

# Trace-element geochemistry of pyrite and arsenopyrite: ore genetic implications for late Archean orogenic gold deposits in southern India

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## ABSTRACT

The distribution of Au and associated trace elements in pyrite and arsenopyrite from late Archean Hutti and Hira-Buddini orogenic gold deposits, eastern Dharwar Craton, southern India was investigated by laser ablation-inductively coupled plasma-mass spectrometry. X-ray element maps acquired by electron probe microanalyser reveal oscillatory zoning of Co and As indicating the crystallization of pyrite and arsenopyrite in an episodic fluid flow regime in which fluid salinity fluctuated due to fault-valve actions. The absence of any relationship between Au and As in pyrite obviate the role of As in the incorporation of Au into pyrite, particularly here and may be generally the case in orogenic gold deposits. On the other hand, positive correlations of Au with Cu, Ag and Te suggest possible influence of these chalcophile elements in the enhanced gold concentration in sulfides. Pb-Bi-Te-Au-Ag bearing micro-particles (<2 µm) are observed exclusively in micro-fractures and pores in arsenopyrite. The absence of replacement features and element gradient suggests direct precipitation of Pb, Bi, Te, Au and Ag from a fluid that was unreactive towards arsenopyrite. An intermittent fall in fluid pressure caused by the fault-valve action would have resulted in the sporadic precipitation of Au, Pb, Ag, Bi and Te.

**KEYWORDS:** pyrite, arsenopyrite, gold, trace elements, Hutti, Hira-Buddini.

## Introduction

PYRITE (FeS<sub>2</sub>) is the dominant sulfide mineral in the Earth's crust and occurs in varied geological environments, from sedimentary to high-grade metamorphic rocks (Craig and Vokes, 1993). It is a common mineral in the Archean orogenic lode-gold deposits. Pyrite and arsenopyrite crystallize in cubic and orthorhombic systems, respectively, with distinct optical properties, such as the cubic habit together with the isotropic nature of pyrite compared to the rhombic habit and characteristic anisotropism of arsenopyrite. Although these two minerals have anionic pairs in their crystal structures, there are differences in the anionic

pairs, i.e. [S-S]<sup>2-</sup> in pyrite and [As-S]<sup>3-</sup> in arsenopyrite (Vaughan and Craig, 1978). Because of their refractory nature, both pyrite and arsenopyrite archive compositional variations of the fluid with which they equilibrate and preserve a record of the history of fluid events (Craig *et al.*, 1998). Therefore, the compositions of these minerals have been used successfully to understand fluid characteristics and depositional environments as well as post-depositional changes in various types of ore deposits (e.g. Craig *et al.*, 1998; Large *et al.*, 2007; Cook *et al.*, 2013; Hazarika *et al.*, 2013). Compositions of pyrite and arsenopyrite from auriferous veins in orogenic gold deposits and associated alteration zones may provide important information enabling one to understand better fluid evolution and various genetic aspects of this type of ore deposit. The present study is an attempt to investigate the ore genetic processes involved in

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the late Archean Hutti and Hira-Buddini orogenic lode-gold deposits by determining the variations in the trace-element composition of zoned pyrite and arsenopyrite. Further, we intend to discuss the distribution of invisible Au in the light of the variation of trace-element distributions in pyrite and arsenopyrite from the altered wall rocks and those from the lode-gold veins.

Gold mineralization at Hutti and Hira-Buddini occurred in two stages. The stage-1 mineralization at Hutti, associated with biotite-plagioclase alteration, occurred at  $\sim 2$  kbar/377–450°C and the stage-2 mineralization, associated with K-feldspar-sericite alteration, formed at 1–1.7 kbar/ $\sim 300^\circ\text{C}$  (Mishra and Pal, 2008; Rogers *et al.*, 2013). The stage-1 amphibolite facies alteration and gold mineralization at Hira-Buddini occurred at  $\sim 510$ –590°C, which was succeeded by the stage-2 greenschist-facies alteration and mineralization (Krienitz *et al.*, 2008). Several studies have suggested the influence of metamorphic and magmatic fluids on the gold mineralization at Hutti and Hira-Buddini (Krienitz *et al.*, 2008; Rogers *et al.*, 2013; Hazarika *et al.*, 2015a, 2016). This contribution discusses the distribution of Au and associated trace elements in pyrite and arsenopyrite from Hutti and Hira-Buddini as a case study, which may have broader implications to other Archean orogenic gold deposits.

## Geological background

The Hutti and Hira-Buddini gold mines occur in the Hutti-Maski greenstone belt located in the eastern Dharwar Craton, India (Fig. 1). The greenstone belt comprises massive to schistose mafic rocks, intermediate to felsic volcanics, interlayered volcanoclastics and late Archean calc-alkaline and TTG plutons. The rocks were metamorphosed to middle amphibolite-facies conditions in a clockwise *P-T* evolutionary path in a subduction setting (Hazarika *et al.*, 2015b). Three regional-scale deformation events have been recognized in the belt (Roy, 1979). The second regional deformation (RD<sub>2</sub>) refolded the pervasive regional schistosity (S<sub>1</sub>) and the first generation isoclinal folds (F<sub>1</sub>) to generate the NW–SE trending F<sub>2</sub> folds. Broad flexures, kinks and minor puckerings represent the last phase of regional deformation (RD<sub>3</sub>). Hutti, currently the largest operational gold mine in India, is a world-class deposit having a proven reserve of >120 t Au, with an average grade of 4.42 g/t Au (Mishra and Pal, 2008). The Hutti mine contains

nine parallel  $\sim$ N–S striking,  $\sim 1$ –3 km long and 2–10 m thick, steeply dipping shear zones, locally referred to as reefs. These reefs contain: (1) quartz + chlorite + sericite + calcite + sulfides + gold  $\pm$  scheelite veins (D<sub>2</sub> veins) within intensely altered and mylonitized wall rocks; and (2) laminated quartz + sericite + calcite + sulfide veins containing native gold (D<sub>3</sub> veins). The shear zones are separated by  $\sim 200$  m of unaltered amphibolite and felsic meta-volcanic rocks (Pal and Mishra, 2002). Among the five mine-scale deformations, the ductile D<sub>2</sub> and ductile-brittle D<sub>3</sub> shearing events correspond to the two stages of gold mineralization at Hutti. The D<sub>2</sub> deformation (stage-1 mineralization) is represented by mylonitic foliation and associated proximal biotite-plagioclase and distal chlorite alteration. The D<sub>3</sub> deformation (stage-2 mineralization) marks the emplacement of laminated quartz veins with associated K-feldspar-sericite alteration and corresponds to the second phase of regional deformation (RD<sub>2</sub>). The D<sub>4</sub> (correspond to RD<sub>3</sub>) and D<sub>5</sub> events are represented by post-mineralization quartz-calcite-chlorite veining and faults, respectively. Further, last two phases of deformation show no evidence of alteration, which might have aided in remobilization of the gold ore (Kolb *et al.*, 2004; Mishra and Pal, 2008; Rogers *et al.*, 2013).

Hira-Buddini, located 19 km east of Hutti, has an estimated reserve of  $\sim 200,000$  t of potentially high-grade ore (6–10 g/t Au) to a depth of 145 m (Curtis and Radhakrishna, 1995). Wall-rock alteration and replacement textures suggest two stages of mineralization. The stage-1 amphibolite facies alteration and mineralization is represented by the biotite-K-feldspar-actinolite-albite-tourmaline-calcite assemblage. Auriferous sigmoidal quartz-calcite veins of extensional origin are associated with the stage-1 mineralization. The chlorite-biotite-albite-tourmaline-quartz assemblage associated with late-stage quartz veining represents the stage-2 greenschist-facies alteration. Both the alteration assemblages contain sulfides and gold (Krienitz *et al.*, 2008). Unlike Hutti, there is no post-mineralization veining in the Hira-Buddini mine (Mishra and Pal, 2008).

