

An uranium series disequilibrium investigation of reduction spheroids in red beds

Autor(en): **Hofmann, Beda A.**

Objektyp: **Article**

Zeitschrift: **Schweizerische mineralogische und petrographische Mitteilungen
= Bulletin suisse de minéralogie et pétrographie**

Band (Jahr): **71 (1991)**

Heft 3

PDF erstellt am: **28.04.2024**

Persistenter Link: <https://doi.org/10.5169/seals-54368>

Nutzungsbedingungen

Die ETH-Bibliothek ist Anbieterin der digitalisierten Zeitschriften. Sie besitzt keine Urheberrechte an den Inhalten der Zeitschriften. Die Rechte liegen in der Regel bei den Herausgebern.

Die auf der Plattform e-periodica veröffentlichten Dokumente stehen für nicht-kommerzielle Zwecke in Lehre und Forschung sowie für die private Nutzung frei zur Verfügung. Einzelne Dateien oder Ausdrucke aus diesem Angebot können zusammen mit diesen Nutzungsbedingungen und den korrekten Herkunftsbezeichnungen weitergegeben werden.

Das Veröffentlichen von Bildern in Print- und Online-Publikationen ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Die systematische Speicherung von Teilen des elektronischen Angebots auf anderen Servern bedarf ebenfalls des schriftlichen Einverständnisses der Rechteinhaber.

Haftungsausschluss

Alle Angaben erfolgen ohne Gewähr für Vollständigkeit oder Richtigkeit. Es wird keine Haftung übernommen für Schäden durch die Verwendung von Informationen aus diesem Online-Angebot oder durch das Fehlen von Informationen. Dies gilt auch für Inhalte Dritter, die über dieses Angebot zugänglich sind.

An uranium series disequilibrium investigation of reduction spheroids in red beds

by Beda A. Hofmann¹

Abstract

Fourteen samples of uranium-rich reduction spheroid cores from Permian red beds of Northern Switzerland (0 to 1051 m below surface) and one similar sample from Oklahoma were investigated for radioactive disequilibria between ^{238}U , ^{234}U and ^{230}Th and for U, Th concentration by alphaspectrometry. Significant disequilibria are common in samples from depths to 230 m, although a few deep samples show moderate disequilibria as well. Most of the observed disequilibria are indicative of leaching or show a complex pattern due to a combination of leaching and deposition of uranium. Uranium concentrations in cores range from 19 to 39 200 ppm and Th concentrations are 8.3 to 317 ppm. The enrichment of Th in reduction spheroid cores demonstrates that this element was relatively mobile during the low-temperature formation of these redox structures during late diagenesis.

Keywords: Reduction spheroids, Permian red beds, Northern Switzerland, uranium series disequilibria.

Zusammenfassung

Vierzehn Proben von uranreichen Reduktionshofkernen aus Redbeds des Nordschweizer Permokarbondrogens (aus Tiefen von 0 bis 1051 m unter der Oberfläche) sowie eine analoge Probe aus Oklahoma wurden mittels Alphaspektroskopie auf radioaktive Ungleichgewichte zwischen ^{238}U , ^{234}U und ^{230}Th untersucht. Signifikante Ungleichgewichte wurden in Proben aus Tiefen bis 230 m festgestellt, einige tiefere Proben zeigten ebenfalls Anzeichen von Ungleichgewichten. Die meisten Ungleichgewichte deuten auf relativ rezentes Weglösen von Uran oder auf komplexe Akkumulations-Lösungs-Vorgänge hin. Urankonzentrationen in den Reduktionshofkernen liegen zwischen 19 und 39 200 ppm, Thoriumkonzentrationen zwischen 8.3 und 317 ppm. Die Anreicherung von Thorium in Reduktionshofkernen deutet auf eine gewisse Mobilität dieses Elementes während der spätdiagenetischen Bildung dieser Redoxstrukturen hin.

Introduction

Reduction spheroids are small-scale redox systems occurring in red beds and in altered crystalline rocks. In the center of bleached haloes of a few mm to several cm diameter, dark cores that are enriched in V, U and other elements are common (CARTER, 1931; EICHHOFF and REINECK, 1952; PERUTZ, 1940; HARRISON, 1975; HOFMANN, 1986, 1990). The mineralogy and geochemistry of reduction spheroids from Northern Switzerland and other localities has been described elsewhere (HOFMANN, 1990; HOFMANN, 1991). Authigenic

roscoelite and uraninite in reduction spheroids from Northern Switzerland most likely were formed during the Jurassic to Cretaceous periods (HOFMANN, 1990).

