SHRIMP measurements of U and Pb isotopes in the Koongarra secondary ore deposit, Northern Australia

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SHRIMP analyses have been conducted for rock samples from the Koongarra secondary ore deposit in Northern Australia to obtain activity ratios of $^{234}\text{U}/^{238}\text{U}$ and isotopic ratios of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{204}\text{Pb}/^{206}\text{Pb}$, and to understand their migration behavior within the secondary ore deposit. Main target minerals for the analyses were iron minerals and kaolinite, which are the main weathering products in this area. The activity ratios of $^{234}\text{U}/^{238}\text{U}$ were based on SHRIMP counts at the mass of uranium metal. The $^{234}\text{U}/^{238}\text{U}$ activity ratios based on counts of uranium oxides were not satisfactory, because the count rates of $^{234}\text{U}^{16}\text{O}$ were affected by interference from the $^{238}\text{U}^{12}\text{C}$ fragment. The activity ratios of $^{234}\text{U}/^{238}\text{U}$ were approximately unity for crystalline iron minerals, whereas the amorphous iron minerals (precursors of the crystalline iron minerals) had also values above unity. The mean residence time of uranium within the iron nodules was estimated to be up to approximately 2–3 million years.

Results of lead isotopes, represented by a diagram of $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$, indicated that the present three samples contained radiogenic lead, common lead and mixture of both components. In addition, the recent radiogenic lead component within the primary ore is dominant in the area closer to the primary ore. The radiogenic lead isotope compositions of samples at greater distances from the primary ore have been affected only by the earlier mobilization event of radiogenic lead. All these results indicate that some geologic event causing migration of the radiogenic lead had occurred before formation of the secondary ore deposit due to the weathering. After the weathering commenced at least 2–3 million years ago, uranium and lead have migrated from the primary ore. While the uranium has dispersed throughout the secondary ore deposit, the lead reached only the area closer to the primary ore probably due to its immobility compared to the uranium.

INTRODUCTION

The prediction of geochemical behavior of elements over very long periods of time is important for the safety assessment of geological disposal of radioactive wastes or for the environmental management of hazardous elements. In natural analogue studies, the long-term behavior of

uranium decay series around uranium ore bodies is particularly useful because the uranium decay series can be used in part as a chronological clock or contains various elements with different geochemical properties. For example, the remobilization process of uranium decay series due to the weathering within the Koongarra secondary ore deposit, Northern Australia, is analogous

to that that might be expected to occur around a repository (Skagius and Wingefors, 1992; Yanase *et al.*, 1998), and has extensively studied.

The Koongarra secondary ore deposit began to form about 1–3 million years ago, that was derived from the whole rock activity ratios of $^{234}\text{U}/^{238}\text{U}$, and from simulations of migration models which include the effect of transport by flowing groundwater and equilibrium sorption (Airey *et al.*, 1986). Also geomorphological studies suggest that the dispersion fan is between one and six million years old (Wyrwoll, 1992). However, the $^{234}\text{U}/^{238}\text{U}$ activity ratios modelled by Airey *et al.* (1986) were obtained from bulk rock samples, in which it is impossible to identify the minerals of importance and their mechanistic role in U retention and radioactive disequilibrium.

Selective extraction (SE) procedures are useful for separating and identifying the constituent mineral phases, and have been applied to the study of U series radionuclides (Yanase *et al.*, 1991, 1996). However, the SE technique does not provide information on the textural relationship between the phases, because crushing and dissolution of the sample are required. Isotopic data for small areas, e.g., individual mineral phases within rock samples or different positions within a grain, are necessary to elucidate the isotopic fractionation mechanisms and migration of U series radionuclides.

Recently, secondary ion mass spectroscopy (SIMS) has been developed as a micro-analytical technique for isotopes in solids and applied to geological samples, and is expected to be useful to confirm data obtained with the SE procedure. The technique was used by Sato *et al.* (1998) to ascertain the feasibility of using a Sensitive High mass-Resolution Ion Micro Probe (SHRIMP), one of the most powerful SIMS instruments, in measurements of weathered rock samples from the Koongarra deposit. Although they provided new data of $^{234}\text{U}/^{238}\text{U}$ activity ratios from individual mineral phases, they analyzed only one rock sample and did not discuss the timescale related to the redistribution of uranium series radionuclides within the dispersion fan. SIMS has also recently

been used in analyzing the lead isotopic composition of uranium and lead minerals in the primary ore body of the Koongarra deposit (Isobe *et al.*, 1998).

