

Comparative chemistry of the platinum and other heavy metals in the marine environment

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Abstract - The complexing abilities and the redox reactions of the platinum metals and their periodic table neighbors are used to interpret their comparative marine chemistries. Two sets of environmental conditions are treated: the oxic milieu where dissolved oxygen gas can initiate redox reactions; and the anoxic milieu where the waters are devoid of oxygen gas. In the latter case reductions of dissolved species may take place with the ever present organic phases. Analyses of seawaters, sediments and ferromanganese minerals are carried out using graphite furnace atomic absorption spectroscopy. All assays are followed with radioactive tracers for yield determination. Isolation of picomolar concentrations of these metals from seawater utilizes anion exchange resins with an ultimate isolation upon one or two beads.

INTRODUCTION

The platinum metals and their periodic table neighbors provide the environmental scientist with a unique opportunity to expand present knowledge of the chemical nature of seawater and the reactions occurring therein (ref. 1). So far there are but a few investigations dedicated to studying their concentrations in various compartments of the ocean environment. In 1969, the following summary was made about the knowledge of the platinum metals' chemistries at the surface of the earth (ref.2): "The behavior of the platinum metals during weathering, the nature of platinum metal species responsible for solubility in natural waters and the abundance of these metals in natural waters are essentially unknown." Although subsequently there have been extensive studies of platinum metals in lunar samples and some basic rocks, little improvement in this situation has been made in recent years.

Several reasons converge to make studies of these heavy metals especially attractive today. First of all, variations in their acidic character and in their redox reactions are systematic. The concentrations in various domains of the oceans may, in principle, be interpreted comparatively through first principles of chemistry. Secondly, there are available techniques for the analyses of platinum metals at environmental levels, often as low as femtomolar in waters and parts per trillion or less in solid phases. Options include neutron activation, atomic absorption and isotope dilution mass spectroscopy. Although a single technique may not be available for all elements of interest, usually it will analyze more than one.

METHODS

Our determination of these metals in marine waters, sediments and organisms is based upon the isolation of anionic forms upon appropriate ion exchange resins with subsequent purification through uptake on a single ion exchange bead. Graphite furnace atomic absorption spectrometry is employed as the determinative step. Both single beam and double beam instruments have been used in our work. In some cases the isolate can be analyzed for more than one element. All steps are followed by radioactive tracers and yields vary between 35 and 90%.

One uncertainty in analytical techniques involving radioactive tracers is the assumption that there is an equilibration of the tracer with all of the species containing the element under assay. In the case of iridium, for example, both the trivalent and tetravalent forms may exist in our samples (ref. 3). Thus, chlorine gas is introduced to the solution to oxidize any reduced forms of iridium to the tetravalent state. Still, there is no certainty that this procedure brings all of the iridium into the same chemical forms. This is a problem common to nearly all trace analyses of elements which can occur in more than one redox state or which form strong complexes in environmental media.

It should be mentioned that there can be difficulties in obtaining commercially the appropriate radionuclides for use as yield tracers in the analytical procedures. This applies especially to those nuclides that are produced in accelerators as opposed to the more readily available fission products. For example, we have been unable to find a source for Pd-103, the cyclotron produced nuclide used to monitor our palladium analyses. A similar situation exists for some enriched stable isotopic preparations of the platinum and other metals which can be used to prepare radioactive tracers through irradiation.

Platinum: Platinum is quantitatively removed from two liters of acidified seawater through uptake on the anion exchange resin Dowex 1 (ref. 3). The waters are initially spiked with Pt-191 tracer (half life of three days) prepared by the neutron irradiation of enriched Pt-190 metal powder (4.19 atom % compared to a natural abundance of 0.0127 atom %). Following elution of the platinum from the resin with hot concentrated nitric acid, the solution is reduced in volume and rotated with a single ion exchange bead which takes up the metal. The platinum is then stripped from the bead with concentrated nitric acid and injected directly into the graphite furnace. The ferromanganese nodules are initially dissolved in 6 N HCl; the sediments are placed into solution with HF. The detection limit, defined as a signal with twice the background, is about 15 pg. Seawater blanks were always less than 40 pg/sample.

