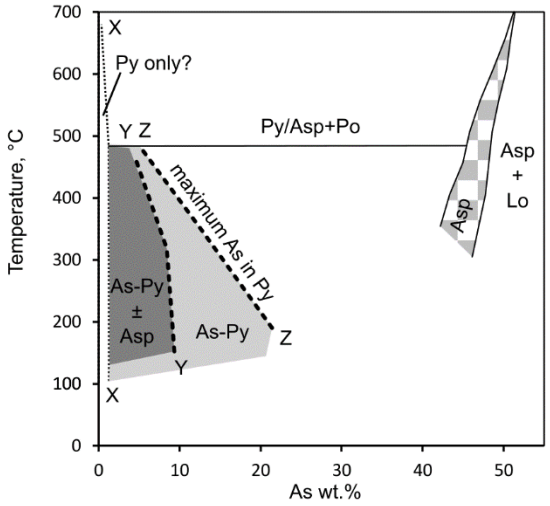
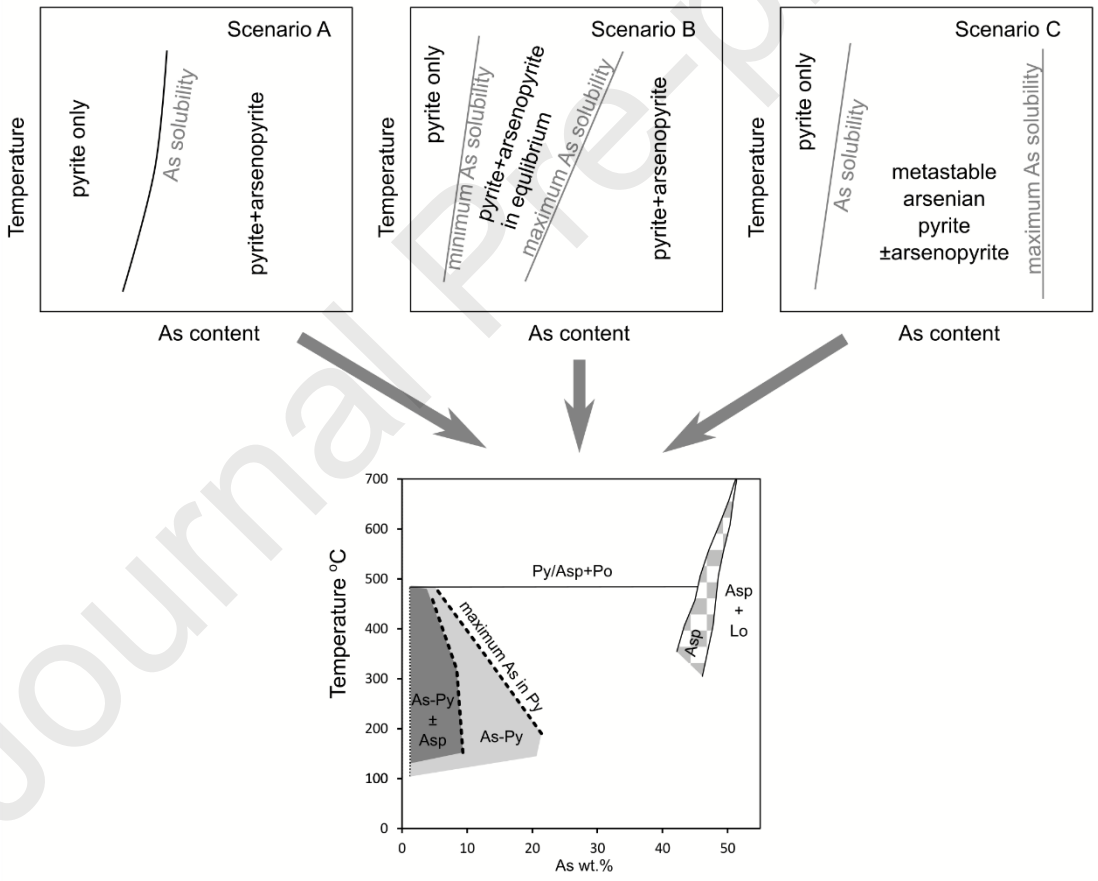


Figure 8

1193



1194

1195 • Pyrite with As above 1 wt. % and called arsenian pyrite is an essential phase in ore deposits

1196 and sedimentary rocks

1197 • Assemblages of arsenopyrite with pyrite containing <1 wt. % are typical in ore deposits

Journal Pre-proofs

1198 • The experimental studies synthesised pyrite with about 1 wt. % in equilibrium with
1199 arsenopyrite
1200 • The scenarios of equilibrium coexistence of arsenopyrite with pyrite containing 5-6 wt. % As
1201 cannot explain many natural assemblages and experimental data
1202 • The scenario of disequilibrium crystallisation of arsenian pyrite offers explanation for sector
1203 zoning in arsenian pyrite and the negative temperature dependence of As content

1204

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