In this study, some $^{234}\text{U}/^{238}\text{U}$ activity ratios using SHRIMP were added for three samples from the Koongarra secondary deposit. The lead isotope composition of samples in the secondary deposit was also measured. The final goal of this investigation is to elucidate geochemical behavior of uranium and lead within the dispersion fan and to estimate the timescale associated with their migration and redistribution.

EXPERIMENTAL

Sample description

In the vicinity of the Koongarra uranium deposit, uranium dissolved from the primary ore has migrated down-gradient by groundwater transport. Along the groundwater flow, a tongue-like secondary ore deposit has developed within the weathering zone as a result of uptake of uranium by weathering products (Snelling, 1992). The secondary ore body lies within 25 m of the ground surface, and is referred to as the “dispersion fan” (Fig. 1). Three weathered rock samples from different positions within the secondary ore deposit have been analyzed in the present study. The rock samples were located in the dispersion fan at similar depths (about 15–20 m) and different distances from the primary ore body, and hence could provide information on the spatial distribution of the uranium and lead within the dispersion fan. These samples were from boreholes DDH58, DDH60 and DDH87, and were denoted DDH58-78, DDH60-65 and DDH87-61, respectively (Snelling, 1992) (see Fig. 1).

In the present three samples, main mineral components are kaolinite, iron minerals and quartz. The kaolinite is considered to result from the weathering of vermiculite, biotite, garnet, feldspar, smectite, and possibly direct from the weathering of chlorite (Edis *et al.*, 1992). The iron minerals occur also as the weathering products, and are considered to influence the distribution of ura-

Fig. 1. Schematic cross section of the Koongarra ore body (modified from Snelling, 1992). The symbols (●) indicate sampling positions.

niun as well as phosphate, manganese etc. (Edis *et al.*, 1992). There seem to be at least two kinds of iron minerals, i.e., amorphous and crystalline phases. High uranium contents (40–70 wt.% uranium) were observed within the crystalline iron mineral phases (Edis *et al.*, 1992; Murakami *et al.*, 1992). The “iron nodule” phase has distinctive morphological features, particularly a complex alveolar structure (Sato *et al.*, 1997). Of the various iron-rich phases, the U content is highest in the nodules, i.e., 1.6–7.7 wt.% in minerals, rather than Fe coatings or fissure filling phases (Sato *et al.*, 1997). It is therefore thought that the crystalline iron nodules have played a dominant role in the retention of uranium in the dispersion fan, to a greater extent than any other mineral phase. Based on polarized optical transmission micrographs, the iron nodules in DDH58–78 were classified into three phases, namely red nodules, brown nodules, and yellow nodules, which mineralogically corresponded to amorphous and

young, paracrystalline and middleaged, and crystalline and old-aged phases, respectively. Samples of DDH60–65 and DDH87–61 contained an amorphous iron mineral, which is a likely precursor phase of the iron nodules (Sato *et al.*, 1997). This fine-grained amorphous phase appears dark brown or black under optical microscopy, and has a strong capacity for U sorption (Sato *et al.*, 1998).

In addition to the three minerals, DDH58–78 and DDH87–61 contain muscovite and TiO_2 , respectively. Besides the rock samples, standard minerals were analyzed to calibrate of peak positions of mass of uranium series radionuclides, and to ascertain whether some isotope ratios are similar to the previously obtained values. For this purpose, we used a Tanzanian uraninite which is at secular radioactive equilibrium (Sato *et al.*, 1998).

