

Investigation of soluble indium chelates for groundwater and hydrothermal fluid tracing

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Abstract—Indium is an excellent tracer with a unique combination of good activation analysis sensitivity retaining most of the advantages of radioactive tracers without creating health or environmental risk, and low background concentration in surface and subsurface fluids. The organic chelating agents ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) were selected to enhance the solubility of In as a tracer within the pH range of groundwater and hydrothermal fluids. The thermal stability of indium chelates of EDTA and NTA was investigated at temperatures from 22 to 240°C. Degradation of In(III)-EDTA, observed at and above 200°C, is attributed to metal dissociation followed by thermal decomposition of the organic ligand. Degradation of In(III)-NTA, observed at temperatures greater than 150°C, is probably due to significant decrease of the thermodynamic formation constant. The results suggest that soluble indium chelates can be used effectively as tracers for surface and groundwater flow and transport studies. The applicability of In(III)-EDTA as a conservative tracer can be extended to low-temperature geothermal reservoirs where ionic chemical tracers are not fully conservative.

INTRODUCTION

METAL organic complexes have been extensively used as tracers in hydrological investigations (HANSON, 1970; LEBECKA and TOMZA, 1977; BEHRENS *et al.*, 1977; NAVADA *et al.*, 1981; DRABAOK, 1982) but little has been reported on their use in hydrothermal systems. Radioactive tracers, such as ^3H , ^{14}C , ^{82}Br , and ^{131}I , have been used effectively in liquid dominated geothermal reservoir studies (GULATI *et al.*, 1978; MCCABE *et al.*, 1983; MCCABE and BARRY, 1985). Such tracers provide great sensitivity to evaluate formation fracture networks and to follow the flow of water between reinjection and production wells (HORNE, 1982). Public approval to utilize radiotracers in large reservoir systems has become difficult to obtain and an alternate method which maintains the great sensitivity of radiation measurement without the need to inject radioactive materials into the reservoirs is desired. Activable tracers in conjunction with activation analysis offer a reasonable compromise between retaining most of the advantages of radioactive tracers and creating low health or environmental risk (KRUGER, 1971). One promising tracer is In which possesses excellent activation properties and is easily prepared as a soluble chelated complex.

Conservation of an external tracer in hydrothermal systems is more difficult to ensure than in groundwater aquifers and oil-field reservoirs owing to the complex chemical environment and high temperatures encountered. Chemical and fluorescent dye tracers are subject to adsorption losses, thermal instability and high natural background (SMART and LAIDLAW, 1977; WAGNER, 1977). Alternatively, several chelated stable-elements, useful as activable tracers,

have low background concentrations in hydrothermal systems. Some of these tracers have good thermal stability and sorption characteristics.

This paper summarizes our investigations concerning the thermal stability of In complexed with the organic ligands ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA). The data indicate the maximum formation temperatures at which these indium chelates can be employed as a conservative tracer of hydrothermal fluid flow. The data also provide for the design of tracer tests in groundwater aquifers and geothermal reservoirs unsuited for ionic chemical tracers. Also, some preliminary results of chelated In adsorption onto graywacke sandstone are discussed briefly.

An optimization analysis by CHRYSIKOPOULOS (1986), based on chemical composition of geothermal effluents and activable tracer requirements, suggested stable ^{51}V , ^{59}Co , ^{115}In and ^{164}Dy isotopes as potential activable tracers. Indium was considered to be an excellent activable tracer because of its unique combination of good detection sensitivity and low background concentration in groundwater and hydrothermal fluids. Indium has two naturally occurring isotopes, ^{113}In and ^{115}In , with isotopic abundance 4.3% and 95.7%, respectively (LEDERER and SHIRLEY, 1978). The cross-section for the $^{115}\text{In}(n,\gamma)^{116m}\text{In}$ reaction is 70 barns, and the 54.12 min half-life of the activation product provides adequate radiation measurement at concentrations far below chemical and dye tracers. The major gamma-ray of ^{116m}In decay has a photopeak energy of 1.2935 MeV at an absolute intensity of 85% (LEDERER and SHIRLEY, 1978). This gamma-ray energy is sufficiently high to reduce the Compton scattering contribution to its full-energy peak (O'KELLEY,

