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Invisible gold: Comparison of Au deposition on pyrite and arsenopyrite

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Abstract

X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), and open circuit potentials were used to compare the size, chemical state, and distribution of adsorbed and reduced gold from Au^{3+} chloride solution on pyrite and arsenopyrite. Many small Au^0 particles grow on the arsenopyrite surface, whereas few, much larger, gold particles appear on pyrite. These results mimic the differences in distribution of gold in some coexisting natural pyrites and arsenopyrites. The rate-limiting step in deposition of gold from Au^{3+} chloride solutions is the reduction of Au^{3+} to Au^+, whereas the open-circuit potential for deposition is determined by the reduction of Au^+ to Au^0. The open-circuit potential of pyrite or arsenopyrite is a corrosion potential. Presence of Au^{3+} shifts the corrosion potential to a value that depends on the relative rates of the reduction of Au^{3+} and the oxidation of the mineral. Open-circuit potential measurements indicate that the rate of deposition of gold on pyrite is controlled almost entirely by the rate of reduction of Au^{3+}. By contrast, the rate of reduction of gold on arsenopyrite is controlled significantly by the rate of oxidation of arsenopyrite.

Introduction

Gold is commonly associated with sulfide minerals such as pyrite and arsenopyrite (Boyle 1980, 1987). Arsenopyrite usually contains more gold than pyrite, and the gold content of arsenian pyrites generally increases with arsenic content (Fleet et al. 1993). Much of this gold is present as "invisible" gold (particles less than 0.1 μm), and many studies (Cabri et al. 1989, 1991; Cathelineau et al. 1989; Cook and Chryssoulis 1990; Friedl et al. 1995; Fleet and Mumin 1997; Genkin et al. 1998) have shown that the gold consists either of submicroscopic metallic particles or is incorporated as "chemically bound" gold. It has been assumed that gold deposits by precipitation induced by changes in temperature, pressure, or pH of the gold-bearing fluid (Romberger 1988; Bowers 1991). Deposition from gold sulfide complexes was proposed as being of importance in these processes (Shenberger and Barnes 1989; Benning and Seward 1996), but in many cases gold chloride complexes also appear to be involved (Helgeson and Garrels 1968; Goleva et al. 1970; Henley 1973). Recent laboratory studies (Jean and Bancroft 1985; Bancroft and Hyland 1990; Mycroft 1993; Möller and Kerstein 1994; Mycroft et al. 1995; Scaini et al. 1997) have shown, however, that adsorption-reduction reactions on surfaces are important in accounting for the existence of some gold deposits (Bakken et al. 1989; Cabri et al. 1989; Cook and Chryssoulis 1990; Knipe et al. 1991, 1992; Fleet et al. 1993; Genkin et al. 1998).

For ease of experiment, most of our previous studies, as well as this study, used the stable $AuCl_4^-$ species in aqueous solutions at 25 °C; $AuCl_2^-$ disproportionates. Most natural systems at 25 °C do not contain significant Au^{3+} complexed with chloride (Vlassopoulos and Wood 1990), but the $AuCl_4^-$ complex provides a simple stable precursor for the Au^+ to Au^0 reduction.

Measured open-circuit potentials of pyrite and arsenopyrite in contact with aqueous solutions are used to provide evidence for the mechanism of the deposition process and a partial explanation of the XPS and SEM observations. This interpretation is based on the electrochemistry of both mineral surfaces and of Au^{3+} and Au^+ in chloride solutions. It has been recognized within the last decade that (incongruent or congruent) dissolution of many semiconducting mineral electrodes, which involves redox processes, also involves solid-state electrochemical processes (Crundwell 1988; Osseo-Asare 1992). Consequently, for pyrite (Mycroft 1993) and arsenopyrite (Maddox 1996) the open-circuit potential is a mixed (or corrosion) potential. A mixed potential results from a balance of spontaneous oxidation and reduction processes to produce no net consumption or production of electrons or holes. A mixed potential is necessarily far from equilibrium under conditions where active corrosion is taking place. The proof that this is the case for pyrite in contact with aqueous solutions at room temperature, and a proposed mechanism for establishment of the mixed potential involves extensive electrochemical investigation and will be presented elsewhere. Here, the details of the mechanism are not of primary importance; recognition of the existence of a mixed potential is sufficient. In pyrite

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and arsenopyrite, the rate of corrosion is measurable electrochemically and is very slow. The linear rate is of the order of a small fraction of a millimeter per year and does not produce visible corrosion over short times; however, it is large enough to measure electrochemically. Corrosion gives rise to surface states that appear as non-stoichiometry of the surface.

