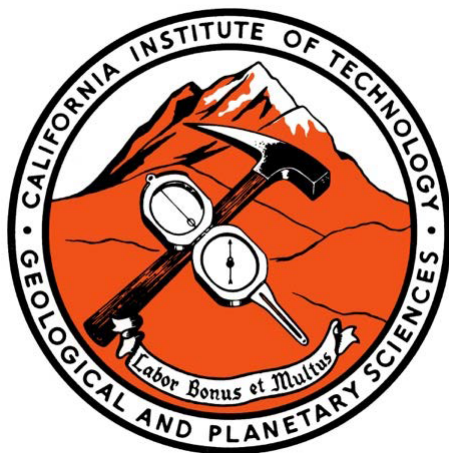


X-RAY ABSORPTION SPECTROSCOPY OF URANIUM IN ZIRCON AND THE REDOX EVOLUTION OF THE CONTINENTAL CRUST

Thesis by
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In Partial Fulfillment of the Requirements for
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ABSTRACT

Zircon is one of the most important minerals for reconstructing Earth history as it can preserve its primary chemical and isotopic composition through weathering, metamorphism, and crustal recycling. While zircon U-Pb geochronology, trace-element analysis, and isotope geochemistry have transformed our understanding of crustal evolution, the ability to recover magmatic redox conditions directly from zircon remains limited. Oxygen fugacity (fO_2) is a thermodynamic parameter used to quantify magma redox, and imparts first-order controls on melt chemistry, mineral stability, volatile speciation, and the long-term coevolution of Earth's interior and surface environments. This thesis develops and applies a zircon-based oxybarometer using uranium X-ray absorption near-edge structure (U XANES) spectroscopy to measure U oxidation states in zircon as a proxy for magmatic fO_2 .

The first part of this work establishes the analytical and experimental foundation for U XANES zircon oxybarometry. Measurements of well-characterized zircon demonstrate that U M₄-edge XANES provides a sensitive and reproducible measure of average U valence and shows that zircon can incorporate uranium across its full range of oxidation states, from entirely U^{IV} to pure U^{VI}. An empirical calibration is then developed using the U M₄-edge spectra of samples with independently constrained fO_2 , allowing zircon U valence to be used as a quantitative proxy for magma redox.

The second part of the thesis applies this new oxybarometer to questions in early Earth geology and long-term crustal evolution. U XANES analyses of Jack Hills zircon provide improved constraints on Hadean and Archean magma redox states and indicate relatively oxidized magmatic conditions on the early Earth. Additionally, metamorphic Jack Hills zircon domains reveal low-temperature, high-pressure metamorphism at 3.35 Ga, consistent with an early onset of mobile-lid tectonics. The final chapter applies the U XANES oxybarometer to zircon grains spanning Earth history, from ~4200 to 55 Ma, producing a robust archive of continental redox evolution through time. This record reveals that major changes in magma redox coincide with transitions in tectonomagmatic processes, mantle dynamics, and the nature of the continental crust. Together, these results expand the breadth of information that can be extracted from zircon to include magmatic oxygen fugacity and provides a new framework for linking mineral-scale redox information to the evolution of Earth's lithosphere, atmosphere, and habitability.

PUBLISHED CONTENT AND CONTRIBUTIONS

Chapter II

Houchin S. K., Tissot F. L. H., Ibañez-Mejia M., Newville M., Lanzirotti A., Pavia F. and Rossman G. (2024) Uranium oxidation states in zircon and other accessory phases. *Geochimica et Cosmochimica Acta* 381, 156–176. <https://doi.org/10.1016/j.gca.2024.07.032>

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Chapter IV

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TABLE OF CONTENTS

Acknowledgments	iii
Abstract	v
Published Content and Contributions.....	vi
Table of Contents.....	vii
List of Illustrations and Tables	ix
Nomenclature.....	xi
Chapter I: Introduction	1
1. Zircon: The Crystal Chronicle of the Continental Crust.....	2
2. Oxygen Fugacity	3
3. Current Constraints on Oxygen Fugacity Through Time	4
4. Uranium, XANES, and Zircon as an Oxybarometer	5
5. Thesis Summary	7
6. Outlook and Future Directions	9
7. Conclusion	10
References	11
Chapter II: Uranium oxidation states in zircon and other accessory phases.....	16
Abstract	17
1. Introduction.....	18
2. Samples and Methods	20
3. Results	27
4. Discussion	34
5. Concluding Remarks	44
References	46
Figures.....	54
Tables	75
Ch. 2 Appendix 1	81
Chapter III: Comparison of uranium M₄, M₅, and L₃ X-ray absorption edges for zircon XANES analysis	104
Abstract	105
1. Introduction.....	106
2. Samples and Methods	107
3. Results	110
4. Discussion	112
5. Conclusions.....	116
References	117
Figures.....	120
Tables	126
Chapter IV: Oxidized Hadean magmas and Archean mobile-lid tectonics revealed by Jack Hills zircon.....	127
Abstract	128
1. Introduction.....	129
2. Samples	130

3. Results.....	131
4. Discussion.....	133
5. Methods.....	141
References.....	145
Figures.....	153
Tables.....	158
Ch. 4. Appendix 1.....	159
Ch. 4. Appendix 2.....	170
 Chapter V: Redox evolution of crustal magmas from uranium M₄-edge XANES analysis of zircon	
Abstract.....	175
1. Introduction.....	176
2. Samples and Methods.....	177
3. Results.....	179
4. Discussion.....	182
5. Conclusions.....	183
References.....	194
Figures.....	195
Tables.....	202
	210

LIST OF ILLUSTRATIONS AND TABLES

Chapter I

Figure 1: Zircon crystal from the Jack Hills, Australia	1
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Chapter II

Figure 1: Example of imaging methods	54
Figure 2: Examples of normalized U M ₄ -edge spectra	55
Figure 3: Example of U L ₃ -edge normalization and EXAFS data processing	56
Figure 4: Assessment of U M ₄ -edge analytical uncertainties	57
Figure 5: Assessment of beam damage	58
Figure 6: Normalized U M ₄ -edge spectra for all zircon grains	59
Figure 7: Normalized U M ₄ -edge spectra for tn, bd, ap, and grt	60
Figure 8: U M ₄ -edge white-line energy of all samples	61
Figure 9: Variation in U M ₄ -edge FWHM with white-line energy for zircon samples	62
Figure 10: Example spectra for dominantly U ^{IV} , U ^V , and U ^{VI} samples	63
Figure 11: U M ₄ -edge PCA analysis	64
Figure 12: Variation in average U ⁿ⁺ with E _{wl} for individual zircon samples	65
Figure 13: k^2 -weighted EXAFS $\chi(k)$ for individual zircon grains	66
Figure 14: U-X interatomic distances determined from EXAFS analysis	67
Figure 15: Impact of crystallographic orientation on U M ₄ -edge spectra	68
Figure 16: α -dose versus average U valence	69
Figure 17: Uranium partitioning between zircons and host rock for HLMC samples	70
Figure 18: Calibration of U XANES oxybarometer	71
Figure 19: Intragrain variations in U M ₄ -edge spectra of FCT zircon	72
Figure 20: Core to rim variations in U M ₄ -edge E _{wl} for FC-1 and FCT zircon	73
Figure 21: Average U M ₄ -edge spectra for FCT accessory phases	74
Table 1: List of samples	75
Table 2: Comparison of published and measured U M ₄ -edge E _{wl} values	76
Table 3: Average E _{wl} and U ⁿ⁺ for all zircon samples	77
Table 4: Reference Zr-X and measured U-X bond lengths from EXAFS analysis	78
Table 5: Data for f_{O_2} – U M ₄ E _{wl} calibration	79
Table 6: Calculated f_{O_2} values for zircon samples	80
<i>Ch. II Appendix 1</i>	
Figure S1: Zircon cathodoluminescence images and μ XRF maps	81
Figure S2: Variations in U ⁿ⁺ /ΣU with U M ₄ -edge E _{wl} for zircon samples	102
Table S1: PCA results for zircon U M ₄ -edge spectra	103

Chapter III

Figure 1: Generalized schematic of the beamline experimental set up	120
Figure 2: Comparison of U XANES edges for dominantly U^{IV} , U^V , and U^{VI} samples	121
Figure 3: Comparison of fitting procedures for U XANES edges	122
Figure 4: Comparison of ΔE , precision, and attenuation depth for U XANES edges	123
Figure 5: Comparison of $E_{wt}-fO_2$ calibration for U XANES edges.....	124
Figure 6: Comparison of zircon L_3 - and M_4 -edge spectra for different lithologies	125
Table 1: List of samples.....	126

Chapter IV

Figure 1: Overview of crystal zoning, U XANES spectra, age, and redox.....	153
Figure 2: Chondrite normalized REE patterns of Jack Hills zircon rims and cores.....	154
Figure 3: Comparison of zircon oxybarometers	155
Figure 4: P-T proxies and estimates for metamorphic zircon rims	156
Figure 5: T/P conditions and tectonic interpretations for metamorphic zircon rims	157
Table 1: Age, fO_2 , Eu/Eu*, P-T and T/P estimates for metamorphic zircon rims	158

Ch. IV Appendix 1

Figure S1: SEM images of Jack Hills zircon grains	160
Figure S2: REE patterns for cores and rims of individual grains.....	161
Figure S3: Relationship between pressure and zircon Eu/Eu*	165
Figure S4: Differences in metamorphic T/P based on method of pressure estimation.....	166
Figure S5: Results of k-means clustering analysis for metamorphic zircon rims.....	167

Ch. IV Appendix 2

μ XRF maps of Jack Hills zircon grains	170
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Chapter V

Figure 1: Global map of zircon sample locations and bedrock age.....	202
Figure 2: Representative U M_4 -edge spectra for dominantly U^{IV} and U^{VI} zircon.....	203
Figure 3: Zircon fO_2 through time	204
Figure 4: Records of surface, crustal, and mantle oxidation	205
Figure 5: Results of onset detection algorithms for age- fO_2 data	206
Figure 6: Box and whisker plots for igneous zircon samples (I-A-S-type).....	207
Figure 7: Secular evolution of key parameters relating to lithospheric redox	208
Figure 8: Oxygen isotopes ($\delta^{18}O_{VSMOW}$) versus fO_2 (ΔFMQ) for zircon samples	209
Table 1: Sample information, ΔFMQ , and age of igneous zircon samples.....	210

NOMENCLATURE

Zircon. Zircon (ZrSiO_4) is a common accessory mineral known for its durability and ability to preserve chemical and isotopic information over long geologic timescales.

Uranium. Uranium is a heavy, radioactive element (atomic number 92). It occurs in trace amounts in rocks and minerals where it behaves as an incompatible element.

Incompatible. An incompatible element or molecule is one that preferentially enters into melts rather than solids during processes such as partial melting and crystallization, leading to its enrichment in evolved melts/ rocks.

Redox. Redox refers to the oxidation–reduction state of a system, which describes the transfer of electrons between chemical species. Oxidized species have lost electrons (which are negatively charged), while reduced species have gained electrons (thereby *reducing* their electric charge).

Valence state. Valence state is the effective charge of an element, determined by the number of electrons it has lost or gained.

Oxygen fugacity ($f\text{O}_2$). Oxygen fugacity is a thermodynamic parameter that describes the chemical potential of oxygen in a system and is used to quantify its redox state.

Oxybarometer. Oxy – related to oxygen; barometer – a tool for measuring pressure. Hence, an oxybarometer is a tool used to measure the effective partial pressure (i.e., fugacity) of oxygen.

XANES. X-ray absorption near-edge structure (XANES) is a spectroscopic technique that measures how X-rays are absorbed by a material as a function of energy, providing information about the oxidation state and local electronic structure of specific elements.

Mafic. Mafic rocks are rich in iron (Fe) and magnesium (Mg), they are typically dark-colored and dense (e.g., basalt).

Felsic. Felsic rocks are rich in silica (SiO_2) and feldspar minerals, they are typically light-colored and less dense than mafic rocks (e.g., granite).

Crust. The crust is Earth's outermost solid layer, composed of mafic oceanic and felsic continental components. It represents the interface between the deep Earth and surface and is the primary site of magma differentiation and long-term geochemical evolution.

Mantle. The mantle is the thick layer of silicate rock between the crust and core and makes up the majority of Earth's volume. Mantle processes drive long-term heat transfer and material circulation through convection, influencing magmatism and tectonic processes.

Tectonics. Tectonics refers to the processes that govern the structure and movement of Earth's lithosphere, including plate motion, deformation, crustal growth and recycling, and the formation of geologic features such as mountains and basins.

Chapter I

INTRODUCTION



Figure 1. Zircon crystal from the Jack Hills, Australia

1. ZIRCON, THE CRYSTAL CHRONICLE OF THE CONTINENTAL CRUST

Zircon is an ideal mineral for studying Earth's evolution. It is extraordinarily resistant to physical and chemical alteration and is able to retain its original composition through weathering, erosion, burial, and metamorphism (Hanchar, 2003). As a result, zircon can survive repeated passage through the rock cycle, including episodes of orogenesis, denudation, metamorphic overgrowth, and re-entrainment into new magmas (Hoskin and Schaltegger, 2003). Zircon can therefore preserve information otherwise lost from the rock record, allowing for complex geologic histories to be reconstructed through microanalytical investigation of distinct growth regions within single mineral grains.

This resilience, combined with zircon's distinctive geochemical behavior, makes it the foundation of one of the most robust geochronologic tools available: U-Pb dating (e.g., Tilton et al., 1955; Davis et al., 2003; Schoene, 2014). During crystallization, zircon readily incorporates radioactive uranium (U) into its crystal structure while strongly excluding its decay product, lead (Pb). This behavior permits the assumption that any lead present in the mineral is dominantly the product of radioactive decay, allowing crystallization ages to be calculated with high precision and accuracy. Because diffusion and alteration of U and Pb in zircon are limited under most geologic conditions (Cherniak and Watson, 2003), the U-Pb system is typically well preserved through subsequent geologic events.

Beyond its widespread use as a geochronometer, zircon incorporates trace elements and isotopes that reflect crystallization conditions, magma sources, and tectonic setting. For instance, Ti concentrations provide estimates of crystallization temperature (Ferry and Watson, 2007), while rare earth element systematics can constrain pressure conditions (Tang et al., 2021) and tectonomagmatic provenance (Grimes et al., 2015). Oxygen isotopes record interaction with surface reservoirs and the incorporation of altered crustal material (Valley, 2003), and Lu-Hf isotopes track the extent of crustal reworking versus juvenile mantle-derived inputs (Vervoort and Kemp, 2016). When integrated with U-Pb ages, these geochemical and isotopic proxies enable temporally resolved reconstructions of magmatic processes through time.

The same durability that makes zircon a robust geochemical archive also gives it extraordinary longevity. Indeed, the oldest known terrestrial materials are detrital zircon crystals from ancient sandstones (Froude et al., 1983; Harrison et al., 2017; Byerly et al., 2018), which can be up to 4.38 billion years old (Valley et al., 2014). These primeval crystals extend the chronicle of Earth's history beyond the age of the oldest known rock,

preserving evidence from intervals where other geologic records have largely been destroyed. Because zircon samples have crystallized and survived from the Hadean to the present, the collective zircon record represents the most continuous single archive of planetary evolution. Developing new analytical techniques for interrogating this archive is therefore a constructive endeavor for unearthing the inner workings of our world.

2. OXYGEN FUGACITY

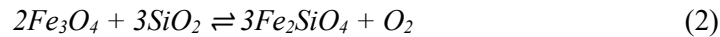
One parameter of magmas that has been hitherto elusive to constrain is oxygen fugacity (fO_2). This thermodynamic variable describes the chemical activity of oxygen and is used to quantify the redox state of geologic systems. By controlling the potential for multivalent elements (e.g., Fe, Ce, V, U) to occur in more oxidized or reduced states fO_2 influences the composition of crystallizing phases and residual liquids, the formation of critical mineral resources, the speciation of volcanic gases, and the long-term co-evolution of the lithosphere and atmosphere (e.g., [Moretti and Neuville, 2021](#)). A thorough overview of the concept of oxygen fugacity, its history, and its practical application to geologic systems is described in detail by [Frost \(1991\)](#) and summarized below.

Oxygen fugacity is related to the chemical potential of oxygen by the equation

$$\mu_{O_2} = \mu_{O_2}^{\circ} + RT \ln(f_{O_2}) \quad (1)$$

Where $\mu_{O_2}^{\circ}$ is the standard state chemical potential of oxygen, T is temperature, and R is the ideal gas constant. Equation (1) illustrates that higher fO_2 corresponds to more oxidizing conditions, whereas lower fO_2 corresponds to more reducing conditions.

Because absolute fO_2 varies with temperature and pressure, it is convenient to discuss the fO_2 of a system relative to mineral equilibria that ‘buffer’ the activity and fugacity of O_2 . One of the most widely used buffers in igneous petrology is the fayalite-magnetite-quartz (FMQ) buffer:



This reaction relates oxidation of ferrous iron (Fe^{II}) in fayalite to ferric iron (Fe^{III}) in magnetite and defines equilibrium fO_2 at given pressure and temperature through the equilibrium constant:

$$K_{eq} = \frac{(a_{Fe_2SiO_4})^3 f_{O_2}}{(a_{SiO_2})^3 (a_{Fe_3O_4})^2} \quad (3)$$

where $a_{\text{Fe}_3\text{O}_4}$, a_{SiO_2} , and $a_{\text{Fe}_2\text{SiO}_4}$ are the activities of magnetite, quartz, and fayalite, respectively. For the pure mineral assemblage fayalite + magnetite + quartz, these activities are commonly taken to be unity, so the equilibrium constant becomes:

$$K_{eq}^{FMQ} = f_{\text{O}_2} \quad (4)$$

So that:

$$\log(f_{\text{O}_2}^{FMQ}) = \frac{-\Delta G_{FMQ}^0}{2.303RT} \quad (5)$$

Where $-\Delta G_{FMQ}^0$ is the change in standard state Gibbs free energy for the fayalite-magnetite-quartz reaction, R is the gas constant, and T is temperature. Measured magma redox states can then be reported as the log unit deviation in f_{O_2} relative to this buffer:

$$\Delta FMQ = \log(f_{\text{O}_2}^{sample}) - \log(f_{\text{O}_2}^{FMQ}) \quad (6)$$

Reporting oxygen fugacity relative to FMQ is useful for two reasons. First, it removes much of the strong temperature and pressure dependence of absolute f_{O_2} , allowing redox states to be compared among magmas of different ages, compositions, and crystallization conditions. Second, because the redox state of the modern upper mantle is approximately $\Delta FMQ \sim 0 \pm 0.5$, the FMQ buffer provides a functional measure for evaluating whether a magma is relatively oxidized or reduced (Cottrell et al., 2025).

3. CURRENT CONSTRAINTS ON OXYGEN FUGACITY THROUGH TIME

Magma f_{O_2} has proven challenging to reconstruct through deep time as existing oxybarometers often require specific mineral assemblages (Ghiorso and Sack, 1991), independent constraints on temperature, pressure, or melt composition (Smythe and Brenan, 2016), and/or preservation of primary magmatic equilibria, all of which may be modified during cooling, alteration, or metamorphism (Cottrell et al., 2025). These limitations have contributed to persistent disagreement over the long-term redox evolution of the mantle. Some studies argue that the mantle has become more oxidized through time (Nicklas et al., 2019; Stagno and Aulbach, 2021; O'Neill and Aulbach, 2022; Zhu et al., 2026), whereas others infer that mantle redox states have remained fairly constant since the Hadean (Li & Lee, 2004; Zhang et al., 2024; Cottrell et al., 2025). Relative to the mantle, the long-term evolution of crustal redox has received comparatively less attention, though several studies provide evidence for a shift in continental magma redox states across the Archean–Proterozoic transition (Bucholz et al., 2018; Meng et al., 2022; Moreira et al., 2023). Given zircon's well-documented ability to preserve primary geochemical

information through time, the development of a reliable zircon-based oxybarometer would be a powerful tool for investigating crustal magma redox conditions across Earth history.

4. URANIUM, XANES, AND ZIRCON AS AN OXYBAROMETER

Several methods for recovering magma redox information from zircon have been proposed. These approaches, however, can be imprecise due to their reliance on Ce and other trace-element concentrations (Trail et al., 2012; Smythe and Brenan, 2016; Loucks et al., 2020), which can be affected by temperature, melt composition, and the presence of co-crystallizing phases. For example, increases in zircon Ce concentrations relative to neighboring REE can arise during cooling at constant fO_2 or through changes in the crystallizing mineral assemblage (Loader et al., 2022). Some trace-element oxybarometers also require difficult to constrain parameters such as melt composition, water activity, or melt polymerization state (Smythe and Brenan, 2016). These requirements are especially limiting for ancient or detrital zircon, where the original host-rock composition and petrologic context may be poorly constrained or entirely unknown. A robust zircon oxybarometer should therefore rely on direct measurement of element oxidation states, rather than concentration alone, while remaining resilient against alteration on geologic timescales.

Although uranium in zircon is typically associated with geochronology, it may also provide a direct means of interrogating magma fO_2 . Uranium is a redox-sensitive element that can occur in silicate melts as U^{IV} , U^V , or U^{VI} with the relative proportions of these species largely controlled by oxygen fugacity. Although U in zircon has commonly been assumed to be tetravalent (Cherniak et al., 1997), previous spectroscopic and experimental studies have shown that zircon can contain appreciable quantities of oxidized U (Vance and Mackey, 1974; Farges and Calas, 1991; Zhang et al., 2003; Burnham and Berry, 2012; Tanaka and Takahashi, 2019). This observation raises the possibility that U valence in zircon may record information about the redox state of the magma from which the crystal grew. Uranium is also promising as a redox tracer because its valence transitions occur over the range of fO_2 conditions relevant to crustal magmas ($\sim$ FMQ-2 to +3). In silicate melts, the $U^{IV} \rightleftharpoons U^V$ and $U^V \rightleftharpoons U^{VI}$ equilibria lie on either side of the Fe^{II} to Fe^{III} transition (Schreiber, 1987), implying that U speciation may be highly sensitive to changes in magma fO_2 . Oxidized U may also represent a substantial fraction of total U at oxygen fugacities typical of crustal magmas, potentially reaching up to $\sim$ 50% near the FMQ buffer (Halse, 2014). Lastly, U concentrations in zircon are known to be resistant to alteration, suggesting

that U oxidation states could be similarly preserved. Together, these characteristics make U-in-zircon an attractive target for developing a magma redox proxy.

X-ray absorption near-edge structure (XANES) spectroscopy is a synchrotron-based technique that probes the electronic structure of specific elements and allows for the direct measurement of element oxidation states (e.g., [Henderson et al., 2014](#)). A XANES-based zircon oxybarometer therefore has the potential to overcome some of the limitations inherent to existing zircon redox proxies. Namely, it does not require assumptions regarding the relationship between magma fO_2 , partitioning behavior, and element concentrations, nor does it necessarily require knowledge of host-rock composition. Because U is commonly present in sufficient abundance for spectroscopic analysis (hundreds to thousands of ppm), U XANES is widely applicable to most zircon-bearing rocks as well as detrital grains. The analytical characteristics of XANES are also well matched to zircon's value as a deep-time archive. Measurements can be made at small spot sizes (typically $<5\mu\text{m}$), allowing U speciation to be investigated within individual growth zones. The technique is also non-destructive, making it compatible with other *in situ* zircon analytical methods, including laser-ablation and secondary ion mass spectrometry for U-Pb geochronology, trace-element analysis, and oxygen and Lu-Hf isotope measurements.

XANES analysis of sulfur speciation in apatite has already demonstrated the potential of X-ray absorption spectroscopy for oxybarometry using igneous accessory phases ([Konecke et al., 2019](#); [Meng et al., 2022](#); [Moreira et al., 2023](#)). Notably, however, applications of this method have commonly focused on apatite inclusions in zircon, with the assumption that the zircon host would shield the apatite inclusions from alteration, as apatite is considerably more susceptible to diffusion and resetting relative to zircon ([Farley, 2000](#); [Cherniak and Watson, 2003](#)). While valuable information can be gleaned from this approach, the S-in-apatite XANES proxy is only precise over a narrow range of fO_2 , from $\sim\text{FMQ}$ to $\text{FMQ}+1.2$, with only first-order estimates of whether a sample is generally reduced or oxidized provided outside this range ([Konecke et al., 2019](#)). U XANES analysis of zircon offers an alternative approach that targets the resilient host mineral itself and may be applicable across a broader range of magmatic redox conditions.

In conclusion, establishing a quantitative relationship between uranium valence in zircon and magmatic fO_2 using XANES spectroscopy would enable determination of crystallization ages and redox conditions from the same element within the same mineral, providing a self-consistent approach for reconstructing magma oxidation states at the scale

of a single pluton or eruption, or across time, from the Hadean to the Holocene. This endeavor is the topic of this thesis.

5. THESIS SUMMARY

Chapter II presents the development and calibration of the U XANES zircon oxybarometer. The chapter begins by describing U XANES data acquisition and processing and establishes the analytical reproducibility and uncertainty associated with measurements of natural zircon samples. While some U L₃-edge data is presented, the chapter focuses on U M₄-edge because of its greater sensitivity for determining average U oxidation states. Each U M₄-edge spectrum is evaluated using the energy of peak absorbance or ‘white-line’ (E_{wl}) to determine average U valence. From the E_{wl} data, we assess the range of U valence states that can be incorporated into zircon and show that zircon can incorporate U of any valence state, from entirely U^{IV} to pure U^{VI}. Potential caveats that may impact U XANES results or complicate interpretation are then considered. These include the orientation between the sample relative to the incoming X-ray beam and detector; beam-induced crystal damage; and self-induced damage from the radioactive decay of U and Th. Each factor was found to have a negligible effect on measured U valence states. Building on these findings, an empirical calibration between U M₄-edge E_{wl} and independently constrained magma fO_2 is constructed and applied to a range of zircon samples to demonstrate the utility and broader applicability of the method. Together, Chapter II establishes U XANES analysis of zircon as a powerful new oxybarometer and outlines methodological approaches for future studies.

Chapter III expands the development of zircon U XANES oxybarometry by comparing the strengths, limitations, and analytical tradeoffs of the U M₄-, M₅-, and L₃-edges. In particular, it considers how edge choice affects sensitivity to U oxidation state, data processing methods, correlation of XANES results to textural features, and overall utility for oxybarometry. Based on these comparisons, it provides recommendations for selecting the most appropriate absorption edge depending on whether the goal is precise oxybarometry, or qualitative assessment of bulk U valence state, particularly the identification of U^V. Additionally, this chapter refines the methodological framework for U XANES zircon analysis and helps establish best practices for future applications of the oxybarometer.

Chapter IV applies the U XANES zircon oxybarometer to some of Earth’s oldest materials, the Jack Hills zircon. U XANES measurements are integrated with SIMS U-Pb

and trace-element analyses to investigate the igneous cores and metamorphic rims of these ancient crystals. This work provides improved constraints on early Earth magmatic redox conditions, narrowing previous estimates from FMQ -4 to +4 (Trail et al., 2011) to FMQ -1 to +1. It also presents the first detailed investigation of metamorphic zircon domains from the Jack Hills, providing some of the earliest constraints on metamorphic P-T conditions. In particular, the identification of low-temperature, high-pressure metamorphism in rims of Archean age indicates that deep underthrusting of crustal fragments was occurring no later than 3.35 Ga, providing evidence for horizontal plate motions and the operation of mobile-lid tectonics in the early Archean.

Chapter V applies the U XANES zircon oxybarometer to more than 750 individual zircon grains spanning nearly all of Earth history, from ~4200 to 55 Ma. By combining this large zircon dataset with the $f\text{O}_2$ calibration and analytical framework developed in the preceding chapters, the chapter presents a robust, long-term record of continental crust redox evolution. The results reveal that significant fluctuations in zircon U oxidation state broadly coincide with major changes in tectonomagmatic processes and atmospheric composition.

A central finding of Chapter V is a pronounced increase in zircon U oxidation states in the Neoproterozoic, between ~2.6-2.0 Ga. This shift occurs during a period of fundamental reorganization in the nature of the continental crust as secular mantle cooling promoted changes in melt generation (Keller and Schoene, 2018), crustal thickness (Palin et al., 2020), and subduction processes (Liu et al., 2020). At the same time, widespread cratonization and increasing continental emergence expanded the interface between the solid Earth and surface environments (Bindeman et al., 2018; Spencer et al., 2019; Reimink and Smye, 2024), enhancing the potential for oxidative weathering, sedimentary recycling, nutrient delivery, and changes in volcanic gas fluxes. Together, these processes coincided with a transition from dominantly TTG-like crustal production toward more diverse and modern-like magmatism (Laurent et al., 2014), suggesting that the rise in continental crust redox state was part of a broader transformation in Earth's tectonomagmatic system. Importantly, the Neoproterozoic increase in crustal redox state predates the major rise in atmospheric oxygen during the Great Oxidation Event at ~2.35 Ga (Farquhar et al., 2000; Partin et al., 2013; Lyons et al., 2014). This temporal relationship suggests that oxidation of the continental crust may have helped trigger atmospheric oxygenation.

Chapter V also evaluates mid-Proterozoic and Phanerozoic fluctuations in zircon U oxidation states and explores how changes in crustal thickness, supercontinent assembly

and breakup, mantle temperature, and subduction styles may have influenced the redox state of continental magmas through time.

6. OUTLOOK AND FUTURE DIRECTIONS

The development of zircon XANES analysis for studying magmatic redox conditions creates opportunities across a range of spatial and temporal scales beyond those explored in this thesis. The small X-ray beam diameter (1–5 μm) enables detailed analysis of intragrain regions, providing an opportunity to investigate redox variations within single zircon crystals. For instance, measurements from the core to rim of individual zircon grains could be used to reconstruct changes in U valence during progressive crystallization of a pluton, magma chamber, or eruptive system, resolving redox evolution over the lifetime of individual magmatic systems. More broadly, the method can be applied to suites of detrital zircon grains to explore regional variations in magma redox across crustal provinces. The non-destructive nature and small analytical volume of XANES also makes it highly compatible with other microanalytical methods such as LA-ICP-MS and SIMS, and particularly valuable for investigating precious extraterrestrial materials where sample availability is severely limited.

Zircon U XANES may also provide a useful tool for investigating the formation of economically important mineral resources. Porphyry copper and other critical metal deposits are commonly associated with oxidized magmas ([Sillitoe, 2010](#); [Sun et al., 2015](#); [Loader et al., 2017](#)), but the processes that generate these deposits remain incompletely understood. Zircon U XANES oxybarometry offers a direct mineral-based approach for evaluating the redox evolution of ore-forming magmas and may help identify the conditions most favorable for metal transport, concentration, and emplacement.

The broader potential of XANES-based mineral oxybarometry extends beyond U in zircon. Zircon XANES analyses could be expanded to other multivalent elements, such as Ce and Eu, providing complementary constraints on magma $f\text{O}_2$ and aiding interpretation of trace-element systematics ([Trail et al., 2015](#)). Preliminary U XANES analyses of apatite and baddeleyite also suggest that other U-bearing minerals can incorporate multivalent uranium (Chapter II), opening the possibility of developing related oxybarometers for rocks in which zircon is absent.

7. CONCLUSION

This thesis develops and applies a zircon-based oxybarometer that uses XANES spectroscopy to measure uranium oxidation states in zircon as a proxy for magma redox. Extending zircon petrochronology to include direct constraints on magmatic $f\text{O}_2$ opens a window into the zircon record that can help shed light on the redox processes that have shaped our planet by creating new links between mineral-scale chemical information and the evolution of continents, atmospheres, and planetary habitability.

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Chapter II

URANIUM OXIDATION STATES IN ZIRCON AND OTHER ACCESSORY PHASES

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ABSTRACT

Zircon and other U-bearing accessory phases are important time-capsules for studying the evolution of Earth and other planetary bodies as these minerals can record both temporal and compositional information regarding their host rocks. In silicate melts, uranium can occur in either the U^{IV} , U^V , or U^{VI} valence state and its redox sensitive nature could, in principle, allow for information on magma oxygen fugacity (fO_2) to be gleaned from U-bearing phases provided they can incorporate multivalent U during crystallization. Currently, however, little is known regarding the details of how U is speciated in these minerals.

In this study, we conducted conventional X-ray absorption near-edge structure (XANES) spectroscopy at the U M_4 -edge on a set of natural zircon ($n=140$), titanite ($n=9$), apatite ($n=7$), baddeleyite ($n=7$), and garnet ($n=2$) samples to determine the oxidation state of U in these crystals. We also collected U L_3 -edge spectra for select zircon samples to investigate the bonding environment of U using extended X-ray absorption fine structure (EXAFS) analysis. The effects of crystallographic orientation and radiation damage on zircon U M_4 -edge spectra are found to be minimal compared to the magnitude of the peak shifts associated with U oxidation state. We find that titanite and garnet contain only tetravalent U, while zircon, apatite, and baddeleyite can contain U of variable valence. Of these phases, zircon shows the greatest variability, with white-line energy, E_{wl} (*i.e.*, peak absorbance) covering a range of >2.0 eV between grains: *i.e.*, the entire energy range expected between pure U^{IV} and pure U^{VI} species. Moreover, a correlation is observed between the E_{wl} of zircon U M_4 -edge spectra (*i.e.*, relative proportions of U^{IV} , U^V , U^{VI}) and the fO_2 of their host rocks. Our results thus establish U oxidation states in zircon as a powerful new tracer of magma redox. Since XANES is non-destructive and can be performed in situ, this technique can be utilized alongside other microanalytical methods (e.g., LA-ICPMS, SIMS) to further expand the breadth of information that can be extracted from single mineral grains.

1. INTRODUCTION

Zircon and other uranium bearing accessory phases (*e.g.*, titanite, apatite, baddeleyite) are key materials for investigating the evolution of Earth's crust as they can be both precisely dated and contain unique geochemical information reflective of the environment in which they formed (Hancher et al., 2003). Zircon grains, in particular, can be extraordinarily long-lived and can retain their original composition through weathering, diagenesis, and metamorphism on protracted, billion-year timescales (Harrison et al., 2017). This durability has resulted in the zircon record being one of the most complete archives of Earth's history. While many methods of interrogating these minerals exist (*e.g.*, U-Pb, O isotopes, and Lu-Hf in zircon), continued development of new tools to study these time capsules is a worthy effort that will provide valuable new insights into Earth's evolution.

One parameter of crustal magmas that has been elusive to constrain is oxygen fugacity (fO_2). This thermodynamic quantity controls the potential for redox-sensitive elements (*e.g.*, iron, vanadium, uranium, or cerium) to occur in more oxidized or reduced states, and it is often the dominant control on the proportions of their different valence states present within a rock or mineral. In the context of igneous petrology, fO_2 serves as a measure of magma oxidation state and has a direct influence on the compositional evolution of the crystallizing phases and residual liquids. For example, high fO_2 magmas will tend to follow a calc-alkaline differentiation trend while low fO_2 magmas follow a tholeiitic trend (*e.g.*, Osborn, 1959; Richards, 2014; Cottrell et al., 2021). Current zircon-based oxybarometers, however, can be unreliable due to their dependence on element concentrations and compositional assumptions, which in practicality are often difficult to constrain (*e.g.*, Trail et al., 2011; Smythe & Brenan, 2016). Given the importance of the U-Pb zircon geochronometer for dating magmatic crystallization, developing a technique that provides the ability to constrain magma redox conditions at the time of equilibration from the same crystals being dated would provide a valuable tool for studying crustal evolution on both long and short timescales.

Though typically considered in the context of geochronology, uranium (U) in zircon has several qualities which make it a promising system for use as a tracer of fO_2 . First, uranium is a redox sensitive element with three oxidation states (U^{IV} , U^V , U^{VI}). Second, although U in zircon is often assumed to be tetravalent (*e.g.*, Cherniak et al., 1997), previous work has shown that zircon can contain appreciable amounts of multivalent U (Vance & Mackey, 1974; Farges & Calas, 1992; Zhang et al., 2003; Burnham and Berry,

2012; Tanaka and Takahashi, 2019). Third, the redox potentials of the $U^{IV} \rightarrow U^V$ and $U^V \rightarrow U^{VI}$ reactions in silicate melts lie on either side of the $Fe^{II} \rightarrow Fe^{III}$ reaction (Schreiber, 1987), implying that uranium should be more sensitive to magma redox states than iron. Fourth, zircon incorporates U at high concentrations (100s-1000s of ppm) (Hancher et al., 2003), enabling spectroscopic investigations of U speciation. And finally, at the fO_2 values relevant to crustal magmas, oxidized U is expected to represent a significant proportion of the total U in the melt (up to 50% at ~FMQ) (Halse, 2014). Given the characteristics listed above, the oxidation state of U in zircon has the potential to be developed into a tracer of magma oxygen fugacity if its valence can be accurately determined.

X-ray absorption spectroscopy (XAS) has proven to be a powerful tool for investigating element oxidation states, as it provides quantitative information on the electronic structure of specific elements within a material. This technique has been used with great success on several redox sensitive elements (*e.g.*, Fe: Kelley & Cottrell, 2009; Berry et al., 2010; Brounce et al., 2015; V: Sutton et al., 2005; Ce: Trail et al., 2015), but to date, few studies have used XAS to investigate U in zircon (Farges & Calas, 1992: L_3 edge; Tanaka & Takahashi, 2019: L_3 and M_5 edge). While these pioneering studies confirmed that zircon can contain oxidized U, they both analyzed a limited number of samples and were primarily focused on metamict zircon grains.

In this study, we investigate the oxidation state of uranium in a large set of natural U-bearing minerals (including zircon, titanite, apatite, baddeleyite, and garnet) using conventional U M_4 -edge X-ray absorption near-edge structure (XANES) spectroscopy. For zircon from select localities, the bonding environment of U in these crystals was also studied using extended X-ray absorption fine structure (EXAFS) analysis (U L_3 -edge). Through careful consideration of the impact of potential systematic biases and confounding factors, such as crystallographic orientation and radiation damage, we show that XAS can provide an accurate and consistent measure of U oxidation states in zircon and other U-bearing minerals. Importantly, our data reveals that the energy of peak absorbance in U M_4 -edge zircon spectra correlates directly with the fO_2 of their host rocks. We discuss how these results open the door for XANES analysis of U in zircon to be used as a probe of magma oxygen fugacity.

2. SAMPLES AND METHODS

2.1 Samples

Mineral samples for this study were selected to cover a range of magma compositions, oxygen fugacities, ages, and tectonic environments. Several samples are also common reference materials and/or contain multiple coexisting U-bearing accessory phases (*e.g.*, FC-1 Duluth Gabbro, Fish Canyon Tuff). The majority of the minerals analyzed are from igneous rocks, although some of the titanite, garnet and baddeleyite grains analyzed are from metamorphic sequences (see [Table 1](#)). For zircon, baddeleyite, titanite, and apatite from reference localities (*e.g.*, FC-1, FCT, Ecstall, Phalaborwa) mineral separation and mounts were made at the Arizona LaserChron Center at University of Arizona. New zircon samples prepared for this study were processed at Caltech (Harney Peak, Sturgeon Lake, Lassen, Long Valley, Pacoima Pegmatite) and the Arizona LaserChron Center (Bishop Tuff). All grains analyzed in this study were concentrated using standard mineral separation techniques (*i.e.*, magnetic and heavy liquid separation). Mineral separates were hand-picked under a binocular microscope and mounted in 1-inch epoxy rounds. The average thickness of the mineral grains investigated is ~50-150 μm . Due to APS safety regulations for actinide research, epoxy sample mounts were encapsulated in 1 mil Kapton film. For samples that had undergone previous LA-ICPMS analyses a subset of grains were chosen such that a representative sampling of other relevant quantities of the larger data set (*i.e.*, U-Pb age, trace element concentrations) were covered. For samples with no pre-existing data for individual grains, crystals with the fewest number of cracks and inclusions were selected for analysis from each sample mount. In total, 140 individual zircon grains from 34 different rock samples were analyzed in this study, as well as 9 titanite from 3 samples, 7 apatite from 4 samples, 7 baddeleyite from 4 samples, and 2 garnet from 2 samples. [Table 1](#) gives a complete list of the samples analyzed, along with their ages and host lithology.

2.2 SEM Imaging

Backscattered electron (BSE) and cathodoluminescence (CL) images of all mineral grains measured in this study were collected prior to XAS analyses. Images were collected using a Zeiss 1550VP FE-SEM at the GPS Division Analytical Facility (Caltech) at an accelerating voltage of 20 keV. These images were used to identify areas of interest and avoid cracks, inclusions, or other imperfections on the grain surfaces. For grains having undergone LA-ICPMS prior to this study, these images allowed positioning of spots for XAS measurements in the same growth region as previous analyses.

2.3 μ XRF mapping

X-ray fluorescence mapping of each grain was conducted at the Advanced Photon Source (APS, Argonne National Laboratory) Beamline 13-IDE prior to XAS analyses. These maps were used to select the location of XAS analyses spots and to avoid subsurface inclusions that were not apparent in BSE or CL images (Fig. 1). Maps were collected using a monochromatic incident X-ray beam focused to 2x2 microns using silicon mirrors (Rh-coated) in a Kirkpatrick-Baez (KB) geometry (Sutton et al., 2017). Fluorescence counts were measured using a seven-element, silicon-drift-diode detector array (SX7, Canberra) with pulse-processing provided by an Xspress 3 digital X-ray processor system (Quantum Detectors). For mapping, an incident beam energy of 17.5 keV was used with an incident flux of $\sim 6.75 \times 10^{11}$ photons/sec. For zircon and baddeleyite samples, false-color RGB images of Ti $K\alpha$, U $L\alpha$, and Ca $K\alpha$ emission intensities were used to select the location of analysis spots and to avoid inclusions, as Ca and Ti tend to have high concentrations in minerals that often occur as zircon inclusions (e.g., apatite, rutile, rock-forming minerals). In some instances, grains were mapped using an incident beam energy closer to the U M₄-edge (3.76 keV with an incident flux of $\sim 3.5 \times 10^{11}$ photons/sec) and the U M β emission intensity was visualized instead of U $L\alpha$. Similarly, RGB maps of Ti $K\alpha$, U $L\alpha$, K $K\alpha$ and Hf $L\alpha$, U $L\alpha$, K $K\alpha$ were used to select analysis locations for apatite and titanite, respectively. It should be noted that mapping and XAS analyses at the 17.5 keV probes into the interior of the crystal (~ 150 μ m attenuation length) while mapping at lower energy (3.76 keV) only probes near surface of the grain (~ 2 μ m attenuation length). Figure 1 shows an example of the imaging procedure conducted for each grain prior to collection of spectra for XANES/ EXAFS analyses. SEM and μ XRF images of all analyzed grains are provided in the Supplementary Materials.

2.4 X-ray Absorption Spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) is an ideal method for studying element oxidation states as the X-ray beam can be finely tuned to precise energies, and thus, used to target specific electronic transitions in individual elements. When the energy of the incident beam matches the energy required to excite a core level electron to a specific bound state, a sudden rise in X-ray absorption is seen (*i.e.*, a sharp peak) in the XAS spectrum. The energy at which this peak occurs depends on the oxidation state of the element being interrogated, with higher oxidation states shifting the absorption peak to higher energies. This prominent peak is often referred to as the “white-line” (E_{wl}), a term

which originates from the early days of X-ray spectroscopy when spectra were recorded onto photographic film and the sharp absorption peaks were expressed as heavily exposed lines on the developed film. Analysis of oxidation states utilizing the features around the peak is referred to as X-ray absorption near-edge structure (XANES) spectroscopy. For U, there is a shift in E_{w1} between U^{IV} and U^{VI} on the order of 2 eV for the M_4 -edge and 4 eV for the L_3 -edge. While the U L_3 absorption edge has a larger shift between U^{IV} and U^{VI} , the U M_4 -edge absorption peak is significantly narrower due to a smaller core-hole lifetime broadening (~ 7.4 eV, vs 3.2 eV, respectively), since the M_4 edge probes the 5f unoccupied states of the U atom. XANES spectroscopy of the lower energy U M_4 -edge thus provides better sensitivity for determining the U oxidation states in a sample (Kvashnina & Butorin, 2022). The higher energy transition of the L_3 -edge, however, is better suited for extended X-ray absorption fine structure analysis (EXAFS). This technique utilizes the post-edge features that arise due to scattering between the target atom and its neighbors to provide structural information on the distances, identity, and coordination of the neighboring atoms. As with mapping at low vs. high energy, analysis of the U M_4 -edge will interrogate the near surface of the sample, while the higher energy of U L_3 -edge analyses will penetrate deeper and interrogate a larger volume of the sample.

The smaller excitation volume of the U M_4 -edge makes this method particularly amenable to zircon studies as the measured U valence will be more closely related to textural and compositional features observed in CL images and information gained from other *in situ* analyses (e.g., SIMS, LA-ICPMS). In this study, conventional total fluorescence yield U M_4 -edge spectra were collected for all grains and U L_3 -edge spectra were collected on a subset of the samples. From the larger sample set, FC-1, FCT, Bishop Tuff, and Ecstall zircons were selected for EXAFS analyses as these samples cover a range of host rock compositions and, except for the Ecstall zircon, have been well-characterized for ages and TREE (trace and rare-earth elements) in numerous prior studies (e.g., FC-1: Orihashi et al., 2008; Ibañez-Mejia et al., 2014; FCT: Schmitz & Bowring, 2001; Gleadow et al., 2015; Bishop Tuff: Crowley et al., 2007; Trail et al., 2015).

It should be noted that high energy resolution fluorescence detection (HERFD) XANES can provide higher resolution at the U M_4 -edge compared to the traditional total fluorescence yield XANES techniques used in this study (e.g., Kvashnina and Butorin, 2022). However, for samples with ppm level U concentrations such as zircon, the improved resolution would increase acquisition times from minutes to hours per spectra at the beamline used and thus significantly reduce the number of samples measurable in each

beamline session. For example, a study of U speciation in contaminated wetland soils (Le Pape et al., 2020) collected 20-25 scans of 20 minutes each to produce spectra with low signal to noise ratios at U concentrations of ~2000 ppm, equating to >6 hours per sample. As one of the aims of the present study is to assess the extent of U valence variability in zircon and other accessory phases from different lithologies, tectonic settings, and time periods, a large number of samples need to be analyzed. Since conventional U M₄-edge XANES is suitable for distinguishing uranium oxidation states, this approach was used here to allow the requisite number of samples (>150 grains) to be analyzed in the time available. Although recent improvements at several beamlines worldwide allow for faster HERFD acquisition times on low-concentration samples, the size of the beam at these end stations are generally $\geq 100\ \mu\text{m}$ in diameter. Since most zircon grains are ~100-500 μm in length, and often contain distinct growth regions and inclusions, a beam size of on the order of 10s of μm or less is required for targeted analyses. While conventional total fluorescence yield XANES was used for this study, we recommend that as beamline capabilities continue to improve, future work utilizing HERFD XANES be undertaken to further enhance our knowledge of U speciation in these minerals.