Palladium: Palladium is isolated from seawater as a cyanide complex onto a small volume of ion exchange resin and then eluted with hot 14 M nitric acid. Initially, Pd-102 (half-life of 17 days) is added as a yield tracer (ref. 4). The eluant is evaporated to dryness and redissolved with 1.5 M hydrochloric acid. The solution and an ion exchange bead are placed into a 1 ml Eppendorf pipette and rotated for at least 12 hours. The bead is directly introduced into the graphite furnace. Blanks range from the detection limit to 0.18 pmol/kg. The detection limit is about 0.11 pmol/kg in two liters of seawater and the precisions are 11% and 7.2% at 0.6 and 1.2 pm/kg respectively.

Ruthenium: An initial isolation involves a coprecipitation of the ruthenium from seawater upon aluminum phosphate (ref. 5). Rock samples are fused with sodium peroxide and the manganese nodules are put into solution with hydrochloric acid. Ru-106 with a half-life of 366 days is used as a yield tracer. The ruthenium was distilled as the tetroxide from a sulfuric acid/potassium permanganate solution. The ruthenium in the distillate is isolated upon an anion exchange bead in 0.5 molar hydrochloric acid and ammonium thiocyanate solution, stripped and determined in the graphite furnace atomic absorption unit. The U.S. Geological Survey Standard peridodite (PCC-1) was used to calibrate the method and our results are in reasonable agreement with those of previous investigators who used neutron activation techniques.

Iridium: Ir-192 (half-life of 74 days), used as a tracer, is prepared by neutron activation of natural iridium (ref. 3). The stable iridium content of the tracer spike is below the detection limit of the technique. Twenty liters of spiked and acidified seawater are treated with a vigorous bubbling of chlorine gas to oxidize any reduced iridium to the tetravalent state. The degassed solution is then passed through an AG-1 ion exchange column which quantitatively retains the iridium. The absorbed iridium is stripped with hot, concentrated nitric acid. Subsequently, the solution is reduced in volume and tumbled with several IRA-900 ion exchange resin beads. The iridium is then stripped from the beads and the solution introduced into the graphite furnace. For seawater samples, the blanks are always less than 20 pg/sample. The seawater iridium values are so low that 100 liters of seawater had to be treated in five batches.

Rhenium: The analytical procedure was traced with the 88.9 hour Re-186 prepared from enriched rhenium (Re-185, 96.85%; Re-187, 3.15%) at the University of Missouri Nuclear Reactor. The seawater assays were made with the assumption that all of the rhenium was in the heptavalent state as perrhenate (Koide et al., manuscript in preparation). One to two liters of Re-185 spiked, acidified seawaters are passed through an AG-1 column. Following elution with 2N nitric acid, the resulting solution was heated for about two days at a low setting of the hot plate. Losses from Re volatility can take place during this step of the procedure. A sodium peroxide fusion of the residue is essential to place the rhenium in a form such that it can then be taken up by a second pass through an AG-1 column. An extraction of the tetraphenyl arsonium perrhenate into chloroform separates the rhenium from molybdenum, an interfering element in the atomic absorption analysis. The evaporated extract is taken up in 6 N HCl and introduced into the graphite tube for assay. Manganese nodules are placed into solution with hydrochloric acid and sediments through a sodium peroxide fusion. The seawater procedure is then followed in each case.

Gold: Two liters of acidified seawater, 0.5 grams of dried sediment, or 0.5 grams of ferromanganese minerals are spiked with carrier-free Au-195 tracer (half-life of 183 days) (Koide et al., manuscript in preparation). The latter two solids are placed into solution with a sodium peroxide fusion and a hydrochloric acid treatment, respectively. The resulting solutions are passed through an AG-1 anion exchange resin and the sorbed gold is

eluted with 8 M nitric acid at 83°C. The eluant is dried, subsequently dissolved in 0.5 M HCl and the gold extracted into a 10% dithizone solution in chloroform. The chloroform is evaporated to dryness; the residue is taken up in 25 microliters of chloroform and quantitatively transferred to a graphite cup for determination by atomic absorption spectroscopy.

SEAWATERS

The concentrations and distributions of these trace metals in the marine system can usually be interpreted with chemical and oceanographic knowledge. Even at femtomolar concentrations platinum and palladium have systematic ocean chemistries. Open ocean, coastal and California Current waters from the eastern Pacific show similar but increased concentrations of platinum with depth (Fig. 1) (refs. 3 and 11). The curves resemble those of nickel which is in the same vertical series of the periodic table. The Pt/Pd ratio in these waters is essentially constant at 4.5. Such profiles reflect biological and scavenging processes which transfer metals from surface to deeper waters. On the other hand, rhenium at picomolar concentrations in seawater is essentially constant with depth, suggesting a most modest involvement in chemical and biological reactions.