1962). The background concentration of In in natural waters is very low. Hot spring waters in Bulgaria contain up to 40 ppb In (SMITH *et al.*, 1978), while In concentration in Pacific Ocean water was found to be 4 ppb (CHOW and SNYDER, 1969). Indium concentration measurements in representative geothermal fluids are sparse. COSNER and APPS (1978) reported that the In content of fluids from geothermal resources in the U.S.A. is less than 100 ppb.

The chemistry of In precludes its use as a simple cationic tracer. Generally, anions tend to be more conservative than cations (STUMM and MORGAN, 1981). Although In exhibits positive oxidation states from one through three, in aqueous solutions only the trivalent state is stable. Hydrolysis of In occurs at pH values as low as 2.7–3.4, with rapid formation of reversible hydrolysis products (BIEDERMANN, 1956). In addition to the mononuclear hydrolysis products of In, several polynuclear hydrolytic species are also formed, such as $\text{In}[\text{In}(\text{OH})_2]_n^{(3+n)+}$, where n is an integer (BIEDERMANN, 1956). Indium can exist in groundwater solution complexed with several common groundwater anions such as chloride (InCl^{2+} , InCl_2^+ , InCl_3^0 , and InClO_4^{4+}) (Ferri, 1972a, b). However, chloride retards In hydrolysis up to pH of 5.5 (BAES and MESMER, 1976). Because the pH of most geothermal and ground waters is greater than ~5, to enhance conservation of In as a tracer in these fluids, it is desirable to chelate the metal to ensure geochemical stability and mobility, as well as to prevent hydroxide precipitation.

Complexation of metal ions by inorganic and organic ligands can either decrease or increase metal adsorption (BENJAMIN and LECKIE, 1981). DAVIS and LECKIE (1978) have suggested some criteria that may help to predict the behavior of a given chelate, but such predictions are not fully reliable. The organic ligands EDTA and NTA were chosen to enhance the solution stability of In for several reasons. These organic chelating agents have low molecular weight and form water-soluble complexes with most metal ions. In particular, the EDTA and NTA complexes of In(III) are very strong. At room temperature the thermodynamic formation constant, K , of In(III)-EDTA is $10^{24.9}$ whereas the K value of In(III)-NTA is $10^{16.9}$ (MARTELL and SMITH, 1974). MOTEKAITIS *et al.* (1982) indicated that the first order rate constants for decomposition of EDTA chelates of divalent metal ions at 310°C are inversely proportional to the thermodynamic constants of the chelates measured at room temperature. The decomposition rate constants for chelates of trivalent metal ions are expected to follow similar trends at elevated temperatures. Therefore, EDTA and NTA are good choices of chelating agents because their formation constants with In(III) compete very well with most of the common cations.

The organic ligands EDTA and NTA have been employed extensively in a variety of commercial operations, such as prevention of scale build-up in

steam generators, decontamination of nuclear facilities, stabilization of fatty-acids, prevention of turbidity formation in wine, photographic and agricultural uses, and in therapeutic removal of poisonous metals ingested by humans (MEANS *et al.*, 1980). These ligands become components of waste waters and they are easily introduced into the environment. EDTA is rather slowly biodegradable and persistent in the environment (TIEDJE, 1977). Further, EDTA has been considered as a principal contributor in the mobilization of radionuclides from radioactive waste burial sites (MEANS *et al.*, 1978). On the other hand, NTA is known to be biodegradable and it is unlikely to be found in water supplies (THOMPSON and DUTHIE, 1971; TIEDJE and MASON, 1974).