The idea of using reduction spheroids as indicators of recent uranium mobility in red beds is based on the presence of localized uranium enrichments in a low-uranium environment resulting in concentration gradients of up to several 1000 ppm over a distance of a few millimeters. In this situation, recent uranium mobility should be manifested by disequilibria of the uranium decay chains.

¹ Naturhistorisches Museum, Bernastrasse 15, CH-3005 Bern.

The goal of this study is to investigate whether relatively recent (< 2 Ma) interactions between uranium phases in the cores of reduction spheroids and porewater took place. In an earlier investigation (HOFMANN et al., 1987) a single sample from the Kaisten well in Northern Switzerland was studied in detail. Notwithstanding the detailed sampling, the interpretation of the data was difficult due to an unsystematic pattern in the results. In the present study, a suite of samples from different boreholes and from two outcrops in Northern Switzerland and Southern Germany were investigated in order to establish the influence of sample depth and groundwater chemistry on the mobility of uranium in the cores of reduction spheroids. Samples are from depths ranging from 0 to 1051 m and host rocks are Permian continental red beds and underlying crystalline basement rocks. For comparative purposes, a single sample of a reduction spheroid from Permian red beds in a shallow well in Oklahoma was also investigated. Groundwaters in these host rocks are rich in V and U (pers. comm. G. BREIT, U.S.G.S.; BREIT et al., 1990), indicating possible active deposition or dissolution of U and V.

A SHORT REVIEW OF OTHER INVESTIGATIONS OF RADIOACTIVE DISEQUILIBRIA IN REDUCTION SPHEROIDS

Research on radioactive disequilibria in reduction spheroids was carried out by several authors. PONSFORD (1955) and DURRANCE et al. (1980) tested samples from Budleigh Salterton (South Devon, U.K.), DYCK and MCCORKELL (1983) studied reduction spheroids from Nova Scotia (Canada) and HOFMANN et al. (1987) investigated material from Kaisten, Northern Switzerland. The results of the earlier study on material from Kaisten will be shortly summarized: HOFMANN et al. (1987) investigated different zones in two adjacent reduction spheroids from Permian red beds in the Kaisten drillhole (230.0 m depth) by detailed small-scale sampling. The majority of the samples showed disequilibria between ^{238}U , ^{234}U and ^{230}Th , but an unequivocal interpretation was not possible due to an unsystematic scatter of the data for different samples. The interpretation given was based on weighted averages for the different zones. These values indicated that recent accumulation of uranium occurred at the edges of the cores. Several samples showed disequilibria indicative of a complex history or of mechanical mixing of zones showing different isotopic ratios during sampling.

These results are now interpreted as being due to dissolution of a minor amount of U minerals in the center of the cores followed by deposition of the dissolved U in the outer core zones and in near-core samples. This interpretation differs from an earlier one (HOFMANN et al., 1987) in that no introduction of U from outside the haloes is assumed. The dissolution of U phases in the cores seems to indicate that the porewaters are not in equilibrium with uraninite and coffinite at 230 m depth at Kaisten. The lack of disequilibria in one core likely is due to very high U concentrations obliterating the effects of removal of a small fraction of total U.

Samples and analytical methods

The samples investigated in this study are from the Nagra-drillholes Kaisten (KAI), Weiach (WEI) and Riniken (RIN), additional samples are from the older wells Zuzgen-1 (ZUZ), Weierfeld (WEF) near Rheinfelden and from surface exposures near Mumpf (MUM) and Weitenau (WT; Southern Germany). The geology of the Kaisten, Weiach and Riniken drillholes is described in detail in PETERS et al. (1989), MATTER et al. (1988a) and MATTER et al. (1988b), respectively. Details of the geology of the Zuzgen and Weierfeld wells are given by BLÜM (1989). The Mumpf samples are from an abandoned quarry exposing clay-rich sandstone. The depth below the original land surface is estimated at 10 m. The Weitenau samples are from an active clay pit, samples are from about 2 m below the present land surface. Host rocks of the investigated reduction spheroids are upper Permian red beds and the crystalline basement (KAI 297, 351). As a measure of the representativeness of the samples, the total weight of the ground samples before analysis is also reported (Tab. 1). The samples taken for this study mostly represent whole cores, no attempt was made to sample the outer core zone only because this would have yielded too small samples in many cases.

