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Corrosion of Spent Nuclear Fuel: The Long-Term Assessment

Rodney C. Ewing

Nuclear Engineering and Radiological Sciences
Materials Science & Engineering
Geological Sciences

University of Michigan
Cooley Bldg., 2355 Bonisteel Boulevard
Ann Arbor, Michigan 48109-2104

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ABSTRACT

Spent nuclear fuel (SNF), essentially UO_2, accounts for over 95% of the total radioactivity of all of the radioactive wastes in the United States that require disposal, disposition or remediation. The UO_2 in SNF is not stable under oxidizing conditions and may also be altered under reducing conditions. The alteration of SNF results in the formation of new uranium phases that can cause the release or retardation of actinide and fission product radionuclides. Over the long term, and depending on the extent to which the secondary uranium phases incorporate fission products and actinides, *these alteration phases become the near-field source term.*

This research program has been a broadly based effort to understand the long-term behavior of SNF and its alteration products in a geologic repository.

Fortunately, our experiments and field studies have established that natural uraninite, UO_{2+x}, and its alteration products are excellent "natural analogues" for the study of the corrosion of UO_2 in SNF. This research program has addressed the following major issues:

1. **What are the *long-term* corrosion products of natural UO_{2+x}, uraninite, under oxidizing and reducing conditions?**
2. **What is the paragenesis or the reaction path for the phases that form during alteration?**
3. **What is the radionuclide content in the corrosion products as compared with the original UO_{2+x}? Do the trace element contents substantiate models developed to predict radionuclide incorporation into the secondary phases?**
4. **Are the corrosion products accurately predicted from geochemical codes (e.g., EQ3/6 or Geochemist's Workbench) that are used in performance assessments? Can these codes be tested by studies of natural analogue sites (e.g., Oklo, Cigar Lake or Pena Blanca).**

As detailed in the summary of results, we have made substantial progress in addressing each of the above issues.

INTRODUCTION

The successful disposal of spent nuclear fuel (SNF) is one of the most serious challenges to the successful completion of the nuclear fuel cycle and the future of nuclear power generation (Ewing, 1999a, 1999b). In the United States, 21 percent of the electricity is generated by 107 commercial nuclear power plants (NPP), each of which generates 20 metric tons of SNF annually. In 1996, the total accumulation of SNF was 33,700 metric tons of heavy metal (MTHM) stored at 70 sites around the country (Richardson, 1997). The end-of-life projection for current nuclear power plants is approximately 86,000 MTHM of SNF. In the proposed nuclear waste repository at Yucca Mountain over 95% of the radioactivity originates from SNF. In 1998, approximately 130,000 MTHM of SNF have accumulated worldwide, most of it located at 236 NPP in 36 countries (Carter and Pigford, 1999). Annual production of SNF is approximately 10,000 MTHM, containing about 100 tons of "reactor grade" plutonium. Any reasonable increase in the proportion of energy production by NPP, i.e., as a substitute for hydrocarbon-based sources of energy, will significantly increase SNF production.

Spent nuclear fuel is essentially UO_2 with approximately 4-5 atomic percent actinide and fission product elements. A number of these elements have long half-lives (^{239}Pu 24,500 years; ^{237}Np 2 million years; ^{129}I 16 million years; ^{79}Se 1.1 millions years; ^{99}Tc 200,000 years); hence, ***the long-term behavior of the UO_2 is an essential concern in the evaluation of the safety and risk of a repository for SNF. One of the unique and scientifically most difficult aspects of the successful disposal of SNF is the extrapolation of short-term laboratory data (hours to years) to the long time periods (10^3 to 10^5 years)*** as required by the performance objectives set in regulations, i.e. 10 CFR 60. The direct verification of these extrapolations or interpolations is not possible, but ***methods must be developed to demonstrate compliance with government regulations and to satisfy the public that there is a reasonable basis for accepting the long-term extrapolations of spent fuel behavior.*** In recent years "natural analogues" for both the repository environment (e.g., the Oklo natural reactors) and nuclear waste form behavior (e.g., corrosion and alteration of uraninite, UO_{2+x}) have been cited as a fundamental means of achieving confirmation of long-term extrapolations (Ewing and Jercinovic, 1987; Ewing, 1991, 1992, 1993a, 1993b, 1999b). In particular, considerable effort has already been made to establish that uraninite, UO_{2+x}, with its impurities, is a good structural and chemical analogue for the analysis of the long-term behavior of the UO_2 in SNF (Fayek et al., 1997a; Janeczek and Ewing, 1991a, 1991b, 1992a, 1992b, 1995, 1996; Janeczek et al., 1993, 1996a, 1996b; Murphy, 1993; Murphy and Pabalan 1995; Murphy et al., 1995; Pearcy et al., 1994).

