Nanoscale Pb clustering and multi-domain Pb-mobility in zircon.

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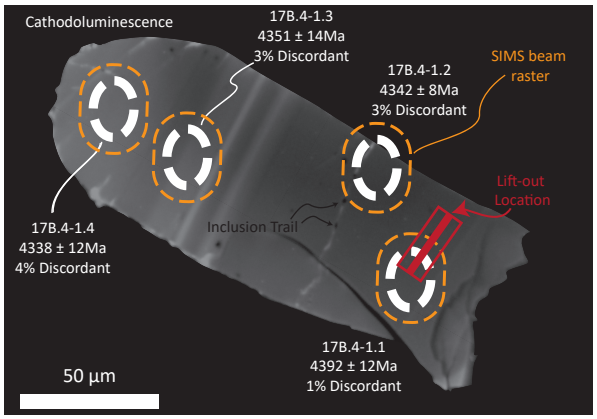
EGU2020
GVPM1.2
D1443

INTRODUCTION AND MOTIVATION

The utility of U-Pb dating of zircon stems from the mineral's widespread occurrence, pristine zircon being both physically and chemically robust, and the ability to evaluate the presence of open system behavior (i.e. "concordance") through comparison of the independent $^{238}U/^{206}Pb$, $^{235}U/^{207}Pb$, and $^{232}Th/^{208}Pb$ decay chains. The phenomenon of discordance is well documented in zircon; however, the nanoscale controls on Pb mobility and Pb loss remain poorly defined. The unique characterization capabilities of atom probe tomography (APT) have documented Pb-rich nanostructures which preserve radiogenic Pb ratios over billions of years. The potential influence of these features on isotope systematics in the subject of this work.



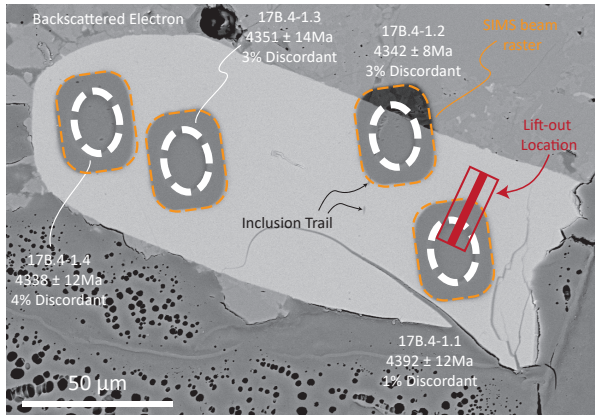
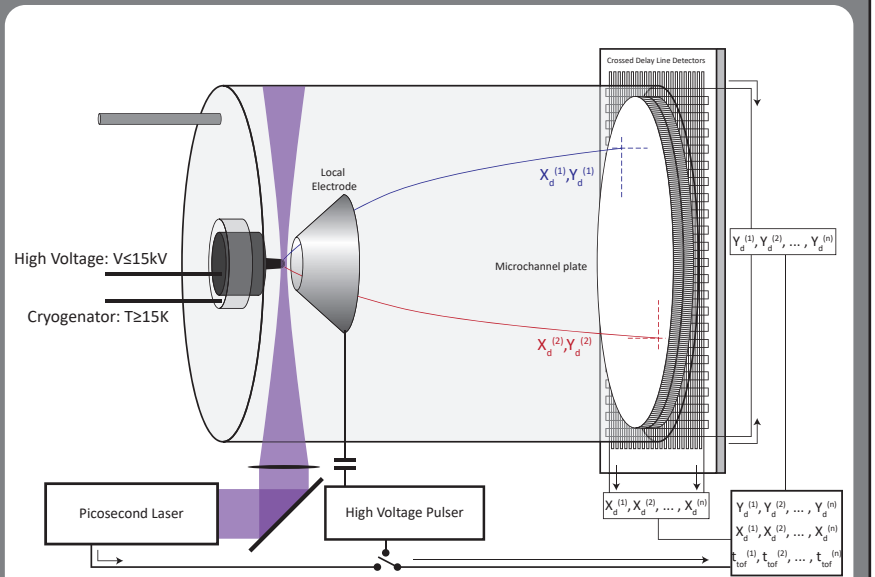


