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MICROSTRUCTURAL INTERACTIONS OF GEOLOGIC MEDIA WITH WASTE RADIONUCLIDES

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A preliminary investigation of the microstructure of four geologic media was undertaken to examine the interaction of Cs, Sr, Gd and U with those media. Since K_D measurements often vary by more than an order of magnitude on rocks of the same strata separated by several feet, it was probable that minor rock components play an important role in radionuclide sorption. A qualitative analysis of the rock surfaces after equilibration with solutions of Cs^+ , Sr^{++} , Gd^{+++} and UO_2^{++} revealed that clay minerals are responsible for all important sorption that takes place on the rocks studied (Magenta dolomite, Bell Canyon silt stone, Eleana shale and clay bearing halite). Thus it is concluded that a relatively small portion of these rocks is actively responsible for sorption characteristics. Gd was bound on all samples, probably as Fe bearing chlorites. Cs was strongly held on the Eleana shale, probably by an illite. Although uranium was associated with an unidentified clay in the halite sample, uranium sorption probably occurred as UO_2CO_3 , which would not significantly retard uranium movement at trace concentrations. Similarly Sr was retained only as $SrSO_4$ on Magenta and this mechanism is not significant at trace levels. These analyses were performed by correlating electron microprobe elemental distribution photomicrographs with x-ray analyses of the four rocks.

Introduction

A feasibility study was undertaken to verify the utility of a micro-structural analysis of selected rocks to yield relevant information on the mechanism of radionuclide sorption on common rock minerals. It is commonly accepted that ion-exchange is the predominant mechanism of radionuclide sorption. However, the major constituents of common rock such as carbonates, silicates and quartz are generally not recognized as good ion-exchangers. It is thus expected that minor rock components would play the predominant role in retarding radionuclide movement in geologic media. Clay minerals are commonly assumed to be responsible for the bulk of ionic sorption on rocks although this fact has not been verified before now. This study has sought correlations between concentrations of test ions on the surface of rocks and the underlying mineralogy in elemental distribution photomicrographs obtained with the automated electron microprobe.

Our main concern in this study is to verify that the electron microprobe analysis is capable of yielding information on the association of test ions with individual minerals. If clays are responsible for the bulk of sorption which takes place in rock assemblages, it is not at all clear at the outset whether the microprobe has the resolution to identify individual clay particles. For this purpose it is felt that relatively concentrated test solutions should be used. At a later time it is felt that concentrations of the test ions may be reduced by using autoradiography in conjunction with microprobe analyses of the test rocks. The use of concentrated solutions would insure that the microprobe could detect the test ion on the surface and would eliminate the need for the time consuming mapping of the surface required when two techniques are used in conjunction.

Experimental

Four rock samples were chosen for this initial study: a sample of Eleana shale taken from the Nevada Test Site at a core depth of 1805 ft., and three core samples from AEC #8 in the Los Medanos area of southeast New Mexico. The New Mexico samples are a Bell Canyon sandstone from a core depth of 4823.4 ft., Magenta dolomite from the Rustler formation at 749.5 ft., and a very dirty salt sample from the Salado at 2186.0 ft. X-ray analyses of these rocks reveal that the Eleana shale is composed primarily of quartz, siderite, and chamosite with minor phases of chlorite, illite, microcline, oligoclase, pyrophyllite, talc, calcite, and traces of pyrite, marcasite, and ferroan dolomite.⁽¹⁾ The Bell Canyon sandstone was composed of quartz calcite, kaolinite, chlorite, a small amount of feldspar and possibly some dolomite. Magenta is primarily dolomite with quartz and gypsum present as minor phases. The dirty salt is primarily halite with 7.8% by weight clay inclusions consisting of montmorillonite, chlorite, kaolinite, illite, mixed layer montmorillonite-chlorite, magnesite and talc.

Samples of these rocks were equilibrated with solutions of Cs, Sr, Gd and U to form an array of 16 rock-ion pairs. Chips of these rocks were allowed to equilibrate for three days at ambient conditions and then rinsed with solutions free of Cs, Sr, Gd or U for one day to remove loosely-bound or soluble ions from the rock surfaces.

Solutions used in these equilibrations were prepared by equilibrating deionized water with powdered samples of the rocks for four days. The rock solids were filtered off, and the pH and Eh of the resultant solution are given in Table I. Since no attempt was made to preclude air from these solutions, the oxidation potential, measured with a bright platinum electrode,

(1) All x-ray analyses were performed by G. T. Gay.

reflects the "irreversible oxygen potential."⁽²⁾ This oxidation potential will assure that uranium remains in the +6 oxidation state, as UO_2^{++} . The other ions in this study have only one oxidation state.