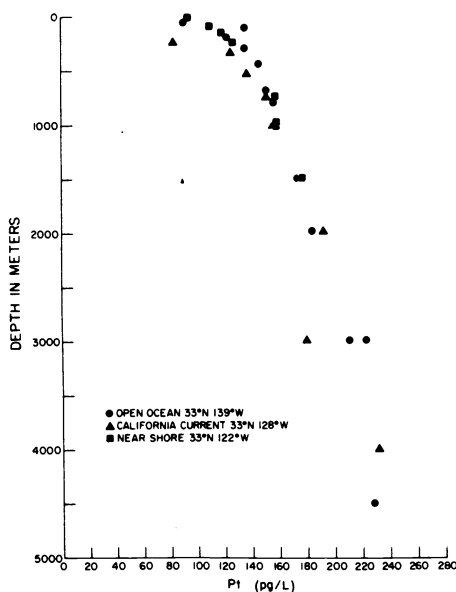


Fig. 1. Platinum concentrations in Pacific Ocean, filtered seawaters.

The speciation of these metals in seawaters provides a stepping stone to understand their chemistries. For example, in his classic equilibrium model of seawater Sillen (ref. 6) concluded that if Au(III) and Au(I) in solution are in equilibrium with elemental gold, then the dominant form of dissolved gold would be the anion AuCl_2^- . Sillen also pointed out that colloidal gold would contribute to the gold burden in seawater.

Platinum and palladium probably exist in seawater as the doubly charged, divalent chloro anions. This is a consequence of the high concentration of chloride ion in seawater. The stability constants of these two complexes have been determined (ref. 7) and are higher for platinum than for palladium. This is consistent with the softer acidic character of platinum. The fourth stepwise stability constant of platinum is several hundred times larger than that for palladium (ref. 7). Both platinum and palladium have higher stability constants with the halides than those of nickel. Thus, a priori one would expect a higher relative concentration of the two platinum metals in seawater than that of nickel relative to their crustal abundances.

The stability constants for the bromo complexes of palladium are several thousand times greater than for the corresponding chloro complexes (ref. 8). However, because of the extremely small concentrations of bromide in seawater, the bromo complexes will be of less importance. The differences between the chloro and bromo complexes of platinum are smaller than those for palladium.

Iridium probably exists in seawater as the trivalent state which does not form as strong complexes with chloride and bromide as platinum and palladium. For example, the addition of the last chloride to Pt(II) to form PtCl_4^- , to Pd(II) to form PdCl_4^- and to Ir(III) to form the complex IrCl_6^- are defined by stability constants of around 100, 24 and about 0.1 (refs. 7 and 9). Hydrolysis reactions are of greater importance for iridium than for palladium and platinum.

Table 1. Some geochemical characteristics of the platinum metals, gold, silver, molybdenum and rhenium. Crustal abundances are from ref. 12.

Element	Atomic Number	Crustal Abundance	Pelagic Sediment Abundance	Manganese Nodule Abundance	Surface Seawater Concn.
on a wt. basis relative to Ru					
Mo	42	4000.	10,000	40,000	10,000,000
Ru	44	1.0	1.0	1.0	<5
Rh	45	1.0			
Pd	46	10.0	2.0	0.01-0.06	20
Ag	47	180.0			100 (ref. 17)
Re	75	1.0	<0.1	<0.1	8000
Os	76	1.0			
Ir	77	1.0	0.8	0.20	1.5
Pt	78	5.0	4.0	20.	100
Au	79	10.0	0.12	<0.002-0.11	

The seawater chemistry of ruthenium probably involves the trivalent state and chloro complexes. The log Ks for the reduction of Ru(IV) to Ru(III) are of the order of 100 to 10,000 (ref. 6). The oxidation to the tetravalent state may occur under favorable circumstances although the occurrence of mixed valence states in solid and liquid phases cannot be excluded. With a pE of seawater of 12, the ratio of Ru(III)/Ru(IV) will be of the order of 100 to 10,000 at equilibrium.