The analytical methods employed for uranium series disequilibrium measurements are described in detail by ROSHOLT (1985). Spiked samples were dissolved in $\text{HF}/\text{HNO}_3/\text{HClO}_4$. Thorium and uranium were separated by ion exchange. Thorium was purified by coprecipitation with zirconium pyrophosphate and lanthanum oxalate, ion exchange and extraction into thenoyltrifluoroacetone (0.25M in benzene). The organic phase was evaporated on stainless steel discs and flame dried. The uranium fraction was further purified by extraction into methyl isobutyl ketone, back-

Tab. 1 Sample description

All samples are from red beds of Permian age

Coordinates: Swiss coordinate system

Samples weights: Total weight of sample from which aliquot has been taken for analysis

WT: Weitenau, 5 km NW of Schopfheim, Germany (625°199/281°000)

Core of single spheroid, 1.32 g.

MUM: Mumpf, Switzerland (636°450/265°900)

Composite sample of spheroid cores, 12 g

WEF: Rheinfelden Weierfeld, Switzerland (WEF), well drilled in 1875

(623°993/266°209). Core of single spheroid with roscoelite and native Cu, depth 53.9 m, 0.90 g

KAI: Kaisten well, Switzerland (644°641/265°624)

KAI130.86m, irregular mineralized zone, rich in Ni-arsenides, 0.58 g

KAI226.94m, core of reduction spheroid (Fig. 1 in HOFMANN, 1990), 0.36 g

KAI297.69m, composite of 4 cores in fault gauge in gneiss, 0.011 g

KAI351.77m, irregular U-mineralized zone surrounded by bleached zone in gneiss, black U-As-phase (low Pb) is main U carrier, 0.17 g

ZUZ: Zuzgen-1 well, Switzerland (635°030/263°400)

ZUZ201.35, core of single spheroid in claystone, 1.35 g

ZUZ227.25, outer zone of core of very large spheroid in clayey sandstone, 1.12 g

RIN: Riniken well, Switzerland (656°604/261°800)

RIN819.40A, core of single, fracture-bound spheroid, 0.28 g

RIN819.40B, weakly mineralized outer zone of core 819.40A, 2.50 g

RIN910.78, mineralized dolomite nodule, 1.62 g

WEI: Weiach well, Switzerland (676°744/268°618)

WEI1021.55, core of single spheroid in claystone, 0.24 g

WEI1050.89, composite of 3 spheroid cores in sandstone, 0.54 g

OK: Oklahoma Co, Oklahoma, USA, well NOTS-6, (35° 42' N 97° 33' W)

Depth 123.3 m, single spheroid core, contains montroseite as main ore mineral, 0.5 g

extraction into water followed by ion exchange and electrodeposition on platinum discs. The spike used contained ^{229}Th and ^{236}U calibrated with a standard uraninite solution (ROSHOLT, 1985). The errors reported are 1 sigma errors based on count statistics only.

Mapping of induced fission tracks as a measure of uranium distribution was performed on polished thin sections using muscovite detectors. Samples were irradiated at the U.S.G.S. Triga reactor facility in Denver. After irradiation, the muscovite detectors were etched with HF.

Results

The results of the alphaspectrometric determinations of U, Th concentrations and of activity ratios are reported on table 2. Uranium concentrations range from 19 to 39 200 ppm and Th concentrations range from 8.3 to 317 ppm. Activity ratios of

$^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ of the deep (> 200 m) samples all are close to unity. Strong disequilibria are present in the surface samples from Northern Switzerland and Germany and in the sample from Oklahoma. Plots of activity ratios versus depth (Figs 1, 2, 3) illustrate the fact that significant disequilibria are most common in samples from depths of 200 m and less.

In a cautious approach to the disequilibrium data, only disequilibria differing from equilibrium by at least twice the stated 1 sigma error and by at least 1% were considered significant. Even with these restrictions, 25 of the 42 reported isotope pairs of the ^{238}U decay chain are out of equilibrium and only in four samples all three pairs are in equilibrium. Generally, deep samples are closer to equilibrium than shallow ones, although one deep sample (WEI1050) shows significant disequilibria.

Samples from Kaisten (KAI 226, 297) that are close to the previously investigated samples

Tab. 2 Results of uranium series disequilibrium measurements: U, Th concentrations and activity ratios (samples are arranged in order of increasing depth).

