

PROJECT SUMMARY

This proposal requests funding to acquire a powder X-ray diffractometer (XRD) for use in Earth Science research and education at Washington University in St. Louis. An existing instrument, the only powder XRD at Washington University, is nearly 30 years old and has developed major problems that prevent its continued operation. In addition, modern instruments incorporate recent design and detector improvements, including the introduction of silicon strip detectors, that compared to the existing instrument provide substantial improvements in precision and accuracy and a reduction in data collection times by a factor of 10 to 100. These improvements make possible experiments in the laboratory that in the past have been generally limited to synchrotron light sources. A new instrument is essential to the research program of the PI, an early career scientist, and will also be used by a number of Earth Science faculty members at Washington University. While the PI plans for extensive use of the proposed instrument, substantial time will be available for use by other researchers and, as with the current XRD, the proposed instrument will be operated as a user facility. An existing user base of seventy distinct users from seven departments at Washington University and the Department of Earth and Atmospheric Sciences at Saint Louis University will be transitioned to the new instrument, providing a large financial support pool that is immediately available to recover operating expenses and partially support the instrument technician.

Intellectual Merit

The proposed instrument will provide data essential to a number of the PI's projects, including research associated with a recent NSF CAREER award, that cannot be acquired on the current system because of generator and goniometer problems and design limitations. High-precision lattice parameter measurements will provide insight into trace element substitution mechanisms in iron oxides and how this affects element release during Fe(II)-catalyzed mineral recrystallization. Rapid collection of data with high signal-to-noise ratio over a wide 2θ range will facilitate modeling of (hk0) bands from phyllosulfates and ferrous smectites having turbostratic stacking in order to assess changes in sheet structure upon redox transformations. Enhanced detection limits of minor phases will allow for the identification of uranium(VI) phosphate nucleation in sediments and secondary phase formation during the Fe(II)-catalyzed recrystallization of iron oxides that contain insoluble substituting elements. The instrument will also enable research by other Earth scientists in areas such as mineral physics, biomineralization, geoarchaeology, sedimentary geology, and carbon sequestration.

Broader Impacts

The proposed instrument will be employed in a number of educational and outreach activities. Postdoctoral scholars, graduate students, and undergraduate students will use the instrument in research activities. High-school interns working with the PI will also use the instrument each summer. The instrument will be used in undergraduate and graduate courses and the PI will provide a short course on powder XRD methods every one to two years. The educational benefits of using advanced analytical instrumentation in undergraduate research will be investigated using student self-assessments. The instrument will substantially enhance the research infrastructure available to Earth scientists in the St. Louis metropolitan area and data collected on the instrument will result in publications in peer-reviewed Earth Science journals. Many of the projects conducted on the instrument will have societal benefits such as improving our understanding of the processes controlling contaminant fate in aquatic systems and mineralization pathways involved in carbon sequestration.

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PROJECT DESCRIPTION

1. INTRODUCTION

Powder X-ray diffraction (XRD) is a core analytical method to Earth Science, serving two distinct but important roles in the field. First, it is a primary research tool used to explore the structure of fine-grained earth materials and to quantify the relative mineralogical composition of rocks, sediments, and soils. Second, powder XRD is an essential characterization tool, identifying crystalline phases in samples in support of broader research projects. These dual roles make access to a powder X-ray diffractometer a critical need for Earth scientists.

The existing powder XRD instrument in the Department of Earth and Planetary Sciences at Washington University in St. Louis is a thirty year old Rigaku DMAX/A. It is at the end of its useful lifetime as it has developed problems with the main power generator and the gearing on the goniometer. In the last three years it has tripped its breaker for no clear reason on multiple occasions, damaging the tube twice because of the immediate voltage and current drop. It also lost control of its water circulation three years ago, causing a tube meltdown. While repairs are made as needed, major components that control the system and distribute power are breaking down. The frequent tube damage caused by unexpected generator failures or breaker trips is taxing the laboratory budget, as no XRD lab expects to replace the X-ray tube once a year. This instrument is the sole powder XRD system available at Washington University and is also used by members of Department of Earth and Atmospheric Sciences at nearby Saint Louis University. This instrument thus plays an essential role in Earth Science research in the St. Louis metropolitan area and its impending failure represents a major challenge for Earth scientists at multiple universities in the area.

Modern instruments offer many advantages that represent a substantial improvement over the existing system. Instruments are now plug-and-play and self-aligning, offering guaranteed stability to better than $0.01^\circ 2\theta$. This facilitates ease of use and ensures high-quality data are collected. These new instruments have been demonstrated to obtain data of the precision, accuracy, and signal-to-noise ratio (S/N) needed for Rietveld refinement of crystal structures and quantitative phase analysis. In addition, silicon strip detectors, originally developed for use at synchrotron light sources and in high-energy physics experiments, are now available for use on laboratory instruments. These detectors act as an array of scintillator strips, counting multiple degrees of 2θ at once with resolution $<0.02^\circ 2\theta$. The silicon strip detector on the proposed system covers roughly 3° in about 200 strips. Depending on experimental setup, these detectors provide a 10- to 90-fold reduction in the data collection time needed for a given S/N. This substantially improves crystalline phase detection limits and allows high-quality data to be collected in a fraction of the time for weakly scattering turbostratic materials. The stability of modern diffractometers combined with advances in detector technology now make it possible to conduct powder XRD measurements in the laboratory that in the past have typically been limited to synchrotron light sources.

The PI, an early career scientist who recently received an NSF CAREER award, has a critical need for high-quality powder XRD measurements. The needed data cannot be obtained from the existing instrument because of stability and precision limitations, and there is a high probability that the instrument will suffer a major malfunction in the near future. Further, the PI has a number of projects that involve the characterization of turbostratic and nanocrystalline earth materials. These minerals have broad, weak scattering features such as asymmetric (hk0) bands. These can be modeled using advanced analysis approaches to extract structural information but this requires data with high S/N that traditionally requires data collection times of up to 24 hours per sample. Concerns about the stability of the current instrument prevent its use for such long collection times. Moreover, it is impractical to study multiple samples, such as in a reaction series, this way as it would monopolize the existing instrument for multiple weeks and be prohibitively expensive because of hourly usage fees. A modern powder XRD instrument employing a silicon strip detector can obtain the same counting statistics in less than 1 hour with better angular precision and accuracy. Similarly, long counting times are needed to detect the presence of minor

constituents in a sample; such measurements would equally benefit from new detector technology combined with a high-precision instrument.

This proposal requests funds to acquire a powder X-ray diffractometer to support the PI's existing and future research projects in mineralogy and geochemistry, including important portions of the research associated with his NSF CAREER award. While frequent use of the instrument by the PI is planned, ample time will be available for use by other researchers. The instrument will thus be run as a user facility following the same access mode as the current instrument in the department. It will be used by other Earth scientists at Washington University and Saint Louis University studying topics such as geoarchaeology, sedimentary geology, biomineralization, mineral physics, and carbon sequestration. It will be used in undergraduate and graduate courses, in the research projects of undergraduate and graduate students and postdoctoral scholars, as part of team projects for undergraduates, as a research tool for local high school students conducting summer internships, and for demonstrations during outreach activities. The instrument will be managed by a technician that manages our current instrument along with our electron microprobe. The existing user base, consisting of over seventy individual researchers from eight departments at two universities, will be transitioned to the new instrument and provides an established large financial support pool to ensure that operating and maintenance costs can be covered.