XAS analyses were performed during four sessions at APS Beamline 13-IDE (GSECARS) (Sutton et al., 2017). Beamline sessions took place in March 2021, September 2021, November 2022, and March 2023. Except for the first session, all measurements were made with samples enclosed within a He atmosphere to reduce atmospheric attenuation and increase signal intensity. Incident energy was selected using a Si (111) double-crystal monochromator calibrated to put the maximum of the first derivative of $\mu(E)$ for an Fe foil at 7110.75 eV. The beamline regularly monitors this calibration. If the Fe K edge changed by more than $\pm 0.5\ \text{eV}$ between sessions, a calibration with multiple foils was redone. For reference, a Y foil was measured at the start of each session so that data could be easily compared with spectra collected at other beamlines. The maximum of the first derivative of $\mu(E)$ for the Y foil was measured at $17044\ \text{eV} \pm 0.25\ \text{eV}$ across all sessions. XAFS data were collected in fluorescence mode using the SX7 solid state detector and all spectra were corrected for detector dead time. Measured spectra were normalized to incident intensity (I_0) measured in a He-filled, 200 mm-long ion chamber, just upstream of the KB mirror optics.

For both the U M₄ and L₃ edges, energy was scanned in 2 eV steps in the pre-edge region (U M₄: ~3700 eV to 3718 eV; U L₃: ~17066 eV to 17151 eV) and in 0.25 eV steps around the edge (U M₄: 3718 eV to 3743 eV; U L₃: 17151 eV to 17181 eV). In the post-

edge region, energy was scanned in steps of $0.05 \text{ \AA}^{-1}$ for the U M₄-edge and $0.08 \text{ \AA}^{-1}$ for the U L₃-edge. This results in a progressively increasing step size moving away from the edge towards higher energy and allowed for high-resolution scans in the regions of greatest interest (around the peak and near post-edge), while keeping the overall time per scan to a minimum. The dwell time at each energy step was 3 seconds for the U M₄-edge and 2 seconds for the U L₃-edge. The number of spots analyzed on each mineral grain varied depending on sample homogeneity. In most cases, only one or two spots were measured on each grain. The number of scans per spot also varied, with high-U grains requiring fewer scans to produce robust spectra. At the M₄-edge, we found that for zircons with typical U concentrations (100s of ppm or more) one scan per spot was typically sufficient to characterize the U oxidation state. All M₄ and L₃ edge spectra collected for an individual grain were averaged together to provide a single spectrum per crystal. Data processing (normalization, peak fitting, PCA, EXAFS transforms, FEFF fitting) was performed using the XAS Viewer program contained within the Larch software package for XAS analysis (Newville, 2013).

2.5 M₄-edge XANES data reduction

Uranium M₄-edge spectra were normalized with a linear function in the pre-edge, but due to variations in the shape and intensity of features in the post-edge region they could not be consistently normalized by their edge jump height. Instead, these data were normalized by their maximum intensity resulting in spectra with a peak height of ~ 1 for easy comparison between samples. A limited number of spectra had anomalous features in the pre-edge region due to diffraction artifacts caused by the proximity of the XANES spot to pre-existing LA-ICPMS pits. These spectra were discarded and are not discussed further.

To determine the E_{wl} , spectra were fit in XAS Viewer using a pseudo-Voigt function with a linear background to model the main spectral peak. The E_{wl} was taken as the centroid of the fit. Fits were also performed using Gaussian and Lorentzian functions; however, the pseudo-Voigt gave consistently better fits (lower χ^2) compared to the other peak shapes. Spectra were fit in the near-edge region from 3715 eV to 3735 eV. Examples of normalized M₄-edge spectra and their best fits are shown in Fig. 2. The quality of the spectra shown in Fig. 2 are typical for grains with high U concentrations (~ 5000 ppm; Fig. 2a) and moderate U concentrations (~ 100 ppm; Fig. 2b) (Lewis et al., 2021).

2.6 L₃-edge EXAFS analysis

L₃-edge spectra were normalized by fitting linear functions to both the pre-edge and post-edge regions from approximately -90 to -35 eV below the edge and +250 to +550 eV above the edge. Using the Larch software package (Newville, 2013), spectra were converted to the EXAFS function, $\chi(k)$, where k is the wave number of the photoelectron emitted by the absorbing atom. Fourier transforms of the spectra were used to translate $\chi(k)$ to $\chi(R)$, where R is the distance (in Å) from the absorbing atom. Theoretical EXAFS oscillations were then calculated from crystallographic information using the FEFF8 program (Ankudinov et al., 1998; Rehr et al., 2009), which models scattering of the emitted photoelectron from the absorbing atoms based on inputs of crystallographic information and the identity of the absorbing atom. For a detailed explanation of EXAFS fitting and interpretation in Larch see Newville (2013, 2014) and Newville & Ravel (2020). Initial FEFF calculations were run using zircon structural information contained within the Larch library from Hazen & Finger (1979) that were modified to reflect U substitution at the Zr site. Fourier transformed spectra were fit from 1 Å to 4 Å in $\chi(R)$ space (Fig 3c) using three single scattering paths (U-O, U-Si, and U-Zr). Due to the limited k -range of the data used for fitting ($<10 \text{ Å}^{-1}$) the maximum resolution between atomic neighbors is $\sim 0.2 \text{ Å}$, which is greater than the separation of the two reference Zr-O distances of 2.11 Å and 2.26 Å (Hazen & Finger, 1979). For this reason, only one U-O scattering path was used in the fit to determine the average U-O bond length in each sample. Examples of the normalization procedure, extracted EXAFS oscillations, and FEFF fitting results are shown in Fig. 3. All U L₃-edge spectra used for EXAFS analysis are available in the Supplementary Materials.

2.7 Anisotropy tests on U M₄-edge spectra

In anisotropic minerals such as zircon, measured X-ray absorption spectra can be affected by differences in crystallographic orientation of the crystal being analyzed relative to the polarization direction of the incident X-ray beam leading to dichroism (Brouder, 1990). To test the possible effect of this phenomenon on measured U M₄-edge zircon spectra, two grains from three samples (Bishop Tuff, Fish Canyon Tuff, and Ecstall pluton) were mounted such that their c-axis was either parallel or perpendicular to the sample surface. These grains were then repeatedly analyzed at the same spot location through a series of stage axial rotations (0, 45, and 90 degrees). In addition, three randomly oriented FC-1 zircon grains were analyzed at the same spot location at stage rotation angles of 0° and 90°. While many zircon grains have a well-developed crystal habit and are typically mounted with the c-axis parallel to the sample surface, FC-1 zircon grains are almost

always anhedral and thus mounted in random orientations relative to the sample surface. Comparison of the large number of spectra collected on FC-1 zircon grains thus allowed investigation of a variety of geometries between the incident beam and the zircon crystallographic axes.

2.8 Raman Spectroscopy

Raman spectroscopy has proven a useful method for assessing the extent of radiation damage (due to radioactive decay) in a zircon crystal as the peak width and center of the Raman bands widen and shift to lower wavenumbers, respectively, with increasing metamictization (*e.g.*, [Nasdala et al., 1995](#); [Palenick et al., 2003](#); [Marsellos & Garver, 2010](#); [Anderson et al., 2020](#)). High U concentration can also distort the crystal structure of zircon and lead to widening of Raman peaks, but this effect is much smaller than the peak broadening due to radiation damage (1s of wavenumbers opposed to 10s). More importantly, previous studies of U oxidation states in zircon have indicated that metamictization may lead to an increase in the proportion of U^{IV} at the expense of higher valence U within amorphous zones ([Zhang et al., 2003](#)), which could complicate the interpretation of our XANES results (see *Section 5.1* for discussion). The same test cannot be performed on other accessory phases due to the lack of a calibration between Raman spectral modifications with alpha fluence, so we cannot ascertain whether the redox states of U in the other accessory phases are primary features or due to some post-crystallization secondary process.

Raman spectra were collected using a Renishaw inVia Raman spectrometer at Caltech (Rossman laboratory) over the range $200\text{-}1100\text{ cm}^{-1}$ using a 514 nm laser and a 3000 l/mm grating. Calibration of the instrument was performed by measuring a Si-wafer and setting the centroid of the prominent Raman band to 520.5 cm^{-1} . Measurements were made in air and at ambient temperature using an exposure time of either 1 or 2 s and with 20-60 scans collected at each spot depending on the crystallinity of sample (more crystalline samples required fewer scans to produce robust spectra). Raman spots were placed near the location of the XAS measurements when possible. Overall, 1-5 spectra were obtained for each grain depending on the intensity of the Raman signal above background. For samples where multiple spectra were collected, the values for the peak widths and Raman shifts were averaged together.

The intensity of the various peaks in a Raman spectrum can be highly dependent on the orientation of the crystal and may be absent altogether in some beam-sample

geometries (Dawson et al., 1971; Anderson et al., 2020). We focused on the $\sim 356 \text{ cm}^{-1} E_g$ vibrational band as this was the most common feature observed in our samples. While the 1008 cm^{-1} Raman band has traditionally been used to assess radiation damage, Anderson et al. (2020) showed that the $356 \text{ cm}^{-1} E_g$ band spans a greater range in full-width at half maximum (FWHM) values indicating that it may be a more useful indicator of radiation damage. Raman peaks were fit using a Gaussian approximation to determine the FWHM and center of each feature. The average 2 standard deviation (SD) uncertainty was determined from multiple measurements on the same grain of the E_g band. For radiation damaged zircon, the uncertainty on the peak width and center of the E_g band are 6 cm^{-1} and 2 cm^{-1} , respectively. Crystalline zircon gave more consistent results with an uncertainty of 0.4 cm^{-1} for both parameters.

3. RESULTS

3.1 U M₄ XANES data consistency & uncertainties

Since data were acquired during multiple session over the span of two years, tests were performed to assess data stability and reproducibility over time. FC-1 zircon was selected as a reference material for this purpose as these crystals appear homogenous in CL images and showed the most consistent spectra amongst samples measured during the first analysis session. As seen in Fig. 4a, the measured U M₄-edge E_{wl} of FC-1 zircon is reproducible within $\pm 0.18 \text{ eV}$ (2SD). This value is larger than the typical 2 SE error of $\pm 0.03 \text{ eV}$ reported by XAS Viewer for the centroid of the fit used to determine the E_{wl} , but we argue that it better represents the precision of an individual measurement on a natural zircon. Indeed, the MSWD of all FC-1 measurements calculated using a 2 SD for each data point of $\pm 0.03 \text{ eV}$ or $\pm 0.18 \text{ eV}$ are, respectively, 37.53 and 1.04, meaning that a large amount of the variance is unexplained if the smaller uncertainty is used. We thus applied a $\pm 0.18 \text{ eV}$ uncertainty to all measurements of individual zircon grains. Where the average E_{wl} for a sample, calculated from measurements of multiple grains, is discussed, the 2 SE uncertainty is used instead: *i.e.*, $2 \text{ SD}/\sqrt{n}$, where n is the number of grains analyzed. Comparison of the average U M₄-edge E_{wl} of FC-1 zircon obtained in each session shows stability within $< 0.1 \text{ eV}$ (Fig. 4b). Given the stability and reproducibility of FC-1 zircon white-line energies, along with their broad availability as a common laboratory reference material for U-Pb geochronology and Lu-Hf isotopes, we recommend that grains of FC-1 zircon also be used as a reference material for future U XANES studies of zircon. Raw FC-

1 material can be obtained by contacting the Arizona LaserChron Center at University of Arizona.

The effect of beam damage on U oxidation states in zircon was assessed by comparing XANES successive scans collected at the same location. [Figure 5](#) shows the results of this test for two zircon grains over the course of three scans. No change in the measured U valence was detected across the repeated scans with the fitted E_{wl} value varying by only ± 0.04 eV (2 SD), indicating that U oxidation states in zircon are not affected by beam-induced damage at the U M_4 -edge energy.

3.2 U M_4 -edge XANES E_{wl} and calculated U valence

Average U M_4 -edge spectra for all mineral grains analyzed in this study are shown in [Fig. 6](#) (zircon) and [Fig. 7](#) (titanite, baddeleyite, apatite, garnet). Due to the large number of samples analyzed in this study, however, we focus on the white-line energy of each spectrum as a proxy for the proportion of the different U oxidation states present in a sample. This allows each spectrum to be represented by a single value that can be plotted against other parameters and provides a simplified means of representing the data. Details regarding the calculation of average U valence from U M_4 E_{wl} are given below.

[Figure 8](#) shows the white-line energies (E_{wl}) of all U M_4 -edge spectra collected for each grain analyzed in this study. Data points represent the average E_{wl} of all spectra collected for an individual grain. The dashed lines in [Fig. 8](#) show the approximate positions of the U^{IV} , U^V , and U^{VI} edges. The position of the U^{IV} edge was determined from the E_{wl} of UO_2 (3726.2 eV) and the energy of the U^V and U^{VI} edges are placed at 1.5 eV and 2.0 eV above this value, respectively, based on data presented by [Kvashnina & Butorin \(2022\)](#) ([Table 2](#)). While the HERFD spectra they present display narrower peaks and improved resolution of post-edge features compared to the traditional U M_4 -edge XANES spectra in this study, the difference in E_{wl} between our most reduced and oxidized samples is similar to that reported between pure U^{IV} and U^{VI} compounds (~ 2.0 eV). Additionally, several other studies have found the U^V edge to be $\sim 75\%$ between the U^{IV} and U^{VI} edges ([Table 2](#)) ([Kvashnina & Butorin, 2022](#), [Leinders et al., 2017](#); [Popa et al., 2016](#); [Halse, 2014](#)), suggesting that the E_{wl} position we assume for U^V is also a reasonable approximation.

Of all mineral phases investigated, zircon shows the greatest variability in E_{wl} (~ 2.0 eV) with samples having spectra consistent with U valence spanning the range from fully reduced (U^{IV}) to fully oxidized (U^{VI}). Apatite and baddeleyite display a narrower range of E_{wl} (~ 0.6 eV and ~ 0.5 eV, respectively), with average values ~ 0.5 eV above the U^{IV} E_{wl}

value, indicating that these phases also incorporate a component of more oxidized U. Titanite samples have the lowest E_{wl} of the samples measured (3726.3 eV average) and show a restricted range in peak energy of ~ 0.2 eV, indicating that titanite incorporates only U^{IV} . Importantly, this restricted range of white-line energies is observed in titanite grains from both the Fish Canyon Tuff and Ecstall localities, while zircon from these same samples indicate a large proportion of oxidized U being present: *i.e.*, even in the presence of oxidized U, titanite only incorporates U^{IV} in its crystal lattice. The two garnet samples measured yield E_{wl} consistent with a dominantly U^{IV} valence, however, these two grains are both andradite garnets separated from skarns. Since garnet forms an array of different solid solutions and can form in a variety of environments, these two samples are not necessarily reflective of U oxidation states in all types of garnet.

As a further indication that zircon can contain multivalent U, we examine the variation in the full width at half-maximum (FWHM) of zircon U M_4 -edge spectra. Fig. 9 plots the FWHM of individual spectra against their white-line energies and shows that the lowest FWHM values occur near the nominal edge energies of the U^{IV} and U^{VI} ions and the highest values occur in between these energies. The FWHM at the low energy end of the range (U^{IV}) is around 4.6 eV and increases to a maximum of ~ 5.6 eV between the U^{IV} and U^V peaks before decreasing to a minimum of ~ 4.7 eV at the energy of the U^V peak. Peak widths at this energy, however, vary from approximately 4.7 eV to 5.2 eV. Between the U^V and U^{VI} edges the width varies from 5.2 eV to 4.5 eV and reaches a minimum of ~ 4.4 eV at the energy of the U^{VI} edge. The observation that the narrowest peak widths occur near the white line energies obtained for zircon samples with pure U^{IV} or U^{VI} content, and the broadest peaks occur between these values, suggests that the latter are composed of multiple, convoluted, spectral peaks. Since a spectrum with a mixed $U^{IV} + U^{VI}$ composition will lead to a broader peak compared to a mix of $U^{IV} + U^V$, the variability in the FWHM at intermediate white-line energies in Fig. 9 may suggest that samples with a broader peak (*e.g.*, HLMC, light blue circles) are predominantly a mixed U^{IV} and U^{VI} composition, while conversely, samples with a lower FWHM are likely a mix of U^{IV} and U^V (*e.g.*, Harney Peak, green circles). For illustrative purposes, the averaged U M_4 -edge spectra for all titanite samples as well as for zircon grains from samples HP44A (Harney Peak) and MC18 (Long Valley) are shown in Fig. 10. These spectra were chosen as they are representative of endmember samples from our dataset with predominantly U^{IV} , U^V , and U^{VI} valences, respectively. Average titanite and MC18 spectra were chosen to represent U^{IV} and U^{VI} as these samples have the lowest and highest E_{wl} amongst our

samples, respectively. Additionally, the MC18 spectrum shows a slight asymmetry on the high-energy side of the peak that is likely due to U^{VI} (Fig. 10 inset). HERFD spectra of U^{VI} compounds often exhibit additional shoulders and peaks in the post-edge region, and while these features are obscured in the traditional XANES spectra collected in this study, the slight shoulder in the MC18 spectra suggests the presence of U^{VI} in these samples. HP44A was selected to represent U^V as its E_{wl} occurs near the nominal energy of the U^V edge ($\sim 75\%$ between U^{IV} and U^{VI} at 3727.7 eV), and of the samples with E_{wl} around this value, HP44A zircon have the narrowest FWHM. Additionally, U^V has been previously observed in zircon (Vance & Mackey, 1974; Zhang et al., 2013).

To confirm that all three valence states of U are indeed present in our data set, we performed a principal component analysis (PCA) on a set of U M_4 spectra comprising those shown in Fig. 10, along with the average spectra for zircon from felsic volcanic rocks, arc-related rocks, SPGs, and anorthosites + syenites we analyzed (Fig. 11a). PCA was performed on this set of endmember and average spectra to reduce the number of non-significant components arising from noise in the spectra of individual grains while maintaining the variability observed in the dataset. Since PCA can be sensitive to normalization, several trials were run varying slightly the pre- and post-edge normalization ranges of the U M_4 spectra. In all trials PCA identified at least three significant components (average variances of 72%, 25% and 3%) whose total variance accounts for $>99\%$ of the variance in the data set (Table S1, Fig 11b), confirming that all three valence states of U are present within the sample set as a whole.

To constrain the average U valence (U^{n+}) of our zircon samples, their U M_4 spectra were fit using a linear combination of the spectra shown in Fig. 10, which were chosen to represent the U^{IV} , U^V , and U^{VI} endmembers (titanite, HP44A zircon, and MC18 zircon, respectively). The results from these analyses (Fig. S2) are consistent with the FWHM values presented in Fig. 9, as the spectra at intermediate white-line energies with the greatest widths are best fit by a combination of U^{IV} , U^V , and U^{VI} , while spectra with narrower peaks but similar E_{wl} are best fit by a combination of predominantly U^{IV} and U^V . While the proportions of each U oxidation state we determined can vary at a given E_{wl} (*i.e.*, can be a mix of U^{IV} , U^V , and U^{VI} or only two of these oxidation states), the average U^{n+} calculated for each sample varies predictably with the E_{wl} of their spectra (Fig. 12). Since the difference in energy between the U^{IV} and U^V edges is larger than the difference between U^V and U^{VI} (1.5 eV versus 0.5 eV, respectively) the variation in U^{n+} with E_{wl} is not expected to be linear, and as such, the following function was used to model the data:

$$U^{n+} = a e^{\left[\frac{E_{wl} - E_{U(IV)}}{b}\right]} + c \quad (1)$$

where a , b , and c are the fitted parameters, E_{wl} is the white-line energy and $E_{U(IV)}$ is the E_{wl} of a reference U^{IV} compound. A best fit to the data is shown by the black curve in [Fig. 12](#) and given below (Equation 2):

$$U^{n+} = 0.53 e^{\left[\frac{E_{wl} - 3726.2}{1.38}\right]} + 3.54 \pm 0.13 (2\sigma) \quad (2)$$

Since measured E_{wl} values can vary slightly between beamlines depending on the calibration used, the U^{n+} values for each sample, calculated using Eq. (2), are discussed for the remainder of the text except where specific E_{wl} values are relevant. Average E_{wl} values and calculated U^{n+} values for zircon samples are given in [Table 3](#).

Amongst the zircon grains analyzed, those from arc-related magmas show the most variation in U^{n+} , with zircon grains spanning the entire valence range from U^{IV} to a mixed U^V and U^{VI} oxidation state. Zircon from the southern Sierra Nevada plutons vary considerably between samples and suggest that crystallization in these plutons occurred under different redox conditions. For example, zircon from the Bullfrog Pluton have the highest U oxidation states measured for a plutonic rock in this study, with an average valence of $U^{5.3+}$. At the low end, zircon from the Paradise and Lone Pine granodiorites and Mt. Whitney granite have average E_{wl} values that are more than 1.0 eV lower than those measured from the Bullfrog Pluton, corresponding to average U valences of $U^{4.1+}$, $U^{4.3+}$, and $U^{4.4+}$, respectively. In particular, one zircon from the Paradise granodiorite has a spectrum indicative of an entirely U^{IV} composition. Zircon from the Hidden Lakes Mafic Complex in the central Sierra Nevada are also quite variable in their U valence, with different samples of this suite ranging from an average of $U^{4.3+}$ to $U^{5.0+}$. Notably, Hidden Lakes zircon grains separated from rocks with cumulate textures have markedly lower U valence and higher U concentrations when compared to zircon from rocks with liquid-like textures (dark blue circles vs. light blue circles in [Fig. 8](#)) ([Lewis et al, 2021](#)). This result is consistent with the greater compatibility of U^{IV} over U^V or U^{VI} in the zircon structure ([Burnham & Berry, 2012](#), [Mallmann et al., 2021](#)).

Zircon from strongly peraluminous granites (SPG) display differences in U oxidation states between grains from Archean (SP-16-52: Sturgeon Lake) and Proterozoic samples (HP44A/HP21C: Harney Peak), with the Archean grains containing a greater proportion of U^{IV} relative to the Proterozoic samples (averages of $U^{4.25+}$ vs. $U^{5.0+}$, respectively). Oxybarometry on these samples by [Bucholz et al. \(2018\)](#) using biotite-whole rock Fe-Mg modeling determined that the oxygen fugacity of the Archean Sturgeon Lake

granite was lower than the fO_2 of the Proterozoic Harney Peak granite (FMQ+0.7 vs. FMQ+1.4, respectively). The results from this study are thus consistent with the idea that Archean SPGs are generally more reduced than their Proterozoic counterparts.

Zircons from felsic volcanic rocks have the highest U valence amongst our samples, with the peaks in their spectra predominantly between the U^V and U^{VI} edges, though some samples fall between the energies expected for U^{IV} and U^V . Zircon from the Lassen volcano and the post-caldera Long Valley eruptions have the highest U valence, close to the pure U^{VI} endmember. In the presence of oxidizing fluids U is readily oxidized to U^{VI} and the shallow magma chambers that feed these systems are more likely to have interacted with such fluids prior to, or during, eruption relative to deeper-seated plutonic rocks.

Finally, and contrary to samples from felsic volcanic rocks, zircons from anorthosites and syenites have average U oxidation states restricted to the lower end of the range, though their spectra are still indicative of a mixed U^{IV} - U^V composition. High K melt concentrations have been shown to have a reducing effect on U (Dominé & Velde, 1985) and may explain the more restricted range in U oxidation states observed in syenite samples relative to zircons from most of the arc-related samples. This is supported by zircon grains from the arc-related high-K Dariv Igneous Complex (DIC) that show U valences as reduced as zircon from syenites.

3.3 $U L_3$ -edge EXAFS analysis

Although U M_4 XANES is better suited for determining oxidation states, EXAFS analysis of U L_3 -edge spectra can provide important structural information, in particular, on whether the incorporation of oxidized U into the zircon lattice is accompanied by any significant structural transformations that could affect the XANES results. EXAFS analyses were performed on a subset of zircon grains from four different samples (FC-1 n=6; FCT n=6, Ecstall n=2, Bishop Tuff n=1) ranging from moderately to highly oxidized (FMQ to FMQ +2.5). The extracted EXAFS oscillations for all samples are shown in Fig. 13 (normalized U L_3 -edge spectra are shown in Fig. S3). The reference Zr-X interatomic distances and the U-X distances determined by FEFF fitting are given in Table 4 and shown in Fig. 14. The U-X bond distances we determine for these samples are generally larger than the reference distances (Hazen & Finger, 1979), though they tend to decrease with increasing U oxidation state, consistent with higher valence ions having a smaller ionic radii and greater attractive force relative to more reduced species. For instance, between

zircon from FC-1 (mostly U^{IV}) and FCT (mixed $U^{IV} + U^{V/VI}$) the average U-O distance decreases by ~ 0.07 Å from slightly larger than the reference distance for FC-1 to approximately the same as the reference Zr-O distance for FCT. This result can largely be explained by the difference in radius between Zr^{IV} (0.98 Å) relative to U^{IV} (1.14 Å) and U^{VI} (1.00 Å) when in 8-fold coordination (Shannon, 1976). Overall, EXAFS analysis indicates that no significant structural transformation occurs in these samples with increasing U valence (*i.e.*, U^{VI} present as uranyl (UO_2^{2+}) which has two U-O bonds at 1.8 Å), rather, we observe a modest reduction in interatomic distances (up to $\sim 3\%$) with increasing valence (Fig 14).

3.4 Effect of crystallographic orientation on calculated U valence

Rotation tests performed on grains mounted with their c-axis parallel or perpendicular to the polarization direction of the incident X-ray beam reveal a very limited impact of dichroism on the calculated E_{wl} from measured U M_4 -edge spectra (Fig. 15). For the zircon grains analyzed (FCT, BT, and Ecstall), the 2 SE uncertainty in the E_{wl} determined for each crystal ranged from ± 0.02 to ± 0.17 eV, with an average 2 SE uncertainty of only ± 0.10 eV for these grains. For FC-1 zircon the 2 SE uncertainty was only ± 0.05 eV. The variability we observe due to crystallographic orientation is similar in magnitude to the shift observed between U-bearing compounds with different crystal structures (~ 0.1 eV) (Kvashnina & Butorin, 2022) and is much smaller than the differences observed between U of different oxidation states. In all cases the average deviation at each orientation is within the uncertainty of the measurement (Fig. 15c). These analyses indicate that variations in E_{wl} due to the geometry between the crystal and X-ray beam are minimal compared to the magnitude of the peak shifts between different U oxidation states. Although crystallographic orientation does not appear to be a significant source of uncertainty, we recommend that spectra be collected for multiple grains from a sample when possible.

3.5 Impact of radiation damage on calculated U valence

To assess the impact of radiation damage on U valence in zircon (due to decay of radioactive elements within the zircon grains), we compare the Raman peak width (E_g band) and average U valence in our samples (Fig. 16). Amongst the zircon grains investigated here, those from the FCT, Ecstall pluton, BT, Lassen, and the Sierra Nevada Plutons have Raman spectra consistent with crystalline zircon (*i.e.*, Raman peaks < 10 cm $^{-1}$

¹ in width). In contrast, grains from four samples (FC-1, HL-17-2, Harney Peak, and Sturgeon Lake) have peak widths between 10 cm⁻¹ and 30 cm⁻¹ indicating various degrees of radiation damage. No clear relationship between Uⁿ⁺ and Raman peak width is visible in the data. FC-1 zircon grains, while ranging from mostly crystalline to heavily radiation damaged, show no resolvable change in their U valence as a function of Raman peak width. Harney Peak zircon (HP44A and HP21C) have Raman peak widths >25 cm⁻¹ and cover a range of valence states, but the two quantities appear uncorrelated. Sturgeon Lake zircon (SP-16-52) show a slightly positive trend with more reduced grains having a narrower Raman peak width. However, the Raman peak widths are all within uncertainty of each other, and this trend is thus inconclusive regarding the effect of radiation damage on U oxidation states in these crystals. Finally, zircon grains from sample HL-17-2 show a somewhat negative trend with more radiation damaged grains containing a greater proportion of U^{IV}.

4. DISCUSSION

4.1 Effect of radiation damage on U_{zrc} oxidation states

Radiation damage is a persistent concern for any zircon investigation method. The decay of radioactive elements, primarily U and Th, in zircon damages the crystal lattice and over time can destroy the short to medium range order of the mineral (*e.g.*, [Farges & Calas, 1991](#); [Nasdala et al., 1995](#)). The time for radiation damage to accumulate to the point where the crystal becomes amorphous or unsuitable for analysis depends on the concentration of radioactive elements and can vary from millions to billions of years. These damaged zones are more susceptible to chemical alteration and can lead to spurious results when not accounted for. Specifically for U speciation, previous work has suggested that heavily radiation damaged zones in zircon may contain a greater proportion of U^{IV} relative to higher valence states ([Zhang et al., 2003](#)).

Our data show that crystalline zircon grains can have average U valences that span the entire range from U^{IV} to U^{VI}, a feature indicating that the measured U oxidation state is a primary signature, and that zircon can incorporate U of any valence during crystallization. As seen on [Fig. 16](#), grains with varying degrees of radiation damage display a similar range of Uⁿ⁺ as crystalline grains, suggesting that they have largely retained their primary U valence state. Examination of grains from the same sample further strengthen this interpretation. For instance, FC-1 zircon grains, which range from mostly crystalline to heavily radiation damaged, show unresolvable change in U valence as a function of Raman

peak width, indicating that even high degrees of radiation damage did not significantly alter the U redox state of FC-1 zircon. Additional evidence comes from the highly radiation damaged grains (Harney Peak and Sturgeon Lake zircon) that have Raman peak widths $>25 \text{ cm}^{-1}$. Despite their clear radiation damage Harney Peak zircon (HP44A and HP21C) display no significant trend in Fig. 16 and cluster near a predominately U^{V} composition. Sturgeon Lake zircon (SP-16-52) show a slightly positive trend with more reduced grains having a narrower Raman peak width. However, given the large uncertainty associated with highly radiation damaged grains ($6 \text{ cm}^{-1} \pm 2 \text{ SD}$) this trend is inconclusive regarding the effect of radiation damage on U oxidation states in these crystals. Overall, radiation damage does not seem to have a reducing effect on the U oxidation state of the grains studied here, despite the old age and high degree of radiation of some samples (*e.g.*, Harney Peak $\sim 1700 \text{ Ma}$; Sturgeon Lake $\sim 2670 \text{ Ma}$). If the U valence composition of the Harney Peak or Sturgeon Lake zircon grains have been altered, it is more probable that U has been oxidized during to fluid alteration, rather than reduced as a result of electron capture during radioactive decay as proposed by Zhang et al. (2003). This, however, is unlikely for the Harney Peak zircon as their host-rocks appear to have experienced little post-crystallization fluid alteration (Nabelek et al., 1992).

In our dataset, zircon grains from only one sample, HL-17-2, show a decrease in U valence with increasing Raman peak width. At first glance, this observation is consistent with the idea that more metamict grains may contain greater proportions of U^{IV} . However, the HL-17-2 zircon grains with more radiation damage also contain significantly more U than crystalline grains (1000s vs. 100s of ppm U), which needs to be considered. XANES analysis and Raman spectroscopy was conducted on four zircon grains from sample HL-17-2 with U concentrations varying from ~ 200 -5000 ppm. In these grains, the proportion of U^{IV} and the width of features present in their Raman spectra both increase with increasing U concentration, ranging from highly radiation damaged and entirely U^{IV} to crystalline with an average valence of $\text{U}^{4.4+}$. Rather than radiation damage, the reduced nature of the high-U grains could simply be a result of U ion partitioning in zircon as experiments under varying redox conditions have showed that U^{IV} is more compatible in zircon than U^{V} or U^{VI} (Burnham & Berry 2012). When the $\text{U}_{\text{zircon}}/\text{U}_{\text{whole rock}}$ ratio of the individual HL-17-2 zircon are plotted against their U valence (Fig. 17), a strong negative trend is observed from high-concentration-low-valence U to low-concentration-high-valence U. As a comparison the $\text{U}_{\text{zircon}}/\text{U}_{\text{whole rock}}$ ratio of samples SNB-14-34 and SNB-16-12, also from the HLMC, are plotted on Fig. 17. For the HL-17-2 zircon, the concentration

of other incompatible elements (*e.g.*, Hf, Y, REE) are also greater in the high-U grains suggesting the melt from which they crystallized was generally more enriched. Together, this suggests that the greater proportion of U^{IV} in the grains with higher U concentration is likely a primary signature resulting from a combination of U ion partitioning behavior and melt composition, and thus, may reflect crystallization of these grains under different conditions rather than a change in their U oxidation state due to metamictization. This is plausible for the HL-17-2 zircon as they were separated from an anorthosite block within the HLHC (Lewis et al., 2021) and zircon crystallization could have occurred in isolated melt pockets interstitial to the cumulate plagioclase grains, which could explain the variability observed in their U valence and TREE signatures. As a final indication that the trend of the HL-17-2 zircon in Fig. 16 is not due to metamictization, their behavior can be contrasted with the much older FC-1 zircon grains (95.7 Ma vs. 1099 Ma, respectively), which show little variation in U redox state (average valence of $U^{4.29+}$), regardless of their extent of radiation damage.

In summary, our data do not preclude the possibility that highly damaged zircon grains could have their U valence states altered, particularly if they have become entirely amorphous, as such grains give spurious results using other *in-situ* zircon methods. Our results, however, show that radiation damage has a minimal effect (within uncertainty) on the U valence determined from U M₄-edge XANES spectra.

4.2 Incorporation of multi-valent U in zircon and U-bearing accessory phases

Our results show that zircon, apatite, and baddeleyite all may incorporate U of variable valence. Raman spectroscopy on the zircon samples shows that crystalline grains (those with Raman peak widths less than 10 cm^{-1}) have average U valences that span the entire range from U^{IV} to U^{VI} , implying that the measured U oxidation state in these zircon grains is a primary signature and that zircon can incorporate U of any valence during crystallization. In contrast to zircon and the other accessory phases investigated, titanite seem to have invariant U valence containing only the reduced species, U^{IV} . Previous work on experimentally grown titanites concluded that U incorporation was greatest in the starting media with the highest Mg concentrations, which these researchers attribute to a coupled substitution in which U replaces Ca while Mg substitutes into an adjacent octahedral site to balance the higher charge of the U atom (Tiepolo et al., 2002; Mazdab, 2009). Given its specificity, the charge balance requirements of this coupled substitution

reaction would be highly unfavorable towards incorporation of oxidized uranium into titanite, regardless of melt oxidation state, which is consistent with our results.

In zircon, U is thought to substitute for Zr in the crystal structure, and thus, it is often assumed that only U^{IV} is incorporated into zircon as Zr is strictly tetravalent. However, along with U, zircon incorporates many other trace elements including yttrium (Y) and REE, which are predominantly trivalent and may provide a charge balancing mechanism for U of higher valence states (Vance & Mackey, 1974), though charge compensation may be accommodated by vacancies as well. Experimental studies have shown that the partition coefficient for uranium substitution into zircon decreases with higher melt oxidation states suggesting a preference for reduced over oxidized U in the zircon structure (Burnham & Berry, 2012). Despite a preference for U^{IV} , zircon seems able to readily incorporate U of any valence state. For example, zircon from the Bishop Tuff typically have elevated U concentrations ranging from ~800-5000 ppm and contain some of the highest proportions of oxidized U amongst our samples. This is likely due to the incompatible nature of U that results in evolved magmas (the zircon which crystallize from them) having generally higher U concentrations compared to more primitive melts regardless of U oxidation state. While experimental studies of lab-grown zircon have not detected an appreciable amount of U^{VI} in samples grown under oxidizing conditions, this could be due to the volatile nature of hexavalent U, which can be easily lost from 1 atm experiments (Burnham & Berry, 2012). Our study of natural samples unambiguously shows that zircon can incorporate penta- and hexavalent U in addition to the tetravalent form. Notably, while some individual zircon grains appear to have an entirely U^{IV} composition, the lowest average U valence calculated for a sample is $U^{4.25+}$, indicating that the incorporation of multivalent U is a common feature of zircon. The factors determining the proportions U^{IV} , U^V , and U^{VI} in a zircon containing multivalent U are currently unconstrained, however, it is likely a result of the P-T-X conditions of the crystallizing melt. For example, the stability field of U^V has been shown to decrease at higher pressures (Halse, 2014), which would result in a greater proportion of U^{VI} in the melt relative to U^V for the same degree of oxidation. While various factors likely play a role in the oxidation path of U, the proportion of oxidized U (either U^V or U^{VI}) has been shown to increase as a function of fO_2 in silicate melts (Halse, 2014) and zircon (Burnham & Berry, 2012).

4.3 U valence as a probe of magma fO_2

The ability of zircon to incorporate U of any valence raises the question of what determines the valence of U in zircon. Redox conditions in the zircon parental magma are likely to exert a first-order control on U speciation in zircon. In fact, zircon grains from samples with independent fO_2 estimates display a strong positive correlation between their calculated U valence (*i.e.*, E_{wl} of their U M₄-edge spectra) and oxygen fugacity (Fig. 18), highlighting the potential for U valence in zircon to be an accurate oxybarometer for igneous systems. The fO_2 values for samples used in this correlation were calculated from a variety of methods and include rocks of diverse lithology, illustrating the robustness of U M₄-edge spectroscopy as a tool for probing magma redox. References and methods used for each fO_2 estimate are given in Table 5 and are outlined in the following paragraph.

The fO_2 values for FC-1, FCT, and LF042-02 were calculated using Fe-Ti oxide pairs by Pasteris (1985), Johnson & Rutherford (1989), and Underwood et al. (2012), respectively. For the Bishop Tuff, fO_2 estimates vary from an average of FMQ+1.1 (Hildreth & Wilson, 2007) to FMQ+2.4 (Trail et al., 2011, 2012). We use the value of Trail et al. (2012) for our calibration, however, as the value determined using Fe-Ti oxide pairs for the Bishop Tuff was shown to be unreliable by Ghiorso & Guild (2013) due to the disequilibrium growth of ilmenite just prior to, or during, eruption and thus does not reflect pre-eruptive conditions within the magma chamber. Modeling in alphaMELTS using whole rock geochemistry and biotite Fe-Mg compositions by Bucholz et al. (2018) were used to calculate fO_2 values for the SPG samples (HP21C, HP44A, SP-16-52). This method was also used for sample SNB-16-9 from the HLMC (Lewis et al., 2021). For samples HP44A and SP-16-52 the average value determined using this method was used for our calibration, however, the values predicted for sample HP21C were poorly defined (from FMQ-1.4 to FMQ+1.1), so the maximum value was used instead. For comparison, the minimum value determined for sample HP44A, also from the Harney Peak granite, was FMQ+1.45. The fO_2 of the Ecstall pluton was estimated to be FMQ+1 $\pm$ 1 based on the occurrence of titanite, which typically only forms at elevated oxygen fugacities (Xirouchakis & Lindsley, 1998; Loucks et al., 2020).

In Fig. 18a, the data were fit using a linear approximation (Equation 3) to provide an empirical relationship between U M₄-edge E_{wl} and the fO_2 of a sample:

$$\Delta FMQ = \frac{(E_{wl} - E_{FMQ=0})}{slope} \quad (3)$$

where E_{wl} is the white-line energy of the spectra (in eV). Since measured E_{wl} values can vary slightly between beamlines, the E_{wl} of FC-1 zircon can be used as a reference to define

$E_{\text{FMQ}=0}$ in Eq. (3), and ΔFMQ values can be calculated from the difference between the E_{wl} of FC-1 zircon and the unknown. For the beamline used in this work (APS 13-IDE), the best fit takes the form:

$$\Delta\text{FMQ} = \frac{(E_{\text{wl}} - 3726.65)}{0.45} \pm 1.0 (2\sigma) \quad (4)$$

A linear approximation provides a good fit to the data; however, it is expected that below a particular $f\text{O}_2$ all U in zircon would be present as entirely U^{IV} and above a particular $f\text{O}_2$ all U would be present as U^{VI} . As such, this model is only able to predict ΔFMQ values within this interval. From Equation (4) and the approximate edge energies of the various U valence states (Fig. 8), the range of $f\text{O}_2$ values over which this model is applicable is FMQ-1 to FMQ+3.5. These values correspond to 3726.2 eV and 3728.2 eV, which are the energies determined for the U^{IV} and U^{VI} edges, respectively. It should be noted, however, that the lowest and highest white-line energies of individual zircon grains are slightly below and above these values (at 3726.0 ± 0.18 eV and 3728.3 ± 0.18 eV; Fig. 8) but are within uncertainty of the nominal edge energies for U^{IV} and U^{VI} . These slight differences in energy may arise due to crystallographic effects, which can lead to variations in white line energy on the order of ~ 0.1 eV (Fig. 15). As such, zircon with white-line energies less than the nominal U^{IV} E_{wl} (3726.2 eV) or greater than the U^{VI} E_{wl} (3728.2 eV) should be treated as having crystallized at an oxygen fugacity equal to or below FMQ-1 or equal to or above FMQ+3.5, respectively. Importantly, while this approach can only predict ΔFMQ values over a limited range, the interval over which this model is valid encompasses the expected redox states of most zircon-bearing magmas. Should U valence be determined using a different technique (for example U L_3 -edge XANES), a more general formalism, relating U valence in zircon to ΔFMQ , would be useful. Such a relationship is provided in Equation 5 below (see Fig. 18b):

$$\Delta\text{FMQ} = 3.07 \ln \left(\frac{U^{n+} - 3.54}{0.53} \right) - 1 \quad (5)$$

Having thus calibrated the system, we then use Eq. (4) to calculate $f\text{O}_2$ values for the zircon samples for which no robust oxygen fugacity estimates were available. The minimum and maximum ΔFMQ values calculated for zircon grains from each of these samples are given in Table 6. Since the variation between E_{wl} and ΔFMQ in our model is linear, the relative difference in $f\text{O}_2$ between samples is similar to the differences in E_{wl} shown in Fig. 8. For example, zircon from the Long Valley Caldera (MC18-2 and MC18-4) have the highest E_{wl} values amongst our samples, with spectra indicative of an almost entirely U^{VI} composition and return $f\text{O}_2$ values at the upper limit of our model (FMQ+3.5).

On the low end, zircon from the syenite samples (91500/KL and Pacoima Pegmatite) return fO_2 values of $\sim$ FMQ and have an average valence of $U^{4.3+}$. We note that our fO_2 estimate for the 91500 zircon is greater than the estimate of Loucks et al. (2020) (FMQ to FMQ+0.5 vs FMQ-1.4, respectively), however, in their model U is assumed to occur almost entirely in the tetravalent state, which we have shown is not the case for this sample. Modification of the Loucks et al. (2020) model to account for a greater proportion of oxidized U in 91500 zircon would result in an increase in the predicted fO_2 , bringing our estimates into better agreement (from FMQ-1.4 to FMQ+0.1).

The oxygen fugacity values we determine for suites of related rocks reveal interesting differences in the redox behavior of these systems. Samples from the DIC (Buchholz et al., 2014, 2017) have tightly clustered white-line energies and range from FMQ-0.5 to +0.5 for this sample suite as a whole ($n=26$). This result is striking as the Dariv zircon were separated from diverse lithologies within the complex, including monzonites, a lamprophyre dike, and a felsic dike. Samples from the Whitney Intrusive Suite in the southern Sierra Nevada (Table 6) also show similar redox states (FMQ-0.01 to +0.5, excluding one outlier at FMQ-1) despite differences in composition and crystallization conditions (Hirt, 2007). The similar fO_2 amongst samples from these two suites suggests that the redox state of these magmas underwent little change during their emplacement and subsequent differentiation. In contrast, zircon samples from the HLMC (Lewis et al., 2021) record markedly different magma redox states between samples, ranging from FMQ-0.9 to +0.4 for the most reduced sample (HL-17-2), to FMQ+1.4 to +2.5 for the most oxidized sample (SNB-16-12). The HLMC samples also show a >1 log unit difference between the average fO_2 of the cumulate (FMQ+0.1) and liquid-like (FMQ+1.4) samples indicating evolving redox conditions within the HLMC. Overall, the fO_2 values we determine for the HLMC agrees well with the estimate of Lewis et al. (2021) for these rocks of $\sim$ FMQ+1 $\pm$ 1. While a thorough investigation into the redox behavior of these systems is beyond the scope of this study, these observations present a compelling direction for future work.

A potential complication to using U valence in zircon as a magma redox proxy is the variable partitioning behavior of U between zircon and melt, as $D_{U(IV)} > D_{U(V)} > D_{U(VI)}$, where $D_{U(i)}$ is the zircon-melt partition coefficient (Burnham & Berry, 2012; Mallmann et al., 2021). While the relationship between U valence and $D_{U(i)}$ warrants further exploration, in most cases the effect of differential partitioning between U ions on the estimated fO_2 should be minimal. Since U is a trace element in most igneous systems, its oxidation state should be buffered by the more abundant redox sensitive species (*e.g.*, Fe, C-O-H-S

gases/liquids), leading to a consistent U valence recorded by zircon for a given oxygen fugacity. However, in the case of zircon crystallization from small degree partial melts or low volumes of residual melt, the preferential uptake of U^{IV} may lead to an underestimation of fO_2 if the redox state of melt is not buffered (*i.e.*, the system is not in equilibrium). As an incompatible element, U concentrations in low degree melts are typically high, leading to correspondingly high concentrations of U incorporated into zircon. Thus, we recommend that care be taken when applying the U M_4 XANES oxybarometer to zircon with exceptionally high U concentrations (*e.g.*, >2000 ppm).

Our results show that U valence in zircon is a powerful proxy for magma redox. Given the near ubiquity of zircon in evolved igneous rocks and their extreme resistance to alteration, the use of U XANES to extract information on magma redox from zircon opens a new way of interrogating the rich zircon record that will allow for the fO_2 of crustal rocks to be reconstructed throughout most of Earth's history.