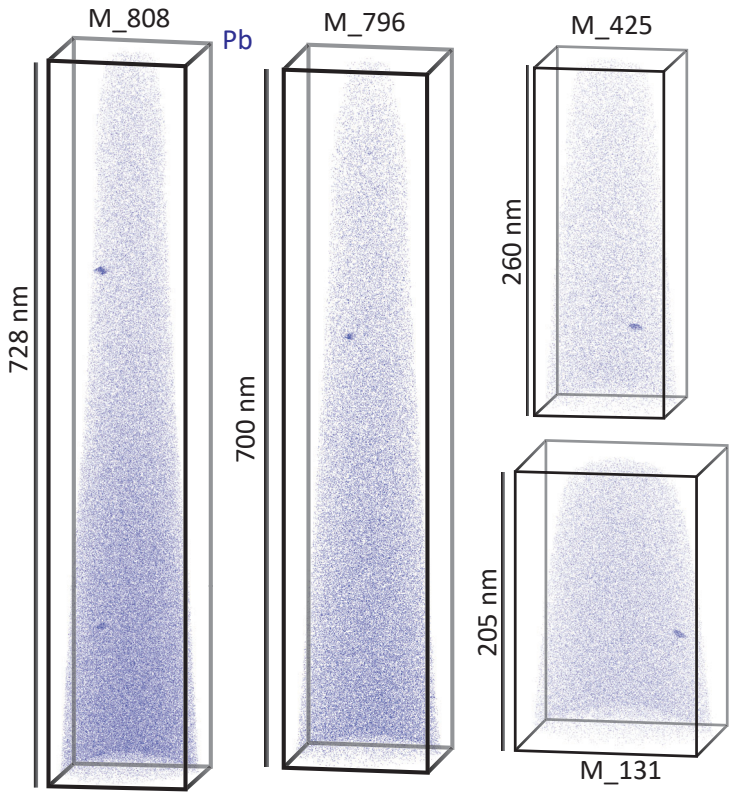
Figure 1: (Above, Left) zircon 17B-4, a 4.39 Ga zircon separated from lunar sample 73235. While ovals and orange outlines show location of SHRIMP-RG U-Pb analyses. Red rectangle shows the location of the atom probe lift-out from which needle shaped specimens were made and subsequently run (see below). (Above, Right) Backscattered electron image of zircon 17B-4 (Blum et al., 2019).
Figure 2: (Below) Reconstructed atom probe data sets showing the nanoscale distribution of Pb within specimens from a 4.39 Ga lunar zircon (Blum et al., 2019)

Atom Probe Tomography

Atom Probe Tomography (APT) is a technique combining time of flight mass spectrometry and projection microscopy. A needle shaped specimen is prepared and field evaporated under high vacuum through laser or voltage pulsing. The identity and initial position of evaporated ions can be reconstructed based on their time of flight and impact on the detector, enabling a three dimensional reconstruction of the specimen with nm scale spatial resolution, and detection limits or ~ 10 parts per million atomic. Reconstructed data sets can be mined for spatial associations as well as nanoscale composition with isotope sensitivity.



(adapted from Gault et al., 2012)



U-Pb Decay and Concordance:

The modeling of distinct isotopic domains and their temporal associations can be understood in the context of time-integrated U and Pb ratios (Figure 3). The $^{238}U \rightarrow {}^{206}Pb$ decay decreases the observed $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios through time. The specific trajectory of ingrowth trends depend on crystallization age, with each terminating on the present data concordia (Bonamici and Blum, in press).

U-Pb Decay and Pb Loss

In the case of Pb loss, Pb will be fractionated from U, but Pb isotopes are not fractionated from one another. As a result, the loss of Pb will induce a lateral translation of Pb ingrowth trajectories depending on the time of Pb loss, and the fraction of Pb lost (Figure 4). Regions experiencing variable amounts of Pb loss will fall along a discordia regression, having an upper concordia intercept at the time of crystallization, and a lower concordia intercept at the time of Pb loss. ***The y-intercept of the present day discordia regression equals the $^{207}Pb/^{206}Pb$ ratio for the lost/mobile Pb component.***