Both EDTA and NTA have the ability of ionizing each one of their carboxyl groups. EDTA can form coordination bonds at six sites, the four oxygen and the two nitrogen sites. The metal complexes of EDTA form five five-membered rings and reduce the charge on the central atom by four. NTA can form coordination bonds at four sites, the three oxygen and one nitrogen sites. The metal complexes of NTA form three five-membered rings and reduce the charge of the central atom by three. Figure 1 illustrates the formation of the EDTA and NTA complexes of In(III). The principal contribution to the stronger stability of In(III)-EDTA over In(III)-NTA is the extra number of rings, or more specifically the stability of the metal complex increases with increasing number of chelate rings (MARTELL and CALVIN, 1952) because of the entropy increase associated with chelate ring formation (BETTS and DAHLINGER, 1959).

The thermal stability of metal chelates is an important consideration for their use in hydrothermal environments. EDTA decomposes at ~200°C by hydrolytic cleavage of the ethylenic C-N bond, producing iminodiacetic acid (IDA) and *N*-2-hydroxyethyl iminodiacetic acid (HEIDA) (SNEGOSKI and VENEZKY, 1974). At higher temperatures breakdown of the primary products of EDTA occurs with loss of CO₂, producing the corresponding methylamines. Further hydrolytic cleavage of HEIDA yields ethylene glycol (MARTELL *et al.*, 1975). NTA does not undergo hydrolytic cleavage below 260°C, but decomposes at about 290°C through a stepwise decarboxylation to *N*-methyliminodiacetic acid, methylsacrosine, and trimethylamine (MARTELL *et al.*, 1975). The observed thermal stability behavior is associated with the ligands themselves rather than the metal-ligand complexes. Certain metal chelates degrade slower than the ligands (VENEZKY and MONIZ, 1969). Also, divalent metal ions stabilize EDTA and thermal dissociation tendencies of the chelates are controlled by the stability constants as well as by the tendency of the metal ion to hydrolyze and precipitate from solution (MOTEKAITIS *et al.*, 1982). However, the stability constants of In(III)-EDTA and In(III)-NTA at elevated temperatures are not available in the literature.

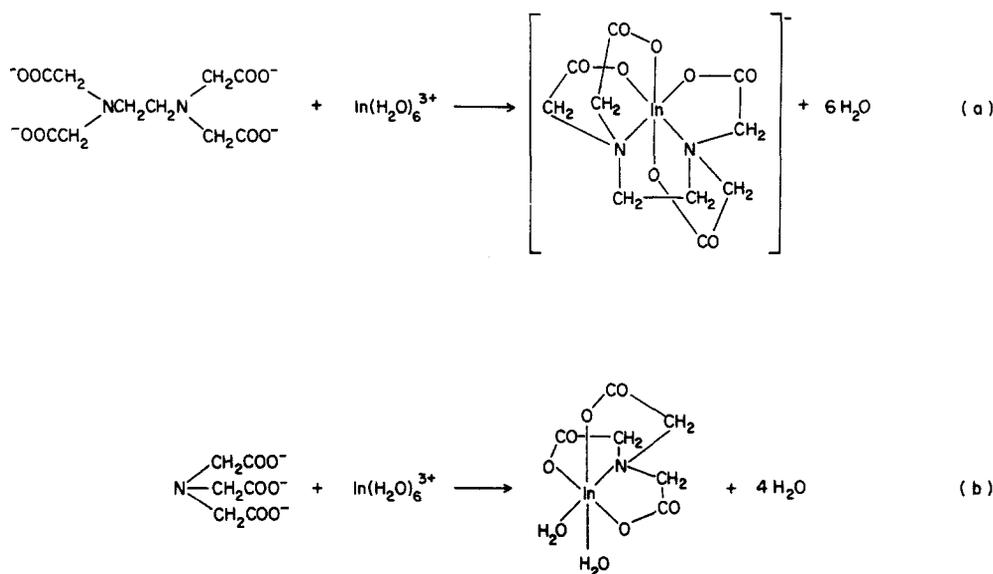


FIG. 1. Structure of (a) In(III)-EDTA and (b) In(III)-NTA complexes. The ratio of metal ion chelated to the chelating molecule is one-to-one.