## Analytical methods

Polished thin sections and mounted blocks of altered wall-rock samples and gold-quartz veins were examined under optical microscope to study the textural features. The samples were further examined using a scanning electron microscope (SEM: JEOL

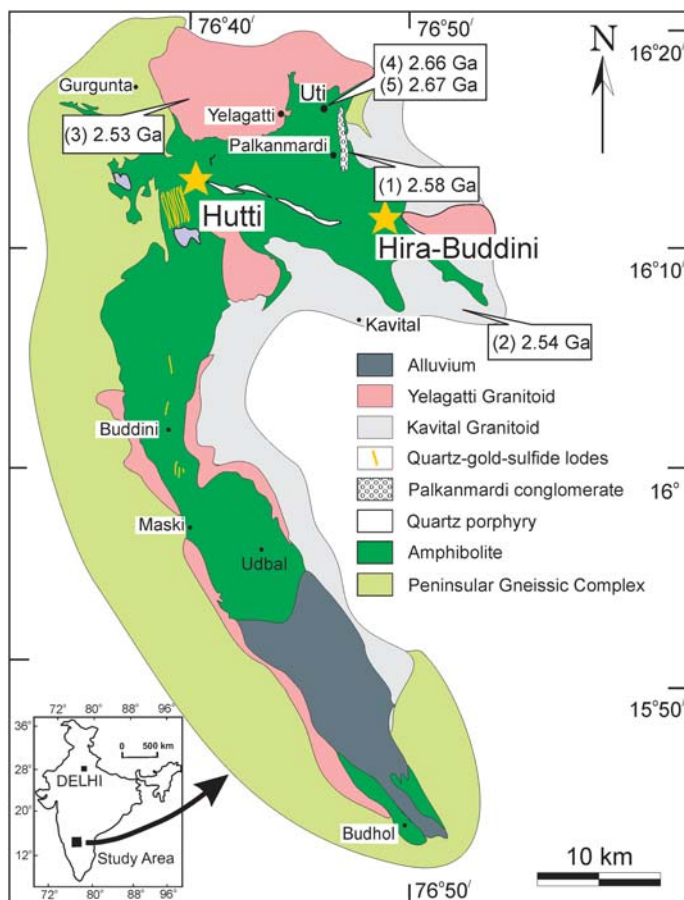


FIG. 1. Geological map of the Hutti-Maski greenstone belt (redrawn from Srikantia, 1995). Location of the Hutti and Hira-Buddini mines are star marked. The known ages of different rock units are shown (not location specific). (1) Vasudev *et al.* (2000), Palkanmardi conglomerate: zircon U-Pb age; (2) Rogers *et al.* (2007), Kavital granitoid: zircon U-Pb age; (3) Anand *et al.* (2014), Yelagatti granitoid: titanite U-Pb age; (4) Anand and Balakrishnan (2010), metabasites: whole rock Sm-Nd age; (5) Hazarika *et al.* (2015b), intercalated volcanoclastic rocks, monazite U-Th-Pb<sub>total</sub> age.

JSM 6490) to identify compositional zoning and micro-textures. Major elements and selected trace elements were analysed at the Indian Institute of Technology (IIT), Kharagpur using a Cameca SX100 electron probe microanalyser (EPMA) equipped with four wavelength dispersive spectrometers. Analysis was performed at 20 kV accelerating voltage and 40 nA beam current. The dwell time was set at 20 s at peak and 10 s at background for Fe and S. For minor elements longer dwell times were used in order to enhance counting statistics. The elements As, Co and Ni were measured with a dwell time of 60 s and Cu, Mo, Te and Se were measured at 100 s. The following standards (and emission lines) were used: FeS<sub>2</sub> (FeK $\alpha$ , SK $\alpha$ ), GaAs (AsL $\alpha$ ), Co

(K $\alpha$ ), Ni (K $\alpha$ ), Cu (K $\alpha$ ), Mo (L $\alpha$ ), Te (L $\alpha$ ), and Se (L $\alpha$ ). X-ray element images were acquired at 20 kV accelerating voltage and 100 nA beam current with 120 ms dwell time and 1  $\mu$ m step size. X-ray lines and crystals used were: AsL $\alpha$  (TAP), CoK $\alpha$  (LLIF), FeK $\alpha$  (LIF) and SK $\alpha$  (PET).

Trace elements were analysed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at IIT Kharagpur using a Cetac 213 nm Nd YAG laser ablation system connected to a Varian 820 quadrupole ICP-MS. The ablation was carried out at 10 Hz pulse frequency, 50  $\mu$ m spot size and 730 V energy. A spot size of 25  $\mu$ m was used for stage-2 arsenopyrite of Hutti due to their very small grain size.

Analyses were performed in peak hopping mode with each analysis consisting of a 20 s background measurement with the laser turned off, and 40 s peak signal measurement with the laser turned on. Calibration was carried out using USGS sulfide standard MASS-1 (Wilson *et al.*, 2002) and the data were reduced offline with the help of the *Glitter*© software (Griffin *et al.*, 2008) using Fe as an internal standard. The measured isotopes are:  $^{53}\text{Cr}$ ,  $^{59}\text{Co}$ ,  $^{60}\text{Ni}$ ,  $^{63}\text{Cu}$ ,  $^{66}\text{Zn}$ ,  $^{75}\text{As}$ ,  $^{77}\text{Se}$ ,  $^{95}\text{Mo}$ ,  $^{107}\text{Ag}$ ,  $^{116}\text{Sn}$ ,  $^{121}\text{Sb}$ ,  $^{125}\text{Te}$ ,  $^{182}\text{W}$ ,  $^{197}\text{Au}$ ,  $^{206}\text{Pb}$  and  $^{209}\text{Bi}$ . NIST612 was analysed as a secondary standard, however, because of matrix mismatch with MASS-1, the estimates were found to be unsatisfactory. Therefore, in the absence of another suitable secondary sulfide standard we chose to use MASS-1 as an unknown for verifying reproducibility. The  $2\sigma$  errors on analyses, as estimated from repeated analyses of MASS-1, are as follows: Co, Ag, Te, W and Sn < 3%; V, Ni, Cu, Mo, Sb, Au, Cr and Se < 5%; Pb and Bi < 12%. The uncertainties on most of the trace elements including Au are within 5% ( $2\sigma$ ); thus MASS-1 can be considered sufficiently homogeneous for these elements except for Pb and Bi, for which the deviation is more than 10%. Time resolved spectra for Au was monitored to distinguish the effect of inclusions, which were not visible at the surface. Representative major- and trace-elements contents of pyrite and arsenopyrite from Hutti and Hira-Buddini are given in Table 1. The full dataset is provided as electronic Appendix A1 (deposited with the Principal Editor of *Mineralogical Magazine* and available from [www.minersoc.org/pages/e\\_journals/dep\\_mat\\_mm.html](http://www.minersoc.org/pages/e_journals/dep_mat_mm.html)).

## Sample description

### Hutti

Gold is mined from nine parallel auriferous reefs each separated by unaltered amphibolites (see Fig. 1b of Hazarika *et al.*, 2016). There are 26 underground working levels at 30 meters interval from the surface. Six samples were selected for the present study, which were collected from 10<sup>th</sup> and 24<sup>th</sup> levels of Zone-I, Strike, Oakley's and Middle reefs. The ore mineralogy at Hutti is dominated by pyrite and arsenopyrite with minor pyrrhotite (Fig. 2). The stage-1 mineralization is characterized by pyrite, arsenopyrite and minor pyrrhotite (Fig. 2c), while in the stage-2 assemblage pyrrhotite instead of pyrite is present together with arsenopyrite (Fig. 2g). Pyrite and arsenopyrite in the proximal alteration zone (stage-1

mineralization) occur along the  $S_2$  foliation, and quartz, calcite and biotite are commonly observed along strain fringes (Fig. 2a,b). Inclusions of quartz, calcite, tourmaline, biotite, ilmenite and occasionally scheelite occur in pyrite and arsenopyrite (Fig. 2b,d). Tourmaline in these rocks show compositional variation from dravite/oxydravite towards magnesio-foitite species, and commonly are Mg rich ( $X_{\text{Mg}} \sim 0.61$ ) with low Na (<0.61 apfu) and high X-site vacancies (Hazarika *et al.*, 2015a). Minor inclusions of pyrrhotite, sphalerite and chalcopyrite are also seen within arsenopyrite and rarely in pyrite. Both arsenopyrite and pyrite sporadically contain inclusions of native gold (Fig. 2e,f).

Arsenopyrite and pyrrhotite in the stage-2 mineralization assemblages are observed in the  $D_3$  quartz-carbonate-scheelite veins within the proximal alteration zone rocks (Fig. 2g) and in the laminated quartz veins (Fig. 2h). In addition to quartz and sulfides, the laminated quartz veins constitute sericite and tourmaline. Tourmaline displays a similar dravite/oxydravite to magnesio-foitite trend with higher Mg content ( $X_{\text{Mg}} \sim 0.77$ ). Native gold typically occurs with arsenopyrite but not as inclusions (Fig. 2h). No visible gold was observed associated with pyrrhotite.

### Hira-Buddini

The Hira-Buddini is a small satellite mine in the Hutti-Maski greenstone belt (Fig. 1) with only five working levels. Three samples were selected for the present study, which were collected from the 4<sup>th</sup> and 5<sup>th</sup> levels. The ore mineralogy at Hira-Buddini is represented by pyrite  $\pm$  pyrrhotite  $\pm$  chalcopyrite with an enigmatic absence of arsenopyrite. Two stages of alteration at Hira-Buddini are shown in Fig. 3(a,b) in a plane-polarized light photomicrograph. Tourmalines from stage-1 assemblage show an oxy-dravite-povondraite (O-P) trend while in the stage-2 alteration assemblages they preserve dravitic composition (Hazarika *et al.*, 2015a). Similarly the associated pyrites can be distinguished on the basis of texture and composition. The anhedral to euhedral pyrite-I (Py I) is associated intimately with early schorlitic tourmalines (Hazarika *et al.*, 2015a) and is typically found as pyritic bands within tourmaline veins in the alteration assemblage (Fig. 3b,d). Tourmaline, together with titanite, calcite and quartz, occurs as inclusions in pyrite-I, which represents the stage-1 alteration. Pyrite-II (Py II) is coarse grained and occurs with

TABLE 1. Representative major- and trace-element compositions of pyrite and arsenopyrite from Hutti and Hira-Buddini.