2. AVAILABLE COMPARABLE EQUIPMENT

The only comparable equipment available at Washington University in St. Louis is a Rigaku DMAX/A powder X-ray diffractometer; the proposed system would replace this instrument. This is the only powder XRD system at Washington University; it was installed in 1982. It has a fixed Cu X-ray tube and a vertical goniometer driven by a single motor, with the 2θ circle directly geared to the θ circle. The diffractometer has fixed slits that can only be changed by the laboratory technician as this requires substantial disassembly of safety features associated with the X-ray tube as well as detector realignment. The detector is a scintillation counter with its energy threshold set to suppress Fe fluorescence from samples. A post-sample graphite monochromator is used to remove the contribution from the Cu K_{β} line and to further suppress sample fluorescence. The instrument was upgraded in the late-1990s with a data box controlled from Material Data Inc., allowing the instrument to be operated from a Windows environment. The JADE data analysis package was purchased at this time. While rich in features, this software package is complex and opaque and thus in practice of limited usefulness to most users. The instrument in its current form cannot accept environment control stages or specialized sample cells.

While this instrument has seen extensive use over its nearly 30 years of continuous operation, it has a number of design limitations and has developed severe operational problems that require its replacement. Specific operational problems include:

- The goniometer loses all angular registration if driven below 3° or above 75° 2θ . The exact origin of the problem cannot be determined but it is likely related to the primary gearing mechanism of the goniometer being severely worn. The only possible repair is replacement of the goniometer; this is cost prohibitive given the instrument age as parts are no longer manufactured. This problem makes analysis of clay minerals difficult and poses severe limitations on the accuracy of lattice parameter determinations
- The goniometer also shows signs of mechanical slipping of the gears in the working range. Diffractometer alignments with NIST standards are not reproducible because of this slippage. This also renders the instrument useless for accurate lattice parameter determination and structure refinements or quantitative phase analysis using Rietveld methods.
- This instrument may have developed a misalignment between θ and 2θ due to mechanical deformation of the goniometer over 30 years of use. As these two circles are directly geared together it is impossible to correct this through realignment.

- The detector high voltage supply shows signs of early stages of failure and requires frequent power cycling even for routine work. The measured intensity of a sample on different days is not always reproducible.
- The graphite monochromator mount is unstable and requires frequent realignment.
- The main power generator for the instrument, including the high voltage supply for the X-ray tube, has become highly unstable. The internal circuit breaker has tripped for unknown reasons three times over the last three years, in one instance damaging an X-ray tube to the extent that a replacement was required. It has also shown instability during current ramp up, with multiple occurrences of the breaker tripping when the current dial lingered for more than 1 to 2 seconds between 25 and 27.5 mA. This instability also damaged an X-ray tube once in the last year, requiring a replacement.
- Three years ago the instrument water flow controller failed abruptly causing a tube meltdown that also slightly damaged the X-ray tube tower.
- The integrated safety system represents a risk of radiation exposure to users, including students. It was designed in a way to allow a technician to have the sample housing and shielding open with X-rays on for alignment purposes. However, this system is configured such that a user could expose their hand to X-rays if they forget to manually close the shutter using a switch on the instrument control panel. Users are trained extensively to prevent this from happening but the system cannot be configured to reduce the risk of user exposure.

These problems and design limitations constrain the use of the instrument to primarily phase identification. In addition, instrument usage is limited to between 10 am and 5 pm on weekdays to ensure that the laboratory technician or a supervising professor monitors the instrument startup so that if instrument failure occurs someone is available to remedy the problem promptly. These problems are also having a financial strain on the laboratory as multiple X-ray tube replacements have been required over the last few years. The normal tube replacement cycle for a system like this is at least 3 to 5 years, often longer. For example, the X-ray tube on a Rigaku DMAX/B instrument that the PI used when at Stanford University had a tube that was 8 years old and still functioning properly, producing nearly its full intensity. Any additional tube failures in the future would overtax the laboratory budget and possibly require the discontinuation of the JADE license and ICDD database subscription. A generator or goniometer failure may require the shutdown of the XRD laboratory. The annual laboratory budget is not configured to cover the cost of catastrophic failure of a major instrument component.

3. PROPOSED INSTRUMENT

Instrument Configuration

The proposed instrument is a Bruker D8 Advance Diffractometer with Davinci Design (see attached quotation). The instrument is configured with a high-precision and high-accuracy vertical goniometer in a θ - θ configuration to maintain a flat sample geometry. The goniometer is guaranteed to have an angular accuracy no worse than $\pm 0.01^\circ$. It is driven by high precision stepper motors with optical encoders to ensure accurate angular positioning. The proposed system has motorized variable-divergence slits and a series of soller slits and beam filters for optimizing the optical configuration to specific experimental setups. A rotating sample stage was selected to minimize preferred orientation effects. This stage accepts a wide array of sample cells, including sealed cells that can maintain anoxic conditions during data collection. The “Davinci Design” represents a plug and play design of the instrument, allowing fast switching of optical components with automated, computer controlled alignment. The software also controls the generator operation, providing features such as an automated initial tube burn in to maximize the useful life of the source. The instrument features two independent safety systems to prevent accidental X-ray exposure.

A Cu X-ray tube with ceramic insulation was selected for long operating life and experimental flexibility. Cu is the ideal tube selection for the research needs of the Department of Earth and Planetary Sciences, including the PI. The short X-ray wavelength from a Mo tube compresses the diffraction pattern to low angles, effectively reducing resolution and making analysis of clay basal reflections difficult. Selection of a Co tube would mitigate Fe fluorescence problems (Co K_{α} fluorescence is below the Fe K-edge) but would increase Mn fluorescence while increasing the angle at which Bragg peaks appear. A Cr tube would mitigate all fluorescence problems but suffers from reduced intensity caused by substantial air attenuation. A Cu tube provides the right balance of intensity, angular distribution of scattering features, and comparability (most published data was collected using Cu K_{α} radiation). The detectors are designed to mitigate contributions of sample fluorescence (see below) and modern software can easily deal with the minor anomalous scattering of Fe near Cu K_{α} wavelengths.

Two detector configurations were selected. The first is a scintillation counter with a graphite pre-monochromator to suppress sample fluorescence and the Cu K_{β} line from the X-ray tube. This configuration can be used to obtain accurate lattice parameters using narrow divergence and detector slits. The second detector selected is a silicon strip detector which can record $3^{\circ} 2\theta$ at once, separated into 192 strips ($\sim 0.016^{\circ}$ resolution). This allows for rapid collection of high-quality data. The reduction in counting time for equivalent S/N (i.e., same number of counts above background) when using a silicon strip detector will vary with each experiment. For typical measurements this will be roughly a factor of 90 (192 strips with $\sim 50\%$ signal reduction from a Ni filter to minimize the Cu K_{β} line). Samples with high Fe fluorescence will see a benefit of roughly half of this (45 times faster data collection) because the threshold setting on the detector will need to be optimized to suppress Fe fluorescence, which also partially reduces the diffracted Cu K_{α} intensity. Even with a conservative estimate that other experimental aspects will reduce this benefit by another factor of 2, it will still be possible to collect data in 1 hour that previously took 24 hours, representing a tremendous gain in potential efficiency and data quality.

The instrument comes packaged with the DIFFRAC suite of data collection and analysis software. The DIFFRAC package includes routines for data collection in various configurations and standard data evaluation, phase analysis, and plotting techniques. The package also comes with the program TOPAS, capable of whole pattern analysis, Rietveld structure refinement, and quantitative phase analysis, among other features. The DIFFRAC+TOPAS software package is well known for its ease of use, making it an excellent choice for an instrument operated as a user facility. The package will suit both novice and advanced users.