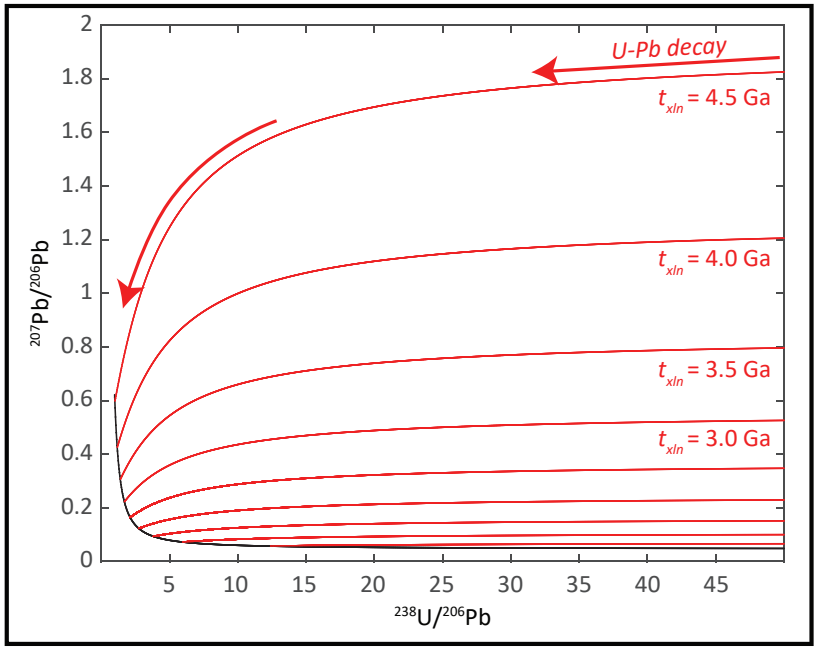
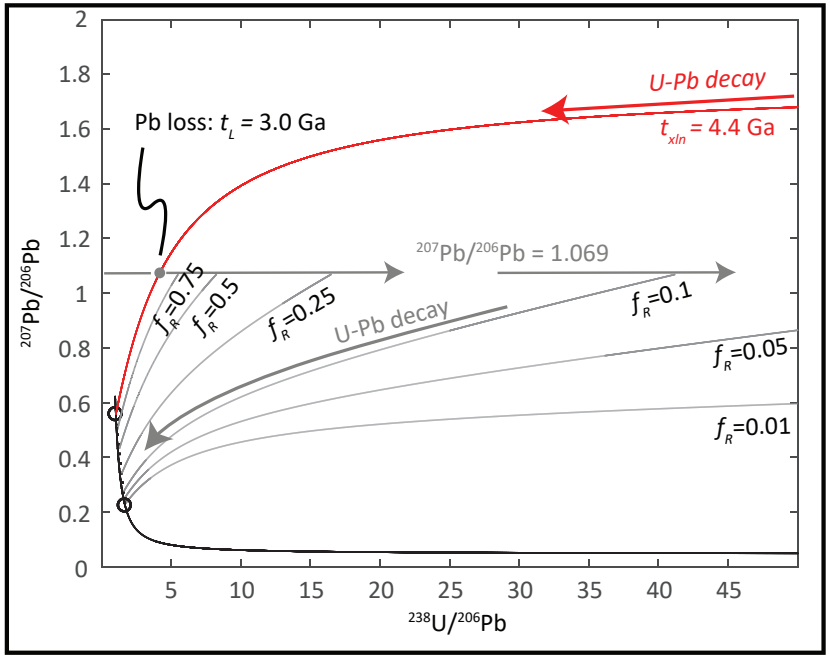


Figure 3: (Above) Inverse concordia showing the time-integrated U and Pb ratios for closed system evolution. All trajectories (red lines) start at 238U/206Pb = ∞, and evolve based on their crystallization age (i.e. their initial U composition). As expected, trajectories terminate at isotope ratios on the present day concordia.



