Western USA Assessment of High Value Materials in Geothermal and Produced Fluids

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ABSTRACT

Water samples were collected from 47 production wells in 12 geothermal fields (Idaho, Nevada, New Mexico, Oregon, and Utah), 25 production wells in the Uinta and Paradox Basins (eastern Utah), 14 groundwater wells in the Tularosa geothermal prospect (New Mexico), and 20 hot/cold springs and groundwaters from the Sevier Thermal Belt (southwestern Utah). These samples were analyzed for major, minor, and trace elements, including transition metals, metalloids, and rare earth elements (REEs). These results are used to characterize the concentrations and potential inventories of strategic, critical, and high value metals (SCVM) in produced fluids.

Most SCVM concentrations in produced waters range from <0.1 to 100 µg/kg; the main exceptions being lithium, which has concentrations that range from <1000 to 26,000 µg/kg. In geothermal waters, gallium, germanium and selenium have concentrations up to 100 µg/kg, and in oil field waters they have concentrations up to 30,000 µg/kg. Most SCVM concentrations range from <10 µg/kg to 100 µg/kg, respectively. Scandium concentrations are up to 10 µg/kg and tellurium concentrations are up to 200 µg/kg. In geothermal waters, REEs have concentrations <0.05 µg/kg and only in a few oil field waters do they get up to 5 µg/kg. The high temperature geothermal resource at Roosevelt Hot Springs has the highest estimated inventory of germanium (20,000 kg) and lithium (7,000 kg), and Patua has the highest estimated inventory of gallium (25,000 kg), selenium (47,000 kg), and tellurium (6.5 kg); Raft River has the highest estimated inventory of scandium (700 kg).

The concentrations of gallium, germanium, lithium, scandium, selenium, and tellurium in produced waters appear to be partly related to reservoir temperature and concentrations of total dissolved salts. Geothermal waters originate as meteoric water whereas oil/gas field waters are typical of basin waters. The relatively high concentration and large inventory of lithium occurring at Roosevelt Hot Springs may be related to granitic-gneissic crystalline rocks, which host the reservoir. Analyses of calcite scales from Dixie Valley indicate enrichments in cobalt, gallium, gold, palladium, selenium and tellurium, and these metals appear to be depositing at deep levels in production wells due to boiling.

1. INTRODUCTION

This project deals with resource assessment of strategic, critical and valuable materials (SCVM) in production fluids and reservoirs across several western states in the USA. SCVM comprise a wide range of diverse elements (e.g., Critical Metals Strategy, DoE, 2011; Energy Critical Elements, American Physical Society and Materials Research Society, 2011), including an alkali metal (Li), noble gases (He, Ne, Ar), metals and metalloids (Ag, Co, Cu, Ga, Ge, In, Ir, Nb, Os, Pt, Pd, Re, Rh, Ru, Se, Te), and rare earth elements (REEs: Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Pr, Nd, Sc, Sm, Tb, Tm, Y, Yb).

Previous work has been directed at targeted studies of subsets of SCVM, typically REEs, primarily in high temperature geothermal fluids from just a few sites in the USA. Accordingly, the aqueous concentrations of REEs are less than a few µg/kg, whereas some metals (Te and Ag) can reach mg/kg level, and aqueous Li can exceed 100 mg/kg (e.g., McKibben and Hardie, 1997; Simmons et al., 2016; Neupane and Wendt, 2017; Nye et al., 2018).

In this study, production fluids and rocks from a number of fields, with reservoir temperatures ranging from 50-250 °C, were sampled and analyzed (Fig. 1). The results have been used to calculate the grades and inventories of SCVM in reservoirs, and the numbers reported herein are provisional. The results are discussed briefly in the light of controls on hydrothermal transport of SCVM.

