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FINAL TECHNICAL REPORT

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by

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DISCLAIMER

SUMMARY OF DOE RESEARCH

Our DOE–sponsored research from 9/1/85 to 1/31/88 resulted in four journal papers published or in press, three journal papers in review, fourteen abstracts, one invited Penrose Conference presentation, one completed thesis, and two theses in preparation. Copies of selected journal papers are included as an Appendix to this report.

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Our studies involved petrographic, fluid inclusion, geochemical and stable isotopic studies of drillcores and fluids from the Salton Sea geothermal system. The SSSDP well State 2–14 (S2–14) was completed on March 17, 1986 and in December we began to analyze samples from this well. About this time we also received drillcores and cuttings from commercial wells completed as part of a Magma Power Co./Dow Chemical Co. drilling program. We also have systematically sampled fluids produced from these wells during flow–testing.

Our initial studies revealed the presence of previously–unrecognized evaporitic anhydrite at depth throughout the geothermal system (McKibben et al., 1988b; Osborn et al., 1988). The high salinity of the Salton Sea geothermal brines previously had been attributed to low–temperature dissolution of surficial evaporitic deposits by meteoric waters. Our microthermometric studies of halite–containing fluid inclusions in the meta–evaporites indicated that the high salinity of the geothermal brines is derived in part from the hydrothermal metamorphism of relatively deeply–buried salt and evaporites. This discovery places constraints on fluid–flow models of the SSGS, as brines are generated partly in situ and need not have migrated great distances.

The next phase of our research concentrated on mineralized fractures in drillcores from the SSSDP well S2–14 (McKibben et al., 1988a). Our mineral assemblage and fluid inclusion data demonstrate the presence of two mineralized fracture systems in the SSGS: an older carbonate–sulfide vein set deposited at higher temperatures and a modern silicate–oxide vein set deposited at present measured downhole temperatures. The fluid inclusion data from the veins record an apparent rapid increase in salinity in the geothermal system at 1–2 km depth, where an interface between two fluid types was inferred to be present based on independent well production data. Therefore, the abundance of modern ore mineralization at 1–2 km depth in the SSGS must be caused by mixing between the two fluid types. We have consequently developed a model for ore mineralization involving heating and upwelling of deep hypersaline brines, with mineralization occurring at the brine interface (McKibben et al., 1987, 1988a). This model has practical applications to commercial development of the SSGS, because it predicts the distribution and salinity of reservoir brines and places constraints on heat and mass flow models (Williams and McKibben, in review).

The results of our sulfur isotopic studies have been submitted to the American Journal of Science (McKibben and Eldridge, in review). We completed a comprehensive study of S isotopic variations among sedimentary host–rock minerals, sulfides in igneous rocks, hydrothermal vein minerals, and aqueous S species in the Salton Sea geothermal system. The original biogenic S isotopic fractionation between SO_4 and H_2S, recorded by $\delta^{34}S$ values of intergrown diagenetic sulfates and sulfides, has been preserved during rapid burial and metamorphism of the Pleistocene deltaic–lacustrine host sediments to lower amphibolite facies conditions. This implies that biogenic S isotopic values may be similarly preserved in metamorphosed sediment–hosted ore deposits.

We observed very dramatic microscopic S isotopic variations within and among sedimentary and hydrothermal minerals. In stratiform sulfides, $\delta^{34}S$ varies by as much as 45 permil over distances of only 0.4 mm, reflecting intimate intergrowths of early diagenetic ($\simeq$–40 permil), late diagenetic ($\simeq$–10 permil) and hydrothermal ($\simeq$0 permil) pyrite generations. The two diagenetic pyrite generations record a transition from open– to closed–system biogenic SO_4 reduction in unconsolidated sediments prior to burial; texturally they might be misinterpreted as recrystallization overgrowths formed during burial metamorphism.

In hydrothermal veins, chalcopyrite crystals are zoned in $\delta^{34}S$ by up to 10 permil over distances of 1 mm, likely recording fractionation caused by sulfide precipitation from fluids with high metal/sulfur ratios. Although vein sulfides intimately envelop sedimentary sulfides in the host rocks, their distinct $\delta^{3}S$ values indicate that, surprisingly, the metal–rich, sulfur–poor hydrothermal fluids do <u>not</u> recycle the sedimentary S. These observations cast doubt on some prevailing theories about the importance of host–rock sulfides in supplying reduced sulfur for ore mineralization from sulfur–poor fluids.