SHRIMP operation

Secondary ion mass spectroscopy (SIMS) is a technique for analyzing the chemical (isotopic)

composition of a solid surface by identifying secondary ions, ejected during primary ion bombardment on the solid surface, with mass spectroscopy. The ability of the instrument to focus the primary ion allows micro-isotopic analysis, and provides spatial information of the sample (Compston *et al.*, 1984). The Sensitive High mass-Resolution Ion Micro Probe (SHRIMP) has been developed at the Research School of Earth Sciences of ANU as a powerful tool for the micro-isotopic analysis. It has been used to measure the U-Th-Pb ages of zircon from a number of locations (Compston *et al.*, 1984; Compston and Pidgeon, 1986; Williams *et al.*, 1996; Meyer *et al.*, 1996). All analyses in this study were made on the SHRIMP II at the ANU. The SHRIMP is optimized for high sensitivity when operating at high mass resolution, which is achieved by the combination of wide slits and a large secondary mass analyzer. Although some smaller ion microprobes can be operated in a similar high mass resolution mode, their sensitivity is greatly diminished, and is more than ten times lower than that of the SHRIMP.

In the SHRIMP measurements, a primary beam of O_2^- at 10 kV accelerating voltage and 5–10 nA beam current was focused to a spot of about 30 μm in diameter on the polished thin section, which was coated with a ~30 nm layer of gold to overcome charging. Each analysis comprised sequential ion count-rate measurements at several mass-stations. The main target nuclides were ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{234}U , ^{235}U , $^{250}(UO)$, and $^{251}(UO)$. The count rate of the SHRIMP II (or sensitivity of SHRIMP II) with the operating conditions was 1.5–2.0 cps/ppm/nA (primary beam current). The background values were obtained at a mass of 0.05 amu higher than that of ^{234}U (~234.03). The mass resolution power was set at ~6000. The time required per spot was about 20 minutes, including several minutes to sputter-clean the target area of the polished section prior to analysis.

Data processing

Isotopic ratios of $^{234}U/^{235}U$, $^{204}Pb/^{206}Pb$, and $^{207}Pb/^{206}Pb$ were measured in the present study. Since count rates of ^{238}U were extremely high rela-

tive to ^{234}U , activity ratios of $^{234}U/^{238}U$ were estimated from count rates of ^{234}U and ^{235}U , using the equation: $A_{234U}/A_{238U} = (\lambda_{234U}/\lambda_{238U})(N_{235U}/N_{238U})(N_{234U}/N_{235U})$, where A_x , N_x and λ_x are activity, content in a mineral and decay constant of nuclide x , respectively. Decay constants of ^{238}U and ^{234}U are 1.551×10^{-10} (y^{-1}) and 2.823×10^{-6} (y^{-1}), respectively (Firestone *et al.*, 1996), and the atomic ratio of $^{235}U/^{238}U$ is 1/137.88 (Firestone *et al.*, 1996). Consequently the activity ratios are given by,

$$A_{234U}/A_{238U} = 132.007 \cdot (N_{234U}/N_{235U}). \quad (1)$$

In using this equation, it is assumed that sputtering and detection efficiency are the same for ^{234}U and ^{238}U . Activity ratios of $^{234}U/^{238}U$ can be estimated not only from isotope ratios of $^{234}U/^{235}U$ (metal-based ratios) but also from those of $^{250}(UO)/^{251}(UO)$ (oxide-based ratios), using the equation: $A_{234U}/A_{238U} = 132.007 \cdot (N_{250UO}/N_{251UO})$.

The oxide-based ratios in some cases provide higher count rates and better counting statistics than the metal-based ratios. However, as shown in Fig. 2, the oxide-based ratios of the kaolinite were generally high compared to the metal-based ratios, and this also applied for several measurements of the iron mineral phases. In addition, the metal-based activity ratios of $^{234}U/^{238}U$ for the Tanzanian uraninite standard were 1.00 ± 0.03 , while the oxide-based ratios were 1.12 ± 0.05 and slightly higher though the sample is at secular radioactive equilibrium. The higher values of the oxide-based activity ratios of $^{234}U/^{238}U$ appear to result from an additional fragment with a very similar mass to $^{250}(UO)$. The most probable explanation is that the peak of $^{234}U^{16}O$ was superimposed by that of $^{238}U^{12}C$. The ability of SIMS to resolve two peaks at a similar mass (M) separated by an interval ΔM is generally given by its mass resolution, $M/\Delta M$. A mass resolution of at least 17000 is necessary to discriminate $^{234}U^{16}O$ (250.0358 amu) from $^{238}U^{12}C$ (250.0504 amu), and this exceeds the mass resolution of the SHRIMP under the present measuring conditions (~6000). For this reason, the uranium oxide peak

