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# RELATIVE CONCENTRATION OF SOLID-PHASE SULFIDE SPECIES IN MARINE SEDIMENTS OVERLYING GAS HYDRATE DEPOSITS: RECOGNITION OF THE ROLE OF ANAEROBIC METHANE OXIDATION IN AUTHIGENIC SULFIDE FORMATION

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Sulfide mineralization in marine sediments occurs when dissolved sulfide, produced by sulfate reduction processes, combines with dissolved iron to form iron sulfide minerals. Sulfide can be produced by oxidation of organic matter or by anaerobic methane oxidation (AMO), which involves the co-consumption of sulfate and methane. The latter process seems especially important within gas hydrate terrains like that of the Blake Ridge (offshore southeastern United States), where appreciable amounts of methane diffuse upward to the base of the sulfate reduction zone, or sulfate-methane interface (SMI).

We examine the sediments of two piston cores collected over the Blake Ridge gas hydrate deposits by sequentially extracting the different phases of sulfide minerals: elemental sulfur ( $S^0$ ), iron monosulfides (FeS), “young” pyrite, and “old” pyrite.  $S^0$  and FeS are extracted using dichloromethane and hot stannous chloride solution, respectively. Youthful pyrite is extracted using cold chromic chloride solution, whereas older pyrite is extracted with hot chromic chloride. We use an improved titration procedure to assay for sulfide-sulfur concentration that involves iodometry and back-titration with sodium thiosulfate solution. Our results show concentrations of elemental sulfur and iron monosulfides vary from ~0.02-0.07 weight percent sulfur with no systematic trends with depth. Young pyrite generally increases in concentration downcore from ~0.04 to peak concentrations approaching 0.17 weight percent sulfur at or near the SMI. Old pyrite concentrations are usually less than 0.05 weight percent sulfur, generally less than young pyrite concentration. Assuming that our procedure actually separates different phases of sulfide sulfur, these results seem consistent with localized sulfide production at the SMI where we expect to see an increased fraction of the young pyrite phase as a result of rapid sulfide mineral formation due to AMO occurring there. We can test this interpretation by determining the sulfur isotopic composition of each sulfide phase. We expect to see enrichments of  $^{34}S$  in the youthful pyrite fraction near the SMI.

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