Justification for Preferred Instrument

The Bruker D8 Advance is capable of high precision, high-accuracy measurements with high S/N. This instrument is generally considered the best available powder XRD system on the market today. In the last year its pricing has improved to now be comparable to Rigaku instruments, which the PI considers to be inferior in terms of data quality, ease of use, and software functionality. The Bruker D8 Advance also provides a platform to expand the X-ray diffraction and scattering capabilities of the Department of Earth and Planetary Sciences in the future. The modular design of the instrument allows for future upgrades such as controlled environment chambers for variable temperature and atmosphere measurements in situ, a capillary mount and associated focusing optics for time-resolved flow-through experiments, and goniometer and optics additions for X-ray reflectivity, grazing-incidence diffraction, small angle X-ray scattering, and texture/preferred orientation measurements.

None of these optic and goniometer upgrades, or the associated applications, are possible on lower-priced diffractometers, such as small benchtop diffractometers like the Bruker D2 Phaser, which cost around \$110,000. In addition, such “mini-XRD” systems employ a low-power generator, producing substantially reduced X-ray flux. A silicon strip detector is needed on such instruments just to approach the S/N available with a simple scintillation counter on the proposed Bruker D8 Advance. Small benchtop diffractometers with silicon strip detectors at best can match the performance of the existing diffractometer and generally lack the goniometer precision needed for the most challenging

measurements. They provided none of the data collection time improvements that make the proposed projects feasible in the laboratory and are suited primarily for phase identification. It is important that the optimal instrument, i.e., the Bruker D8 Advance, be acquired if the new system is to meet the needs of Earth scientists at Washington University for the next few decades.

4. INSTRUMENT MANAGEMENT PLAN

4.1. Instrument Oversight

PI Catalano will be responsible for primary oversight of the instrument. Prof. Brad Jolliff (biosketch attached) will serve in a backup role and be fully trained on the operation of this instrument. Major instrumentation in the Department of Earth and Planetary Sciences often has two faculty supervisors in case problems develop while one is on travel. While Prof. Jolliff does not have substantial active projects requiring the instrument he has extensive experience with X-ray diffraction, including as the faculty supervisor for the current instrument. Day-to-day operation will be managed by Paul Carpenter, a technical staff member of the Department of Earth and Planetary Sciences. Mr. Carpenter currently splits his time between managing the electron microprobe and the existing XRD, which are located in neighboring labs.

4.2. Technical Support Availability

Primary instrument technical support will be provided by Paul Carpenter. The department supports Mr. Carpenter, with this supplemented by user fees obtain from both the XRD and electron microprobe labs. Mr. Carpenter is available during business hours Monday through Friday and trains users in both instrument operation and basic data analysis.

4.3. User Access Policies

The primary expected users are faculty, postdoctoral scientists, graduate students, undergraduate students, visiting scientists, and summer high school interns. All users are required to complete university-wide laboratory safety training followed by a 2-hour instrument training. The instrument training teaches users how to safely operate the instrument. Users that do not demonstrate this ability are not allowed to use the instrument. Once trained, users have access to a web-based system for scheduling time on the instrument. While the current instrument has a high usage rate, seeing use on >85% of available days, it is normally possible to schedule time within a week. For routine phase identification on a single sample this can often be fit in within 1 to 2 days. Access for general users is currently restricted to between 10 am and 5 pm on weekdays to ensure that an instrument malfunction can be corrected promptly; this has happened fairly frequently with the current instrument because of age. With a new instrument a similar access plan would be maintained for most users. Select users with more complex research tasks will be trained as expert users on the new instrument. Training will involve a more detailed understanding of the operation of the instrument and an assessment of the user's ability to work safely. This will be restricted to graduate students, postdoctoral researchers, faculty, and other senior scientists. These expert users will be granted access to the instrument on weekend and evenings to pursue measurements requiring longer counting times or with time-sensitive samples.

4.4. Anticipated User Fees

The existing fee structure will initially be maintained. Washington University users will be charged \$20 per hour for use and external academic and government users \$30 per hour. Training and technician-assisted time is billed at a higher rate: \$25 per hour for users from the Department of Earth and Planetary Sciences, \$30 per hour for other Washington University users, and \$50 per hour for external academic and government users. These usage fees have been set to ensure enough income for maintenance of software and database licenses, instrument repair (including saving funds over multiple years for eventual tube replacement), sample preparation consumables, sample holders (these need

replacement after extensive use), and minor technician support. It is unclear how hourly use will change with the new instrument. It will have new capabilities and, for some users, greater access time, potentially increasing hourly usage. It will also collect better data faster, which could potentially lead to a decrease in the hourly usage. Users will be encouraged to take advantage of the better data quality available on this instrument and a substantial drop in total hours used per year is not expected. However, after 6 months of operation the hourly usage, average per sample data collection time, and lab expenses will be evaluated and the hourly fees may be revised. It is expected that the cost of obtaining quality data per sample will be lower even if the hourly fee is raised because of the substantial improvement in data collection speed afforded by the proposed instrument.

4.5. Data Access and Archival

The data collected on the new XRD will be stored on the PC that controls the instrument. This data will only be accessible in the XRD laboratory. For security purposes the data will not be made available over the internet. Users will be able to email their data to themselves or transfer data via a memory stick. This has worked well for the current instrument. Data will be archived nightly to an internal server to ensure that the data is preserved in the event of a computer failure.

4.6. Installation Location

The XRD will be installed in existing space in the Earth and Planetary Sciences Building (opened 2004). This XRD laboratory is fully climate controlled and has 230 ft² of floor space and 10 ft ceilings. The XRD laboratory has existing electrical and cooling water supplies for the instrument and has a connected laboratory space (also about 230 ft²) for sample preparation.

5. PROPOSED USES IN RESEARCH PROJECTS

The proposed instrument acquisition is essential to a number of projects in the Department of Earth and Planetary Sciences at Washington University in St. Louis. A series of major research projects by the PI that require a modern powder XRD system are described below. These are followed by additional example Earth science projects by auxiliary users. Uses of the proposed instrument for educational and outreach activities are described in Section 6.

5.1 Main Projects by the PI

Two components of the PI's CAREER grant and two additional projects are described.

Trace Element Release from Iron Oxides during Biogeochemical Iron Cycling

Detrital and authigenic iron oxides commonly occur in soil, sedimentary, and aqueous systems as primary grains, overgrowths, cements, ooids, concretions, and major ore bodies [1]. Microbially-mediated iron redox cycling may occur during sediment burial, diagenesis, hydrocarbon fluid migration, and changes in soil hydrologic state [2-5], resulting in secondary abiotic reactions between aqueous Fe(II) and solid Fe(III) oxides. These reactions catalyze dynamic recrystallization of iron oxide minerals through localized and simultaneous oxidative adsorption of Fe(II) and reductive dissolution of Fe(III); recrystallization continues long after the fluid composition indicates that chemical equilibrium has been reached. We have recently demonstrated that this recrystallization causes the repartitioning of trace elements, such as Ni and Zn, between the mineral bulk, mineral surface, and aqueous solution [6], with adsorbed trace elements becoming progressively incorporated in regions of overgrowth and incorporated elements released at sites of dissolution. This previously unknown trace element cycling may substantially alter the distribution of these element in modern and ancient systems, affecting the interpretation of ocean composition proxies, the availability of micronutrients, and the fate of water contaminants.

The PI's group is currently investigating trace element release from iron oxides caused by aqueous Fe(II) and how it is affected by fluid and mineral composition. A series of goethites and hematites containing a range of Ni(II) or Zn(II) concentrations (0.5 to 5 mol%) have been synthesized.

Ni- and Zn-substituted iron oxides containing Al(III), Cr(III), and Sn(IV) co-dopants over a similar range of bulk compositions have also been prepared. Spectroscopic measurements and dissolution experiments show that these elements substitute into crystallographic sites and that their distribution is generally uniform through the particles. The co-dopants have been found to inhibit Ni and Zn release, possibly because these insoluble elements buildup on and passivate the surface.