This proposal is based on the study of uraninite and the naturally occurring alteration products of UO_{2+x} under oxidizing and reducing conditions.

The UO_2 in SNF is not stable under oxidizing conditions. In oxic solutions, uranium has a strong tendency to exist as U^{6+} in the uranyl molecule, UO_2^{2+}. Uranyl ions react with a wide variety of inorganic and organic anions to form complexes and solid phases. Throughout most of the natural range of pH, U^{6+} forms strong complexes with oxygen-bearing ions including CO_3^{2-}, HCO^{3-}, SO_4^{2-}, PO_4^{3-}, and

AsO_4^{3-}, which are present in most oxidized stream and subsurface waters. In arid environments, the U^{6+} ion can precipitate as a wide variety of uranyl oxide hydrates, uranyl silicates and uranyl phosphates. This is well demonstrated in experimental work, e.g., in long term drip tests on UO_2 (Wronkiewicz et al., 1992, 1996, 1997; Buck et al., 1997; Wronkiewicz and Buck, 1999; Finch et al., 1999) and is confirmed by natural occurrences of UO_2 in which a wide variety of uranyl phases form as alteration products (Finch and Ewing, 1989, 1991a, 1991b, 1991c, 1992a, 1992b, 1992c, 1993, 1994, 1997; Finch et al., 1998; Pearcy et al., 1994). The most striking feature of these studies is the extremely close parallel between the paragenetic sequences (i.e. phase formation sequence) of the very long term (10 year tests) (Wronkiewicz et al.,1996, 1997; Wronkiewicz and Buck, 1999; Finch et al., 1999) and the young (therefore, low-Pb uraninites) deposits of Nopal I in Mexico (Pearcy et al., 1994). Thus, both experiments utilizing drip tests and the study of natural uranium deposits may be used to simulate the reaction progress expected for the UO_2 in spent fuel in the proposed Yucca Mountain repository (Finch and Ewing, 1992c; Wronkiewicz et al., 1996, 1997)

Under oxidizing conditions, the reaction kinetics of the conversion of UO_2 to a uranyl phase is rapid, and results in nearly complete dissolution of the original UO_2 (Murphy and Pabalan, 1995). Wronkiewicz et al. (1996) estimated that UO_2 pellets in their experiments (90°C) would have been completely altered within 660 years, concluding:

> ***"The speed at which the UO_2 reactions occurred suggests that an advanced stage of uranyl alteration phase development can occur almost instantaneously within the constraints of the time-scale expected for repository disposal."***

These results imply that alteration and subsequent trace element migration may occur simply due to the exposure of SNF to moisture in an unsaturated repository setting. The results are further supported by kinetic and thermodynamic models of UO_2 corrosion (e.g., Bruno et al., 1995; 1996, 1998) in which the final steps of the corrosion process are the precipitation and subsequent dissolution of the secondary uranyl phases.

The rapid matrix dissolution of the UO_2 in an oxidizing environment will result in a release of actinide and fission product elements, which appears to be preferentially incorporated into the structures of the uranyl phases formed during the corrosion of UO_2 (Ewing et al., 2000). Unfortunately, there are a wide variety of uranyl phases (approximately two hundred mineral names for these phases, see for example Cejka and Urbanec, 1990; Baran, 1992; Fleischer and Mandarino, 1995; Burns, 1999); and they are poorly described, their structures are often not known, and critical parameters such as their thermodynamic stability have not been determined experimentally.

Most importantly, there has been only a limited determination of the capacity of these phases to incorporate and retard the mobility of the released actinides and fission products. The fate of these radionuclides is critical to the performance assessment of a spent fuel repository in an oxidizing or reducing environment. A

basic understanding of the compositions, structures and stabilities of these phases is essential to the DOE environmental remediation program.