| Location<br>Mineral<br>Sample # | Hutti  |       |       |       |       |        |       | Hira-Buddini |        |        |        |        |       |        |       |
|---------------------------------|--------|-------|-------|-------|-------|--------|-------|--------------|--------|--------|--------|--------|-------|--------|-------|
|                                 | Py     | Py    | Py    | Py    | Py    | Py     | Py    | Py I         | Py I   | Py I   | Py I   | Py II  | Py II | Py II  | Py II |
|                                 | SHU1A  |       | ZHU7B |       | ZHU1A |        |       | HBM3A        |        | HB02-4 |        | HBM2B  |       | HB02-4 |       |
| S (wt.%)                        | 53.73  | 52.87 | 53.03 | 52.71 | 52.19 | 51.79  | 52.42 | 52.02        | 53.31  | 53.28  | 52.85  | 52.43  | 52.18 | 53.25  | 51.85 |
| Fe                              | 46.17  | 46.23 | 46.58 | 46.53 | 46.28 | 46.18  | 46.40 | 46.21        | 45.57  | 45.18  | 44.59  | 46.49  | 46.10 | 46.40  | 46.67 |
| As                              | 0.04   | 0.75  | 0.46  | 0.63  | 0.38  | 0.44   | 0.27  | 0.07         | 0.04   | 0.04   | 0.08   | 0.04   | 0.03  | 0.06   | 0.04  |
| V (ppm)                         | bdl    | 17.95 | bdl   | bdl   | 6.70  | 3.37   | 5.96  | bdl          | bdl    | bdl    | 1.65   | bdl    | bdl   | bdl    | bdl   |
| Co                              | 2831.3 | 90.07 | 12.11 | 3.28  | 615.1 | 1019.0 | 292.5 | 8082.0       | 4717.0 | 5802.0 | 7545.0 | 640.5  | 624.3 | 5.81   | 76.48 |
| Ni                              | 623.1  | 133.6 | 71.32 | 88.05 | 340.7 | 239.2  | 157.4 | 21.72        | 2.94   | 21.03  | 3.71   | 113.30 | 300.0 | 15.52  | 85.78 |
| Cu                              | 0.36   | 0.96  | 0.62  | 0.40  | 0.52  | 54.76  | 0.18  | 1.12         | 0.14   | 13.37  | 6.21   | 0.71   | 0.11  | 1.84   | 3.12  |
| Zn                              | 0.32   | 1.67  | 1.04  | 0.87  | 2.62  | 4.85   | 0.81  | 0.74         | bdl    | 0.85   | 1.82   | 0.65   | 0.58  | 0.44   | 0.54  |
| Mo                              | 0.06   | bdl   | 0.00  | bdl   | 0.01  | 0.01   | 0.01  | 0.03         | 0.02   | 0.03   | 0.03   | bdl    | 0.01  | bdl    | 0.02  |
| Ag                              | 0.14   | 0.16  | 0.03  | 0.03  | 0.06  | 0.26   | 0.05  | 0.07         | 0.01   | 0.23   | 0.09   | bdl    | 0.01  | 0.07   | 0.32  |
| Sb                              | 0.04   | 2.80  | 0.08  | 0.43  | 0.45  | 1.00   | 0.78  | 0.77         | 0.02   | 10.03  | 0.93   | 0.04   | 0.05  | 1.13   | 5.23  |
| Te                              | 5.28   | 0.17  | 0.12  | 0.14  | 1.74  | 1.49   | 0.42  | 0.98         | 0.02   | 5.44   | 2.10   | 0.43   | 0.71  | 1.10   | 3.20  |
| W                               | bdl    | 11.89 | 0.01  | 2.45  | 0.04  | 3.52   | 14.60 | 0.38         | bdl    | bdl    | 0.10   | bdl    | bdl   | bdl    | 0.23  |
| Au                              | bdl    | 0.36  | 0.10  | 0.13  | 0.10  | 0.45   | 0.05  | 0.01         | bdl    | 0.12   | 0.02   | 0.01   | bdl   | 0.01   | 0.05  |
| Pb                              | 8.13   | 2.19  | 0.68  | 0.89  | 2.47  | 2.60   | 1.16  | 2.08         | 0.07   | 34.72  | 3.60   | bdl    | 0.14  | 3.26   | 64.29 |
| Bi                              | 0.53   | 4.15  | 0.45  | 0.60  | 0.77  | 1.80   | 1.05  | 2.08         | 0.07   | 9.68   | 6.01   | bdl    | 0.06  | 2.10   | 13.90 |
| Cr                              | bdl    | 1.83  | bdl   | bdl   | 0.95  | 5.15   | 2.82  | bdl          | bdl    | bdl    | bdl    | bdl    | bdl   | bdl    | bdl   |
| Se                              | 24.85  | 15.10 | 13.85 | 23.78 | 10.54 | 16.31  | 19.40 | 32.57        | 16.89  | 29.05  | 19.69  | 50.12  | 54.96 | 22.72  | 40.61 |
| Sn                              | bdl    | 0.32  | bdl   | 0.11  | 0.05  | 0.10   | 0.07  | 0.05         | bdl    | 0.05   | 0.15   | bdl    | 0.05  | bdl    | 0.04  |

All data are presented in ppm (LA-ICP-MS) except S, Fe and As that are in wt.% (EPMA).

Bdl: below detection limit.

TABLE 1. (cont.)

| Location<br>Mineral<br>Sample # | Hira-Buddini |       |       |       | Hutti (Stage-1) |       |       |       |        |       |        |       | Hutti (Stage-2) |        |        |        |
|---------------------------------|--------------|-------|-------|-------|-----------------|-------|-------|-------|--------|-------|--------|-------|-----------------|--------|--------|--------|
|                                 | Py II        | Py II | Py II | Py II | Apy I           | Apy I | Apy I | Apy I | Apy I  | Apy I | Apy I  | Apy I | Apy II          | Apy II | Apy II | Apy II |
|                                 | HBM3A        |       | HBM3B |       | SHU1A           |       | ZHU9A |       | OHU5   |       | ZHU1A  |       | QV2             |        |        |        |
| S (wt.%)                        | 52.08        | 52.07 | 51.44 | 52.38 | 22.47           | 23.20 | 21.93 | 22.43 | 21.13  | 21.54 | 20.56  | 21.94 | 20.16           | 22.11  | 22.52  | 21.82  |
| Fe                              | 46.62        | 46.61 | 46.71 | 46.88 | 35.24           | 35.63 | 35.29 | 35.38 | 34.80  | 35.36 | 34.74  | 35.34 | 34.75           | 34.11  | 34.95  | 34.69  |
| As                              | 0.09         | 0.05  | 0.04  | 0.04  | 41.53           | 40.58 | 42.26 | 41.05 | 42.52  | 41.91 | 43.76  | 41.95 | 44.63           | 43.88  | 40.85  | 43.11  |
| V (ppm)                         | bdl          | bdl   | bdl   | bdl   | bdl             | bdl   | bdl   | bdl   | bdl    | bdl   | bdl    | 48.52 | bdl             | bdl    | 18.20  | bdl    |
| Co                              | 0.47         | 9.72  | 24.62 | 8.87  | 244.6           | 1293  | 105.7 | 122.9 | 1146.0 | 377.3 | 2422.0 | 736.7 | 3818.0          | 54.75  | 352.1  | 335.3  |
| Ni                              | 80.37        | 11.14 | 59.78 | 74.91 | 329.5           | 362.5 | 371.5 | 215.3 | 285.9  | 108.8 | 404.6  | 222.2 | 1877.0          | 101.2  | 564.9  | 598.0  |
| Cu                              | 378.2        | 172.5 | 1.60  | 0.75  | 0.21            | 0.43  | bdl   | 0.29  | 1.41   | 16.48 | 11.23  | 5.44  | 4.55            | 1.03   | 9.77   | 3.69   |
| Zn                              | 5.90         | 1.33  | 2.11  | 0.60  | 0.71            | 0.95  | 0.70  | bdl   | 0.39   | 1.22  | 1.33   | 1.59  | 11.75           | 1.57   | 5652.0 | 13.66  |
| Mo                              | 0.08         | bdl   | 0.01  | bdl   | 0.07            | 0.10  | 0.19  | 0.02  | 3.03   | 5.35  | 0.25   | 3.85  | 2.50            | 47.41  | 16.61  | 3.93   |
| Ag                              | 0.77         | 0.55  | 0.06  | 0.01  | 1.17            | 0.08  | 0.03  | 0.01  | 0.28   | 9.49  | 0.40   | 0.79  | 22.01           | 3.46   | 10.47  | 25.76  |
| Sb                              | 2.71         | 3.75  | 2.11  | 0.17  | 101.9           | 45.96 | 95.16 | 84.30 | 113.9  | 159.5 | 19.34  | 134.2 | 104.8           | 389.6  | 383.1  | 196.6  |
| Te                              | 4.67         | 10.83 | 0.09  | 0.16  | 2.03            | 13.47 | 9.77  | 9.49  | 6.12   | 20.04 | 114.6  | 253.9 | 27.41           | 81.35  | 107.3  | 312.3  |
| W                               | 0.40         | 0.33  | 7.67  | bdl   | 1.45            | 0.08  | 1.10  | 0.08  | 0.01   | 0.85  | 0.17   | 5.45  | 1.57            | 2.80   | 85.84  | 14.22  |
| Au                              | 0.06         | 0.34  | 0.01  | 0.03  | 1.24            | 14.18 | 0.43  | 43.18 | 1.74   | 40.30 | 0.43   | 1.52  | 1.09            | 6.66   | 14.54  | 3.73   |
| Pb                              | 65.30        | 55.92 | 13.42 | 1.49  | 0.74            | 0.82  | 0.34  | 0.04  | 2.68   | 10.41 | 8.76   | 7.12  | 3111            | 697.9  | 11410  | 54183  |
| Bi                              | 5.18         | 8.79  | 1.09  | 0.78  | 0.95            | 0.70  | 1.30  | 0.41  | 4.45   | 11.72 | 2.67   | 5.37  | 220.6           | 214.4  | 3278   | 1099   |
| Cr                              | bdl          | bdl   | bdl   | bdl   | bdl             | bdl   | bdl   | bdl   | bdl    | bdl   | bdl    | 21.83 | 2616.0          | 250.0  | 401.40 | 564.9  |
| Se                              | 52.98        | 73.02 | 28.91 | 20.32 | 44.65           | 34.87 | 61.98 | 32.67 | 22.68  | 63.73 | 33.91  | 97.61 | 61.80           | 67.56  | 98.56  | 94.38  |
| Sn                              | 0.05         | 0.05  | 0.09  | bdl   | 0.11            | 0.06  | bdl   | 0.09  | bdl    | 0.92  | 0.07   | 0.60  | bdl             | bdl    | 3.53   | 1.82   |