4.4 Intra-grains variations in U M_4 -edge spectra

The concentrations of uranium and other trace elements are known to vary within different growth zones of the same zircon crystal due to evolving conditions in the crystallizing melt. The small analytical spot size (1-5 μm) of XANES measurements enables probing of individual growth zones within a zircon crystal and thus allows for their interrogation on an intra-grain level. To explore how U oxidation state can vary within a single zircon, measurements were made at several points across individual FCT zircon grains as these crystals typically have complex growth patterns and oscillatory zonation in CL images. Analysis locations and their corresponding spectra for two FCT grains are shown in Fig. 19. Across these transects both crystals show a decrease in U oxidation state from the core to the rim of the crystal. While zircon FCT_2-1 in Fig. 19 contains an antecrystic (or xenocrystic) core analyzed at point A (which may not reflect conditions of the erupted Fish Canyon Tuff liquid), a general rim-ward decrease in U^{n+} is observed amongst most of the FCT zircon analyzed in this study. Fig. 20a shows the average U valence of individual spot locations plotted against the location of the analysis point for five FCT and eight FC-1 zircons. The location is plotted as the fractional distance of the measurement point along a line from the center of the grain to the edge of the crystal (Fig. 20b). This quantity is used to serve as a rough approximation of the zircon growth stage that each analysis targeted. From the core rim-ward, FCT zircon show a general decrease in average U valence, although there is an increase in variability at the grain rims. FC-1

zircon on the other hand, appear homogenous in CL images and likewise show little variation in U^{n+} with distance from the center of the grain. The spread in U oxidation states at FCT grain edges may be the result of sampling zircon that completed their growth at different stages of magmatic evolution, or which completed their growth in different locations within the magma chamber if the entire melt was not in equilibrium. For example, grains with a greater abundance of oxidized U at their margins could have grown from a melt which had interacted with oxidizing fluids in the near surface just prior to or during eruption. During the main stage of zircon growth, however, the parental melt to the FCT zircon grains appears to have been evolving towards a more reduced state. [Cottrell et al. \(2021\)](#), and references therein, show that degassing of a C-O-H-S vapor from a magma chamber can lower fO_2 and may explain the general rim-ward decrease in U oxidation state observed in FCT zircons. There is still much to be explored regarding intra-grain variations in U oxidation states and the possible driving mechanisms, but this exercise shows that U XANES can be used to gain insight into the crystallization history of single zircon grains and can elucidate redox changes occurring within an individual magma body during its evolution.

4.5 Variation in U valence between coexisting phases

Samples with coexisting U-bearing accessory phases show differences in the U valence of the different minerals. Minerals from the FCT show the greatest variability between phases with E_{wl} varying across 1.25 eV from 3727.55 eV ($\sim U^{5+}$) for zircon, to 3726.3 eV (entirely U^{IV}) for titanite, while the E_{wl} of apatite is intermediate at 3726.9 eV ([Fig. 21](#)). Zircon and baddeleyite from FC-1 are also distinct in their peak positions with baddeleyite having a slightly higher proportion of oxidized U relative to zircon ([Fig. 8](#)). The variability in white line energy observed between zircon and coexisting apatite or baddeleyite may either reflect a preference for a particular U oxidation state in these minerals (similar to titanite incorporating only reduced U), or crystallization of these phases during different stages of magmatic evolution. One possibility, for instance, would be that early crystallization of titanite, which only incorporates U^{IV} , could modify the average U valence of in the parental melt, and thus that recorded by the zircon. A simple mass balance calculation shows that this hypothesis is unlikely. For instance, FCT samples contain $\sim 0.5\%$ titanite, with titanite and whole rock U concentrations of 50-100 ppm and 4-5 ppm, respectively ([Bachmann et al., 2002](#); [Schmitz & Bowring, 2001](#)). This means that only between 5% and 12.5% of the total U content in the rock is hosted by titanite, a value

too small to have a noticeable effect on the valence of U incorporated into FCT zircon (at our current level of precision). Furthermore, if titanite crystallization were to impart a control on the U valence recorded by FCT zircon it would be expected to lower the proportion of U^{IV} and lead to progressively higher valence U incorporated into zircon as crystallization progresses (assuming co-crystallization of these phases). However, an opposite trend is observed in the FCT, with E_{wl} decreasing from the core rim-ward for most zircon grains (Fig. 19). As a trace element, U concentrations in crustal rocks are low, generally between 1-10 ppm, and thus, its redox state may be buffered by more abundant species (*e.g.*, Fe, H_2O , and C-O-H-S gases) if only a particular oxidation state is removed during crystallization. While the impact of titanite crystallization on U valence in zircon appears minimal for the FCT, this may not be the case for all samples. For example, if zircon and titanite co-crystallize within isolated melt pockets or from low-degree partial melts, titanite may impart a stronger effect on zircon U valence. As such, future work examining the relationship between U valence in these phases from a more diverse set of lithologies should be undertaken.

4.6 Implications for U isotope fractionation

Solution measurements of $^{238}U/^{235}U$ in pooled zircons fractions (100s-1000s of single crystals) (Hiess et al. 2012, Livermore et al., 2018) and single grains (Tissot et al., 2019) show variability in $\delta^{238}U$ of ~ 0.6 ‰, with even greater fractionations (up to 4.8 ‰) between zircon and titanite from the same sample. Laser ablation MC-ICPMS data show a similar spread in zircon, and an even larger range in titanite, from -3.5 ± 2.2 ‰ to $+13.1 \pm 3.4$ ‰ (Yamamoto et al., 2021). These variations indicate the presence of significant uranium isotope fractionations during magmatic processes, whose origin are currently unconstrained. For heavy elements such as uranium, equilibrium isotope fractionations can be driven by: 1) difference in coordination environments, for instance between crystals and melt, with heavy isotopes concentrating where coordination numbers are low and valence is high, or 2) changes in the size and shape of the atomic nucleus between odd and even-numbered isotopes, known as the nuclear field shift effect (NFSE), resulting in isotopes with odd numbers of neutrons behaving as if they had a smaller mass, which for U leads to preferential incorporation of heavy isotopes in reduced species (Bigeleisen, 1996a, 1996b). While the magnitude of the effects seen in titanite almost certainly indicates a kinetic origin for some U isotope fractionations (Tissot & Ibanez-Mejia, 2021), the more subtle variations seen in zircon could be redox driven. As such, future work performing coupled

investigation of U-isotope fractionation and U speciation in zircon from different samples and between zircon and coexisting accessory phases may help elucidate the driver of high-temperature U-isotope fractionation.

5. CONCLUDING REMARKS

We conducted a systematic investigation of the oxidation state of uranium in several important U-bearing accessory phases using U M₄-edge XANES. The data (Figs. 6 to 8) reveals that zircon, apatite, and baddeleyite can contain multivalent uranium, while titanite contains only U^{IV}. The garnet samples investigated herein also appear to only contain U^{IV}, but this may not be the case for all types of garnet as only two grains of similar composition were analyzed. Of the minerals we investigated, zircon shows the greatest variability in the proportions of the different U oxidation states it can incorporate, with spectra indicative of nearly pure U^{IV}, U^V, and U^{VI} compositions as well as mixtures of these species.

The potential effects of systematic biases on zircon U M₄-edge white-line energies were investigated. Repeat measurements on the same spot shows that beam damage does not affect U oxidation states in zircon (Fig. 5), while rotation tests indicate that crystallographic effects (*i.e.*, sample orientation) have a minimal effect on the measured E_{wl} of U M₄-edge spectra (Fig. 15). Similarly, comparison of Raman peak width vs. zircon Uⁿ⁺ indicates that radiation damage also has little effect on U M₄-edge spectra (Fig. 16). Instead, our results show that the U M₄-edge E_{wl} (and Uⁿ⁺) of zircon samples is strongly correlated with the parental magma fO_2 , indicating that U oxidation states in zircon as determined by XANES can be used as a tracer of magma redox (Fig. 18).

This new approach has several advantages over other zircon-based oxybarometers that use Ce and other trace element concentrations to infer magma redox states (*e.g.*, Trail et al. 2011; Smythe & Brenan, 2016; Loucks, 2020). First, the concentration of trace elements in zircon can vary due to a variety of factors other than oxygen fugacity, such as melt composition and temperature (*e.g.*, Zou et al., 2019; Loader et al., 2022). In particular, Loader et al. (2022) showed that increases in Ce-anomalies, which form the basis of several zircon oxybarometers, can occur due to cooling at constant fO_2 or due to the presence of certain co-crystallizing phases. Second, these methods can rely on difficult to constrain parameters such as the activity of H₂O or melt polymerization (*e.g.*, Smythe & Brenan, 2016). Third, they often require the composition of the melt be known or estimated from whole rock compositions (Trail et al., 2011; Smythe & Brenan, 2016). Lastly, the oxidation

state of U is assumed to be exclusively tetravalent in the model formulations of the [Smythe & Brenan \(2016\)](#) and [Loucks et al. \(2020\)](#) oxybarometers, which we show here is not the case, leading to a misestimation of fO_2 for zircon containing oxidized uranium. XANES, on the other hand, is a direct measure of an element's oxidation state and should be more closely related to melt fO_2 compared to element concentrations. Since U is typically present in sufficient amounts to produce reliable spectra for most zircon crystals (100s of ppm or more), this technique is widely applicable to most zircon-bearing lithologies and even single detrital zircon crystals. Furthermore, U XANES does not necessitate knowledge of the host rock composition, so this approach could be particularly useful for studies of zircon that have been removed from their original context, such as in detrital settings. Additionally, the small analytical spot size ($<2\mu\text{m}$) and non-destructive nature of XANES make this method amenable to investigating magma redox changes within individual zircon growth zones and allows this technique to be used in conjunction with other *in situ* zircon methods (*e.g.*, LA-ICPMS, SIMS). In summary, U M_4 -edge XANES analysis of zircon can provide a reliable and straightforward method for interrogating magma redox conditions from the global scale to that of a single pluton or eruption, and throughout Earth's history from the Hadean to the present.

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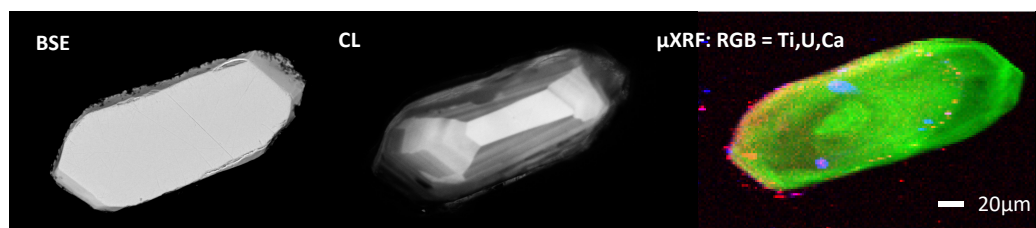


Figure 1. Example of imaging methods used prior to XAS analysis. All images are of zircon sample Ec_zrc_2-3 from the Ecstall pluton. The μ XRF map visualizes the Ti K α , U L α , and Ca K α emission intensities.

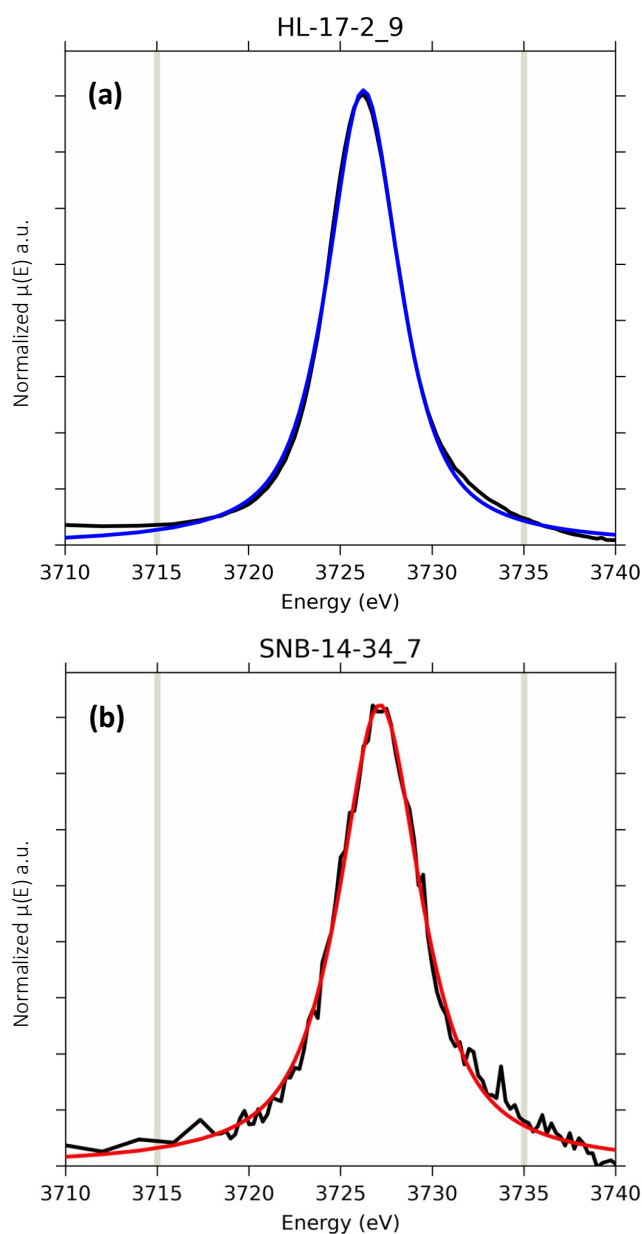


Figure 2. Examples of normalized U M₄-edge spectra (black lines) and best fit curves for zircon grains with **(a)** high U concentrations (blue line: HL-17-2_9 ~5000 ppm U) and **(b)** low U concentrations (red line: SNB-14-34_7 ~100 ppm U). Vertical lines show the bounds of the fit.

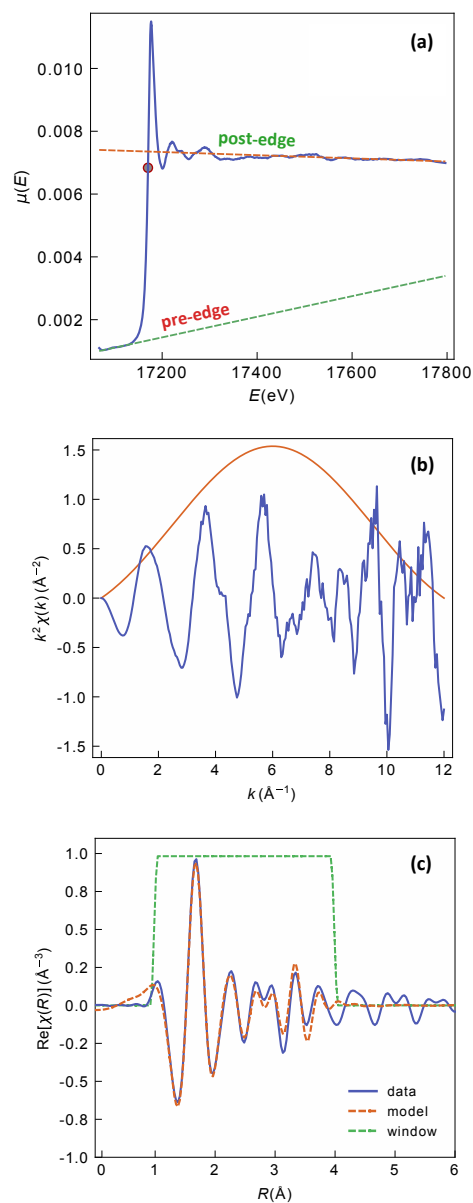


Figure 3. Example of U L_3 -edge normalization and EXAFS data processing for zircon FCT 2-1. **(a)** Raw $\mu(E)$ with the pre- and post-edge functions used for normalization. **(b)** Extracted EXAFS oscillations and window used for the Fourier transform. **(c)** Data and best fit from FEFF modeling.

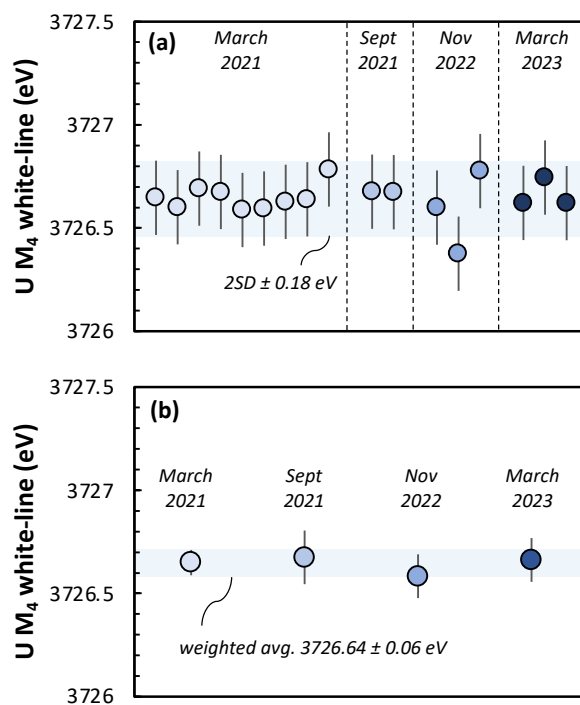


Figure 4. (a) White-line energy of individual FC-1 zircon grains measured during each analysis session. Colored bar represents the ± 2 SD uncertainty of the data across all sessions (± 0.18 eV). (b) Average white-line energies of FC-1 zircon measured during each analysis session. Vertical error bars are the 2 SE uncertainty for that analysis session.

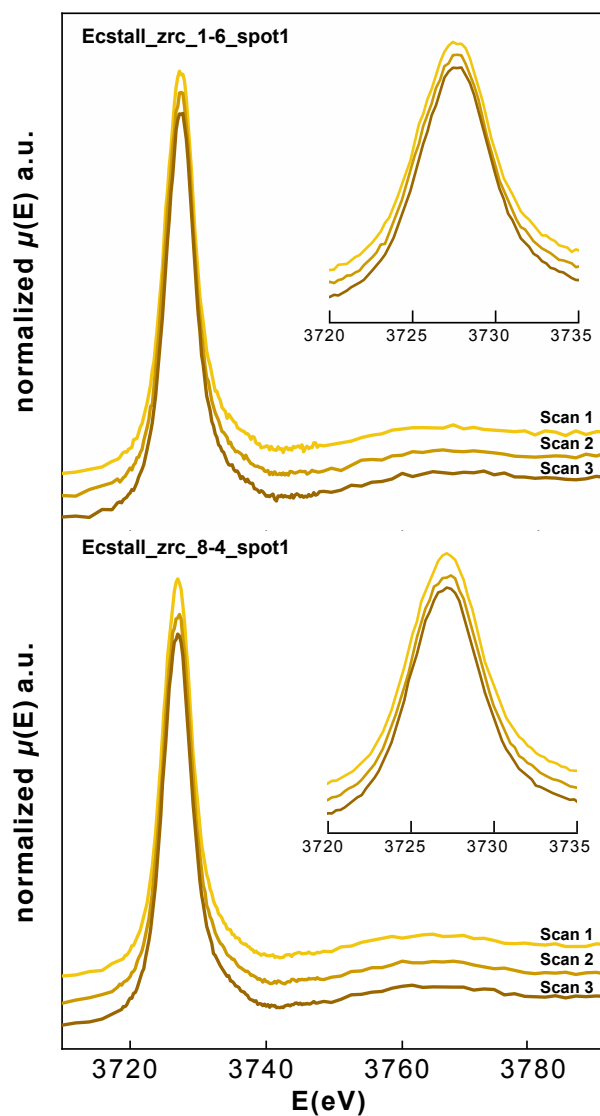


Figure 5. Results of repeated XANES scans at the same location for two zircon grains. The variation in fitted E_{wl} varies by ± 0.04 eV (2 SD) between the three scans indicating that beam damage does not affect U oxidation states in zircon.

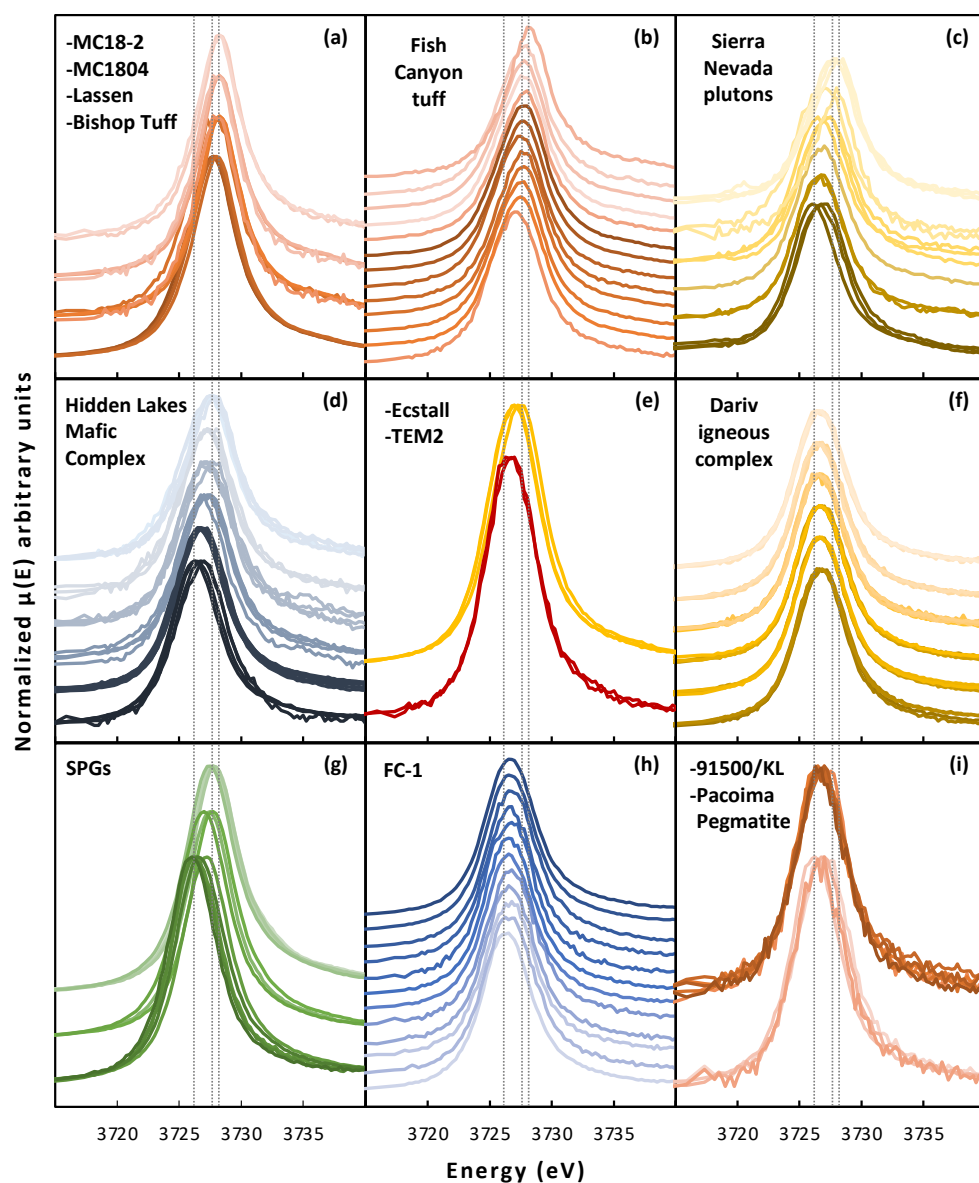


Figure 6. Normalized U M₄-edge spectra for all zircon grains. Dotted lines show the approximate edge energies of the U^{IV}, U^V, and U^{VI} ions (from left to right, respectively). From top to bottom: **(a)** MC18-04, MC18-02, LF042-02, Bishop Tuff; **(b)** Fish Canyon Tuff; **(c)** Bullfrog, Dragon, Independence, Mt. Whitney, Lone Pine, Paradise; **(d)** SNB-16-12, SNB-16-9, SNB-14-34, SNB-16-6, SNB-14-40, HL-17-2; **(e)** Ecstall, TEM2; **(f)** MO-11-14, MO-11-12, MO-11-16, MO-11-19, MO-11-23, MO-11-26; **(g)** HP44A, HP21C, SP-16-52; **(h)** FC-1; **(i)** 91500/KL, Pacoima Pegmatite.

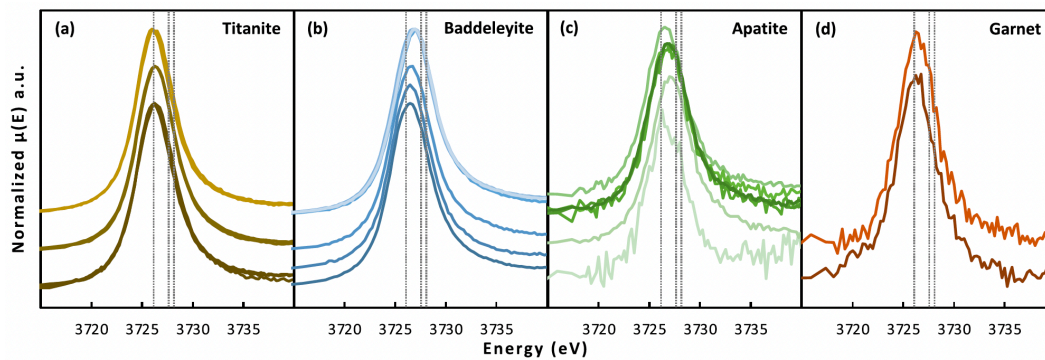


Figure 7. Normalized U M₄-edge spectra for all titanite, baddeleyite, apatite, and garnet grains. Dotted lines as in Fig. 5. From top to bottom: **(a)** BLR-1, Ecstall, Fish Canyon Tuff; **(b)** FC-1, Kovdor, Phalaborwa, Burma; **(c)** Durango, Fish Canyon Tuff, MAD2, McClure; **(d)** Jumbo Black, KI-88.

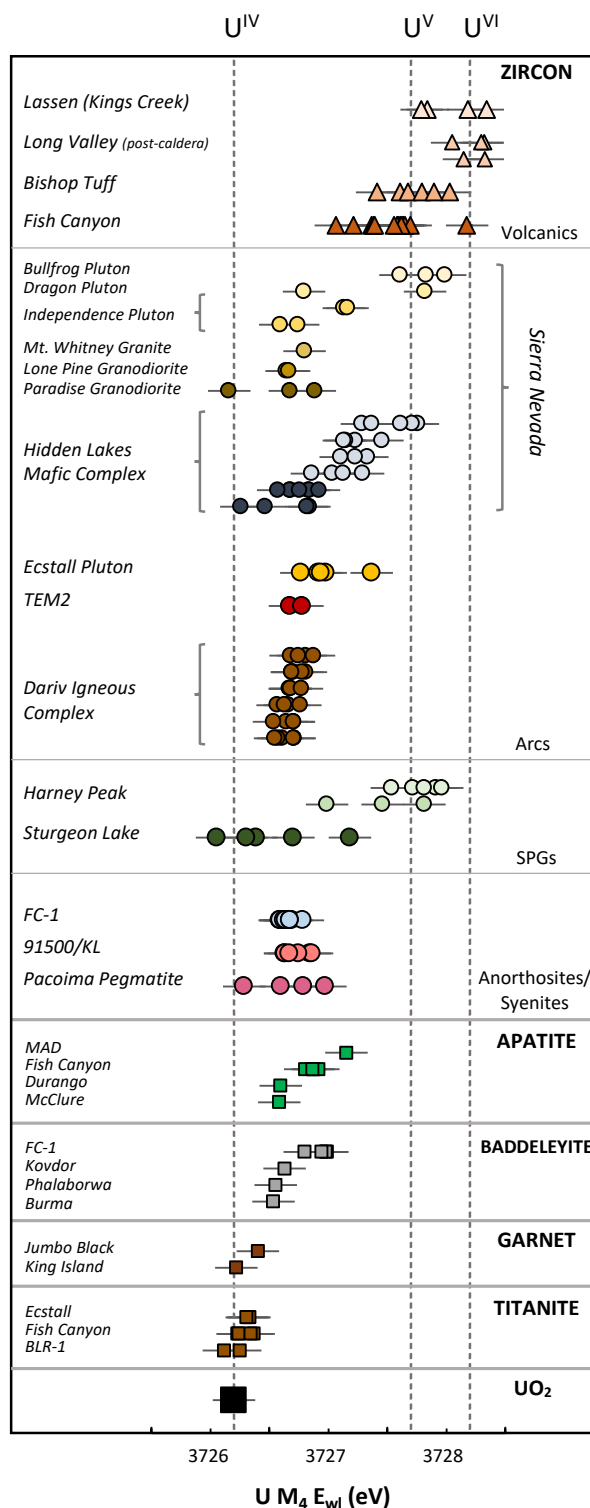


Figure 8. U M₄-edge white-line energy of all samples analyzed in this study. Data points represent the average white-line energy of all spectra collected for an individual grain. Horizontal error bars are the 2 SD uncertainty of the peak position (± 0.18 eV). Vertical dashed lines show the approximate edge energies of the U^{IV} , U^V , and U^{VI} ions.

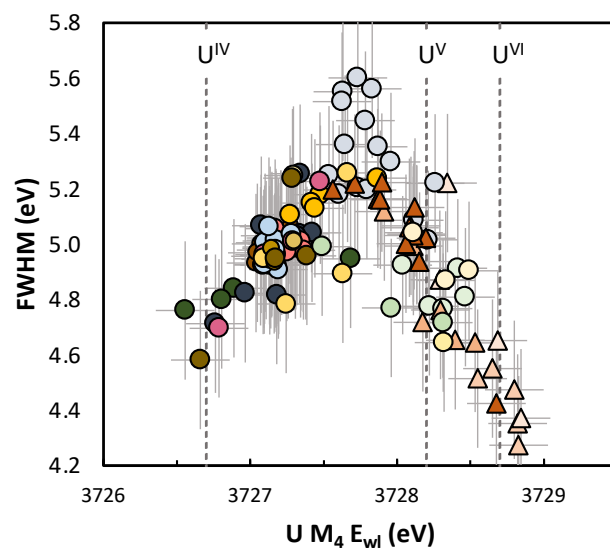


Figure 9. Variation in U M₄-edge FWHM with white-line energy for zircon samples. Symbols as in Fig. 8.

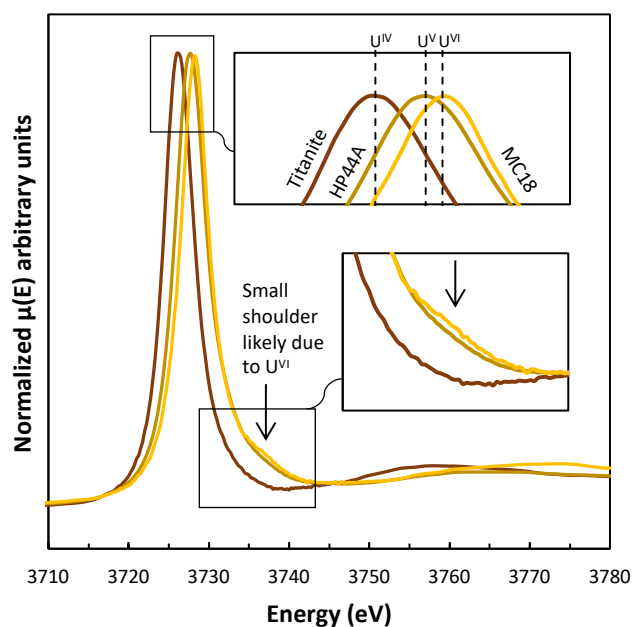


Figure 10. Example spectra for samples with dominantly U^{IV} , U^V , and U^{VI} compositions: titanite (all samples), HP44A (zircon), MC18 (zircon), respectively. Spectra are averages of all scans collected for that sample and represent multiple grains. Note the small shoulder in the MC18 spectrum indicative of U^{VI} .

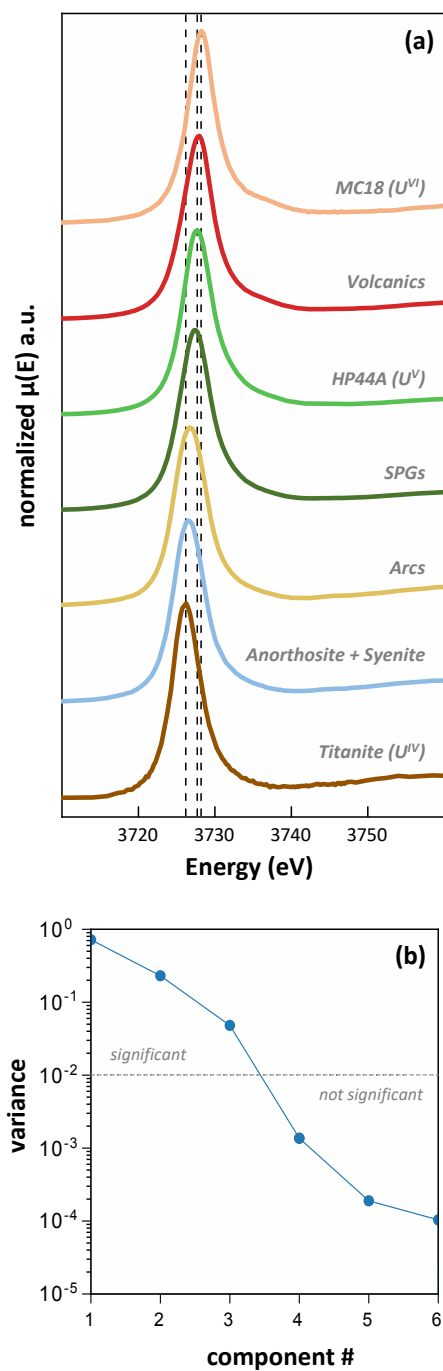


Figure 11. (a) Average U M4-edge spectra used for principal component analysis. PCA was performed from 3710-3790 eV, a smaller energy range is plotted to highlight differences in E_{wl} . **(b)** Example SCREE plot showing the variance of the components.

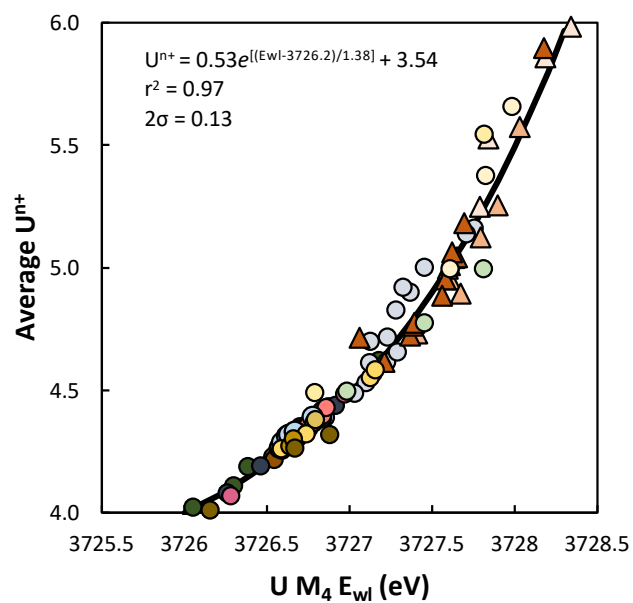


Figure 12. Variation in average U^{n+} with E_{wl} for individual zircon samples. Black line is the best fit to the data given by Eq (2). Symbols as in Fig. 8.

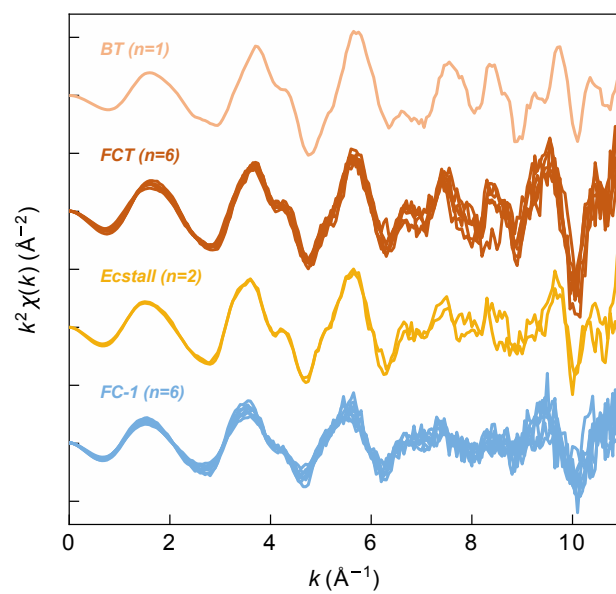


Figure 13. k^2 -weighted EXAFS $\chi(k)$ for individual zircon grains.

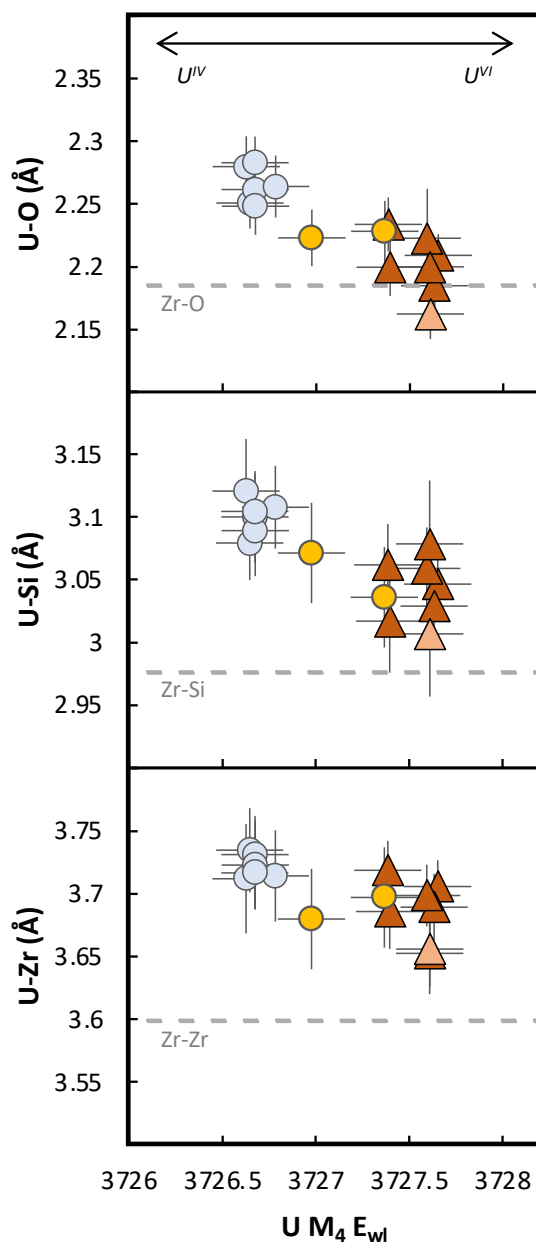


Figure 14. U-X interatomic distances determined from EXAFS analysis. From top to bottom: U-O, U-Si, U-Zr. Dashed lines indicate the reference Zr-X distances. Symbols as in Fig. 8. (FC-1: blue circle; Ecstall: orange circle; FCT: red triangle; BT: pink triangle).

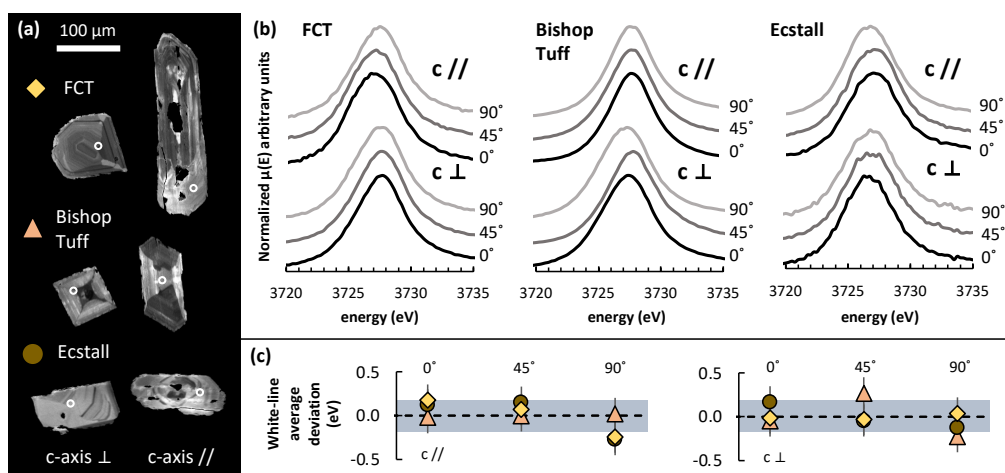


Figure 15. (a) CL images of grains analyzed to test the effect of crystallographic orientation on U M₄-edge spectra. The right column are the grains mounted with their c-axis approximately parallel to the mount surface. White circle shows the location of the analysis spot. Image shows grains in the 0° orientation. (b) Spectra for FCT, Bishop Tuff, and Ecstall zircons collected at each orientation. (c) Average deviation from the mean white-line energy for each grain measured at each orientation. Symbols for each sample are shown in (a) FCT: yellow diamonds; Bishop Tuff: pink triangles; Ecstall: brown circles. Colored bar represents the ± 0.18 eV uncertainty (2 SD) of the white-line energy.

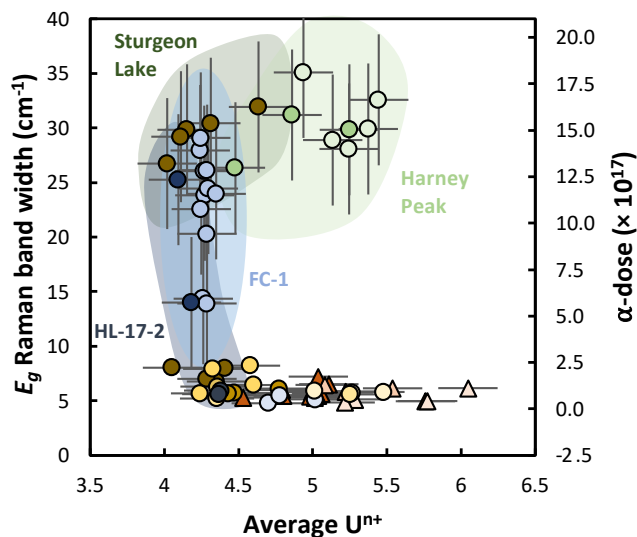


Figure 16. Raman peak width/ α -dose vs. average U valence. α -dose calculated using the method of Härtel et al. (2022). Symbols are the same as in Fig. 7. Horizontal error bars are the 2 SD uncertainty on the U valence (± 0.2 eV), vertical error bars are the average 2 SD uncertainty of the Raman peak width (6 cm^{-1} for grains with peak width $>10 \text{ cm}^{-1}$ and 0.4 cm^{-1} for grains with peak width $<10 \text{ cm}^{-1}$). Symbols as in Fig. 8.

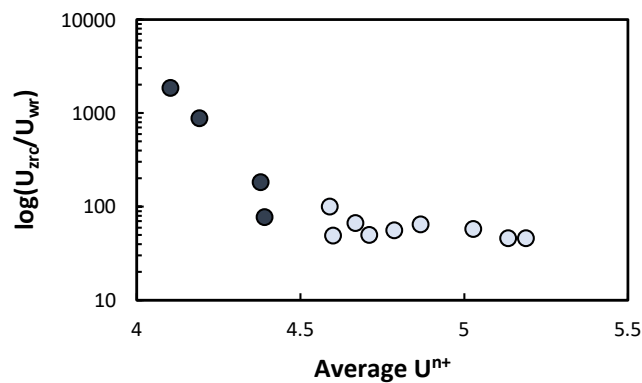


Figure 17. Uranium partitioning between zircons and host rock for HLMC samples. HL-17-2 (anorthosite, dark blue circles) and SNB-14-34 and SNB-16-12 (monzodiorites, light blue circles). The U valence of HL-17-2 zircons decreases systematically with increasing U concentration indicating a preference for U^{IV} over $U^{V/VI}$ in the zircon structure.

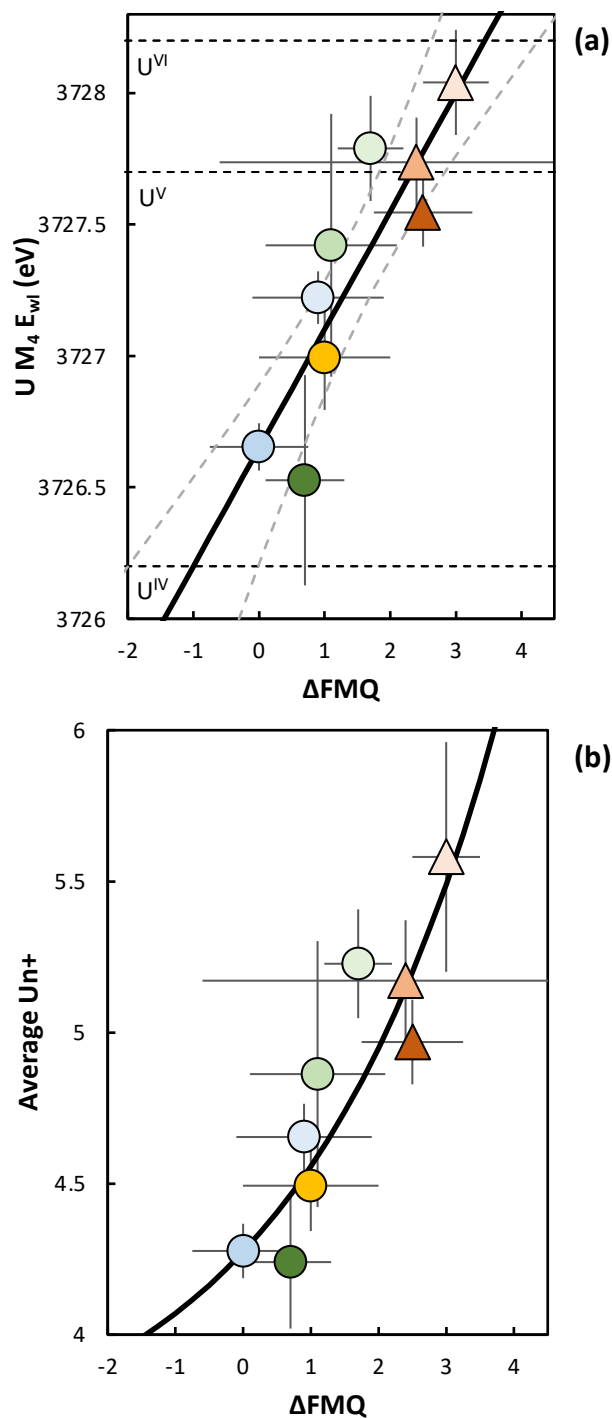


Figure 18. Variation in oxygen fugacity relative to the FMQ buffer with (a) $U M_4 E_{wl}$ and (b) average U^{n+} . Vertical error bars are the 2 SE for each sample. Horizontal error bars are from the published fO_2 estimates given in Table 5. Dashed line in (a) shows the 95% confidence interval of the fit. Symbols as in Fig. 8.