The marine environment can be divided into two milieus for the consideration of chemical reactions of the metals: the oxic environment where dissolved oxygen gas can initiate redox reactions; and the anoxic environment where the waters are devoid of oxygen gas. Here, reductions of some dissolved species may take place through interactions with the ubiquitous organic phases.

First of all, the factors that govern the comparative amounts of these heavy metals in seawaters will be considered. The relative concentrations of platinum, palladium, iridium and ruthenium in seawaters are interpretable on the basis of their complexing abilities with the available ligands (Table 1). For example, platinum is markedly enriched over palladium in seawater compared to sediment or crustal values. The Pt/Pd ratio in seawater is 5; in crustal rock 0.5. This can be explained by the softer acidic character of Pt(II) relative to Pd(II) and the stronger stabilization in seawater through complex formation of platinum with such ligands as chloride and bromide (ref. 10). On the other hand, iridium has seawater concentrations less than those of platinum or palladium (ref. 11): the Pt:Pd:Ir ratios are 100:20:1.5. Their sediment or crustal abundances are more similar (Pt:Pd:Ir = 4:2.0:0.8). The hydrophobicity of iridium comes about as a consequence of its weaker complexing abilities with the halides and of a stronger tendency to hydrolyze.

In the oxidation process, which results in the incorporation of oxidizable platinum metals in the ferromanganese concretions (see below), it may be initially assumed that such metals are removed from seawater with equal efficiency, i.e., the relative seawater concentrations are reflected in these solids. This appears to be the case for iridium and platinum, for example. The Pt/Ir ratio in seawater is about 100 (Table 1). In the ferromanganese minerals, the Pt/Ir ratio increases with increasing platinum concentrations and the nodule values cluster about 100 (Fig. 2). The outlier at 300 is as yet unexplained. Lower values may result from dilution of the ferromanganese phases with detrital components whose Pt/Ir ratios are lower, reflecting crustal abundances.

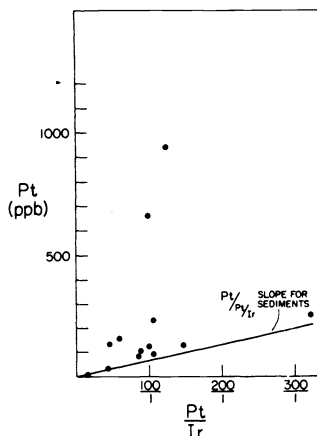


Fig. 2. The Pt/Ir ratio vs the platinum concentrations in Pacific Manganese nodules.

Using similar reasoning we can predict the ruthenium concentration in seawater (ref. 5). As yet we can only place an upper limit at 5 pg/liter experimentally. The Pt/Ru ratio in the ferromanganese minerals fluctuates around 20. Thus, assuming that both platinum and ruthenium are oxidized effectively during mineral formation and are removed from seawater in amounts relative to their seawater concentrations, we estimate 6 pg/l as the concentrations or ruthenium in surface waters where the Pt concentrations are 120 pg/l. This is close to the upper limit we have placed on these waters experimentally.

Of this group of elements rhenium has the lowest pelagic sediment concentration, as well as the lowest crustal abundance (Table 1). However, it has an extraordinarily high seawater concentration compared to neighboring elements in the periodic table. This is a result of its occurrence in seawaters as the highly unreactive perrhenate ion. The removal of this species from seawater requires a reduction to the tetravalent state (see below).

THE OXIC ENVIRONMENT

The geochemical characteristics of the metals to be considered are given in Table 1. Except where indicated, the analyses were performed in our laboratories. Of interest are their fractionations going from the earth's crust to seawater and from seawater to the solid phases that precipitate under oxidizing or reducing conditions.

There are a number of metals in seawaters whose dissolved states can be oxidized to insoluble, higher oxidation states. Perhaps, most notorious is manganese which can go from divalent to the tetravalent forms in the build-up of the ferromanganese minerals. Accompanying manganese are cerium (going from III to IV), lead (going from II to IV) and cobalt (going from II to III). All of these elements, oxidized by dissolved oxygen gas, are markedly enriched in these accretions.