Before beginning a detailed study of all 16 rock-ion pairs, it was felt that an initial screening of the rock-ion pairs could be used to eliminate from the matrix those pairs which have little mutual affinity. This initial screening analysis consisted of contacting the rocks with very concentrated test ion solutions (1.0 M in the case of Cs, Sr and Gd, and 0.1 M in the case of U) and then examining each rock for test ion accumulations on the surface. If no accumulation was observed with the automated electron microprobe, operated in the wave length dispersive mode, it was felt that this rock-ion pair could be safely deleted from the matrix. In this manner six rock-ion pairs were eliminated from the matrix as shown in Table II.

Of these rock-ion pairs for which test ions were observed on the surface, the salt sample was found to pick up test ions only in areas of high silicon, representative of clay minerals. Cs was retained on the Eleana shale while Sr was retained as either a relatively insoluble carbonate or sulfate on the Magenta, Bell Canyon sandstone and the dirty salt. Gd was retained on every sample while uranium was retained on both the Magenta as UO_2CO_3 and the clay in the salt sample.

In the case of SrSO_4 , SrCO_3 and UO_2CO_3 formation on the above rocks, these ions were so strongly sorbed that their presence completely masked

(2) Merkle, F. G., "Oxidation-reduction processes in Soil," in Chemistry of the Soil, F. G. Bear (ed) (ACA Monograph 126). New York, Reinhold 1955, pp. 200-218.

TABLE I

pH and Eh of Solutions Equilibrated with Indicated Rocks

	<u>Magenta</u>	<u>Bell Canyon Silt Stone</u>	<u>Eleana Shale</u>	<u>Dirty Salt</u>
pH	6.96	7.69	7.77	6.98
Eh (volts)	0.58	0.53	0.52	0.53

TABLE II

Detection of Test Ions with Automated Electron Microprobe

	<u>Magenta</u>	<u>Bell Canyon Silt Stone</u>	<u>Eleana Shale</u>	<u>Dirty Salt</u>
Cs	-	-	+	-
Sr	+	+	-	+
Gd	+	+	+	+
U	+	-	-	+

+ Indicates the presence of the ion on the rock

- Indicates that ion was undetected. Approximate detection limit for each ion is given in parentheses: Cs (0.05%), Sr (0.03%), Gd (0.13%), U (0.1%).

other active species on the rocks. Since the solubility products of these compounds are too large to make them effective as binding agents for the very dilute solutions expected in situ, the concentration of Sr was reduced to 50 ppm in the more detailed study presented below while U was reduced to 1000 ppm. Calculations using solubility products and the bicarbonate equilibrium indicate that for Sr concentrations less than 10 ppm, no precipitate formation is expected, while for uranium, this limit is 1 ppm.

In our more detailed study, solution concentrations were set at 2.5×10^4 ppm Cs, 50 ppm Sr, 1.0×10^4 ppm Gd and 1000 ppm uranium. Solutions were prepared, as before, by being equilibrated with the rocks prior to addition of the test ion. The rock samples were ground to flatness with No. 600 carborundum paper. Chips of the rocks were then equilibrated in solutions to form the ten rock-ion pairs which had positive responses in the screening analysis. These rocks were rinsed as before and examined with the microprobe. On all elemental distribution photomicrographs (EDPM) light areas indicate the presence of the selected element. These EDPM's are 200X so that the distance between grid lines is approximately 36μ . Since exposure times vary from one EDPM to the next, all results are interpreted only in a qualitative manner. Similarly the identification of minerals must be considered tentative at this time.

