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Impurity heterogeneity in natural pyrite and its relation to internal electric fields mapped using remote laser beam induced current

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ABSTRACT

Regions of band-bending in naturally occurring semiconducting sulfides are thought to drive electrochemical reactions with passing fluids. Metal bearing fluids within the right pH range interact with the electric fields at the surface resulting in precious metal ore genesis, even in under-saturated solutions. Metal reduction at the surface occurs via field assisted electron transfer from the semiconductor bulk to the ion in solution via surface states. Better understanding the role these regions and their texturing play on nucleating ore growth requires imaging of electric field distributions near the sulfide surface and correlation with underlying elemental heterogeneity. In this paper we discuss PIXE measurements made on the CSIRO Nuclear Microprobe and correlate elemental maps with laser beam induced current maps of the electric field distribution.

1. Introduction

Naturally occurring semiconducting metal sulfides such as pyrite possess electrical properties which depend on their crystal structure as well as formation sequence, subsequent diagenesis, metamorphic activity and natural weathering [1,2]. These settings and their influence on paragenesis results in a wide variety of habits, impurity levels and their heterogeneity throughout the mineral. Large impurity gradients in natural samples are not uncommon particularly close to hydrothermally altered rims. Impurity heterogeneity, structural imperfections and small changes in stoichiometry can lead to large variation in electrical properties [2–4]. Illustrating the scale of spread in natural assemblages, an early compilation by Pridmore et al. on the resistivity of natural pyrite found *n*-type samples to vary over four orders of magnitude, with *p*-type samples tending to have higher resistivities but a smaller spread [1]. Likewise, low co-ordination surface sites due to conchoidal fracture for example can result in bandgap narrowing and heterogeneous electrical properties at the surface [5,6]. In theory then, the band structure constants including minimum gap, the electron and hole Fermi levels, positions of the conduction and valence band edges as well as their density of states can all vary within a single mineral phase [7].

Of interest to this work however is the occurrence of neighbouring *p* and *n*-type regions with a shared boundary most commonly seen in zoned pyrites and their relationship to gold ore-genesis. Such regions have been observed by Marion et al. [8] and exist in many zoned pyrites such as those from Carlin and Bendigo-type deposits [9,10]. Semiconductor theory tells us that these metallurgically clean interfaces result in the establishment of an in-built micro-junction. The resultant potential difference across the junction can be characterised by its open circuit voltage V_{oc} or a short circuit photocurrent if suitably irradiated by light. Similarly, band offsets between mixed sulfide phases such as pyrite and galena can also lead to heterojunctions. A complex mineral assemblage can be thought of as a three dimensional circuit which controls the flow of free carriers [2]. Any electric fields established close to the surface are able to interact with passing fluids resulting in enhanced abiotic and biotic oxidative attack and electroless autocatalytic adsorption [11,12] of precious metals like Au and Ag (an electrochemical process). In this process, micro-galvanic action [13,14] between the *p* and *n*-regions of the junction results in the dissolution of the *n*-type material with electrons liberated passing to the *p*-side via a diffusion current where they are transported to the surface and quantum mechanically tunnel via surface states to reduce noble metal ions in solution. Under short circuit conditions prevalent due to the fluid shunting the device, the junction becomes slightly forward biassed i.e. the diffusion current outweighs the drift current.

In this work we attempt to observe these micro-junctios in pyrite and correlate their existence to PIXE measurements of local

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mineralogy and impurity heterogeneity. Arsenian pyrites from Otago New Zealand were chosen as native gold is often associated with As rich pyrites and in particular fracture lines and borders between mixed sulfide phases. The assemblage consisted of a black shale host with large 0.5–2 mm euhedral grains scattered about. Heterogeneity in the electric-field distribution near the surface of these grains was mapped using Remote laser beam induced current (LBIC) [15] microscopy. By correlating PIXE and LBIC measurements we hope to observe *p-n* junctions responsible for gold precipitation.

2. Particle induced X-ray emission (PIXE)

Technique minimum detection levels in the ppm range offered by PIXE make it ideally suited to investigate elemental heterogeneity in natural minerals that lead to variation in electrical properties [16]. To this end a 3 MeV proton beam from the University of Melbourne Pelletron was used on the CSIRO NMP [17] to map minor and trace element concentrations across several Otago pyrite grains (only one is shown here). Two large area hyperpure Ge X-ray detectors are mounted at ±45° to either side of the mineral face. Only the minor and trace level distributions in relation to the Fe distribution will be discussed here. The MicrodaQ data collection system in *x*-stage step mode [18] was used to scan a $\sim$3.5 mm × 1.5 mm region in 2 μm steps encompassing both the long euhedral and smaller subhedral grain shown in the photograph in Fig. 1. Accumulated charge at each pixel was set at 50 pC to ensure ppm sensitivity across common impurities found in metal sulfides. A 300 μm Al filter damps contributions from Fe and S to reduce pileup for the applied beam currents of 3–5 nA. The second X-ray detector included a 250 μm Be filter to collect all elements including S in the sulphide. As such it is of little interest in this paper. Results generated with GeoPIXE [19] on the trace channel are summarised in Figs. 2 and 3. The elements shown are those known to alter the electrical behaviour of pyrite [1]. Ni has not been included as it has recently been shown by Lehner et al. to form a deep level [20] and is not expected to play a large role in determining local dopant type.