Significance of Research Program to the EMSP

An integral part of the performance assessment of a repository will be the interpolated behavior of UO_2 in SNF during alteration and corrosion. This research program will provide a basis for establishing the extent to which models of alteration and corrosion processes used in the performance assessment of the near-field repository environment are useful or valid. For example, it is essential that the presently large uncertainties inherent in these models be reduced (see for example the discussion by Ahn, 1996a, 1996b). Studies of natural samples of great age and appropriate geochemical environments offer a means to improve the understanding of the sources of error while decreasing uncertainties in the corrosion models.

This research focuses on near-field phenomena, that is waste form degradation. The successful understanding of relevant phenomena in the near-field <u>reduces uncertainties</u> in the total system performance assessment because:

- The radionuclides are initially located within the UO_2 matrix of the spent fuel. Initially, these waste forms (spent fuel or vitrified high-level waste) are the only part of the repository that is radioactive. ***The successful performance of the waste form, or subsequent incorporation of radionuclides into alteration products of the corrosion process, results in near-field containment.*** This strategy is much preferred to the geologic isolation approach that presumes inherent release and movement of radionuclides, and relies on long travel times, dilution, dispersion, and sorption to restrict transport.

- ***The chemistry and physics of the UO_2 corrosion and alteration, which lead to an understanding of subsequent release or retention of radionuclides over a given range of environmental conditions, is inherently more simply modeled and extrapolated over time*** than the use of coupled hydrologic, geochemical and geophysical models of far-field radionuclide transport in of a geologic repository. That is, the extrapolation of the corrosion behavior of the UO_2 over long periods rests on a firmer scientific foundation than the extrapolated behavior of, as an example, hydrologic systems that are site specific and highly dependent on specific boundary conditions that are more difficult to model over long time periods (e.g., climate and recharge).

- ***Naturally occurring UO_2 and its alteration products provide fundamental data for the "confirmation" of the extrapolated behavior of the UO_2 in spent fuel over long periods of time (millions to billions of years).*** This approach holds great potential for the confirmation of performance assessments of near-field behavior. Uraninite provides one of the rare opportunities in which studies of a natural material can provide unambiguous data for the long-term behavior of SNF.

Finally, we note that uranium is the most abundant actinide element in the DOE complex and the dominant element present in SNF. The results of this research

program are broadly applicable to DOE's efforts to clean up its numerous sites, such as at Fernald, Ohio, and Paducah, Kentucky, as well as dispose of defense and commercially generated SNFs. This research also provides data that are required to evaluate the long term behavior of fuel held in storage sites, both in pools or in dry casks.

RESEARCH REPORT (2000 - 2004)

The major advances resulting from this research program include:

Thermodynamic Prediction of Observed U^{6+} Phases. Analyses have shown that Blind Prediction Modelling (BPM) fails to predict the reported U^{6+} mineralogy in the weathering horizon of the 2 Ga old supergene-weathered Oklo-Okélobondo and Bangombé U-deposits and their natural fission chain reactors (Salah 2000; Jensen et al., 2002). The major problems appeared to be: 1) the lack of thermodynamic data on key uranyl phases and 2) that important species, such as SO_4^{2-} and PO_4^{3-} were not always included in the modelling. We have developed an empirical model that provides for the calculation of this much-needed thermodynamic data (Clark et al., 1998; Chen et al., 1999a). Using a method that sums the polyhedral contributions for the structural components, the thermodynamic parameters for key uranyl phases have been calculated. Based on this updated data, Eh-pH diagrams predict that coffinite and $U(HPO_4)_2.2H_2O$ are stable U^{4+} phases under reducing conditions, and uranopilite, torbernite and bassetite will become stable as conditions become oxidizing. These phases are in accord with mineralogical observations. Previous BPM often omitted P and S and hence failed to predict the uranyl minerals observed at Bangombé. These new modelling results stress the importance of SO_4^{2-} and PO_4^{3-} resulting from dissolution of accessory apatite, monazite and sulphides in the retardation of U owing to the formation of uranyl sulphates and phosphates. This is a very specific example of the use of a natural analogue site to test conceptual models used in a performance assessment. These results have been published in *Radiochimica Acta* 90, 761-769 (2002).