2. SAMPLING

Hot springs (37-83 °C) and production wells were sampled for waters. The methodology for acquiring fluid samples from geothermal wells depended on several factors, including the location(s) and availability of pipeline sample ports and temperature-pressure conditions. Where the wells are pumped to produce geothermal fluid, samples were acquired with stainless steel coiled tubing submerged in an ice bath to prevent gas phase separation. Where the wells are self-flowing and fluid production is two-phase, a mini-separator was attached to the pipeline to collect separate water and gas samples.

Oil and gas production wells were sampled for produced waters from the wellhead or separators. Some separators have a valve located on the bottom of the tank, which permitted acquisition of a sample that was relatively free of hydrocarbons. Other separator tanks were only accessible from the top, and to acquire a water sample, a bailer was lowered to the bottom of a tank through a layer of liquid hydrocarbons. Where the wellhead fluid could be sampled, a mixture of hydrocarbons and water were collected into a large clean bucket. Field treatment of samples was impractical, and most were contaminated with hydrocarbons. Hence, water samples were processed in the lab by letting them stand for 48 hours to allow immiscible liquid hydrocarbons to rise and separate from the underlying water, after which aliquots of water were decanted and treated.

Treated waters were filtered using a 0.45 µm Millipore filter kit into high density polyethylene plastic bottles (HDP) and then acidified with nitric acid (HNO₃) to pH 2. All HDP bottles were acid cleaned prior to filling with filtered water samples. To check for
contamination, field blanks were prepared, in which deionized water (>12 MΩ-cm) from the lab was carried into the field and then subjected to field filtration and acidification.

Rock samples were collected from drill cuttings and field outcrops. Drill cuttings were obtained for wells drilled at Beowawe, Dixie Valley, and Roosevelt Hot Springs, and from wells drilled in the Uinta and Paradox basins. Outcrop samples in the Sevier Thermal Belt were obtained from exposures of reservoir host rocks, volcanic rocks, and travertine deposits.

Samples of pipe scales made of calcite were supplied by Terra-Gen from two wells at Dixie Valley. These scales formed on small diameter coiled tubing that had been inserted into the well to continuously supply anti-scalant to the feed points at reservoir depths. The calcite likely deposited due to boiling and separation of gas from the liquid.

Figure 1. Production fluid sampling sites. Abbreviations: C=Covenant; Nc=Newcastle; Ro=Roosevelt Hot Springs; Sevier TB=Sevier Thermal Belt (orange); Th=Thermo. Base map is from Ryan et al. (2009).

3. ANALYTICAL METHODS

Aliquots (50ml) of filtered and acidified water were analyzed at the University of Minnesota geochemistry lab. Major elements were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES), and major anions (Cl, F, SO₄) were analyzed by ion chromatography. Minor and trace cations were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Blanks and standards for trace elements were prepared and utilized for calibrating analytical results. The detection limits for trace elements, transition metals, and metalloids are 100 µg/kg (Li), 1-2 µg/kg (Al & Se), 0.1-0.2 µg/kg (Sr, Mn, Fe, Ge, As, W, Au), 0.05 µg/kg (Sc, Co, Ni, Cu, Ga, Y, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sb, Te, Ta, Rh, Ir, Pt, Ti, Pb), and 0.01 µg/kg (In, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U). At these detection limits, the accuracy and precision of results for standards is within 20% of their known elemental concentrations. Untreated waters were analyzed for pH and bicarbonate at the Utah Department of Health laboratory in Salt Lake City. Rock and mineral samples (~1.5 grams of solids) were dissolved into an aqueous solution using strong acids (HCl, HNO₃, HF), sealed vessels, and a microwave digester. The solutions were analyzed for trace elements via standard addition by ICP-MS. Many elements, including Sc, Co, Cu, Zn, Ga, Nb, Sb, La, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb, were within 20% accuracy and precision. The analytical results for As, Ru, Rh, Sb, Te, showed much stronger variance in precision exceeding 50%.