3. Remote laser beam induced current

The remote LBIC method uses dual micromanipulator probes placed on either side of the mineral under study to capture a portion of the modulated lateral photocurrent induced by a focused 1–2 μm 633 nm laser spot as it is scanned across its surface [21]. Due to the large leakage current (or small dynamic resistance) in these natural junctions in addition to shorting material around the edges etc., this current is typically buried in the noise requiring the use of sophisticated AC methods and lock-in-amplifiers [21]. A typical LBIC response for this "remote" configuration is bipolar as noted in Fig. 3. Also shown is the equivalent circuit for the junction and ohmic contacts. A full description of the system used in this study is given elsewhere [21]. Note that LBIC measures an AC short circuit current or photovoltage phasor with both real and imaginary components. All images presented here are the magnitude of the short circuit photocurrent vector Fig. 4.

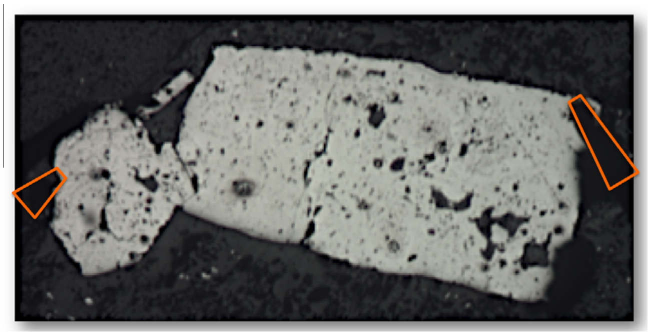

Fig. 1. Photograph of the Otago arsenian pyrite sample studied in this work. The sample dimensions are approximately 3 mm long by 1 mm high. Note the location of the electrical probes contacting both extreme edges made for LBIC measurements to ensue.

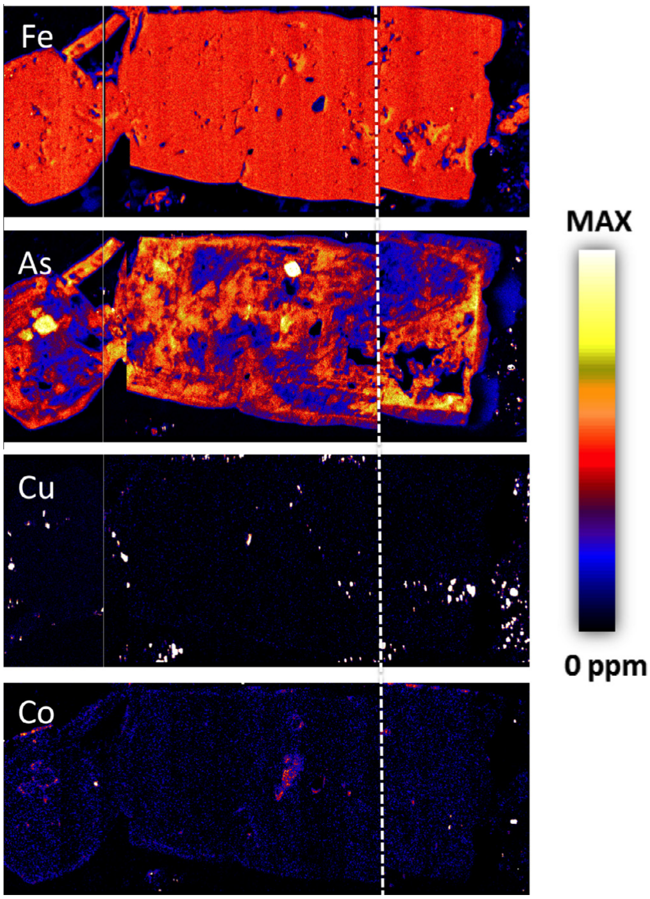

Fig. 2. PIXE elemental images of the dominant electrically active impurities in pyrite mapped across an approximate size of 3 mm wide by 1 mm high. As dominates the electrical properties anywhere across the mineral bar the small inclusions of chalcopyrite (see Cu image).

An LBIC short-circuit photocurrent image of the entire region shown in Fig. 1 as a function of laser modulation frequency is given in Fig. 5 (scale is on the bottom). For reasons discussed elsewhere, the large component close to the probe contacts shown in the 75 Hz image is due to thermoelectric currents due to high laser powers. At higher modulation frequencies this component decreases due to the minerals thermal mass and the structure revealed should be that due to electric fields near the surface due to impurity and mixed sulphide heterogeneity.

4. Discussion

For brevity the full analysis cannot be discussed here and a more full analysis will be published later. PIXE tells us that the majority of both grains contains an As rich overprint related to metamorphic activity late in paragenesis. These As impurities form shallow acceptor levels in pyrite resulting in a *p*-type doping throughout most of the crystal bulk [1]. Likewise, the elemental