To understand the chemical controls on trace element release and the inhibitory effects of insoluble co-dopants it is essential to evaluate the substitution mechanism of the substituting elements and the effect this has on the iron oxide structure. Identifying any secondary phases that form from co-dopant precipitation during reaction is also of great importance. Precise XRD data with high S/N are thus critical to this project. The proposed XRD system will be used to obtain the data needed to address outstanding questions regarding substitution mechanism and secondary phase formation. Precise lattice parameter measurements will be determined for the different single-element and co-doped substitution series. These measurements require an accurate goniometer and data collection to high 2θ and are not possible on the current instrument. Linear changes in lattice parameters with increasing element substitution following Vegard's Law are expected if a single substitution mechanism is involved over the entire composition range. Deviation from linearity would indicate a change in mechanism. For example, Ni substitution in hematite may initially be coupled to proton or water incorporation ("hydrohematite") [7-9], but at higher doping levels could involve anion vacancy formation for charge balance. Rietveld structure refinements will be conducted on data from samples with the highest doping levels to investigate structural changes associated with element doping. Special attention will be focused on the Fe site occupancy as a reduction in this parameter may indicate water/proton incorporation [9]. Chemical composition measurements will be used to constrain the fractional occupancy of this site by substituting elements.

Post-reaction samples will be analyzed in airtight specimen holders to investigate structural changes and secondary phase formation. Fe(II) can cause release of up to 30% of the substituting element(s) [10] and its adsorption may produce a delocalized electron in the structure [11,12]. Lattice parameter measurements will be used to evaluate structural changes caused by Fe(II) incorporation (increase in lattice parameters expected from addition of delocalized electron) and substituting element release (lattice parameter change depends on relative size of element to Fe^{3+}). Linewidths will be monitored in case the active volume of the mineral undergoing recrystallization is limited to a surface region that is thinner than the penetration depth of the beam. The possible formation of secondary insoluble phases on the Al, Cr, and Sn-substituted iron oxides after reaction with Fe(II) will be investigated using the silicon strip detector in order to obtain data with a high S/N. This detector should provide at least a factor of 5 to 10 improvement in theoretical detection limits for secondary phases over the current system based on counting statistics and the range of background count rates expected; improvement in practical detection limits will likely be greater because of the improved instrument stability and ability to employ longer data collection times. These studies will be coupled with transmission electron microscopy and X-ray photoelectron spectroscopy measurements to determine the mechanism through which insoluble co-dopants inhibit trace element release during iron oxide recrystallization.

Transformations of Phyllomanganates during Biogeochemical Cycling and Trace Element Fate

Biogeochemical processes result in the cycling of manganese between reduced and oxidized states. Similar to iron, secondary abiotic reactions may occur between aqueous Mn(II) and solid Mn(IV/III) oxides during such redox cycling. Past studies suggest that these reactions may affect the structure and average oxidation of manganese oxides [13-19], but the reactions that occur in these systems are poorly understood and the resulting impact on trace element fate is unknown. The mechanisms involved in these secondary manganese reactions are challenging to explore because, unlike iron [11,20-24], isotopic methods, including isotope-labeled Mössbauer spectroscopy, cannot be employed as manganese is monoisotopic and Mössbauer inactive.

The PI's group is approaching this knowledge gap in manganese biogeochemistry by evaluating the compositional and structural changes of manganese oxides that results from reaction with aqueous

Mn(II). The project focus is on the phylломanganate minerals δ -MnO₂ and hexagonal birnessite, which are the predominant phases that form during manganese redox cycling [13-16,25-27]. These phases are nanocrystalline and composed of sheets of Mn⁴⁺O₆ octahedra; the sheets show turbostratic stacking, similar to smectites. Vacancies and substitution of Mn(III) for Mn(IV) gives the sheets a net negative charge; interlayer cations that readily exchange are present for charge balance. The two phylломanganates under investigation differ in that δ -MnO₂ has little Mn(III) substitution but a substantial vacancy content, whereas hexagonal birnessite has fewer vacancies but greater Mn(III) substitution for Mn(IV). Reaction with Mn(II) may induce the following structural changes in phylломanganates: (1) Mn(II) adsorption over and capping of vacancy sites; (2) Mn(II) oxidative adsorption, randomly filling vacancies in the phylломanganate sheet as Mn(III) and reducing a sheet Mn(IV) to Mn(III); (3) Mn(II) oxidative adsorption producing an ordered array of Mn(III), altering the sheet symmetry from hexagonal to orthorhombic; (4) oxidative Mn(II) adsorption on sheet edges, causing sheet growth and reduction of sheet Mn(IV/III) to Mn(III/II). Reaction 4 may be favored at high ionic strength, such as in marine systems and sedimentary brines, where the high electrolyte concentration suppressed Mn(II) cation exchange. Electron transfer from the sheet edged to Mn(III) sites in the particle interior may generate Mn(II), which will then be released to the interlayer and lost via cation exchange, leaving behind a vacancy. As vacancy content greatly affects the capacity of phylломanganates to bind trace elements [28-30] and conduct electrons [31], these structural changes may substantially alter the ability of phylломanganate to modify the composition of natural waters and modify the energy yield available to microbial metabolic processes.

Investigating these potential structural changes is challenging because of the turbostratic nature of the phylломanganates of interest, preventing traditional structure refinements. Powder XRD measurements are critical to investigating phylломanganate structure and structural changes as they are one of the few tools directly sensitive to changes in vacancy content, vacancy capping, and sheet symmetry that can be applied to these materials. XRD methods developed to analyze the structure of lamellar materials like smectites [32-37] are applicable to phylломanganates and provide substantial insight into the mineral structure. These methods have been successfully applied in the past to evaluate structural features of natural and synthetic phylломanganates [15,28,38-44]. These methods require powder XRD patterns with high S/N over a broad 2 θ range. This allows for modeling of the weak and broad (hk0) bands [33,37], present in the XRD pattern of any turbostratic material, to evaluate sheet structure. On a conventional powder diffractometer data collection times of approximately 24 hours per sample are needed to obtain data having the requisite S/N and 2 θ range. Such measurements are infeasible on the current XRD system at Washington University because of instrument instability. The proposed instrument, when using a silicon strip detector, will provide the required S/N in 1 hour of data collection, making it feasible to analyze a series of samples to identify the systematic dependence of structural changes on fluid composition and reaction time. These X-ray scattering studies will be coupled to Mn K-edge EXAFS measurements, which provides complementary structural information [16], and chemical analyses for the average oxidation state of Mn. This structural and chemical information will then be used to assess how Mn(II) affects trace element fate by altering the adsorption capacity of phylломanganates or causing trace element release during Mn(II)-induced phylломanganate restructuring.

Oxidative Transformations of Fe(II)-Bearing Smectites

Iron-rich clay redox transformations affect the fate of contaminants [45,46] and may be important components of the iron cycle [5,47-49]. While the reduction and reoxidation of Fe(III)-bearing dioctahedral smectites has been studied extensively [47,48,50-53], the oxidation of Fe(II)-smectites, which are primarily trioctahedral, has been rarely investigated even though these minerals are of substantial geological and environmental importance. Mafic rock weathering on the early Earth prior to the Great Oxidation Event, under anoxic conditions in modern terrestrial systems, and on Mars prior to global oxidation and desiccation is predicted to result in Fe(II)-bearing smectites [54]. Limited occurrences of ferrous smectites have been observed in weathered basalt on the ocean floor, in Iceland,

California, Connecticut, Japan, and India, and at the Atlantis II Deep in the Red Sea [54-61]. The chemical behavior of these trioctahedral smectites is difficult to investigate because of their instability in air; ferrous smectite samples from the field often oxidize before they can be studied.