In Situ Isotopic Analysis & High-Resolution Transmission Electron Microscopy (HRTEM) of UO_2: One of the challenges in using natural uranium deposits, such as the Cigar Lake Deposit in Canada or the Oklo natural reactors in Gabon, as analogues for the long-term behavior of spent nuclear fuel has been the need to understand their complicated history of repeated alteration and criticality events (in the case of Oklo). In collaboration with Mostafa Fayek (now at Oak Ridge National Laboratory) we have used highly accurate *in situ* isotopic analyses by secondary ionization mass spectrometry (SIMS) to make measurements of the complexly intergrown uranium minerals and their alteration products. The first study was of the uranium minerals at the Cigar Lake Deposit of the Athabasca Basin in Canada. By a combination of SIMS and HRTEM, we were able to demonstrate that the nanoscale formation of alteration products, such as coffinite ($USiO_4$) and calciouranoite ($CaU_2O_7\ 5H_2O$), has a profound and misleading effect on the results of conventional fluorination analyses. Using our nanoscale techniques, we were able to clearly identify 3 stages of alteration in the Cigar Lake uraninites (Fayek et al, 2002). We have extended this approach to studies of the Oklo-Okélobondo natural fission reactors in Gabon (Fayek et al., 2002). In this case, we were able to

determine the timing of separate criticality events and subsequent alteration events. Most importantly, we have been able to determine by isotopic analysis that the reactor zones nearest the surface have reacted more extensively with groundwaters of meteoric origin. We have now combined the high-resolution SIMS analysis with advanced microscopy techniques, such as high-angle annular dark-field imaging scanning transmission electron microscopy (HAADF-STEM) to put together a detailed description of the alteration processes of uraninite in the reactor cores at Oklo and Bangombé (Fayek et al.submitted).

UO_2 Incorporation of ^{99}Tc. ^{99}Tc is a long-lived radioactive fission product with a half-life of 2.13×10^5 years and a fission yield of 6.13% in nuclear reactors, making ^{99}Tc a prominent contributor to dose in safety assessments of nuclear waste repositories. Under Eh-pH conditions corresponding to the oxidative corrosion of SNF, which is constrained by the stability of uranyl phases relative to that of the UO_{2+x} phase, TcO_4^- is the predominant species of technetium with log $[TcO_4^-]/[TcO(OH)_2^0] > 2.15$ over the range of pH = 4 – 10. The low solubility of $TcO_2 \cdot H_2O$ and high adsorption of Tc^{4+} by geological materials (e.g. clays), results in a groundwater concentration of Tc^{4+} of less than 10^{-8} m (Chen et al., 1999c). This implies that the incorporation of Tc^{4+} into alteration uranyl phases is not an important retardation mechanism. In contrast, TcO_4^- is highly soluble and weakly adsorbed in the near-field. Thus, the incorporation of Tc^{7+} into the structure of oxidized uranyl phases that might be expected to occur as an alteration product of SNF will actually result in under-bonding at the U^{6+} site, destabilize the structure. This suggests that significant substitution of (TcO_4^-) will not occur in uranyl phases. These results have been published in the *Journal of Nuclear Materials* 278, 225-232 (2000).

Uraninite, UO_{2+x}, Incorporation of Trace Elements. Uraninite and associated alteration products from the Colorado Plateau were studied in detail by optical microscopy, electron microprobe analysis (EMPA), scanning electron microscopy (SEM) and backscattered electron (BSE) imaging in order to determine the behavior and fate of trace elements such as Pb, Ca, Si, Th, Zr, and REE during corrosion under oxidizing conditions. The long-term alteration products and processes of uraninite provide insight into the corrosion of UO_2 in SNF. Uraninite, schoepite, calciouranoite, uranophane, fourmarierite, a Fe-rich uranyl phase, and coffinite were identified. The primary uraninite and alteration phases generally have low trace element contents, with the exception of coffinite from Caribou Mine, Colorado. The trace element content of uraninite (Zr, Ti, Th and REEs) were in general, lower than the values measured in secondary uranyl phases, suggesting that trace elements are preferentially incorporated into the structures of the secondary uranyl phases. A compositional profile of a concentric structure in schoepite shows that alteration results in a loss of U, Pb and Zr and the incorporation of Si, Ti, Ca and P. Concentric structures are usually composed of both uraninite and uranyl phases, while micro-fractures are common in the secondary phases. This work has been published in *Radiochimica Acta* (Zhao and Ewing, 2000).