Several of the platinum metals (platinum, ruthenium and iridium) also show this behavior (ref. 5, 10, and 11). Platinum, which can be oxidized from the divalent state to the tetravalent state is markedly enriched in the ferromanganese minerals, compared to its vertical periodic table neighbor, palladium, which only occupies the divalent state in natural waters. Where the Pt/Pd weight ratio in seawater is about five, the Pt/Pd ratios in ferromanganese nodules can attain values as high as 1300. In general, nodules with high Pt/Pd ratios also are enriched in cobalt. The oxidation process, involving dissolved oxygen gas, can be illustrated in the following way. Some ferromanganese nodules rest upon sub-oxic sediments, i.e., those devoid of dissolved oxygen gas in their interstitial waters. The tops of the nodules, on the other hand, are exposed to seawaters containing dissolved oxygen. The tops contain Pt concentrations around a hundred or so parts per billion, while the bottoms contain platinum at levels of a part per billion or less. The accommodation of cobalt in the tops and bottoms of the nodules parallels that of platinum.

Gold and silver are unusually low in ferromanganese minerals reflecting the stabilities of their chloro complexes and their resistance to oxidation in oxygenated seawaters. Molybdenum possesses a rather unique geochemical characteristic -- it is enriched in solids that precipitate under oxidizing conditions as well as in those that precipitate under reducing conditions (ref. 13). The uptake onto ferromanganese nodules typifies the former and appears to be a sorption process that involves both iron and manganese oxides. There exists at present a confusion over what parameters regulate the uptake process. Our data shows a strong covariance between molybdenum and manganese in pelagic sediments suggesting a role of the manganese oxides in the uptake process.

Although rhenium and manganese are members of the same vertical row in the periodic table, the former differs from the latter in that it is depleted in ferromanganese minerals. Rhenium has a stable septavalent state in seawater which is not readily oxidized, whereas the soluble divalent manganese is unstable thermodynamically in oxygenated waters with respect to oxidation to the tetravalent state. Rhenium, on the other hand, has a strong geochemical coherence with molybdenum in anoxic environments.

THE ANOXIC ENVIRONMENT

There are a number of elements whose dissolved species in seawater can be reduced to insoluble lower oxidation states in anoxic environments. For example hexavalent molybdenum as molybdate can be reduced to the four or five valent forms (ref. 14). Chromate, a hexavalent form of chromium, can be reduced to the much less soluble trivalent chromous species. Uranium primarily exists in seawater as the carbanato complex $UO_2(CO)_3$ but can be reduced to the tetravalent state in the formation of such minerals as phosphorites. In general anions are reduced to cationic species which hydrolyze or form insoluble sulfides. We have assayed a number of elements which in principle might be reduced under anoxic conditions (ref. 15): gold from Au(I) or Au(III) to Au(0); rhenium from Re(VII) to Re(IV) and molybdenum from Mo(VI) to Mo(V) or Mo(IV). The abundances of these elements in deposits that probably have been subjected to anoxic conditions are compared with those

Table 2. The concentrations of some potentially reducible elements in anoxic and oxic deposits (ref. 15).

Sediment	Mo ppm	Re ppb	Au ppb	Ag ppm
HYDROTHERMAL DEPOSITS				
Sphalerite, Guaymas Chimney	1.5	6	420	13
Chalcopyrite, East Pacific Rise	11	11	1.7	
Green Seamount crater pit	170	273	107	3.3
PHOSPHORITES				
PD-15-18	53	63	<0.1	
Concretion	7.6	44	<0.1	
ANOXIC COASTAL SEDIMENTS				
Chile Core, 11-12 cm	67	93	1.3	0.81
Peru Core, 2-3 cm	15	8	4.5	0.36
Saanich Inlet, 14 cm	18.5	6.9	<0.1	0.17
FERROMANGANESE MINERALS				
DWBD-4	423		<0.1	
PELAGIC SEDIMENTS				
SCAN 29PB	15.5	0.1	6.	
CRM-11G	17	<0.15	0.43	
CRUSTAL ROCKS (ref. 12)				
	1.5	0.5	4	0.07

from oxic environments (ferromanganese minerals and pelagic sediments) and with crustal abundances (Table 2). The data are from investigations in our laboratories.