It is important to understand the structural transformations caused by oxidation of Fe(II)-smectites in order to assess their abundance through geologic time, how they are involved in iron cycling, and the potential for these phases to serve as electron donors in microbial metabolic pathways. Ferrous saponite was synthesized and the structural transformations that occur upon oxidation are currently being studied. A series of oxidants and a range of chemical conditions and oxidation rates are being investigated, as is the effect of post-oxidation recrystallization. Fe K-edge EXAFS and Mössbauer spectroscopies provide insight into the changes in local structure and Fe coordination environment following oxidation, but powder XRD provides the only available probe of medium- to long-range structure. As for the phyllosulfates described above, the XRD patterns produced by the turbostratic phases under investigation have broad, low-intensity features, requiring long counting times (10 to 20 hours per sample) to obtain data with the S/N needed to extract structural information from the (hk0) bands of the diffraction patterns. Modeling of these bands can provide information on structural transformations of the sheet, including a transition from trioctahedral to dioctahedral and, for the latter case, whether the product has a *cis*- or *trans*-vacant octahedral sheet. The needed measurements cannot be made on the current instrument because of the limited angular range and inability to operate for extended periods of time. In addition, the current instrument cannot accept sample holders that maintain anaerobic conditions; such holders are available for the proposed instrument. The proposed XRD instrument with the silicon strip detector will be employed to obtain rapid (1 hour) full powder XRD patterns on these materials. The available airtight sample cells will prevent oxidation during measurements. Modeling of the (hk0) bands [33,37] will be used to assess structural changes in the ferrous smectite sheet upon oxidation.

Uranium Phosphate Precipitation in Subsurface Sediments

Uranium contamination of the subsurface is a widespread environmental problem resulting from Cold War-era weapon and energy production activities. In some locations uranium(VI) phosphate minerals have formed because of the high phosphate content of the uranium waste fluid [62-65]. A number of remediation methods have been proposed for other locations with the goal of precipitating uranium phosphate minerals in place [66-73], as these phases have low solubility and geological occurrences demonstrate their relative stability [74-81]. The PI's group is investigating the chemical conditions under which nucleation of uranium phosphates occurs in subsurface sediments. The proposed XRD instrument will be used to collect data with high S/N in select 2θ regions where the strongest diffraction lines of possible uranium(VI) phosphate minerals occur. As for the iron oxide project described above, the proposed instrument will provide a substantial improvement in detection limits over the current instrument, facilitating the identification of the early precipitation behavior of uranium phosphate minerals. The proposed XRD measurements will be complemented by EXAFS spectroscopy and electron microscopy studies.

5.2 Example Projects from Earth Science Auxiliary Users

Listed below are a series of example projects for auxiliary Earth science users that will employ the proposed XRD system. These auxiliary users are all based in the Department of Earth and Planetary Sciences at Washington University in St. Louis and have received funding in the past from the NSF Division of Earth Sciences. As requested in the Grant Proposal Guide, short biosketches for these auxiliary users are attached.

Connection of Crystal Structure with Thermal Diffusivity and Spectral Properties (PI: Anne M. Hofmeister)

Prof. Hofmeister conducts dual research programs in heat transport of Earth and planetary materials and laboratory spectroscopy of candidate materials for astrophysical environments. Many physical properties of substances are tied to their long-range structure or lack thereof. For both studies, Dr. Hofmeister's group is constructing databases of minerals and other solids. For many of their samples, polytypes exist, so confirmation of the crystal structure is important [82,83]. Powder XRD is an easy and reliable means of doing so. Their group also uses this method to characterize samples after heating [84]. In addition, Hofmeister's group has recently discovered that the inverse of thermal diffusivity is proportional to thermal expansivity times temperature [85,86]. Exploring this fascinating tie of heat transport to behavior of the crystal lattice is the subject of a recent grant proposal. Expanding and improving the XRD facilities, with the possibility of later addition of an environmental chamber, would advance this research.

Characterization of Biological Apatite and Its Synthetic Analogs (PI: Jill Dill Pasteris)

Prof. Pasteris' research group is involved in several collaborative studies of biological apatite and synthetic carbonated apatite that mimics many of the latter's properties. The group relies heavily on Raman spectroscopy for characterization of these materials, but their interpretations would benefit greatly from complementary information provided by high-quality X-ray diffraction analysis. Ph.D. candidate Zhen Li's research focuses on characterizing the most highly mineralized bone material known to exist, which contains about 95 wt.% apatite rather than the 50-60 wt.% mineral in typical bone. This hypermineralized bone, obtained from the Smithsonian Institution and from French colleagues, comes from the rostrum of an unusual beaked whale. The size of the nanocrystals of bone apatite is difficult to determine. Application of the Scherrer equation to XRD data would be very useful for this purpose. Both Pasteris and Li also are part of an interdisciplinary group (from the schools of Engineering, Medicine, and Arts and Sciences) that is exploring the material properties of biological transition zones in which unmineralized tendon grades into fully mineralized bone, as in the rotator cuff. In addition to characterizing (by TEM) biological tissue, these researchers create synthetic analogs to biomineralized tissue. It is extremely important in such syntheses to be able to distinguish among several calcium phosphate phases that may precipitate in the experiments, as well as to be able to detect (at a low concentration) and quantify contaminating phases. Again, high quality XRD data also would permit assessment of apatite crystallite size in the precipitates. Lastly, Pasteris collaborates with a synthetic chemist at Franklin and Marshall College, whose group synthesizes hydroxylapatites with different amounts of substitution of carbonate for phosphate. Such materials require XRD evaluation of their degree of crystallinity and crystallite size, as well as XRD screening for contaminant phases. The goal of the Pasteris group's research is to understand how the specific chemical features of biological apatite control its properties, for instance, crystallite size, shape, and solubility. The research has wide-ranging applications beyond the medical issues of bone health and development of synthetic replacements for defective bones and teeth. Carbonated apatites are useful in the remediation of heavy metals, such as lead, from contaminated soil and water. As a carbonate-containing phase of low solubility that occurs in large geologic deposits (phosphorites), carbonated apatite is also of interest in carbon sequestration.

Mineral Formation during Carbon Capture and Storage (PI: Philip Skemer)

Carbon capture and storage (CCS) is being actively pursued to mitigate the environmental consequences of fossil fuel emissions. CCS involves collecting anthropogenic carbon dioxide (CO₂) and sequestering it in an environmentally safe manner or recycling it for other industrial purposes. Prof. Skemer and collaborators are engaged in the study of mineralization that occurs during these processes, using in situ nuclear magnetic resonance (NMR) spectroscopic techniques at high pressure and temperature. Their spectroscopic tools provide information on the rate of reactions and in the near term will explore the spatial heterogeneity of these. However, NMR spectra cannot provide unique phase identification in some cases because of similarities in the nature of chemical bonding of certain key

minerals. For these cases phase identification by XRD is a required analytical technique. Therefore, Dr. Skemer will use the proposed XRD system for rapid and precise phase identification after each experiment. This information will be related back to the spectroscopic data to understand the mineralization pathways and kinetics related to geological sequestration of CO₂.

