

## AN OCCURRENCE OF MAGMATIC SPHALERITE, GRANITEVILLE QUARRY, STATEN ISLAND, NEW YORK

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### ABSTRACT

Despite the thermally refractory character of zinc sulfide, the deposition of sphalerite is almost invariably the result of relatively low-temperature hydrothermal processes. However, a few rare occurrences are known in which sphalerite has been reported to be a magmatic mineral. We describe an occurrence of microscopic crystals of sphalerite enclosed selectively in the albite component of the quartz–albite granophyre, which constitutes the groundmass of a pyroxene trondhjemite that was produced by the marginal fusion of a xenolith of Lockatong argillite enclosed in the Palisades diabase sill in the Graniteville quarry, Staten Island, New York. The petrographic characteristics and the euhedral character of the sphalerite strongly support the interpretation that these crystals are part of the magmatic suite. Based on phase-equilibrium diagrams for the system albite – quartz and the system diopside – nepheline – silica, we conclude that the zinc sulfide probably crystallized from a silicate melt between 1073° and 1062°C. Possible sources of the zinc and sulfur are (1) the sedimentary xenolith, which is now a hornfels containing 20–54 ppm of zinc, and (2) the basaltic magma of the sill, which crystallized to a diabase containing 50 ppm of zinc. The latter hypothesis involves diffusion of zinc and sulfide ions across the liquid–liquid boundary between the co-existing basaltic magma of the sill and the trondhjemitic magma derived from the xenolith.

*Keywords:* sphalerite, zinc sulfide, magmatic ZnS, fused xenolith, Palisades sill, Staten Island, New York.

### SOMMAIRE

Malgré le caractère réfractaire du la sphalérite, dont la déposition se fait généralement en milieu hydrothermal à basse température, il existe quelques rares exemples de sphalérite primaire. Nous décrivons la présence de cristaux microscopiques de sphalérite dans l'albite d'une intercroissance granophyrique de quartz et d'albite. Cette intercroissance forme la pâte d'une trondhjemite à pyroxène, produit de cristallisation d'un magma issu de la fusion partielle d'une enclave d'argillite (Formation de Lockatong) dans le filon-couche de Palisades, qui affleure dans la carrière de Graniteville, sur l'île de Staten (New York). D'après les textures et sa nature idiomorphe, la sphalérite semble magmatique. Les diagrammes de phase pour les systèmes albite – quartz et diopside – néphéline – silice montrent que le sulfure de zinc a probablement cristallisé d'un magma entre 1073° et 1062°C. Le zinc et le soufre auraient une origine soit dans l'enclave d'argillite, maintenant une cornéenne contenant entre 20 et 54 ppm de Zn, soit dans le magma basaltique, dont le produit, une diabase, en contient 50 ppm. Dans le second cas, les ions de Zn et de S auraient à traverser l'interface entre les deux liquides en présence.

(Traduit par la Rédaction)

*Mots-clés:* sphalérite, sulfure de zinc, ZnS magmatique, enclave fondue, filon-couche de Palisades, île de Staten, New York.

### INTRODUCTION

Sphalerite is a remarkably refractory sulfide, with a melting point in excess of 1800°C (Kullerud 1966). Nevertheless, all economic deposits of sphalerite are of hydrothermal origin, and occurrences of magmatic sphalerite are rare (Ramdohr 1980, p. 519). However, a few occurrences of magmatic sphalerite have been

reported. Desborough (1963) reported the occurrence in Missouri of sphalerite of apparently magmatic origin; it occurs as disseminated grains in unaltered intrusive tabular bodies of olivine diabase, coarse ophitic gabbro, and layered gabbro. He indicated that, because of its lack of distinctive optical properties, sphalerite may easily be overlooked or mistaken for ilmenite in microscopic examination of thin and polished

sections. He also reported that sphalerite may be a rare constituent of magmatic droplets of iron, nickel, and copper sulfides in mafic igneous rocks. Wilson (1953) stated that some zinc may enter the magmatic Cu–Ni–Fe sulfides, although zinc typically reaches its maximum concentration in a mafic magma at a much later stage than the formation of the magmatic sulfides. Naldrett (1989) pointed out that zinc is conspicuously absent in magmatic sulfide ore, although some of the magmatic sulfide ores of Sudbury average 100–200 ppm of zinc, and some copper-rich stringers contain up to 3700 ppm of zinc. According to Naldrett (1989, p. 52), the sulfide melt – silicate melt partition coefficient of zinc is about 1, and, consequently, zinc does not concentrate in sulfide melts. In this paper, we report evidence for the direct crystallization of magmatic sphalerite from a felsic silicate melt.