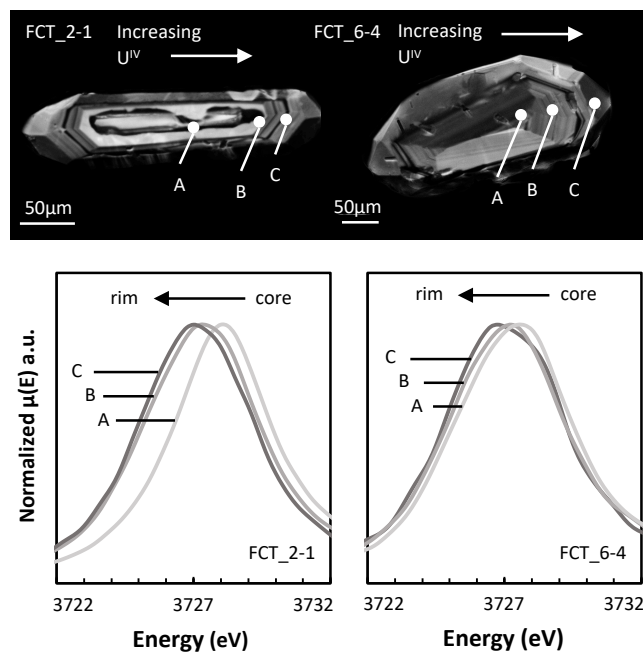


Figure 19. CL images for two FCT zircons and their corresponding spectra collected along a transect parallel to the c-axis. Both crystals show a rim-ward decrease in white-line energy.

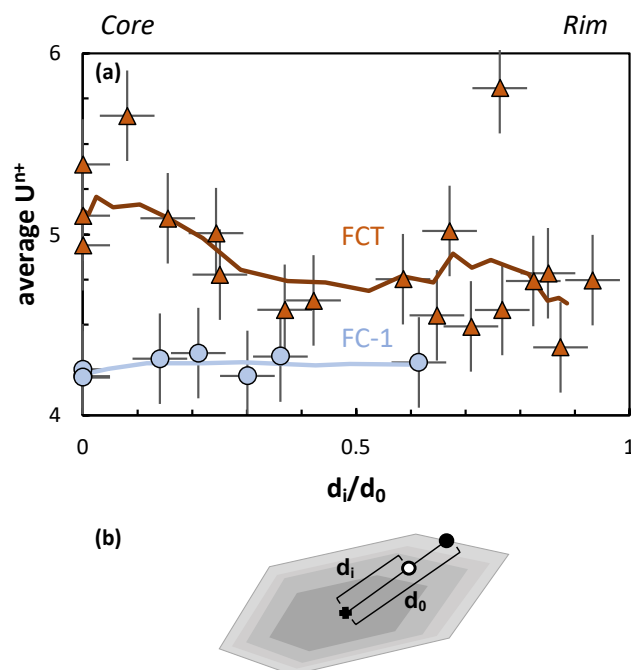


Figure 20. (a) Variation in U valence for FCT and FC-1 zircon plotted against the fractional distance from the approximate center of the grain. Only FCT samples with multiple spot locations are shown. Solid lines are the moving average of the data points ($n=5$). **(b)** Cartoon illustrating formulation of the fractional distance plotted in (a).

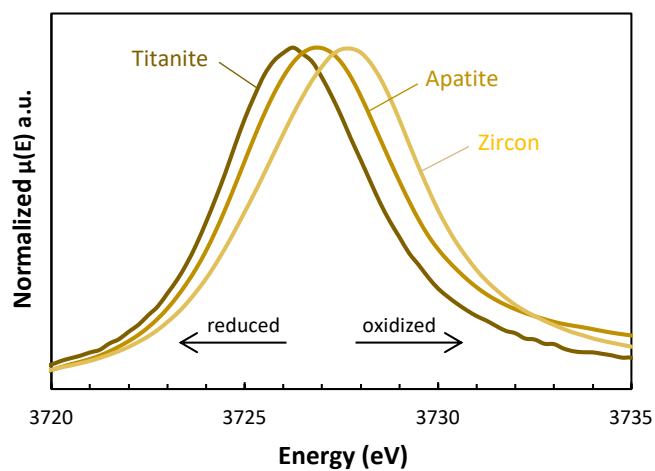


Figure 21. Average U M₄-edge spectra for titanite, apatite, and zircon from Fish Canyon Tuff.

Table 1. List of samples analyzed in this study along with their host lithology, age, and the analyzed phases.

SAMPLE	LITHOLOGY	AGE (Ma)	PHASES (n = # grains)	REF.
Volcanics				
Lassen (LF042-02)	<i>rhyodacite</i>	0.035	zircon (n=4)	1
Long Valley (MC18-02,04)	<i>pumice/ rhyolite</i>	0.1-0.16	zircon (n=5)	2
Bishop Tuff (BT)	<i>ignimbrite</i>	0.76	zircon (n=6)	3,4
Fish Canyon Tuff (FCT)	<i>dacite</i>	28.4	zircon (n=15), titanite (n=4), apatite (n=4)	5
Arcs				
<u><i>Sierra Nevada Plutons</i></u>				
Mt. Whitney granite (W-35)	<i>granite</i>	85.3	zircon (n=1)	6,7
Paradise granodiorite (KC-17,-19)	<i>granodiorite</i>	87	zircon (n=4)	6,7
Lone Pine granodiorite (LP-9)	<i>granodiorite</i>	89.8	zircon (n=2)	6,7
Dragon pluton (Dragon1)	<i>granodiorite</i>	102	zircon (n=3)	6,7
Bullfrog pluton (14BF-2, 3)	<i>granite</i>	102.3	zircon (n=3)	6,7
Independence pluton (11SN15,31)	<i>granite</i>	100.5-104	zircon (n=4)	6,7
<u><i>Hidden Lakes Mafic Complex</i></u>				
HL-17-02	<i>anorthosite</i>	95.7	zircon (n=4)	8
SNB-14-40	<i>cumulate monzonite</i>	90.5	zircon (n=7)	8
SNB-14-34	<i>liquid-like monzodiorite</i>	96.5	zircon (n=4)	8
SNB-16-12	<i>liquid-like monzodiorite</i>	90.5	zircon (n=5)	8
SNB-16-6	<i>liquid-like monzodiorite</i>	95.1	zircon (n=3)	8
SNB-16-9	<i>liquid-like monzonite</i>	95.6	zircon (n=4)	8
<u><i>Dariv laneous Complex</i></u>				
MO-11-12	<i>monzogabbro</i>	502	zircon (n=4)	9
MO-11-14	<i>monzodiorite</i>	502	zircon (n=4)	9
MO-11-16	<i>felsic dike</i>	502	zircon (n=5)	9
MO-11-19	<i>lamprophyre dike</i>	502	zircon (n=5)	9
MO-11-26	<i>quartz monzonite</i>	502	zircon (n=4)	9
MO-11-23	<i>monzonite</i>	502	zircon (n=4)	9
Ecstall Pluton	<i>granodiorite</i>	91.5	zircon (n=5), titanite (n=3)	10
Temora II	<i>diorite</i>	416.8	zircon (n=2)	11
SPGs				
Harney Peak (HP44A, HP21C)	<i>granite</i>	1700	zircon (n=8)	12,13
Sturgeon Lake (SP-16-52)	<i>granite</i>	2671	zircon (n=5)	12
Anorthosites/ Syenites				
FC-1	<i>anorthosite</i>	1099	zircon (n=11), baddeleyite (n=4)	14,15
91500/ KL	<i>syenite</i>	1065.4	zircon (n=6)	16
Pacoima Canyon Pegmatite	<i>syenite</i>	1200	zircon (n=4)	17
Other accessory phases				
BLR-1	<i>metamorphic megacryst</i>	1047.1	titanite (n=2)	18
Jumbo Black	<i>skarn</i>	-	garnet (n=1)	-
King Island (KI-88)	<i>skarn</i>	-	garnet (n=1)	-
Durango	<i>volcanic iron deposit</i>	31.44	apatite (n=1)	19
McClure	<i>hbl-bt-syenite</i>	523.5	apatite (n=1)	20
MAD2	<i>carbonatite</i>	474.25	apatite (n=1)	21
Kovdor	<i>carbonatite</i>	379.1	baddeleyite (n=1)	22
Burma/Myanmar	<i>metamorphic belt</i>	35-24	baddeleyite (n=1)	23
Phalaborwa	<i>carbonatite</i>	2060.6	baddeleyite (n=1)	24

1) Underwood et al. (2012); 2) Hildreth (2004); 3) Hildreth & Wilson (2007); 4) Crowley et al. (2007); 5) Schmitz & Bowring (2001); 6) Chen & Moore (1982); 7) Moore (1963); 8) Hirt (2007); 9) Lewis et al. (2021); 10) Bucholz et al. (2014, 2017); 11) Butler et al. (2002); 12) Black et al. (2004); 12) Bucholz et al. (2018); 13) Nabelek et al. (1992); 14) Paces & Miller (1993); 15) Ibanez-Mejia et al. (2014); 16) Wiedenbeck et al. (1995, 2004); 17) Barth et al. (2001); 18) Aleinikoff et al. (2007); 19) Chew et al. (2016); 20) Schoene & Bowring (2006); 21) Thomson et al. (2012); 22) Rodionov et al. (2012); 23) Davies et al. (2019); 24) Reichmann et al. (1995).

Table 2. Published U M_4 E_{wl} values for the three U oxidation states compared with values from this study.
Values are in eV.

U^{IV}	U^V	U^{VI}	$(U^V - U^{IV})/(U^{VI} - U^{IV})$	Ref.
3725.0	3726.5	3727.0	0.75	Kvashnina & Butorin (2022)
3725.2	3726.4	3726.8	0.75	Leinders et al. (2017)
3724.5	3725.5	3726.2	0.6	Popa et al. (2016)
3725.1	3726.2	3726.7	0.7	Halse (2014)
3726.20	3727.70	3728.20	0.75	This study

Table 3. Average E_{wl} and U^{n+} for all zircon samples.

Sample	average E_{wl} (eV)	average U^{n+}
<i>Volcanics</i>		
LF042-02	3728.04	5.59
MC18-2	3728.22	5.85
MC18-4	3728.24	5.88
BT	3727.74	5.18
FCT	3727.55	4.98
<i>Arcs</i>		
Bullfrog	3727.81	5.26
Dragon	3727.31	4.81
Independence (11SN31)	3726.67	4.30
Independence (11SN15)	3727.15	4.60
Mt. Whitney	3726.80	4.37
Lone Pine	3726.66	4.29
Paradise	3726.57	4.26
SNB-16-12	3727.55	4.97
SNB-16-9	3727.22	4.66
SNB-14-34	3727.24	4.68
SNB-16-6	3727.08	4.56
SNB-14-40	3726.76	4.35
HL-17-2	3726.60	4.27
Ecstall	3726.99	4.50
TEM2	3726.73	4.33
MO-11-14	3726.78	4.36
MO-11-16	3726.74	4.33
MO-11-26	3726.66	4.29
MO-11-23	3726.65	4.28
MO-11-19	3726.63	4.27
<i>SPGs</i>		
HP44A	3727.79	5.24
HP21C	3727.42	4.87
SP-16-52	3726.53	4.25
<i>Anorthosites/Syenites</i>		
FC-1	3726.65	4.29
91500/KL	3726.73	4.33
Pacoima Pegmatite	3726.66	4.30

Table 4. Reference Zr-X bond lengths and best fit values for U-X bond lengths from EXAFS analysis of U substitution in zircon. All distances are in Å.

Sample	U-O	U-Si	U-Zr	sO2	eO
FCT 1.2-1	2.21 ± 0.02	3.05 ± 0.03	3.71 ± 0.02	0.80 ± 0.16	8.3 ± 1.7
FCT 1.1-7	2.18 ± 0.03	3.03 ± 0.03	3.69 ± 0.03	0.93 ± 0.27	5.7 ± 2.6
FCT 1.6-4	2.23 ± 0.02	3.06 ± 0.03	3.72 ± 0.02	0.87 ± 0.23	10.5 ± 2.0
FCT 1.6-7	2.22 ± 0.04	3.06 ± 0.03	3.70 ± 0.02	0.92 ± 0.24	8.0 ± 2.2
FCT 1.8-1	2.20 ± 0.02	3.08 ± 0.05	3.65 ± 0.03	0.64 ± 0.16	6.8 ± 2.5
FCT 2.1-1	2.20 ± 0.02	3.02 ± 0.04	3.69 ± 0.03	0.82 ± 0.22	6.9 ± 2.6
FC1 1.3-1	2.25 ± 0.02	3.08 ± 0.03	3.73 ± 0.03	0.65 ± 0.16	7.4 ± 2.0
FC1 1.4-5	2.26 ± 0.02	3.10 ± 0.04	3.73 ± 0.03	0.74 ± 0.17	8.5 ± 1.8
FC1 1.9-1	2.28 ± 0.02	3.12 ± 0.04	3.71 ± 0.04	0.69 ± 0.20	9.3 ± 2.1
FC1 1.10-7	2.26 ± 0.02	3.11 ± 0.03	3.71 ± 0.04	0.56 ± 0.17	7.9 ± 2.3
FC1 2.1-1	2.25 ± 0.02	3.09 ± 0.04	3.72 ± 0.04	0.80 ± 0.22	7.8 ± 2.1
FC1 2.2-1	2.28 ± 0.02	3.10 ± 0.03	3.72 ± 0.03	0.82 ± 0.22	10.9 ± 1.8
Ec 1-6	2.23 ± 0.02	3.04 ± 0.03	3.70 ± 0.03	0.90 ± 0.27	7.5 ± 2.4
Ec 2-3	2.22 ± 0.02	3.07 ± 0.04	3.68 ± 0.05	0.98 ± 0.37	6.4 ± 2.0
BT 1-3	2.16 ± 0.02	3.01 ± 0.05	3.66 ± 0.03	0.77 ± 0.22	3.8 ± 2.6
Average	U-O	U-Si	U-Zr		
FCT	2.21	3.05	3.69	-	-
FC-1	2.26	3.10	3.72	-	-
Ec	2.23	3.05	3.69	-	-
BT	2.16	3.01	3.66	-	-
	Zr-O	Zr-Si	Zr-Zr		
Reference^a	2.18	2.98	3.60	-	-

^a Hazen & Finger, 1979

Table 5. White-line energy, fO_2 estimate, method of fO_2 determination, and references used for calibration of the U M_4 -edge XANES oxybarometer in Fig. 18.

Sample	White-line (eV)	ΔFMQ	Method	Reference
LF042-02	3728.04	3.0 ± 0.5	Fe-Ti oxides	<i>Underwood et al. (2012)</i>
BT	3727.74	2.4 ± 3.1	Ce in zrc	<i>Trail et al. (2011, 2015)</i>
FCT	3727.55	2.5 ± 0.8	Fe-Ti oxides	<i>Johnson & Rutherford (1989)</i>
HP44A	3727.79	1.7 ± 0.5	Biotite Fe-Mg modeling	<i>Bucholz et al. (2018)</i>
HP21C	3727.42	1.1 ± 1.0	Biotite Fe-Mg modeling	<i>Bucholz et al. (2018)</i>
SNB-16-9	3727.22	0.9 ± 1.0	Biotite Fe-Mg modeling	<i>Lewis et al. (2021)</i>
Ecstall	3726.99	1.0 ± 1.0	Petrology	<i>estimate (titanite present)</i>
SP-16-52	3726.53	0.7 ± 0.6	Biotite Fe-Mg modeling	<i>Bucholz et al. (2018)</i>
FC-1	3726.65	0.0 ± 1.0	Fe-Ti oxides	<i>Pasteris (1985)</i>

To maintain consistency, published fO_2 values were recalculated as deviations from the fayalite-magnetite-quartz buffer (ΔFMQ) when necessary.

Table 6. fO_2 values of zircon samples* calculated using Eq. (3).

Sample		ΔFMQ min	ΔFMQ max
Long Valley Caldera			
MC18-2	$n=3$	+3.1	>+3.5
MC18-4	$n=2$	+3.3	>+3.5
Sierra Nevada			
Bullfrog Pluton	$n=3$	+2.1	+3.0
Dragon Pluton	$n=2$	+0.3	+2.6
Independence Pluton	$n=4$	-0.1	+1.1
<u>Whitney Intrusive Suite</u>			
Mt. Whitney granite	$n=1$	+0.3	+0.3
Lone Pine granodiorite	$n=2$	-0.01	+0.04
Paradise granodiorite	$n=4$	-1	+0.5
<u>Hidden Lakes Mafic Complex</u>			
SNB-16-12	$n=5$	+1.4	+2.5
SNB-14-34	$n=4$	+1.1	+1.8
SNB-16-6	$n=4$	+0.5	+1.4
SNB-14-40	$n=7$	-0.2	+0.6
HL-17-2	$n=4$	-0.9	+0.4
TEM2	$n=2$	+0.1	+0.3
Dariv Igneous Complex	$n=26$	-0.5	+0.5
91500/KL	$n=6$	0	+0.5
Pacoima Pegmatite	$n=4$	-1.0	+0.6

*samples used for calibration of Eq. (3) are excluded.

CHAPTER 2 APPENDIX 1

Zircon CL and μ XRF maps

Fig. S1. *Lassen (Kings Creek): LF042-02*

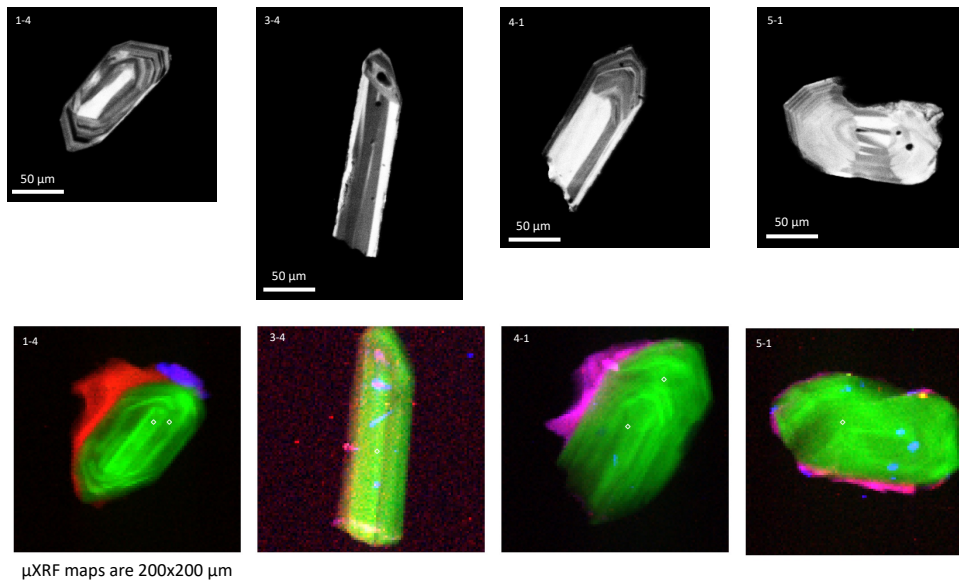
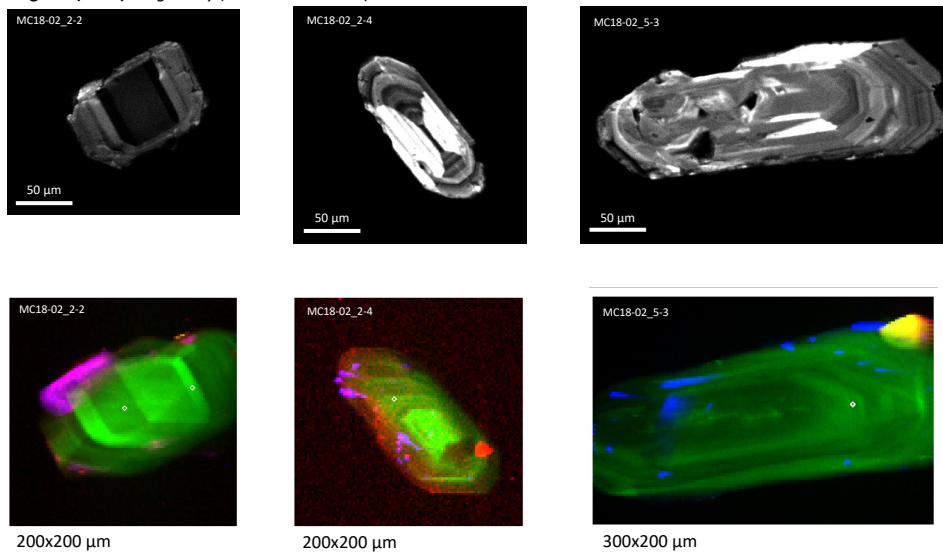
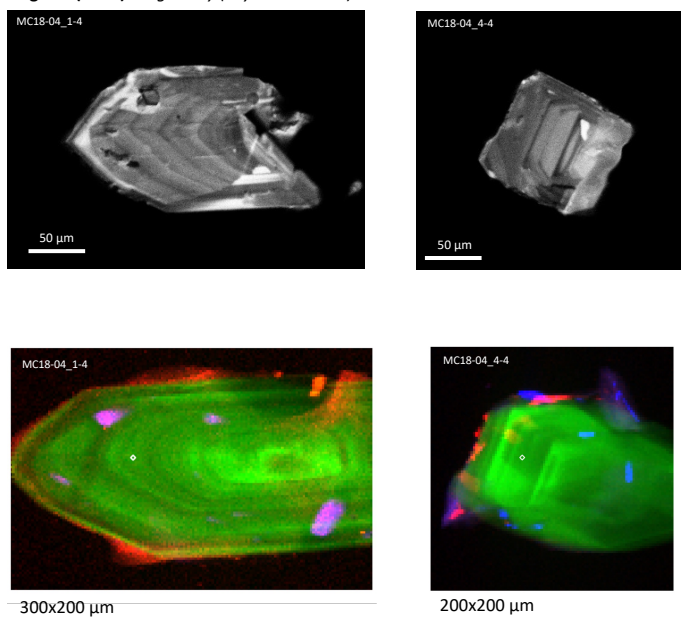


Fig. S1. (cont.) *Long Valley (West Moat Coulee): MC18-02*



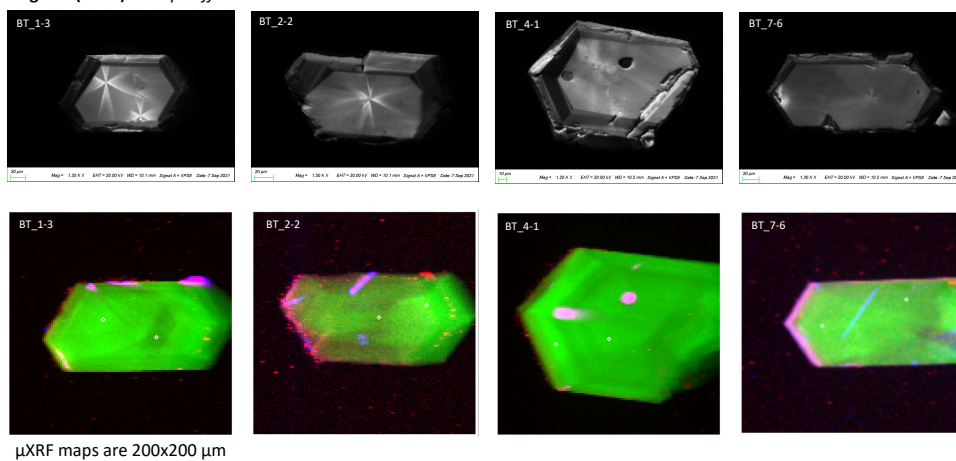
RGB: Ti ($K\alpha$); U ($L\alpha$); Ca ($K\alpha$)

Fig. S1. (cont.) Long Valley (Dry Creek Dome): MC18-04



RGB: Ti ($K\alpha$); U ($L\alpha$); Ca ($K\alpha$)

Fig. S1. (cont.) Bishop Tuff



μXRF maps are 200x200 μm

RGB: Ti ($K\alpha$); U ($L\alpha$); Ca ($K\alpha$)

Fig. S1. (cont.) Fish Canyon Tuff

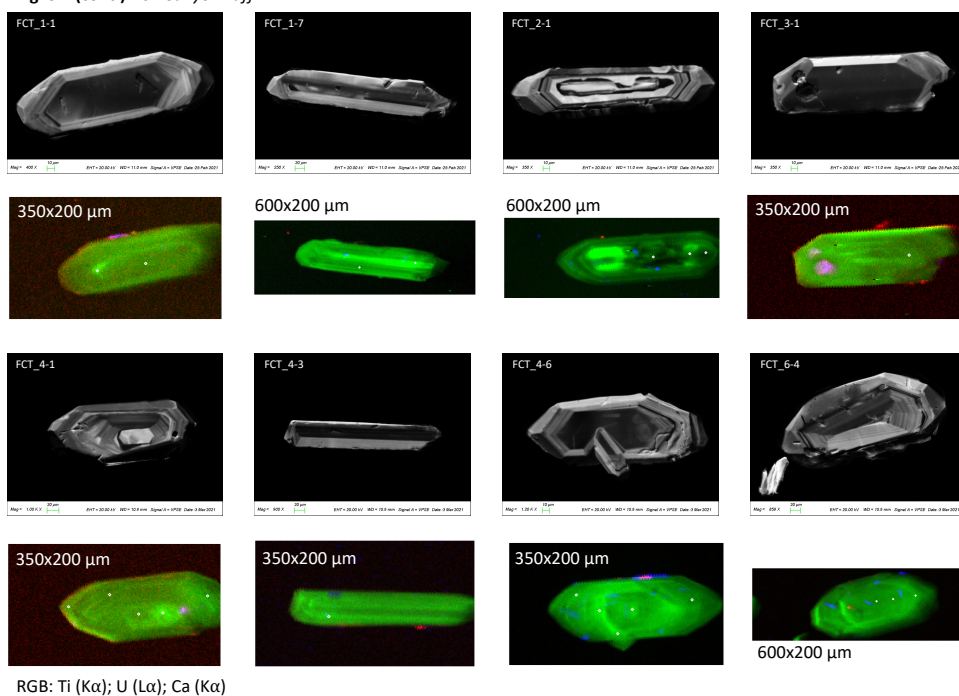


Fig. S1. (cont.) Fish Canyon Tuff (cont.)

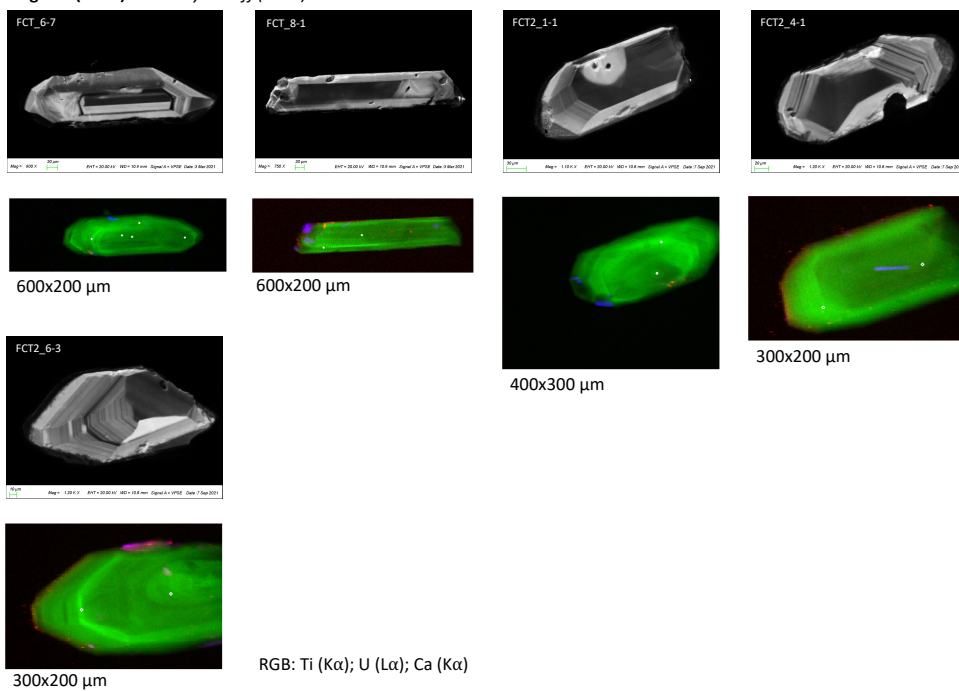
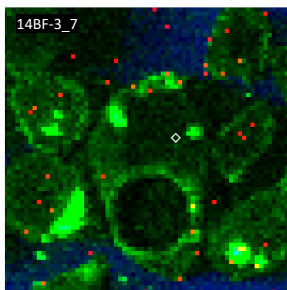
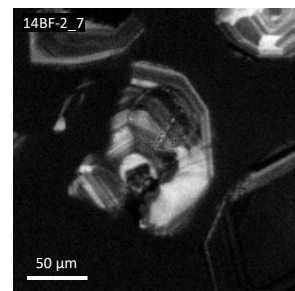
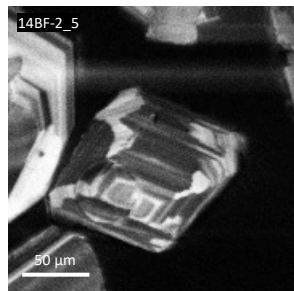
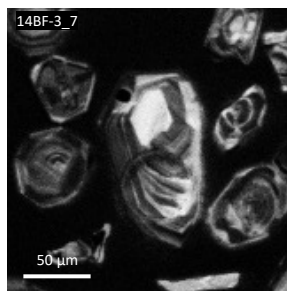
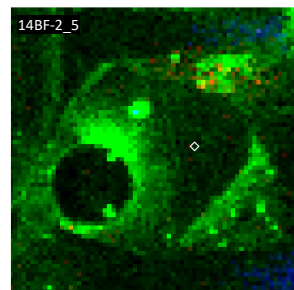


Fig. S1. (cont.) Bullfrog Pluton

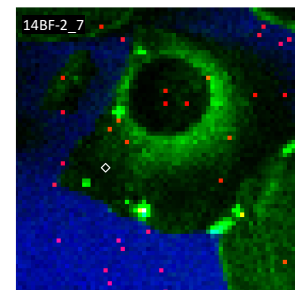


200x200 μm

RGB: Ti (Kα); U (Mβ); Ca (Kα)

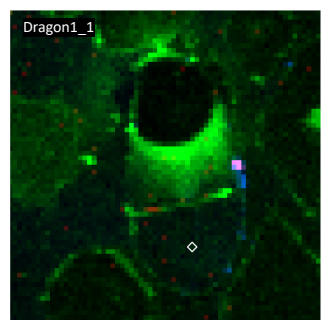
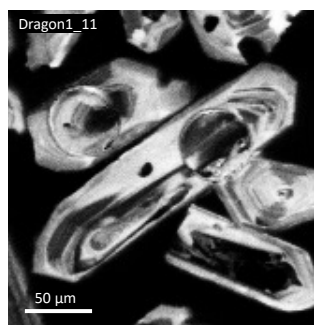
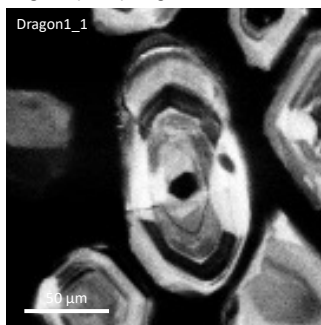


200x200 μm

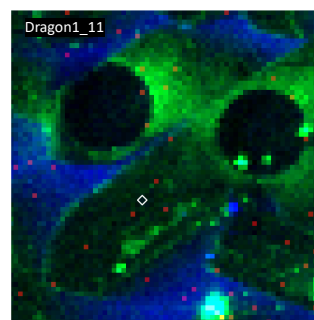


200x200 μm

Fig. S1. (cont.) Dragon Pluton

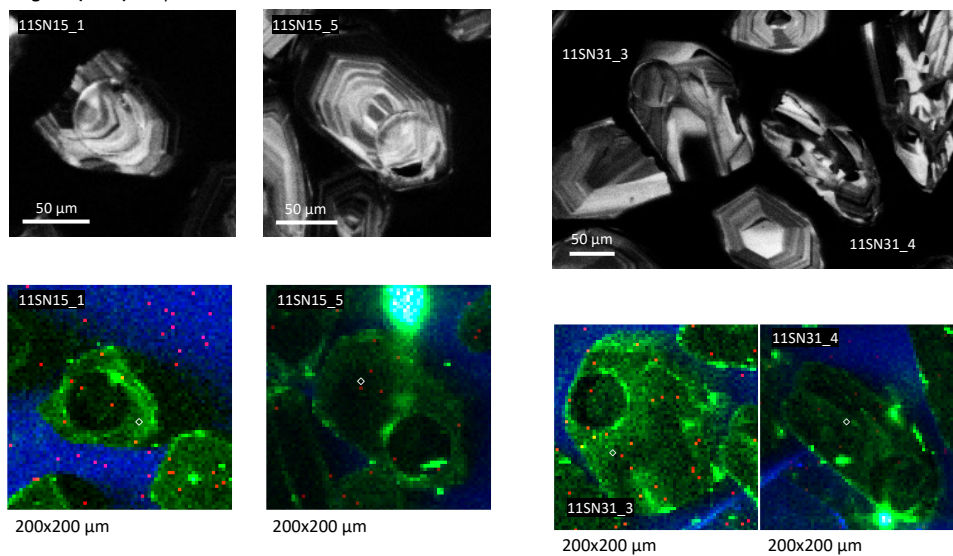


200x200 μm

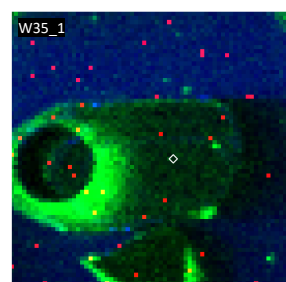
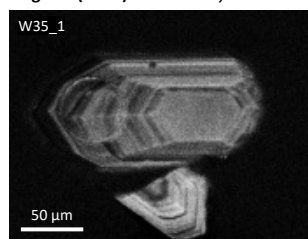
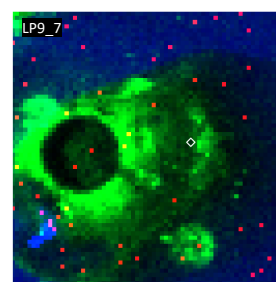
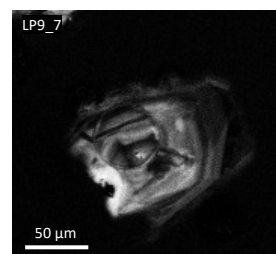
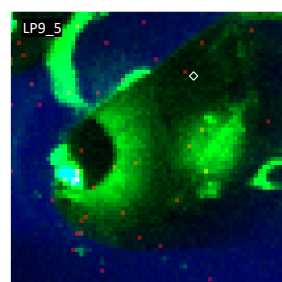
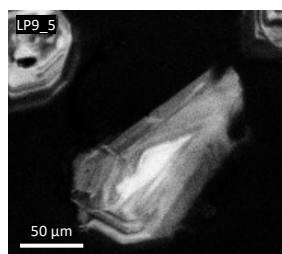


200x200 μm

RGB: Ti (Kα); U (Mβ); Ca (Kα)

Fig. S1. (cont.) Independence Pluton

RGB: Ti ($K\alpha$); U ($M\beta$); Ca ($K\alpha$)

Fig. S1. (cont.) Mt. Whitney Granite**Lone Pine Granodiorite**

RGB: Ti ($K\alpha$); U ($M\beta$); Ca ($K\alpha$)

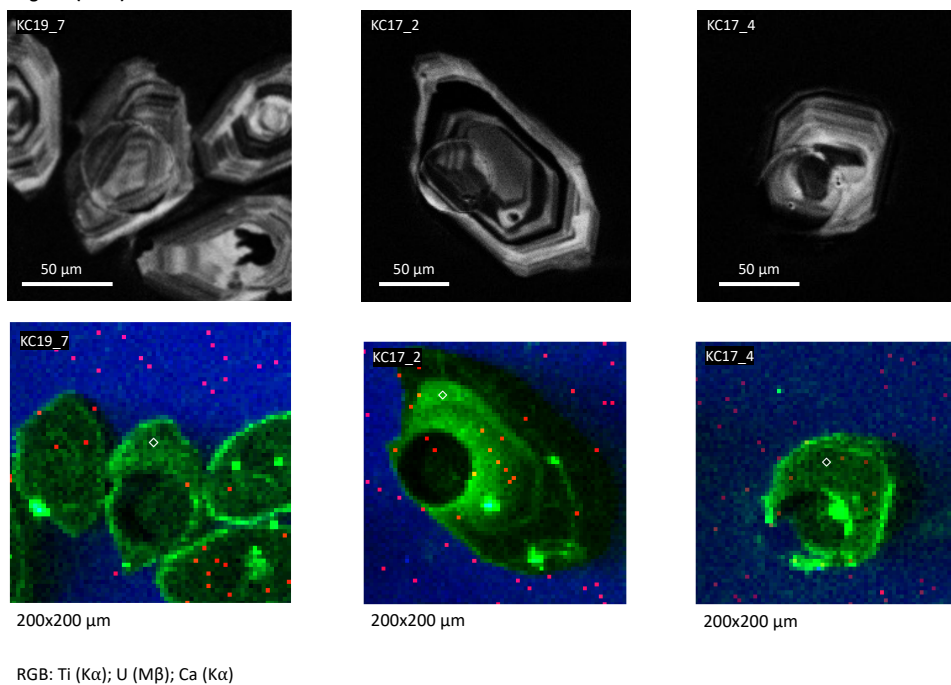
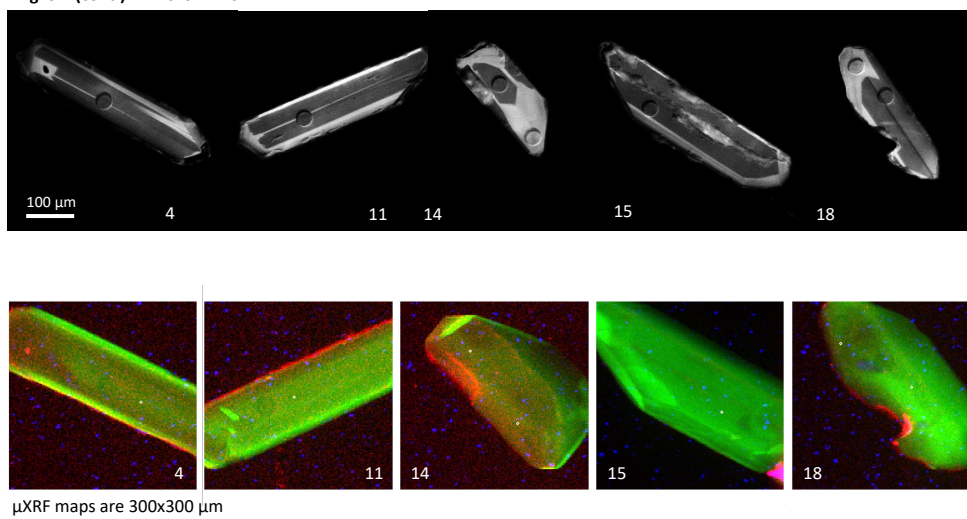
Fig. S1. (cont.) *Paradise Granodiorite*Fig. S1. (cont.) *HLMC: SNB-16-12*

Fig. S1. (cont.) HLMC: SNB-16-9

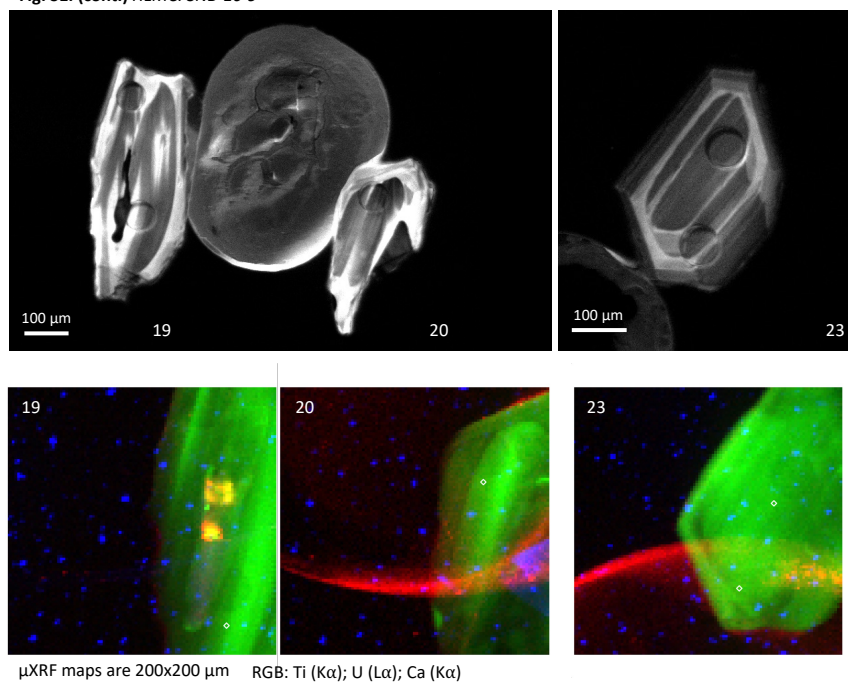
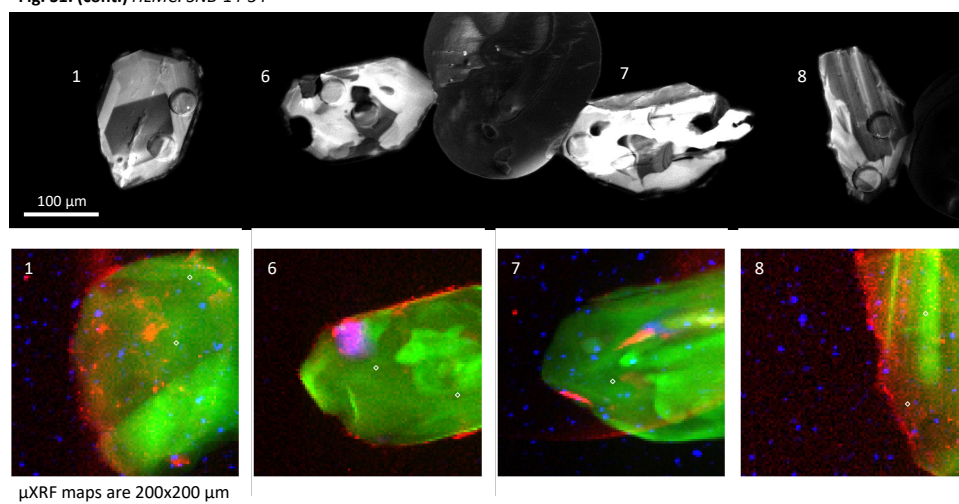
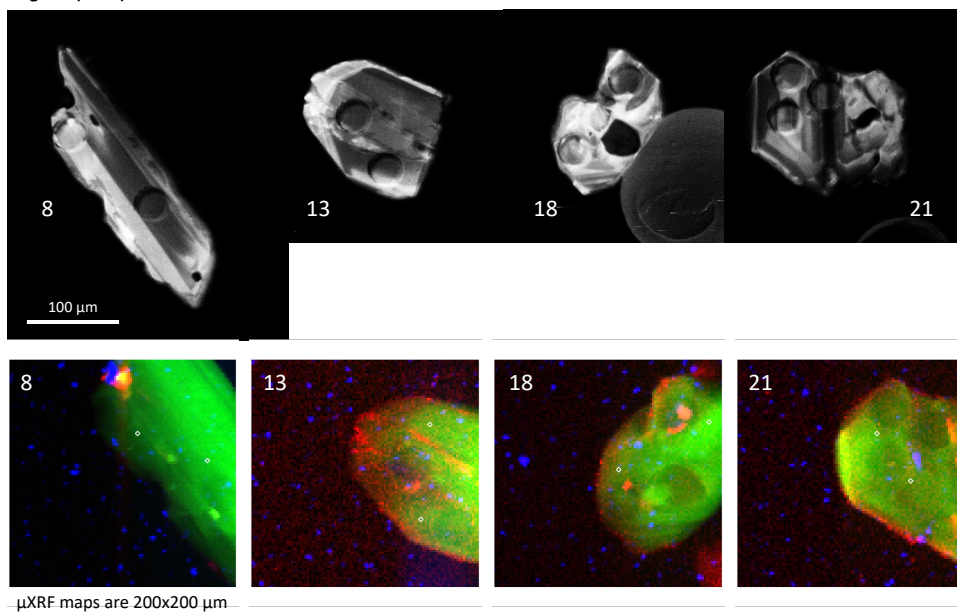


Fig. S1. (cont.) HLMC: SNB-14-34



RGB: Ti (Kα); U (Lα); Ca (Kα)

Fig. S1. (cont.) HLMC: SNB-16-6



RGB: Ti (Kα); U (Lα); Ca (Kα)