All data are presented in ppm (LA-ICP-MS) except S, Fe and As that are in wt.% (EPMA).

Bdl: below detection limit.

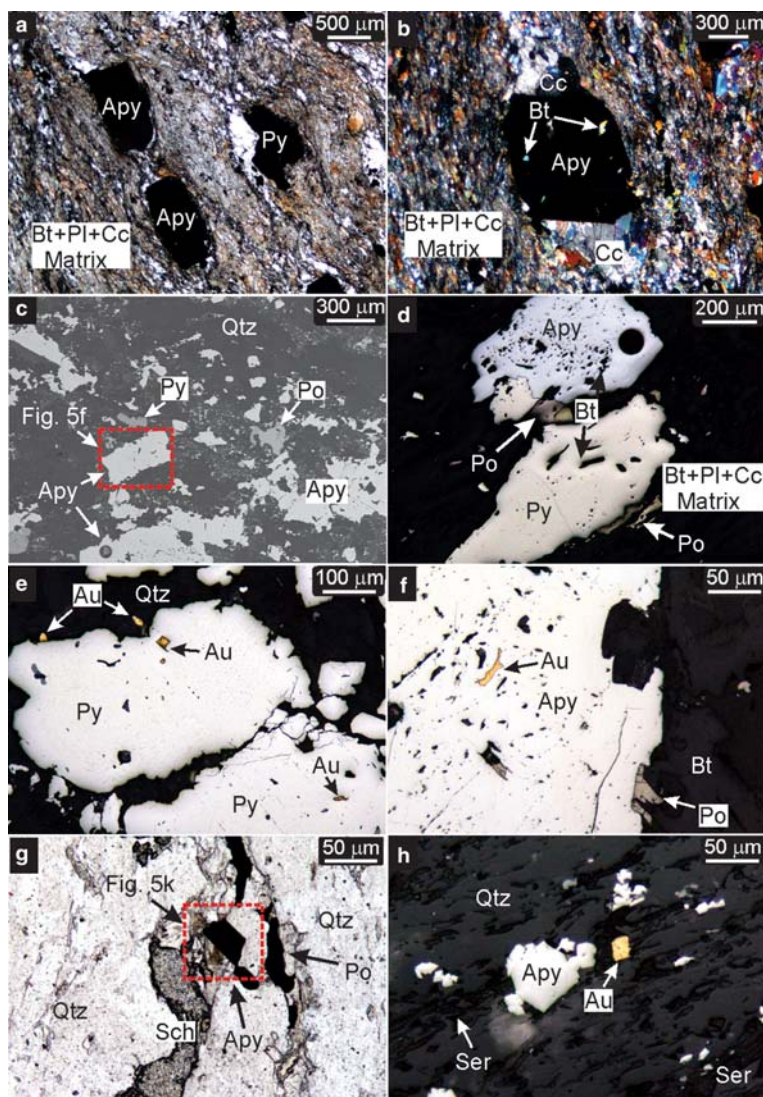


FIG. 2. Transmitted light photomicrographs (*a,b,g*), scanning electron microscopy (SEM) back-scatter electron (BSE) image (*c*), and reflected light photomicrographs (*d-f,h*) of different textural associations of ore minerals from Hutti. (*a*) Arsenopyrite and pyrite grains aligned parallel to  $S_2$  foliation in stage-1 alteration assemblage; (*b*) warping of arsenopyrite by biotite defined  $S_2$  foliation, wherein strain fringes are occupied by calcite, quartz and biotite; (*c*) SEM-BSE image and (*d*) reflected light photomicrograph of stage-1 alteration assemblage showing buffered assemblage Py + Apy + Po; (*e,f*) occurrence of gold as inclusions and at the margins of pyrite and arsenopyrite; (*g*) stage-2 alteration assemblage showing occurrence of arsenopyrite and pyrrhotite with scheelite in  $D_3$  veins within proximal biotite alteration zone; (*h*) native gold and arsenopyrite in laminated quartz ( $D_3$ ) veins. Key: Bt: biotite; Cc: calcite; Apy: arsenopyrite; Py: pyrite; Po: pyrrhotite; Sch: scheelite; Qtz: quartz; Pl: plagioclase; Ser: sericite.

later dravitic tourmalines either in quartz-veins (Fig. 3c) that crosscut the earlier alteration assemblage (early schorlitic tourmalines and Py I with actinolites) or is associated intimately with

biotite that replace stage-1 actinolite (Fig. 3e,f). Native gold occurs in the mineralized quartz veins and as minute grains in contact with pyrite in the altered rocks (Fig. 3f).

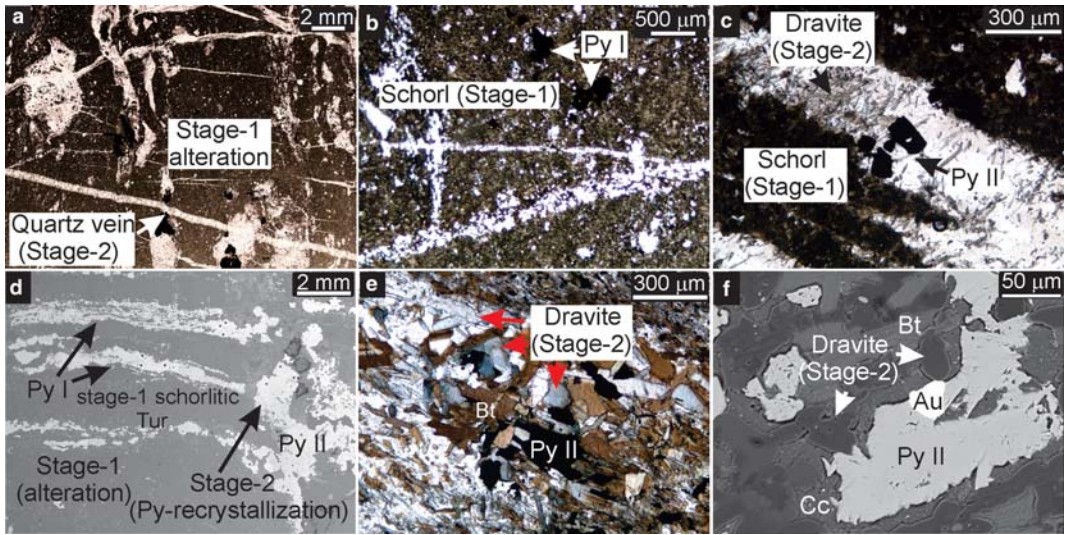


FIG. 3. Transmitted light photomicrographs (a,b,c,e) and BSE images (d,f) documenting alteration and mineralization at Hira-Buddini. (a) stage-1 alteration assemblage transected by stage-2 quartz-tourmaline vein; (b) Py I in stage-1 alteration assemblage; (c) magnified image of stage-1 (schorlitic) assemblage and stage-2 dravite-quartz vein with Py II; (d) stage-1 pyrite bands (Py I) and stage-2 coarse grained recrystallized Py II; (e) Py II in stage-2 alteration assemblage with biotite and later dravitic tourmaline; (f) stage-2 assemblage showing association of Py II, later tourmaline, calcite, biotite and native gold.

