J. Ind. Geophys. Union, 30(2) (2026), 142-147
https://doi.org/10.71122/JIGU.30(2)2026.0015

# Acanthite ($Ag_2S$) as an indicator of late-stage silver mineralization in the Zawar Pb–Zn system, Rajasthan, India: Insights from Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) microtextural studies

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**ABSTRACT**

This study investigates the occurrence, microtextural characteristics and chemical composition of acanthite ($Ag_2S$) in the Zawar deposit, Rajasthan, India, to understand the conditions and the paragenetic relationship of silver mineralization in this classic carbonate-hosted Mississippi Valley Type (MVT) ore deposit. Silver in Zawar, traditionally considered a by-product of lead (Pb) and zinc (Zn) extraction, is shown here to occur as late-stage acanthite developed as distinctive veins and star-shaped aggregates along the weak zones and micro-fractures within earlier-formed pyrite. Scanning Electron Microscopy (SEM) reveals that these acanthite crystals are confined to structurally controlled micro-openings, indicating precipitation from late stage fluids that exploited pre-existing sulfide microstructures. Energy-dispersive X-ray spectroscopy (EDS) confirms a dominantly silver (Ag) and, sulfur (S) composition, and only minor iron (Fe) and calcium (Ca), suggesting limited solid solution or sub-microscopic inclusions of associated sulfides. The dominance of monoclinic acanthite in carbonate-hosted, structurally focused sites, is fully consistent with the deposition from basinal brines at low temperatures. These textural and geochemical observations, collectively indicate that silver enrichment at Zawar is genetically linked to the waning stages of MVT-type hydrothermal activity.

**Keywords:** Silver, Acanthite, Hydrothermal mineralization, Micro-textural Studies, Zawar.

## INTRODUCTION

Globally, silver production is dominated by Australia, Mexico, China, Peru, and Russia, while India, though among the top three consumers, contributes only a small share of the 6,10,000 tonnes worldwide reserve in 2023, indicating a heavy reliance on imports (Indian Minerals Yearbook, 2023). Total reserve of silver in India is about 7700 tonnes, mainly found as a by-product from lead, zinc, copper, and gold refining in Rajasthan, Jharkhand, and Andhra Pradesh, and its strategic importance is growing with rising industrial demand in electronics, solar energy, and storage sectors. The Zawar deposit of Rajasthan, is one of the economically significant carbonate-hosted Pb-Zn orefields and an important historical centre for silver production (Haldar, 2004). Mining in this belt has been active since at least medieval times, with archaeological evidence for large-scale lead zinc smelting, from poly metallic ores in the Zawar hills. Modern operations by Hindustan Zinc Limited (HZL) at Mochia, Balaria, Zawarmala and Baroi, continue to produce Zn–Pb ore with silver recovered as a significant by-product. Although the principal ore minerals are galena (PbS) and sphalerite (ZnS), silver is hosted both in solid solution within these sulphides and in discrete silver minerals. Classical mineralogical work on Zawar describes small amounts of argentite and native silver associated with the main sulphide assemblage (Mookherjee, 1964).

Generally, Silver sulfide ($Ag_2S$) occurs in three temperature-dependent polymorphs that share the same chemical composition but differ in structure and stability (Sadovnikov et al., 2015). At low temperatures, the stable phase is α-$Ag_2S$ (acanthite), which has a monoclinic structure with relatively ordered $Ag^+$ positions and forms the common silver ore mineral in most deposits. On heating above ~177 °C, acanthite transforms to β-$Ag_2S$ (argentite), a high-temperature polymorph with a cubic (isometric) structure in which $Ag^+$ ions become partially disordered and highly mobile in nature, this phase is usually preserved only as acanthite pseudomorphs after argentite because it inverts on cooling (Sadovnikov et al., 2015). At still higher temperatures (typically above ~600 °C under experimental conditions), $Ag_2S$ transforms further to γ-$Ag_2S$, another high-symmetry cubic phase with even greater $Ag^+$ mobility and structural disorder. The objective of this study is to characterize the morphology, microtextural setting, and chemical composition of acanthite in the Zawar deposit using SEM and EDS analyses, in order to understand the nature of silver mineralization

## GEOLOGY OF THE STUDY AREA

The Zawar deposit lies within the highly mineralised Proterozoic Aravalli Supergroup of the Aravalli Craton in NW India (Deb et al., 1989). Stratigraphically, mineralisation occurs in a siliciclastic–dolomitic carbonate succession of the Middle Aravalli Group, within the Zawar Formation (Mukherjee and Bhattacharya, 2021). The belt is characterised by two major superposed folds, the hook-shaped Main Zawar Fold (MZF) and the antiformal anticline Zawarmala Fold, developed under lower greenschist facies metamorphism and hosting several important mines, including Balaria, Mochia Magra, Baroi Magra and Zawarmala (Roy, 1995). The regional geology of the area is depicted in Figure 1.