At the reduced concentration levels, Sr was found only as SrSO_4 on the Magenta sample as shown in Figure 1. Strontium was not detectable on either the Bell Canyon sandstone or the dirty salt. Hence, none of the rocks demonstrated any significant affinity for strontium. In the case of uranium sorption on Magenta, most of the surface Mg and Ca were replaced by uranium, probably as UO_2CO_3 as shown in Figure 2. A normal dolomite distribution for Ca and Mg would almost completely cover the

photomicrograph. Although U is also positively correlated with K, Al, Si and Mg as shown in Figure 3, a positive statement that U is sorbed by a clay mineral would be difficult to make on the basis of this series because the uranyl carbonate is so prevalent. On the other hand, uranium is not associated with quartz at coordinates (3,1) or a mineral resembling illite at (-1,-1). In the case of the clay inclusions in the dirty salt, U is associated with the clay rich areas as shown in Figure 4 and 5. Here, U is strongly correlated with Mg, Al, Fe and Si. This behavior may be indicative of saponite-chlorite in view of the negative correlation with K; (5) however, it is likely that uranium has entered a simple exchange reaction with Magnesite to form UO_2CO_3 . Ca is present as gypsum and demonstrates no affinity for U. Similarly, pyrite, FeS_2 , retains no U. A clay, likely kaolinite, which has Na substituted for K, demonstrates no affinity for U at (-2,1). An illite at (4,-1) shows no affinity for U.

The only sample showing any Cs sorption was the Eleana Shale as shown in Figure 6 and 7. Cs was strongly correlated with K, Al, Si, Mg and Fe. This clay is likely illite-vermiculite which is renowned for its affinity to cesium. Areas showing no cesium take up are ferroan dolomite at (-3,4), quartz (+3,-2) and siderite (-3,0).

Gadolinium was sorbed on all four rock samples. The EDPM (elemental distribution photomicrographs) for the Eleana shale are shown in Figure 8. The light streak running at 45° above horizontal in the top right quadrant reveals the negative correlation of Gd for K. A positive correlation is obtained for Mg, Al, Si and Fe, possibly chamosite or chlorite. In the

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- (3) Bodine, M. C. Jr., "Geochemistry and mineralogy of silicate assemblages associated with Permian Basin evaporites," New Mexico Bureau of Mines and Mineral Resources Circular 159 (1977).

Bell Canyon sandstone shown in Figures 9 and 10, once again there is a strong preference of Gd for Fe, Mg, Al and Si indicative of chlorite. An area of dolomite at (3,1) shows no Gd affinity. The dirty salt sample is shown in Figures 11 and 12 reveals that Gd is taken up in a clay pocket which is positively correlated with Fe, Mg, Al and Si, possibly chlorite. When K is associated with Al and Si, possibly illite, as at (-2,-1), Gd is not retained. Anhydrite (-3,1) is not associated with Gd. Lastly, Figure 13 shows the interaction of gadolinium with Magenta. Here it is seen that Gd is sorbed in several areas, such as (4,2), which are high in K, Al, Si, Mg and Fe (not shown) as well as having a more dispersed pattern which generally correlated with dolomite. This last effect is more than likely caused by displacing the carbonate-bicarbonate equilibrium to form a hydroxide which is relatively insoluble. Hydroxide formation should not occur at Gd concentrations below 10^3 ppm.

An attempt was made to come up with a better characterization of the mineral phases which are associated with Cs and Gd. For this characterization, geologic thin sections were prepared without cover slides so that the section could be examined both with the petrographic microscope and the electron microprobe. In the case of the Bell Canyon sandstone, this effort was somewhat successful as we were able to obtain a semi-quantitative analysis of the mineral which retained gadolinium. This mineral is chlorite. For the other specimens, the results are at present inconclusive.

Conclusions

Although the results of this study are not to be construed as anything but preliminary, we may make several conclusions. Firstly, at the high concentrations considered in this study, clay minerals appear to be responsible

for all of the important sorption which takes place between Cs^+ , Ud^{+++} and UO_2^{++} and Eleana Shale, Magenta dolomite, Bell Canyon sandstone and clay bearing halite. It may then be concluded that a relatively small portion of these rocks are actively responsible for sorption characteristics. Gadolinium was bound in all samples, probably as iron bearing clay, with a probable active mineral being chlorite. Cesium was retained by the Eleana Shale, in which illite is the probable active mineral. Although illite was also present in the clay bearing halite, no cesium retention was observed in this case. A possible explanation for Cs not being observed in the halite sample is that the illite may be too finely dispersed to build up Cs concentration above the microprobe detection limits. Strontium was not significantly retained on any samples as SrSO_4 is not formed at trace concentrations.

Although the clays observed in this study were in some cases finely divided, as in the case of the illite clay in the halite sample, frequently clays of a given type formed easily recognized patterns or were present in detrital grains large enough to be observed directly. This fact allowed tentative identification of the minerals as well as allowing identification of associations between the test ions and the individual minerals by electron microprobe techniques.