Both rhenium and molybdenum show unusual enrichments in the anoxic sediments -- the hydrothermal deposits, the phosphorites and the coastal sediments -- compared to their crustal abundances. The reduction of molybdenum and rhenium in anoxic regimes to lower valence states can explain these results. For rhenium, the process of enrichment involves the presence of perrhenate in seawaters. Since rhenium in igneous rocks probably exists in reduced states, the first appearance of perrhenate in natural waters took place with the onset of an oxidizing atmosphere and hence oxidizing waters. Thus, the oldest sediments enriched in rhenium may signal the advent of an oxidizing environment.

Platinum is markedly depleted in anoxic deposits relative to crustal concentrations. For example, in sulfide minerals from hydrothermal sediments, the platinum concentrations are more often than not less than 0.2 ppb whereas in crustal rocks and in pelagic sediments the values are usually greater than several ppb (ref. 15).

Silver and gold are only enriched in the hydrothermal deposits and the enrichments are quite remarkable (Table 2). We suspect that these enrichments are a consequence of (1) the precipitation of the highly insoluble Au(I) and Ag(I) sulfides (ref. 12) or (2) their reduction to the elemental state by hydrogen sulfide. Hot gold solutions can be reduced to metallic gold at high temperatures (ref. 16). The hot waters associated with the hydrothermal vents, combined with the high hydrogen sulfide concentrations of the waters, provide an appropriate situation for the deposition of elemental gold.

There is some laboratory evidence for the reduction of gold from solution to the elemental state during the formation of sulfides (ref. 17). Gold appears to grow upon the mineral surfaces. The reduction is auto-catalyzed and the metal accumulates on the surfaces as spheroids and is unevenly distributed. A variety of sulfide minerals reduced gold and include pyrite (FeS_2), sphalerite (ZnS), galena (PbS) and chalcopyrite (CuFeS_2).

The redox chemistry of gold may be influenced by aquatic plants. Fresh water algae (*Chlorella vulgaris*) accumulate both monovalent and trivalent species of gold from solution (ref. 18). When the organisms, which had been exposed to gold for periods which lead to saturation, were allowed to stand for two days either in the light or dark, they changed color from green to purple. The spectra of the algal suspensions showed absorption bands near 525 nm, similar to that of elemental colloidal gold particles. Thus, a mechanism to produce colloidal gold in marine systems may be related to primary plant productivity.

The softer acidic characters of both Au(I) and Au(III) compared to that of the transitional element platinum emphasize the higher degrees of interactions of the former with sulfur. Thus, the comparative enrichments of gold and the depletion of platinum in the sulfides may be interpreted on the strong affinities of Type B elements such as gold for sulfur and on the strong chloro-complexes of platinum which keep this metal in solution.

In one case we have observed a remarkable enrichment of both platinum and gold in an anoxic deposit near the Whites Point sewer outfall off the coast of Los Angeles. Here, the platinum values on a dry weight basis varied between 1.3 and 2.0 ppm dry weight and the gold between 0.3 and 0.9 ppm. Clearly, the enrichments must relate to the high anthropogenic fluxes of these elements in the domestic waste discharges. Silver is also enriched with concentrations between 12 and 20 ppm.

The enrichments of molybdenum and rhenium in anoxic coastal sediments vary from site to site but the Mo/Re ratio hovers about 1000. Clearly, the important factors that govern the sedimentary concentrations of these two metals include the rates of accumulation, the mineral phases in which the molybdenum and rhenium are accommodated and the exact nature of the deposit, i.e., sub-oxic, anoxic, etc.

The enrichments of molybdenum and rhenium in the phosphorites are in accord with previously measured enrichments of uranium, which is reduced from the hexavalent to the tetravalent state before incorporation into the minerals. Either during formation or after deposition, the solid phosphate phases are in an electron rich milieu which can remove molybdenum and rhenium from solution through reduction.

A FOOTNOTE

Sometimes a mineral can form under either oxidizing or reducing conditions. Its trace constituents can often be decisive in identifying the environmental parameters. For example, some calcium phosphates are associated with deposits underlying areas of high organic productivity where reducing conditions exist. On the other hand, there are widespread deposits of these phosphates in the shallow areas of the tropical oceans where intergrowth with manganese and ferric oxide minerals is common (ref. 19). The former minerals have high concentrations of uranium (existing to a large extent in the tetravalent state); the latter have low concentrations. In the first case uranium is reduced to the tetravalent state such that its increased ionic radius is similar enough to that of calcium that it can readily substitute in the crystal structure.

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