Chemical speciation of Ag in galena by EPR spectroscopy

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ABSTRACT
Electron paramagnetic resonance (EPR) spectroscopy has been used to study the valence state of silver in “argentiferous” galena samples from the Apuane Alps (Tuscany, Italy) mining district. This method was used to reveal primary metallic silver (Ag$^0$) in galena. Both thermodynamic data and experimental studies suggest that galena and native silver can stably coexist, but have not been reported as a primary (hypogene) assemblage in natural samples. EPR spectroscopy proved to be a suitable tool to solve this problem, because this technique is capable of detecting paramagnetic species down to the ppb level, even in a highly absorbent matrix such as galena.

A detailed SEM-EDS investigation could not detect metallic silver (or gold) in galena samples, but did reveal small (few micrometers) inclusions of Ag-bearing phases, in which silver has a formal valence of +1. On the other hand, EPR spectra indicated the presence in galena of pairs and clusters of elemental silver atoms, which may be associated with pairs of metallic gold, or with silver-gold hetero-atomic pairs. Therefore, SEM/EDS and EPR are complementary techniques, revealing the presence of both Ag$^+$ and Ag$^0$.

The Ag(Au) metallic species were apparently deposited on the galena surface during its growth from mineralizing fluids. Their scarcity, and the presence of larger amounts of Ag$^{1+}$ phases, suggest that the assemblage galena-metallic silver was stable only under peculiar physical and chemical conditions. The formation of Ag$^+$ was presumably linked to local and rare chemical fluctuations of the hydrothermal environment, characterized by low activities of S, Sb, Bi (Cu….) and high activity of Ag in the fluids. The occurrence of both homo- and hetero-atomic pairs suggests either different kinetics of pair formation, or possible fluctuations in the composition of the hydrothermal fluids, which alternatively carried Ag or Au species, or both.

INTRODUCTION
The widespread association of precious metals with base metal sulfide ores is well known. Therefore, many systematic investigations of the processes by which precious metals accumulate on metal sulfide surfaces have been undertaken (Bancroft and Jean 1982; Starling et al. 1989; Cabri 1992; Foya et al. 1999; Cabri et al. 2000, and references therein). Particular efforts were made to study the valence state of precious metals in sulfides, and to address their nearest chemical environment. This topic is of great scientific and economic interest because an accurate knowledge of the modes of occurrence (e.g., sub-microscopic inclusions vs. structurally bound atoms) of precious metals in sulfides is essential to optimize metal recovery, improve metallurgical techniques, and gather more information on ore-forming processes.

Experimental evidence of valences of noble metals in sulfides frequently leads to controversy because noble metals often occur in small amounts, close to the detection limits of many techniques, and are unevenly distributed in minerals (Cabri 1992). In particular, the most common techniques for valence studies of dispersed precious metals in sulfides are XANES and Mössbauer spectroscopy, whereas electron paramagnetic (or spin) resonance (EPR or ESR) studies are comparatively scarce (e.g., van Moort et al. 1995; McQueen et al. 2001). However, a potential advantage of this technique is the ability to detect paramagnetic species down to the ppb level (Weil et al. 1994).

Di Benedetto et al. (2002) have recently reviewed the applications of magnetic techniques, including EPR and direct magnetic measurements, to the study of valence state and site symmetries of transition elements in mineral sulfides and sulfosalts. While EPR has been profitably applied to the characterization of Ag properties in some materials (Michalik et al. 1996; Mitrikas et al. 1999), no data are published, to our knowledge, concerning Ag speciation in galena as studied by paramagnetic resonance spectroscopies. In this paper, to evaluate