### Compositional zoning in pyrite and arsenopyrite

Pyrites from Hutti have relatively high As-contents (390–9353 ppm) compared to the Hira-Buddini

pyrites (Py I, 333–765; Py II, 260–863 ppm) and show a broad negative correlation with sulfur (Fig. 4). The Fe contents of the Hutti pyrites are near stoichiometric, ranging from 32.83 to 33.92 at.%, and show no relation with As concentrations. Pyrite-I

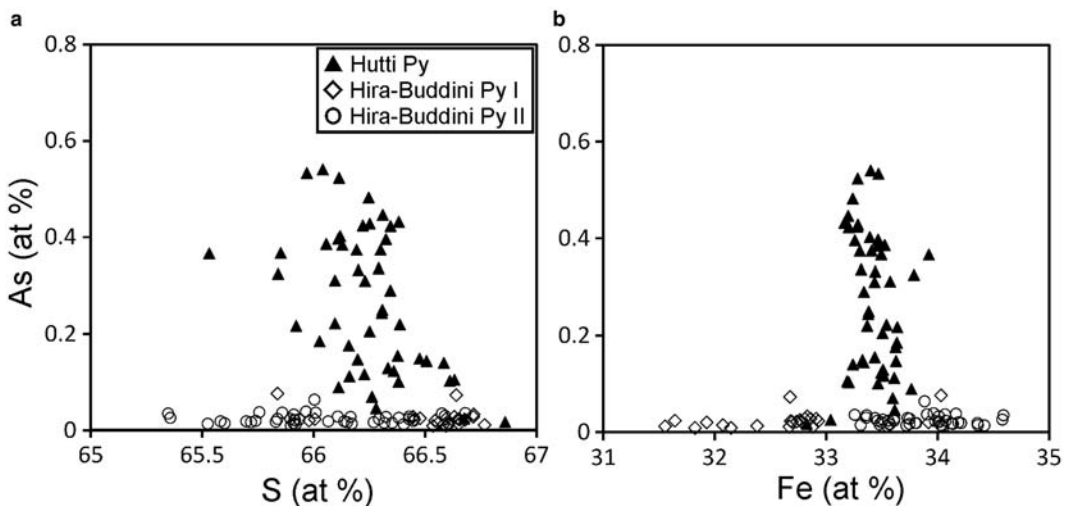


FIG. 4. Plots showing relationship of S (at.%) and Fe (at.%) with As (at.%) in pyrite from Hutti and Hira-Buddini. Note the crude negative correlation between S and As in pyrite from Hutti and very low content of As in Hira-Buddini pyrite.

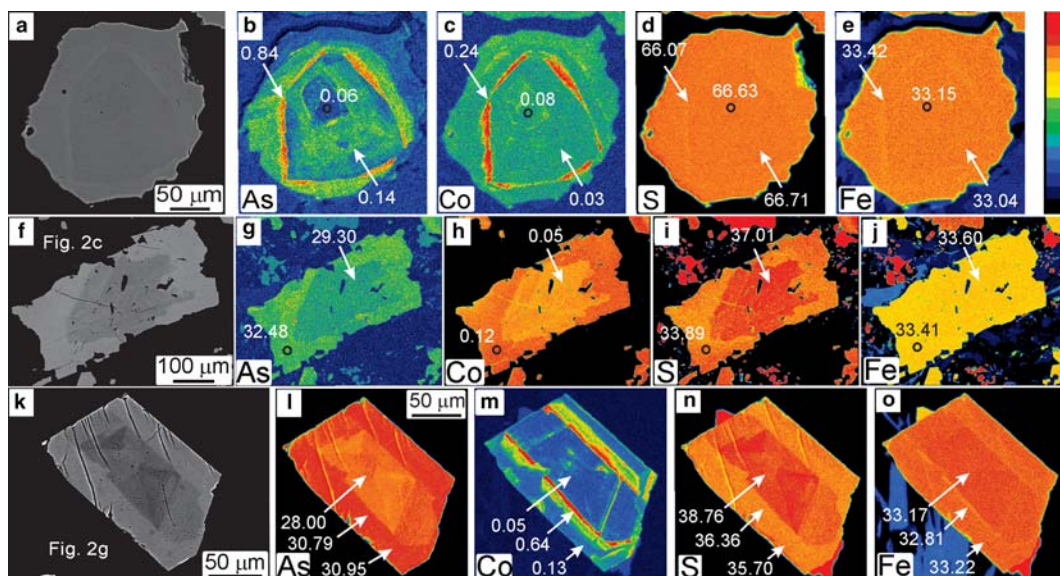


FIG. 5. BSE-images and X-ray element maps of pyrite (a–e), arsenopyrite (f–j) from stage-1 assemblage (Fig. 2c) and arsenopyrite (k–o) from stage-2 assemblage (Fig. 2g) in Hutti. The numbers display concentrations (in wt.% for b, c, h and m; in at.% for others) at respective analytical spots.

of Hira-Buddini shows variable and distinctly lower concentrations of Fe (31.56–34.03 at.%) compared to Py II, in which the Fe-content varies over a smaller

range (33.26–34.59 at.%). The Hira-Buddini pyrites show no correlation between As, Fe and S (Fig. 4). Texturally constrained arsenopyrite from stage-1 and

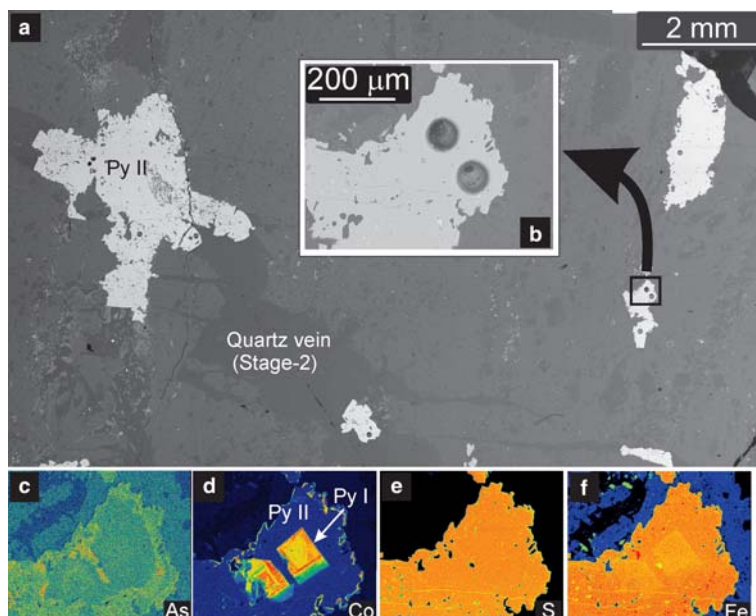


FIG. 6. (a) BSE image of altered wall-rock sample from Hira-Buddini. Late-stage quartz veins cut across stage-1 alteration assemblage. (b) BSE image and (c–f) X-ray element images of pyrite from Hira-Buddini. Note the similar nature of zoning in Co and Fe and reverse zoning in As. The dark circles in ‘b’ are laser ablation spots.

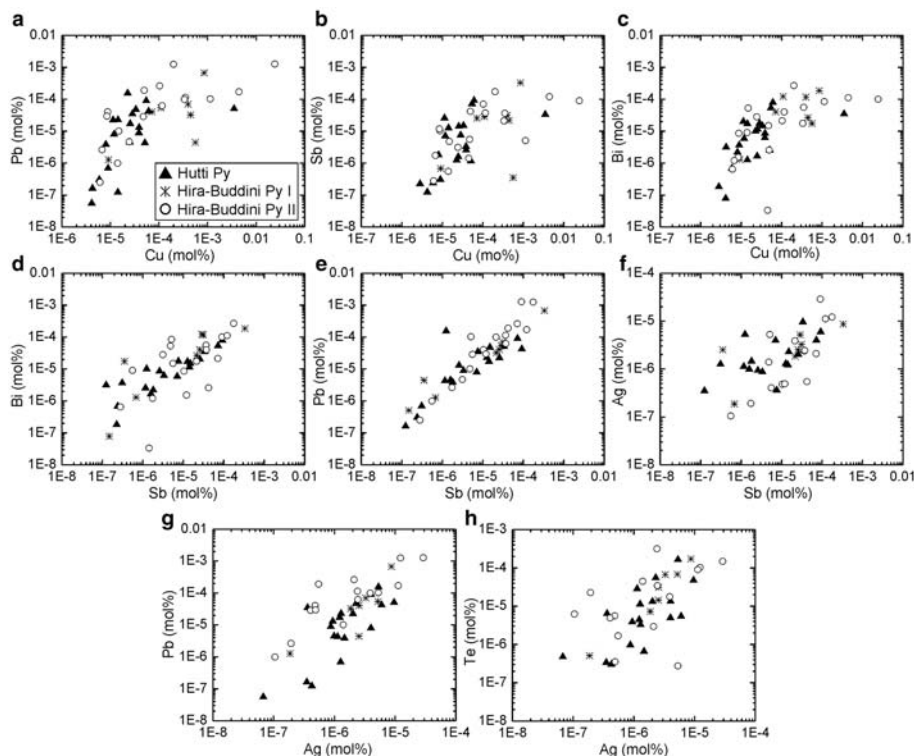


FIG. 7. Bivariate plots (in mol.%) showing the correlation of trace elements (chalcophiles) in pyrite from Hutti and Hira-Buddini.

stage-2 assemblages preserves similar major-element contents. Arsenopyrite from the stage-1 assemblage at Hutti has an As-concentration in the range 28.26 to 32.93 at.%, with reciprocal variations in S-content from 38.13 to 33.41 at.%. Similarly, the stage-2 arsenopyrite has As-contents ranging from 29.08 to 32.24 at.%, with a corresponding variation in S-content from 37.48 to 34.03 at.%. Such inverse correlation of S- and As-contents in arsenopyrite represents the  $S \leftrightarrow As$  diadochy in an environment of changing sulfur fugacity (e.g. Kretschmar and Scott, 1976; Sharp *et al.*, 1985; Morey *et al.*, 2008).