Metallic gold is deposited from chloride solutions containing Au^{3+} in two steps: Reduction of Au^{3+} to Au^{+}, which is rate-determining, followed by a much faster reduction of Au^{+} to Au^{0} (Herrera Gallego et al. 1975; Schalch et al. 1976). Thus, formation of Au^{0} actually occurs from a Au^{+} complex. The mechanism of Au deposition has another feature. The rate of disproportionation of Au^{+} to Au^{3+} and Au^{0} is very slow but observable (Lingane 1962). Solutions containing $AuCl_4^-$ in contact with Au^{0} undergo the reverse of the disproportionation reaction of Au^{+} to Au^{3+} and Au^{0}. In the absence of Au^{0}, small amounts of impurities in solution or even rough surfaces can cause the reduction of Au^{3+}. Consequently, there is always a small amount of Au^{+} present in Au^{3+} solutions, and at the short times involved in spontaneous deposition of gold, the potential of a gold electrode is determined by the one-electron reaction of Au^{+} to Au^{0}. This potential, of course, is a pseudo steady-state potential, not an equilibrium potential. At times of the order of 100 h (Lingane 1962), disproportionation equilibrium is essentially complete, and the potential reaches its three-electron equilibrium value, which is a combination of the one- and two-electron processes.

Here we show that "invisible" gold can be formed by adsorption and reduction of Au^{3+} from chloride solution on pyrite and arsenopyrite surfaces. More importantly, more gold of smaller particle size occurs on arsenopyrite than on pyrite if the minerals are in the same or in separate solutions, and this difference mimics recent field observations of pyrite-arsenopyrite assemblages.

Experimental methods

The pyrite from Logrono, Spain, contained no arsenic; (see Mycroft 1993 for characterization). Arsenopyrite from Quebec, Canada was homogeneous, with 12 electron microprobe (wavelength dispersive) analyses over three grains giving the average composition $FeAs_{0.97}S_{1.1}$. The gold solution contained $KAuCl_4$ (10^{-4} or 10^{-5} M) and KCl (1 *M*) in doubly distilled deionized water, with pH adjusted to 3 with HCl. The plates (10 × 10 × 5 mm) of pyrite or arsenopyrite were cut using a water-cooled diamond saw and were either polished (800 and 1200 grit SiC and then 0.25 μm diamond dust) or fractured, then immersed in the solution electrolyte for 10 min in a polytetrafluoroethylene (PTFE) beaker at room temperature without stirring. Six experiments were carried out with both minerals present in the same beaker, but not in contact with each other. Three experiments were performed with the two minerals separately (total of six). No experiments were performed where the two minerals were in direct contact.

After washing with doubly distilled deionized water, the plates were transferred immediately into the vacuum chamber of either the XPS or the FESEM. A modified SSX-100 X-ray photoelectron spectrometer with monochromatic Al*K*α X-rays was used. Binding energies were calibrated with the Au 4f$_{7/2}$ line of high purity gold foil, which has a binding energy E = 84.0 eV. Narrow scan analysis was performed using a 300 μm spot size and 25 eV pass energy. A Hitachi S-4500 field emission SEM (cold cathode electron source, accelerator voltage 3–15 keV) was used to provide the high resolution micrographs.

Electrodes were cut with a diamond drill parallel to a prominent crystal face to give disks of diameter 6.4 mm. After wet polishing (as above), the electrodes were placed in a conventional three-electrode cell with electrolyte (as above) degassed by a stream of purified nitrogen. Open circuit potentials [vs. the saturated calomel electrode (SCE), which has a potential 0.244 V vs. the standard hydrogen electrode (SHE) at 25 °C] were monitored by a EG&G PAR Model 273 potentiostat-galvanostat.