We also determined $\delta^{34}S$ for H_2S and SO_4 in geothermal fluids sampled during well flow–tests. In the deep hypersaline brines, H_2S ($\simeq$0 permil) and SO_4 ($\simeq$20 permil) are in dilute solution S isotopic equilibrium at 300°C, indicating that salinity effects on isotopic fractionation are negligible under these conditions. $\delta^{34}S$ for total fluid S is equal to the mean $\delta^{34}S$ value of stratiform evaporitic anhydrite in the host sediments ($\simeq$10 permil). These observations indicate that H_2S is generated by partial ($\simeq$ 50 %) hydrothermal reduction of evaporitic SO_4, probably by interaction with Fe^{2+} in the reduced, metal–rich brines. This situation represents a valuable active analog of processes thought to be responsible for ore deposition in many hydrothermal ore deposits.

Although vein sulfide $\delta^{34}S$ values cluster near 0 permil, there is little or no magmatic contribution of S to ore formation in the Salton Sea geothermal system. Altered diabase sills at 3 km depth are overprinted by at least two hydrothermal sulfide–depositing events.

Few experimental data exist to evaluate the speciation and thermodynamics of metal chloride complexes in saline fluids at elevated temperatures appropriate for the SSGS. Therefore, it is necessary to determine such information empirically. Our database from the Salton Sea geothermal system includes a series of 44 nearly isothermal ($\simeq$300°C) Na–Ca–K–Cl brine analyses covering a range of total chloride concentrations from 3–6 molal (Williams and McKibben, in review). In such brines only 4–9 water molecules exist per ion, and the low dielectric constant of water further reduces the degree of ionization. Consequently, the predominant metal chloride species in these brines should be neutral or high ligand number chloride complexes.

Published thermodynamic data on alkali chloride solutions indicate that activity coefficients remain relatively constant at high salinities at elevated temperatures. Therefore, isothermal plots of log total metal molality versus log total chloride molality will yield slopes corresponding to the mean ligand number of the metal chloride complexes, assuming that a single mineral controls a given metal's solubility and that pH and mH_2S remain relatively constant over the salinity range.

From such plots we have determined the mean ligand numbers for several metal chloride complexes in the Salton Sea brines (McKibben et al., in review). For Zn, our data yield a mean ligand number of 2.1 (Figure 6), in excellent agreement with lower–salinity experimental data. Similar determinations for all base metals indicate that the dominant chloride complexes are: $PbCl_3^-$, $ZnCl_2^0$, $CdCl_2^0$, $CuCl_3^{2-}$, and $MnCl_2^0$. Fe data are complicated by the presence of both Fe^{2+} and Fe^{3+} in the brines, yielding a mean ligand number of 4.4. This implies that Fe is carried by mixtures of $FeCl_4^-$ and $FeCl_5^-$ complexes. These empirical speciation data allow more accurate calculation of metal sulfide solubilities in the SSGS brines, with obvious applications to scaling problems.

List of publications sponsored by grant DE–FG03–85ER13408

JOURNAL PAPERS

McKibben, M. A., Williams, A. E., Elders, W. A., Eldridge, C. S., (1987) Saline brines and metallogenesis in a sediment–filled rift: the Salton Sea geothermal system, California, U.S.A. Applied Geochemistry, Vol. 2, p. 563–578. (Invited paper)

McKibben, M. A., Andes, J. P., Jr., Williams, A. E., (1988a) Active ore–formation at a brine interface in metamorphosed deltaic–lacustrine sediments: the Salton Sea geothermal system, California. Economic Geology, Vol. 83, No. 3. In press, accepted December 1987.

McKibben, M. A., Williams, A. E., Okubo, S. (1988b) Metamorphosed Plio–Pleistocene evaporites and the origins of hypersaline brines in the Salton Sea geothermal system, California: fluid inclusion evidence. Geochimica et Cosmochimica Acta, Vol. 52, p. 1047–1056.

Charles, R. W., Janecky, D. R., Goff, F., McKibben, M. A., (1988) Chemographic and thermodynamic analysis of the paragenesis of the major phases in the vicinity of the 6120 ft (1866 m) flow–zone, California State well 2–14; Journal of Geophysical Research, Vol. 93. In press, accepted March, 1988.