#### X-ray element images

Both pyrite and arsenopyrite from the stage-1 assemblage, and arsenopyrite from the stage-2 assemblage at Hutti, record compositional zoning as evident in BSE images and X-ray element maps. Pyrite from the stage-1 assemblage shows complex and oscillatory zoning of As and Co, whereas no

remarkable zoning is observed in Fe and S (Fig. 5a–e). The lack of S zonation in pyrite is an artefact of the difficulty in imaging small relative differences in S contents; however, the compositional variation is recognizable in Fig. 4a. The core is relatively poorer in As and Co compared to the outer zone, which is separated from the core by an intermediate zone that is slightly poorer in Co than the core but richer in As. The outermost zone is rimmed by a thin discontinuous zone showing a sharp decrease in As and Co, followed by a slight Co increase. Arsenopyrite from the stage-1 assemblage (Apy I) shows an As- and Co-poor, and S-rich core, which is surrounded by an As- and Co-rich, and S-poor mantle (Fig. 5f–j). Arsenopyrite from stage-2 assemblage (Apy II) shows a similarly As-poor and S-rich core bounded by an As-rich and S-poor mantle. However, Co in Apy II shows oscillatory zoning, where a Co-poor core is surrounded by a Co-rich intermediate zone, which is rimmed by a Co-poor outer zone (Fig. 5k–o). The observed increase in arsenic from core to rim in Py, Apy I and

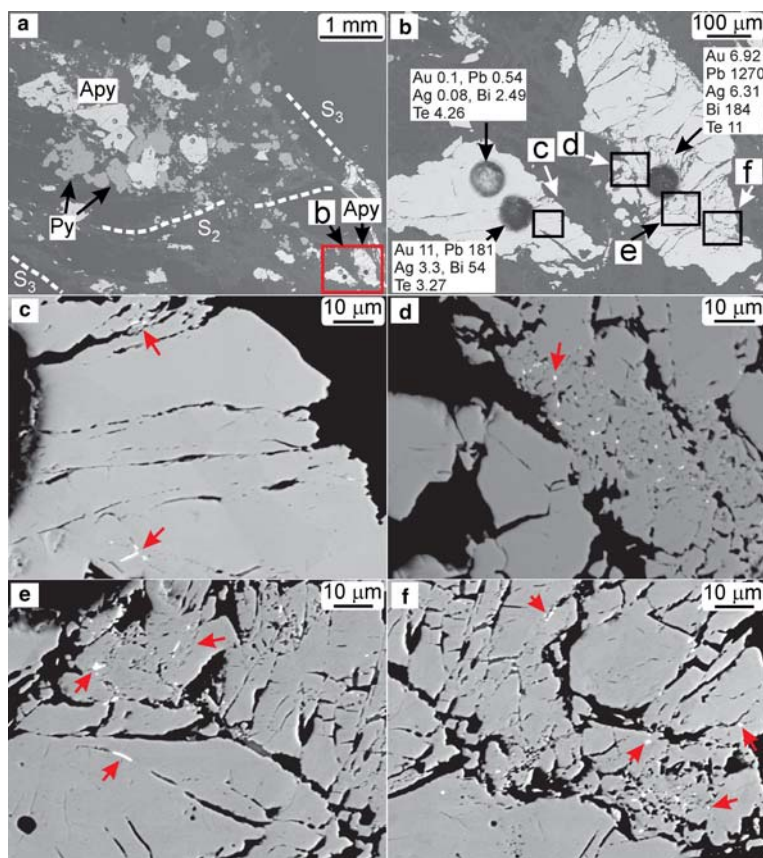


FIG. 8. (a) Pyrite-arsenopyrite association in proximal alteration zone of Hutti showing brittle deformation in arsenopyrite; (b) magnified BSE image of the inset in (a) displaying high contents of trace elements along fractures; (c–f) magnified BSE image of insets in (b) showing bright phases (marked by red arrows) occurring along microfractures. The dark circles in (b) are the laser ablation spots with the respective trace-element contents (in ppm) shown.

Apy II is inversely related to S. The Apy I does not have the intermediate Co- and As-rich zone. Py and Apy II although precipitated during two different stages show a similarity in their zoning patterns for As. There is even a complementary relation between Fe in Py and Fe in Apy II. Cobalt in Py decreases from core to rim except at the enriched intermediate zone. In Apy I, Co and S are lower compared to Apy II, but Fe is higher. Note that the stage-1 pyrite and arsenopyrite both show corroded zonal margins while stage-2 arsenopyrite is non-corroded (Fig. 5) implying that if the stage-1 pyrite and arsenopyrite were affected during stage-2, no material was added to their margins, instead they underwent dissolution. Small amounts of later pyrrhotite have grown on Apy II.

The Hira-Buddini pyrites show rather simple zoning compared to the Hutti pyrites. A BSE image

of an altered wall-rock sample, is shown in Fig. 6a in which a stage-2 quartz vein is seen to crosscut the stage-1 alteration assemblage. The X-ray element maps (Fig. 6c–f) show preservation of a Co-rich and As-, Fe-poor core mantled by a Co-poor, As-, Fe-rich outer zone in a pyrite grain proximal to the stage-2 quartz veins.

### Trace-element contents

Pyrite and arsenopyrite show distinct trace-element contents in Hutti. Hira-Buddini pyrites are in general depleted in As and enriched in Co compared to pyrites from Hutti (Table 1 and electronic Appendix A1 available from [www.minersoc.org/pages/e\\_journals/dep\\_mat\\_mm.html](http://www.minersoc.org/pages/e_journals/dep_mat_mm.html)). The As and Co contents in Hutti pyrites have values

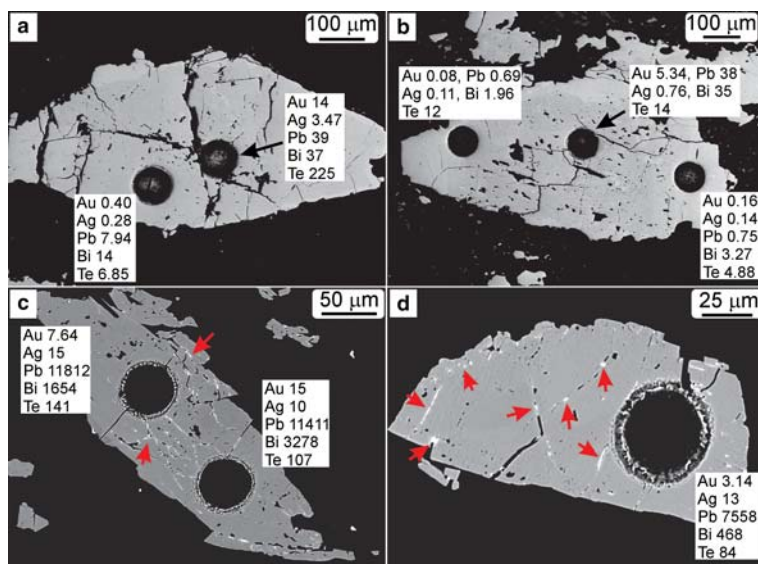


FIG. 9. (a,b) BSE images of Apy I from proximal alteration rock, and (c,d) Apy II from laminated quartz veins showing variation in trace-element contents along micro-fractures and undeformed zones. Note the bright trace-element rich inclusions and micro-veinlets (marked by red arrows) in Apy II. The dark circles are the laser ablation spots.

in the range of 0.04–0.93 wt.% and 3–2831 ppm, respectively. Hira-Buddini pyrites, on the other hand, preserve very low As values of 0.03–0.08 wt.% and 0.03–0.09 wt.% for Py I and Py II, respectively. The Co contents in Hira-Buddini pyrites are distinct for two generations with very high concentration in Py I (4717–13,946 ppm) compared to Py II (<1–1333 ppm). Arsenopyrites in Hutti contain consistently higher Au (Apy I: 0.08–43.18 ppm; Apy II 4.17–51.93 ppm) than the pyrites (<1 ppm). Arsenopyrites are also enriched in other trace elements such as Sb, Bi, Pb, Ag, Cu, Mo and Te. The concentrations of chalcophile elements such as Cu, Sb, Pb, Ag, and Bi in pyrites from both Hutti and Hira-Buddini show similar geochemical behaviour (Fig. 7). However, no such correlation among the trace elements is observed in the bivariate plots in arsenopyrites.

Both Apy I (in proximal alteration assemblage) and Apy II (in laminated quartz veins) show brittle deformation in Hutti. Figure 8a,b shows BSE images of pyrite-arsenopyrite association from stage-1 mineralization, where Apy I shows brittle deformation perpendicular to the  $S_3$  foliation. Figure 8b is the magnified BSE image of the inset in Fig. 8a showing elevated concentrations of trace elements in the fractures compared to those in the inclusion-free undeformed zones. The insets in Fig. 8b are magnified in Fig. 8c–f, which show

bright phases along micro-fractures/pores in arsenopyrite. It is noteworthy that such bright phases do not exceed 2 μm in size, exclusively occur along the highly fractured zones and are not observed in the undeformed areas. LA-ICP-MS analyses of these fractured zones in arsenopyrite show elevated concentrations of Pb, Bi, Sb, Te, Au and Ag compared to the concentrations in fracture/inclusion free zones (Figs 8 and 9). Although, arsenopyrite grains from the proximally altered rocks consistently show elevated contents of trace elements along fractures, bright phases in BSE images are not always encountered (Fig. 9a,b). However, the consistent higher trace-element contents indicate the possible occurrence of nanoparticles, which were not discernible using the scanning electron microscope. Figure 9c,d displays BSE images of two arsenopyrite grains from the laminated quartz veins (stage-2 mineralization) that show bright veinlets along micro-fractures. The laser ablation of the bright phases consistently shows higher contents of Pb and Bi in varying ratios, and thus may indicate the possible occurrence of Pb-Bi sulfosalts.