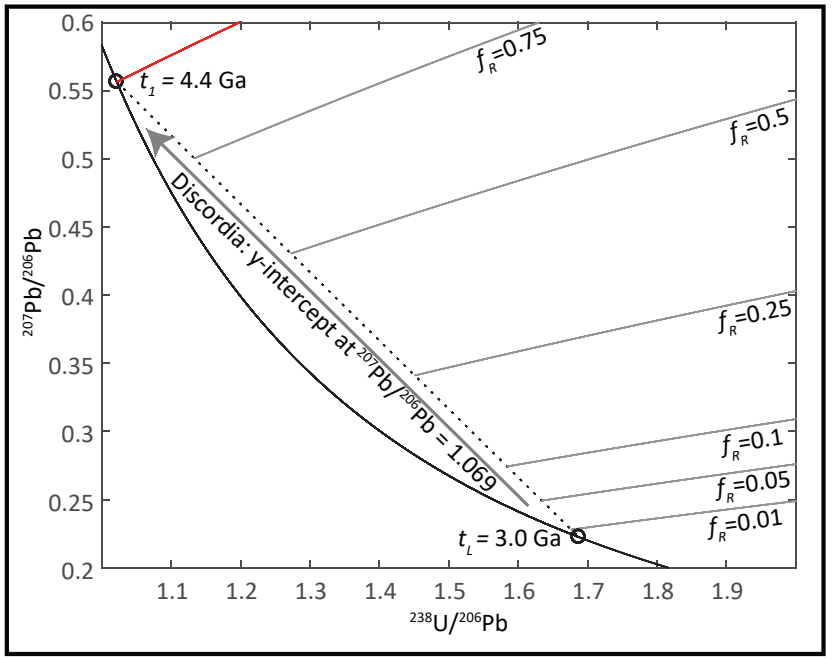


Figure 4: (Near, right) Inverse Concordia showing the ingrowth and Pb loss trajectories for a zircon having a crystallization age of t_1 = 4.4 Ga, and experiencing Pb loss at time t_L = 3.0 Ga. Red lines show time integrated U-Pb evolution, while grey lines show trajectories following Pb loss. (Far right) close up of panel, showing discordia regression, as well as (1) the temporal significance of the upper and lower concordia intercepts, and (2) the regression of the discordant analyses, intercepting the y-axis at the isotope composition of the mobile Pb component during Pb loss.

U-Pb Decay and Concordance:

For zircons grains with low common Pb components, clusters form as radiogenic Pb segregates and is trapped within defect domains (e.g. Valley et al., 2015; Blum et al., 2018). In a simple model for cluster formation, the $^{207}Pb/^{206}Pb$ ratios within the clusters are a function of the crystallization age, and time of clustering (Figure 5); as long as the crystallization age is known, the $^{207}Pb/^{206}Pb$ ratio can be used to determine the age of cluster formation.

Traditional analysis of zircon by microanalytical techniques (SIMS, LA-ICP-MS) integrate large portions of the zircon grain; as long as Pb has not reorganized and on the micron scale, microanalysis reintegrates nanodomains and returns bulk ratios consistent with closed system behavior (Figures 5, 6).