Results and discussion

Scanning electron micrographs and X-ray photoelectron spectra

Samples of pyrite and arsenopyrite, both in the same container, are depicted in the micrographs of Figures 1 and 2. Typical low magnification (Figs. 1a and 1b) show a denser distribution of small Au^{0} particles on arsenopyrite, and fewer, much larger particles on pyrite. At higher magnification (Figs. 2a and 2b), the particles on arsenopyrite have diameters 20–50 nm; the single composite particle on pyrite is about 380 nm in size. The Au 4f XPS spectra (Figs. 3a and 3b) show mainly bulk gold (E = 84.0 eV), with some small particle gold ($E \leq 85.6$ eV) (Cordes and Harsdorff 1988; Mycroft et al. 1995) and also Au^{+} at E = 85.8–86.0 eV (Fig. 3b). The surface sensitivity of XPS precludes quantification of the total amount of gold on the surfaces. However, both narrow region spectra were obtained using 35 scans, so that direct comparison of the relative intensities could be made. From Figure 3b, the peak height for bulk gold on arsenopyrite is about seven times larger than that on pyrite, indicating that the amount of gold is at most seven times greater on arsenopyrite.

Similar results were obtained when the minerals were placed in different solutions in different containers; both polished and fractured arsenopyrite plates showed small gold particles of diameter 20–30 nm. The XPS spectra from polished (Fig. 4) and fractured plates in a 10^{-5}M $KAuCl_4$ solution shows bulk gold (E = 84.0 eV) from these small particles, and an intense broad peak at E = 84.5 eV from even smaller particles. Pyrite reacted under identical conditions showed fewer but larger gold particles, and again there is evidence from the XPS spectra for both small particle gold and Au^{+}. The two surfaces, pyrite and arsenopyrite, thus produce particles of bulk

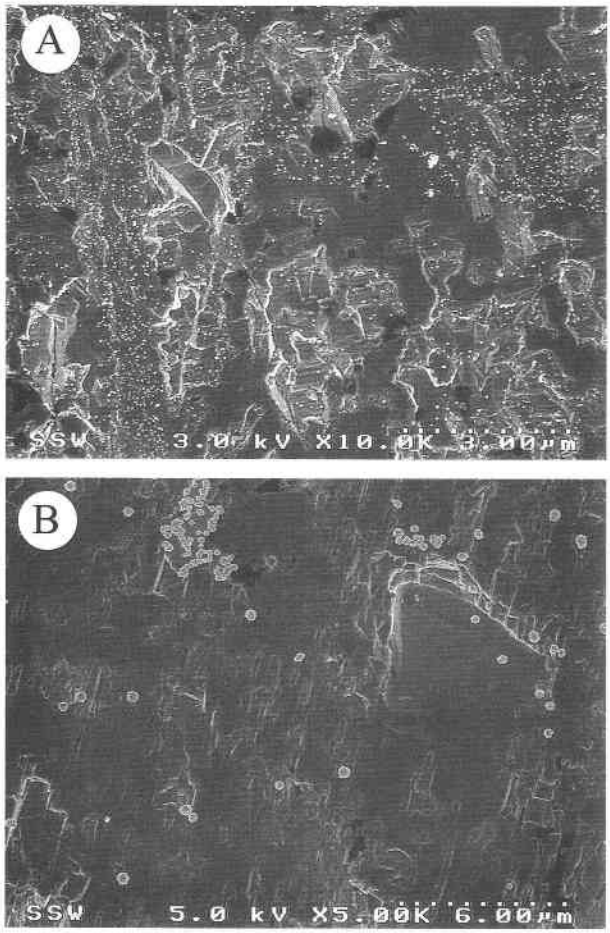

FIGURE 1. Low magnification SEM micrographs for (**a**) arsenopyrite and (**b**) pyrite plates after immersion for 10 min in a solution of 10^{-4} *M* $KAuCl_4$ and 1 *M* KCl, pH = 3.