Pyrites from Hutti are relatively enriched in As compared to those from Hira-Buddini. The Au:As ratio of all analyses fall below a 1:1000 line (Fig. 10a). However, unlike other documented coupled geochemical behaviours of As and Au

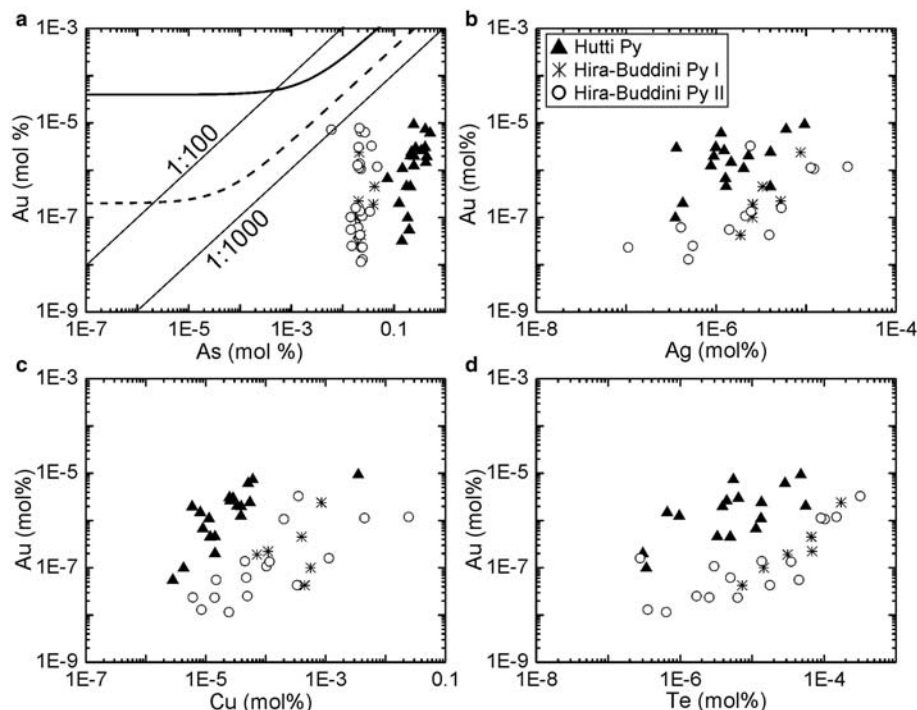


FIG. 10. Logarithmic plots of Au vs. As (a), Ag (b), Cu (c) and Te (d) for pyrites from Hutti and Hira-Buddini. The thick curve in (a) denotes the solubility limit of Au in pyrite ( $C_{Au} = 0.02 \times C_{As} + 4 \times 10^{-5}$ ) as suggested by Reich *et al.* (2005). The dashed line marks the maximum solubility limit of Au in pyrite ( $C_{Au} = 0.004 \times C_{As} + 2 \times 10^{-7}$ ) from orogenic gold deposits as suggested by Deditius *et al.* (2014). Note the lack of any correlation between Au and As in (a), and crude positive correlations with Ag, Cu and Te (b–d).

in pyrite from diverse physico-chemical environments, the data presented here show no convincing As–Au correlation. On the other hand, gold contents show a positive correlation with Cu, Ag and Te, with dissimilar correlation ratios (Fig. 10b–d).

## Discussion

### Compositional zonation: genetic implications

Previous studies in Hutti and Hira-Buddini have established distinct compositions and sources of ore-forming fluids (Krienitz *et al.*, 2008; Rogers *et al.*, 2013; Hazarika *et al.*, 2015a). Regardless of involvement of dissimilar fluids sourced from mafic greenstone (in Hutti) and granitoids (in Hira-Buddini), the trace-element concentrations in pyrite showed no marked variation except for As and Co contents (Table 1). The observed negative correlation between S and As suggests the

substitution of S by  $As^{1-}$  in the pyrite from Hutti, which indicates relatively reducing conditions of formation (Simon *et al.*, 1999a; Deditius *et al.*, 2008). The low  $Fe^{3+}/Fe^{2+}$  ratio (Hazarika *et al.*, 2015a) in tourmalines from the same samples is also consistent with a reducing environment. The observed complex zoning pattern in pyrite and arsenopyrite suggests coupling between As and Co in the hydrothermal fluid. Trace elements such as As, Co, Cu, Ni, Pb and Au occupy common growth zones in pyrite (Deditius *et al.*, 2009). Thus, it is unlikely that there is any crystallographic control on the observed occasional divergent As and Co zoning in pyrite (Fig. 5b,c). Hence, the observed oscillatory zoning in pyrite and arsenopyrite with sharp boundaries between zones mark abrupt changes in the composition of the ore-forming hydrothermal fluid. Removal of the trace elements by continued precipitation may result in their lower concentrations in later developed zones unless their rate of supply is faster than the rate of crystal

growth. Progressive mineral precipitation during wall-rock alteration by hydrothermal fluid would result in gradual compositional change in precipitating minerals. Therefore, the sharp oscillatory zoning in pyrite and arsenopyrite may be explained by operation of two independent mechanisms: (1) phase separation, where a fluid separates into two components; and (2) mixing of fluids of two different compositions (Deditius *et al.*, 2009).

Similar behaviour of Co and As in the hydrothermal solution is evident. Thermodynamic modelling of Co transport in hydrothermal fluids suggests that tetrahedral  $\text{CoCl}_4^{2-}$  is the dominant Co-carrying complex above 250°C and in moderate to low salinity (6 m NaCl solution) (Liu *et al.*, 2011; Migdisov *et al.*, 2011). Further, Liu *et al.* (2011) proposed that a drop in temperature and/or small drop in salinity of low saline hydrothermal fluids results in the decrease in the stability of  $\text{CoCl}_4^{2-}$  leading to the precipitation of Co. The low Co content in the core of pyrite and arsenopyrite implies their precipitation from a relatively high-saline fluid, the intermediate Co- and As-rich zone represent a brief drop in salinity followed by an increase. Such sudden changes in fluid salinity may be ascribed to pulsating fluid salinity during rapid fluid-pressure fluctuations caused by seismogenic fault failure, which is a common mechanism in lode-gold deposits (Sibson *et al.*, 1988; Wilkinson and Johnston, 1996). Fault-valve action-induced phase separation has been proposed previously to have occurred at Hutti (Kolb *et al.*, 2005; Mishra and Pal, 2008). Peterson and Mavrogenes (2014) observed sharp, cyclic textural and compositional zoning in pyrite from Porgera gold deposit, Papua New Guinea. Based on the cyclicity of the zoning pattern and lack of intermediate compositions in the pyrites studied, the authors suggested a repeated and sudden change in fluid pressure and transient fluid flow regime. The sharp oscillatory compositional zoning of Co and As in sulfides at Hutti are most probably the consequence of phase separation caused by fluid-pressure fluctuations during subsequent events of seismogenic fault failures. Tourmaline and scheelite compositions of stage-2 assemblage in D<sub>3</sub> quartz-carbonate veins also indicate cyclicity in the fluid influx related to a drop in fluid pressure and phase separation (Hazarika *et al.*, 2016).

In Hira-Buddini, Co composition shows an inverse relation with that of Fe, indicating replacement of Fe by Co in the pyrite structure. The remarkable abrupt decrease in Co concentration from core to outer zone and preservation of typical

euhedral cubic form of the core indicate subsequent pyrite growth with a break or sudden change in fluid composition. The Co-rich euhedral core represents Py I that is overgrown by later Co-poor, As-rich Py II, which fills up the vein during stage-2 pyrite growth. This interpretation is consistent with the high Co-contents of banded Py I that co-exist with early tourmaline in the stage-1 assemblage (Fig. 3b).