EXPERIMENTAL METHODS

Analytical-reagent grade high-purity (99.99%) In was used with disodium salts of EDTA and NTA. Indium, in powder form, was dissolved in nitric acid, and the chelate solutions were formed with a chelon-to-metal mole ratio of 10, to maintain a high ratio of complexed to free metal concentrations. Stock solution concentrations were prepared over two orders of magnitude above the low end of detection limit at good sensitivity. The solution pH was adjusted with NaOH. Milli-Q water was used in preparing all stock solutions. The calculated ionic strength of the In(III)-EDTA and In(III)-NTA solutions was 0.22 and 0.12 M, respectively. The pH values cited in this paper were those measured at room temperature.

The rock used for the adsorption experiments was a metamorphic graywacke of western California, similar to the graywacke sandstone prevalent at The Geysers geothermal field in California. Microscopic observations performed by SATOMI (1982) indicate that this graywacke consists of quartz (29.4%), feldspar (30.4%), epidote, apatite and sphene (trace), shale and metabasalt (5.8%), and cementing materials (34.4%). The graywacke was crushed in a single-runner rock grinder and separated into mesh size ranges through Tyler sieves. Three averaged rock size fractions were obtained: 1.28, 0.94 and 0.46 mm, where the average rock size of each range was assumed to be the mean of the lower and upper sieve sizes. The specific surface areas were estimated at 1.905, 2.026 and 2.191 m²/g, respectively, measured with a pore-volume analyzer utilizing the BET low temperature multilayer gas adsorption technique (BRUNAUER *et al.*, 1938).

Indium concentrations were determined by comparator radioactivation analysis. This method requires only relative measurements and it is based on identical irradiation and counting treatment of standards and samples (KRUGER, 1971). The comparator standard and sample enclosed in scintillation capsules, were simultaneously irradiated in the Stanford Linear Accelerator Center (SLAC) ²⁵²Cf neutron source for a 10 min period at a thermal neutron flux of 2×10^6 n cm⁻² s⁻¹. Following activation and a 30 min delay, the sample activity was measured with a NaI(Tl) well scintillation

detector for a 5 min count interval. The gamma-ray spectra were recorded on an 1024-channel analyzer, calibrated so that the 0.66 MeV ¹³⁷Cs photopeak was registered in channel 113. The integrated count of channels 209–245, corresponding to the 1.29 MeV peak of ^{116m}In, provides good efficiency and resolution relatively to the ¹³⁷Cs full-energy peak. The background count-rate within this channel interval was less than 4 cpm.

The thermal stability experiments were conducted over 20–30 day periods at 150, 200 and 240°C. Aluminium pressure vessels of approximately 40 ml volume and gold-plated interior wall, were filled with 10 ml indium chelate solution. Gold-plated pressure vessels were used to minimize interactions between tracer solution and vessel wall. The vessels were closed with threaded aluminium caps and sample leakage was prevented by a 0.16 cm thick Teflon-disc seal. Elevated temperatures were obtained with a Blue-M mechanical convection oven maintaining constant temperature within $\pm 0.5^\circ\text{C}$. At the end of a heating period, the vessels were taken from the air-bath, quickly quenched by immersion in a cool water-bath, and the samples were transferred to centrifuge tubes. After centrifugation, 2 ml of the supernatant liquid were transferred from each centrifuge tube to scintillation capsules for neutron irradiation and gamma-ray spectroscopy.

Batch adsorption experiments were conducted at room temperature to characterize the In(III)-EDTA adsorption onto graywacke. The experiments were run with three size fractions and five In(III)-EDTA concentrations. Polycarbonate tubes were filled with 5 g of rock and 40 ml of chelate solution. The tubes were connected to a rotating rack for a 3 day period to provide adequate reaction time for the attainment of equilibrium in all samples. At the end of equilibration period the slurries were centrifuged and 2 ml aliquots of the supernatant liquid were transferred to scintillation capsules, followed by soluble In concentration determination.