4. SCVM CONCENTRATIONS & INVENTORIES IN PRODUCED WATERS

The concentrations of most SCVM in produced waters range from <0.1 to 100 µg/kg. Lithium, however, has concentrations that range from <1000 to 26,000 µg/kg. Other elements that attain relatively high concentrations are gallium (10-80 µg/kg geothermal; 10-10,000 µg/kg Uinta and Paradox Basins), germanium (1-70 µg/kg geothermal; 10-500 µg/kg Uinta and Paradox Basins), scandium (0.1-2.0 µg/kg geothermal; 5-10 µg/kg Uinta and Paradox Basins), selenium (1-100 µg/kg geothermal; 10-20,000 µg/kg Uinta and Paradox Basins), and tellurium (0.1-10 µg/kg geothermal; 0.1-500 µg/kg Uinta and Paradox Basins). Small concentrations of rhodium in the range of 0.1-1.0 µg/kg were measured in water samples from Roosevelt Hot Springs, San Emidio, Soda Lake, and the Sevier thermal belt, and up to 10 µg/kg in Uinta and Paradox basin waters. Iridium concentrations of 0.1-0.3 µg/kg were measured in water samples from Puta and the Uinta Basin. Geothermal waters contain very low concentrations of REEs, below the analytical detection limits of 0.01 µg/kg, in accord with large amounts of published data on neutral pH thermal waters (Neupane and Wendt, 2017). The concentrations of some REEs in Uinta Basin waters, by contrast, range from 0.05 to 5 ppb, notably lanthanum, cerium, and europium. The concentrations of REEs in the Paradox Basin waters were below detection, which because of the high total dissolved salts (TDS) was probably on the order of 0.15 µg/kg.
Figure 2. Average concentrations (μg/kg) of gallium, germanium, lithium, scandium, selenium, and tellurium in produced waters from geothermal fields plotted against estimates of inventories in reservoirs.
Figure 3. Concentrations (μg/kg) of gallium, germanium, lithium, scandium, selenium, and tellurium in produced waters from the Uinta and Paradox basins, plotted against estimates of inventories in reservoirs.
Figure 4a. Comparison of the range of concentrations of gallium, germanium and lithium in produced geothermal waters and in rock samples collected from wells at Dixie Valley (DV), Beowawe (Be), Roosevelt Hot Springs (RHS), Paradox Basin (Px) and Uinta Basin (Ui).
Figure 4b. Comparison of the range of concentrations of scandium, selenium, and tellurium in produced geothermal waters and in rock samples collected from wells at Dixie Valley (DV), Beowawe (Be), Roosevelt Hot Springs (RHS), Paradox Basin (Px) and Uinta Basin (Ui).
Inventories of SCVM in geothermal reservoir waters were calculated by multiplying the average concentrations in produced fluids by the reservoir volume, assuming a porosity of 15%. The reservoir volume was estimated from the plan distribution of production wells multiplied by 1 km, which represents an arbitrarily assigned, but geologically reasonable, reservoir thickness. In the case of the Uinta and Paradox Basin wells, the known histories of water production were used to calculate the reservoir water volumes. Figures 2 and 3 graphically portray the concentrations of gallium, germanium, lithium, scandium, and tellurium versus reservoir inventories. Among the geothermal fields, the Roosevelt Hot Spring reservoir appears to have the largest endowments of germanium (20,000 kg) and lithium (7 million kg), the Patua reservoir appears to have the largest endowments of gallium (25,000 kg), selenium (47,000 kg), and tellurium (2500 kg), and the Raft River reservoir appears to have the large endowment of scandium (700 kg). By comparison, the Uinta Basin has larger inventories of gallium (>100,000 kg). All reported values of SCVM concentrations and inventories are provisional.

The ranges of gallium, germanium, lithium, scandium, selenium, and tellurium concentrations in rock samples are graphically portrayed along with concentrations of these elements in produced waters in Figure 4. The aqueous elemental concentrations are generally much lower than the rock concentrations. Furthermore, the aqueous and rock concentrations show poor correlation, especially selenium and tellurium in the Paradox Basin samples. These data trends suggest that there is no direct relationship between the concentrations of SCVMs in rocks versus produced waters.