Fig. S1. (cont.) HLMC: SNB-14-40

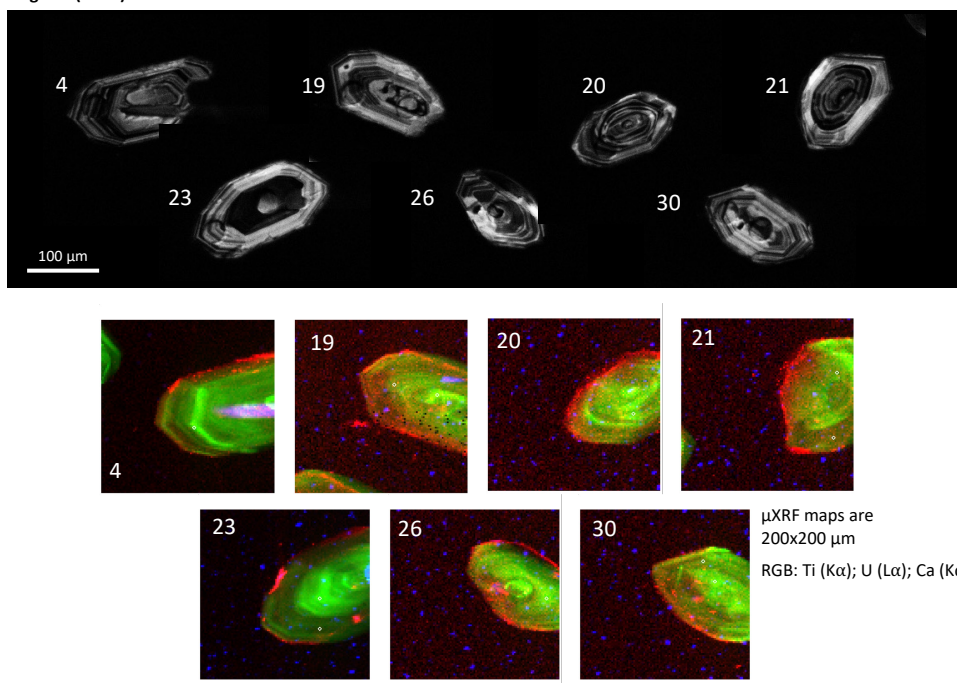
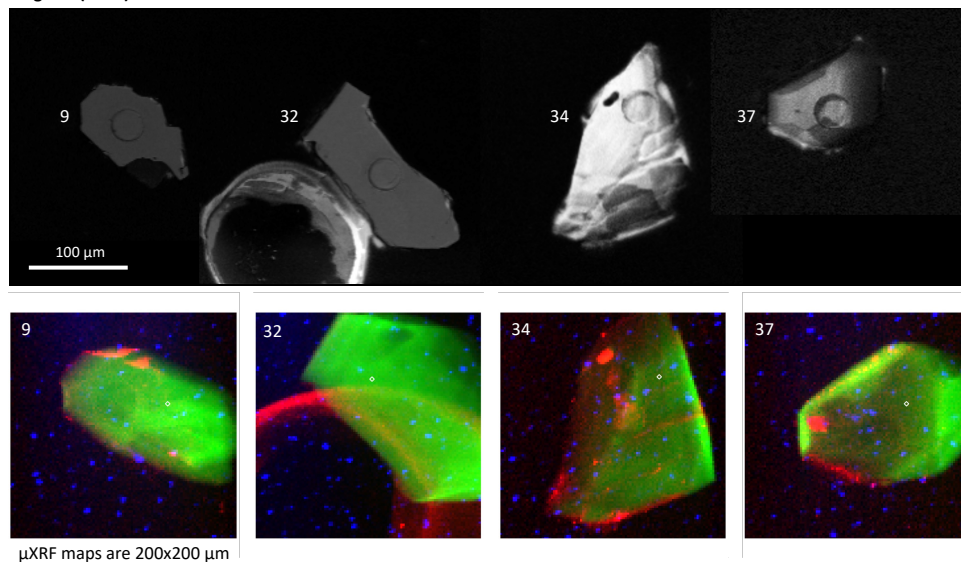
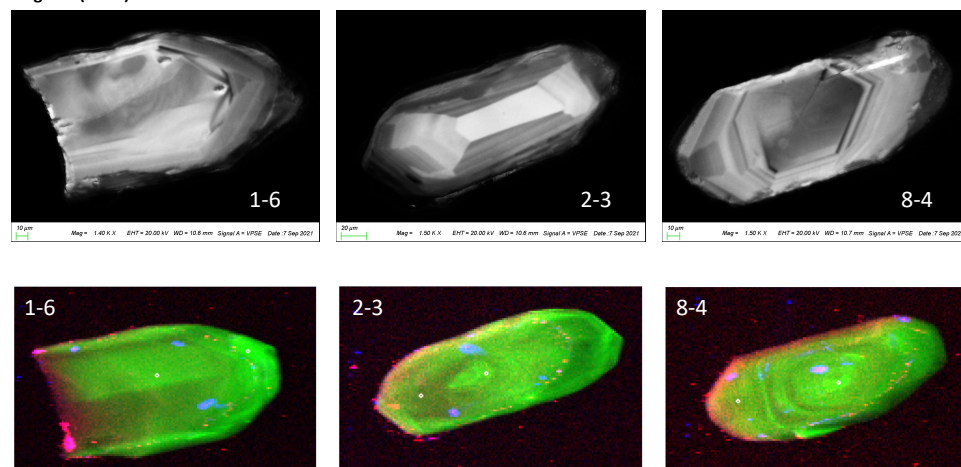


Fig. S1. (cont.) HLMC: HL-17-2



RGB: Ti (K α); U (L α); Ca (K α)

Fig. S1. (cont.) Ecstall



RGB: Ti (K α); U (L α); Ca (K α)

Fig. S1. (cont.) TEM2

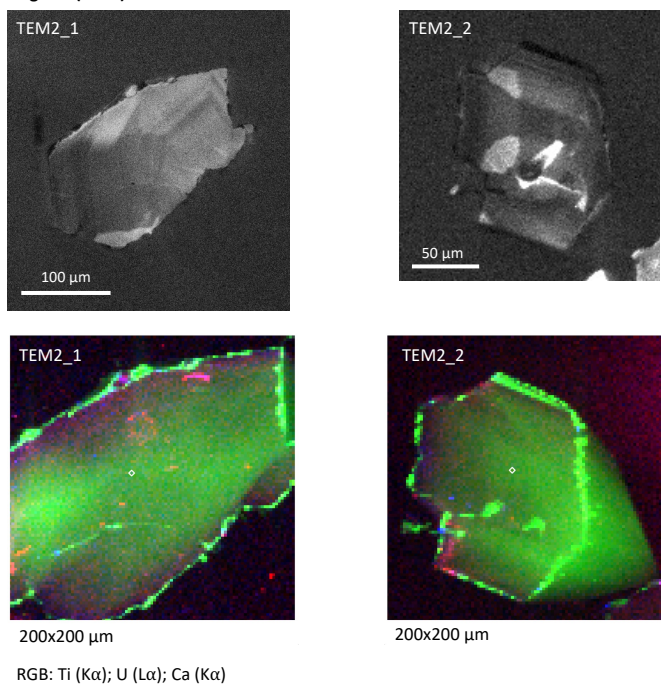
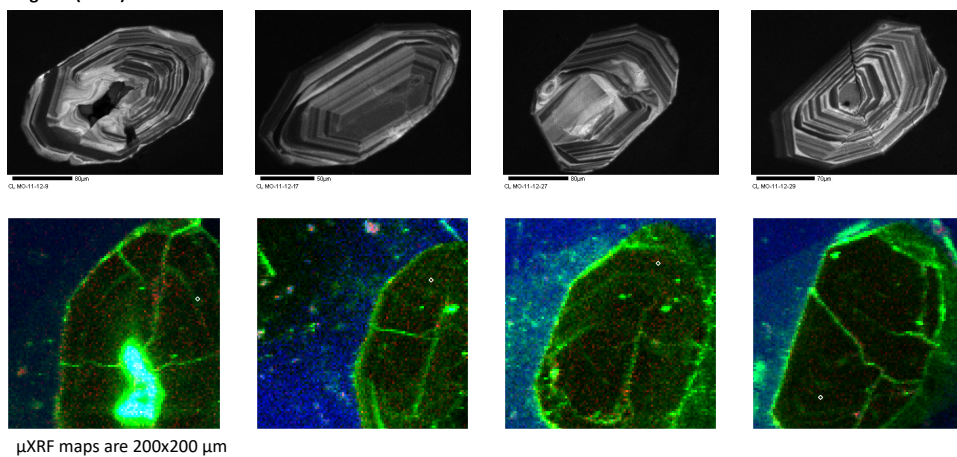
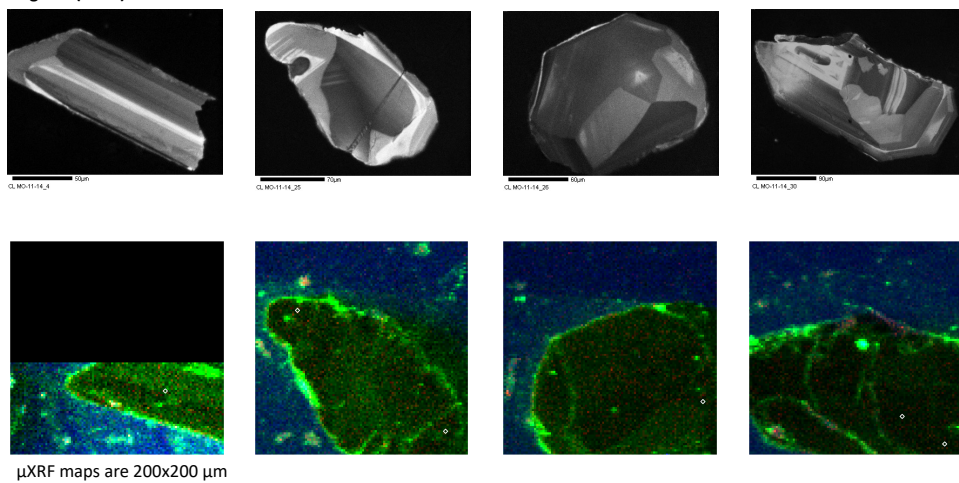


Fig. S1. (cont.) Dariv: MO-11-12



RGB: Ti ($K\alpha$); U ($M\beta$); Ca ($K\alpha$)

Fig. S1. (cont.) Dariv: MO-11-14



RGB: Ti ($K\alpha$); U ($M\beta$); Ca ($K\alpha$)

Fig. S1. (cont.) Dariv: MO-11-16

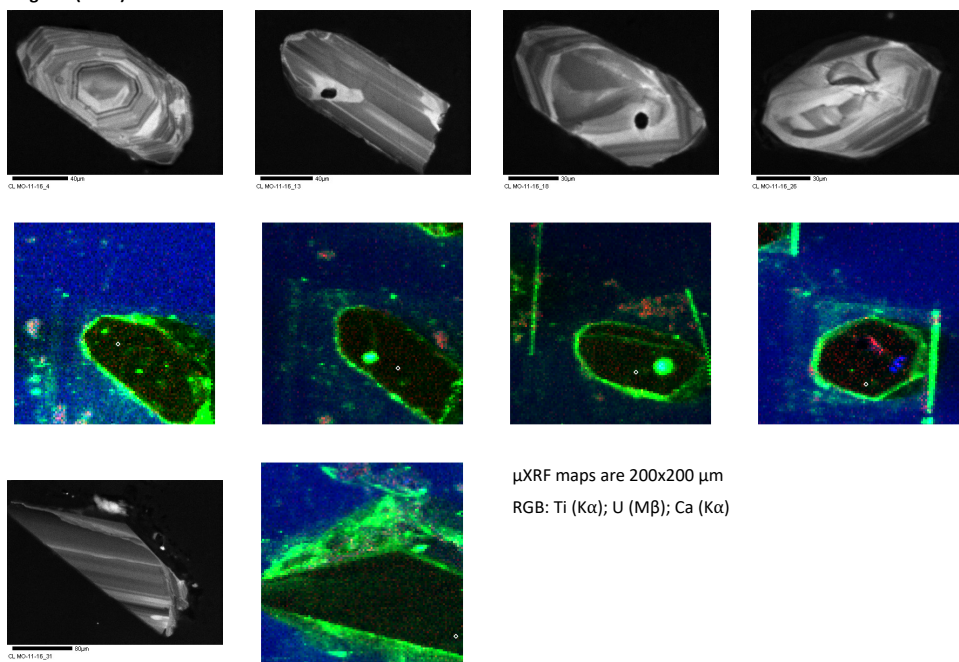
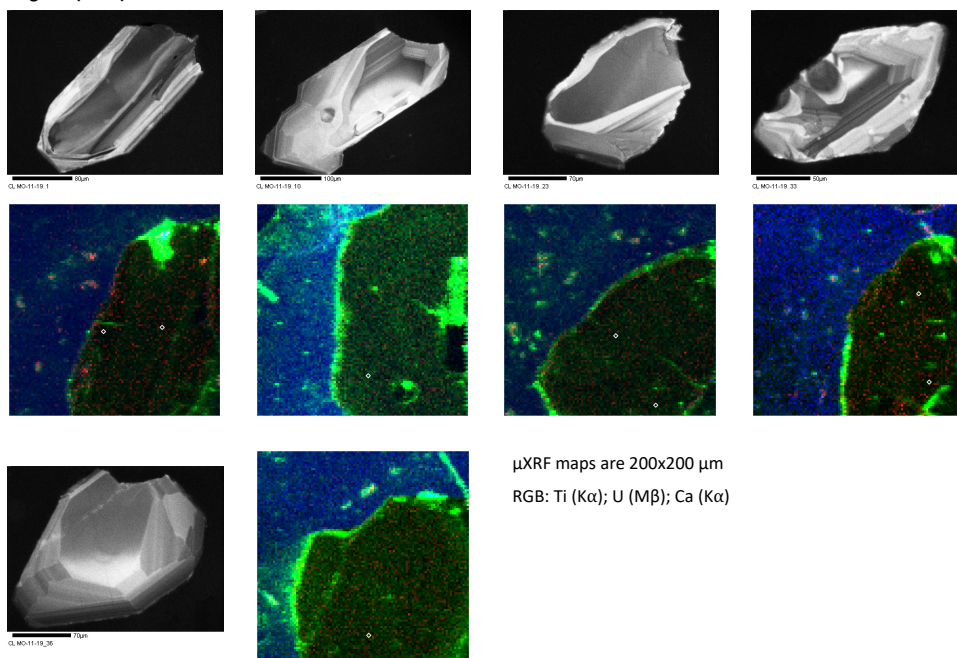
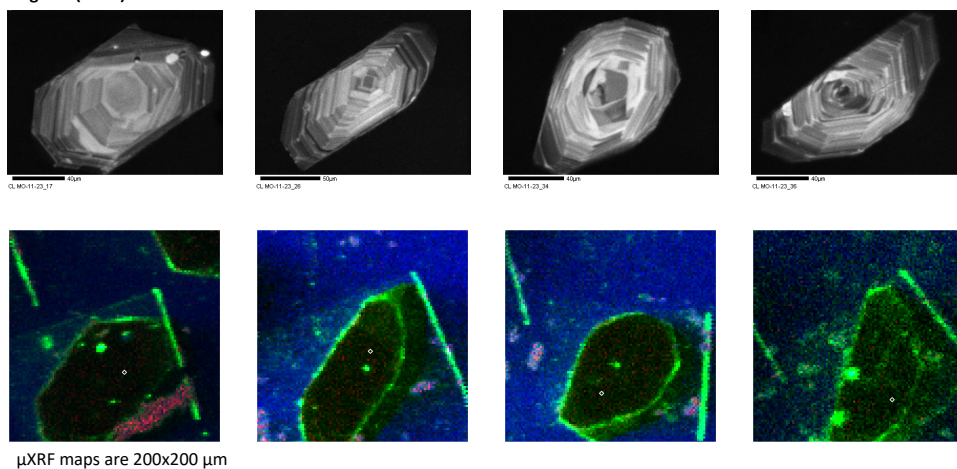
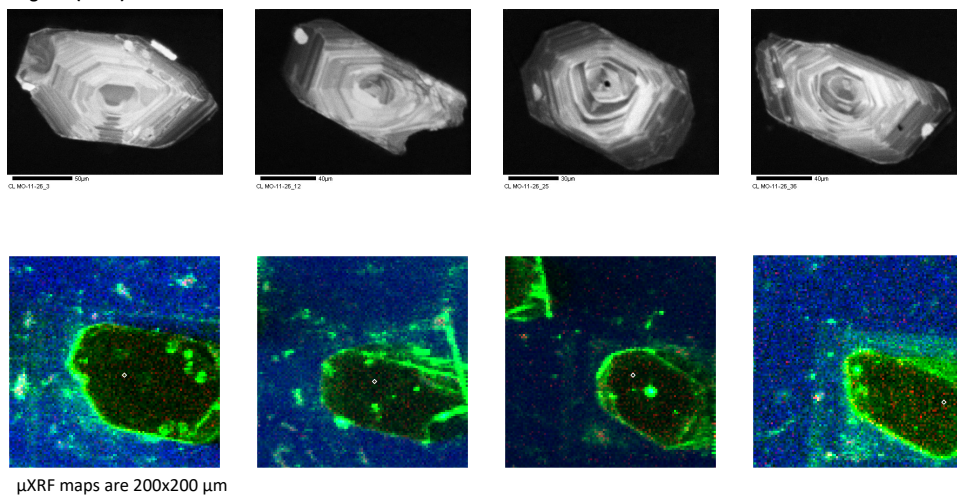


Fig. S1. (cont.) *Dariv: MO-11-19*Fig. S1. (cont.) *Dariv: MO-11-23*

RGB: Ti (Kα); U (Mβ); Ca (Kα)

Fig. S1. (cont.) *Dariv: MO-11-26*

RGB: Ti ($K\alpha$); U ($M\beta$); Ca ($K\alpha$)

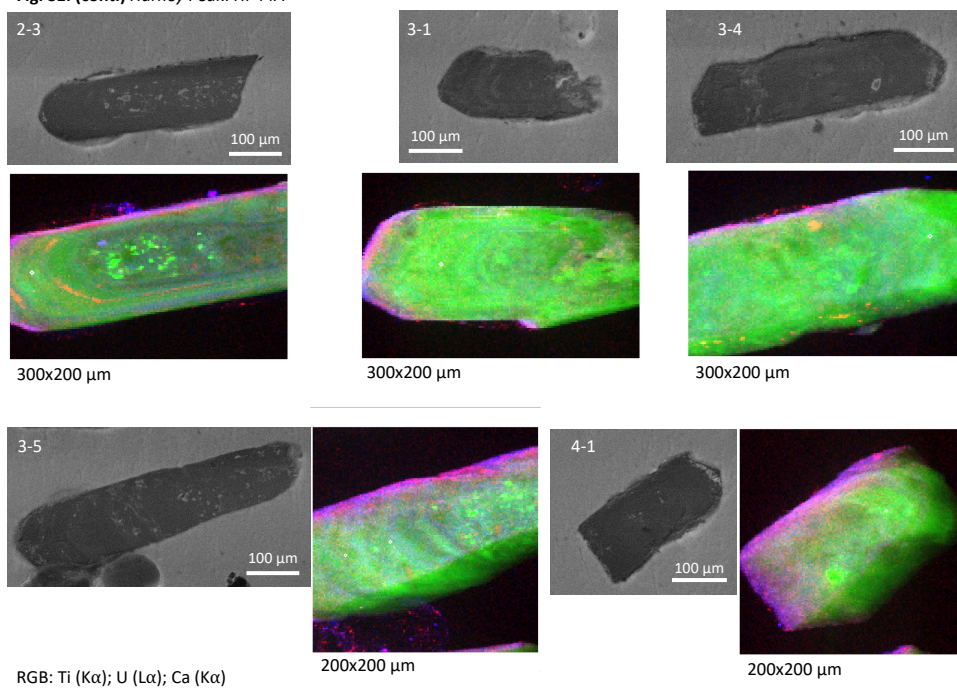
Fig. S1. (cont.) *Harney Peak: HP44A*

Fig. S1. (cont.) Harney Peak: HP21C

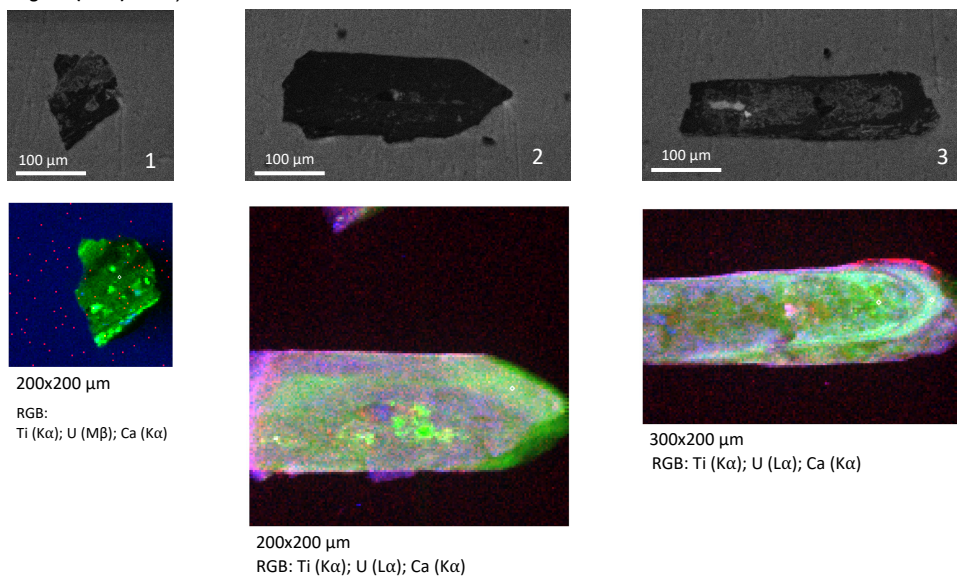


Fig. S1. (cont.) Sturgeon Lake: SP-16-52

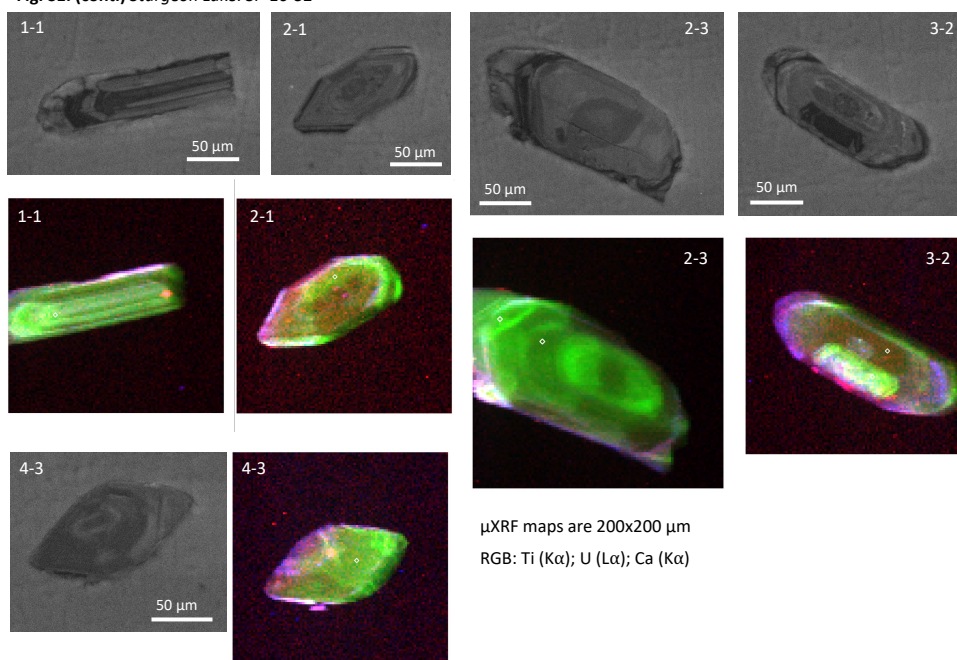
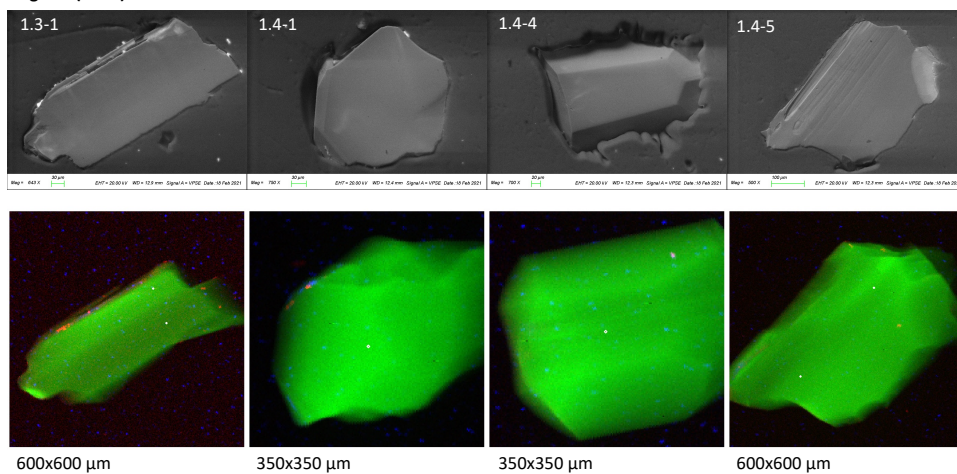
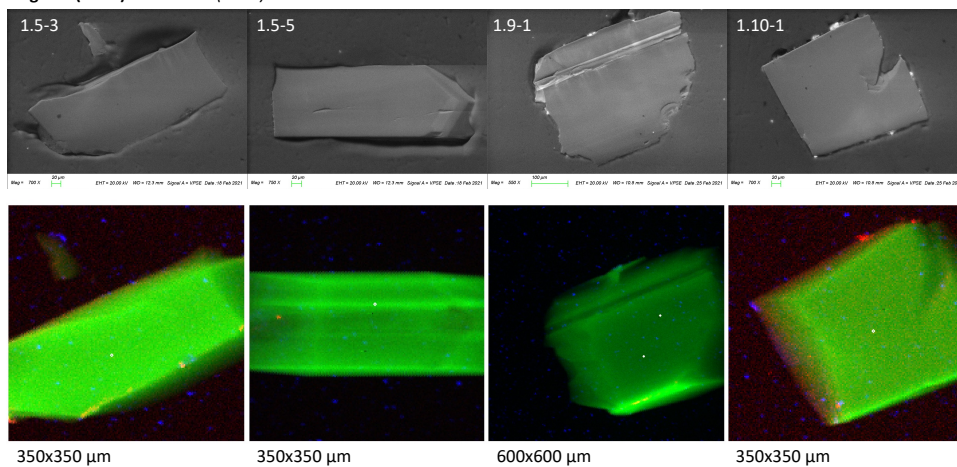


Fig. S1. (cont.) FC-1 zircon



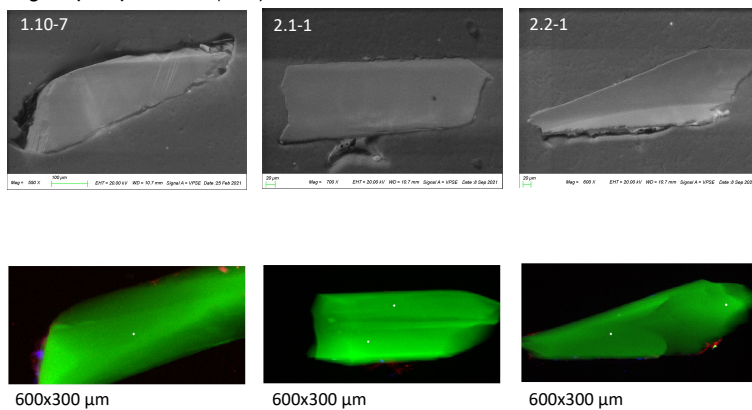
RGB: Ti ($K\alpha$); U ($L\alpha$); Ca ($K\alpha$)

Fig. S1. (cont.) FC-1 zircon (cont.)



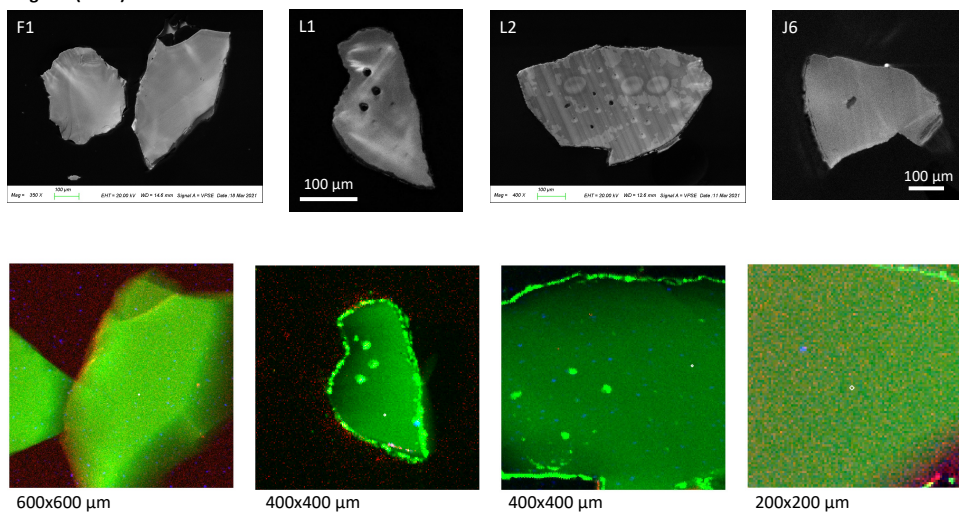
RGB: Ti ($K\alpha$); U ($L\alpha$); Ca ($K\alpha$)

Fig. S1. (cont.) FC-1 zircon (cont.)



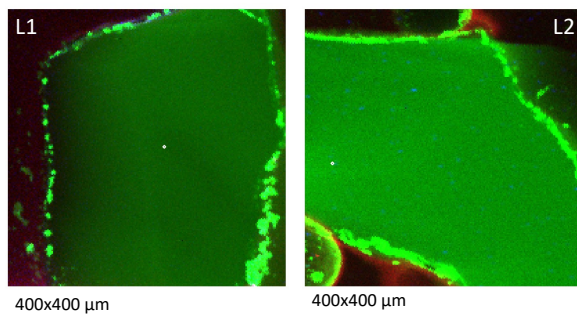
RGB: Ti (Kα); U (Lα); Ca (Kα)

Fig. S1. (cont.) 91500 zircon



RGB: Ti (Kα); U (Lα); Ca (Kα)

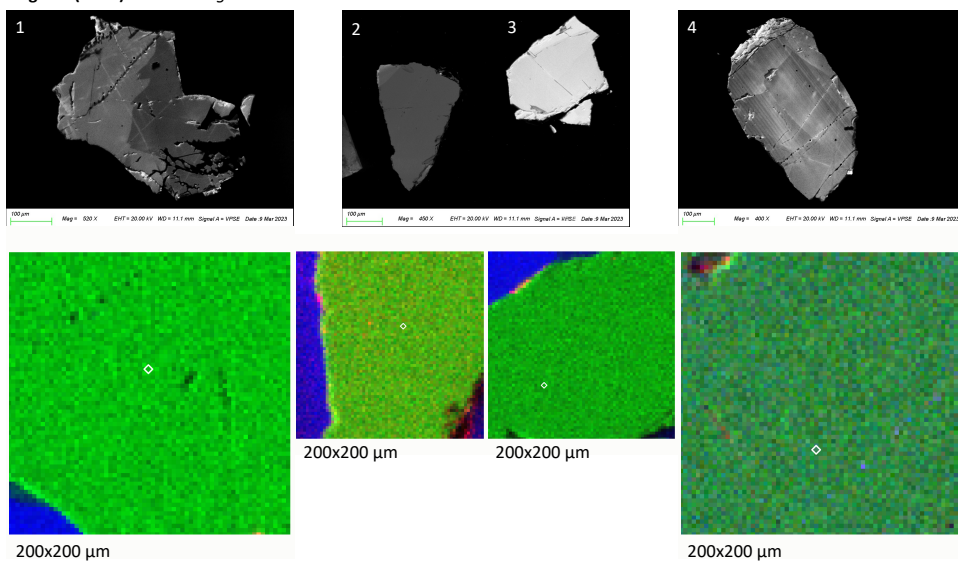
Fig. S1. (cont.) KL zircon



*No CL images for the KL zircon grains

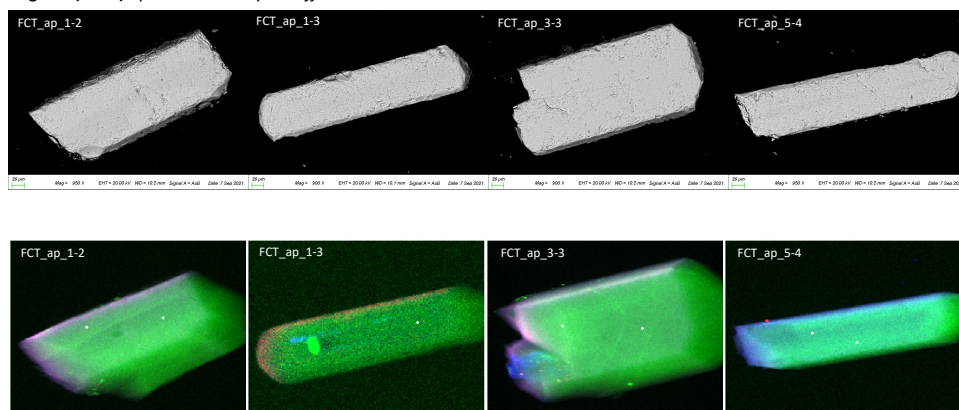
RGB: Ti ($K\alpha$); U ($L\alpha$); Ca ($K\alpha$)

Fig. S1. (cont.) Pacoima Pegmatite



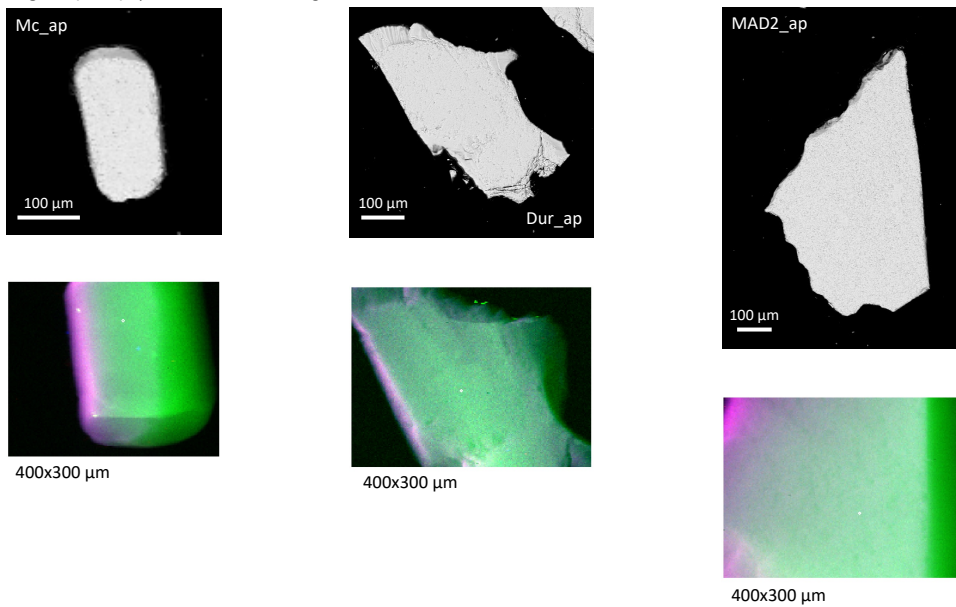
RGB: Ti ($K\alpha$); U ($M\beta$); Ca ($K\alpha$)

Fig. S1. (cont.) Apatite: Fish Canyon Tuff



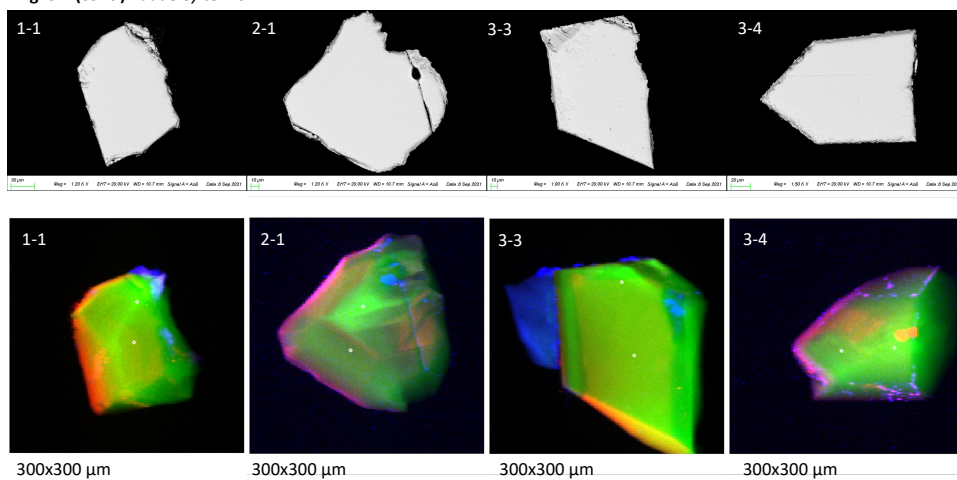
RGB: Ti ($K\alpha$); U ($L\alpha$); K ($K\alpha$)

Fig. S1. (cont.) Apatite: McClure, Durango, MAD2



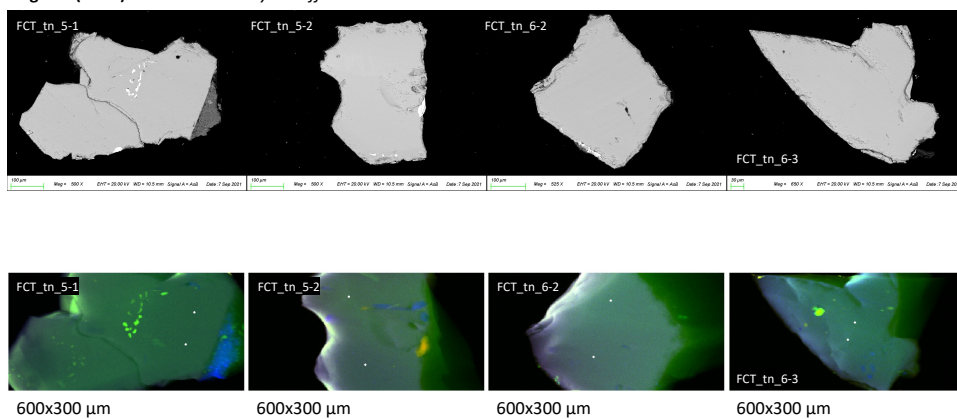
RGB: Ti ($K\alpha$); U ($L\alpha$); K ($K\alpha$)

Fig. S1. (cont.) Baddeleyite: FC-1

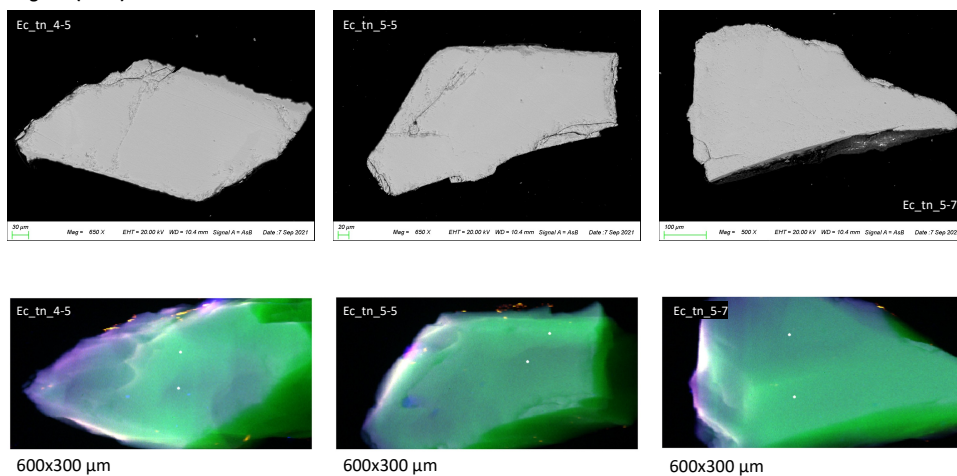


RGB: Ti ($K\alpha$); U (La); Ca ($K\alpha$)

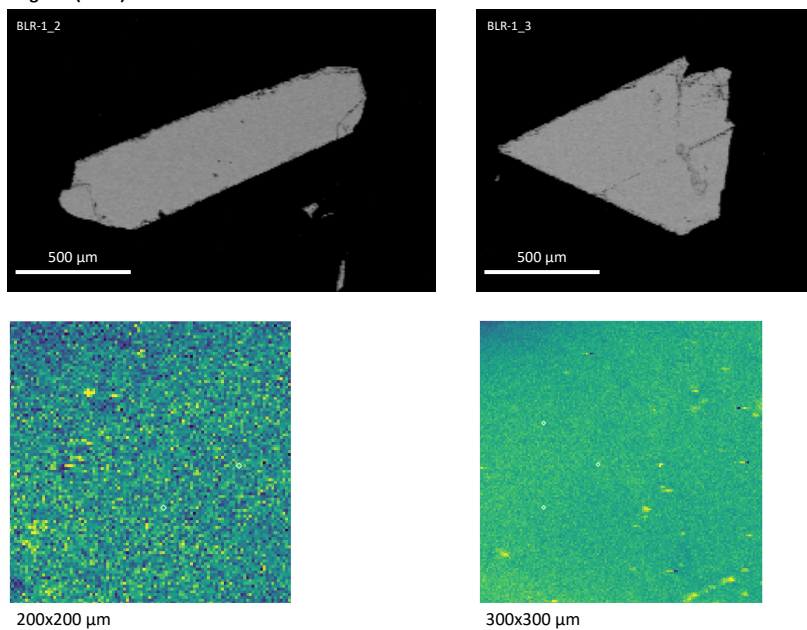
Fig. S1. (cont.) Titanite: Fish Canyon Tuff



RGB: Hf (La); U (La); K ($K\alpha$)

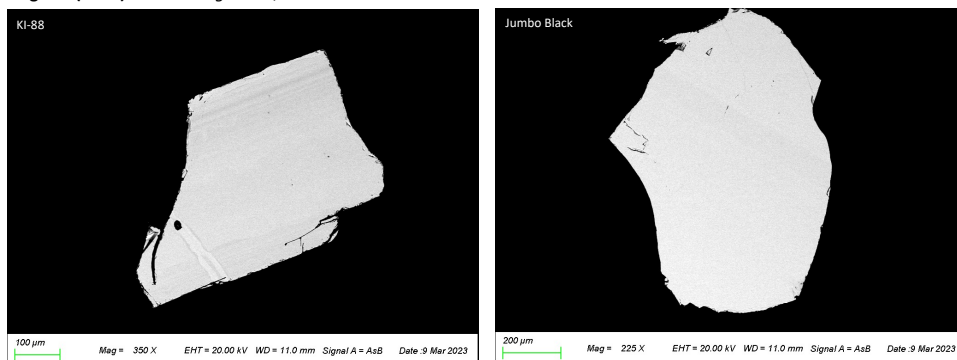
Fig. S1. (cont.) Titanite: Ecstall

RGB: Hf ($L\alpha$); U ($L\alpha$); K ($K\alpha$)

Fig. S1. (cont.) Titanite: BLR-1

Map is only U ($L\alpha$); blue low U, yellow high U

Fig. S1. (cont.) Garnet: King Island, Jumbo Black



No μ XRF maps collected for the garnet samples.

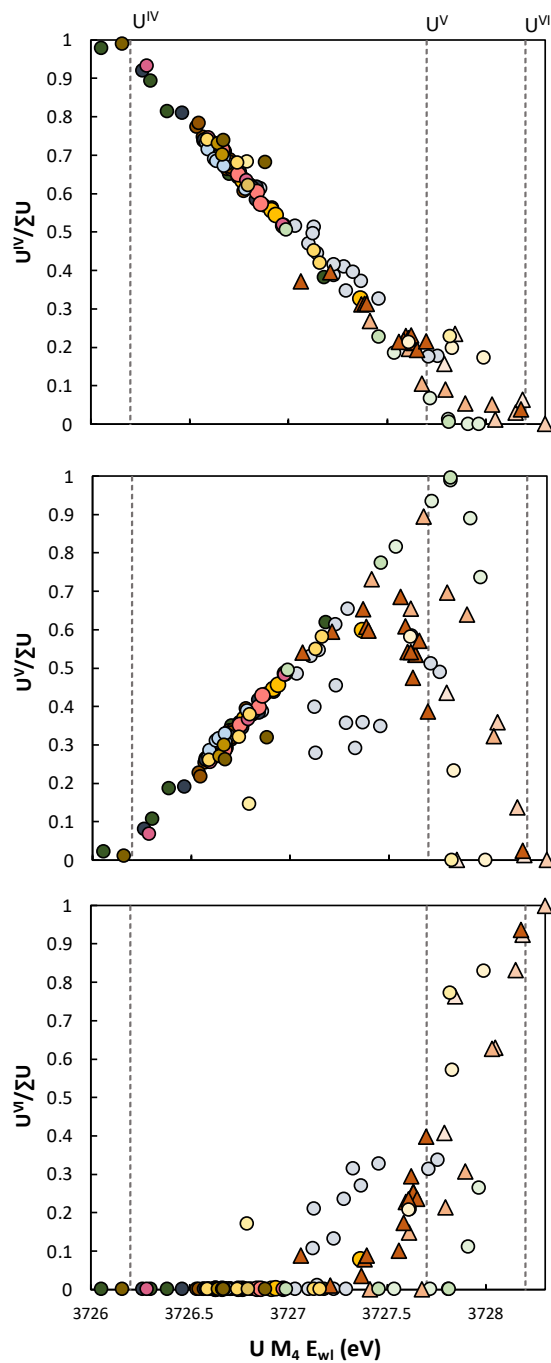


Figure S2. Variations in $U^{n+}/\sum U$ with $U M_4$ -edge E_{wl} for zircon samples. Symbols as in Fig. 8 of the main text.

Table S1. PCA results for zircon U M₄-edge spectra.

Trial #	PC1	PC2	PC3	sum
1	0.79	0.17	0.04	0.998
2	0.63	0.35	0.02	0.999
3	0.65	0.34	0.01	0.999
4	0.84	0.14	0.02	0.998
5	0.72	0.23	0.05	0.999
Average	0.72	0.25	0.03	0.999

Chapter III

COMPARISON OF URANIUM M₄, M₅, AND L₃ X-RAY ABSORPTION EDGES FOR ZIRCON XANES ANALYSIS

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ABSTRACT

X-ray absorption near-edge structure (XANES) spectroscopy provides a direct measure of element oxidation states in minerals, making it a powerful tool for reconstructing magma oxygen fugacity (fO_2). Uranium XANES analysis of zircon has emerged as a promising oxybarometer, however, uranium has multiple absorption edges (M_4 , M_5 , and L_3) that probe different electronic transitions, and their relative strengths and limitations for zircon analysis have not been systematically evaluated. Here, we compare M_4 -, M_5 -, and L_3 -edge XANES spectra from a diverse suite of zircon samples spanning a range of lithologies, ages, and parental magma redox states to determine which absorption edge is best suited for characterizing U valence and magma redox states. We find that the U M_4 -edge provides the most robust oxybarometer with the lowest analytical uncertainties, highest sensitivity to redox variations, and a sufficiently short attenuation depth that XANES results can be directly correlated with discrete growth zones observed in zircon SEM images. The M_5 -edge yields similar but less sensitive results, though it may be preferable for high-K minerals where potassium K-edge interference can complicate M_4 -edge analyses. While the L_3 -edge provides less precise fO_2 estimates, it offers valuable complementary information on bulk U valence states through diagnostic post-edge features. These findings establish a framework for selecting the optimal U absorption edge for XANES studies of zircon and other U-bearing accessory minerals.