Fig. 2. Plots of metal-based and oxide-based $^{234}\text{U}/^{238}\text{U}$ activity ratios obtained with the SHRIMP for iron minerals and kaolinite in the Koongarra secondary ore deposit.

from $^{234}\text{U}^{16}\text{O}$ could not be separated from that of $^{238}\text{U}^{12}\text{C}$. Consequently, the metal-based activity ratios of $^{234}\text{U}/^{238}\text{U}$ were used in this study.

RESULTS AND DISCUSSION

Uranium series disequilibria in the iron minerals and kaolinite

The iron minerals and kaolinite were subjected to detailed SHRIMP measurements to obtain $^{234}\text{U}/^{238}\text{U}$ activity ratios because they are main minerals in the present samples. Quartz grains were excluded from the quantitative measurements be-

cause of its extremely low uranium content. In Fig. 2, most of metal-based activity ratios of $^{234}\text{U}/^{238}\text{U}$ on iron minerals are close to unity (0.98 ± 0.18). On the other hand, higher values of the $^{234}\text{U}/^{238}\text{U}$ activity ratios were obtained from kaolinite grains (1.35 ± 0.24). If a system has been closed and a sufficient time (at least 1 My) has passed after the uptake of uranium, the activity ratio approaches unity. One possible explanation of the slightly higher values of $^{234}\text{U}/^{238}\text{U}$ on the kaolinite is that this mineral has not been closed, and has hence allowed inflow or outflow of groundwaters containing uranium within the grains. If the kaolinite is an open system, the isotopic composition of the groundwaters would be equilibrated with this mineral (Lowson *et al.*, 1986; Yanase *et al.*, 1991). However, studies of the groundwater geochemistry in the Koongarra uranium deposit showed that $^{234}\text{U}/^{238}\text{U}$ activity ratios of groundwater were below unity in the surficial weathered zone (shallower than about 20 m depth), and greater than unity in the deeper unweathered zone (>30 m depth) (Yanase *et al.*, 1995; Payne *et al.*, 1992). Although there are no data on the $^{234}\text{U}/^{238}\text{U}$ activity ratios of the groundwater at the present three positions (DDH58-78, DDH60-65, and DDH87-61), the groundwater activity ratios are presumably below unity, because the sampling positions are located in the weathered zone. Therefore it appears unlikely that isotope exchange with the groundwater could lead to the observed pattern of disequilibria in the mineral phases.

The mechanisms leading to lower $^{234}\text{U}/^{238}\text{U}$ ratios in groundwaters and higher ratios in mineral phases are still under discussion. One possible explanation of the higher ratios in the resistant mineral phases is the mechanism of α -recoil (Yanase *et al.*, 1991, 1996; Sheng and Kuroda, 1986a, b). It has been postulated that α -recoil occurs when ^{238}U present at the edge of an iron nodule (or other mineral grain) decays to ^{234}Th . The recoiling ^{234}Th nucleus is transferred to the adjoining kaolinite (or other minerals) as a consequence of α -recoil, and ^{234}U , a daughter nuclide of the ^{234}Th , accumulates in this phase. This mechanism would be favored by the recoil of ^{234}U

into a relatively uranium-poor phase (such as kaolinite). While the α -recoil mechanism provides a reasonable explanation of the observed ^{234}U excess in the kaolinite phase, it should be noted that the range of the recoiling nucleus has been calculated to be approximately 20 nm (Hashimoto *et al.*, 1985). This is quite small compared to the distances of the analyzed kaolinite spots from the adjacent iron minerals, and to the spot-size of the SHRIMP. This implies that another geochemical process, such as diffusion of the daughter nucleus, should also be considered.