To test the possibility that some SCVM elements might be depositing as scales in geothermal wells (e.g., Simmons et al., 2016b), six samples of calcite scale from Dixie Valley were analyzed. One sample (28-33A; Table 3-Tab Dixie Valley Calcite Scales) contains anomalous concentrations of cobalt (4,000 µg/kg), gallium (800 µg/kg), germanium (45 µg/kg), selenium (14,000 µg/kg), tellurium (4000 µg/kg), gold (20,000 µg/kg) and palladium (500 µg/kg). Trace amounts (10-100 µg/kg) of yttrium, niobium, rhodium, lanthanum, cerium, neodymium, europium, gadolinium, and rhenium were also measured. These data suggest that some SCVM deposit from produced fluids before reaching the surface, likely due to boiling in the well. A comparison of the data for produced waters, calcite scales, and subsurface rocks based on drill cuttings is shown in Figure 5. Calcite precipitation in the well appears to be very effective at concentrating most elements from produced geothermal water, except for As and Sb. Thus, where flashing or boiling is occurring in self-flowing wells (i.e. Beowawe, Dixie Valley, and Roosevelt Hot Springs), a significant portion of the reservoir aqueous SCVM might be sequestered in scales before reaching the surface.

Figure 5. Comparison of the range of concentrations of metals in produced geothermal waters (black bold line), calcite scales (grey-filled area) and subsurface lithologies based on drill cuttings (rocks-white filled area between thin black lines) from wells at Dixie Valley.
All thermal waters in the Sevier Thermal Belt are near neutral pH, and isotopically are similar to local meteoric water (Simmons et al., 2015). Based on the major anion compositions, thermal waters are classified as chloride and hybrid chloride-sulfate or sulfate-chloride waters, with chloride concentrations that range from ~100 to 5000 mg/kg, sulfate concentrations that range from ~40 to 2000 mg/kg, and bicarbonate concentrations that range from ~50 to 500 mg/kg. Roosevelt Hot Springs is a chloride water having reservoir host rocks made of crystalline Precambrian gneiss/Tertiary granite. Thermo waters are sulfate-chloride waters, with elevated bicarbonate; reservoir host rocks are made of Paleozoic-Mesozoic marine carbonates and siliciclastic units. Crater, Hatton, Joseph, and Meadow hot springs are chloride-sulfate waters and Monroe is a sulfate-chloride water. The Covenant oil field water comprises saline (12,000 mg/kg Cl) chloride water, and the reservoir is hosted by Jurassic quartz sandstone sealed by mudstone and evaporites. Although TDS values of Sevier Thermal Belt waters overlap the whole set of produced geothermal waters, there is poor correlation between TDS and temperature.

Produced thermal waters at Roosevelt Hot Springs and Thermo originate as deeply circulated meteoric waters that have been modified by hot water-rock interaction (>250°C). Geological evidence suggests that the main deep lithology is made up of crystalline basement rocks (i.e., gneiss, granite); however, the precise sources of Cl, SO₄, and HCO₃ are unclear and they could be derived from magmatic intrusions (Simmons et al., 2015). At reservoir depths, there is indication that thermal waters are partially modified by interaction with Paleozoic-Mesozoic sedimentary rocks. During continued ascent to the surface, steam-loss through boiling affects the concentrations of aqueous and gaseous constituents.

Where waters reach shallow aquifers, they are affected by dilution and outflow under the influence of hydraulic gradients. The compositions of hot spring waters suggest they are fed by separate, isolated geothermal systems, albeit with modest resource temperature (<150°C), judging from aqueous silica concentrations and quartz-silica equilibration temperatures. Simmons et al. (2015) infer from high Mg and high Cl/Br ratios coupled with enrichments in SO₄, and to a lesser extent HCO₃, that these waters are strongly modified by interaction with salts and clays in alluvial basin fill. They may have also interacted with brine pore fluids in subjacent Mesozoic-Paleozoic sedimentary rocks.