#### GEOLOGICAL SETTING AND PETROGRAPHY

Benimoff & Sclar (1984, 1988) described an occurrence of a partly fused xenolith of Lockatong argillite in the Palisades sill of Staten Island, New York. The melt probably contained at least 70%  $\text{SiO}_2$  and was characterized by an exceptionally high Na/K ratio, which reflects the Na-rich, K-poor parental argillite. After cationic diffusion across the liquid–liquid boundary separating the magma of the sill from the newly generated siliceous magma derived from the argillite, the latter crystallized to a pyroxene trondhjemite that contains phenocrysts of augite and discrete crystals of albite enclosed in a groundmass of albite–quartz granophyre. The trondhjemite envelops the xenolith as a zone 5–12 cm thick. Enclosed selectively in the albite of the albite–quartz granophyre, we found, in thin sections, about a dozen isolated euhedral to subhedral crystals of sphalerite 30–70  $\mu\text{m}$  in diameter (Figs. 1, 2). These crystals are transparent, with a

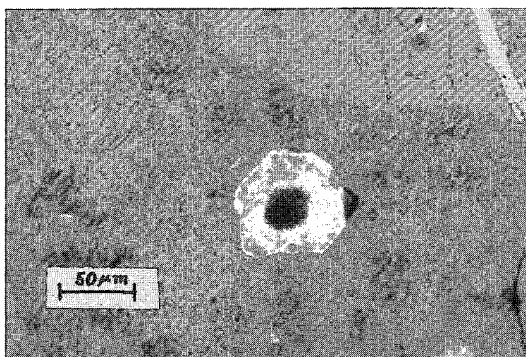


FIG. 2. Photomicrograph of zoned subhedral ZnS crystal enclosed in turbid albite of the quartz–albite granophyre. 360 $\times$ . Plane-polarized light.

high refringence. They are isotropic and optically zoned, with a dark-brown core and pale brown to colorless rim. Also enclosed in the trondhjemite are minute interstitial anhedral grains of Ni- and Co-bearing pyrrhotite, although nowhere is the pyrrhotite in contact with the sphalerite crystals.

The euhedral grains of zinc sulfide typically have the shape of an equilateral triangle, the corners of which are truncated (Figs. 3, 4). This results in a six-sided form with alternating long and short sides that resembles most closely the crystallographic form of an isometric positive tetrahedron modified by a negative tetrahedron. This morphology is characteristic of sphalerite. Nevertheless, such a morphology is not incompatible with the hexagonal symmetry of wurtzite if the grains are considered to be basal (0001) sections or near-basal sections. However, the absence of anisotropic longitudinal *c*-axis sections suggests that the crystals that nucleated in the trondhjemite magma were sphalerite and not wurtzite. Some of the euhedral

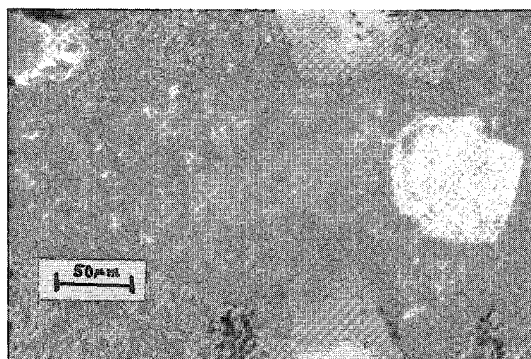


FIG. 1. Photomicrograph of a euhedral crystal of ZnS that is probably a simple twin. Note turbid albite host for the ZnS crystal and relatively clear associated quartz. 360 $\times$ . Plane-polarized light.

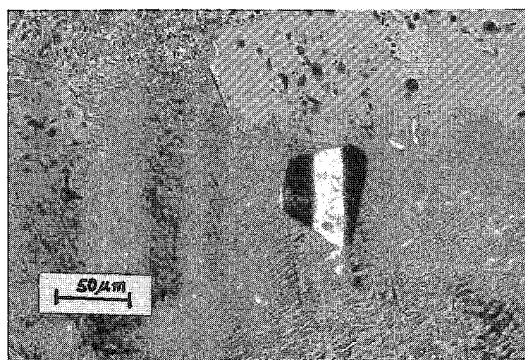


FIG. 3. Photomicrograph of euhedral trigonal ZnS crystal showing internal reflections enclosed in turbid albite of the quartz–albite granophyre. 360 $\times$ . Plane-polarized light.

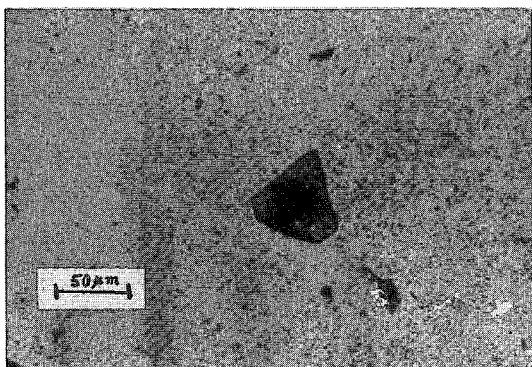


FIG. 4. Photomicrograph of trigonal zoned crystal of ZnS in turbid albite of the quartz-albite granophyre. 360 $\times$ . Plane-polarized light.