	U ppm	Th ppm	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{238}\text{U}$	$^{230}\text{Th}/^{234}\text{U}$	$^{228}\text{Th}/^{232}\text{Th}$
WT	35.7 ± 0.4	15.9 ± 0.6	2.58 ± 0.02	4.32 ± 0.05	1.68 ± 0.02	2.04 ± 0.08
MUM	19.0 ± 0.2	9.8 ± 0.2	0.80 ± 0.01	3.74 ± 0.05	4.69 ± 0.07	1.67 ± 0.04
WEF54	2057 ± 25	14.4 ± 0.7	1.007 ± 0.003	1.18 ± 0.02	1.17 ± 0.02	1.78 ± 0.11
KAI130	5268 ± 65	34.5 ± 1.8	0.878 ± 0.004	0.93 ± 0.01	1.06 ± 0.01	1.14 ± 0.07
ZUZ201	1781 ± 21	20.4 ± 1.0	1.098 ± 0.005	1.15 ± 0.01	1.05 ± 0.01	1.96 ± 0.09
KAI226	264 ± 3	14.1 ± 0.7	1.021 ± 0.008	1.02 ± 0.01	1.00 ± 0.01	1.57 ± 0.12
ZUZ227	114 ± 1.3	15.9 ± 0.6	0.996 ± 0.009	0.98 ± 0.01	0.99 ± 0.01	1.59 ± 0.06
KAI297	11924 ± 136	317 ± 7	1.001 ± 0.003	0.99 ± 0.01	0.99 ± 0.01	0.91 ± 0.02
KAI351	39200 ± 480	282 ± 27	0.981 ± 0.007	0.93 ± 0.01	0.94 ± 0.01	8.07 ± 0.45
RIN910	2164 ± 26	22.8 ± 1.1	1.008 ± 0.004	0.96 ± 0.01	0.96 ± 0.01	3.59 ± 0.14
RIN819K	1954 ± 22	46.1 ± 1.7	1.005 ± 0.005	1.09 ± 0.01	1.08 ± 0.01	0.94 ± 0.04
RIN819R	152 ± 2	18.2 ± 0.5	0.999 ± 0.007	1.02 ± 0.01	1.02 ± 0.01	1.14 ± 0.03
WEI1021	1879 ± 21	19.2 ± 2.1	1.009 ± 0.006	1.02 ± 0.01	1.01 ± 0.01	7.91 ± 0.44
WEI1050	1064 ± 13	8.3 ± 0.6	1.051 ± 0.005	1.12 ± 0.01	1.06 ± 0.01	1.53 ± 0.12
O K	48.8 ± 0.6	9.5 ± 0.3	0.548 ± 0.007	0.76 ± 0.01	1.39 ± 0.02	2.14 ± 0.05

(HOFMANN et al., 1987, KAI 230 m), are in equilibrium. Sample KAI351 is slightly deficient in ^{230}Th . Considering the low Pb content of this sample (HOFMANN, 1990), this is taken as a possible indication of a low age (323^{+33}_{-25} Ka).

The surface samples MUM and WT show strong disequilibria. Disequilibria in sample MUM are in accordance with single stage leaching while the activity ratios of sample WT must be explained by a combination of leaching, causing

the high $^{230}\text{Th}/^{238}\text{U}$ activity ratio of 4.32, and of uranium accumulation, responsible for the high $^{234}\text{U}/^{238}\text{U}$ activity ratio of 2.58. Compared with the subsurface samples, samples MUM and WT are low in uranium. Minimum pre-leaching uranium concentrations based on $^{230}\text{Th}/^{238}\text{U}$ activity ratios (assuming very recent leaching) are 71 ppm for MUM and 154 ppm for WT. These values are still relatively low but are comparable to some of the deep samples.

