

## Formation of modern and Paleozoic stratiform barite at cold methane seeps on continental margins: Comment and Reply

### COMMENT

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The proposal of Torres et al. (2003), that Paleozoic barite deposits in Nevada, Arkansas, and China formed at cold seafloor methane seeps, is an important addition to the large literature on the genesis of bedded barite. However, we would like to point out that Torres et al. use flawed criteria to exclude a hydrothermal origin for these and other barite deposits, and as a consequence, their larger conclusions are open to question. The diagnostic criteria set forth for hydrothermal barite are: (1) Sr that is less radiogenic than contemporaneous seawater Sr, (2)  $\delta^{34}\text{S}$  values within 2‰ of contemporaneous seawater sulfate, and (3) associated polymetallic sulfide deposits. These criteria take into account spreading-ridge hydrothermal systems that can deposit barite in association with volcanogenic massive sulfide deposits of Zn, Cu, and Pb. They do not apply to sedimentary-exhalative hydrothermal systems that can form both bedded barite deposits and the sediment-hosted massive sulfide deposits of Zn, Pb, and Ag ( $\pm$ barite) that account for the bulk of the world's known Zn and Pb reserves. Whereas spreading-ridge hydrothermal systems arise from seawater convection through hot volcanic rocks, sedimentary-exhalative hydrothermal systems arise from the ascent of basinal brines through sedimentary sequences into intracratonic or continental margin seas. There are barite deposits throughout the world that are clearly products of sedimentary-exhalative hydrothermal systems and show none of the criteria set forth by Torres et al. as diagnostic of a hydrothermal origin. To cite just a few examples, at Jason and Tom in western Canada, at Meggen and Rammelsberg in Germany, and at Red Dog in northwest Alaska, barite occurs both intergrown with sulfide minerals and as barite-only deposits above or lateral to massive sulfide bodies. At all these localities, the barite contains Sr that is more radiogenic than contemporaneous seawater Sr (Turner, 1991; Maynard et al., 1995; Ayuso et al., 2000) reflecting scavenging of Sr and other elements from continental detritus in underlying sediments. The barites do not show  $\delta^{34}\text{S}$  values within 2‰ of contemporaneous seawater sulfate, but rather can extend up to 30‰ higher (Goodfellow et al., 1993; Johnson et al., 2003). Barite-only deposits occur not only in close association with sulfide deposits but also far removed from them (tens of km), although commonly at the same stratigraphic horizons (e.g., Lydon et al., 1979).

We agree with Torres et al. that the presence of polymetallic sulfide deposits supports a hydrothermal origin for associated barite, but it is important to note that the absence of sulfides does not preclude a hydrothermal origin. Whether a hydrothermal fluid precipitates base metals, barium, or both can depend on the redox chemistry of the fluid (Lydon et al., 1979; Emsbo, 2000). Barite is more soluble in reduced fluids with low concentrations of sulfate, whereas base metals are only soluble in oxidized fluids with low concentrations of  $\text{H}_2\text{S}$ . Thus, barite-only deposits are to be expected not only at cold seeps, as pointed out by Torres et al., but also at sites where hot,  $\text{H}_2\text{S}$ -stable fluids are vented. We would also like to point out that methane venting is by no means restricted to cold seeps as Torres et al. seem to imply. Hydrothermal methane is known to be venting today on the modern seafloor (e.g., Simoneit et al., 1988; Canet et al., 2003), and methane expulsion is known to have been a key element of the sedimentary-exhalative hydrothermal system that formed the Red Dog sulfide + barite deposits (Johnson et al., 2003), which contains the largest zinc and barite resource ever discovered.

We believe that use of the hydrothermal-barite definition proposed by Torres et al. obscures relationships between hydrocarbon and brine-expulsion events and the thermal evolution of ancient basins. Our own work on this problem has led to the important discovery (Emsbo et al., 1999; Emsbo, 2000) that the Nevada barite belt, long considered a typical example of metal-free barite occurrences (e.g., Torres et al., 2003), also contains barite deposits that carry significant gold. As for the modern seafloor, we are intrigued by the Peru margin barite locality because it contains strikingly radiogenic Sr (Torres et al., 2003). This suggests to us an exciting possibility, namely that this locality may be the surface expression of deep-seated fluids (cf. Aquilina et al., 1997) that represent a nascent sedimentary-exhalative hydrothermal system.