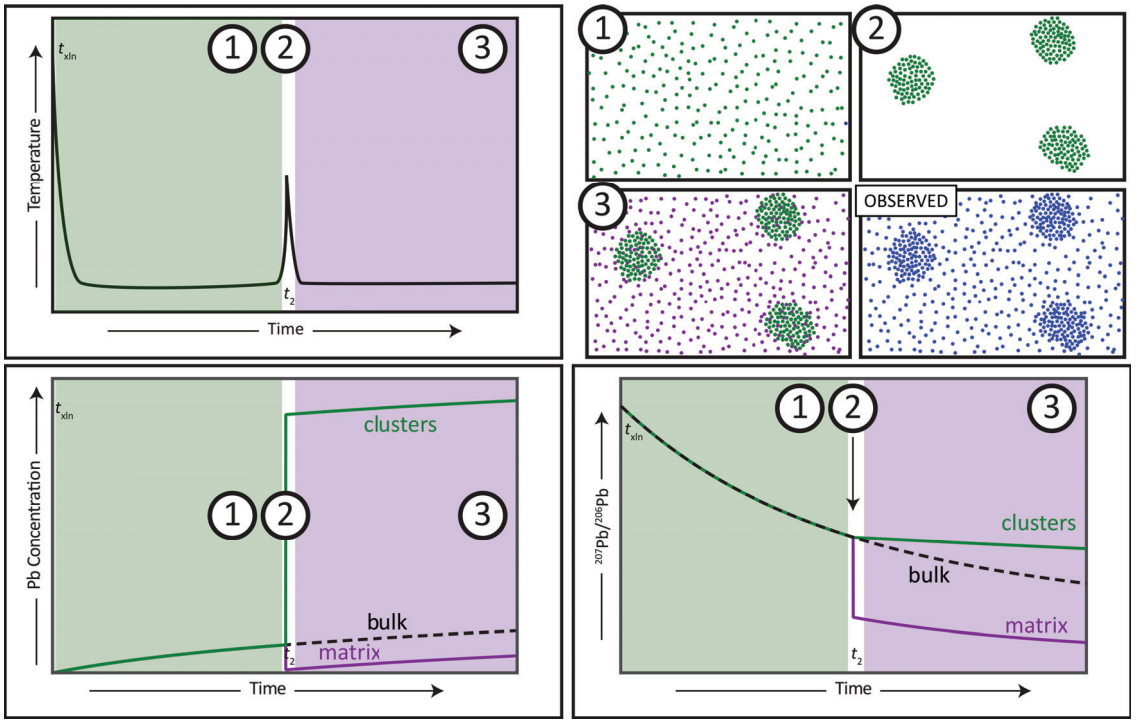


Figure 5: (Above) Schematic illustration of clustering and age modeling. Clustering associated with high temperature episodes (top left), drives early formed radiogenic Pb into clusters (top right), and generates systematic differences in Pb concentration and isotope ratios throughout the zircon (bottom left and right).The fact that clusters preserve isotope ratios over billions of years suggest they are stable over geologic time.

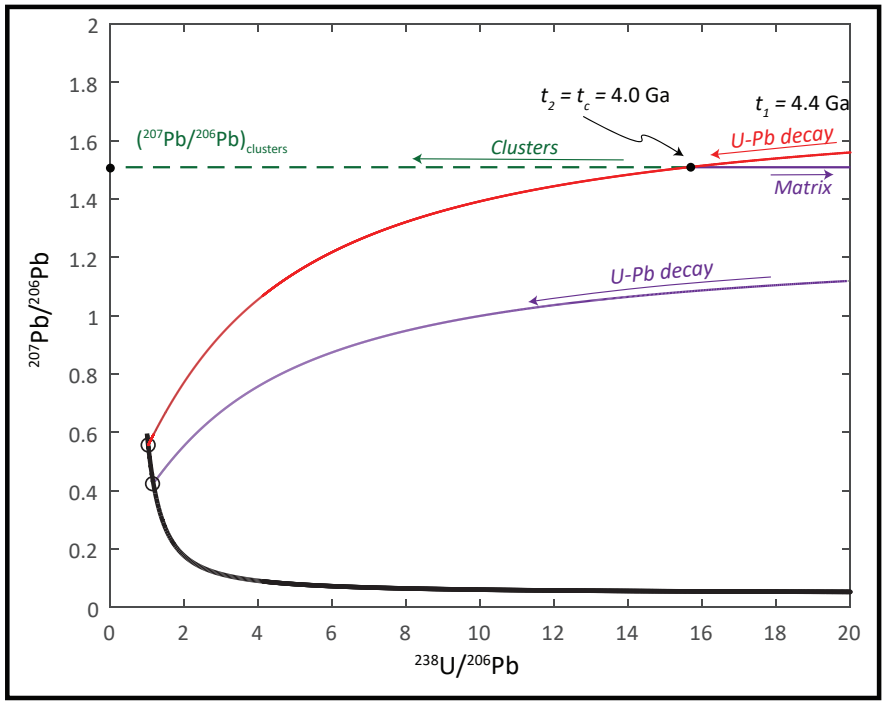
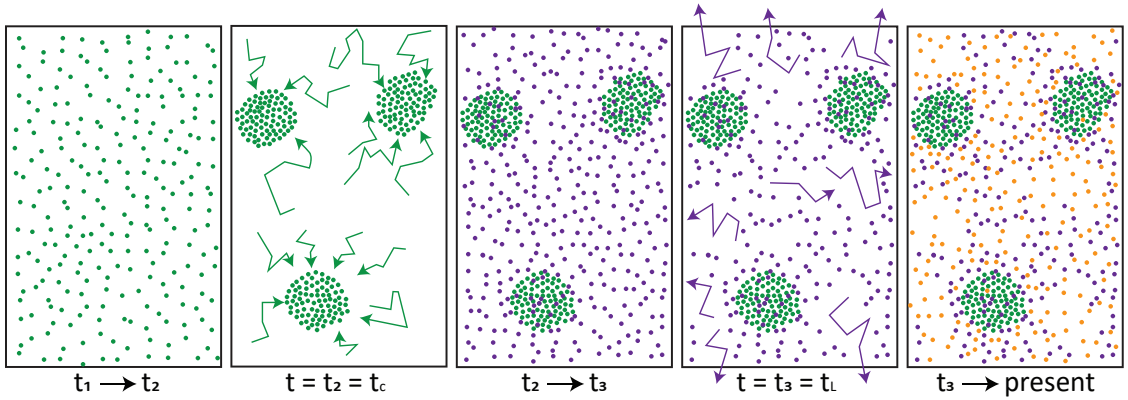


