4.1.81

AVS: Myth or reality?

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Acid volatile sulfide (AVS) is an "operationally defined" component of anoxic sediments consisting of the hydrogen sulfide that is evolved from sediment as a result of acidification with HCl. It is a commonly measured form of S(-II) in sediments and is often determined in association with total reduced sulfide (TRS). The most abundant form of S(-II) in most sediments is pyrite and pyrite-S is generally taken to be equal to the TRS – AVS.

AVS has received the most attention as representing a pool of metastable iron sulfide minerals, most notably mackinawite and geigite. In recent years, AVS has also received conisderable attention in attempts to assay the toxicity of metals in sediments where it is held that many metals are not toxic if the concentration of AVS exceeds that of simultaneously extracted metals.

It is becoming increasingly clear that AVS can comprise a wide variety of dissolved, nanoparticulate and solid phase components, and that these potential components can vary in their relative abundance between different sediments and with depth within a given sediment. In some cases AVS may even mainly consist of an acid-soluble fraction of fine grained pyrite. In marine sediments, it is almost always impossible to directly establish the existence of any iron sulfide minerals other than pyrite. Indirect approaches, such as using pore water $Fe(II)$ and ΣH_2S concentrations to calculate apparent saturation states with respect to metastable iron sulfide minerals are fraught with many problems including uncertainties about the solubility of these minerals.

There is an extensive literature which treats AVS as FeS and uses this definition to intepret the distribution of AVS and its role in pyrite formation. Furthermore, the ambiguities in the chemical nature of AVS raise serious questions about whether or not it always represents a reactive pool of S(-II) for precipitation with toxic metals. Clearly a more sophisticated approach to sedimentary sulfides is necessary.

Normally, it is not possible to define with confidence the S(-II) species present in AVS or their relative contribution. Although it can be argued that AVS is a reality since an acid soluble fraction of the sulfide component of sediments does exist, we contend that its utility as a definable and, therefore useful, chemical component of sediments is largely mythological.

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Chemical potentials of dissolved species in marine sediment porewaters

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In the marine sciences, especially in the interpretation of ocean drilling data, diffusion is usually (and conveniently) described by a simple Fick's law of the following form:

$$J_i = -D_i(T) \nabla C_i$$

expression in which J_i is the flux of the diffusing species, ∇C_i its concentration gradient and $D_i(T)$ its temperature-dependent diffusion coefficient. This expression does not recognize the fact that diffusion in electrolyte solutions is a coupled process (ionic diffusion is driven by the concentration gradients of *all* charged species). Moreover, in oceanic sediments, the temperature gradient built up by the cooling of the oceanic crust is superimposed to the concentration gradients of dissolved elements in porewaters. Temperature and concentrations are combined into chemical potentials that are rarely used as individual values, except in linear combinations for the calculation of either ionic products or equilibrium constants. Irreversible thermody-namics places chemical potentials in a central position as the driving force for diffusion. The direct transformation of ionic concentrations into ionic chemical potentials is not possible because ionic chemical potentials are conventional properties with no physical meaning. It is nevertheless possible to write a diffusion equation expressing ionic fluxes as a function of the chemical potential gradients of electrically neutral combinations of cations and anions (i.e. dissolved mean electrolytes), which are thermodynamic (measurable) quantities whose values do not depend on any extra-thermodynamic convention. This meets the concept of "independently diffusing substances" introduced by Haase (1965).

In this work the model of the Na-K-Ca-Mg-Ba-Sr-Cl-SO$_4$-H$_2$O system (Monnin, 1999) elaborated using Pitzer's ion interaction model is thus extended by including consistent values of the standard chemical potentials of dissolved species.

The present approach is developed to study the correlation between temperature and the concentration of a non-reactive species like magnesium in the sediment porewaters of the Eastern flank of the Juan de Fuca ridge.

References

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