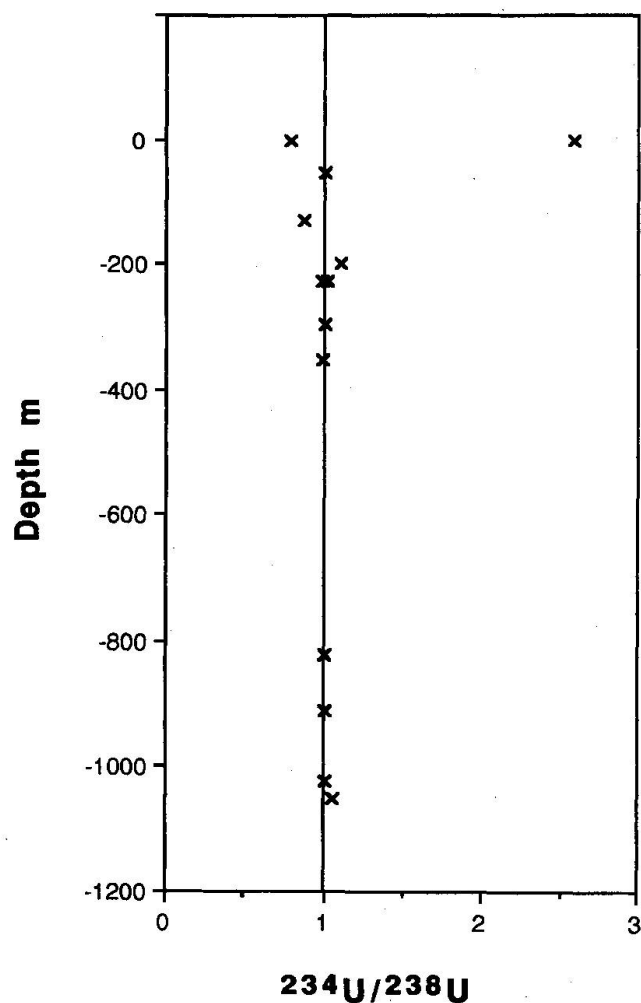


Fig. 1 Plot of $^{234}\text{U}/^{238}\text{U}$ activity ratios against sampling depth. Permian of Northern Switzerland / SW Germany. Symbol size is equal or larger than errors.

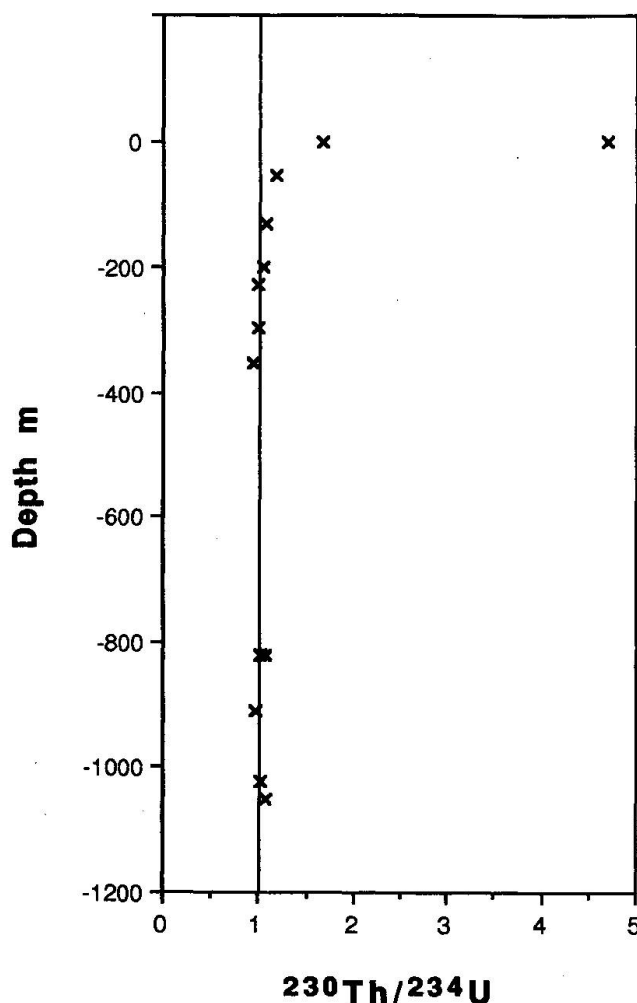


Fig. 2 Plot of $^{230}\text{Th}/^{234}\text{U}$ activity ratios against sampling depth. Permian of Northern Switzerland / SW Germany. Symbol size is equal or larger than errors.

The Oklahoma sample shows a strikingly low $^{234}\text{U}/^{238}\text{U}$ activity ratio of 0.55 and a low $^{230}\text{Th}/^{238}\text{U}$ activity ratio of 0.76.

^{232}Th THORIUM CONCENTRATIONS

During earlier investigations (HOFMANN et al., 1987; HOFMANN, 1990), ambiguous results were obtained as to whether ^{232}Th is enriched in reduction spheroid cores or not. This question has important implications regarding the low-temperature mobility of thorium and of geochemically similar artificial actinides that may be present in radioactive waste. No Th enrichments were found using XRF- (HOFMANN, 1990) and ICP methods (HOFMANN, 1991). However, a few samples of uranium minerals with Th contents well above the

detection limit of the microprobe were identified by HOFMANN (1990). Alphaspectrometric measurements indicated Th enrichments in cores at Kaisten 230 m (HOFMANN et al., 1987). Background concentrations of Th in the clayey Permian red beds of the Kaisten well were found to be 16 to 18 ppm (HOFMANN et al., 1987). Compared to this, the measurements presented in this paper show elevated Th concentrations for samples RIN819K, KAI130, KAI297 and KAI351. The uranium phase in sample KAI351 was previously analyzed with the microprobe showing 72.68% UO_2 and 0.55% ThO_2 (64.07% U and 0.48% Th, HOFMANN, 1990, table 3). Assuming all U and Th in sample KAI351 measured in this study is present in this uranium phase, the Th content of the uranium phase based on alphaspectrometry is $0.46 \pm 0.04\%$ which compares very well with the microprobe analysis.