MAGENTA - STRONTIUM

Strontium Distribution

Sulfur Distribution

Magnesium Distribution

Calcium Distribution

Figure 1. Elemental distribution photomicrographs (EDPM) of Sr contaminated Magenta. The predominant Sr phase is SrSO_4 where Sr replaces Ca in gypsum. (200X)

MAGENTA - URANIUM

Uranium Distribution

Magnesium Distribution

Calcium Distribution

Figure 2. EDPM of uranium contaminated Magenta. The predominant U phase appears to be UO_2CO_3 as Mg and Ca are dramatically reduced from a normal dolomite distribution as shown in Fig. 1. (200x)

MAGENTA - URANIUM

Potassium Distribution

Aluminum Distribution

Silicon Distribution

Figure 3. EDPM of uranium contaminated Magenta. Attempts to correlate U with K, Al and Si are difficult because of the strong masking by the predominant UO_2CO_3 . (200X)

DIRTY SALT - URANIUM

Uranium Distribution

Magnesium Distribution

Chlorine Distribution

Aluminum Distribution

Silicon Distribution

Figure 4. EDM of uranium contaminated dirty salt. Uranium is associated with clay rich areas and not NaCl. Upper right portion of uranium EDM is missing because of a topographical effect. The predominant U phase is likely UO_2CO_3 , from reaction with Magnesite. (200X)

DIRTY SALT - URANIUM

Iron Distribution

Potassium Distribution

Sodium Distribution

Sulfur Distribution

Calcium Distribution

Figure 5. EDPM of U contaminated dirty salt. When Fe is associated with clay, Fe is correlated with U while K, Na, S and Ca are not correlated. However, the positive correlation with iron bearing clay is not definitive in view of the reaction of U with Magnesite. (200x)

ELEANA SHALE - CESIUM

Cesium Distribution

Potassium Distribution

Aluminum Distribution

Silicon Distribution

Figure 6. EDPM of cesium contaminated Eleana Shale. Cs is associated with K, Al and Si indicative of illite-vermiculite. (200X)

ELEANA SHALE - CESIUM

Iron Distribution

Magnesium Distribution

Calcium Distribution

Figure 7. EDPM of Cs contaminated Eleana Shale. Cs is associated with Fe except for the ferroan dolomite at (-3,4). Cs is also correlated with Mg. (200x)

ELEANA SHALE - GADOLINIUM

Gadolinium Distribution

Potassium Distribution

Magnesium Distribution

Iron Distribution

Aluminum Distribution

Silicon Distribution

Figure 8. EDPM of gadolinium contaminated Eleana Shale. A light streak of Gd running from the origin into the top right quadrant reveals a negative correlation for K and positive association with Fe, Mg, Al, Si, indicative of chamosite or chlorite. (200X)

BELL CANYON - GADOLINIUM

Gadolinium Distribution

Iron Distribution

Magnesium Distribution

Aluminum Distribution

Silicon Distribution

Figure 9. EDM of gadolinium contaminated Bell Canyon sandstone. Gd is associated with Fe, Mg, Al and Si, indicative of chlorite. (200X)

BELL CANYON - GADOLINIUM

Calcium Distribution

Potassium Distribution

Sodium Distribution

Figure 10. EDPM of gadolinium contaminated Bell Canyon sandstone. The sorptive mineral contains some K but no Ca or Na. Dolomite at (3,1) is not retaining Gd. (200X)

DIRTY SALT - GADOLINIUM

Gadolinium Distribution

Aluminum Distribution

Silicon Distribution

Magnesium Distribution

Chlorine Distribution

Figure 11. EDPM of gadolinium contaminated dirty salt. Gd is concentrated in clay pocket, possibly as a chlorite. (200X)

DIRTY SALT - GADOLINIUM

Gadolinium Distribution

Iron Distribution

Potassium Distribution

Calcium Distribution

Sulfur Distribution

Figure 12. EDM of gadolinium contaminated dirty salt. Gd is not associated with pyrite, anhydrite or illite. (200X)

MAGENTA - GADOLINIUM

Gadolinium Distribution

Potassium Distribution

Aluminum Distribution

Silicon Distribution

Magnesium Distribution

Calcium Distribution

Figure 13. EDPM of gadolinium contaminated Magenta. Gd is associated with clay at (4,2) which is high in K, Al, Si and Mg, possibly chlorite. Also there is a diffuse Gd pattern associated generally with dolomite which is likely a concentration effect. (200X)

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