Acid-volatile sulfide (AVS) — A comment

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Abstract

The review by Rickard and Morse (this volume) adequately summarizes our current understanding with respect to acid-volatile sulfides (AVS). At the same time, this review addresses some of the misunderstandings with regard to measurements and dynamics of this important sedimentary sulfur pool. In this invited commentary, we identify some aspects that deserve more attention in our point of view, in particular with regard to the modeling of iron–sulfur interactions in sediments.

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1. Introduction

Rickard and Morse (this volume) have compiled and digested the available literature on acid-volatile sulfides (AVS), sedimentary sulfur pools that generate gaseous \( \text{H}_2\text{S} \) following addition of 1 N HCl or a related acidification procedure. Undoubtedly, this manuscript will show to be an invaluable resource for sedimentary bio-geochemists interested in the details of sulfur chemistry and mineralogy. The authors clearly communicate and re-iterate the problems with and misunderstandings regarding AVS measurements and its dynamics. Moreover, they advocate the need for a detailed characterization of the compounds contributing to the operational AVS pool. However, we believe that the emphasis on mineralogy and solution chemistry may have introduced some bias in the overview. The plea for detail in inorganic chemistry by Rickard and Morse (this volume) may overshadow more pressing questions in S-cycling. Therefore, in this invited commentary, we would like to focus on the following points:

- Usefulness of the AVS concept
- The role of macrofauna in AVS cycling
- The required complexity of S-cycling models
- Applicability of reaction mechanisms and rate laws
- Importance of dissolved fractions in AVS
- The implications for early diagenetic modeling.

Our viewpoints and arguments may be biased and sometimes diverge from those of Rickard and Morse (this volume), but we do hope that they provide an impetus to further study the dynamics of sedimentary AVS.

2. Operational pools out of the window?

AVS represents the operational pool of sedimentary substances generating \( \text{H}_2\text{S} \) gas upon HCl addition. Rickard and Morse (this volume) systematically review all dissolved, colloidal and particulate compounds that potentially contribute to this operationally defined pool of
reduced sulfur. They pose the question whether “it is not time to simply do away with the AVS concept altogether”. Instead, they strongly advocate dealing more directly with the behavior of the compounds that actually comprise the AVS. While we agree that AVS at present is treated as a black box (their Fig. 24) and that much happens within that box (their Fig. 25), we disagree that we should abandon the concept of operationally defined pools like AVS.

AVS is not the only important operationally defined biogeochemical pool, and a comparable situation occurs in the study of organic carbon. In a very similar way, sedimentary carbon is often partitioned into acid-volatile compounds (AVC, mainly assumed to be carbonates) and non-acid-volatile compounds (NAVC, typically interpreted as organic matter). And equally, this partitioning also has its problems. Firstly, there is the non-100% specificity of the extraction procedure. Some organic carbon is acid-volatile, while conversely, the supposed pool of organic carbon contains significant fractions of elemental, black carbon. Secondly, there is the continuum between dissolved and particulate phases. Rickard and Morse (this volume) have made a strong case concerning the presence of molecular clusters FeS$_{aq}$ and FeS nanoparticles in the pore water. In a very similar way, the distinction between dissolved and particulate organic carbon is also rather fuzzy (Gustafsson and Gschwend, 1997). Nonetheless, despite these well-known limitations, significant progress has been obtained in our understanding of organic carbon cycling using the above operational partitioning of carbon. While certain scientific questions require detailed study of compounds and processes occurring within the AVS black box, some other scientific questions can be addressed at the level of operational pools. And sometimes, because of method limitations, the operational level remains the only level of choice.

Moreover, we note that there could also be a downside to opening the AVS black box: research efforts may be focused on those components for which analytical tools are available. This can divert attention from compounds and processes for which we lack tools, but which may be equally significant. In fact, the comprehensive review by Rickard and Morse provides a nice illustration of “biased” knowledge inside the AVS black box. This knowledge is essentially obtained through research efforts that are constrained by the presently available instrumentation.

3. There is more biology than microbiology

Our knowledge of the sedimentary sulfur cycle is biased toward sulfate reduction and iron sulfide formation at the expense of sulfide oxidation. Jørgensen (1977) elegantly demonstrated that almost all sulfide generated during sulfate reduction is re-oxidized. Berner and Westrich (1985) took this further, and showed that not only sulfide oxidizing bacteria are important to close the cycle, but also bioturbating animals. In the review of Rickard and Morse (this volume), the role of benthic animals is hardly touched upon. Yet macrofaunal activity seems essential in the S-cycle, and many aspects of these complex macrofaunal–geochemical interactions have been little studied so far.

