

**STUDY TITLE:** Study of Barite Solubility and the Release of Trace Components to the Marine Environment

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**CONTRACT NUMBER:** 1435-01-03-CT-70000

**SPONSORING OCS REGION:** Gulf of Mexico

**FISCAL YEARS OF PROJECT FUNDING:** 2003; 2004; 2005; 2006; 2007

**COMPLETION DATE OF PROJECT:** December 2007

**COSTS:** FY 2003: \$1,293; 2004: \$170,418; FY 2005: \$36,572; FY 2006: \$6,966; FY 2007: \$754; **CUMULATIVE PROJECT COST:** \$221,633

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**KEY WORDS:** barite; solubility; seawater; barium; mercury; cadmium; trace metals

**BACKGROUND:** The mineral barite (barium sulfate) is frequently used as a weighting agent in drilling fluid and is discharged into the marine environment when no longer needed. Some barite ores contain elevated levels of mercury (Hg), cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), and other trace metals. There is concern that these metals may be released into the marine environment from drilling fluid and cause adverse environmental affects. In 1993 the USEPA established regulations for the maximum concentrations of Hg and Cd in barite ore that is used in drilling fluid in the Gulf of Mexico.

**OBJECTIVES:** The study had three major objectives. The first objective was to identify the location of the trace metals in the barite mineral and determine if the trace metals were primarily associated with small mineral inclusions in the barite matrix. The second objective was to determine the solubility of barium and trace metals in several types of barite exposed to seawater under conditions found in the water column of the outer continental shelf or in shelf sediment. The third objective was to determine the solubility of barium and trace metals from barite as a function of pH to (1) help identify the likely phases that contain the trace metals and (2) provide one analog for assessing metal release from barite as it move through the digestive tract of an organism.

**DESCRIPTION:** Several types of barite were selected for the study and included barite samples that either met the EPA (USEPA 1993) requirements of containing less than 1 ug/g Hg and less than 3 ug/g Cd or exceeded these USEPA requirements for barite that is used in the Gulf of Mexico. The mineralogy of the barite samples was examined using x-ray diffraction, electron and x-ray beam analysis, scanning electron microscopy analysis, and x-ray microprobe analysis. The release of barium and trace metals in seawater was examined over a period of several months. Also the release of metals from barite into sediment pore water was determined over a period of several months under both oxic and anoxic conditions. The release of metals from barite as a function of pH was determined over a range of pH from 2.2 to 6 using a phthalate buffer system and at time intervals of minutes to 48 hours.

**SIGNIFICANT CONCLUSIONS:** Laboratory tests conducted on several fine grained industrial barite samples indicate that mercury and other trace metals are not released in significant quantities into seawater or pore water of marine sediment. Methylmercury concentrations in pore water were very low indicating the mercury in barite is not available for methylation in sediment. The trace metals in barite are located primarily in small sulfide mineral inclusions. The solubility of mercury from barite in acidic solutions was very low with <0.03% of the total mercury leached. However, significant percentages of other trace metals were leached in acidic solutions.

**STUDY RESULTS:** Mineralogical analysis of barite particles identified small inclusions including: quartz, iron oxide, iron sulfide, zinc sulfide, Mn sulfide, silicate minerals, and phosphate minerals. Copper, Pb, and Hg were associated with sulfide mineral inclusions. Mercury and lead were also observed in separate minute inclusions. Cadmium was not detected within any minerals.

The solubility of Ba and selected metals in barite was examined over periods of hours to months under environmental conditions (salinity 30 ppt, temperature 4° and 20°C, pH 7-9, and pressure 14 and 500 psi). At a pH of 7.3, the solubility of Cu, Hg, and Zn was almost double of that at higher pH. Temperature and pressure did not affect the solubility of trace metals. When barite was leached in static seawater for months, several metals (Cd, Cu, Hg, Mn, and Zn) gradually increased over time. Lead did not change significantly after the first 2 hours of contact and Ba decreased over the 6 months of leaching from approximately 35 µg/L to 10 µg/L.

Barite particles were exposed to flowing seawater at pH 8 for 24 hours. The release rate of Cd, Cu, Hg, Pb, and Zn from the particles into the seawater was greatest during the first several hours and after 24 hours, the concentrations of dissolved metals in the flowing seawater were similar to the concentrations found in coastal seawater.

When barite is mixed into oxic surface sediment, the release of metals to the water column and pore water is greatly reduced compared to that from barite alone. Barite dissolves in anoxic sediment resulting in high concentrations of Ba, Fe, and Mn in pore water. However, the anoxic pore water concentrations of Cd, Cu, Pb, Hg, methylmercury, and Zn are well below the USEPA Water Quality Criteria (WQC), presumably due to the formation of insoluble metal sulfides. Methylmercury

concentrations in pore water were very low indicating the Hg in barite is not available for methylation. These results from laboratory experiments are consistent with studies of field samples taken near drilling sites in the GOM where Trefry et al (2003) reported that methylmercury was not elevated in anoxic sediment that contained barite.

The solubility of metals from barite in acidic solutions provides an indication of the bioavailability of metals if barite is ingested by deposit feeding animals. Several metals were relatively insoluble in acidic solutions including Ba, Fe, and Hg with only <0.03%, <2%, and <0.06%, respectively, of the total metal leached. In contrast, Cd, Cu, Pb, and Zn were relatively soluble with as much as 100%, 45%, 8%, and 35% respectively, of the total metal leached at pH 2.2. The correlation between the concentrations of these four metals in the leachates suggests these metals were present as a zinc phase such as sphalerite.

**STUDY PRODUCTS:** Battelle. 2007. Study of barite solubility and the release of trace components to the marine environment. A final report for the U.S. Dept of Interior, Minerals Management Service Gulf of Mexico Region. OCS Study MMS 2007-061. Contract No. 1435-01-03-CT-70000. 161 pp.

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