Mineralogical Indicators of Paleoenvironmental Conditions: Understanding Human Migration and Climate Change in the Quaternary (PI: Jennifer R. Smith)

Prof. Smith works in Quaternary geology and geoarchaeology, with a focus on paleoenvironmental reconstruction. She has several active projects that would involve XRD analysis, and would benefit from increased capabilities for quantitative phase analysis. In Egypt, Smith has been working on Pleistocene calcium carbonate and ironstone spring deposits; the specific mineralogy of these precipitates is critical to understanding the environmental conditions of deposition. Climatically induced changes in groundwater source and chemistry related to regional shifts in monsoonal rainfall can be reconstructed using these spring deposits. Similarly, In the United Arab Emirates (Dubai), Smith has been examining the evidence for aridification since ~5 ka, and investigating the nature of water resources available to Bronze Age occupants of the region. Evaporites are a significant component of the Holocene sedimentary record in this region, and may form either from surface or shallow subsurface water. Characterizing these evaporites through XRD would provide important constraints on groundwater and surface water chemistry and the evolution thereof. In Sudan, Smith is generating a record of Holocene landscapes along the Nile River; this work would both document recent fluctuations in Nile behavior and establish the environmental conditions associated with major changes in the subsistence strategies of prehistoric occupants of the region. Smith intends to use XRD to examine the clay mineralogy of Nile overbank deposits as a key indicator of change in both Nile behavior and in local pedogenesis. Finally, Smith also has a done pilot work for a project in Iraq which would similarly examine the clay mineralogy of Holocene Tigris-Euphrates alluvium as one part of a multi-proxy study aimed at understanding shifting environments in southern Iraq as a context for and possible influence on early urbanism.

6. PROPOSED USES IN EDUCATIONAL AND OUTREACH ACTIVITIES

The current XRD system is used in many educational and outreach activities. A new system will ensure that these activities are maintained and that additional activities can be implemented.

6.1. Direct Educational Uses

The proposed XRD instrument will be used for student research and in undergraduate and graduate courses. In the past three years the current system has been used by 4 postdoctoral scholars, 12 graduate students, and 11 undergraduate students in the Department of Earth and Planetary Sciences and the associated Pathfinder Program in Environmental Sustainability at Washington University. The XRD is the most widely used instrument by undergraduates in the department because of its relatively simple mode of operation and the widespread need for the identification of crystalline phases in geologic materials. Data from the instrument has contributed to graduate and undergraduate theses in both the Department of Earth and Planetary Sciences and the Environmental Studies Program. This instrument has also been used by graduate students from the Department of Earth and Atmospheric Sciences at Saint Louis University, which lacks a powder XRD system. The proposed instrument will continue to be used in the research and training of undergraduate and graduate students and postdoctoral scholars in the St. Louis area. Student usage is expected to increase as faculty members have been reluctant to have their students use the current instrument because of its unreliability. The improved capabilities and ease of use of the new instrument and the expansion of the Department of Earth and Planetary Sciences' undergraduate program with the new Environmental Earth Sciences major may also increase undergraduate student usage.

The PI will provide two additional educational contributions related to student use of the instrument. First, the PI will provide a short course on powder XRD methods, including quantitative

phase analysis via Rietveld methods. This will occur every one to two years, depending on student demand, in fall semester so that undergraduates can employ XRD methods in their senior honors research. Second, the PI will be developing a program to assess the outcomes and educational benefits of undergraduate research in the Department of Earth and Planetary Sciences at Washington University as part of his recently-awarded CAREER grant. Research has become an integral component of undergraduate education in STEM fields, including Earth Science, and is the most common method through which inquiry-based learning activities are implemented at the college level [87]. Unlike courses, the educational outcomes and benefits of research activities are rarely assessed. The program that the PI will develop includes student self-assessments using the Undergraduate Research Student Self-Assessment (URSSA) tool developed at the University of Colorado through support from the NSF. This tool can be customized to a specific department's needs; at Washington University, URSSA will be specifically customized to assess the educational benefits of the use of advanced instrumentation, including powder XRD, in undergraduate research. The results of this activity and the specific recommendations it generates will be reported in the Journal of Geoscience Education.

The proposed XRD system will also be used in undergraduate and graduate courses. XRD is introduced to undergraduate majors in the required course EPSc 352 Earth Materials taught by Prof. Pasteris. Students in this course will learn about XRD through demonstrations using the new instrument. XRD is further explored at the graduate level in EPSc 511 Minerals in Aqueous Environments, taught by the PI. The new XRD will be used in the teaching of various aspects of mineralogy and crystallography, including crystal structure refinements, clay mineralogy, phyllosilicate polytypes, turbostratic materials, and Vegard's law.

6.2. Outreach Activities

The proposed XRD system will also be used in departmental outreach activities. During Women in Science Day every November, female students from St. Louis City Public High Schools visit Washington University for hands-on activities and to learn about careers in science. Multiple demonstrations are provided in the Department of Earth and Planetary Sciences; the new XRD may be included in the "Minerals and Crystal Growth" demonstration. The other major outreach activity involves summer high school student research internships coordinated with the St. Louis-based Students and Teachers as Research Scientists (STARS) program, which places local high school students in laboratories at local research universities and institutions. The PI has hosted one STARS student each of the last three years; each has been trained on the current XRD system and used this instrument in his or her summer research project. The PI will continue to host 1-2 STARS high school students each summer (as committed in his CAREER grant) and each will use the proposed XRD system in her or his research.

7. ADDITIONAL BROADER IMPACTS

As documented above, the proposed XRD instrument acquisition will sustain key educational activities, including inquiry-based learning through undergraduate research. It will be used in activities to encourage high school students, including female students from the urban St. Louis City school district, to pursue careers in STEM fields. The acquisition will enhance the research infrastructure in the St. Louis metropolitan area, providing a replacement XRD instrument with expanded capabilities for use by Earth scientists at both Washington and Saint Louis Universities. The instrument will also serve as a user facility for many science and engineering researchers at Washington University that make up the extensive existing user base of the current instrument. Data collected on this instrument will result in numerous publications in Earth Science journals. Eight such articles have been published in 2011 using data collected on the current instrument, and the PI's group has one additional paper in review and one in preparation. This publication rate should increase with the new instrument's substantially improved data quality and ease of use. Finally, many of the studies that will be conducted using the proposed XRD system have societal benefits as they improve our understanding of the processes controlling contaminant fate in aquatic systems and the geochemical reactions involved in carbon sequestration.

8. RESULTS FROM PRIOR NSF SUPPORT

ETBC: Hidden iron oxide redox processes during biogeochemical iron cycling: Controls on nanoscale transformations and the fate of contaminants (EAR-0818354, \$340,505, 8/15/08 – 7/31/12).

This single-PI project explores nanoscale surface transformations of the iron(III) oxides hematite and goethite activated by aqueous Fe(II) and how these transformation affect nutrient availability and contaminant fate. The grant is currently on a 1-year no cost extension as some residual funds remained because of the unexpected departure of a graduate student for personal reasons part way through the project. These residual funds are supporting graduate student Andrew Friedrich until his graduation in May 2012. Major findings of this project include:

Fe(II)-Induced Hematite Surface Transformations

Structural transformations of three different surfaces of hematite reacted Fe(II) at both pH 3 and 7 were characterized using surface X-ray scattering. Aqueous Fe(II) induces surface transformations on the scale of a few monolayers in size (<1 nm in scale) that vary with crystallographic orientation yet appear to be independent of pH. These structural studies have been complemented with resonant anomalous X-ray reflectivity (RAXR) measurements of the Fe(II)-reacted hematite surfaces. This method is capable of observing Fe(II) on Fe(III)-oxide surface because of crystallographic effects that make most of the Fe(III) invisible. However, no Fe(II) was observed on any surface, indicating that the electron liberated from oxidative adsorption of Fe(II) does not transfer to a different surface site but rather is injected into the bulk structure. This had not been clear from previous studies using isotope tracers as the electron location could not be probed directly. This work resulted in one publication:

- Catalano J.G., Fenter P., Park C., Zhang Z., Rosso K.M. (2010) Structure and oxidation state of hematite surfaces reacted with aqueous Fe(II) at acidic and neutral pH. *Geochimica et Cosmochimica Acta* **74**, 1498-1512.