### *Invisible gold and associated elements*

Previous studies suggest the occurrence of invisible gold in pyrite and arsenopyrite both as lattice bound ( $\text{Au}^{1+}$ ) and as nanoparticles ( $\text{Au}^0$ ) (Simon *et al.*, 1999a; Cabri *et al.*, 2000). The negative correlation between Fe and  $\text{Au}^{1+}$  as observed in many earlier studies have led to the conclusion that  $\text{Au}^{1+}$  replaces Fe in pyrite (Johan *et al.*, 1989; Marcoux *et al.*, 1989; Tamocai *et al.*, 1997; Wu and Delbove, 1989). There is a general consensus based on available data from diverse geological environments that points towards a positive correlation between Au and As in arsenian pyrite (Cook and Chrysosoulis, 1990; Simon *et al.*, 1999b; Large *et al.*, 2009). Cook and Chrysosoulis (1990) have suggested the occurrence of structure bound Au in arsenian pyrite by substituting Fe and S with Au and As, respectively. The study on the distribution of invisible gold in arsenian pyrite carried out by Reich *et al.* (2005) revealed that the maximum amount of structure-bound Au as a function of As content in pyrite can be defined by the equation  $C_{\text{Au}} = 0.02 \times C_{\text{As}} + 4 \times 10^{-5}$ , with  $\sim 0.02$  molar ratio of Au to As. These authors observed a wedge-shaped distribution of data on the Au-As plot bounded by the line defined by the aforementioned equation. Deditius *et al.* (2014) reviewed Au and As values in pyrite from orogenic gold deposits, and suggested that the maximum solubility limit of Au in arsenian pyrite is defined by the line  $C_{\text{Au}} = 0.004 \times C_{\text{As}} + 2 \times 10^{-7}$  in the Au-As plot. All the data generated during the course of the present study on pyrites from Hutti and Hira-Buddini plot below the solubility curve  $C_{\text{Au}} = 0.004 \times C_{\text{As}} + 2 \times 10^{-7}$  (Deditius *et al.*, 2014) in the Au-As plot (Fig. 10a), illustrating very low contents of invisible gold in pyrites in greenstone-hosted orogenic gold deposits. In contrast, pyrites in Kundarkocha sediment-hosted gold deposits in eastern India display elevated contents of invisible gold (up to 500 ppm); the majority of analyses indicate Au to As molar ratios of more than 0.02 (Hazarika *et al.*, 2013).

There is a marked positive correlation between Cu, Pb, Sb, Bi, Ag and Te in pyrites from both Hutti and Hira-Buddini (Fig. 7). The lack of any correlation between As and Au in pyrites (Fig. 10a) indicates decoupled As-Au behaviour in the hydrothermal systems studied. In contrast, the positive correlation of Au with Ag, Cu and Te (Fig. 10b–d) indicate their geochemical similarity. The high contents of Au, Te and other chalcophile elements in As-free colloform pyrite within vent chimneys from the Silurian Yaman-Kasy volcanic-hosted deposit was attributed to the presence of micro-inclusions, which were interpreted to have exsolved from pyrite (Maslennikov *et al.*, 2009). Ciobanu *et al.* (2012) demonstrated incorporation of Au coupled with chalcophile elements into As-free pyrite by mineral-fluid interaction. The positive correlation of Au with Cu, Te and Ag, and geochemical resemblance between trace elements (Cu, Sb, Pb, Ag and Bi) in Hutti and Hira-Buddini suggest incorporation of Au, Ag, Cu, Te, Pb, Sb and Bi into pyrite by mineral-fluid interactions as envisaged by Ciobanu *et al.* (2012). However, the mode of occurrence of these elements in pyrite, either as lattice bound or nanoparticles, cannot be ascertained from the present study. High-angle annular dark-field–scanning transmission electron microscopic (HAADF-STEM) studies on these pyrite samples would provide a better understanding of the trace-element associations and mechanisms of their incorporation. The presented data demonstrate that Au incorporation into pyrite in Archean gold systems may be free of the effect of arsenic, and instead is coupled with the contents of chalcophile elements.

The observed geochemical correlation between Au and chalcophile elements in pyrite (Fig. 10b–d) is not unusual and has previously been reported by several workers (Cook *et al.*, 2009; Ciobanu *et al.*, 2012). The broad positive correlation between Cu and Au in the Dongping and Huangtuliang deposits, China, was related to the small chalcopyrite inclusions within pyrite (Cook *et al.*, 2009). Based on constraints from ionic charge and radii, Chouinard *et al.* (2005) proposed coupled substitution of  $\text{Au}^{3+} + \text{Cu}^+ \leftrightarrow 2\text{Fe}^{2+}$  for the incorporation of Au into pyrite, which was consistent with the oxidizing conditions of the high sulfidation Pascua epithermal deposit. However, spectroscopic studies in arsenian pyrite revealed the occurrence of gold either as structurally bound  $\text{Au}^{1+}$  and/or nano-inclusions of free gold ( $\text{Au}^0$ ) (Simon *et al.*, 1999a, b; Deditius *et al.*, 2009) and no report so far has been made to validate the occurrence of  $\text{Au}^{3+}$  in

pyrite (Deditius *et al.*, 2014). Structurally bound gold ( $\text{Au}^{1+}$ ) can be coordinated to two or four S atoms in the pyrite structure, and due to the significantly higher ionic radius of  $\text{Au}^{1+}$ , its incorporation causes considerable distortion in the pyrite structure (Simon *et al.*, 1999a). The near neutral to slightly alkaline pH, and reducing/low  $f_{\text{O}_2}$  conditions of hydrothermal alteration at Hutti (Mishra and Pal, 2008; Hazarika *et al.*, 2015a) precludes the occurrence of  $\text{Au}^{3+}$  in the fluid. Compositions of tourmalines associated with Py I in Hira-Buddini indicate oxidizing conditions for stage-1 alteration. However, reducing conditions were prevalent during the stage-2 alteration as marked by later dravitic tourmalines that are associated with Py II (Hazarika *et al.*, 2015a). Hence, the coupled behaviour of Au and Cu in pyrites from Hutti and Hira-Buddini cannot be explained by the substitution scheme  $\text{Au}^{3+} + \text{Cu}^+ \leftrightarrow 2\text{Fe}^{2+}$  as proposed by Chouinard *et al.* (2005), and remains still unresolved.

Although no remarkable correlation amongst trace elements is seen in arsenopyrite analyses, trace elements such as Pb, Bi, Te, Au and Ag showed elevated contents along fractures. Such enriched concentrations are most likely due to the ablation of bright micrometre-sized phases that occur along the micro-fractures. The restricted occurrences of these bright Pb-Bi-Te-Au-Ag bearing phases along the micro-fractures indicate their precipitation along micro-pores during syn-deformation alteration. Ciobanu *et al.* (2012) recognized significant geochemical similarity between Au and chalcophile elements such as Cu, Pb, Bi and Ag in As-free pyrites from the Dongping Au-polymetallic sulfide telluride deposit, North China Craton. The HAADF-STEM study carried out by these authors revealed Au-Ag-Te-Pb nanoparticles within pyrite, suggesting devolatilization-induced precipitation of Au-Ag-Te-Pb nanoparticles within micro-fractures in pyrite from Te-rich vapours. Striking features in arsenopyrite from Hutti such as the absence of notable alterations of arsenopyrite grains adjacent to fractures, several magnitudes higher contents of trace elements along the fractures and exclusive occurrences of Pb-Te-Bi-Au-Ag bearing phases along micro-fractures and pores suggest the introduction of trace elements from the fluid, which precipitated as Au-chalcophile micro-particles. Thermodynamic calculations suggest low aqueous Te concentrations in hydrothermal fluid; indicating vapour-phase transport of Te (McPhail, 1995). The geochemical correlation between chalcophile elements (in pyrite), and high contents of Pb, Ag, Bi, Au together with Te in arsenopyrite may

indicate their similar partition behaviour in the hydrothermal fluid. Thus, hydrothermal fluids carrying Te vapours (McPhail, 1995) and chalcophile elements (CE) most probably precipitate Au-CE-rich micro- to nanoparticles along fractures due to super saturation (Ciobanu *et al.*, 2012) during fluid-pressure fluctuations.

## Conclusions

The most notable difference in the ore mineralogy between Hutti and Hira-Buddini deposits is the absence of arsenopyrite in Hira-Buddini. The As-deficient environment in Hira-Buddini is also evident from the very low As contents (260–863 ppm) in the pyrites compared to those from Hutti (390–9353 ppm). Pyrite and arsenopyrite from Hutti preserve oscillatory Co and As zoning that most probably resulted from repeated phase separations during fluid-pressure fluctuations in an episodic flow regime. The  $S \leftrightarrow As$  diadochy in arsenopyrite, as displayed by the preservation of S-rich, As-poor core and S-poor, As-rich mantle indicates arsenopyrite precipitation in conditions of changing  $f_{S_2}/f_{As_2}$  ratio in the fluid. The lack of any correlation between As and Au, and positive correlations of Au with Cu, Ag and Te suggest incorporation of Au into pyrite coupled with chalcophile elements, but not as a function of its arsenic content. Micrometre- to sub-micrometre-sized Au-chalcophile-rich particles were precipitated along micro-fractures/pores in arsenopyrite from ore-bearing fluids. Such an inference rests on the following convincing observations: (1) elevated contents of Au, Pb, Te, Bi and Ag along fractures in arsenopyrite; (2) exclusive occurrence of bright Pb-Te-Bi-Au-Ag bearing micro-particles ( $<2 \mu m$ ) along the micro-fractures/pores in brittle deformed arsenopyrites; and (3) lack of alteration signature in arsenopyrite adjacent to the fractures, which could have remobilized trace elements from the host arsenopyrite. This study demonstrates coupled behaviour of Au and chalcophile elements (Ag, Cu, Te, Sb, Bi and Pb) in the Hutti and Hira-Buddini late Archean orogenic lode-gold deposits. The incorporation of Au into pyrite in such deposits is most probably a function of mineral fluid interactions without any effect of arsenic content.

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