In Figure 7, gallium, germanium, lithium, scandium, selenium and tellurium concentrations in produced geothermal waters are compared to Sevier Thermal Belt waters as a function of temperature. The first thing to note is that the Sevier Thermal Belt waters, in comparison to all the produced thermal waters, are generally low to intermediate in the range of concentrations of gallium, germanium, and scandium, similar to the range of concentrations for selenium and lithium, and higher in concentrations of tellurium. Secondly, the hottest production water at Roosevelt Hot Springs has the highest concentrations of germanium, lithium, and scandium, and close to the highest concentrations of selenium; by contrast, the relatively cool production water at Thermo is associated with low concentrations of gallium, germanium, lithium, scandium, selenium and tellurium. Thirdly, germanium and lithium show positive correlation with temperature, in contrast to gallium, scandium, selenium and tellurium, which show no correlation. From these trends, it seems that temperature control on the concentrations of SCVM elements is restricted to germanium and lithium.
Figure 7. Concentrations (μg/kg) of gallium, germanium, lithium, scandium, selenium, and tellurium in Sevier Thermal Belt and produced geothermal waters (Fig. 2) plotted against measured or quartz-silica equilibration temperatures.
Figure 8. Concentrations (μg/kg) of gallium, germanium, lithium, scandium, selenium, and tellurium in Sevier Thermal Belt and produced geothermal waters (Fig. 2) plotted against total dissolved salts (mg/kg). The most saline water is from the Covenant oil field.
In Figure 8, gallium, germanium, lithium, scandium, selenium and tellurium concentrations in produced geothermal waters are compared to Sevier Thermal Belt waters as a function of TDS. Tellurium shows the strongest correlation with TDS, with the highest concentration being found in the most saline water from Covenant oil field. Scandium and selenium also show coherent correlations with TDS. If the Covenant oil field water is omitted, then in all other thermal waters, lithium shows a strong correlation with TDS. For gallium and germanium correlations with TDS are weak, which is consistent with formation of hydroxyl complexes (Wood and Samson, 2006). Scandium also tends to form hydroxyl complexes (Williams-Jones and Vasyukova, 2018), but the elevated concentrations measured in Paradox basin waters suggest high TDS help to mobilize this element. Overall the trends imply that the influence of TDS on the concentrations of lithium, scandium, selenium and tellurium in thermal waters is important, but less so for gallium and germanium.

6. SUMMARY

The concentrations of SCVM in produced waters range from <0.1 to 100 µg/kg, and they are relatively low level, with the exception of lithium, which has much higher concentrations and which ranges from 10 to 26,000 µg/kg. Relatively high concentrations of gallium, germanium, scandium, selenium, and tellurium were also detected. Geothermal production waters, however, contain very low concentrations of REEs, except for some elevated results for lanthanum, cerium, and europium in Uinta Basin waters.

The Roosevelt Hot Springs geothermal reservoir appears to have the largest endowments of germanium (20,000 kg) and lithium (7 million kg), the Patua geothermal reservoir appears to have the largest endowments of gallium (25,000 kg), selenium (47,000 kg), and tellurium (2500 kg), and the Raft River geothermal reservoir appears to have the large endowment of scandium (700 kg). By comparison, the Uinta Basin has larger inventories of gallium (>100,000 kg). These estimates are provisional, and they were calculated using geologically reasonable values for reservoir volumes and porosities.

The concentrations of gallium, germanium, lithium, scandium, selenium, and tellurium in produced waters appear to be partly controlled by reservoir temperature and concentrations of total dissolved salts. The relatively high concentration and large endowment of lithium occurring at Roosevelt Hot Springs appears to be related to hot water interaction with crystalline granitic rocks, which host the reservoir and the hydrothermal system, and elevated concentrations of TDS. Analyses of calcite scales from Dixie Valley show that cobalt, gallium, gold, palladium, selenium and tellurium are depositing at deep levels in production wells due to boiling.

7. ACKNOWLEDGMENTS

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