Retardation of Radionuclides in the Oklo Natural Reactors. The natural fission reactors in Gabon have been studied in detail by optical microscopy, BSE, and EMPA to determine the source term, extent of uraninite alteration, and the means of retardation of nuclear reaction products during their 2 Ga year long

geological history. A detailed study of the recently excavated Okélobondo reactor zone was conducted. This reactor zone consists of a ~ 55 cm thick reactor core overlain by a typically less than 60 cm thick hydrothermal alteration halo, *argile de pile*. The reactor core mainly consists of uraninite (≤ 90 vol.%), galena, illite, and minor chlorite. The *argile de pile* consists mainly of chlorite cut by fine illite veinlets. The uraninite has been subjected to minor degree of coffinitization ($UO_2 \rightarrow USiO_4.nH_2O$). Several accessory phases occur in the reactor zone of which U-Zr-silicate, monazite, sulfides, and sulfur-arsenides are particularly important with respect to retardation of fissiogenic elements. The "unaltered" uraninite is relatively pure and consists of 87.01± 0.72 to 91.24±0.91 wt.% UO_2 and 5.66±0.61 to 7.22±0.53 wt.% PbO. The major impurities are SiO_2 (≤ 0.78±0.11 wt.%), CaO (≤ 1.84±0.09 wt.%), and FeO (≤ 0.55±0.04 wt.%). The concentration of fissiogenic trace elements is low: ZrO_2 ≤ 0.09±0.04 wt.%, ThO_2 ≤ 0.20±0.11 wt.%, Ce_2O_3 ≤ 0.09±0.02 wt.%, and Nd_2O_3 ≤ 0.10±0.06 wt.%, but showed a distinct variation with location in the reactor zone. The concentration of the fissiogenic trace elements was higher (ZrO_2 ≤ 24.29 wt.%, ThO_2 ≤ 0.31 wt.%, Ce_2O_3 ≤ 0.75 wt.%, and Nd_2O_3 ≤ 0.50 wt.%) in U-Zr-silicate observed in fracture veinlets and mineral coatings in the reactor zone. Inferred from mineral chemistry, the fissiogenic Zr (including $^{90}Sr \rightarrow {}^{90}Zr$), Ce, Nd, and Th (daughter of $^{238}U(n,\gamma,2\beta)^{239}Pu(n,\gamma)^{240}Pu$ and $^{235}U(n,\gamma)^{236}U$) are well-retained in uraninite and retarded by the U-Zr-silicate during migration. Fissiogenic LREE may also have been incorporated into rare monazite. Fissiogenic Ru, including ^{99}Ru a daughter of ^{99}Tc, was mainly retained in ruthenium sulfur-arsenides (± Pb, Co, and Ni), such as ruthenarsenite and ruarsite. This work was published in the *Bulletin of the Geological Society of America* (Jensen and Ewing, 2001).

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SUMMARY OF IMPACTS OF THE RESEARCH PROGRAM

Impact on International Programs. During the past three years, my research group at the University of Michigan has had an active program of research on uranium-bearing phases, the corrosion products of uraninite, and the UO_2 in SNF. The work has benefited from numerous collaborations, many of them international. As an example, Professor Ewing was a participant in the European Union project to study radionuclide migration around the Oklo reactors in Gabon. The EU program supported collaborations with scientists in Denmark, Poland, France, Spain and Japan. He participates in a new European initiative to study radionuclide release from the Bangombé reactor under oxidizing conditions. As a result of this collaboration, Professor Ewing now has an extensive research collection of Oklo samples that provide the basis for future work. Through a NATO program there is an active collaboration with Russian colleagues at the Khlopin Radium Institute in St. Petersburg and through a BES/DOE program we collaborate with the IGEM of the Russian Academy of Science in Moscow in studies of minerals suitable for use as actinide waste forms. We are continuing our collaboration with Dr. F. Chen at the Guangzhou Institute of Geochemistry of the Chinese Academy of Sciences.