Interfacial Water Ordering on Iron Oxide Surfaces

The structure of interfacial water affects the rates and mechanisms of reaction at mineral surfaces, including electron transfer from aqueous Fe(II) and bacterial cytochromes [88-91]. The arrangement and dynamics of interfacial water is expected to vary with the crystallographic orientation of the surface. This in turn could affect the rate and mechanisms of Fe(II) adsorption and thus potentially play a role in the orientation-dependence of Fe(II)-induced structural transformations. Prior to this NSF project the water structure on only the hematite (012) surface had been characterized in situ [92]. These measurements have been extended to the (110) and (001) surfaces; the corundum (001) surface was also studied for comparison. As for Fe(II)-induced transformations, the (110) and (012) surfaces display similar water ordering while the structure of water near the (001) surface differs. Whether water structure and surface transformation have a causal relationship or are both simply the result of fundamental variations in the properties of hematite surfaces is under investigation. This work has resulted in two publications:

- Catalano J.G., Fenter P.A., Park C. (2009) Water ordering and relaxations at the hematite (110)-water interface. *Geochimica et Cosmochimica Acta* **73**, 2242-2251.
- Catalano J.G. (2011) Weak interfacial water ordering on isostructural hematite and corundum (001) surfaces. *Geochimica et Cosmochimica Acta* **75**, 2062-2071.

Fe(II)-Promoted Cation Incorporation into and Release from Iron Oxide Surfaces

Fe(II)-induced transformations of iron oxide surfaces through atom exchange and electron transfer reactions may affect the speciation of sorbing contaminant species. Adsorbed elements structurally compatible with iron oxide structures, such as Ni [93], could potentially be incorporated, providing a long-term sink for contaminants but also reducing the bioavailability of micronutrients. EXAFS spectra demonstrate that sorbed Ni(II) speciation is substantially altered by Fe(II)-induced mineral recrystallization, with 30 to 50% of the sorbed Ni being incorporated into hematite and goethite. Fe(II)-catalyzed recrystallization also leads to the release of Ni back into aqueous solution in similar

systems containing Ni pre-incorporated in goethite and hematite. This previously unknown trace element cycling may substantially alter the fate of trace elements in both modern and ancient geological systems.

Further studies have demonstrated that: (1) this cycling extends to Zn; (2) Fe(II)-catalyzed metal release from iron oxides occurs on the same timescale as isotope equilibration; (3) product inhibition occurs, indicating that the system equilibrates rather than being passivated (in the absence of other dopants); (4) there is a defined and systematic dependence of metal release on Fe(II) and surface site concentrations; (5) metal release increases with increasing pH and is exceeded by the background rate of proton-promoted mineral recrystallization at pH 4; (6) Cu release is coupled to Cu reduction by Fe(II), producing CuO and Cu particles; (7) Mn(III) and Co(III) release is coupled to their reduction. This work resulted in one publication, one manuscript in review, and one manuscript in preparation:

- Frierdich A.J., Luo Y., Catalano J.G. (2011) Trace element cycling through iron oxide minerals during redox-driven dynamic recrystallization. *Geology* **39**, 1083-1086.
- Frierdich A.J., Catalano J.G. (2011) Controls on Fe(II)-activated trace element release from goethite and hematite. *Environmental Science & Technology*, submitted.
- Frierdich A.J., Catalano J.G. (2011) Redox processes involved in Fe(II)-catalyzed Cu, Mn, and Co release from iron oxides. In preparation for *Geochimica et Cosmochimica Acta*.

Effect of Fe(II) on Arsenate Adsorption

In contrast to metals like Ni, oxoanions are generally structurally incompatible with iron oxides. There is some evidence of P and Si incorporation into hematite through forced coprecipitation [94,95], but such incorporation appears to be uncommon in nature [1]. We investigated the effect of Fe(II) on arsenate adsorption and found little observable difference in the macroscopic uptake behavior of As(V) onto both hematite and goethite over a range of pH conditions (4 to 7). As K-edge EXAFS spectroscopy showed that, in contrast to the Ni studies, no change in the coordination environment of adsorbed As(V) occurs when Fe(II) was added to the system at pH 4 or 7, even at Fe(II) concentrations as high as 1 mM. This suggests that either As(V) inhibits Fe(II)-induced surface transformations or that As(V) adsorption is not effected by such a process. As(V) was found to reduce Fe(II) sorption through competitive effects at low Fe(II) concentrations. This work has resulted in one publication:

- Catalano J.G., Luo Y., Otemuyiwa B.T. (2011) Effect of aqueous Fe(II) on arsenate sorption on goethite and hematite. *Environmental Science & Technology*, doi: 10.1021/es202445w.

Characterization of Natural Biogenic Iron and Manganese Oxides

Active Fe and Mn biomineralization in a shallow karst cave environment was examined to investigate redox-driven mineral transformations and their effect on trace element fate. Unfortunately, the Fe oxide deposits were rare and transient and not suitable for extensive comparative studies, but widespread areas of active Mn oxide deposition provided an opportunity to explore similar processes for the Mn system. We have found a substantial variation in Mn oxide mineral structure at different sites in the cave. Specifically, while all samples appeared to have a layer structure intermediate between δ -MnO₂ and hexagonal birnessite, those from groundwater seeps, which contain elevated sustained Mn(II) concentrations, have a more birnessite-like character. δ -MnO₂-like materials occur in the cave stream, where aqueous Mn(II) concentrations are lower, but contain trace elements (Co, Ni, Zn, Ba) at concentrations 10 to 500 times greater than at the groundwater seeps. There is a clear inverse relationship between solid phase trace element concentration and both aqueous Mn(II) concentration and Mn oxide structure. These structural variations with local Mn(II) concentrations agree with past studies of biogenic Mn oxides [13,25]. Variation in Mn(II) concentrations among the sampling sites may thus be the primary control on the ability of these phases to take up trace elements from the groundwater seeps and cave streams. This work resulted in one publication and one manuscript in preparation:

- Frierdich A.J., Hasenmueller E.A., Catalano J.G. (2011) Composition and structure of nanocrystalline Fe and Mn oxide cave deposits: Implications for trace element mobility in karst systems. *Chemical Geology* **284**, 82-96.

- Frierdich A.J., Catalano J.G. (2011) Distribution and speciation of trace elements in iron and manganese oxide cave deposits. In preparation for *Geochimica et Cosmochimica Acta*.

Education and Public Outreach

This project has supported the training of three graduate students (two currently; one left the Ph.D. program for personal reasons), six undergraduate students (including four female students interested in pursuing careers in science and engineering and one Iraq War veteran), and a postdoctoral researcher. This project also facilitated 6-week summer internships for three local high school students. Two graduate students and the postdoctoral researcher gained experience serving as research mentors for undergraduate and high school students. This proposal has also supported the training of three graduate students in synchrotron-based analytical methods.

The PI has also conducted three outreach activities associated with this proposal. A presentation was given at the Synchrotron Environmental Sciences IV meeting in December 2008 on applications of resonant X-ray scattering in molecular environmental sciences. This meeting was heavily attended by geosciences graduate students, and the goal of the talk was to reach out to this group to make them aware of new techniques they could use in biogeochemical research to probe interfacial redox reactions. A similar talk was given by the PI at the 2010 Advanced Photon Source Users Meeting to a group of actinide scientists. The PI also served on a panel discussion on nuclear energy in October 2008 that was organized by undergraduate students at Washington University and attended by both students and members of the general public. The PI discussed how natural and stimulated biogeochemical processes can affect the migration of nuclear waste in the environment.