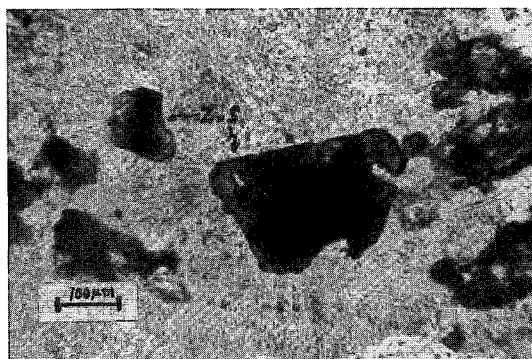


FIG. 5. Photomicrograph of crystals of ZnS in turbid albite of the quartz-albite granophyre. Note embayments in larger crystal. 140 $\times$ . Plane-polarized light.

crystals show deep embayments (Fig. 5) that may be indicative of magmatic resorption.

#### ELECTRON-MICROPROBE DATA

Compositional data were obtained with an ARL electron microprobe using wavelength-dispersion analysis. Standards were synthetic ZnO for zinc and pyrite for iron and sulfur. Operating conditions were 15 kV and 40 nA. The raw data were corrected for atomic number, absorption, and fluorescence effects (ZAF). Results of the electron-microprobe analysis (Fig. 6) show that these isotropic grains are zoned zinc sulfide, with a relatively high-iron core (10–16 mole % FeS) and low-iron rim (1–5 mole % FeS). The core-rim boundaries are abrupt and show concentration gradients in excess of 3 mole % FeS per  $\mu\text{m}$ . Some of the grains have an asymmetrically zoned rim composed of alternating relatively high-iron (5 mole % FeS) and relatively low-iron (1 mole % FeS) zones.

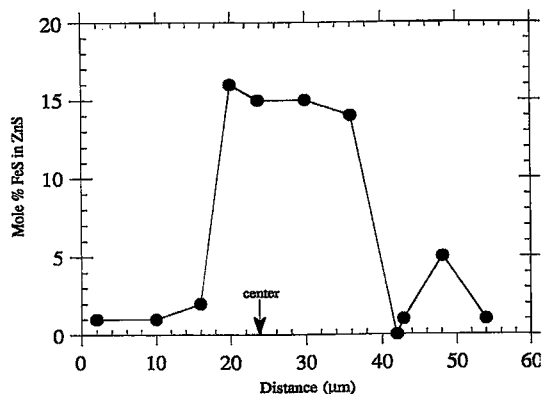


FIG. 6. Typical zoning profile of the magmatic ZnS crystals, showing the distribution of iron as determined by electron-microprobe analysis.

#### ORIGIN OF THE SPHALERITE

The crystallization history of the trondhjemite may be interpreted by means of the dry one-atmosphere phase-equilibrium diagrams for the system albite – silica of Schairer & Bowen (1956) and the system diopside – nepheline – silica of Schairer & Yoder (1960). The albite-quartz granophyre is considered to be a eutectic of albite and quartz with a melting temperature of 1062°C. Petrographic relationships indicate that the sphalerite is part of the magmatic suite and that it probably crystallized from the silicate melt at temperatures between 1062° and 1073°C (before the albite of the quartz-albite granophyre and after the augite phenocrysts and early discrete crystals of albite). Based on the geological setting, pressure at the time of crystallization was probably less than 2 kilobars. A possible source of the zinc and sulfur was the sedimentary xenolith (now a hornfels), which contains 20–54 ppm of zinc. Another possible source of the zinc and sulfur is the surrounding uncontaminated diabase, which contains 50 ppm of zinc. Zinc and sulfide ions could have diffused from the basaltic magma across the liquid-liquid boundary between the coexisting basaltic and trondhjemitic magmas.

The equilibrium boundary between sphalerite (low-temperature polymorph) and wurtzite (high-temperature polymorph) in pure ZnS occurs at 1020°C at 1 atmosphere (Kullerud 1966); the pressure-dependence of the inversion is not known. The inversion temperature is lowered to about 960°C with 15 mole % of FeS in solid solution (Kullerud 1966). These phase relationships in the ZnS-FeS system suggest that wurtzite should have nucleated as the equilibrium phase in the temperature interval 1062–1073°C and then inverted to sphalerite on cooling below the solidus, but the morphology of the ZnS crystals suggests, at first, that

sphalerite was the magmatic phase. However, it is important to note that several of the polytypes of wurtzite (3R, 9R, 12R, 15R, 21R) have symmetry  $R3m$  (Kostov & Minčeva-Stefanova 1982). It is possible, therefore, that the magmatic ZnS crystals developed as thin tabular forms of wurtzite parallel to (0001). They would display trigonal outlines like tourmaline and appear optically isotropic regardless of whether they inverted to sphalerite. Such an occurrence of wurtzite would be compatible with the estimated temperature of crystallization and the equilibrium relationships between wurtzite and sphalerite.

Toulmin *et al.* (1991) have recently reviewed the binary system (ZnS–FeS) with specific reference to the FeS content of sphalerite in association with pyrite and pyrrhotite as a function of temperature and pressure. However, the absence of pyrite and pyrrhotite in direct association with the Graniteville sphalerite precludes the application of their conclusions to this occurrence.

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