The estimated uncertainty of the experimental data includes uncertainties in volumetry, gravimetry (<0.3%) as well as counting error. The counting error is significant when the half-life of a radionuclide is short compared to the counting time, because decay occurs during the measure-

ment period and correction of the observed count-rate is required. Self-shielding effects in the activation were eliminated by employment of dilute homogeneous samples. Neutron flux gradient errors were minimized by simultaneous irradiation of samples and standards. Additional details of experimental and analytical procedures are given by CHRYSIKOPOULOS (1986).

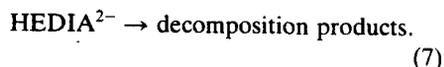
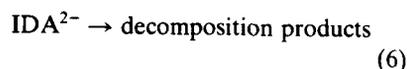
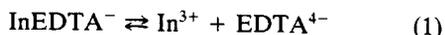
RESULTS AND DISCUSSION

At room temperature and solution pH greater than pK_4 10.26 (EDTA), pK_3 9.73 (NTA) (PRIBIL, 1972) the chelates of In are completely formed and the only major species present in solution are InEDTA^- and InNTA^0 . However, groundwater and hydrothermal fluids exist at $\text{pH} < 10$ (TSAI *et al.*, 1978). Therefore, all experiments were conducted at pH 6.9 and complete formation of the chelates under investigation was ensured by the presence of excess ligand. Concentrations of the successive deprotonated species of EDTA and NTA present in solution at room temperatures can be calculated precisely. However, determination of these species at elevated temperatures can not be accomplished without detailed solution equilibria and ligand protonation constants. These data were not necessary for the analysis of the experimental data. Quantitative determination of soluble In concentration by neutron activation delineates total metal concentration as a chelate rather than dissociated metal ion still in solution, because uncomplexed In remains in solution only at $\text{pH} < 3.4$ (BIEDERMANN, 1956).

The results of the In(III)-EDTA and In(III)-NTA thermal stability investigations are shown in Figs 2 and 3, respectively. The data obtained at 150°C indicate that the In concentration of both chelates remained constant over the experimental period of 20 days. The calculated standard error of the mean soluble In concentration is ± 5.2 ppm and ± 4.9 ppm for 505 ppm initial concentrations of In(III)-EDTA and In(III)-NTA, respectively. Because these organic ligands do not decompose thermally at 150°C (MARTELL *et al.*, 1975), there are no additional indium chelates formed with ligand decomposition products present in solution. Therefore, it appears that a temperature of 150°C has little effect on the thermal stability of In(III)-EDTA and In(III)-NTA complexes.

At 200°C the soluble In concentration of 505 ppm In(III)-EDTA solution was not constant with time. For the first 16 days the change in the total soluble In concentration, if any, was in the range of experimental error. Within 14 additional days the soluble metal concentration decreased to a level 32% of its original value. The observed degradation kinetics can be attributed to the chelating characteristics of the intermediate thermal decomposition products of EDTA; IDA and HEIDA. A chelating efficiency of EDTA degradation products at 200°C was suggested by VENEZKY and MONIZ (1969). However, the ability

of IDA and HEIDA to chelate metal cations at room temperature is significant, but several orders of magnitude lower than that of EDTA (MARTELL and SMITH, 1974). Because EDTA decomposition at 200°C is relatively fast (MARTELL *et al.*, 1975), the observed stabilization of EDTA is due to coordination with In. Stabilization of EDTA complexed with monovalent and divalent metal ions at elevated temperatures was observed by VENEZKY and MONIZ (1969) and MOTEKAITIS *et al.* (1982). A dissociation-controlled mechanism for In(III)-EDTA degradation at 200°C can be described as follows:



Therefore, the solubility of In at 200°C is a function of the thermal decomposition rate not only of EDTA but also of IDA and HEIDA.

