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Alkali elements (Na, K, Rb) and alkaline earth elements (Mg, Ca, Sr, Ba) in the anoxic brine of Orca Basin, northern Gulf of Mexico

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Abstract

A profile of filtered seawater and brine samples was collected in the summer of 2003 from a depth of 1500 m down to the bottom of the anoxic, hypersaline Orca Basin (northern Gulf of Mexico). Using ion chromatography and inductively coupled plasma mass spectrometry (ICP-MS), these samples were analyzed for alkali cations (Na^+, K^+, Rb^+), alkaline earth cations (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}), and the major anions chloride (Cl^-) and sulfate (SO_4^{2-}). Major ion concentrations in the brine are consistent with previous studies, confirming that Na plus Cl make up more than 95% of its composition, hence governing its density and hydrodynamic stability. Binary mixing plots across the interface between deep Gulf of Mexico seawater and the anoxic brine are generally linear, but display substantial deviations from conservative behavior at the steepest part of the pycnocline for all analytes except Na, Cl, and Ca. Negative deviations signify localized cation removal by an adsorption or ion-exchange process, probably associated with the dense layers of particles that are trapped there. Especially strong Mg removal may be indicative of dolomitization, whereby the concomitant release of Ca counters its adsorption, resulting in zero net Ca removal. A positive deviation for sulfate is attributed to bacterial sulfide oxidation.

Concentrations of Rb, Sr, and Ba in the homogeneous brine, reported here for the first time, are enriched by factors of 1.5, 1.4, and ~9, respectively, with respect to the overlying seawater. Unlike Ca and Sr, Ba concentrations in the brine are clearly controlled by the solubility of its sulfate salt (barite), causing a maximum of 670 nmol/kg at the interface. Several independent lines of evidence suggest that the brine is formed outside the basin, most likely by the interaction of seawater with regionally extensive evaporite deposits. A simple mass balance shows that the dissolution of about 280 g of halite per kg of seawater can account for the extreme concentrations of Na and Cl in the Orca Basin brine. The same mass balance was applied to a number of minor constituents (K, Rb, Mg, Ca, Sr, SO_4, Br, total iodine) in order to calculate what abundances in the halite are required to reproduce their concentrations in the brine as measured in the present work and by others. The results are entirely compatible with the composition of the Jurassic Louann Salt, specifically with the median of compositions published for a transect spanning early to late stage halites. Elevated abundances of K and Rb point to contributions from bittern facies modified by prior diagenetic contact with seawater.

Keywords: Orca Basin; Hypersaline; Anoxic; Alkali elements; Alkaline earth elements; Evaporite

1. Introduction

Submarine anoxic brine pools are undoubtedly among the most chemically exotic oceanic environments

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known. They are created by processes that deform the seafloor, exposing ancient evaporite deposits to ambient seawater and simultaneously excavating a deep basin to hold the resulting hypersaline solution. Such a coincidence of circumstances is rare and has only been encountered and studied in a handful of locations, including geothermal brines in the Red Sea (Swallow and Crease, 1965; Backer and Schoell, 1972), the cold brines of the Tyro, Bannock, Urania, L'Atalante, and Discovery Basins in the eastern Mediterranean Sea (Jongsma et al., 1983; Scientific staff of Cruise *Bannock* 1984-12, 1985; MEDRIFF Consortium, 1995), and the solitary cold brine of the Orca Basin in the northern Gulf of Mexico (Shokes et al., 1977).

The extreme salinity of these brines gives rise to a pronounced density gradient, or pycnocline, severely restricting the free exchange of water and solutes across the interface with the overlying seawater (de Lange et al., 1990c). As biogenic particles continue to rain onto the brine from the euphotic zone, organic matter is bacterially remineralized, causing depletion of oxygen followed by a gradual build-up of dissolved sulfide. Because of the tremendous hydrodynamic stability and consequent longevity of such a system, this process eventually renders the brine fully anoxic. The concomitant shift in redox potential converts many elements to their most reduced, often more soluble forms. The brines are therefore typically highly enriched in dissolved iron and manganese (Brewer and Spencer, 1969; Trefry et al., 1984) as well as in various trace metals that readily adsorb onto reactive iron and manganese oxyhydroxide surfaces but are released as these carriers reductively decompose in the anoxic water (Schijf et al., 1995). In addition, the concentrations of certain elements may be buffered by the solubility of precipitates whose formation in the open ocean is thermodynamically or kinetically unfavorable, namely transition metal sulfides (Saager et al., 1993), alkaline earth sulfates (Krumgalz et al., 1999), and dolomite (de Lange et al., 1990a). This exceptional array of physical and chemical processes also affects the underlying sediments, which may be characterized by intricate lamination due to the absence of bioturbation and bottom currents, prolonged preservation of microfossils and plant debris (Sheu and Presley, 1986b), elevated contents of organic matter and iron sulfides (the latter imparting a distinctive jet-black color), or the conspicuous presence of normally uncommon minerals like gypsum (Scientific staff of Cruise *Bannock* 1984-12, 1985) and hematite (Sheu and Presley, 1986a).

The Orca Basin, discovered in 1975–76, is located on the continental slope of the northern Gulf of Mexico, centered at 26°55′ N 91°20′ W (Shokes et al., 1977). Whereas similar intraslope depressions are found throughout this area of active salt diapirism, Orca Basin appears to be the only one that contains anoxic brine (Trabant and Presley, 1978). The brine pool, with an estimated total volume of ~5 km^3, only partially fills the basin which covers about 400 km^2. Orca Basin is roughly J-shaped, consisting of two interconnected sub-basins separated by a saddle, a small one to the north and a much larger one to the south. Maximum depth in each of the two sub-basins is at least 2400 m. The vertical extent of the brine layer at these deepest points is approximately 200 m. Based on ^{14}C dating of a sudden transition from gray sediments (assumed to have been deposited in an oxygenated environment) to black ones in a long piston core taken near the center of the saddle, Addy and Behrens (1980) put the beginning of brine emplacement around 8000 years BP. Downward decreasing salinity in the sediment pore waters indicates that the brine did not originate beneath the Orca Basin, but was introduced from somewhere outside. This was confirmed by seismic evidence for salt exposure on the seafloor to the north and southeast (Addy and Behrens, 1980) and by the discovery of a 'brine river', flowing into Orca Basin from the upper slope (Brooks et al., 1990). Addy and Behrens (1980) noted that the level of the brine is below the sill and that accumulation may thus be ongoing. Geochemical studies of the Orca Basin have shown that the composition of the brine with respect to a number of components (Na^+, Cl^-, Br^-, SO_4^{2-}, Ar) is compatible with the dissolution, in ambient seawater, of ~300 g/L of halite from a regionally extensive evaporite deposit known as the Louann Salt (Sheu, 1990).

In this work I present data from a new series of filtered water samples that were collected in the summer of 2003 and span the complete transition from deep Gulf of Mexico seawater to homogeneous brine at high resolution. Precise measurements of major ion concentrations by ion chromatography confirm the dominance of Na plus Cl in the brine and their effect on its physical properties. The use of inductively coupled plasma mass spectrometry (ICP-MS) enabled the first reported analyses of Rb, Sr, and Ba. Simple mass balances, binary mixing plots, and solubility calculations are employed to investigate the source of the brine, while striving to explain observed deviations from conservative behavior at the seawater–brine interface in terms of redox–chemical processes, enhanced scavenging within the dense layers of particles trapped by the pycnocline, and the potential precipitation of alkaline earth sulfates (barite) and carbonates (dolomite) occurring both at the interface and within the brine itself.