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LETTER REPORT

TITLE: Review of "The geochemistry of Ca, Sr, Ba and Ra sulfates in some deep brines from the Palo Duro Basin, Texas," D. Langmuir & D. Melchior, Geochim. Cosmochim. Acta 49, 2423-2432, 1985.

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The subject paper presents the chemical composition (Na, K, Ca, Mg, Sr, Ba, Ra, Cl, SO<sub>4</sub>, Br and pH) of five brines from the Wolfcamp Formation (carbonate) and granite wash facies of the Palo Duro Basin, Texas. The authors evaluate the solubility data for gypsum, anhydrite, celestite, barite and RaSO<sub>4</sub> at the temperature (32-40°C), pressure (67-130 bars) and ionic strength (2.9-4.8m) of the brines. Their treatment involves the use of the Pitzer equations and comparison to available solubility data. The purpose of the study is to evaluate solubility controls on the alkaline earths, focusing mainly on radium and strontium. These waters are located stratigraphically below the lower San Andres Formation which is the candidate horizon for a high-level waste repository in Deaf Smith County, Texas. If leakage were to occur from the waste package it may contact these fluids. The authors examine the mineral saturation indices for Ca, Sr, Ba and Ra sulfates to determine if solubility controls exist. They also examine the possibility of adsorption and solid solution as removal processes for radium.

As there is little thermodynamic data for RaSO<sub>4</sub> the authors make well-justified assumptions for calculating its solubility product as well as its distribution coefficient in the phases barite, celestite and anhydrite and the distribution coefficient of RaCO<sub>3</sub> in aragonite and calcite.

Their calculations show RaSO<sub>4</sub> to be 5-6 orders of magnitude undersaturated in all 5 brines while gypsum, anhydrite and celestite are saturated in all of them and barite is saturated in 3 of the 5. These results imply that while Ca, Sr and Ba are solubility controlled, radium in these solutions is not solubility controlled by RaSO<sub>4</sub>, which is the least soluble radium phase. The absence of any of these sulfates in drill cores (except for anhydrite in one case) suggests that the fluids acquired their composition while passing through another part of the

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section. Radium control by adsorption is unlikely as  $^{226}\text{Ra}$  is in secular equilibrium with  $^{222}\text{Rn}$  and  $^{228}\text{Ra}$  is in secular equilibrium with  $^{224}\text{Ra}$ .

The distribution coefficients for the solid solution calculations are dependent on temperature and the mole fraction incorporated in the solid is also dependent on the solution activities of  $\text{Ra}^{2+}$  and  $\text{M}^{2+}$ . The authors provide one example of this calculation for the brine from Sawyer #1, Zone 5 demonstrating that radium is incorporated most strongly in barite, then celestite. I have calculated the logarithm of the mole fraction of radium in the considered phases in all 5 sampled brines to demonstrate that although the relative importance of the phases remains unchanged, the absolute amount of Ra which can be incorporated is dependent on the individual solution chemistries and temperatures (see Table 1).

Table 1: Log Mole Fraction of Radium

	Sawyer #1 Zone 5	Sawyer #1 Zone 4	Mansfield #1 Zone 1	Mansfield #1 Zone 2	Zeeck #1 Zone 3
barite	-4.99	-6.67	-5.45	-5.96	-4.33
celestite	-6.66	-7.66	-7.02	-7.11	-6.79
anhydrite	-8.03	-9.21	-8.91	-9.02	-8.50
aragonite	-10.81	-11.86	-11.52	-11.66	-11.16
calcite	-10.88	-11.93	-11.59	-11.73	-11.23
T °C	32	38	40	39	38

The authors suggest that solid solution is the controlling mechanism for the concentration of radium in the solutions. Although this cannot at present be proven, it is a reasonable explanation. Solubility and adsorption controls can be eliminated; an additional explanation for the levels is that there is too little radium available from the rocks to be dissolved into the solutions. The authors point out that since anhydrite (and celestite to a lesser degree) has retrograde solubility above  $\sim 50^\circ\text{C}$  it may form near the waste package, which will lower the sulfate concentration in the fluids and may result in decreased precipitation of barite, etc. in the far field. Since barite incorporates much more radium than anhydrite, near field precipitation may allow a larger amount of radium and strontium to remain in solution and to be transported. This scenario would only be important if the fluids around the waste package were similar to those in the lower Wolfcamp Formation (i.e. high sulfate) and if these fluids remained quantitatively important when they mixed with the Wolfcamp fluids, resulting in a significantly lower total sulfate concentration in the final solutions.