The results obtained from the In(III)-NTA run at 200°C (Fig. 3) show that the decrease in soluble In concentration started simultaneously with the initiation of the experiment. The In concentration decreased steadily from 505 ppm to approximately 95 ppm within a period of 11 days. The concentration remained stable at 95 ppm for the rest of the experiment. An additional experiment, at 200°C and 322 ppm In(III)-NTA, was performed to examine the dependence of the equilibrium In concentration on the initial solution concentration. The results of this investigation are shown in Fig. 4. The In concentration decreased from 322 ppm to 35 ppm within 5 days. The data obtained during the following 12 day period indicate no further decline in soluble In concentration, with an average value of 33 ppm. The scatter of the experimental data is attributed to In detection limitations of the available apparatus. The equilibrium In concentration at 200°C is shown to be dependent on the initial In(III)-NTA concentration. NTA does not decompose thermally below 260°C (MARTELL *et al.*, 1975). Therefore, the decrease in soluble In concentration at 200°C may be due to an equilibrium shift of the In(III)-NTA chelate. Because the chelate solutions were adjusted to pH 6.9, uncomplexed In species were probably sorbed onto the pressure vessel walls and precipitated as indium hydroxide. The data imply that the thermodynamic formation constant of the In(III)-NTA decreases considerably at 200°C . However, complex dissoci-

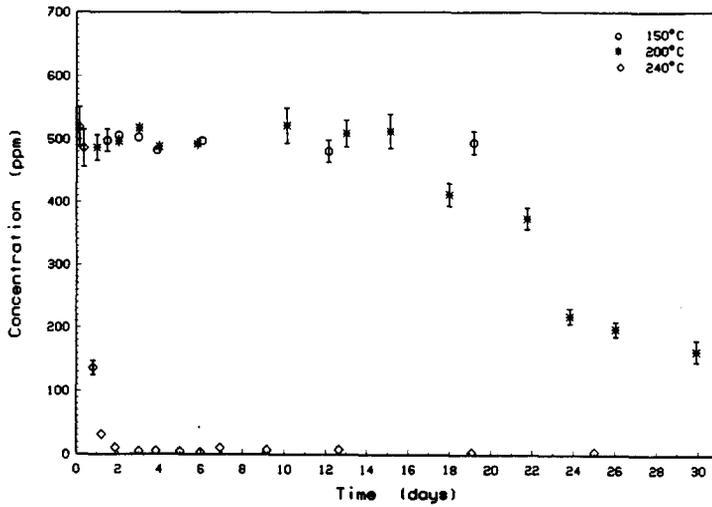


FIG. 2. Persistence of 505 ppm In(III)-EDTA at 150, 200 and 240°C as a function of time.

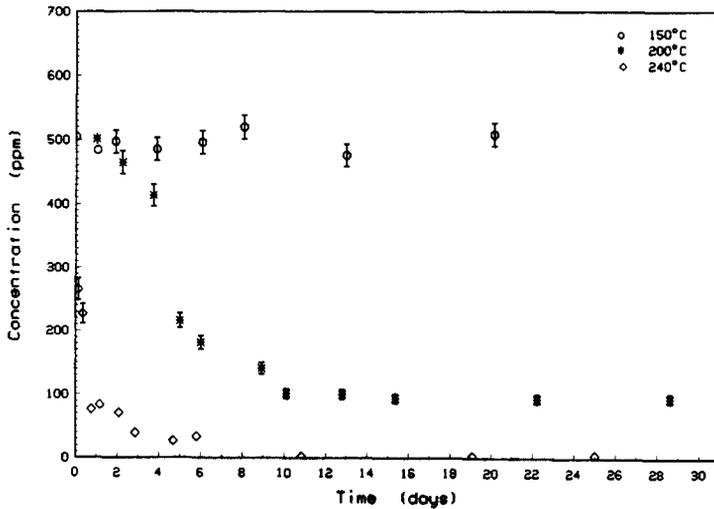


FIG. 3. Persistence of 505 ppm In(III)-NTA at 150, 200 and 240°C as a function of time.