1. INTRODUCTION

X-ray absorption near edge structure (XANES) spectroscopy is an increasingly important tool in Earth and planetary sciences (*e.g.*, see review by [Moretti and Neuville, 2021](#)). This technique probes the electronic structure of atoms and provides direct information about an element's oxidation state and local coordination environment. In particular, for multivalent elements, the energy position of the main absorption peak varies systematically with the valence state of the element being interrogated, shifting to higher energy as oxidation state increases (*e.g.*, [Henderson et al., 2014](#)). In petrologic contexts, the potential for an element to occur in an oxidized or reduced states is primarily a function of the oxygen fugacity (fO_2) during crystallization. This fundamental parameter influences the partitioning behavior of many redox-sensitive elements (*e.g.*, Fe, V, Cr, U) between minerals, melts, and fluids, thereby governing the stability of mineral phases and the composition of magmatic volatiles ([Cottrell et al., 2021](#); [Mallmann et al., 2021](#)). In turn, fO_2 imposes a first-order control on the geochemical and physical properties of Earth's interior and the composition of the atmosphere, with secular variations in magma redox conditions being linked to changes in mantle dynamics, crustal recycling, and surface oxidation through Earth history ([Buchholz et al., 2018](#); [Kadoya et al., 2020](#); [Moreira et al., 2023](#); [Hirschmann, 2023](#); [Houchin et al., 2026](#)). As a result, methods capable of directly determining element oxidation states in robust mineral archives provide a valuable means of reconstructing the fO_2 of magmatic systems and, by extension, the redox evolution of Earth's interior and surface environments.

Investigation of magma redox states, whether on the scale of a single pluton or across Earth's history requires a mineral archive that can incorporate multiple valence states of the same element, can be precisely dated, and is able to retain its primary composition through the vagaries of weathering, erosion, diagenesis, and metamorphism. For this task the mineral zircon is ideally suited. Indeed, zircon can incorporate multivalent uranium during crystallization and the proportion of oxidized uranium varies predictably with magma fO_2 ([Houchin et al., 2024](#)). Second, the incorporation of uranium in zircon forms the basis of one of the most robust and widely applied geochronometers: the U-Pb system (*e.g.*, [Tilton et al., 1955](#); [Davis et al., 2003](#); [Schoene, 2014](#)). Lastly, zircon is one of the most resilient minerals to physiochemical alteration and is able to withstand processing through the rock cycle with its primary geochemical signatures intact ([Hoskin and Schaltegger, 2003](#)). Indeed, the oldest known terrestrial materials are detrital zircon grains preserved in ancient sandstones, which pre-date the oldest known rocks by several

hundred million years (Valley et al., 2014; Harrison, 2020; Drabon et al., 2024). As such the zircon record provides, arguably, the most complete single-mineral archive of Earth's evolution.

In our previous work we showed that U M₄-edge XANES analysis of zircon is a robust oxybarometer (Houchin et al., 2024). Uranium can, however, be interrogated at several X-ray absorption edges that probe different electronic transitions (M_{4,5} XANES probes 3d to 5f electronic transitions and L₃ XANES probes the 2p to 6d transition) (Halse, 2014; Leinders et al., 2020; Kvashnina and Butorin, 2022), and the advantages/limitations of each edge remains to be determined. Here, we investigate a suite of zircon samples at the uranium M₄, M₅, and L₃-edges in order to determine which absorption edge is best suited for zircon analysis. In particular, we assess the relative sensitivity of each edge for determining the dominant U valence state present in a sample, and by extension, for quantifying magma fO_2 . Criteria for a robust oxybarometer include: i) a straightforward, consistent, and reproducible fitting procedure; ii) a clear systematic relationship between E_{wl} and magma fO_2 ; and iii) the ability to precisely correlate the location of XANES analysis spots with the textural and compositional features apparent in backscattered electron (BSE) and cathodoluminescence (CL) images. The last point is particularly important as zircon often have complex crystallization histories and may record evolving redox conditions during primary igneous crystallization or altogether different redox conditions due to re-entrainment in a later batch of magma or secondary growth during metamorphism. For determining the dominant U valence state present in a sample, X-ray absorption spectra should show clear variations in the position and shape of absorption features with changes in element oxidation state. Ideally, with diagnostic features occurring both around the main absorption peak and in the pre-edge or post-edge regions. Identifying which absorption edge optimally captures these related, but distinct, pieces of information is critical for guiding future synchrotron studies that aim either to reconstruct magma redox conditions or to probe the chemical behavior of uranium in zircon and the melts from which they crystallize.

2. SAMPLES AND METHODS

2.1 Samples

Zircon samples used for comparison of the various U X-ray absorption edges in this study were previously measured by Houchin et al. (2024) and were chosen to cover a broad range of lithologies, ages, and redox states of their host rocks. BLR-1 titanite, a

common geochronology standard, was also measured. Titanite has been shown to contain solely tetravalent uranium, regardless of the redox state of its host rock (Tiepolo et al., 2002; Houchin et al., 2024) and thus serves as a reliable U^{IV} reference material with similar U concentrations as zircon. An additional set of zircon samples were measured at the U M_4 - and L_3 -edges to further assess the utility of these edges for previously uncharacterized samples. A full sample list is given in Table 1.

2.2 Sample imaging and characterization

Individual mineral grains were first characterized using scanning electron microscopy (SEM) with BSE and CL images collected to document internal growth structures, locate cracks or inclusions that might compromise spectroscopic measurements, and to guide the selection of analysis points. SEM characterization was conducted using a Zeiss 1550VP FE-SEM at the GPS Division Analytical Facility (Caltech) using an accelerating voltage of 15-20 kV. At the synchrotron, prior to XANES measurements, each grain was mapped using micro-X-ray fluorescence (μ XRF) to determine the spatial distribution of uranium and to identify subsurface inclusions that were not visible in SEM images. These μ XRF maps were then used to precisely position analysis spots in regions of interest within each crystal. Finally, XANES measurements were made at the selected locations. This multi-step workflow ensures that spectroscopic measurements are performed on well-characterized, inclusion-free regions of each grain, thereby maximizing the reliability of information derived from the XANES data.

2.3 μ XRF and XANES analysis

Uranium M_4 -edge spectra were collected at the Advanced Photon Source (APS), Argonne National Laboratory, Beamline 13-ID-E and at the National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory, Beamline 4-BM. Uranium L_3 -edge and M_5 -edge spectra were collected at APS 13-ID-E and NSLS-II 4-BM, respectively.

The experimental set up and data acquisition procedures at these beamlines are broadly similar. A schematic representation of the beamline end station is shown in Figure 1. Both beamlines utilize Kirkpatrick-Baez mirrors to deliver focused X-rays with tunable energy using a Si(111) double-crystal monochromator, with fluorescence counts (I_f) measured using a seven element, silicon-drift-diode detector array (SX7, Canberra) positioned at 90° from the incident beam and at 45° from the sample surface. Incident intensity (I_0) is measured in a He-filled ion chamber just upstream from the focusing mirror optics.

Samples at both beamlines are placed inside a He-atmosphere to reduce attenuation of the fluorescence signal. At APS 13-ID-E, μ XRF mapping was conducted at ~ 17.5 keV (around the U $L\alpha$ emission line) or at ~ 3.76 keV (around the U $M\beta$ emission line). All μ XRF mapping conducted at NSLS-II 4-BM was collected near the energy of the U $M\beta$ emission line. False-color RGB images were generated using either the U $L\alpha$ or U $M\beta$ emission intensities to visualize the distribution of uranium in each crystal, with Ti $K\alpha$ and Ca $K\alpha$ emission intensities used to avoid inclusions, as Ca and Ti tend to have high concentrations in minerals that often occur as zircon inclusions (*e.g.*, apatite, rutile, rock-forming minerals). The location of XAS analysis spots were selected directly from these maps to ensure accurate placement. XANES spot sizes at APS 13-ID-E and NSLS-II 4-BM are ~ 1 μm and ~ 5 μm , respectively. For each of the U X-ray edges we investigated (M_4 , M_5 , and L_3) energy was scanned in 2.0-5.0 eV steps below the edge, 0.2 eV steps around the edge, and 2.0 eV steps above the edge. Using this approach, XANES spectra take approximately 5-6 minutes to collect per scan, with several scans typically collected per grain and/or analysis point. Because a larger energy range is typically measured in the pre- and post-edge regions for L_3 -edge scans, these measurements usually take slightly longer than scans at the $M_{4,5}$ -edge, though the choice of step size and dwell time has a greater impact on the time needed per analysis.

Grains of the FC-1 zircon reference material were analyzed at both APS 13-ID-E and NSLS-II 4-BM in order to calibrate results between beamlines (Houchin et al., 2024). The energy of peak absorption at the M_4 -edge for the FC-1 samples was ~ 0.15 eV lower at NSLS-II 4-BM relative to APS 13-ID-E and all M_4 -edge spectra acquired at NSLS-II were shifted accordingly. No corrections were made to M_5 - or L_3 -edge spectra as these data were only collected at NSLS-II or at APS, respectively. Nonetheless, we recommend that several grains of FC-1 zircon be measured at the edge of interest during any XAS experiment involving zircon, so that data collected at different beamlines or during different sessions can be easily correlated.

2.4 Data processing

Comparison of XAS measurements with other geochemical data requires reducing spectra to a single representative variable that can be plotted against other parameters. Here we use the energy of peak absorption, or white-line (E_{wl}) as a proxy for average U valence (U^{n+}) and as the basis for calibrating relationships between XANES spectra and magma $f\text{O}_2$. In U M_4 - and M_5 -edge spectra the edge jump is negligible, allowing a linear

background to account for differences in absorption between the pre- and post-edge regions without affecting the centroid of the modeled absorption peak that defines E_{wl} (Fig. 2A,B). In contrast, U L₃-edge spectra exhibit a pronounced difference between pre- and post-edge absorption, requiring a step function (e.g., arc tangent or error function) to accurately model the main absorption peak (Fig. 2C). To evaluate the robustness and reproducibility of peak fitting, all spectra were modeled using Gaussian, Lorentzian, and pseudo-Voigt functions. A linear background was applied to U M₄- and M₅-edge spectra, whereas the U L₃-edge step was modeled using an arc-tangent step function. For the L₃-edge, E_{wl} was taken as the centroid of the combined peak and arc tangent fit. All data processing (e.g., normalization, peak fitting) was performed using the LARCH software package (Newville, 2013).

3. RESULTS

3.1 Overview of spectral features

Uranium M₄- and M₅-edge spectra appear broadly similar, consisting of a single sharp peak with a minimal intensity contrast between the pre- and post-edge regions (Fig. 2A,B). In both cases peak positions shift systematically towards higher energy with increasing U valence. For samples with E_{wl} values approaching the nominal position of the U^{VI} edge, a small shoulder develops on the high energy side of the main peak. The full width at half maximum (FWHM) of the M₄- and M₅-edge peaks are also comparable, ranging from ~4.5 eV for samples dominated by a single valence state to ~5.5 eV for mixed valence samples where the observed absorption feature represents the convolution of multiple spectral peaks (Houchin et al., 2024; Fig. 9). Importantly, however, the difference in energy between the nominal U^{IV} and U^{VI} peak positions ($\Delta E_{U^{VI}-U^{IV}}$) is greater for the M₄-edge compared to the M₅-edge (~2.5 eV versus ~1.6 eV, respectively) allowing U valence to be resolved with greater sensitivity from M₄-edge spectra.

In zircon L₃-edge spectra, the main peak likewise shifts to higher energy with increasing U oxidation state as expected. This trend contrasts, however, with a previous study that reported the main peak of KUO₃ spectra (a pure U^V compound) occurring at a higher energy than that of UO₃, which contains exclusively U^{VI} (Leinders et al., 2020). The KUO₃ peak presented in Leinders et al., 2020, however, is highly asymmetric and the non-linear white-line behavior observed for KUO₃ and UO₃ likely arises from differences in the crystal structures of these compounds. Conversely, as uranium is a trace element in zircon, the crystallographic environment is broadly similar regardless of the U valence state and a systematic relationship between U valence and E_{wl} is observed. In addition to the shifts in

energy, systematic differences in peak intensity are observed among the various U oxidation states. Whereas the U^{IV} and U^{VI} peaks reach similar intensities above the edge-step, the U^V peak is comparatively subdued, reaching ~50% of the normalized intensity of the U^{IV} and U^{VI} peaks. Consequently, samples containing appreciable proportions of U^V may exhibit lower intensity peaks relative to samples of mixed U^{IV} and U^{VI} valence states. In the post-edge region of U L_3 -edge spectra, a broad feature occurs between 17,190 to 17,250 eV (Feature A, Fig. 2C), centered near ~17,213 eV for U^{IV} , ~17,217 eV for U^V , ~17,230 eV for U^{VI} . In U^{VI} -rich spectra this feature is broader and commonly resolves into two distinct humps. A second feature occurs between 17,275 to 17,315 eV (Feature B) that is most pronounced in samples containing significant U^{VI} , whereas it is absent in U^V dominated samples (Fig. 2C). Notably, zircon samples inferred to contain appreciable U^V all crystallized from peraluminous melts; this observation is explored further in the Discussion (Section 4.2).

3.2 Peak fitting

Figure 3 shows the mean and distribution (box-and-whisker plots) of E_{wl} for each sample and absorption edge as determined from fits using Gaussian, Lorentzian, or pseudo-Voigt functions. For M_4 -edge spectra, the choice of peak shape has a negligible effect on the results with most samples displaying nearly identical distributions, and average E_{wl} values varying by less than 0.05 eV (~0.3 times the measurement uncertainty) depending on the function used to model the main absorption feature. With the exception of Sturgeon Lake and Lassen zircon, the choice of peak shape also has a negligible impact on the modeled E_{wl} value of M_5 -edge spectra. In contrast, L_3 -edge spectra are highly sensitive to the choice of peak shape, with mean E_{wl} values differing by as much as 2.5 eV (~3 times the measurement uncertainty) as a result of the function used to model the absorption edge. This sensitivity is reflected not only in the shift in mean values but also in substantially more variable distributions of E_{wl} depending on the selected peak function. From the average results of each peak fitting method for each sample we find that $\Delta E_{U^{VI}-U^{IV}}$ is ~2.5 eV at the M_4 -edge, ~1.6 eV at the M_5 -edge, and ~4.5 eV at the L_3 -edge.

3.3 Principal component analysis

Principal component analysis (PCA) can be used to determine the number of significant components that make up a collection of spectra. While the components themselves may not have physical meaning, the number of significant components reflects

the number of unique spectra (*i.e.*, valence states) needed to explain the observed variance. Previous PCA of zircon U M₄-edge spectra was conducted by [Houchin et al. \(2024\)](#) and indicated that three components were needed to fully describe the zircon spectra. Here, PCA was used to investigate the variance in zircon U L₃-edge spectra. This analysis, likewise, revealed three significant components, confirming that U^{IV}, U^V, and U^{VI} are all capable of being incorporated into zircon.

4. DISCUSSION

4.1 Comparison of uranium edges for zircon U XANES oxybarometry

To determine which of the uranium absorption edges investigated are best suited for zircon oxybarometry we assess each according to the criteria outlined in the introduction.

4.1.1 Peak fitting and uncertainties

For the M_{4,5}-edges modeling the main absorption edge is straightforward, using only a linear background and single peak function, and provides consistent results regardless of the choice of peak shape (Fig. 3A,B). While generally insensitive to peak shape, the best fits (lowest χ^2) are obtained using a pseudo-Voigt to model the peak for both M₄- and M₅-edges. Gaussian and Lorentzian functions are thought to represent, peak broadening due to instrumental uncertainty and the finite core-hole lifetime of the excited state, respectively ([Henderson et al., 2014](#)). A pseudo-Voigt is essentially a convolution of Gaussian and Lorentzian peaks shapes and thus can capture both broadening effects. Conversely, E_{wl} values obtained from fitting of L₃-edge XANES are highly dependent on the choice of peak shape (Fig. 3C), though, as with the M_{4,5}-edges, a pseudo-Voigt function gives the most consistent results. Overall, the M_{4,5}-edges show greater reproducibility relative to the L₃-edge for redox estimates based on fitted E_{wl} values. In all cases, however, using a pseudo-Voigt function to model the absorption edge gives the most consistent results and this approach is recommended for future studies.

The average uncertainties on modeled E_{wl} values reported by the LARCH program are ~0.02 eV for the M_{4,5}-edges and ~0.1 eV for the L₃-edge. We argue, however, that the 2 standard deviation (SD) uncertainty based on repeat measurements of FC-1 zircon, which shows consistent U valence across mineral grains, better represents the precision associated with the measurement of individual mineral grains. For the M₄, M₅, and L₃-edges the calculated uncertainties on the white-line energy are ± 0.18 eV, ± 0.22 eV, and ± 0.86 eV,

respectively. As $\Delta E_{U^{VI}-U^{IV}}$ varies with each absorption edge we ratio the 2 SD uncertainty with the total energy range going from pure U^{IV} to pure U^{VI} to calculate their % uncertainty $[(2SD/\Delta E_{U^{VI}-U^{IV}})*100]$ to directly compare the sensitivity of each edge. For individual measurements, this analysis shows that the M_4 -edge provides the greatest sensitivity, with a relative uncertainty of only 8%, compared the M_5 - and L_3 -edges which have relative uncertainties of 15% and 20%, respectively (Fig 4A).

4.1.2 Correlation of XANES analysis spots with zircon growth zones

For zircon with a typical density of 4.65 g/cm^3 the $1/e$ attenuation depth is $\sim 3.4 \text{ }\mu\text{m}$ at the M_4 -edge, $\sim 3.1 \text{ }\mu\text{m}$ at the M_5 -edge, and $\sim 200 \text{ }\mu\text{m}$ at the L_3 -edge (Fig 4B) (<https://xraydb.xrayabsorption.org/>). Analysis at the $M_{4,5}$ -edges can thus be directly correlated with textural features apparent in SEM images. Most zircon are $\leq 200 \text{ }\mu\text{m}$ across the a-b axis (due to their tetragonal crystal habit most zircon grains are mounted with the a-b axis parallel to the mount surface), such that the higher energy of the L_3 -edge will deeply, or completely, penetrate through the crystal. Uranium L_3 -edge XANES spectra will thus reflect bulk analysis of U speciation within a mineral grain, even if the beam diameter may be small ($\leq 5 \text{ }\mu\text{m}$).

4.1.3 E_{wl} and magma fO_2 calibration

Figure 5 shows zircon E_{wl} values for the different U edges plotted against independent estimates of magma fO_2 . While there is a clear relationship between E_{wl} and fO_2 for each absorption edge, the M_4 -edge calibration is the most well-constrained, with a root mean squared error (RMSE) of $\pm 0.49 \text{ log } fO_2$ units, compared to the M_5 - and L_3 -edges which have RMSEs of ± 0.63 and ± 0.52 , respectively. While the RMSE is similar for each calibration, the 2 SE uncertainties on L_3 E_{wl} values are significantly larger than for the $M_{4,5}$ -edge samples. The combined 1σ uncertainty in ΔFMQ from adding in quadrature the RMSE on the fit with the propagated analytical uncertainty, is ± 0.53 , ± 0.69 , and $\pm 0.77 \text{ log } fO_2$ units for the U M_4 -, M_5 -, and L_3 -edge, respectively. Additionally, the lower intensity of the U^V peak at the L_3 -edge (Fig. 2C) leads to a more complex relationship between E_{wl} and average U valence when compared to the $M_{4,5}$ -edges, as the U^{VI} or U^{VI} peaks dominate the signal in L_3 -edge spectra of mixed valence. For this reason, L_3 -edge E_{wl} values tend to cluster at either low or high energy (Fig. 4C), as opposed to showing an even distribution across the range of energy between the U^{IV} and U^{VI} peak positions as observed for the U M_4 -edge. In particular, the Harney Peak zircon, which are dominated by U^V , show

significantly lower $L_3 E_{wl}$ values relative to M_4 -edge results; while FC-1, which has a mixed U^{IV} and U^{VI} signal, returns relatively higher L_3 -edge E_{wl} compared to the M_4 -edge (Fig. 5).

The greater resolution of the $M_{4,5}$ -edges compared to the L_3 -edge arises from the nature of the electronic transitions being interrogated. Analysis of the U $M_{4,5}$ -edges involves 3d to 5f electronic transitions and directly probes the outer 5f electron orbitals that are most responsible for chemical bonding. $M_{4,5}$ -edge XANES spectra are thus more sensitive to variations in oxidation state compared to L_3 -edge XANES which interrogates the inner 2p to 6d transitions (Kvashnina and Butorin, 2022). The width of the main peak in a XANES spectrum is also inversely proportional to the core-hole lifetime of the core level from which the photoelectron is excited (Henderson et al., 2014), and the significantly broader peak of the L_3 -edge arises from a shorter 2p core-hole lifetime relative to the 3d core-hole lifetime associated with the $M_{4,5}$ -edges.

4.1.4 Summary of criteria for successful U XANES oxybarometer

Based on the criteria outlined for a robust mineral oxybarometer, we find that the U M_4 -edge best fulfills these specifications (Fig. 4C): (i) the peak fitting procedure is straightforward and highly reproducible, with a <10% relative uncertainty on the white-line energy, (ii) spectra E_{wl} exhibit a strong correlation with independent estimates of magma fO_2 , and (iii) analysis spots can be precisely placed and directly linked to zircon textural feature observed in SEM images. While the M_5 - and L_3 -edges can also serve as magma redox proxies, fO_2 estimates derived from these edges are associated with larger uncertainties and, in the case of the L_3 -edge, reflect bulk rather than spatially resolved values. Although potassium interference is negligible for zircon due to its low K concentrations, the proximity of the potassium K-edge (~3.6 keV) to the post-edge region of the U M_4 -edge can introduce spectral distortions in potassium-rich phases, complicating background modeling and white-line energy determination. In such cases, the U M_5 -edge avoids this interference and may therefore provide more reliable results for future studies of U-bearing accessory minerals with measurable potassium contents (*e.g.*, apatite, monazite).

4.2 Determination of bulk U valence state and identification of U^V

When grouped according to host rock lithology, zircon U L_3 -edge spectra show systematic variations that reflect the compositional and structural characteristics of the crystallizing melt. Based on the broad classification of their host rocks, we classify the

samples into four group: felsic volcanic rocks, arc-related granitoids, strongly-peraluminous granites (SPGs), and Archean granitoids (Fig. 6).

Zircon from Phanerozoic felsic volcanic rocks have L₃-edge spectra exhibiting dominantly U^{VI} characteristics (i.e., high E_{wl} , broad double-hump centered near 17,230 eV, and a second post-edge feature around 17,290 eV; Fig. 2C) reflecting the generally oxidized nature of extrusive felsic rocks, which may arise from high H₂O contents (Kelley and Cottrell, 2009) and/or preferential loss of Fe²⁺ during fractional crystallization (Luo et al., 2024). Arc magmas are derived from flux melting of the mantle-wedge with contributions from subducted slab fluids and oxidized crustal material, resulting in magmas with relatively high fO_2 , commonly ranging from FMQ to FMQ+2 or higher (Kelley and Cottrell, 2009; Cottrell et al., 2021). At these conditions, both U^{IV} and U^{VI} are stable in the melt and zircon from arc magmas record this mixed U^{IV} and U^{VI} signature. This is reflected in their intermediate E_{wl} values and post-edge features exhibiting the broad double-hump characteristic of U^{VI} (Fig. 2C, Feature A) but shifted to a position intermediate between the energy of Feature A in U^{IV} and U^{VI} spectra (Fig. 6). Felsic-intermediate magmas in the Archean are generally thought to be more reduced than their modern counterparts (Moreira et al., 2023; Ge et al., 2023). This is reflected in the L₃-edge spectra of zircon from these rocks that show characteristics of a dominantly U^{IV} composition (e.g., E_{wl} , position of Feature A), with a minor contribution from U^{VI}. Uranium L₃-edge spectra of zircon from Archean and Proterozoic SPGs show characteristics consistent with a high proportion of U^V. Enrichment of Nb^V and Ta^V has been documented in peraluminous melts and attributed to the stabilization of pentavalent HFSE complexes within the Al-rich polymerized network (Linnen and Keppler, 1997), which may suggest a broad affinity for pentavalent HSFEs in peraluminous melts. Zircon that crystallize from peraluminous magmas also typically have higher Al concentrations (Trail et al., 2017), which can serve to charge balance U^V via the reaction: $U^{5+} + Al^{3+} \rightleftharpoons Zr^{4+} + Si^{4+}$. The distinct shape and intermediate E_{wl} between U^{IV} and U^{VI} further supports the conclusion that a considerable proportion of U^V is present in zircon from SPGs. We note that the current SPG zircon dataset contains only Archean and Proterozoic samples and further U XANES studies of Phanerozoic SPG zircon is needed to see if the stabilization of U^V in peraluminous melts is consistent across Earth history.

Uranium M₄-edge analysis of zircon grains from the samples as described above are shown in Fig. 6B. These spectra show a clear shift in E_{wl} between groups that broadly mirrors the shift in L₃-edge E_{wl} . Zircon from Archean rocks exhibit peaks with the lowest

E_{wl} , reflecting a dominantly U^{IV} composition. Conversely, zircon from Phanerozoic felsic volcanic rocks show the highest E_{wl} values and hence the greatest proportion of U^{VI} . Zircon from arcs and SPGs both have intermediate E_{wl} , with zircon from arc-related rocks typically exhibiting higher FWHM values due to convolution of the U^{IV} and U^{VI} peaks, rather than their spectra being mostly composed of a single peak as is the case with the U^V dominated zircon from SPGs (see [Houchin et al., 2024](#); Fig. 9).

While U M_4 -spectra show clearly resolvable differences in E_{wl} and are ideally suited for XANES oxybarometry as outlined above, identifying whether samples with intermediate E_{wl} contain a mixture of U^{IV} and U^{VI} or are a mixture of U^V and U^{IV} and/or U^{VI} can be difficult. The overall peak shape and additional post-edge features in L_3 -edge spectra, however, can provide a robust means of qualitatively identifying the dominant U valence states that are present in a sample. In particular, if samples with intermediate E_{wl} contain U^V or are a mix of tetra- and hexavalent uranium.

5. CONCLUSIONS

As presented throughout this manuscript, each U X-ray absorption edge has distinct advantages depending on the nature of the problem under investigation. The M_4 -edge is best suited for zircon oxybarometry as these measurements yield the lowest analytical uncertainties and provided high spatial resolution due to the short attenuation depth of X-rays at this energy, allowing XANES results to be directly linked with discrete zircon growth regions observed in SEM images. The M_5 -edge yields spectra that are similar in shape to the M_4 -edge but with a lower $\Delta E_{U^{VI}-U^{IV}}$ and thus lower sensitivity for estimating magma redox states. Due to interferences from potassium in the post-edge of M_4 -edge spectra, however, the M_5 -edge may be well-suited for future U XANES investigations of minerals with high-K concentrations. While the L_3 -edge is less precise for oxybarometry than the $M_{4,5}$ -edges, it provides important information on the bulk U valence state in a sample making it well suited for studies of element partitioning and melt polymerization. We hope that this comparative analysis serves as a useful guide for future U XANES studies of zircon and other U-bearing minerals.

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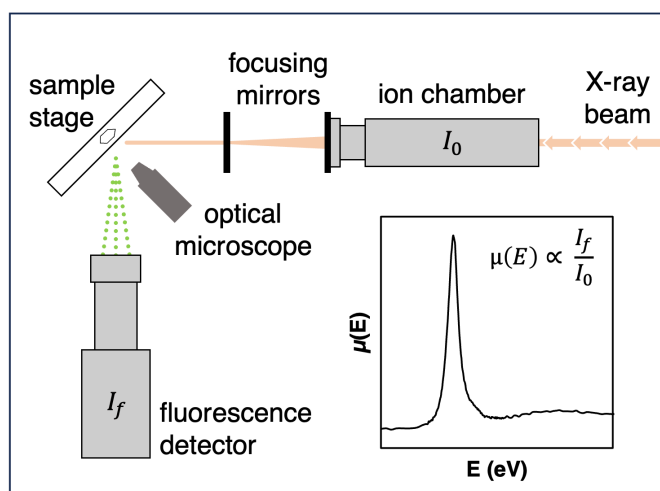


Figure 1. Generalized schematic of the experimental set up at the beamlines used in this study.

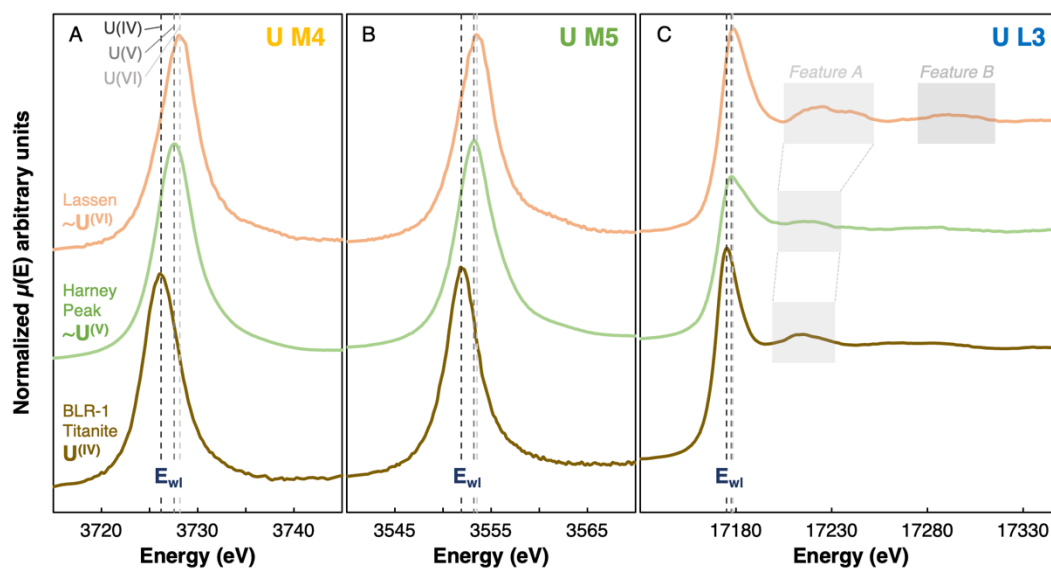


Figure 2. Comparison of uranium M₄-, M₅-, and L₃-edge XANES spectra for samples containing dominantly U^{IV}, U^V, and U^{VI} valence states. A) M₄-edge, B) M₅-edge, C) L₃-edge. Dashed lines show the approximate location of the U^{IV}, U^V, and U^{VI} white-line energies. Colored boxes in panel C highlight post-edge features of L₃-edge spectra (see main text for details).

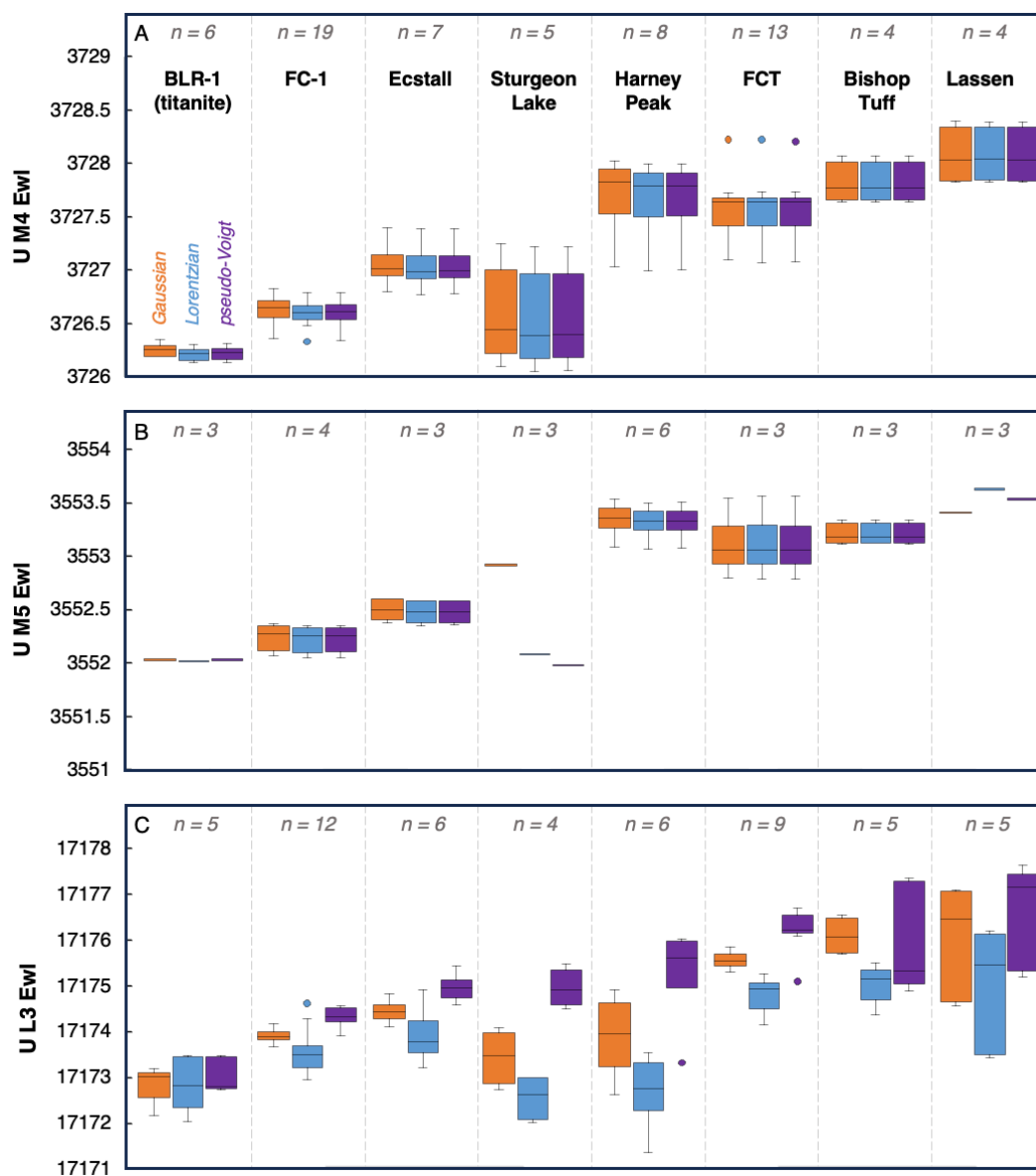


Figure 3. Box-and-whisker plots comparing fitting procedures for M_4 -, M_5 -, and L_3 -edge XANES spectra using Gaussian (orange), Lorentzian (blue), or pseudo-Voigt (purple) peak shapes. A) M_4 -edge, B) M_5 -edge, C) L_3 -edge. For each sample and edge, n is the number of grains measured.

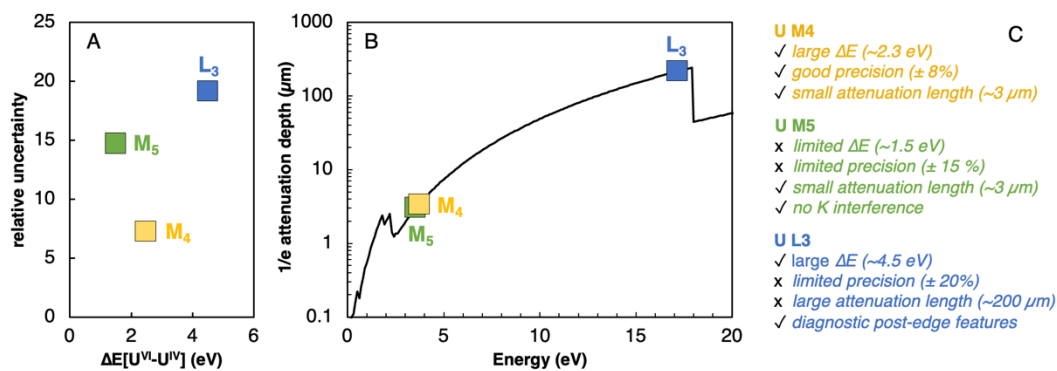


Figure 4. Comparison of ΔE , precision, and X-ray attenuation depth for M_4 -, M_5 -, and L_3 -edges. A) $\Delta E_{U^{VI}-U^{IV}}$ versus % uncertainty. B) 1/e X-ray attenuation depth. C) Pros and cons for zircon XANES oxybarometry for each of the U absorption edges investigated.

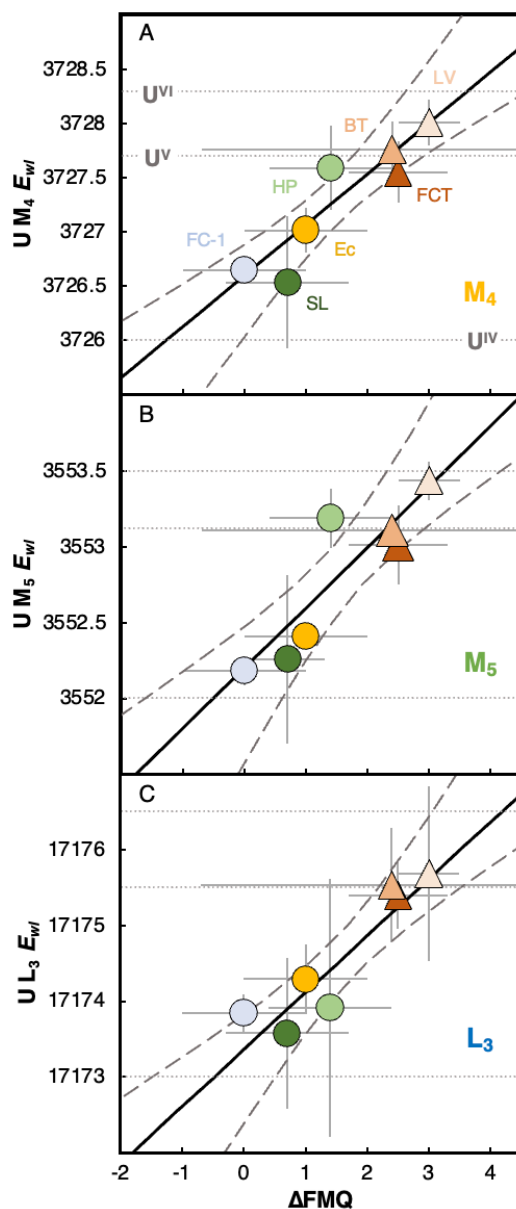


Figure 5. Comparison of U XANES calibration curves for M_4 -, M_5 -, and L_3 -edge XANES oxybarometry. A) M_4 -edge, B) M_5 -edge, C) L_3 -edge. Horizontal dotted lines are the nominal white-line energies of U^{IV} , U^V , and U^{VI} . Thick black line is the best-fit and gray dashed lines are the 95% confidence interval. Vertical error bars are the 2 SE for each sample. Horizontal error bars are from the published fO_2 estimates for each sample. SL = Sturgeon Lake; Ec = Ecstall pluton; HP = Harney Peak; FCT = Fish Canyon Tuff; BT = Bishop Tuff; LV = Lassen Volcano.

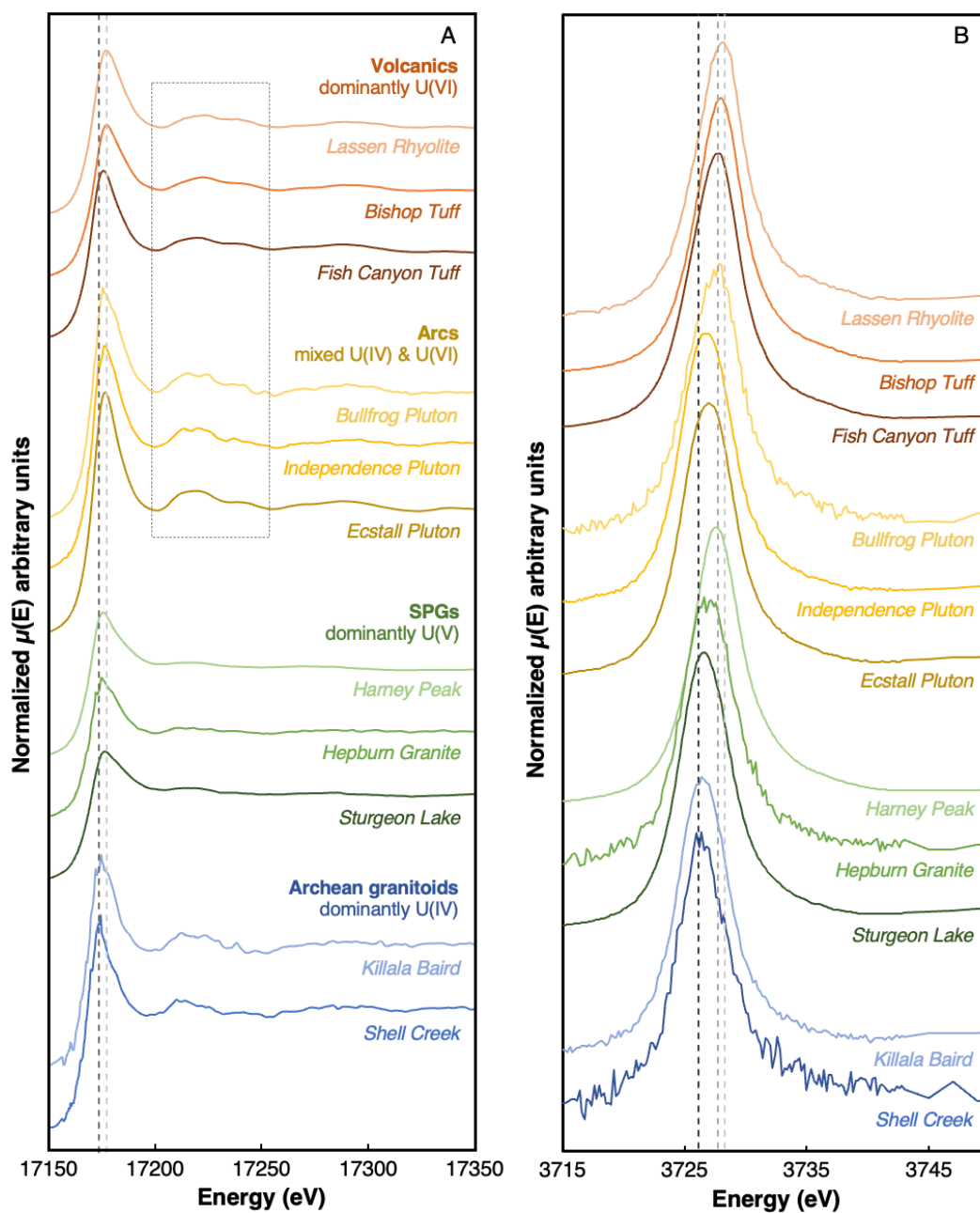


Figure 6. Comparison of zircon L₃- and M₄-edge spectra for samples of different lithology. A) L₃-edge, B) M₄-edge. Dashed box in A highlights the diagnostic U^{VI} double hump post-edge feature that is most prominent in zircon from Phanerozoic felsic volcanic rocks and arc-related rocks.

Table 1. List of samples analyzed in this study.

Sample	Lithology	Age (Ma)	Edge	Reference
<i>Volcanics</i>				
Lassen	<i>rhyolite</i>	0.035	M ₄ , M ₅ , L ₃	<i>Underwood et al. (2012)</i>
Bishop Tuff	<i>rhyolite</i>	0.76	M ₄ , M ₅ , L ₃	<i>Hildreth & Wilson (2007)</i>
Fish Canyon Tuff	<i>dacite</i>	28.4	M ₄ , M ₅ , L ₃	<i>Schmitz & Bowring (2001)</i>
<i>Arc granitoids</i>				
Ecstall Pluton	<i>granodiorite</i>	91.5	M ₄ , M ₅ , L ₃	<i>Butler et al. (2002)</i>
Bullfrog Pluton	<i>granite</i>	102	M ₄ , L ₃	<i>Chen & Moore (1982)</i>
Independence Pluton	<i>granite</i>	100-104	M ₄ , L ₃	<i>Chen & Moore (1982)</i>
<i>SPGs</i>				
Harney Peak Granite	<i>granite</i>	1750	M ₄ , M ₅ , L ₃	<i>Bucholz et al. (2018)</i>
Hepburn Granite	<i>granite</i>	1898	M ₄ , L ₃	<i>Lalonde (1989)</i>
Sturgeon Lake Granite	<i>granite</i>	2602	M ₄ , M ₅ , L ₃	<i>Bucholz et al. (2018)</i>
<i>Archean granitoids</i>				
Killala Baird Batholith	<i>TTG</i>	2681	M ₄ , L ₃	<i>Corfu & Andrews (1987)</i>
Shell Creek	<i>monzonite</i>	2878	M ₄ , L ₃	<i>Frost & Fanning (2005)</i>
<i>Titanite</i>				
BLR-1	<i>metamorphic megacryst</i>	1047	M ₄ , M ₅ , L ₃	<i>Aleinikoff et al. (2007)</i>

Chapter IV

OXIDIZED HADEAN MAGMAS AND ARCHEAN MOBILE-LID
TECTONICS REVEALED BY JACK HILLS ZIRCON

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ABSTRACT

Mobile-lid tectonics is a first-order feature characterizing the modern Earth, yet its origins remain enigmatic due to a scarcity of ancient terrestrial materials. Detrital zircons provide the most complete archive of Earth's early crust, and preserve the only record extending beyond ~4.0 Ga. Here, we combine U XANES oxybarometry with U-Pb and trace element analysis to investigate the igneous cores and metamorphic rims of Hadean-Archean zircon from the Jack Hills, Australia. Igneous cores record consistent, moderately oxidized magma conditions (FMQ-1 to +1), challenging notions of a highly reduced early Earth and supporting models that evoke efficient mantle convection throughout the Hadean. In contrast, redox states and trace element contents show that metamorphic rims record (i) high- $f\text{O}_2$ and high-intermediate T/P conditions (FMQ+1.6 to +2.5; >600 °C/GPa) and (ii) low- $f\text{O}_2$ and generally lower T/P conditions (FMQ-0.2 to +0.5; <500 °C/GPa). While only high T/P conditions are observed in Hadean zircon rims, Archean rims (~3.35 Ga) preserve both the low and high T/P signatures, a pattern typical of large-scale plate underthrusting. These findings imply Earth's mantle had near-modern redox states by 4.15 Ga and that mobile-lid tectonics was active by the early Archean, at the latest.