Williams, A. E., and McKibben, M. A., A brine interface in the Salton Sea geothermal system, California: fluid geochemical and isotopic distribution. In review, Geochimica et Cosmochimica Acta. Submitted May, 1988.

McKibben, M. A., and Eldridge, C. S., Sulfur isotopic variations among minerals and aqueous S species in the Salton Sea geothermal system: a SHRIMP ion microprobe and conventional study. In review, American Journal of Science. Submitted May, 1988.

McKibben, M. A., Eldridge, C. S., and Williams, A. E., Sulfur and Base metal transport in the Salton Sea geothermal brines. In review, Geothermal Resources Council Transactions. Submitted June, 1988.

THESES

Andes, J. P. Jr., Mineralogic and fluid inclusion study of ore–mineralized fractures in drillhole State 2–14, Salton Sea Scientific Drilling Project, California, U.S.A. U. C. Riverside, December 1987.

Osborn, W. L., Mineralogy, genesis and metamorphism of non–marine evaporites in the host rocks of the Salton Sea geothermal system; Thesis, U. C. Riverside, September 1988.

Gonzalez, C. M., Chemical and thermal history of MoS_2–mineralized fractures in the VC–2a drillcore, Valles Caldera, New Mexico. U. C. Riverside, December, 1988.

ABSTRACTS

McKibben, M. A., Williams, A. E., Andes, J. P. Jr., Oakes, C. S., Elders, W. A. (1986) Metamorphosed Plio–Pleistocene evaporites in the Salton Sea geothermal system, Salton Trough rift, California; Geol. Soc. Am. Abstr. with Progr., V. 18, p. 690.

McKibben, M. A., Elders, W. A., Williams, A. E., Eldridge, S. S. (1986) Metamorphosed Plio–Pleistocene Evaporites and the origins of salinity and sulfur in the Salton Sea geothermal system; EOS, v. 67, p. 1258.

Andes, J. P. Jr., McKibben. M. A. (1987) Thermal and chemical history of mineralized fractures in cores from the Salton Sea Scientific Drilling Project; EOS, v. 68, p. 439.

McKibben, M. A. (1987) Fluid inclusions in metamorphosed Plio–Pleistocene evaporites from the Salton Sea geothermal system, Salton Trough rift zone, California. Proceedings, American Current Research on Fluid Inclusions (ACROFI), Socorro, New Mexico, 3 p.

McKibben, M. A., Andes, J. P. Jr., Williams, A. E. (1987) Ore–forming processes in the Salton Sea geothermal system, California: new insights from the SSSDP cores; Geol. Soc. Amer., Abstr. with Progr., v. 19, p. 766.

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Eldridge, C. S., McKibben, M. A. (1988) Sulfur isotope systematics and ore genesis in the Salton Sea geothermal system; Geol. Soc. Amer., Abstr. with Progr., Vol. 20 (submitted).

Osborn, W. L., McKibben, M. A., Williams, A. E. (1988) Formation, diagenesis and metamorphism of lacustrine sulfates under high geothermal gradients in an active continental rift zone; Geol. Soc. Amer., Abstr. with Progr., Vol. 20 (submitted).

McKibben, M. A., Williams, A. E. (1988) Metal chloride speciation in saline hydrothermal fluids; Geol. Soc. Amer., Abstr. with Progr., Vol. 20 (submitted).

McKibben, M. A., Eldridge, C. S. (1989) Sulfur isotope systematics and ore genesis in sediment–hosted geothermal systems; Soc. Econ. Geol., Fall Mtg., Symposium on Hydrothermal Fluids, Abstracts with Program, (submitted).

Williams, A. E., McKibben, M. A. (1989) Geochemistry of hydrothermal fluids in sediment–hosted geothermal systems; Soc. Econ. Geol., Fall Mtg., Symposium on Hydrothermal Fluids, Abstracts with Program, (submitted).

APPENDIX

Selected journal papers sponsored by grant DE–FG03–85ER13408.

McKibben, M. A., Williams, A. E., Elders, W. A., Eldridge, C. S., (1987) Saline brines and metallogenesis in a sediment–filled rift: the Salton Sea geothermal system, California, U.S.A. Applied Geochemistry, Vol. 2, p. 563–578.

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McKibben, M. A., Eldridge, C. S., and Williams, A. E., Sulfur and Base metal transport in the Salton Sea geothermal brines. In review, Geothermal Resources Council Transactions. Submitted June, 1988.