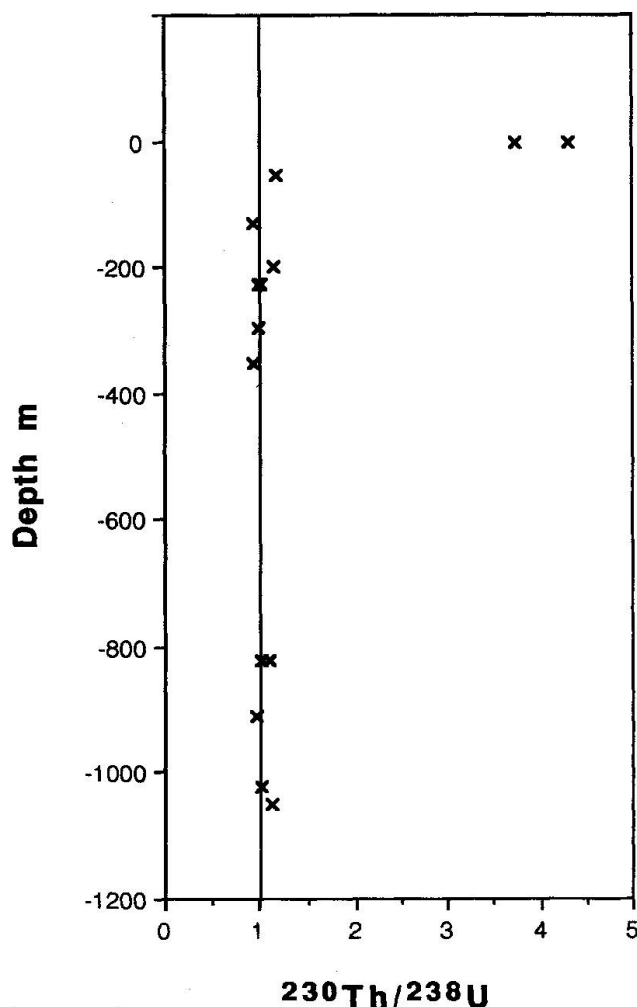


Fig. 3 Plot of $^{230}\text{Th}/^{238}\text{U}$ activity ratios against sampling depth. Permian of Northern Switzerland / SW Germany. Symbol size is equal or larger than errors.

URANIUM DISTRIBUTION IN REDUCTION SPHEROIDS AND HOST ROCKS

The spatial distribution of uranium in reduction spheroid cores and in host rocks was investigated by fission track mapping on samples from the Kaisten drillhole. The distribution of uranium in the host rock and in the bleached haloes was found to be very homogeneous, with a majority of the uranium bound to the finegrained clay matrix and a minor part bound to detrital minerals like zircon and monazite. The uranium concentration gradient at the border of the cores is very steep. Over a distance of 1 to 2 mm the uranium concentration increases from background (± 5 ppm) to several 1000 ppm (Fig. 4). No difference of uranium concentration was found between the red host rock and the bleached haloes, and there is no evidence of uranium accumulation at the border between red host rock and bleached haloes. Car-

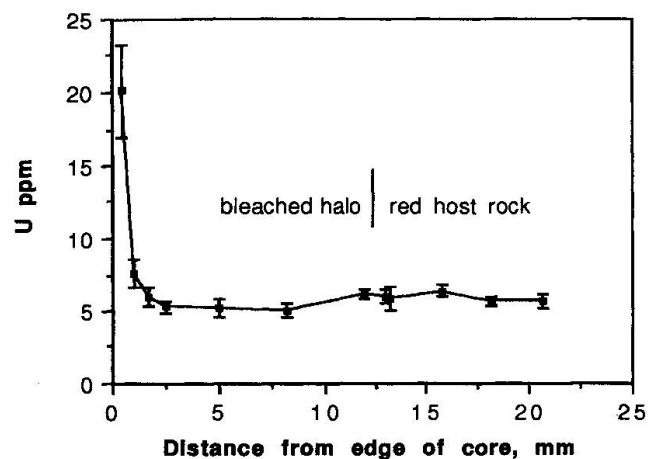


Fig. 4 Detailed profile of uranium concentration at the edge of the core of a reduction spheroid (Kaisten 230.0 m) derived from a fission track map. Track densities in the core were too high for counting (> 1000 ppm U).

bonate concretions generally have uranium concentrations (1–2 ppm) that are much lower than those of the host rock, but occasionally they contain small inclusions of uranium-rich phases.