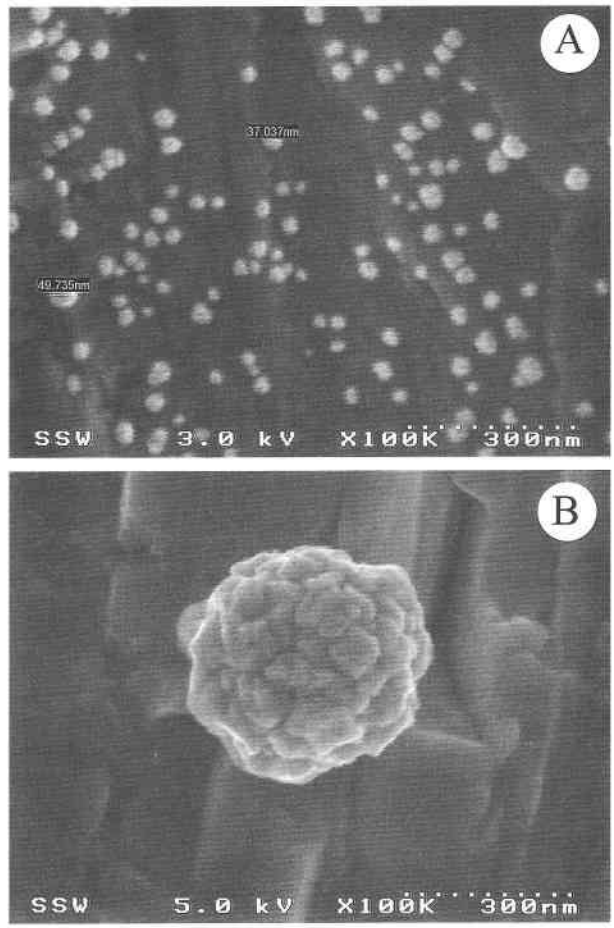

FIGURE 2. As in Figure 1, but at high magnification.

gold and microscopic gold, as well as Au^+. Repeated experiments showed that arsenopyrite concentrates gold more effectively than pyrite under the same conditions, with smaller particles on arsenopyrite than on pyrite.

Open-circuit potentials

The open-circuit potential of pyrite is about 0.28 V SCE for pyrite at pH = 3 (Mycroft 1993; Wei and Osseo-Asare 1996), and about 0 V SCE for arsenopyrite at pH = 3 (Maddox 1996). Figure 5 shows that deposition of gold on surfaces of either pyrite or arsenopyrite occurs at potentials positive to their open-circuit potentials, and thus involves oxidation of the mineral surface and spontaneous reduction of Au^{3+} to Au^+ and Au^0. In other words, the role of Au^{3+}/Au^+ solutions is to provide an alternate reduction path (reduction to Au^0) that combines with the oxidation of the mineral surface to shift the open-circuit potential toward the faster of the two processes. Even in the initial absence of Au^+, reduction by pyrite is sufficiently rapid that some Au^+ and gold nuclei are formed rapidly and the potential shifts toward that of the $AuCl_2^-/Au$ couple. Conventional corrosion theory (Bockris and Reddy 1973) shows that the corrosion potential and rate of corrosion are determined by the relative rates at open circuit of the contributing oxidation and reduction reactions; the corrosion potential lies closer to the process with the faster rate, whereas the rate of corrosion is determined by the process with the slower rate.

The potential for deposition of gold on pyrite from $AuCl_4^-$ solutions lies within about ±30 mV of the potential for deposition of gold on gold, under the same conditions (Mycroft 1993). Exact comparisons are difficult because of the difficulty in reproducing the small concentrations of Au^+ in these solutions, but the general conclusion is that the two deposition potentials lie very close to one another. The open-circuit potentials (Fig. 5) for Au deposition on pyrite and for deposition of gold are assumed identical. Even allowing for uncertainty in the relative positions of the two potentials, it is clear from corrosion theory that the deposition is controlled by the rate of reduction of Au^{3+}; the rate of oxidation of the pyrite surface is relatively slow. The potential of the pyrite electrode (Fig. 5) in contact with solutions of 1×10^{-4} *M* $AuCl_4^-$ starts at a value corresponding to about 2×10^{-6} M $AuCl_2^-$ and rises to a steady-state value corresponding