![Fig. 1. Mineral fraction of AVS as a function of total dissolved sulfide (µmol l$^{-1}$). Curves are shown for AVS of 10 µmol g$^{-1}$ and porosities (φ) of 0.6, 0.7, 0.8 and 0.9 and for φ of 0.7 with AVS concentrations of 5, 50 and 100 µmol g$^{-1}$.](image-url)
Burrowing, feeding and relocation of benthic animals results in the displacement and mixing of sediment particles (bioturbation; Meysman et al., 2003a). Since most of the sedimentary AVS is in the particulate form (see Fig. 1), benthic animals are the primary transport agent for AVS. Bioturbation results in the transport of AVS from the site of formation to the site of oxidation and thus is an essential component of the sedimentary AVS cycle (Aller, 1977; Berner and Westrich, 1985). Animal burrows and burrow networks penetrate deeply into the sulfidic zones of sediments. To enable life in an anoxic environment, burrows are oxygenated and well-flushed. This ventilation of burrows results in the removal of dissolved AVS components, while the associated oxygen transfer into deeper layers enhances the oxidation of both dissolved and particular sulfide. In addition, deposit-feeding animals ingest particles while feeding. This has a number of consequences for AVS. Animals may avoid AVS-rich particles, and this particle selectivity may induce heterogeneity and compound-dependent transport properties. Also, AVS-rich particles that are ingested will experience gut conditions that differ from the bulk sediment in many respects, including pH, surfactants and enzymes. The consequences of such particle ingestion by macrofauna on the sedimentary AVS cycle are largely unknown.

4. Modeling sulfur cycling in marine sediments

A crucial aspect of early diagenesis is the strong coupling between different elementary cycles. As a consequence, the sedimentary sulfur cycle cannot be studied in a stand-alone fashion, but must be synchronously assessed with the cycling of carbon, nitrogen, iron and manganese. In terms of modeling, this imposes some significant challenges. Only quite recently, numerical diagenetic models have been developed that fully address the combined C–N–S–Mn–P–Fe cycling in marine sediments (Boudreau, 1996; Van Cappellen and Wang, 1996; Wang and Van Cappellen, 1996; Hunter et al., 1998; Wijsman et al., 2002; Berg et al., 2003; Meysman et al., 2003b; Furukawa et al., 2004). Because each elemental cycle requires at least a couple of key chemical species to be modeled, these models must include at least a minimal set of 20–40 compounds. Additional complexity results from the non-linear reaction kinetics which entail the coupling of cycles, and the strongly divergent time scale of the reactions involved (the problem of numerical “stiffness”). So for a typical one-dimensional grid of 100 depth layers, one requires the solution of a coupled set of 2000–4000 of non-linear, stiff differential equations. By nature, such reactive transport models are notorious consumers of memory and run-time resources, and unfortunately, there is no technical way to work around this intrinsic constraint. As a result, even with the high-performance hardware of today, early diagenetic models must be economical with the numbers of chemical species and the type of reactions that are included in the model formulation.

4.1. How much detail inside the AVS box?

Effectively, the present generation of diagenetic models only includes a simplified scheme of sulfur cycling, which does not “peek” into the AVS box. Even in the most complex model formulation adopted up to present (Van Cappellen and Wang, 1996; Wijsman et al., 2002; Meysman et al., 2003b), there are only three S-species in the pore water (SO$_4^{2-}$, H$_2$S, HS$^-$) and three compounds in the solid phase (S$_0$ representing elemental sulfur, FeS representing a solid iron sulfide, and FeS$_2$ representing pyrite). This representation in current diagenetic models differs rather markedly from the conceptual model for natural sulfidic systems as endorsed by Rickard and Morse (their Fig. 25).