Discussion

The results of this study show that recent mobility of uranium, evidenced by disequilibria between ^{238}U , ^{234}U and ^{230}Th was common in Permian red beds in Northern Switzerland to depths of about 230 m and affected uranium minerals in the cores of reduction spheroids. Below a depth of roughly 230 m, disequilibria are rare and less pronounced. Pore fluids are considered to be closer to chemical equilibrium with uraninite and coffinite at these depths. Evidence of uranium accumulation is present in one surface sample and in ZUZ201, in both cases based on $^{234}\text{U}/^{238}\text{U}$ activity ratios only while Th/U activity ratios are indicative of leaching. These results are consistent with the reinterpretation of results from detailed sampling of KAI 230 m (HOFMANN et al., 1987), where uranium leaching most likely caused the observed activity ratio profiles. A comparison with groundwater data from Permian red beds and from the overlying Triassic Buntsandstein (data from WITTWER, 1986) shows that in the depth range where U mobility has been evidenced in this study, U concentrations in the groundwater are significantly higher (15 ppb) than in deeper red beds (0.2 to 0.5 ppb).

Elevated concentrations of ^{232}Th were found in four samples of reduction spheroid cores, confirming the presence of Th established by microprobe analysis (HOFMANN, 1990). Thorium is gen-

erally considered to be an immobile element under the low temperature conditions that prevailed during the formation of reduction spheroids. The evidence presented here shows that at least in some cases thorium is mobile together with uranium allowing Th/U ratios in the fluid phase (as reflected in the composition of uranium minerals) as high as 0.0072/0.0075 (KAI351, from alpha-spectrometry and microprobe, respectively). Interestingly, the uranium phase in this sample is intergrown with a Sr-Ce-La-Nd-arsenate-phosphate (kemmilitzite). Possibly the LREE and Th were carried together in the solution from which these minerals were precipitated. The low Pb content of this uranium phase (HOFMANN, 1990) and a ^{230}Th deficiency indicate that this uranium mineral and the associated transport of U, Th and LREE could be as young as 323^{+33}_{-25} Ka. These results are supported by reports from Wales (PARNELL and EAKIN, 1989) and SW Colorado (HOUSTON and MURPHY, 1970) where Th-bearing, U-rich organic matter of diagenetic origin was found. These lines of evidence for thorium mobility also pose some doubts on the assumption that ^{230}Th is strictly immobile.

The presence of a steep uranium concentration gradient (Fig. 4) at the edge of the cores shows the difficulty of adequately sampling different zones for uranium series disequilibrium investigations. Ideally, low-uranium zones directly adjacent to the cores would best show evidence of recent uranium loss from the core and accumulation in a near core zone. Due to the somewhat irregular shape of the cores and the presence of small, high-U "subcores", it would be difficult to obtain a contamination-free sample of sufficient size from this zone.

The data of the Oklahoma sample (OK) are most likely indicative of continuous leaching of ^{234}U or precursors over long periods of time leading to a depletion of both ^{234}U and its daughter product ^{230}Th relative to ^{238}U . This interpretation is consistent with high uranium concentrations and $^{234}\text{U}/^{238}\text{U}$ activity ratios > 1 in groundwaters from this site (G. BREIT, pers. comm. 1990).

Conclusions

^{238}U , ^{234}Th and ^{230}Th are at or close to radioactive equilibrium below about 230 m depth in Permian red beds in Northern Switzerland indicating that no significant chemical perturbation occurred within the last 2 Ma. Above 230 m depth, disequilibria increase to the surface indicating active dissolution and/or reprecipitation of uranium phases. During the formation of reduction spher-

oids, thorium was mobile to a certain extent allowing the coprecipitation with uranium in minerals. This thorium mobility is probably due to the presence of unknown complexing agents that also allowed LREE transport. This study demonstrates the suitability of reduction spots in tracing recent uranium mobility in red beds.

Acknowledgements

This research was supported by a postdoctoral research grant provided by Nagra (National Cooperative for the Storage of radioactive waste, Baden, Switzerland).

I wish to thank B.J. Szabo, J.N. Rosholt, C.A. Bush and D. Muhs for the permission to use their lab and for help during the preparation and measurement of the uranium series samples. G.N. Breit kindly supplied the sample from Oklahoma. R.A. Zielinski introduced me to the art of fission track mapping. The delicate work of preparing polished thin sections of clays was performed by J. Megert (Mineralog.-petrograph. Institut, University of Berne).