Another possible explanation of the higher $^{234}\text{U}/^{238}\text{U}$ ratios is that ^{234}Th , the short-lived daughter nuclide of ^{238}U , is adsorbed on clay and iron minerals produced by the weathering of host rock, and the ^{234}Th and its daughter nuclide, ^{234}U , are subsequently fixed in the minerals (Ohnuki *et al.*, 1990). In this case, the $^{234}\text{U}/^{238}\text{U}$ ratios in the weathering products are greater than unity and those in the groundwaters are below unity.

Figure 3 shows metal-based $^{234}\text{U}/^{238}\text{U}$ activity ratios on different iron mineral phases of the three

Fig. 3. Metal-based $^{234}\text{U}/^{238}\text{U}$ activity ratios at different types of iron minerals in the Koongarra secondary ore deposit. Labels of the x-axis of Y, B, R, Crys and Amor represent yellow nodule, brown nodule, red nodule, crystalline iron minerals and amorphous iron minerals, respectively.

rock samples. Among a large number of data close to unity, slightly higher values than unity seem to be also obtained on two mineral phases, namely amorphous red iron minerals of DDH58-78 and amorphous iron minerals of DDH60-65. Although the number of data is quite small, it is probable that the amorphous iron minerals have also slightly higher $^{234}\text{U}/^{238}\text{U}$ activity ratios in addition to unity. Since the amorphous iron minerals are the precursors of the crystalline iron minerals, this hypothesis implies that the amorphous iron minerals are partly open systems and that transformation of the amorphous iron minerals to the crystallite eventually leads to the closing of the system, after which inflow and outflow of uranium are prevented because of changes in its structure. In such a closed system, the $^{234}\text{U}/^{238}\text{U}$ ratios will approach unity.

On the basis of the above hypothesis, we can estimate the period during which the amorphous iron minerals have transformed to the crystalline phases. In a closed system with a commencing $^{234}\text{U}/^{238}\text{U}$ activity ratio of x , the ratio (AR) as a function of time (t) is expressed by the following equation,

$$AR = \frac{e^{-\lambda_{238\text{U}} \cdot t} - e^{-\lambda_{234\text{U}} \cdot t} + x \cdot e^{-\lambda_{234\text{U}} \cdot t}}{e^{-\lambda_{238\text{U}} \cdot t}} \quad (2)$$

where $\lambda_{234\text{U}}$ and $\lambda_{238\text{U}}$ are decay constants of ^{234}U and ^{238}U respectively. Figure 4 shows the change in the $^{234}\text{U}/^{238}\text{U}$ activity ratio of 1.5, a maximum value in Fig. 3, with increasing time calculated from Eq. (2). It is apparent from this figure that approximately 2–3 million years is required for a system with a $^{234}\text{U}/^{238}\text{U}$ activity ratio of 1.5 to reach secular equilibrium. Although SHRIMP data contain uncertainty as shown in Fig. 3, the mean residence period of uranium within the iron minerals examined in this study appears to be approximately 2–3 million years, assuming that the crystalline iron minerals have formed from an amorphous iron mineral with a maximum $^{234}\text{U}/^{238}\text{U}$ isotope ratio of approximately 1.5. As calculated by Airey *et al.* (1986), the secondary ore deposit be-

Fig. 4. Evolution of $^{234}\text{U}/^{238}\text{U}$ ratios as a function of time (years). The initial value of 1.5 is the activity ratio of the amorphous iron minerals measured by the SHRIMP.

gan to form about 1–3 million years ago. Therefore the value obtained in the present study indicates that the uranium leached from the primary ore has been deposited in the nodules during the evolution of the secondary ore body, and retained in the nodules for a considerable period. However, it should be noted that the $^{234}\text{U}/^{238}\text{U}$ isotope ratio in the amorphous iron minerals may have varied throughout geological time, which means that there is some uncertainty about the length of time required for isotopic equilibrium to be achieved.