Firstly, the Rickard and Morse model is simpler in the sense that it exclusively focuses on reaction mechanisms governing concentrations of the compounds that constitute AVS. This “box” perspective reveals a certain bias towards laboratory studies of reaction kinetics, and is particularly reflected by the fact that their governing equation set (35)–(44) is specified in terms of ordinary differential equations. In natural sediments, however, concentrations are intrinsically determined by a balance between transport and reaction processes. This leads to the characteristic partial differential form of the equation set used in early diagenetic modeling (Boudreau, 1997). We believe that transport effects could well be an important factor in the dynamics of the AVS concentrations. For example, aqueous FeS$_{aq}$ clusters and FeS nanoparticles will have different (slower) diffusion properties as compared to the compounds HS$^-$ and H$_2$S, which are traditionally considered to make up dissolved fraction of the AVS (d-AVS). So, in environments where these dissolved FeS compounds are important, the apparent transport of d-AVS will be slower than expected.

Secondly, the Rickard and Morse model is far more complex in the sense that many more compounds are included than in the usual early diagenetic formulation. For the solid phase, the Rickard and Morse concept involves a moderate model modification: in addition to mackinawite FeS, they include greigite Fe$_2$S$_4$, but do not consider solid elemental sulfur S$_0$. However, in the pore water, the traditional description which only
includes HS⁻ and H₂S, is greatly expanded to include the complex FeHS⁺, aqueous clusters FeSₐq, nanoparticles FeS, and polysulfides Sₓ⁻.

However, a model is by definition a simplified representation of nature, developed for a certain purpose. So when the purpose is to understand sulfur cycling in sediments, then adding this proposed detail in species composition begs two questions. Given the above economy constraints on the formulation of diagenetic models, a first issue concerns the cost-benefit of such additional complexity. In other words, how much does the addition of an extra sulfur compound improve the overall model quality and predictions? To this end, the model developer needs quantitative data on the importance of the species at hand. Species can be important in terms of absolute concentrations, or in terms of intermediate species in reaction rate mechanisms. In the case of AVS, one can ask how much FeHS⁺, aqueous FeSₐq clusters and FeS nanoparticles contribute to the d-AVS as compared to ΣH₂S? Or equally, why or when should we incorporate greigite or organic sulfur as additional solid phase compounds? In this light, the present review by Morse and Rickard is rather disappointing to modelers looking for clear-cut answers. Hard quantitative information on the importance of all the species inside the extended AVS box (their Fig. 25) is either dug deep or even absent. A second and related issue is that of data availability. Extending the model with new compounds creates additional degrees of freedom within the model, thus requiring more extensive data sets to validate the model formulation. The question then becomes whether such data is readily available or will become available?

4.2. From the beaker to the bay

Over the last decades, laboratory studies have identified new reactions involved in the production and consumption of AVS-related compounds, and the corresponding rate laws have been derived in dedicated kinetic experiments (e.g., Rickard, 1995, 1997). Rickard and Morse (this volume) review this accumulated knowledge in detail, and as a result, advocate the inclusion of these detailed mechanisms in models of sediment geochemistry. Some of these mechanisms have already trickled down into diagenetic models, such as the differentiation between pyrite formation via the H₂S and polysulfide mechanisms (Wijsman et al., 2002; Meysman et al., 2003b). Yet, as discussed above, the usual representation of sulfur cycling is still far less sophisticated as the conceptual scheme proposed by Rickard and Morse (this volume, Fig. 25). So what is hampering the extrapolation of these laboratory results (the “beaker”) to actual sedimentary environments (the “bay”)?

Some answers are readily given by Rickard and Morse (this volume). First of all, for some reactions the mechanism and/or kinetic rate law is presently unknown (e.g. oxidation of mineral FeS, formation of greigite). For some other reactions, the rate law has been elaborated, yet the actual values for the parameters in this rate

Fig. 2. Thickness of sediment water film covering mineral surfaces (µm) as a function of porosity. Calculations have been made for low, intermediate and high specific surface areas (5, 10 and 25 m² g⁻¹, respectively).
law are highly uncertain (e.g. solubility coefficient of mineral FeS and the dissociation constant of FeSaq). However, even when rate law expressions and parameters have been carefully determined in laboratory studies, there is still a huge barrier to overcome, which is hardly touched upon in Rickard and Morse (this volume). A serious quandary in model development is the relevance for the field situation of rate laws and parameters derived from carefully controlled solution experiments. Sedimentary environments are dominated by mineral–water interfaces and any compound (whether truly dissolved, cluster form or nanoparticle) in the interstitial spaces of the sediment is always within reach of a mineral surface. Fig. 2 shows the average thickness of the water layer covering sedimentary particle surfaces as a function of porosity. For a typical porosity of 0.7 and a specific surface area of 10 m² g⁻¹ (Mayer, 1994), there is only 0.7 cm³ of water per 7.8 m² of sediment surface. In other words, an average water film of less than 1 μm covers each mineral surface. While this calculation may be questioned regarding details, it clearly indicates the prominent role of mineral surfaces. Diffusion coefficients for dissolved components are typically 10⁻⁶ cm² s⁻¹ or higher, implying that a dissolved component diffuses in less than a fraction of 1 s to and from a mineral surface. Mineral formation mechanisms and kinetic rate laws in these surface-rich environments may therefore differ from those occurring and studied in aqueous environments in the absence of surfaces. The relative importance of transport processes versus reaction controlling factors is another complication that arises when extrapolating laboratory kinetics to the field. Many reactants diffuse to the site of reaction and this may be the overall rate-limiting step downsizing the importance of mineral precipitation reaction kinetics.

