The conditions necessary for the formation of metastibnite are not clear. Clark (this issue) attributes formation of metastibnite at Mina Alacrán, Copiapó, Chile to oxidation from stibnite, but the metastibnite found at The Geysers and at Steamboat Springs may be primary (see White, 1967; for a discussion of the geochemistry of the waters of both locations). Sulfur isotopic analyses (Geochron Laboratories, Cambridge, Massachusetts) yield the following information for sulfur-bearing species from the metastibnite location at The Geysers: metastibnite;  $\delta S^{34} = -6.7 \circ/_{oo}$ ; cinnabar,  $+2.3 \circ/_{oo}$ ; native sulfur,  $-2.9^{\circ}/_{oo}$ ; and sulfate (boussingaultite plus unidentified material),  $-0.9 \circ/_{oo}$ . These data suggest that a gas phase, probably H<sub>2</sub>S, is involved in the formation of primary metastibnite because its sulfur is appreciably lighter than the S of the other species. This explanation would also account for its occurring as coatings in cracks but not as complete veins.

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# SUPERGENE METASTIBNITE FROM MINA ALACRÁN, PAMPA LARGA, COPIAPÓ, CHILE

# ALAN H. CLARK, Department of Geological Sciences, Queen's University, Kingston, Ontario, Canada

#### ABSTRACT

Metastibnite is confirmed as an oxidation product of stibnite in the Alacrán deposit. Electron microprobe analysis yields a composition close to stoichiometric  $Sb_2S_3$ , but with a slight sulfur-deficiency.

Although the status of the rare mineral, metastibnite, as amorphous red  $Sb_2S_3$  is generally accepted (e.g. Palache *et al.*, 1944; Hey, 1955), there appear to have been no quantitative analytical studies since the investigations of Davy (1920) and Lindgren and Abbott (1931).

A reddish-brown powdery coating on stibnite in a specimen from the dumps of the Alacrán Ag-As-Sb mine (Lat.  $27^{\circ}36'$  S.; Long.  $70^{\circ}11'$  W.) in the Pampa Larga mining district of northern Chile (Parker, Salas and Pérez, 1963), has been identified as metastibnite. The coating occurs in fractures in bladed stibnite aggregates, associated with minor, massive cinnabar in a barite gangue. It was at first taken to be *yuyo*, a powdery mixture of cinnabar and iron-, copper-, and antimony oxides, which is a widespread oxidation product of cinnabar-bearing ores in northern Chile (Domeyko, 1864).

However, X-ray examination of a carefully separated fraction of the powder, using a NONIUS Guinier-de Wolff focussing camera, revealed only several faint and diffuse  $\alpha$ -quartz lines, and none which could be ascribed to metallic sulfides or oxides. Ore microscopic study of an impregnated polished mount of the powder showed that its major constituent, apparently amorphous, is a bluish-white, slightly translucent mineral, displaying moderate anisotropism in air, and intense orange-red internal reflections under oil immersion. These properties correspond to those observed for metastibnite by Ramdohr (1937; 1970). Identification of this phase as metastibnite was confirmed by electron microprobe analysis; only antimony and sulfur were detected in several grains showing an irregular, cauliflower-form habit.

Quantitative analysis, using synthetic  $Sb_2S_3$  as a standard, yielded a composition which is slightly sulfur-deficient with respect to stoichiometric  $Sb_2S_3$  (Table 1), whereas the associated hypogene stibnite shows no significant departure from that composition. It may be noted that stibnite, a major constituent of the Alacrán veins, here coexists with realgar, orpiment, and native arsenic, and contains up to 0.6 weight percent As in the earliest vein assemblages, while the later-formed stibnite, such as that associated with the metastibnite, is essentially arsenic-free.

The significance of the low Sb+S analytical total yielded by the

	$\mathrm{Sb}_2\mathrm{S}_3$	Late-stage hypogene stibnite	Supergene metastibnite
$\mathbf{Sb}$	71,69	71.62	71.50
As	<u> </u>	tr.	n.d.
S	28.31	28.35	26.56
Total	100.00	99.97	98.06

 TABLE 1. ANALYTICAL DATA FOR STIBNITE AND METASTIBNITE,

 MINA ALACRÁN, PAMPA LARGA, CHILE

# MINERALOGICAL NOTES

metastibnite is unclear; this mineral may contain minor amounts of oxygen or other light elements (cf. Davy, 1920). The Mina Alacrán metastibnite lacks lead, but the material from the Socavón mine, Oruro, Bolivia, described by Davy (1920) and Lindgren and Abbott (1931) apparently represents a valid plumbian variety, since there is no indication that the samples analysed by the latter authors were grossly impure (cf. Palache et al., 1944).

In other documented occurrences, metastibnite has apparently formed under hypogene conditions, whether as a powdery impregnation of siliceous sinters in fumarolic centers (Becker, 1888; Brookins, this issue), or as more competent, mammillary aggregates in the Bolivian tin-silver deposits (Day, 1920; Lindgren and Abbott, 1931; Ahlfeld, 1940). At Mina Alacrán, however, the amorphous antimony tri-sulfide appears to represent a product of the *in silu*, post-Miocene (Sillitoe, Mortimer and Clark, 1968) oxidation of stibnite. This alteration does not appear to have involved large compositional changes, but may have resulted from colloidal reprecipitation during the deposition of supergene chalcedony.

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