1. INTRODUCTION

Mobile-lid tectonics is the fundamental feature of modern Earth geodynamics that drives the rich geological diversity of our world. When this unique tectonic mode first developed is, however, an intensely debated topic owing to the self-erasing nature of this process ([Harrison, 2024](#)). Like a palimpsest, the record of Earth's early evolution has been obfuscated by eons of subduction, orogenesis, and crustal recycling. With only scattered remnants of our planet's formative years available for study, and hardly any known rock older than ~4.0 Ga ([Bowring and Williams, 1999](#); [Sole et al., 2025](#)) the most complete early terrestrial archive at our disposal are detrital crystals of the remarkably resilient mineral zircon ([Harrison, 2020](#)). Most notably, zircon from the Jack Hills, Australia (~3.0-4.38 Ga), have provided unparalleled insight into the processes and conditions prevailing in the Hadean and early Archean ([Wilde et al., 2001](#); [Valley et al., 2014](#); [Harrison et al., 2017](#); [Carley et al., 2022](#)). Yet, their potential to elucidate the nature of metamorphism on the early Earth is unexplored.

On modern Earth, metamorphic thermobaric ratios (T/P) are intrinsically linked to tectonic settings ([Brown and Johnson, 2019](#)). Low T/P values (<375 °C/GPa) are associated with the subduction or imbrication of cold crust in accretionary and collisional orogens and are indicative of convergent boundary tectonics. Intermediate T/P values (375-775 °C/GPa) are associated with mountains belts in collisional orogens, also suggesting mobile-lid processes. High T/P metamorphism (>775 °C/GPa) can result from crustal thickening or from arc- or plume-related magmatism in either mobile or stagnant-lid tectonic regimes. Conveniently, zircon grains formed in different metamorphic environments exhibit distinct physiochemical characteristics depending on the pressure-temperature conditions and composition of their protolith. For instance, metamorphic zircon formed in low T/P conditions (*e.g.*, eclogite facies) often exhibits weakly negative to positive Eu anomalies due to the breakdown of plagioclase ([Rubatto, 2017](#)), while intermediate or high T/P zircon (*e.g.*, granulite facies) may have elevated Ti concentrations and show enrichments in LREE due to the breakdown of monazite ([Strong et al., 2022](#)). In cathodoluminescence (CL) images, high-grade metamorphic zircon or zircon crystallized from anatectic melts often manifests as discrete CL-bright rims that mantle relict cores ([Rubatto, 2017](#); [Du et al., 2023](#)). These highly luminescent rims are typically homogenous, exhibit weak to no oscillatory zonation, and show a sharp boundary that may truncate or embay the primary zonation of their relict core. In contrast, metamorphic zircon domains formed at lower P-T conditions often appear dark or patchy and may show clear signs of fluid alteration (see

Rubatto (2017), for a concise comparison of metamorphic zircon textures). Using the physiochemical characteristics outlined above, identification and investigation of metamorphic domains within ancient zircon can shed light on early Earth metamorphism and geodynamics.

Oxygen fugacity (fO_2) can also be an indicator of tectonic process and is an important factor for understanding the coevolution of the solid-Earth and atmosphere. For instance, arc-related rocks generally exhibit higher fO_2 relative to modern MORB (~FMQ-1 to +3 *versus* FMQ-1 to 0, respectively, where FMQ denotes the fO_2 of the Fayalite-Magnetite-Quartz buffer) (Cottrell et al., 2021). In the context of metamorphism, granulite-facies rocks often record high fO_2 (~FMQ > 0) (Harlov, 1992; Singh and Prakash, 2019) resulting from the breakdown of hydrous minerals, while deeply subducted rocks generally record lower fO_2 (~FMQ ≤ 0) (Aulbach et al., 2019) with a general decrease in oxygen fugacity with depth (Stagno and Fei, 2020). Magma fO_2 also dictates the speciation of volcanic gases, influencing atmospheric composition. Redox estimates for the early continental crust, however, vary widely (FMQ-6 to +6) (Trail et al., 2011; Yang et al., 2014), leaving questions regarding the evolution of the lithosphere, atmosphere, and potential habitability open.

Here, we seek to illuminate the tectonic setting and redox conditions of continental-type crust on the early Earth by investigating the igneous cores and metamorphic rims of a suite of Jack Hills zircon (JHZ) using a combination of SIMS U-Pb geochronology and trace element analysis, in conjunction with a new zircon-based oxybarometer based on U M₄-edge X-ray absorption near-edge structure spectroscopy (U XANES) (Houchin et al., 2024).

2. SAMPLES

From a collection of JHZ, a suite of grains exhibiting CL-bright rims with morphologies characteristic of growth during high-grade metamorphism were identified. In such settings, new zircon domains (i.e., rims) can potentially form via subsolidus recrystallization or by precipitation from fluids and/or partial melts. For this reason, we describe the CL-bright rim domains simply as *metamorphic zircon*. As recommended by (Yakymchuk, 2023), this term does not specify where along a P-T path or by what mechanism newly formed zircon grew.

Approximately 1600 grains were surveyed, and from these, 16 grains with rims wide enough for analysis (>10 μm) were selected. SIMS and U XANES analyses were

performed on both the cores and rims of these grains. An additional 18 igneous grains previously measured for U-Pb and trace elements (Carley et al., 2022) were also analyzed using U XANES. Representative CL images of the samples are shown in Fig. 1A. Annotated images of all investigated grains are provided in the Supporting Information (*SI Appendix*, Fig. S1). To ensure reliability of the data, SEM images were collected before and after analyses and data from spots placed on cracks were discarded. Samples showing geochemical indicators of alteration (*e.g.*, high Ca) were also excluded from interpretations (see Methods for a detailed explanation of the filtering criteria). In total, trace element data for four rims and three cores were filtered out along with data for four of the additional igneous grains. No U-Pb analyses or U XANES results were discarded as none of these analysis spots were placed on cracks. U-Pb ages for grain rims are generally concordant ($\pm 10\%$) with the exception of two analyses showing $>60\%$ discordance. The $^{207}\text{Pb}/^{206}\text{Pb}$ dates of the discordant grains, however, are well within the 2SD uncertainty of other rim domains and show similar $f\text{O}_2$ and trace element compositions as concordant samples. As such, these grains were not filtered from the dataset. Nevertheless, we note that their inclusion or exclusion does not change the conclusions of this study.

3. RESULTS

3.1 Age and XANES $f\text{O}_2$

The ages of igneous zircon cores investigated define two groups corresponding to the two main peaks documented in the JHZ age spectrum at 4150-3950 Ma and 3450-3300 Ma (Fig 1b). The $f\text{O}_2$ of the igneous cores are remarkably consistent, varying between $\sim\text{FMQ}-1$ to $+1$, with an average of $\text{FMQ}-0.2 \pm 0.2$ (2 SE) for Hadean cores and $\text{FMQ}-0.5 \pm 0.2$ (2 SE) for Archean cores. In all cases, grain rims are more oxidized than their corresponding core and can be sorted into two categories: high- $f\text{O}_2$ rims ($\text{FMQ}+1.6$ to $+2.5$) and low- $f\text{O}_2$ rims ($\text{FMQ}-0.2$ to $+0.5$) (Fig 1b).

3.2 Trace element systematics

The two types of rims identified on the basis of $f\text{O}_2$ also display clear trace element systematics characteristic of different formation environments. We focus on Th/U, Ti, Eu/Eu*, and chondrite-normalized REE concentration patterns for interpretation and comparison with other samples. REE patterns for the rim domains and the range of REE for igneous cores are plotted in Fig. 2. REE patterns for each individual grains' core and rim are available in the Supplementary Materials (Chapter 4, Appendix 1, Fig. S2).

Th/U ratios are commonly used to distinguish igneous ($\text{Th/U} > 0.1$) from metamorphic zircon ($\text{Th/U} < 0.1$). This simple distinction, however, is not always applicable as zircon formed at high metamorphic grades may also have high Th/U ratios due to the prograde breakdown of monazite and other Th bearing phases (Yakymchuk et al., 2018). While $\text{Th/U} > 0.1$ is not unique to igneous zircon, high Th/U can be a preliminary indicator of growth at high P-T conditions for zircon domains inferred to be metamorphic based on morphology or other geochemical signatures (Rubatto, 2017; Yakymchuk et al., 2018). Except for one analysis, all CL-bright rim domains show $\text{Th}_i/\text{U}_i > 0.1$ pointing to a high-grade metamorphic origin (subscript *i* denotes age-corrected values). Igneous cores and grains also have Th_i/U_i ratios > 0.1 consistent with their magmatic origin.

Titanium substitution in zircon forms the basis of a robust geothermometer (Watson and Harrison, 2005; Ferry and Watson, 2007) that has been widely applied to studies of both igneous and metamorphic zircon. The igneous cores studied here have Ti-temperatures consistent with other magmatic JHZ grains ($\sim 600\text{--}750^\circ\text{C}$), while the metamorphic rims show generally higher T with the high- $f\text{O}_2$ rims in the $\sim 700\text{--}940^\circ\text{C}$ range and the low- $f\text{O}_2$ rims in the $\sim 640\text{--}825^\circ\text{C}$ range. Since the activity of SiO_2 and TiO_2 are unconstrained for detrital grains, we assume a value of unity for each parameter and apply a typical uncertainty of $\pm 60^\circ\text{C}$ for individual measurements as this range encompasses the potential effects of overestimating either parameter (Ferry and Watson, 2007). Ti in zircon can also be affected by secondary alteration, this however, typically leads to increased Ti concentrations and hence higher calculated T. As such, the Ti-in-zircon temperatures we report are more likely to be maximum rather than minimum values.

Zircon Eu anomalies ($\text{Eu}/\text{Eu}^* = \text{Eu}_\text{N}/\sqrt{(\text{Sm}_\text{N} \cdot \text{Gd}_\text{N})}$) are typically attributed to plagioclase fractionation or breakdown and often related to the pressure of melt generation (Rubatto, 2017; Tang et al., 2021). Europium exists in two valence states, Eu^{2+} and Eu^{3+} , the former being highly compatible in plagioclase and leading to preferential incorporation of Eu during plagioclase crystallization (see inset Fig. 2A). This depletes Eu from the melt and results in a negative Eu anomaly ($\text{Eu}/\text{Eu}^* < 1$) in zircon. Conversely, during high-pressure metamorphism the breakdown of plagioclase liberates excess Eu, resulting in zircon from HP-UHP rocks exhibiting weakly negative to positive Eu/Eu^* (Rubatto, 2017). Igneous cores have Eu/Eu^* of 0.1-0.4, typical of other JHZ and indicative of crystallization from melts in equilibrium with plagioclase. High- $f\text{O}_2$ rim domains ($n=5$) are mostly within the upper portion of this range having Eu/Eu^* values of 0.2-0.6. Low- $f\text{O}_2$ domains ($n = 7$)

exhibit generally higher Eu anomalies with all but two samples having $\text{Eu}/\text{Eu}^* > 0.6$ and two grains showing $\text{Eu}/\text{Eu}^* > 1$.

REE diagrams of grain cores are consistent with igneous JHZ from other studies (Carley et al., 2022) supporting their magmatic nature. Relative to the igneous cores, high- $f\text{O}_2$ rims are enriched in LREE and have REE patterns that resemble metamorphic zircon formed at granulite facies conditions (Hoskin and Black, 2000; Reimink et al., 2014; Strong et al., 2022) (Fig 2A). Low- $f\text{O}_2$ rims, on the other hand, have generally higher Eu/Eu^* and REE patterns that overlap with the field for metamorphic zircon from HP-UHP felsic rocks (Wu et al., 2007; Liu et al., 2012; Li et al., 2014; Chen et al., 2015; Du et al., 2023) (Fig. 2B).

4. DISCUSSION

4.1 U XANES versus trace element oxybarometers

As a direct measure of an element's oxidation states, XANES offers advantages over trace element-based redox proxies. We compare our U XANES oxybarometry results with two common trace element-based oxybarometers (Trail et al., 2012; Loucks et al., 2020). The model of Loucks et al. (2020) (Fig. 3A), which uses zircon Ce, U, and Ti concentrations, predicts a similar range in $f\text{O}_2$ but fails to capture the systematic core-rim relationships revealed by U XANES: *e.g.*, rims more oxidized than cores (Fig. 3A). Additionally, this model predicts that grain cores evenly populate a range of >3 log units (FMQ-1 to +2), while U XANES records a much more limited range of <2 log units ($\sim$ FMQ-1 to +1), with 90% of cores falling within an even tighter range of only 1 log unit (FMQ-1 to 0) (Fig. 1C). The method of Trail et al. (2012), which uses zircon Ce anomalies and Ti concentrations to compute $f\text{O}_2$, returns an even greater spread of ~ 10 log units (Fig. 3B) and predicts grain rims to be more reduced than grain cores. Using their model, oxidation states of the igneous cores vary from FMQ+1 to -4.5 and rims from FMQ-3 to -9, the latter being an impossibly low value, below the iron-wüstite buffer, where no FeO should be present in the melt. Since neither trace element based oxybarometers have been calibrated for metamorphic zircon, they may not be applicable to assessment of the metamorphic zircon rims. In contrast, because the U XANES oxybarometer relies on direct measurement of U oxidation states, it is applicable to zircon of any origin. Focusing solely on the grain cores, where both trace element based oxybarometers should be applicable, our data show that these proxies fail to constrain the redox states with the same level of accuracy and precision as the U XANES approach (Fig 3C).

The discrepancy between U XANES and other zircon redox proxies arises from the dependency of zircon trace element composition on a variety of factors other than fO_2 (e.g., melt composition, temperature) (Loader et al., 2022). For instance, trivalent REEs become more compatible with increasing temperature leading to subdued Ce anomalies in high-T zircon (Zou et al., 2019). Additionally, the breakdown of monazite (Yakymchuk et al., 2018) and/or fluid mobilization of LREEs during the breakdown of hydrous minerals (Strong et al., 2022) can greatly enrich the resulting melts/fluids in LREEs, effectively reducing the magnitude of zircon Ce anomalies (Reimink et al., 2014). Indeed, we not only observe a decrease in Ce/Ce* with increasing temperature in the zircon rims and cores studied here (Fig. 3D), but Ce/Ce* also appears to decrease as ΔFMQ determined from U oxidation states increases (Fig. 3E). This result is contrary to the expected trend of increasing Ce/Ce* with increasing oxidation state (Trail et al., 2012). High fO_2 can result from high H₂O content (Ge et al., 2023) and the breakdown of hydrous minerals during upper amphibolite to granulite-facies metamorphism could generate fluids and/or partial melts that are rich in water and incompatible elements (e.g., LREEs) leading to subdued Ce/Ce* despite high fO_2 . This behavior readily explains the low fO_2 values predicted for the metamorphic rims by the model of Trail et al. (2012). We find that the ratio Ce/U, however, is well correlated with fO_2 in our samples (Fig. 3F). This is expected as the compatibility of oxidized Ce and U in zircon exhibit opposite behaviors, with Ce becoming more compatible and U less compatible as their oxidation states increase. Although zircon Ce/U ratios are factored into the oxybarometer of Loucks et al. (2020), their model treats U oxidation state in silicate melts as a constant across the entire fO_2 range of their calibration data set (~FMQ-5 to +3), despite previous work showing that U valence varies with melt oxygen fugacity (Schreiber, 1983; Burnham and Berry, 2012; Halse, 2014). For the reasons outlined above, zircon oxybarometry based on trace element concentrations should be treated with skepticism and inferences based on these proxies should be revisited. Throughout this study, only U XANES redox estimates are used for interpretation and discussion.

4.2 Magma redox conditions

Our U XANES and SIMS analyses of igneous zircon cores indicate a remarkable consistency of magma redox conditions and trace element compositions from the Hadean to Archean, suggesting (i) that early Earth magmas formed under relatively oxidized conditions (~FMQ-1 to +1), and (ii) that similar magma sources and modes of formation

were in operation from ~4.15 Ga to ~3.35 Ga. A subset of our igneous zircon cores were previously measured for oxygen isotopes and show mantle-like values ($\delta^{18}\text{O} \approx 5\text{--}6\text{‰}$ relative to VSMOW), implying that the redox state of the upper mantle during the Hadean was also near the FMQ buffer. Although fractional crystallization is required for partial melts of the mantle to reach zircon saturation, this process is expected to change oxygen fugacity by less than ± 1 log unit and the measured $f\text{O}_2$ should generally reflect that of the source (Cottrell et al., 2021). This result is inconsistent with claims that the crust and upper mantle of the early Earth were highly reduced (Yang et al., 2014; Stagno and Fei, 2020; Sossi et al., 2020), instead supporting the notion of relatively oxidized conditions during the early stages of Earth's evolution (Pahlevan et al., 2019; Kuwahara et al., 2023; Zhang et al., 2024). As the identity of gaseous species released during volcanic eruptions is a function of magma redox state (Zahnle et al., 2007), this result also has implications for early Earth atmospheric composition and habitability.

While trace element-based zircon oxybarometry has previously been used to explore magma redox conditions in the Hadean, estimates for individual grains were highly variable. For instance, results from Trail et al. (2011) vary across almost nine orders of magnitude from ~FMQ-5 to +4, with zircon from mantle equilibrated melts ranging from ~FMQ-2 to +4. Likewise, $f\text{O}_2$ values for JHZ zircon using the method of Loucks et al. (2020) range from ~FMQ-5 to +3 (Ge et al., 2023). Our results place much tighter bounds on the redox states of the JHZ source magmas, to within ± 1 log unit of the FMQ buffer throughout the Hadean and early Archean, with an average value of FMQ-0.3 $\pm$ 0.7 (2 SD).

4.3 Metamorphic Conditions

As the igneous zircon cores we studied are alike in composition and oxidation state, their source rocks were likely formed through similar processes, and their zircon rims presumably formed during metamorphism of geochemically similar protoliths. Differences in metamorphic conditions should thus be the primary driver affecting geochemical variations in the rims. While it is possible that grains were eroded from their source rocks, incorporated into sediments, and subsequently metamorphosed, the lack of an evident garnet signature (e.g., HREE depletion) favors a granitoid or arkosic protolith (Chen and Zheng, 2017), as their lower Al content relative to pelitic protoliths leads to less garnet growth during metamorphism.

Metamorphic conditions during zircon rim growth were constrained using Ti concentrations and Eu anomalies as proxies for temperature and pressure, respectively (Fig.

4A). While the Ti-in-zircon thermometer is robust (Watson and Harrison, 2005; Ferry and Watson, 2007), pressure estimates based on zircon Eu/Eu* come with greater uncertainties and may be influenced by other factors. The potential effects of Eu redox state (Yakymchuk et al., 2023), titanite co-crystallization (Loader et al., 2017), and assimilation/fractional crystallization (Bell and Kirkpatrick, 2021) on zircon Eu/Eu* were evaluated and found unlikely to account for the Eu anomalies observed in the zircon rims. Elevated Eu/Eu* is therefore interpreted to primarily reflect the high-pressure breakdown of plagioclase. Detailed discussion of these caveats and calculation of pressure from zircon Eu/Eu* can be found in Methods.

4.4 High- fO_2 rims

High- fO_2 metamorphic domains record oxidation states consistent with granulite-facies metamorphism (Harlov, 1992; Singh and Prakash, 2019) (Fig. 1C) and have trace element compositions resembling zircon from Archean and Proterozoic gneisses (Fig. 2A) (Hoskin and Black, 2000; Reimink et al., 2014; Strong et al., 2022; Kaempf et al., 2024). P-T conditions for these analog samples (Fig. 2; *SI Appendix*) cover P and T of, respectively, 0.45-0.7 GPa and 600-850 °C (Hoskin and Black, 2000; Strong et al., 2022; Kaempf et al., 2024), which overlaps with the range of values calculated for the high- fO_2 rims based on Eu/Eu* and Ti concentrations (0.1-2.1 GPa and 694-939 °C), though pressures for the high- fO_2 rims calculated from Eu/Eu* are generally greater (~1 GPa average). The P-T conditions for high- fO_2 rims plot within the HP-granulite and granulite facies fields (Fig. 4B) and record intermediate to high T/P ratios of 596-1565 °C/GPa.

High oxygen fugacity is often correlated with high H_2O (Ge et al., 2023) and the oxidized nature of the high- fO_2 domains likely arises from the breakdown of hydrous minerals during prograde metamorphism. The breakdown of monazite at high-T can also explain the enrichments in LREEs and high Th/U (>0.1) observed in the high- fO_2 rims. Oxidation states may also be enhanced by the incompatible nature of Fe^{3+} relative to Fe^{2+} during anatexis, leading to elevated fO_2 within low degree partial melts (Tang et al., 2018). Consistent with these interpretations, the P-T conditions determined for the high- fO_2 rims lie above the wet basalt solidus where hydrous partial melting would be expected.

4.5 Low- fO_2 rims

Low- fO_2 metamorphic rims show similar trace element systematics to metamorphic zircon from HP-UHP felsic gneisses and migmatites of the Mesozoic Dabie-

Sulu orogen (Wu et al., 2007; Li et al., 2014; Chen et al., 2015) and Proterozoic Miyun Group (Du et al., 2023), both of which are examples of continental collision zones (Fig. 2B). Rocks from the Dabie-Sulu orogen record peak pressures ≥ 4.5 GPa (Wang et al., 2023), with most new zircon growth thought to have occurred at ~ 1 -3 GPa (Wu et al., 2007; Liu et al., 2012; Li et al., 2014; Chen et al., 2015; Wang et al., 2023). Peak pressure estimated for the Miyun Group rocks are ~ 1.2 GPa (Zhang et al., 2019). Zircon from both of these units are characterized by weakly negative to positive Eu anomalies, moderate HREE/LREE values, and Ti-temperatures of 650-850 °C (Wu et al., 2007; Li et al., 2014; Chen et al., 2015; Du et al., 2023). Additionally, zircon with similar CL-bright rims to our samples have been observed in both localities. The geochemical characteristics listed above are also common to zircon from jadeitites (Fu et al., 2010; Lei et al., 2016), a rock type unique to low T/P environments. Zircon with weakly negative to positive Eu anomalies are also found within eclogites, though typically these samples have much flatter HREE patterns (Rubatto and Hermann, 2007; DesOrmeau et al., 2015) due to the greater proportion of garnet relative to rocks derived from felsic protoliths. As the JHZ source rocks are thought to be broadly granitic (Harrison et al., 2017; Turner et al., 2020) HP-UHP quartzofeldspathic orthogneisses are the preferred analog for the low- fO_2 domains.

While most low- fO_2 rims exhibit high-pressure signatures, two rims show strongly negative Eu anomalies suggesting formation at lower pressure. We thus categorize the low- fO_2 rims as either low T/P (n=5) or high T/P (n=2) domains (Fig. 4A). For the rims with weakly negative to positive Eu anomalies (0.6 to >1), the calculated P ranges from 1.1 to 2.9 GPa, which closely matches the pressure range determined for zircon formation within the Dabie-Sulu orogen. Average P-T values for the high Eu/Eu* samples fall mostly within the eclogite facies field (Fig. 4B), with T/P ratios ranging from 268-514 °C/GPa. Notably, the two rims with Eu/Eu* > 1 yield pressures above the albite breakdown reaction as would be expected for zircon exhibiting positive Eu anomalies. Conversely, the low- fO_2 rims with strongly negative Eu anomalies (0.08 and 0.17) suggest formation at lower pressure, and hence, show high T/P of 1337 and 1423 °C/GPa.

4.6 Tectonic Implications

The nature of early Earth tectonics is enigmatic, with a spectrum of geodynamic scenarios having been proposed (Korenaga, 2021; Lourenço and Rozel, 2023; Harrison, 2024; Hawkesworth et al., 2024). While important nuances exist, we broadly classify these as *mobile-lid* or *stagnant-lid* tectonics. Here, *mobile-lid* encompasses any tectonic mode

that involves horizontal movement and collision of crustal fragments capable of driving plate-scale underthrusting (*e.g.*, imbrication, subcretion, subduction) and the generation of low T/P metamorphic conditions. This includes sluggish- and squishy-lid tectonics as well as modern-style plate tectonic regimes. In contrast, stagnant-lid tectonics are dominated by vertical lithospheric motions (*e.g.*, sagduction, delamination, plume tectonics) and primarily generate high T/P metamorphism.

In this framework, the geochemical signatures recorded by metamorphic zircon can be used to constrain the tectonic regime in which they formed. The range of T/P values and inferred tectonic setting of each rim group are summarized in Fig. 5 and outlined below. While high-T/P metamorphism in the Hadean is consistent with either mobile- or stagnant-lid processes, the simultaneous appearance of low T/P and high T/P conditions at ~ 3.35 Ga suggests that plate-scale underthrusting was operational by then (Fig. 5A). The identification of coeval and geographically proximal intermediate T/P and high T/P conditions (known as ‘paired metamorphic belts’) recorded by whole rock samples around 2800-2500 Ma (Fig. 5B) has been argued to represent the onset of mobile-lid tectonics (Brown and Johnson, 2019). By this same reasoning, the paired low and high T/P values recorded by metamorphic zircon rims of similar age in this study suggest this process was ongoing by ~ 3.35 Ga in the Yilgarn craton. This places a minimum age for the onset of mobile-lid tectonics before the estimates of refs. (Smithies et al., 2007; Brown and Johnson, 2019; Hawkesworth et al., 2024) and in agreement with numerous other studies that suggest mobile-lid tectonics was in operation by the early Archean (Bell et al., 2014; Bauer et al., 2020; Nutman et al., 2020; Turner et al., 2020; Aarons et al., 2020; Korenaga, 2021; Drabon et al., 2022) (Fig. 5C). This conclusion is reinforced by a variety of other zircon geochemical proxies. For instance, zircon Lu-Hf isotopic data from the Jack Hills (Bell et al., 2014) and other Hadean-Archean samples (Bauer et al., 2020; Drabon et al., 2022) show a shift towards chondritic ϵ_{Hf} values between 3.8-3.6 Ga, signaling an influx of juvenile magmatism thought to be driven by mobile-lid processes. Increases in zircon Sc/Yb and U/Nb in zircon from the Barberton Greenstone Belt also suggest a shift towards arc-like magmatism during this interval (Drabon et al., 2022).

Although the high T/P conditions recorded by Hadean zircon rims cannot be uniquely attributed to a stagnant- or mobile-lid regime, the consistent f_{O_2} , Ti-temperatures, and REE compositions between Hadean and Archean igneous zircon cores suggests similar modes of magma generation across the 4.15-3.35 Ga interval and a Hadean onset of mobile-lid tectonics is allowed by our data. The paucity of low T/P zircon domains in the

Hadean may reflect preservation biases rather than an absence of mobile-lid processes. Higher mantle temperatures in the Hadean and early Archean may have induced frequent slab breakoff and greater extents of slab melting (Van Hunen and Van Den Berg, 2008), limiting the potential for exhumation and preservation of metamorphic zircon formed in deeply underthrust mafic (oceanic-like) crust. In contrast, zircon formed during collision between continental-type crustal blocks are more likely to be exhumed and preserved due to the greater buoyancy of their host rocks. Indeed, the low- $f\text{O}_2$ rim domains are markedly more similar to metamorphic zircon from HP-UHP orthogneisses (Fig. 2C) than zircon from eclogites (Rubatto, 2017) and minerals subjected to low T/P conditions under hotter Hadean-Archean geotherms may not have survived until collisions between proto-continents became widespread.

The morphologic appearance and geochemical signatures of the CL-bright zircon rims are most consistent with a high-grade metamorphic origin, however, the possibility that they formed from igneous processes (*i.e.*, due to incorporation of older cores into a younger magma) cannot be ruled out entirely. If this were the case, the interpretation that the CL-bright rims provide a record of mobile-lid processes on the early Earth would only be strengthened. Indeed, in the Phanerozoic, high- $f\text{O}_2$ melts ($\sim\text{FMQ}+2$ or greater) are almost always a signature of arc magmatism (Cottrell et al., 2021) (Fig. 1C). In our dataset, zircon rims that record redox states of $\sim\text{FMQ}+2$ date as far back as 4.15 Ga. This would suggest that settings similar to modern arcs capable of generating high- $f\text{O}_2$ magmas existed during the Hadean. As detailed throughout the manuscript, however, the rims are more likely to have a metamorphic origin, and our preferred interpretation is that the high- $f\text{O}_2$ rims are a product of granulite-facies metamorphism.

Further supporting the notion that the CL-bright rims have a metamorphic origin, the ages of the Archean rims ($\sim 3.4\text{--}3.3$ Ga) align with the timing of a known high-grade metamorphic event in the Narryer Gneiss Complex (NGC), adjacent to the Jack Hills (Nutman et al., 1991; Kinny and Nutman, 1996; Wilde and Spaggiari, 2007). Zircon with metamorphic domains formed around 3.4-3.3 Ga occur within multiple units of the NGC and have been interpreted as products of anatexis during migmatization of these units (Kinny and Nutman, 1996). It has been proposed that this widespread metamorphism reflects collision of proto-continental blocks during the early amalgamation of the Narryer Terrane as units that record distinct histories prior to ~ 3.3 Ga begin to share a similar thermal history after this time (Nutman et al., 1991). Our results help to confirm this

hypothesis as low and intermediate T/P conditions are a signature of convergent plate environments.

While the intermediate-low T/P conditions recorded by Archean zircon rims in this study provide a minimum age for the operation of mobile-lid tectonics (~ 3.35 Ga), the relatively oxidized nature of the igneous cores may point to an earlier onset. Early mantle oxidation has been attributed to Fe^{2+} disproportionation during core-mantle segregation, with metallic Fe^0 sequestered into the core and Fe^{3+} retained in the lower mantle (Frost and McCammon, 2008; Kuwahara et al., 2023). For this deep oxidized reservoir to influence crustal magmas, effective mixing involving the lower and upper mantle would be required. Mantle mixing rates are commonly linked to the prevailing tectonic regime, with mobile-lid tectonics characterized by efficient convection and fast mantle mixing rates (< 0.5 Gyr), whereas stagnant-lid regimes are typically associated with slower convection and longer mixing times (> 1 Gyr) (Debaille et al., 2013; Al Asad and Lau, 2024). The relatively rapid homogenization of radiogenic ^{142}Nd anomalies in terrestrial mantle-derived rocks suggests mantle stirring times of ~ 400 Myr since the Hadean (Hyung and Jacobsen, 2020), and with core formation largely complete by ~ 4.5 Ga, an oxidized reservoir in the lower mantle could have been entrained into the upper mantle by approximately 4.1 Ga. Although efficient mantle stirring can, in principle, occur beneath an immobile lithosphere, such rapid convection would be expected to promote horizontal plate motions, even if mantle and lithosphere dynamics are partially decoupled as in sluggish- or squishy-lid tectonic modes. We argue that the presence of oxidized magmas as early as 4.15 Ga (Fig 1C) lends credence to the idea that efficient mantle convection, and consequently, mobile-lid processes, may have been active throughout the Hadean.

This study of igneous and metamorphic JHZ shows that magmas were relatively oxidized by ~ 4.1 Ga and that continental-type crust was moving and being deeply underthrust by at least 3.35 Ga. These findings suggest that the nascent Earth was geodynamically active and similar to our modern world, with efficient mantle convection, crustal recycling, and mobile-lid processes coupling the evolution of the surface and interior early on in our planet's history. Investigation of igneous and metamorphic zircon from other Hadean and Archean terranes using U XANES in conjunction with U-Pb and trace element analyses will help refine estimates for the onset of mobile-lid tectonics and further elucidate the enigmatic origins of Earth's unique tectonic regime.

5. METHODS

5.1 U M_4 -edge XANES

XANES analyses were conducted over two sessions at the APS Beamline 13-ID-E (GSECARS) (Sutton et al., 2017). The methods used are identical to those detailed in (Houchin et al., 2024) and are summarized below. Incident energy was selected using a Si (111) double crystal monochromator and calibrated to put the maximum of the first derivative of $\mu(E)$ for an Fe foil at 7110.75 eV. XANES data were collected in fluorescence mode using the SX7 solid state detector. To reduce atmospheric attenuation and increase signal intensity all measurements were made within a He atmosphere. Measured spectra were normalized to incident intensity (I_0) measured in a He-filled, 200 mm-long ion chamber, just upstream of the KB mirror optics.

U M_4 XANES spectra were collected from ~3700-3800 eV. Energy was scanned in 2 eV steps in the pre-edge region (~3700-3715 eV) and 0.25 eV steps around the edge (3715-3745 eV). In the post-edge region energy was scanned in 0.05 Å⁻¹ steps resulting in an increasing step size moving towards higher energy. This allowed for high-resolution data in the regions of interest while keeping the overall time per scan to a minimum. Prior to XANES analysis μ XRF maps were collected for each grain using an incident energy of 17.5 keV during the first session and 3.76 keV during the second session. RGB images of Ti K α , Ca K α , and either U L α (17.5 keV) or U M β (3.76 keV) were used to ensure accurate placement of analysis points and to avoid inclusions not apparent in SEM images. μ XRF maps of all grains are available in the Supporting Information.

Calculation of fO_2 from zircon U M_4 -edge XANES spectra is based on the energy of peak absorption, or white-line (E_{wl}), which has been shown to be well correlated with independent estimates of magma redox state (Houchin et al., 2024). Analysis of XANES spectra was performed using the Larix software package (Newville, 2013), with E_{wl} for each zircon domain determined by fitting spectra using a pseudo-Voigt function with a linear background in the region around the peak (~3715-3735 eV). To ensure data consistency, grains of FC-1 zircon were measured during each session, as this sample shows particularly stable U XANES results varying by less than 0.2 eV between grains (Houchin et al., 2024). The peak positions of FC-1 zircon were consistent between sessions, and thus no corrections were made to the data. Typical uncertainties using this approach are ± 0.18 eV (2SD) for E_{wl} . Oxygen fugacity, relative to the fayalite-quartz-magnetite (FMQ) buffer, was calculated from E_{wl} using the equation:

$$\Delta FMQ = \frac{E_{wl} - E_{FC1}}{0.45} \pm 0.5 \text{ } 1\sigma$$

Where E_{FC1} is the E_{wl} value of the FC-1 zircon standard. Further details regarding spectra normalization, fitting procedures, and estimation of fO_2 from U M₄-edge XANES spectra are described in [Houchin et al. \(2024\)](#).

5.2 SIMS U-Pb

U-Pb analysis was performed at UCLA using the CAMECA ims1290 and an analytical method similar to ([Barboni et al., 2025](#)) but with a different primary beam. Analyses were undertaken with a 1 nA O₃⁻ beam focused to a ca. 5 μm diameter spot, with the Hyperion-II oxygen ion source ([Liu et al., 2018](#)) held at -13kV and the sample stage held at 10kV. Oxygen flooding to 1-2x10⁻⁵ torr was used in the sample chamber to enhance ionization of Pb. Pb/U relative sensitivity factors (RSF) were calculated using a power law relationship between UO₂/U vs Pb/U for the zircon age standard AS3 ([Paces and Miller, 1993](#)). Zircon standard 91500 ([Wiedenbeck et al., 2004](#)) was used to estimate Th and U concentrations based on Th/⁹⁴Zr₂O and U/⁹⁴Zr₂O. A common Pb correction based on the abundance of ²⁰⁴Pb was applied, assuming surface contamination by southern California environmental Pb ([Sañudo-Wilhelmy and Flegal, 1994](#)).

5.3 SIMS trace element analysis

REEs, Ca, P, Ti, Y, and Hf were measured with a Cameca IMS-7f GEO ion microprobe at the Caltech Microanalysis Center. A -13.5 keV O⁻ primary ion beam of ~5 nA and ~10 μm in size was used to sputter the surface of the zircon. Positive secondary ions at nominal +8.5 keV were counted with an electron multiplier at low mass resolution with 80 eV of energy filtering. Interferences from molecular ions were eliminated by energy filtering and deconvolutions of the HREE secondary ion signals. Si was used as a reference element and NBS610 glass as a standard to determine the relative sensitivity factors for the elements of interest.

5.4 SIMS Oxygen isotopes

Oxygen isotope analyses were performed at UCLA using the CAMECA ims1290 ion microprobe. A 2nA Cs⁺ beam was focused to a 10μm spot and accelerated at 10kV onto a sample stage held at -10kV. A normal incidence electron flood gun was used for charge compensation. ¹⁶O and ¹⁸O were analyzed by multicollection for 10 cycles of 10s

each, and the instrumental mass fractionation was determined using the zircon standard AS3 (Duluth Gabbro; 5.34 ‰ SMOW) (Trail et al., 2007).

5.5 Data filtering

To ensure reliability of data and interpretations, zircon samples were filtered based on several criteria. SEM images were collected before and after SIMS analysis and data from spots deemed to have been placed on cracks were excluded from interpretation. Secondary filtering is based on geochemical indicators of alteration. For igneous zircon, we use the LREE index (Bell et al., 2019) to filter altered samples, with a threshold of $\text{LREE-I} < 20$ used to distinguish altered grains. Metamorphic zircon may exhibit flatter REE patterns compared with igneous grains (Strong et al., 2022), and hence, commonly return low LREE-I values making this filtering criteria unsuitable for assessing alteration of metamorphic zircon. Instead, metamorphic domains with $\text{Ca} > 100$ ppm were excluded from the interpretation (Fig 3b), as high Ca concentrations can indicate mobilization of high-field-strength elements (i.e., Ti), compromising temperature estimates (Takehara et al., 2018). This threshold aligns with Ca limits used in other studies (Grimes et al., 2015; Mixon et al., 2024).

5.6 Pressure estimates from zircon Eu/Eu^*

Other than pressure, several other factors may modulate zircon Eu anomalies. In particular, high $f\text{O}_2$ may stabilize more Eu^{3+} leading to zircon with subdued Eu anomalies (Trail et al., 2012; Yakymchuk et al., 2023). The rims exhibiting high Eu/Eu^* , however, formed at an oxygen fugacity close to the FMQ buffer where abundant Eu^{2+} should be present in the melt. Titanite fractionation has also been shown to raise zircon Eu anomalies towards positive values (Loader et al., 2017), but titanite typically forms at $\Delta\text{FMQ} \geq +1$ (Xirouchakis and Lindsley, 1998), well above the $f\text{O}_2$ conditions of the high Eu/Eu^* zircon rims. Zircon Eu/Eu^* can also be affected by assimilation and fractional crystallization (Bell and Kirkpatrick, 2021). These processes, however, are more important during the evolution of large magmatic systems and should have a limited effect on the Eu/Eu^* values of metamorphic zircon grown from low degree anatectic melts or at subsolidus conditions. High $f\text{O}_2$, titanite co-crystallization, assimilation, and fractional crystallization can thus be ruled out as significant factors controlling Eu anomalies in the metamorphic zircon rims.

Pressure estimates for zircon rims were derived from Eu/Eu^* using the calibration of Tang et al. (2021) in combination with modeling results of zircon Eu/Eu^* behavior

during partial melting (Yakymchuk et al., 2023). The calibration of Tang et al. (2021) likely overestimates pressure and we take results from this model as a maximum estimate. The minimum pressure estimate is set at 1 GPa below the maximum as this range encompasses all the potential values of Eu/Eu* predicted by the model results of Yakymchuk et al. (2023) (*SI Appendix*, Fig. S3). This approach conservatively constrains pressure within a 1 GPa range. Neither study considers zircon with positive Eu anomalies, so a value of Eu/Eu* = 1 is used to calculate pressure estimates for zircon with Eu/Eu* > 1 (corresponding to ~2-3 GPa). To corroborate the pressure estimates derived from Eu/Eu*, the REE patterns of the CL-bright rims were compared with well-characterized metamorphic zircon from samples with independent P-T constraints (Fig. 2; *SI Appendix*). To maintain internal consistency of the dataset, however, only the pressures derived from Eu/Eu* are used for calculations and displayed in figures within the main text (e.g., Table 1, Fig. 4). If pressure values based on comparison with analog samples are averaged with the values derived from Eu/Eu*, the contrast between P-T conditions for the high- fO_2 and low- fO_2 rims becomes even sharper (*SI appendix* Fig. S4), further strengthening our overall conclusions.

5.7 Statistical tests

To assess the statistical significance of the three rim groups (high fO_2 & high T/P; low fO_2 & low T/P; low fO_2 & high T/P) a k-means clustering analysis and Kruskal-Wallis tests were performed. The clusters identified by the k-means algorithm are identical to the to those in Fig. 4 (*SI Appendix* Fig. S5) and differences in fO_2 and pressure between groups were found to be significant by the Kruskal-Wallis test.

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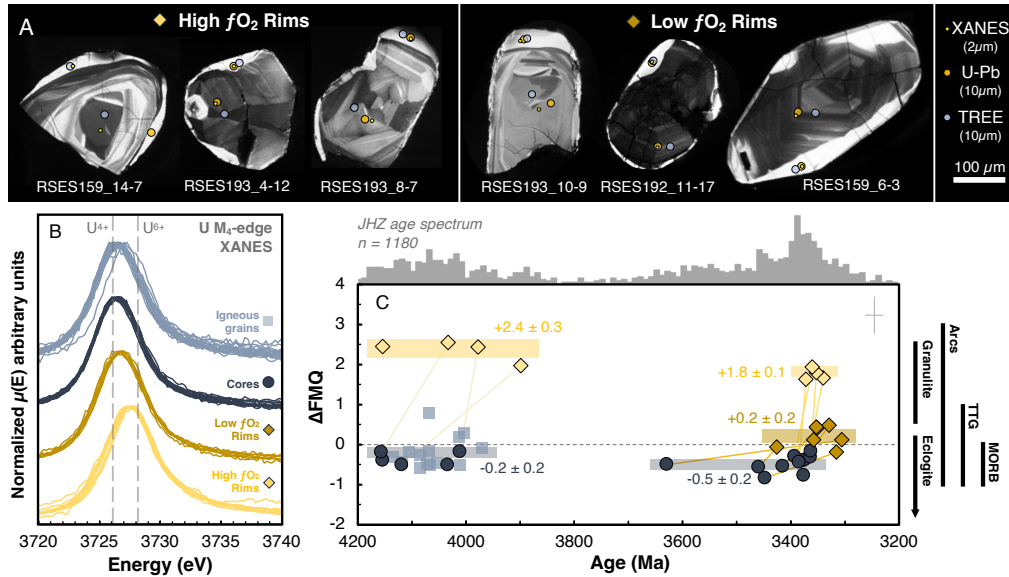


Figure 1. Overview of crystal zoning, U XANES spectra, age, and redox for studied zircon samples. (A) Example images of Jack Hills zircon with CL-bright metamorphic rims. (B) Normalized U M₄-edge XANES spectra for all zircon domains analyzed in this study. Dashed lines show the approximate locations of the U⁴⁺ and U⁶⁺ white-line energies. (C) Oxygen fugacity relative to the Fayalite-Magnetite-Quartz (FMQ) buffer vs age for the cores and rims of JHZ grains. Tie-lines connect a grain's core and rim. Rims are grouped based on their age and fO_2 . Cross shows the 1 σ uncertainty for individual measurements. Colored bars show the mean and 2 SE in ΔFMQ for each group. Grey histogram is the age spectrum for JHZ (Condie et al., 2009; Carley et al., 2022). Ranges in fO_2 for various rock types from: (Cottrell et al., 2021; Houchin et al., 2024) arcs; (Moreira et al., 2023) TTG; (Harlov, 1992; Singh and Prakash, 2019) granulite; (Aulbach et al., 2019) MORB/ eclogite xenoliths.

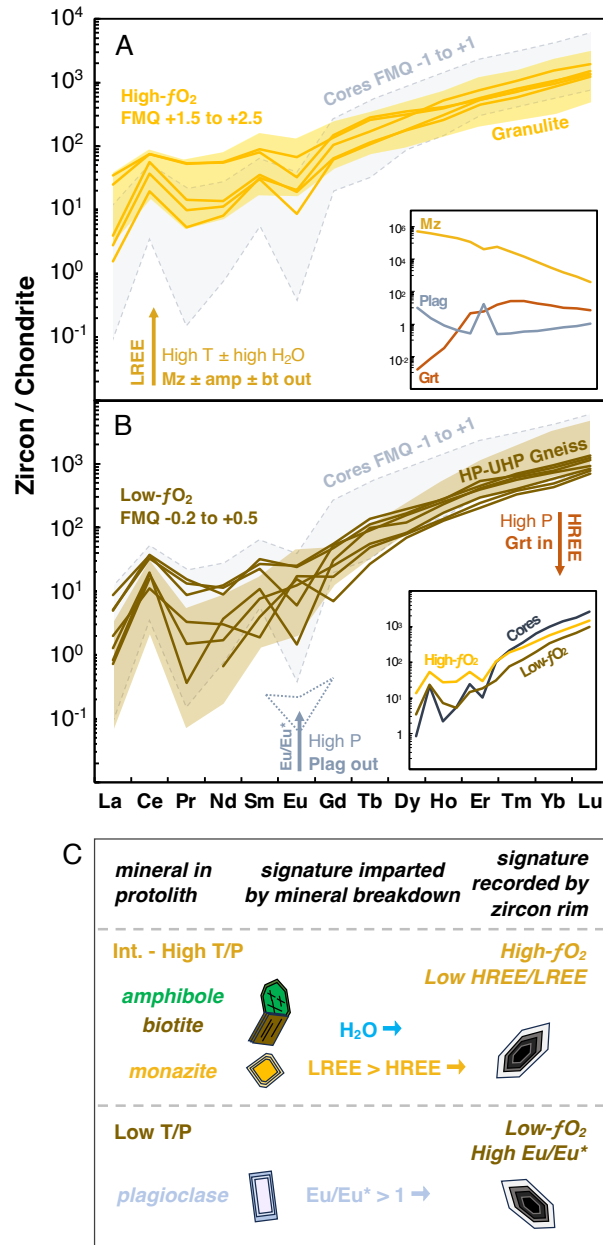


Figure 2. Chondrite normalized REE patterns of Jack Hills zircon rims and cores. (A) REE patterns of high- fO_2 rims (orange lines). The light blue shaded region shows the range of REE patterns from igneous cores analyzed in this study, while the orange shaded region shows that of zircon domains formed during granulite-facies metamorphism (Hoskin and Black, 2000; Reimink et al., 2014; Strong et al., 2022). Inset shows typical REE patterns for monazite (Mz), plagioclase (Plag), and garnet (Grt). (B) REE patterns of low- fO_2 rims (brown lines). Brown shaded region is the range of average REE patterns for metamorphic zircon from HP-UHP felsic gneisses (Wu et al., 2007; Liu et al., 2012; Li et al., 2014; Chen et al., 2015; Du et al., 2023). Light blue shaded region as in (A). Inset shows the average REE pattern for each zircon group (cores, and low-/high- fO_2 rims). (C) Key phases whose breakdown is responsible for generating the observed trace element signatures in each rim group.