Lead isotope ratios

The stable lead isotopes present in the earth are ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb . The isotopic abundances in current terrestrial lead are 1.41% of ^{204}Pb , 24.1% of ^{206}Pb , 22.1% of ^{207}Pb and 52.4% of ^{208}Pb (Firestone *et al.*, 1996). In a system containing significant uranium or thorium, the relative abundances are different from the average terrestrial values. While the ^{204}Pb abundance remains constant, the amounts of ^{206}Pb , ^{207}Pb and ^{208}Pb continue to increase because the decay of ^{238}U , ^{235}U , and ^{232}Th yields the stable isotopes ^{206}Pb , ^{207}Pb , and ^{208}Pb , respectively. Thus, the lead isotopic composition in the Koongarra ore deposit

could provide information on the timescale of uranium migration, and also on the migration behavior of lead (Isobe *et al.*, 1998).

Lead produced from the radioactive decay of uranium and thorium is called radiogenic lead, whereas that which existed at the formation of the Earth 4.5 billion years ago is called primordial or primeval lead. The isotopic composition of primordial lead is represented by the measured values of troilite in iron meteorites, in which uranium and thorium compositions are extremely low compared to lead. Thus, the radiogenic component is absent within the instrumental measurement error. Values of 9.307 for $^{206}\text{Pb}/^{204}\text{Pb}$ and 10.294 for $^{207}\text{Pb}/^{204}\text{Pb}$ were reported as the primordial lead ratios by Tatsumoto *et al.* (1973). The current average terrestrial lead (mentioned above) essentially contains the radiogenic lead formed since the formation of the Earth, as well as the primordial lead, and is here referred to as “common lead”.

The lead isotope compositions of different samples are presented on a diagram of $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{204}\text{Pb}/^{206}\text{Pb}$ (Fig. 5). Experimental points in the upper-right corner of the diagram represent the common lead component of the host rock of the Koongarra deposit. The data points in the lower-left show a significant influence of radiogenic lead isotopes from uranium decay. Figure 5 shows that the secondary ore deposit contains both radiogenic lead and common lead. The data points form a line between these two end members, indicating the mixture of both types of lead in different proportions. The interception of the least-squares regression line with the $^{207}\text{Pb}/^{206}\text{Pb}$ axis corresponds to the isotopic ratio of the radiogenic lead component. Values of this intercept for the analyses of minerals in DDH60-65 and DDH87-61 samples are 0.122 and 0.111, respectively, whereas that for DDH58-78 is 0.09.

The isotope ratios obtained for samples from the secondary ore body in the present study should be compared with the results obtained for the primary ore body by Isobe *et al.* (1998). These authors reported that there were two distinctive lead isotopic compositions in the primary ore zone. As might be expected, both were highly radiogenic,

Fig. 5. Plots of isotope ratios of $^{207}\text{Pb}/^{206}\text{Pb}$ versus those of $^{204}\text{Pb}/^{206}\text{Pb}$ for different minerals in samples DDH58-78, DDH60-65, and DDH87-61.

and therefore the data fall to the bottom left in Fig. 5. However, the lead isotope ratios differed between uranium-rich minerals and lead-rich sulfides. In the primary uraninite and secondary uranium minerals, the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio was 0.077 and 0.079, respectively. In contrast, the sulfides, such as galena, chalcopyrite and pyrite gave higher $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, in the range 0.108 to 0.134. The higher ratios in the sulfide minerals indicate that lead migrated from the primary ore-zone during a geological event that preceded the mobilization of uranium. The values of the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in samples DDH60-65 and DDH87-61 obtained in the present work (0.11 to 0.12) therefore suggest that the radiogenic lead component at these locations is derived from the radiogenic lead which migrated from the primary ore body before the secondary ore formation.

In the DDH58-78 sample, the common lead was predominantly detected in the kaolinite, while the radiogenic lead was found in the iron minerals (Fig. 5). The intercept of the regression line of the DDH58-78 analyses with the vertical axis is 0.090, and is therefore lower than that for DDH60-65 and DDH87-61. As discussed above, the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios of uranium minerals are approximately 0.078 in the primary ore body, which is lower than that of the lead-rich sulfide minerals (Isobe *et al.*, 1998). The DDH58 bore hole is closer to the primary ore body than DDH60 and DDH87, and the isotope ratios imply that radiogenic lead in the

primary ore body has migrated as far as DDH58, but not as far as the other two boreholes. The lead isotope compositions of samples from DDH60 and DDH87 are only affected by the earlier mobilization event, which only involved lead.