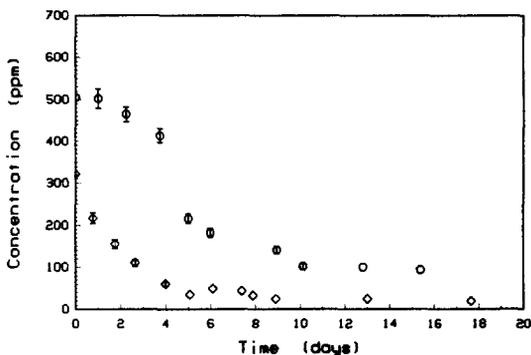
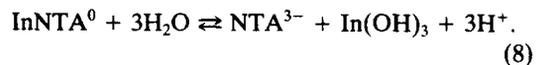


FIG. 4. Effect of initial In(III)-NTA concentration on the equilibrium chelate concentration at 200°C. Circles represent solutions containing 505 ppm total In. Diamonds represent solutions containing 322 ppm total In.

ation increases with indium-ion hydrolysis and precipitation from solution at pH 6.9. The overall reaction at a temperature of 200°C may be written as follows:



A comparison of In(III)-EDTA and In(III)-NTA results at 200°C indicates that the enhancement of In solubility by EDTA is superior than that of NTA, implying that In liberation is inversely proportional to the magnitude of metal-ligand formation constant.

At 240°C the data were not suitable for quantitative analysis because the time required for the first few pressure vessels to reach air-bath temperature was an appreciable fraction of each heating period. Both of the indium chelates showed rapid decomposition.

The room temperature adsorption experiments with In(III)-EDTA concentrations ranging from 50 to 1500 ppm, in contact with graywacke of 1.28, 0.94 and 0.46 mm rock size fractions indicate that any adsorption, if present, is within experimental error. The adsorption mechanism of metal-ligand involves either an ion exchange of elements in the rock structure for cations in solution or physical adsorption. Ion exchange has a low activation energy and the approach to equilibrium is fast, while physical adsorption is a reversible and rapid process caused by nonspecific secondary binding mechanisms. Adsorption of cations in the presence of EDTA onto the clays kaolinite or montmorillonite, two of the main cementing constituents of the graywacke, have fast equilibrium kinetics in the order of 30 min (MAEST *et al.*, 1985). Therefore, the 3 day equilibration period for the adsorption experiments was sufficiently long. The insignificant In adsorption observed in these experiments indicate that the thermal degradation data were not subject to adsorption losses. However, due to the large volume of solution and the low rock surface-area used in the adsorption experiments no reliable conclusions can be drawn about the adsorption process.

From all the metal cations present in hydrothermal fluids and subsurface formation, only Fe(III) could displace In from its chelate complex. The ferric cation may be an important displacing reactant because the thermodynamic formation constant of Fe(III)-EDTA, $K = 10^{25}$, is slightly higher compared to In(III)-EDTA formation constant (MARTELL and SMITH, 1974). Although the formation rate of indium(III) ion with EDTA is rapid (OMORI *et al.*, 1984), the substitution reaction between Fe(III) and In(III)-EDTA complex is very slow in weakly acid solutions (DAS, 1974). Therefore, In substitution from EDTA complex is probably unlikely to occur in a dynamically flowing environment. However, the role of metal cations in affecting In solubility in the presence of EDTA requires further study.

CONCLUSIONS

Chelated In is a reliable activable tracer for studying the dynamic behavior of surface and ground waters as well as low to moderate temperature hydrothermal systems. The organic ligands EDTA and NTA, employed to enhance In solubility in the pH range of surface and subsurface natural fluids, form stable time persistent complexes with In. Their formation constants with In(III) compete very well with most of the common metal cations, minimizing metal displacing reactions.

It has been demonstrated experimentally that In(III)-EDTA and In(III)-NTA are degraded at and above 200°C through a metal dissociation mechanism. The experimental data show that EDTA is more favorable than NTA for In chelation at

elevated temperatures, because In liberation is inversely proportional to the magnitude of metal ligand formation constant. The observed EDTA stabilization towards thermal degradation at 200°C is attributed to metal coordination of the organic ligand.

The In(III)-EDTA and In(III)-NTA complexes are conservative tracers at low temperatures. However, In(III)-EDTA can be used effectively as a conservative tracer in hydrothermal systems and particularly geothermal reservoirs with formation temperatures below 200°C and tracer transit times of approximately 20 days or less.

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