



Acid volatile sulfide (AVS)

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Abstract

The sequestration of sulfur within sedimentary pyrite is a major sink in the global biogeochemical sulfur cycle and has consequent impacts on the related cycles of carbon and oxygen. In many sedimentary environments, a zone exists which releases H₂S if treated with acid. The materials that produce this sulfide are described as acid volatile sulfides or AVS and the sulfide which is evolved and collected by this treatment is called acid volatile sulfide (AVS-S). In this research review we show that AVS represents part of a complex and dynamic biogeochemical system which is not defined simply by the analysis of AVS-S.

During the 40 years since R.A. Berner first defined the concept of acid volatile sulfide, a number of scientific myths have developed regarding the nature and composition of AVS and its role in the global sulfur cycle. We show that:

- AVS is not equivalent to FeS and solid FeS phases have rarely been identified in marine sediments. AVS is a complex and variable component which does not represent any singular or simple group of sediment components.
- The commonly used extraction methods do not quantitatively extract AVS minerals (mackinawite and greigite) without also significantly releasing sulfide from pyrite.
- AVS varies geographically and AVS is not the same component or set of components wherever it is found.
- The solubilities of FeS and Fe₃S₄ in neutral to alkaline systems are presently poorly constrained and pore water saturation state calculations cannot be used to support the presence of specific AVS minerals.
- The colored zone in sediments does not reflect the distribution of AVS.
- AVS is not always a minor fraction of total reduced sulfide (TRS) which dominantly occurs near the sediment–water interface. AVS minerals are not required precursors for pyrite formation.

A better understanding of the sedimentary sulfur system, including its nature, formation and transformations, is a key component in understanding the evolution of the Earth and its future development. However, some basic parameters, such as the solubility and composition of the metastable iron sulfide solids, are still not constrained. Even the presence of these minerals in most sedimentary systems remains equivocal. Aqueous FeS clusters appear to be ubiquitous and appear to have significant geochemical and biological roles. The roles of organisms, especially in modifying rates and products, remain a key area of research.

Although AVS may have served its purpose in the earlier exploratory days of the study of sedimentary sulfides, the concept is now probably more of a hindrance than a help in advancing this field. It is reasonable to question if it is not time to simply do away with the AVS concept altogether and get on with the business of trying to deal more directly with the behavior of the more

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important components known to fall within the group of sulfide species that contribute to sulfide that is volatilized when acid is added to a sediment.

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1. Introduction

One of the controlling aspects of the interrelated global biogeochemical cycles of carbon, oxygen and sulfur is the removal of sulfur from the ocean–atmosphere system and its burial in sediments. Observations of anoxic sediments show a common sulfide-rich zone at depth which includes a variety of precipitated and dissolved iron and sulfur species (Fig. 1). Adding HCl to this material results in the evolution of H₂S gas that is derived from the “acid volatile sulfide(s)” (AVS) component of sedimentary sulfides.

In fine-grained marine sediments this zone commonly includes bluish to gray colored material which was referred to as “blue mud” by early navigators. The formation of this blue mud and the disappearance of sulfate from the interstitial waters was one of the early observations of the first marine science expedition of HMS Challenger in 1873–1876 (Murray and

Renard, 1891; Murray and Irving, 1895). In some sediments, especially in freshwater systems, wetlands and euxinic basins, the sulfide-rich zone includes a black-colored layer which has a finite thickness. Metastable iron sulfides have been widely identified with this black sulfide-rich zone because of their black color and the fact that they tend to dissolve with HCl to produce H₂S gas. There have also been solubility considerations which have attempted to demonstrate that the concentration of dissolved Fe(II) in this zone is controlled by the solubility of iron(II) monosulfide. This black, sulfide-rich material has been widely identified with acid volatile sulfide or AVS. The current paradigm is that sulfide is first removed by reaction with Fe(II) to form metastable iron sulfides in this black or AVS zone which then transforms on aging to pyrite.

Probably the seminal paper for the concept sedimentary AVS as an “operationally defined” component of anoxic sediments was that of Berner (1964a). He defined AVS in terms of the source of H₂S evolved from sediments by adding 1 N HCl. This approach measures both solid phase HCl-reactive sulfide minerals and sulfide dissolved in pore waters (which operationally includes iron sulfide clusters and nanoparticles). A variant of the basic AVS method is the simultaneously extractable metal (SEM)–AVS approach. In this technique, the metals, mainly iron, extracted by the HCl addition are also analyzed in an attempt to assess their potential toxicity.

The measurement of AVS-S in sediments is operationally simple. It has therefore been widely used in the marine community and in areas of environmental science to such an extent that these types of investigations appear to have developed a dynamic of their own. However, it is a simple variety of the common successive leaching approach to unraveling the complexities of natural systems. As such it suffers from the same problems of interpretation of results.

In this research review, we examine the results of the progress that has been made experimentally and theoretically in understanding the chemistry and mineralogy of the Fe–S system in low or ambient temperature aqueous systems. We consider evidence for the composition of the dissolved substances in laboratory AVS-

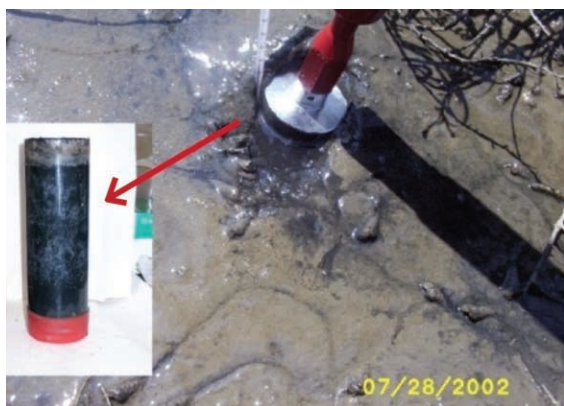


Fig. 1. AVS from a salt marsh. The zone that produces the acid volatile sulfides is generally the black material, classically situated just below the sediment–water interface. A plug-in core is pictured as being taken from the sediment and the resultant core section is inset. The surface sediments are typically a brown-red color at least partially including iron (oxy)hydroxides. The black color is conventionally related to metastable iron sulfide minerals such as mackinawite, FeS, and greigite, Fe₃S₄, although, as discussed in the text, these are rarely actually identified. The black AVS zone emits a strong odor of H₂S, indicating that much of the AVS evolved in acid treatment is derived from dissolved S(-II). Even cursory visual examination of the inset core shows a quite complex color structure within the black zone, suggesting the complexity of AVS (photo: courtesy of Chloe Heywood).

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