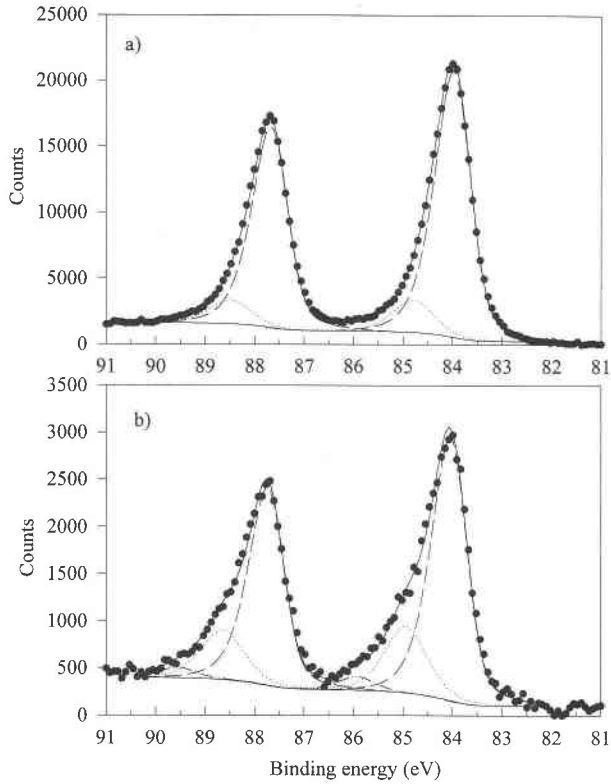

FIGURE 3. Au 4f XPS spectra for (**a**) arsenopyrite and (**b**) pyrite plates after immersion for 10 min in a solution of 10^{-4} *M* $KAuCl_4$ and 1 *M* KCl, pH = 3. Each spectrum results from 35 scans. Filled circles = actual data. Long dashes = bulk gold metal. Short dashes = small particle gold. Dot-dashes = Au^+. Solid line = composite fit.

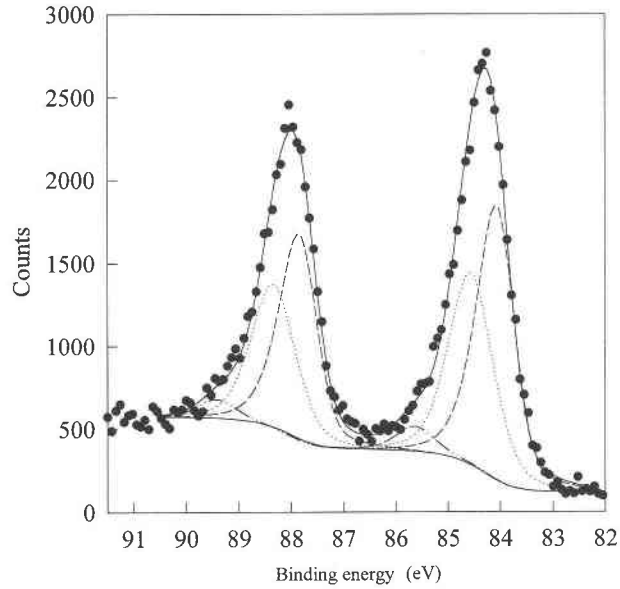

FIGURE 4. Au 4f XPS spectra from a arsenopyrite plate after immersion for 10 min in a solution of 10^{-5} *M* $KAuCl_4$ and 1 *M* KCl, pH = 3. Filled circles = actual data. Long dashes = bulk gold metal. Short dashes = small particle gold. Dot-dashes = Au^+. Solid line = composite fit.

to about 3×10^{-6} M $AuCl_2^-$. These values are calculated from the Nernst equation for the potential and the standard potential for reduction of $AuCl_2^-$ at 25 °C (Lingane 1962; Bard et al. 1985):

$$AuCl_2^- + e^- = Au + 2Cl^- \quad E^0 = 0.910 \text{ V SCE} \quad (1)$$

In contrast, the open-circuit potential for deposition of gold on arsenopyrite lies well below that for the deposition of gold on gold, so that the deposition is influenced strongly by the rate of oxidation of the arsenopyrite surface. It is known (Bancroft and Hyland 1990; Mycroft 1993; Mycroft et al. 1995) that the sites of oxidation of pyrite surfaces and reduction of Au^{3+} are coincident. Therefore, the surface of arsenopyrite oxidizes more rapidly than that of pyrite under the same conditions. More rapid oxidation leads to more nucleation sites on arsenopyrite, whereas the slower oxidation of pyrite leads to preferential growth on gold particles already deposited rather than the further oxidation of the surface. Gold complexes in solution thus serve as probes for the rate of oxidation of the mineral relative to the rate of reduction of Au^{3+} to Au^0. It must be emphasized that the open-circuit potentials of the minerals, as well as those of the mineral surfaces in the presence of Au^{3+}, are corrosion potentials, which are determined kinetically, not thermodynamically.