The iron mineral phases have accumulated not only uranium, but also radiogenic lead, to a much greater extent than the kaolinite (Fig. 5). In the DDH58-78 sample, nearest the primary ore body, the radiogenic lead component is predominantly found in the iron minerals. At DDH60, the radiogenic lead occurs in the amorphous iron mineral. Finally, at DDH87, which is furthest downgradient, the radiogenic lead is concentrated to a greatest extent in the TiO_2 grains.

The data for the DDH60-65 sample suggest that the radiogenic lead has a tendency to accumulate in the amorphous iron minerals rather than the crystalline phases. In DDH58-78, however, the radiogenic lead is observed in the crystalline phases. A possible explanation of this discrepancy for DDH58-78 is that the radiogenic lead was initially accumulated in the amorphous iron minerals and remained during the transformation to the crystalline phases. The fact that the iron nodules in DDH60-65 do not contain the radiogenic lead indicates that the radiogenic lead migrating from the primary ore deposit did not reach as far as DDH60-65, which is at a greater distance from the primary ore deposit. Slightly higher values of the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios of the radiogenic lead com-

ponent in the DDH60-65 sample might imply that the origin of the radiogenic lead at this location would be the lead-rich sulfides at the primary ore. The distribution of lead isotopes in the DDH87-61 sample appears to be influenced by the presence of titanium oxides with high radiogenic lead content.

In conclusion, there seem to be three sources of lead in the secondary ore body: (1) common lead in the Koongarra host rock, (2) radiogenic lead which was mobilized during a geologic event before the secondary ore formation, and (3) radiogenic lead which has migrated from the primary ore concurrently or subsequent to the secondary ore formation. The recent lead component is dominant in the area closer to the primary ore (represented in this study by the DDH58-78 sample). Samples at greater distances from the primary ore (such as DDH87-61) have not been affected by the more recent lead migration, and the isotopic composition in this case is dominated by the lead signature from the earlier lead-mobilizing event. As well as having different spatial trends, the distribution of lead isotopes also differ in terms of the association of Pb isotopes with particular minerals. The SHRIMP provides a unique opportunity to study and interpret the mineral association of lead isotopes.

CONCLUSION

The SHRIMP analyses have been conducted for the samples of the Koongarra secondary ore deposit to obtain activity ratios of $^{234}\text{U}/^{238}\text{U}$ and isotopic ratios of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{204}\text{Pb}/^{206}\text{Pb}$, and to understand their migration behavior within the secondary ore deposit. Activity ratios of $^{234}\text{U}/^{238}\text{U}$ based on the metal and the oxides were compared and the metal-based ratios were found to be less variable and acceptable for both iron minerals and kaolinite. The oxide-based count rates of ^{250}UO were explained by interference from a similar mass due to combination of ^{238}U and ^{12}C . Closer values to unity of activity ratios of $^{234}\text{U}/^{238}\text{U}$ for crystalline iron minerals and slightly higher values for amorphous iron minerals suggested that the mean

residence time of uranium within the iron minerals was up to 2–3 million years.

Results of lead isotopes, represented by a diagram of $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$, indicated that the present three samples contained radiogenic lead, common lead and mixture of both components. In addition, the recent radiogenic lead component within the primary ore is dominant in the area closer to the primary ore (represented in this study by the DDH58-78 sample). The radiogenic lead isotope compositions of samples at greater distances from the primary ore (such as DDH87-61) have been affected only by the earlier mobilization event of radiogenic lead. All these results indicate that some geologic event causing migration of the radiogenic lead had occurred before formation of the secondary ore deposit due to the weathering. After the weathering commenced at least 2–3 million years ago, uranium and lead have migrated from the primary ore. While the uranium has dispersed throughout the secondary ore deposit, the lead reached only the area closer to the primary ore probably due to its immobility compared to the uranium.

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