Note that we certainly do not dispute the utmost importance of kinetic studies. Laboratory experiments have provided sedimentary geochemists and diagenetic modelers with essential knowledge regarding the pH dependence of pathways and the identity of reactants and products (e.g. H₂ formation). However, uncovering the reaction mechanisms in the laboratory provides only the first step in our understanding. The translation to the knowledge to heterogeneous, natural sediments seems a daunting task for future research on sedimentary sulfur cycling.

4.3. Fitting AVS data

In the calibration of diagenetic models, AVS data are characteristically incorporated, yet without posing deep questions with regard to the actual AVS extraction procedure. The available AVS data is typically used in a straightforward way to constrain the model profile of a single solid FeS model compound, thus implicitly equalizing AVS to mineral stoichiometric FeS. Rickard and Morse (this volume) refer to this practice of interchanging AVS and mineral FeS as “a dangerous assumption”. Moreover, statements like “aqueous Fe clusters make up a significant fraction of the AVS of many natural aqueous and sedimentary environments...” create the impression that the dissolved fraction (d-AVS) is quantitatively significant in total (t-AVS).

From a quantitative point of view, we feel that Rickard and Morse (this volume) overly dramatize the problem. Firstly, most AVS data are reported from studies where most pore water is removed from the sediment before doing the AVS extraction. Accordingly, the numbers reported approach mineral (m-AVS) concentrations. Secondly, even when the AVS data are obtained by leaching the total sediment, the discrepancy between t-AVS and m-AVS seems less dangerous than acclaimed. While this may be the case for natural waters, it is unlikely that the dissolved fraction contributes significantly to t-AVS in most marine sediments. Fig. 1 shows the fraction of AVS that is in mineral form, as a function of total dissolved sulfide concentration for a characteristic range of marine sediments. A set of curves is represented, varying the porosity φ from low (0.6) to high (0.9), and the total AVS concentration from low (5 μmol g⁻¹) to high (100 μmol g⁻¹). It is only in high-porosity (φ>0.8) and low t-AVS (<10 μmol g⁻¹) conditions, coinciding with high ΣH₂S concentrations (>1 mM), that d-AVS contributes more than a few percent.

Accordingly, the question of AVS not being equal FeS seems to reduce to the solid phase. How much pyrite co-leaches during AVS extraction, and how important is greigite and organic sulfur? While we agree with Rickard and Morse that in situ electrochemical methods (Luther et al., 2001) are one but very promising way to go forward, we strongly believe that a method allowing characterization of solid phase AVS components in situ should be on top of our wish list.

4.4. Mass balance closure in S-models

The basic critique of Rickard and Morse (this volume) with respect to the current generation of diagenetic models is that the present description of
S-cycling is not detailed enough. Additional species should be incorporated inside the AVS-box, and hence, additional formation and consumption reaction mechanisms associated to these compounds should be included as well. Although a pertinent question, one can ask whether there are no other (and perhaps more disturbing) issues concerning the S-cycle in diagenetic models. In this respect, we believe that one important issue has been greatly overlooked. A considerable fraction of the recently published diagenetic models, violate the fundamental constraint of mass balance closure in a rather subtle way. The problem in these models is that the species set for which reactive transport equations are written does not match the set of species that feature in the reaction set. The underlying problem is basically one of a logically consistent model construction, and theoretically, the problem can occur within any elemental cycle. However, in the practice of early diagenetic modeling, the problem has specifically affected the description of the S-cycle. In other words, in some of the recent diagenetic models, the S-cycle is “leaky”, which seriously weakens the conclusions drawn from the corresponding model simulations.