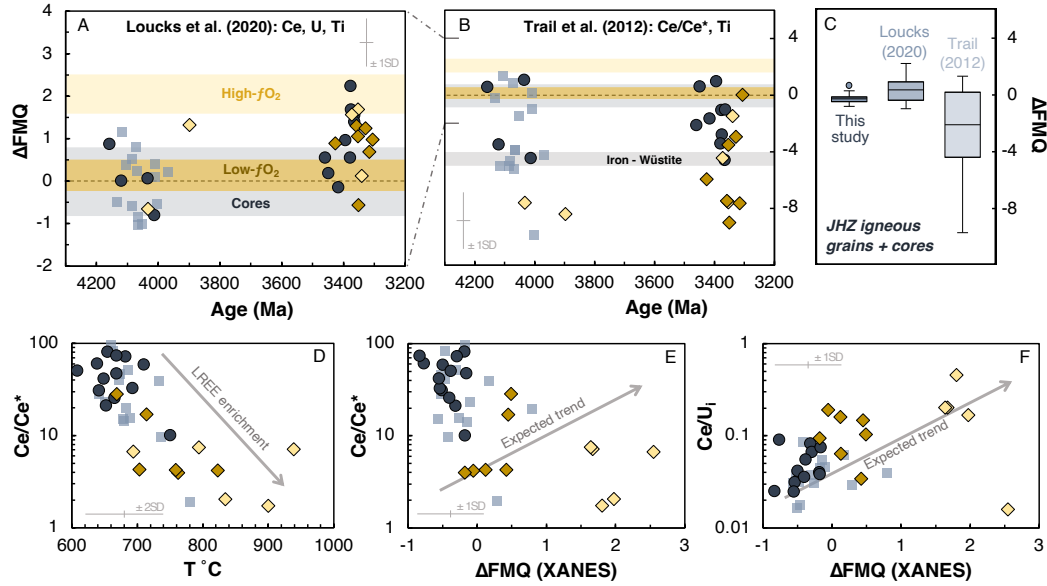


Figure 3. Comparison of oxygen fugacity estimates calculated using U XANES and trace element-based zircon oxybarometers. (A) Loucks et al., 2020 (Loucks et al., 2020) (B) Trail et al., 2012 (Trail et al., 2012). Grey cross in (A,B) shows the $\pm 1\sigma$ uncertainty in ΔFMQ reported for each method (vertical) and a typical U-Pb uncertainty of ± 25 Ma (horizontal). Colored bands represent the full range of $f\text{O}_2$ determined for each sample group using U XANES (Fig. 1C). (C) Box and whisker plot showing the distribution of $f\text{O}_2$ values for igneous JHZ using U XANES, Loucks et al. (2020), and Trail et al. (2012) methods. (D) Ce anomaly vs temperature, (E) Ce anomaly vs U XANES oxybarometry results, (F) Ce/U_i vs U XANES results, where U_i is the age-corrected U concentration.

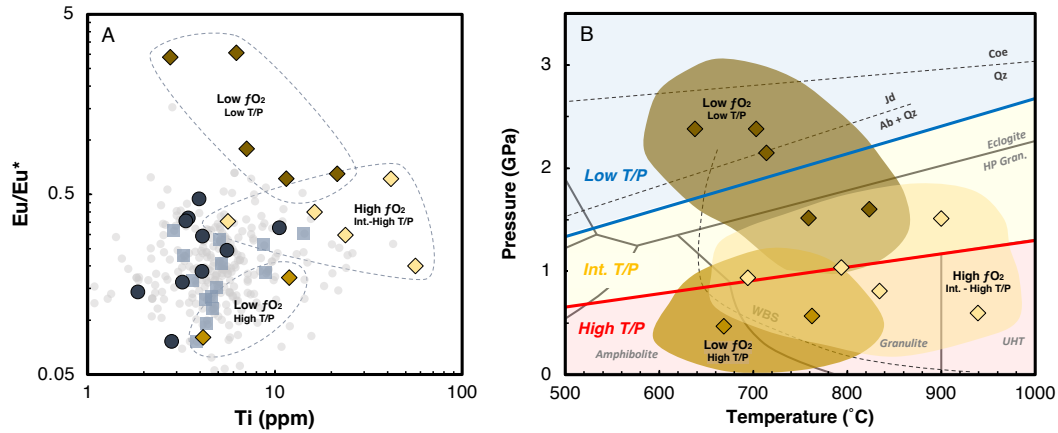


Figure 4. P-T proxies and estimates for metamorphic zircon rims. (A) Zircon Eu anomaly vs Ti concentrations for metamorphic zircon rims and igneous cores. Symbols as in Fig 1c, except “low- $f\text{O}_2$, low T/P” samples shown in darker brown color. Light grey circles are a compilation of igneous JHZ data (Carley et al., 2022). (B) Estimated P-T ranges for each zircon rim domain. Brown/yellow regions are the probability ranges for each group based on 2D kernel density estimation with P and T uncertainties of ± 0.5 GPa and ± 60 $^{\circ}\text{C}$ applied to each data point. P-T ranges are superimposed over a metamorphic facies diagram modified from (Palin et al., 2020). Facies boundaries are marked by solid lines and key phase transitions by dashed lines. Blue, yellow, and red fields represent ranges of thermobaric ratios for low T/P ($<375^{\circ}\text{C}/\text{GPa}$, blue), intermediate T/P ($375\text{--}775^{\circ}\text{C}/\text{GPa}$, yellow), and high T/P ($>775^{\circ}\text{C}/\text{GPa}$ red) (Brown and Johnson, 2019). Jd = jadeite; Ab = albite; Qz = quartz; Coe = coesite; WBS = wet basalt solidus.

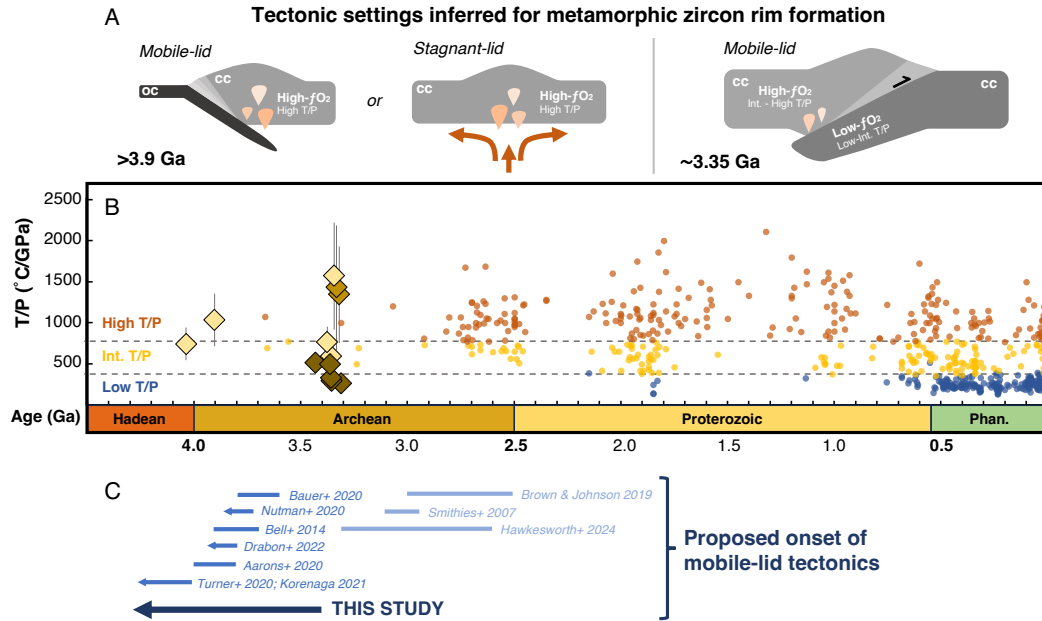


Figure 5. Summary of T/P conditions and tectonic interpretations for metamorphic zircon rims. (A) Schematic cartoon depicting the proposed tectonic setting for each rim type (cc – continental crust; oc – oceanic crust). (B) Global compilation of whole rock metamorphic T/P ratios (red, yellow, blue circles) (Brown and Johnson, 2019) and T/P estimates for metamorphic zircon rims (symbols as in Fig. 4, error bars are 1σ). (C) Timing proposed for the onset of mobile-lid tectonics based on data from this study compared with a collection of estimates from literature sources (Smithies et al., 2007; Bell et al., 2014; Brown and Johnson, 2019; Bauer et al., 2020; Turner et al., 2020; Aarons et al., 2020; Korenaga, 2021; Drabon et al., 2022; Hawkesworth et al., 2024).

Table 1. Age, fO_2 , Eu/Eu*, P-T and T/P estimates for metamorphic zircon rims.

Sample	$^{207}\text{Pb}/^{206}\text{Pb}$ Age (Ma)	ΔFMQ	Eu/Eu*	$P_{\text{Eu/Eu}^*}$ (GPa)	T (°C)	T/P (°C/GPa)
High fO_2; High T/P						
RSES159_14-7_rim	3899	2.0	0.30	0.81	835	1030
RSES192_4-16_rim	4033	2.5	0.35	0.94	694	738
RSES193_4-12_rim	3340	1.7	0.20	0.60	939	1565
RSES193_8-7_rim	3353	1.8	0.61	1.51	900	596
RSES193_10-6_rim	3372	1.6	0.40	1.04	794	763
Low fO_2; Low T/P						
RSES159_15-19_rim	3306	0.1	>1	2.38	638	268
RSES159_20-6_rim	3351	0.4	>1	2.38	703	295
RSES193_10-9_rim	3353	0.4	0.90	2.15	714	332
RSES192_11-17_rim	3426	-0.1	0.65	1.60	823	514
RSES192_18-8_rim	3358	0.1	0.61	1.52	759	499
Low fO_2; High T/P						
RSES192_6-15_rim	3316	-0.2	0.17	0.57	762	1337
RSES159_6-3_rim	3329	0.5	0.08	0.47	669	1423

Only rims with reliable trace element analyses were used to calculate T/P and included in the table.

CHAPTER 4 APPENDIX 1

Supporting Information

Analog zircon samples for REE pattern comparison and P-T estimates

To help corroborate the P-T estimates based on Ti concentrations and Eu/Eu* of the zircon rims, their REE patterns were compared with metamorphic zircon from different tectonic settings.

For the high- fO_2 rims, the samples used for comparison are metamorphic zircon domains from the Winnipeg River terrane ([Strong et al., 2022](#)) and Idiwhaa gneiss ([Reimink et al., 2014](#)), Canada, and Proterozoic gneisses from Queensland, Australia ([Hoskin and Black, 2000](#)). For the Idiwhaa gneiss, REE patterns are from 3.4-3.3 Ga zircon domains ([Reimink et al., 2014](#); their Phase III & VI), and P-T estimates are from ([Kaempf et al., 2024](#)) which identified a granulite-facies metamorphic event of this age in the Idiwhaa gneiss (0.45-0.62 GPa; 725-780 °C). [Strong et al. \(2022\)](#) and [Hoskin and Black \(2000\)](#) provide REE patterns for metamorphic zircon and report pressure-temperature estimates of 0.7 GPa/650-850 °C and 0.65 GPa/750 °C, respectively. Based on these studies, the overall range in P-T for the granulite facies zircon are 0.45-0.7 GPa and 600-850 °C.

Samples used for comparison with the low- fO_2 rims are from the Proterozoic Miyun group and Mesozoic Dabie-Sulu orogen, both in northern China. For the Miyun group, zircon REE patterns are from [Du et al. \(2023\)](#), and P-T estimates are from [Zhang et al. \(2019\)](#), who give values of ~1.2 GPa and approximately 650-850 °C. Zircon REE patterns and P-T estimates for the Dabie-Sulu orogen are from refs. ([Wu et al., 2007](#); [Liu et al., 2012](#); [Li et al., 2014](#); [Chen et al., 2015](#)) with additional P-T estimates from [Wang et al. \(2023\)](#). Pressure estimates for the Dabie-Sulu terrane range as high as 7 GPa, though most new zircon growth in Dabie-Sulu is thought to have occurred between 1-3 GPa ([Wang et al., 2023](#)). For instance, [Li et al. \(2014\)](#) and [Liu et al. \(2012\)](#) estimate zircon formation in the Sulu terrane at ~2.1 GPa and between 1-2 GPa, respectively, while [Chen et al. \(2015\)](#) gives a range of 1-4 GPa. Overall, the P-T estimates for the HP-UHP zircon we use as analogs in this study generally fall between 1-3 GPa and 650-850 °C.

Fig. S1. SEM images of all zircon grains.

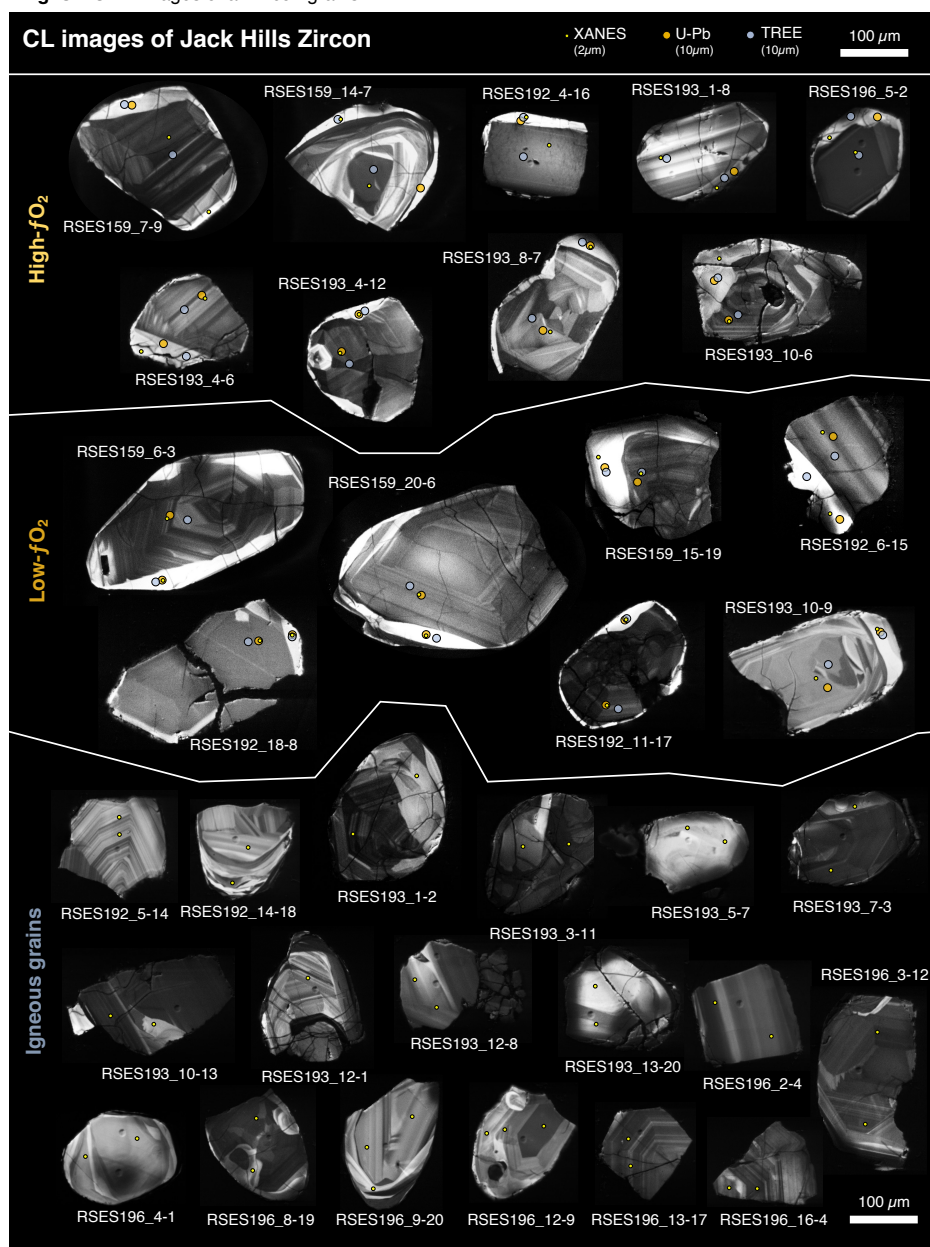


Fig. S2. REE patterns of rims and cores for individual zircon grains.

High- fO_2 (intermediate-high T/P)

Cores - dark blue lines; Rims - orange lines; discarded analyses - dashed lines

ΔfO_2 is the difference in oxygen fugacity and Δt is the difference in age between rim and core.

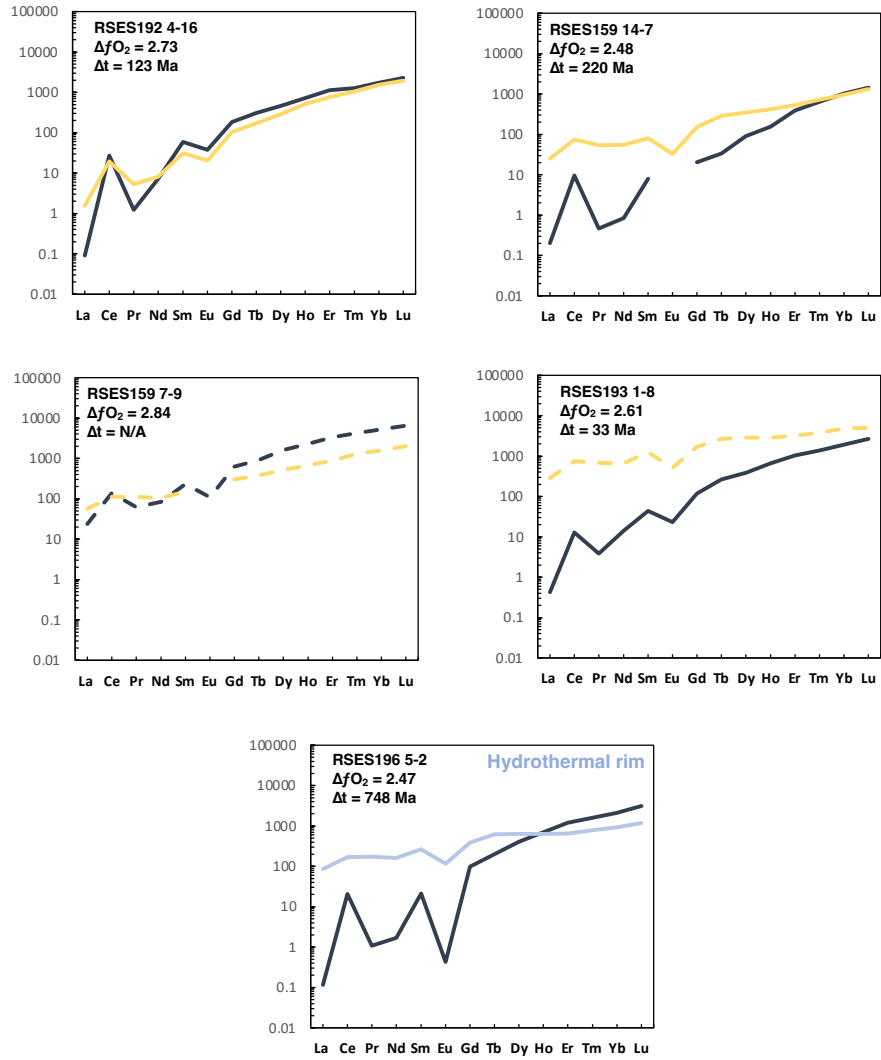


Fig. S2 (cont.)

High- fO_2 (intermediate-high T/P)

Cores - dark blue lines; Rims - orange lines; discarded analyses - dashed lines

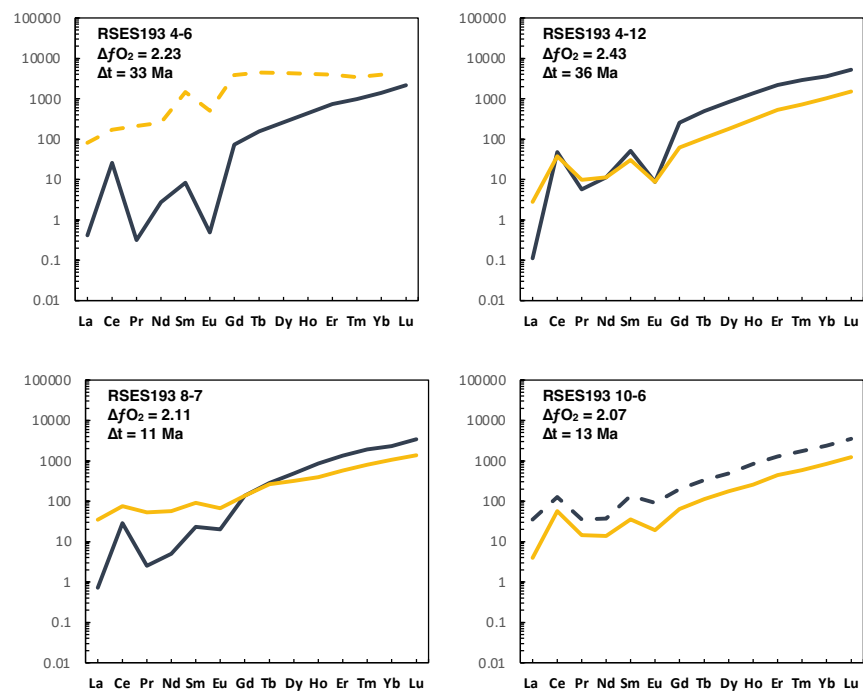


Fig. S2 (cont.)

Low- fO_2 (low T/P)

Cores - dark blue lines; Rims - brown lines; discarded analyses - dashed lines

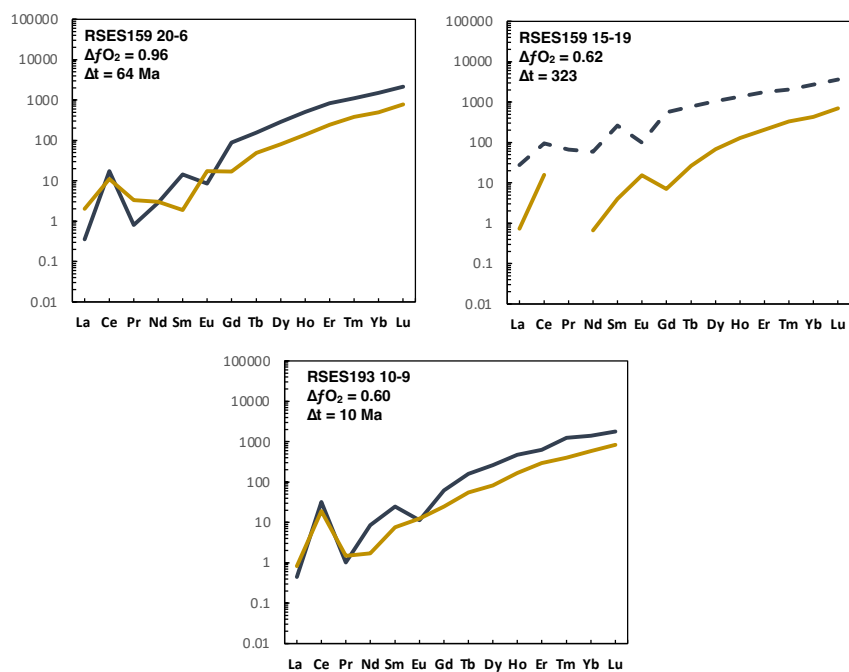
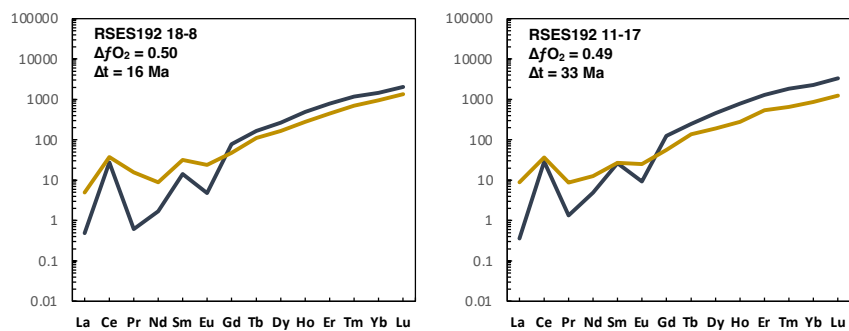
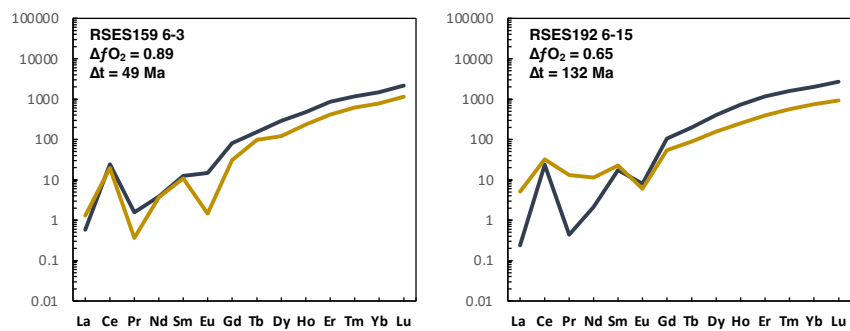
Low- fO_2 (intermediate T/P)

Fig. S2 (cont.)

Low- fO_2 (high T/P)

Cores - dark blue lines; Rims - brown lines; discarded analyses - dashed lines



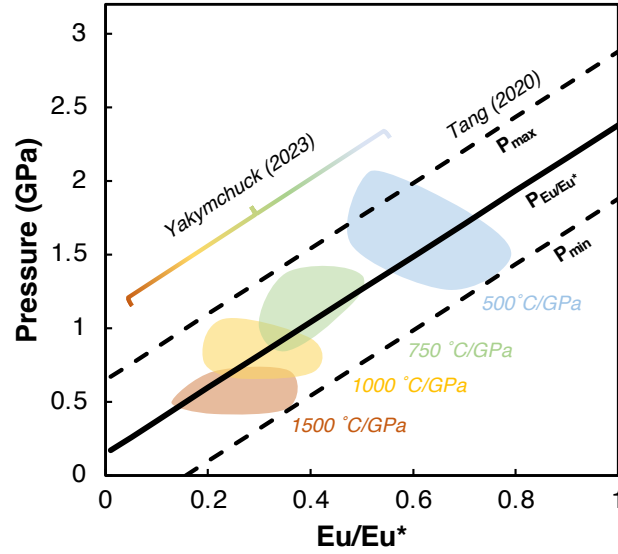


Fig. S3. Relationship between pressure and zircon Eu/Eu*. Colored regions correspond to the range of values predicted by modeling of zircon Eu/Eu* during partial melting of metabasite under different geothermal gradients (Yakymchuk et al., 2023). Upper dashed line is the calibration of Tang et al. (2021) used as a maximum pressure estimate. Lower dashed line is the minimum pressure estimate set at 1 GPa below the maximum value to encompass the range of zircon Eu/Eu* values determined by Yakymchuk et al. (2023). Solid line is the average pressure used for calculation of metamorphic T/P ratios in the main text. A value of $\text{Eu}/\text{Eu}^* = 1$ is used to estimate pressure for zircon with positive Eu-anomalies.

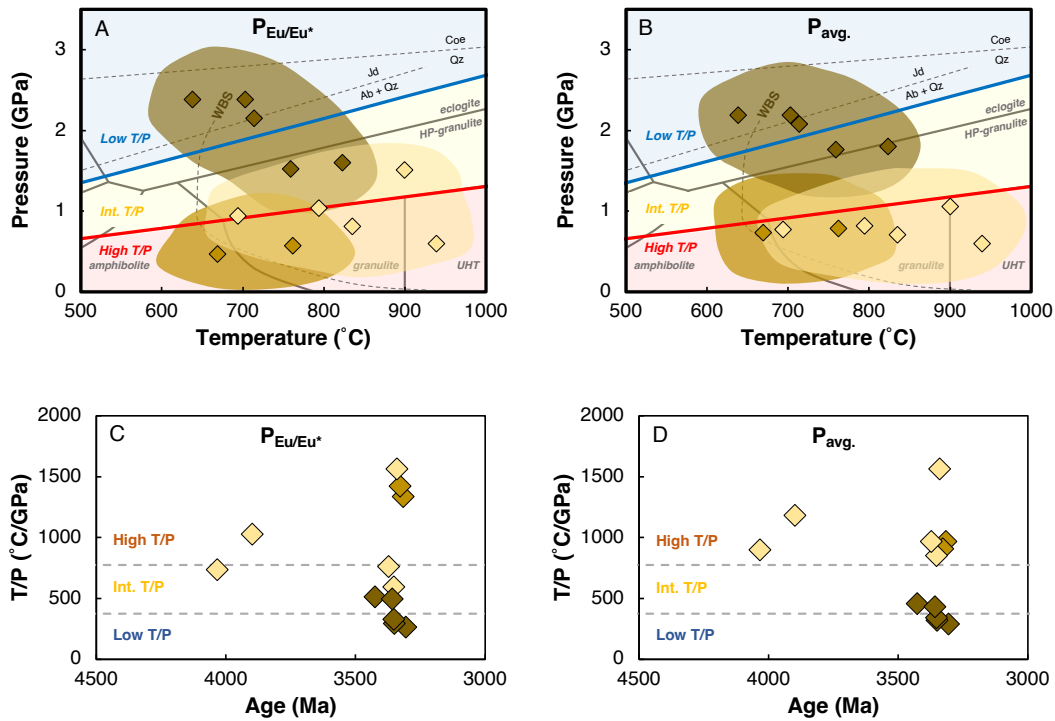


Fig. S4. Differences in P-T and T/P conditions based on method of pressure estimation. (A) P-T conditions for metamorphic rims where pressure is derived only from Eu/Eu* (same values as presented in Fig. 4B of the main text). (B) P-T conditions for metamorphic rims where pressure is the average between Eu/Eu* derived values and values estimated from comparison with analog samples (Fig. 2; *SI Appendix*). (A,B) Brown/yellow regions are the probability ranges for each group based on 2D kernel density estimation with pressure and temperature uncertainties of ± 0.5 GPa and ± 60 °C applied to each data point. Facies boundaries are marked by solid lines and key phase transitions are marked by dashed lines. Colored lines and fields represent thermobaric ratios for low T/P ($<375^{\circ}\text{C/GPa}$, blue), intermediate T/P ($375\text{--}775^{\circ}\text{C/GPa}$, yellow), high T/P ($>775^{\circ}\text{C/GPa}$ red) (Brown and Johnson, 2019). Jd = jadeite; Ab = albite; Qz = quartz; Coe = coesite; WBS = wet basalt solidus. (C) T/P vs. age calculated using pressure values in (A). (D) T/P vs. age calculated using pressure values in (B). Overall, using $P_{\text{avg.}}$ values results in greater separation between low T/P and high T/P sample groups (B,D), however, the key finding that coexisting low T/P and high T/P conditions appear in the Archean is unchanged.

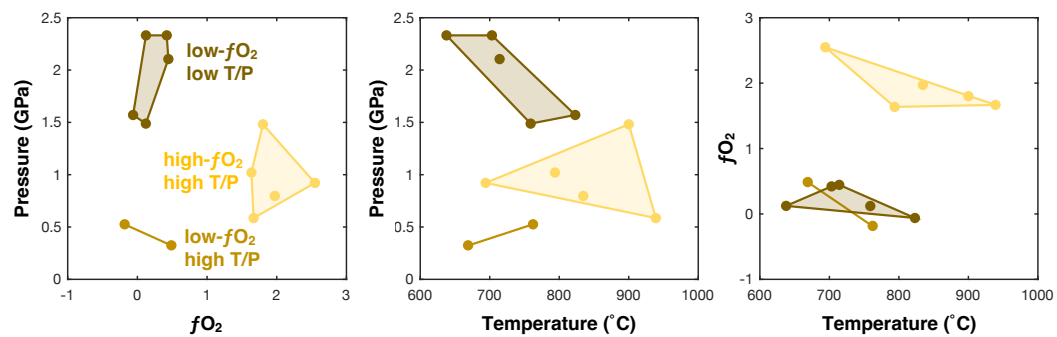
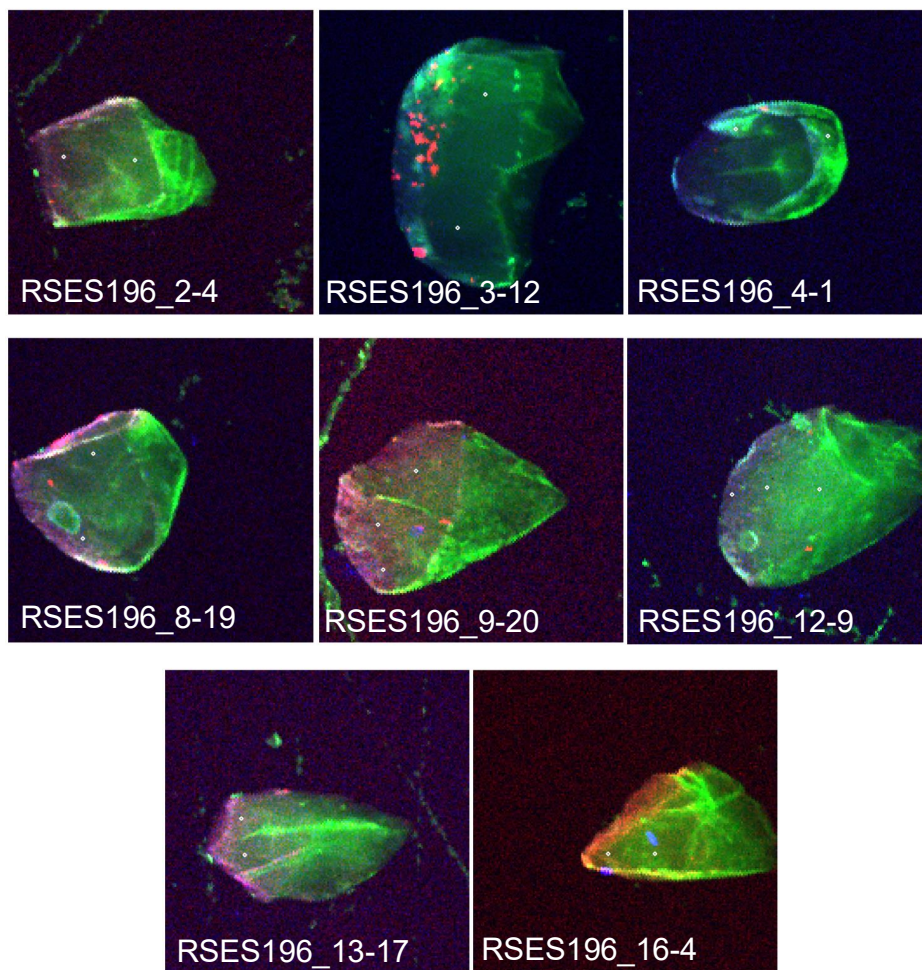


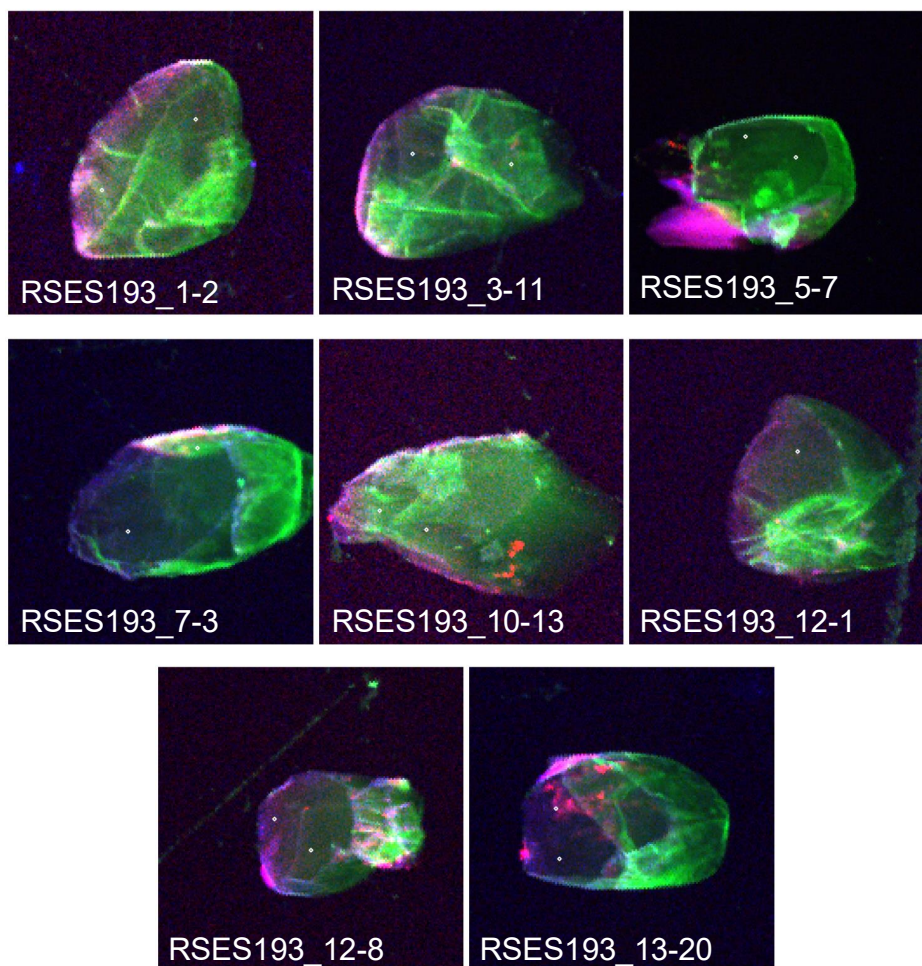
Fig. S5. Results of k-means clustering analysis for metamorphic zircon rims. This analysis confirms the existence of three rim groups defined by distinct pressure and fO_2 conditions.

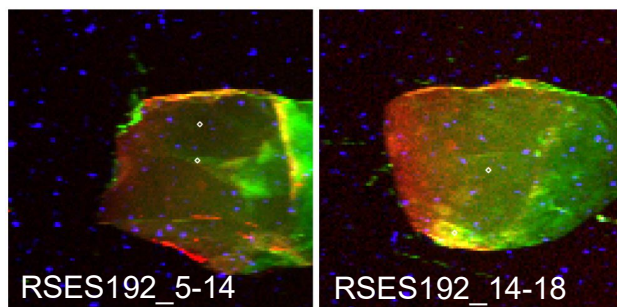
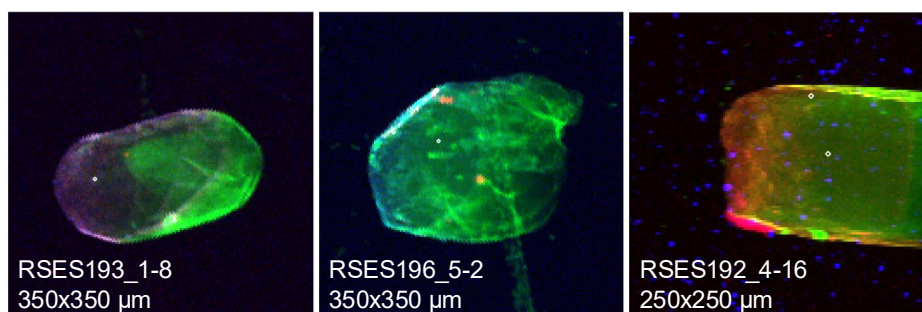
REFERENCES APPENDIX CHAPTER 4

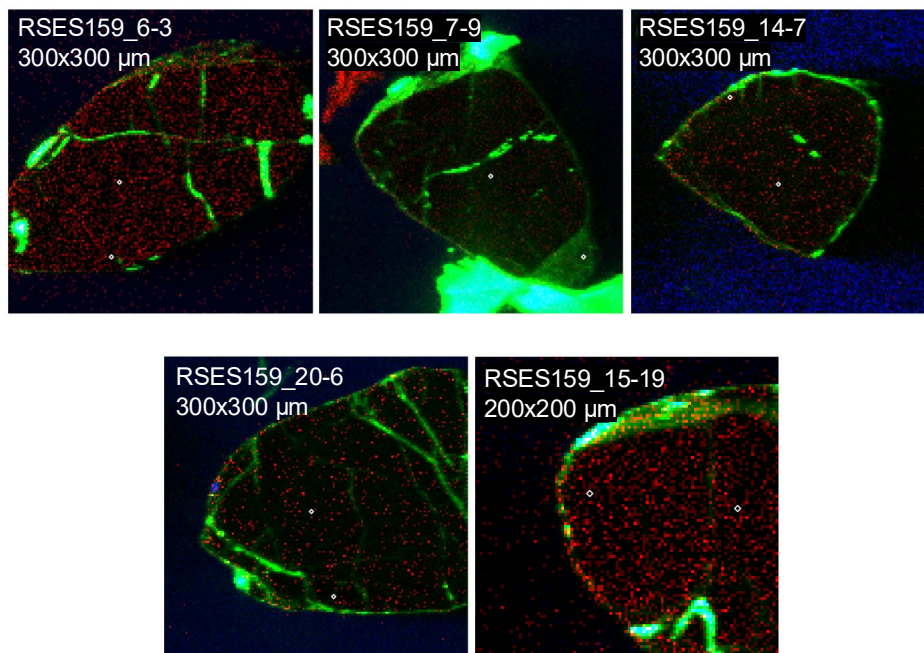
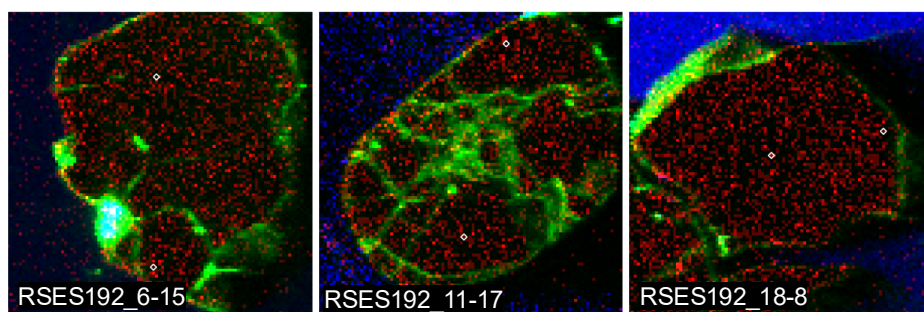
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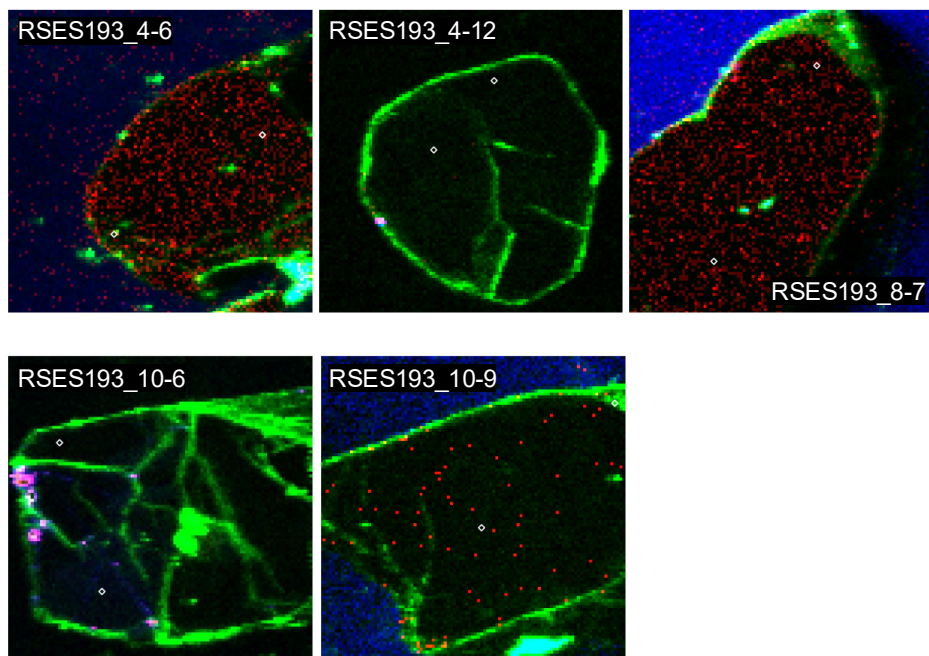
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CHAPTER 4 APPENDIX 2 **μ XRF maps of Jack Hills zircon grains****IGNEOUS GRAINS** **μ XRF MAPS RSES196**RGB = Ti $K\alpha$, U $L\alpha$, Ca $K\alpha$ All maps are 350x350 μ m

IGNEOUS GRAINS **μ XRF MAPS RSES193**RGB = Ti $K\alpha$, U $L\alpha$, Ca $K\alpha$ All maps are 350x350 μ m

IGNEOUS GRAINS **μ XRF MAPS RSES192**RGB = Ti $K\alpha$, U $L\alpha$, Ca $K\alpha$ All maps are 250x250 μ m**RIM-CORE GRAINS** **μ XRF MAPS RSES196**RGB = Ti $K\alpha$, U $L\alpha$, Ca $K\alpha$ 

RIM-CORE GRAINS **μ XRF MAPS RSES159**RGB = Ti $K\alpha$, U $M\beta$, Ca $K\alpha$ **RIM-CORE GRAINS** **μ XRF MAPS RSES192**RGB = Ti $K\alpha$, U $M\beta$, Ca $K\alpha$ All maps are 200x200 μ m

RIM-CORE GRAINS **μ XRF MAPS RSES193**RGB = Ti $K\alpha$, U $M\beta$, Ca $K\alpha$ All maps are 250x250 μ m

Chapter V

REDOX EVOLUTION OF CRUSTAL MAGMAS FROM URANIUM M₄-EDGE XANES ANALYSIS OF ZIRCON

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