This corrosion mechanism for deposition of gold is not expected to occur with gold sulfide complexes. The relevant standard potentials at 25 °C are (1) for the reduction of $Au(HS)_2^-$, using stability data (Benning and Seward

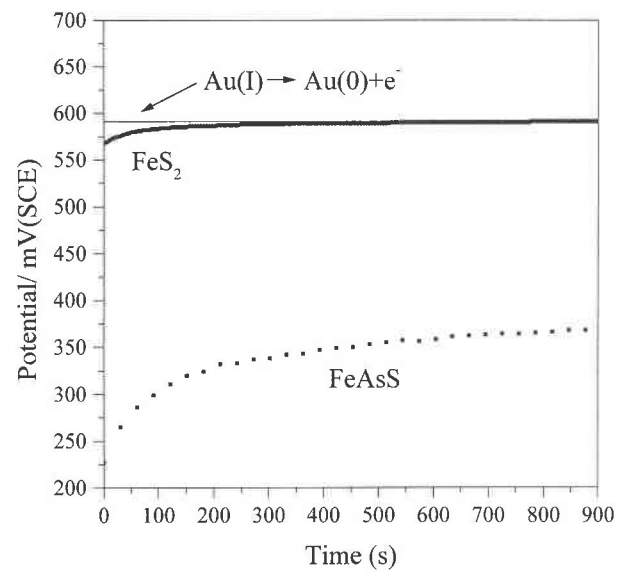

FIGURE 5. Open-circuit potentials for arsenopyrite and pyrite electrodes rotated at 500/m in 10^{-4} *M* $KAuCl_4$ and 1 *M* KCl, pH = 3 after 20 min immersion. Top solid line = potential for deposition of gold on gold ($AuCl_2^- + e^- = Au + 2Cl^-$); see text.

1996) and the standard potential for reduction of Au^+ to Au (Bard et al. 1985):

$$Au(HS)_2^- + H^+ + e^- = Au + H_2S + HS^-$$
$$E^0 = 0.093 \text{ V SCE} \quad (2)$$

or the analog of the reduction of $AuCl_2^-$:

$$Au(HS)_2^- + e^- = Au + 2HS^-$$
$$E^0 = -0.321 \text{ V SCE} \quad (3)$$

(2) for reduction of AuHS, again using stability data (Benning and Seward 1996) and the standard potential for reduction of Au^+ to Au:

$$AuHS + H^+ + e^- = Au + H_2S$$
$$E^0 = 0.548 \text{ V SCE} \quad (4)$$

Under non-standard conditions, but comparable total ligand concentrations and pH values, low concentrations of gold complexes shift the potential significantly in a negative direction relative to the standard potential (see Fig. 5, where the potential for Eq. 1 falls from 0.910 to 0.590 V). Thus the actual potentials for deposition of gold from gold sulfide complexes can lie close to or even below the open-circuit potential for pyrite, and probably also below that for arsenopyrite. If the deposition potential is more negative than the open-circuit potential, oxidation of the mineral surface is no longer possible; if slightly more positive, the rate of corrosion of the mineral surface is small and much smaller than the rate in the presence of gold chloride complexes. Support for this interpretation is found in recent results on the reaction of AuHS with pyrite (Scaini et al. 1998) that show that reduction of Au^+ to Au occurs only very slowly compared to reduction from gold chloride complexes.

The mineral electrodes used in this study were cut and polished, which no doubt produces non-stoichiometric surfaces. It has been claimed (Chaturvedi et al. 1996) that a stoichiometric surface of pyrite can be prepared by cleaning in vacuum with a He^+ beam followed by thermal annealing. We suggest that any natural sample of pyrite will contain grain boundaries and fracture surfaces with non-stoichiometric surface states. In contact with aqueous media, spontaneous corrosion of the surfaces can both create and enhance similar surface states. Therefore, we believe that use of polished surfaces, which are essential for extensive electrochemical investigations, is justified.

Traces of molecular oxygen can oxidize pyrite, but we suggest that any effects are minor compared to the effect of Au^+/Au^{3+} chloride complexes for both electrochemical experiments (where O was excluded as rigorously as possible) and equilibration experiments conducted without exclusion of atmospheric oxygen.

Our studies do not detect the relatively high amounts of "chemical gold" found by Mössbauer spectroscopy on some recently studied Siberian arsenopyrites (Genkin et al. 1998). However, detailed studies of pyrite and arsenopyrite by microbeam techniques, electron probe microanalysis, and SIMS (Genkin et al. 1998) show the same trends reported here: The arsenopyrites generally have more gold more uniformly distributed than the pyrites, and the subsurface inclusions of gold are smaller in the arsenopyrites than in the pyrites. Our results point even more strongly than those of Genkin et al. (1998) to the role of adsorption and reduction in the formation of Siberian gold deposits and possibly others. Our results also at least partially explain why arsenic can act as a pathfinder for gold deposits.

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