Impact on Review and Advisory Committees. Within the United States, Professor Ewing serves on many committees associated with DOE projects. He served as a member of the Committee for the "Peer Review of the Total System Performance Assessment – Viability Assessment of the Yucca Mountain Repository", as a member of the National Research Council's committee on "Alternative High-Level Waste Treatments at the INEEL Site", and on the NSF committee for "Opportunites in Mineral and Rock Physics and Chemistry." He has been a member of the program committees for the Materials Research Society symposium, "Scientific Basis for Nuclear Waste Management", a consultant for the Advisory Committee on Nuclear Waste of the Nuclear Regulatory Commission, and

serves on an international review committee of the waste form development program in France (VESTALE Program) . He is presently a member of the Board of Radioactive Waste Management of the National Research Council. Professor Ewing received a Guggenheim Fellowship (2002) for to study the impact of the nuclear fuel cycle on the environment. Since 2000, Professor Ewing has given 27 invited presentations on various aspects of nuclear waste management. All of these activities have provided opportunities to present the results of this EMSP-supported program.

Impact on Education & Infrastructure. Most important to the long-term impact of the EMSP-supported program is the training of graduate students and post-doctoral fellows in the field of radioactive waste management. Professor Ewing's group has trained a number of scientists who are now prominent in the nuclear waste management field (e.g., G. Lumpkin at Cambridge University in the U.K., W. Gong at the Vitreous State Laboratory at Catholic University, R. Finch at ANL, Peter Burns at Notre Dame, Mostafa Fayek at ORNL, Kate Helean at UC-Davis, Julia McAnallen at the Nuclear Regulatory Commission, Janusz Janeczek at the University of Silesia, and Keld Jensen at the National Institute of Occupational Health in Denmark). The present EMSP program at the University of Michigan supports or has supported: C. Palenik (Ph.D. candidate in Geological Sciences, recipient of Office of Civilian Radioactive Waste Management Fellowship); K. Traexler (Ph.D. candidate in Nuclear Engineering and Radiological Sciences), F. Skomurski (Ph.D. candidate in Geological Sciences), Keld Jensen (Ph.D. candidate and post-doctoral fellow), Farong Chen (post-doctoral fellow), Satoshi Utsunomiya (post-doctoral fellow).

COLLABORATIVE INTERACTIONS

Because of our long involvement in this field, particularly with international scientists, the EMSP program allowed us to maintain long-term collaborations with colleagues working on various aspects of uranium chemistry. .

The main collaborations are listed below:

Dr. Peter Burns	**Notre Dame University** structural studies and refinements of uranium minerals
Professor Udo Becker	**University of Michigan** surface science studies
Dr. Jordi Bruno	**QuantiSci, Barcelona, Spain** leaching studies of uranium minerals; solution chemistry of actinides
Dr. Ignasi Casas	**Department of Chemistry** **UPC, Barcelona, Spain** leaching studies of uranium minerals
Dr. Fanrong Chen	**Guangzhou Institute of Geochemistry** Chinese Academy of Sciences, Wushan, P.R. China geochemical modeling of uranium-phase dissolution
Professor Sue Clark	**Department of Chemistry**

	Washington State University structure-based models of solubility
Dr. Mostafa Fayek	**Center of Isotope Geochemistry** **Oak Ridge National Laboratory** isotopic studies of uranium deposits
Professor Frank Hawthorne	**Department of Geological Sciences** **University of Manitoba** crystal structure refinements of uranium minerals
Professor Janusz Janeczek	**Faculty of Earth Sciences** **University of Silesia** mineralogy and geochemistry of the Oklo reactors
Dr. Keld Jensen	**National Institute of Occupational Health, Denmark** mineralogy and geochemistry of Oklo natural reactors
Dr. Gregory Lumpkin	**Cambridge University, United Kingdom** structural and TEM studies of waste forms and U^{6+} phases
Professor Takashi Murakami	**Mineralogical Institute,** **Tokyo University** studies of uranium phases by FEG-TEM and x-ray diffraction analysis
Professor Alex Navrotsky	**University of California, Davis** Calorimetric studies of waste forms and U^{6+} phases
Dr. Juan de Pablo	**Department of Chemical Engineering** **UPC, Barcelona, Spain** leaching studies of uranium minerals

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The principal investigator's name (this proposal) is indicated in **bold type** in the list of cited references.

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