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### REPLY

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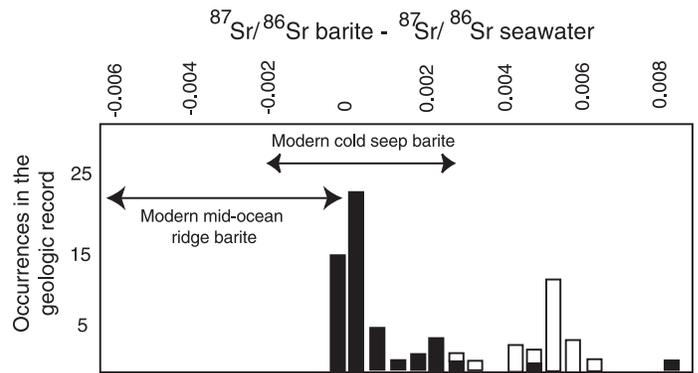
Maynard and Okita (1991) divided ancient bedded barite deposits into two major types: (1) continental margin type, which lacks significant accumulations of base metals, such as the Nevada and Arkansas deposits; and (2) cratonic rift type, which contains significant Pb and Zn, such as the Meggen and Rammelsberg deposits in Germany, and Jason and Tom deposits in Canada. The tectonic setting of the second type should be broadly interpreted and may include outer miogeoclinal and marginal embayment settings, with a continental affinity, and commonly with more carbonates in the section than the continental margin-type deposits. Some localities with base-metal-rich deposits also contain distant barite-only occurrences at similar stratigraphic horizons.

The proposed tectonic settings for the “metal-bearing” and “metal-barren” deposits of Maynard and Okita (1991) were also shown to correlate with the strontium isotopic composition of the barite, as illustrated in Figure 1 (modified from Maynard et al., 1995). This figure also compares these Paleozoic deposits to two classes of modern barites. Strontium values for cratonic-type deposits are all significantly more radiogenic than seawater, while values for continental margin-type deposits coincide closely with modern cold seep barites.

Our postulated mechanism at cold seep sites was not intended to address the cratonic-type barite deposits or any districts that contain significant base metals. Our model pertains exclusively to continental margin-type, metal-barren barites such as those in Nevada and Arkansas, United States, in Sonora, Mexico, and in some Chinese deposits, as stated in our paper.

Among the previously postulated genetic mechanisms for continental margin-type barite was precipitation at or near sediment-covered oceanic ridges in hydrothermal vents; thus the criteria presented in our paper specifically addressed oceanic spreading systems. The range of isotopic composition measured in barite formed at modern oceanic spreading systems includes samples collected at white smokers, black smokers and sedimented ridges, all of which have clear nonradiogenic Sr isotope signatures (Figure 1, data from Paytan et al., 2002). Nevertheless, we agree with Emsbo and Johnson (2004) that by calling the barite precipitated at modern spreading ridges “hydrothermal barite,” we applied a usage of this term that is too limited, because ancient sedimentary-exhalative (cratonic-type) systems are also hydrothermal. There are no appropriate modern analogues to ancient sedimentary-exhalative cratonic hydrothermal deposits, and our comparisons of Paleozoic barren barite were made solely to modern well-documented examples. Thus our hydrothermal barite example is for modern ridge exhalative barites, which in no way changes the conclusions of our paper.

Emsbo and Johnson (2004) state that some Nevada barites are not metal-free and have been found to contain gold; we emphasize that these deposits do contain modest amounts of Fe and lesser Mn, but trivial amounts of Zn, Pb, and Ag. We further believe that the Sr isotopic signal of the Nevada deposits clearly eliminates a cratonic-type sedimentary-



**Figure 1.**  $^{87}\text{Sr}/^{86}\text{Sr}$  composition of barite expressed as difference from coeval seawater (redrawn from Maynard et al., 1995). Data differentiate barites originating in continental margin setting (black bars) from more radiogenic cratonic-type samples (white bars). Isotopic composition ranges of modern cold seep and oceanic ridge barite (Paytan et al., 2002) are also shown.

exhalative origin (Maynard et al., 1995), and that their lithologic and depositional framework supports a cold seep origin for these deposits (Torres et al., 2003). Emsbo and Johnson also suggest that modern cold seeps on the Peru margin may represent the expression of a “nascent sedimentary-exhalative hydrothermal system.” In the case of Peru, the radiogenic Sr data indeed reflect deep-seated fluids, but the cold seep waters are not associated with any recognized nascent hydrothermal activity or a sedimentary-exhalative tectonic setting (e.g., Kukowski and Pecher, 1999, and references therein). Instead, the radiogenic Sr results from fluid flow over a continental basement, transport through the accretionary margin sediment, and cold discharge at the seafloor, as discussed by Torres et al. (1996).

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