CAREER: Nanoscale Mineral Transformations during Biogeochemical Cycling and the Fate of Trace Elements and Nutrients (EAR-1056480, \$460,000, 3/15/2011 – 2/29/2016)

This grant was designed to scientifically follow-up on EAR-0818354 with a substantial education component and more expansive studies of minerals transformation during biogeochemical cycling, including the effects of organic ligands and insoluble dopants and the processes that occur in manganese systems. The PI learned in December 2010 that this grant would be awarded; the proposed start date was 8/1/2011 and no notice was given at that time that this would change. In mid-March 2011 the grant was unexpectedly awarded with an immediate start date. While obviously grateful for the award, the PI had been planning for an August 1 start date and did not have student projects or educational activities specific to this grant scheduled for spring and summer 2011. Work on this grant as of the submission date (late September 2011) has thus been limited to preliminary experiments in three areas. The first investigated the effects of organic ligands on hematite surface transformations. Oxalate was found to cause only minor dissolution; a similar effect was seen on an isostructural corundum surface in control experiments, suggesting that, as expected, the mechanism does not involve electron transfer. In the presence of Fe(II) and oxalate, the hematite surface demonstrated rapid and substantial restructuring, far in excess of what is caused by Fe(II) in the absence of organic ligands. The second study investigated the effect of Mn(II) on phyllosulfate structure. EXAFS spectroscopy shows that Mn(II) adsorption alters the sheet structure of hexagonal birnessite. Sodium exchange and saturation after reaction indicates that the change in EXAFS spectra caused by reaction with Mn(II) is not simply due to Mn(II) cation exchange into the interlayer, suggesting that the sheet structure changes in an irreversible manner. The third project involves the effect of insoluble substituting elements on metal release during iron oxide recrystallization, described in Section 5.1. The PI is currently developing plans for implementing assessments of the impact of undergraduate research on student learning in his department and similar assessments for a local program that places high school students in summer research internships at universities and research centers. In addition, the PI will begin developing a new undergraduate course for non-majors on the topic of Geology and Human Health in the winter and spring of 2012.

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Publications:

Five Related Publications:

- Catalano J.G.**, Luo Y., Otemuyiwa B.T. (2011) Effect of aqueous Fe(II) on arsenate sorption on goethite and hematite. *Environmental Science & Technology*, doi: 10.1021/es202445w
- Friedrich A.J., Luo Y., **Catalano J.G.** (2011) Trace element cycling through iron oxide minerals during redox-driven dynamic recrystallization. *Geology* **39**, 1083-1086.
- Friedrich A.J., **Catalano J.G.** (2011) Composition and structure of nanocrystalline Fe and Mn oxide cave deposits: Implications for trace element mobility in karst systems. *Chemical Geology* **284**, 82-96.
- Luo Y., Giammar D.E., Huhmann B.L., **Catalano J.G.** (2011) Speciation of selenium, arsenic, and zinc in Class C fly ash. *Energy & Fuels* **25**, 2980-2987.
- Catalano J.G.**, Fenter P., Park C., Zhang Z., Rosso K.M. (2010) Structure and oxidation state of hematite surfaces reacted with aqueous Fe(II) at acidic and neutral pH. *Geochimica et Cosmochimica Acta* **74**, 1498-1512.

Five Other Significant Publications:

- Catalano J.G.** (2011) Weak interfacial water ordering on isostructural hematite and corundum (001) surfaces. *Geochimica et Cosmochimica Acta* **75**, 2062-2071.
- Catalano J.G.**, Fenter P.A., Park C. (2009) Water ordering and relaxations at the hematite (110)-water interface. *Geochimica et Cosmochimica Acta* **73**, 2242-2251.
- Catalano J.G.**, Park C., Fenter P., Zhang Z. (2008) Simultaneous inner- and outer-sphere arsenate adsorption on corundum and hematite. *Geochimica et Cosmochimica Acta* **72**, 1986-2004.
- Catalano J.G.**, McKinley J.P., Zachara J.M., Heald S.M., Smith S.C., Brown G.E., Jr. (2006) Changes in uranium speciation through a depth sequence of contaminated Hanford sediments. *Environmental Science & Technology* **40**, 2517-2524.

Catalano J.G., Brown G.E., Jr. (2004) Analysis of uranyl-bearing phases by EXAFS spectroscopy: Interferences, multiple scattering, accuracy of structural parameters, and spectral differences. *American Mineralogist* **89**, 1004-1021.

Synergistic Activities:

1. **Mentor**, Students and Teachers As Research Scientists (STARS) program (2009-Present)
2. **Reviewer**, National Science Foundation, EAR-Geobiology and Low-Temperature Geochemistry (2008-Present) and EAR-Instrumentation and Facilities (2009-Present)
3. **Panelist** (2009-2010) and **Chair** (2011), Chemical, Biological, and Environmental Scattering Proposal Review Panel, Advanced Photon Source
4. **Panelist**, Green Action's 7th Hour Panel Discussion, "Facts and Fission... nuclear power and the 2008 election", Washington University, October 30, 2008
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FACILITIES, EQUIPMENT, AND OTHER RESOURCES

The Department of Earth and Planetary Sciences occupies the 155,000 square foot Earth and Planetary Sciences Building at Washington University, opened in 2004. The building contains laboratory, office, and classroom space. The laboratories of the PI and all auxiliary users are located in this building and each are equipped to meet the research needs of the individual faculty members. A laboratory space already exists for the proposed instrument; this has all of the necessary electrical, network, and water connections needed for the instrument, and has a connected sample preparation laboratory. Additional major equipment available in the department for complementary studies includes:

- Agilent Technologies model 5500 Atomic Force Microscope (AFM)
- JEOL JXA-8200 electron microprobe
- Siemens SRS-200 and SRS-300 sequential X-ray fluorescence spectrometers
- HoloLab 5000-532 and 5000-633 Raman microprobes
- Nicolet Nexus 670 FTIR spectrometer
- Thermo Delta V Plus isotope ratio mass spectrometer
- Thermo MAT 252 stable isotope mass spectrometer
- Thermo Neptune multicollector inductively-coupled plasma mass spectrometer

In the basement of the Earth and Planetary Sciences Building are facilities operated by the Nano Research Facility, a National Nanoscience Infrastructure Network site, and the Center for Materials Innovation. Major equipment available for use includes:

- JEOL 2100F scanning field emission transmission electron microscope [(S)TEM] equipped with an electron-energy-loss spectrometer, a high resolution CCD camera, and an array of BF, DF, and HAADF detectors
- JEOL JSM-7001FLV field-emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray spectrometer and a electron backscattered diffraction detector
- FEI Nova 2300 scanning electron microscope
- FEI Sprit transmission electron microscope
- Malvern Zetasizer ZS for dynamic light scattering (DLS) and zeta potential measurements
- Perkin Elmer Elan DRC II inductively-couple plasma mass spectrometer
- Perkin Elmer Optima 7300DV inductively-couple plasma optical emission spectrometer

Data Management Plan

The proposed instrument will generate electronic data in the form of scattered intensity versus the scattering angle, 2θ . The datafiles will contain a header with additional information regarding the experimental configuration. The datafiles will be in a standard format from the instrument manufacturer Bruker. This format is widely used and freeware is available to convert it to other commonly used XRD data formats. Some files will also be generated from the analysis of the data using the included analysis software. As this is an instrument acquisition, all data generated will belong to the organizations funding the scientific projects that use the instrument. This proposal will itself not result in any data collection beyond running standards for alignment and calibration. It is assumed that the scientists collecting data on the instrument would conform to the data sharing policies of the funding organization. No specific provisions have been made for the distribution of the data collected on this instrument, although the laboratory manager will provide the calibration files upon email request if someone were to request such data.

All data collected on the proposed instrument will be backed up electronically on a nightly basis and archived. It is intended to permanently store all data as the size of the data files are not prohibitively large. Only instrument users will have access to the data. It will not be accessible over the internet for security reasons.