To illustrate the problem, we can write down a stripped-down reaction set of marine early diagenesis, only considering those reactions that involve sulfur species. This reaction set does not consider acid–base effects, and describes a simplified S-cycle in marine sediments. Hydrogen sulfide is generated by sulfate reduction

\[
R_1 : \text{CH}_2\text{CHOH} + 1/2\text{SO}_4^{2-} + \text{H}^+ \rightarrow \text{CO}_2 + 1/2\text{H}_2\text{S} + \text{H}_2\text{O}.
\]

Some of the sulfide is re-oxidized by iron (hydr)oxides generating elemental sulfur

\[
R_2 : \text{FeOOH} + 1/2\text{H}_2\text{S} + \text{H}^+ \rightarrow \text{Fe}^{2+} + 1/2\text{S}_0 + 2\text{H}_2\text{O}.
\]

Furthermore, mineral FeS is formed via the single pathway

\[
R_3 : \text{Fe}^{2+} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}^+.
\]

This mineral FeS may be further transformed into pyrite by two competing mechanisms

\[
R_4 : \text{FeS} + \text{S}_0 \rightarrow \text{FeS}_2
\]

\[
R_5 : \text{FeS} + \text{H}_2\text{S} \rightarrow \text{FeS}_2 + \text{H}_2
\]

Finally, reduced sulfur compounds can be re-oxidized upon contact with oxygen

\[
R_6 : \text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + 2\text{H}^+
\]

\[
R_7 : \text{S}_0 + 3/2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+
\]

\[
R_8 : \text{FeS} + 2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{SO}_4^{2-}
\]

\[
R_9 : \text{FeS}_2 + 7/2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+.
\]

The sulfur cycle in diagenetic models typically includes a subset of the above reactions. Yet, this selection of reactions should be accompanied by an adequate selection of model species to obtain a consistent model formulation. Some diagenetic models are lacking in this regard, and are subject to “mass leakage”. Up to present, two specific types of model formulation have been developed that display such “leakage”. One way is to include reaction R2 which produces elemental sulfur S0, but not incorporate S0 as a model species (e.g. Van Cappellen and Wang, 1996; Wang and Van Cappellen, 1996; Hunter et al., 1998; Furukawa et al., 2004). This way, the model does not follow the concentration of S0, and hence, S0 can accumulate in an unlimited way “outside the model” (without the modeler knowing). Such accumulation of S0 is not realistic for actual sediments. To close the sulfur cycle, one must include a removal mechanism of S0, such as the pyrite formation pathway R4, or the re-oxidation reaction with oxygen R7. Note that the latter re-oxidation reaction consumes oxygen and releases protons. Accordingly, when the model leaks S0, the penetration depth of O2 and the pH calculation can be biased. A leaky sulfur cycle might be one explanation why the pH profiles generated by many early diagenetic model formulations strongly deviate from data. A second “leaky” model formulation is to include the pyrite pathway R5, but not include a diagenetic equation for hydrogen (Wijsman et al., 2002). Similar to S0 in the first case, H2 can now accumulate in an unlimited way outside the model. Such accumulation of H2 is highly unrealistic, as hydrogen is highly reactive and concentrations are typically in the nanomolar range in natural sediments. To close the mass balance, one must include a removal mechanism of H2, e.g. involving it into mineralization reactions of organic matter (for details see Meysman et al., 2003b). Again, the unlimitedly accumulation of H2 outside the model can distort the model predictions. For example, this model artefact explains the discrepancy between the observed penetration depth of O2 and that
predicted by the diagenetic model of Wijsman et al. (2002).

In conclusion, it seems that the diagenetic modeling community should learn how to walk before trying to run. Especially because the landscape of early diagenesis provides some intrinsically rough modeling terrain (many interactions with strong non-linearities and widely different time-scales). The present generation of diagenetic models is still in an early developmental stage, and not enough experience has been built up to consider them routine and robust modeling tools. The modeling community should first develop consistent formulations, and verify and validate the associated model codes, before implementing new, detailed mechanistic knowledge. However, not all the mechanisms and detail that has been elaborated in the laboratory should be downright included in diagenetic models. Experimental scientists need to assess the importance of species and pathways in the overall picture of S-cycling, and convey this information to the modeling community. It is only through interaction and co-operation that modelers learn walking and experimental scientists remain with both feet on the ground.

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