References

- BÜM, W. (1989): Faciesanalyse im Rotliegenden des Nordschweizer Permokarbon-Trogs (Hochrhein-Region zwischen Basel und Laufenburg). *Eclogae geol. Helv.*, 82, 455–489.
- BREIT, G.N., MOSIER, E.L., SCHLOTTMANN, J.L. and PAPP, C.S.E. (1990): Rock/water interactions and groundwater contamination in Permian rocks, Central Oklahoma Aquifer. In: *Environmental Forum 1990*. U.S. Geol. Surv. Open File Report 90–288, p. 14 (abstract).
- CARTER, G.E.L. (1931): An occurrence of vanadiferous nodules in the Permian beds of South Devon. *Mineralog. Mag.*, 22, 609–613.
- DURRANCE, E.M., MEADS, R.E., BRINDLEY, R.K. and STARK, A.G.W. (1980): Radioactive disequilibrium in uranium-bearing nodules from the New Red Sandstone (Permian-Triassic) of Budleigh Salterton, Devon. *Proc. Ussher Soc.*, 5, 81–88.
- DYCK, W. and McCORKELL, R.H. (1983): A study of uranium-rich reduction spheroids in sandstones from Pugwash Harbour, Nova Scotia. *Canadian J. Earth Sci.*, 20, 1738–1746.
- EICHHOFF, H.J. and REINECK, H.E. (1952): Uran-Vanadiumkerne mit Verfärbungshöfen in Gesteinen. *N. Jb. Miner.*, 11/12, 294–314.
- HARRISON, R.K. (1975): Concretionary concentrations of the rarer elements in permo-triassic red beds of south-west England. *Bull. geol. Surv. Great Britain*, 52, 1–26.
- HOFMANN, B. (1986): Small-scale multi-element accumulations in Permian red beds of Northern Switzerland. *N. Jb. Miner. Mh. Jg.* 1986, H.8, 367–375.
- HOFMANN, B., DEARLOVE, J.P.L., IVANOVICH, M., LEVER, D.A., GREEN, D.C., BÄRTSCHI, P. and PETERS, T.J. (1987): Evidence of fossil and recent diffusive element migration in reduction haloes from Permian red beds of Northern Switzerland. In: CÔME, B. and

- CHAPMAN, N.A. (eds), Natural analogues in radioactive waste disposal, Commission of the European Communities. Graham and Trotman, 217–238.
- HOFMANN, B. (1990): Reduction spheroids from Northern Switzerland: Mineralogy, geochemistry and genetic models. *Chem. Geol.*, 81, 55–81.
- HOFMANN, B. (1991): Mineralogy and geochemistry of reduction spheroids in red beds. *Mineralogy and Petrology*, 44, 107–124.
- HOUSTON, R.S. and MURPHY, J.F. (1970): Thorium- and titanium bearing organic material in the Dakota Sandstone near Durango, Colorado. *U.S. Geol. Surv. Prof. Pap.* 700-C, C138–C144.
- MATTER, A., PETERS, T.J., BLÄSI, H.-R., MEYER, J., ISCHI, H. and MEYER, CH. (1988a): Sondierbohrung Weiach, Geologie. Nagra Technical Report 86–01, 438 p., Baden, Switzerland.
- MATTER, A., PETERS, T.J., ISENSCHMID, CH., BLÄSI, H.-R. and ZIEGLER, H.-J. (1988b): Sondierbohrung Riniken, Geologie. Nagra Technical Report 86–02, 198 p. Baden, Switzerland.
- PARNELL, J. and EAKIN, P. (1989): Thorium-bitumen mineralization in Silurian sandstones, Welsh Borderland. *Mineralogical Magazine*, 53, 111–116.
- PERUTZ, M. (1940): Radioactive nodules from Devonshire, England. *Mineralog. Petrograph. Mitt.*, 51, 141–161.
- PETERS, T.J., MATTER, A., MEYER, J., ISENSCHMID, CH. and ZIEGLER, H.-J. (1989): Sondierbohrung Kaisten, Geologie. Nagra Technical Report 86–04, 286 p., Baden, Switzerland.
- PONSFORD, D.R.A. (1955): II. Radioactivity studies of some British sedimentary rocks. *Bull. Geol. Surv. Great Britain*, 10, 24–44.
- ROSHOLT, J.N. (1985): Uranium-trend systematics for dating Quarternary sediments. *U. S. Geol. Surv. Open-File Report* 85–298, 34 p.
- WITTWER, C. (1986): Probenahmen und chemische Analysen von Grundwässern aus den Sondierbohrungen. Nagra Technical Report 85–49, 142 p., Baden, Switzerland.

Manuscript received June 3, 1991; accepted July 10, 1991.