Figure 6: (Left) U-Pb decay and isotope evolution of a zircon having a crystallization age of t_1 = 4.4 Ga, and experiencing a clustering episode at 4.0 Ga, (no subsequent Pb migration). Early Pb is driven into clusters, increasing their $^{238}U/^{206}Pb$ ratios. No parent or daughter product is lost from the system, and thus micron scale analyses which re-integrate matrix and cluster domains will return a concordant, closed system age (e.g. Valley et al., 2015). Note: For zircon that experiences simultaneous Pb clustering and Pb loss, clusters preserve the same isotope ratio as the mobile Pb component during Pb loss, and thus the discordant regression will have a y-intercept equivalent to the $^{207}Pb/^{206}Pb$ ratio of clusters (e.g. Peterman et al., 2016).

Traditional interpretations of discordance and Pb-loss have not considered multistage histories, in which differential trapping of Pb can influence the observed Pb loss systematics. This work presents the graphical foundations for Pb clustering, as well as the implications for differential Pb loss due to Pb trapping.



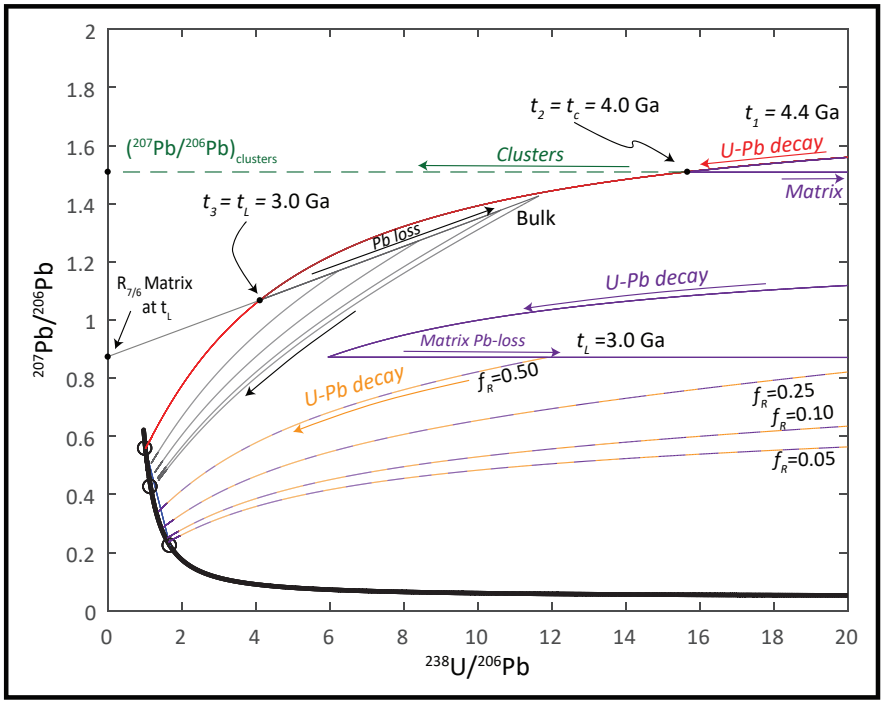
We model the potential influence of clustering on Pb loss and U-Pb isotope systematics following a set of end member boundary conditions, including:

1. ^{238}U and ^{235}U are homogeneously distributed and immobile
2. Initial and common Pb components are negligible.
3. Intermediate daughter behavior is negligible
4. Pb migration is rapid, and "to completion"
5. **Pb is trapped within clusters, and not re-mobilized in later Pb migration events.**

For such a scenario, the trapping of early radiogenic Pb changes both the amount and isotope ratio of mobile Pb at the time of Pb loss, systematically changing the discordant regression and its temporal significance (Figure 7).

The loss of radiogenic Pb following a clustering event will systematically shift the discordia regression, having a distinct y-intercept (i.e. the $^{207}Pb/^{206}Pb$ ratio of the mobile Pb component at the time of Pb loss). In the context of the presented model, this is equivalent to the $^{207}Pb/^{206}Pb$ composition of the matrix at time $t = t_L$.

With the knowledge of a crystallization age, and a clustering age, the timing of Pb loss can be determined, but is not equivalent to the lower concordia intercept of the discordant regression.



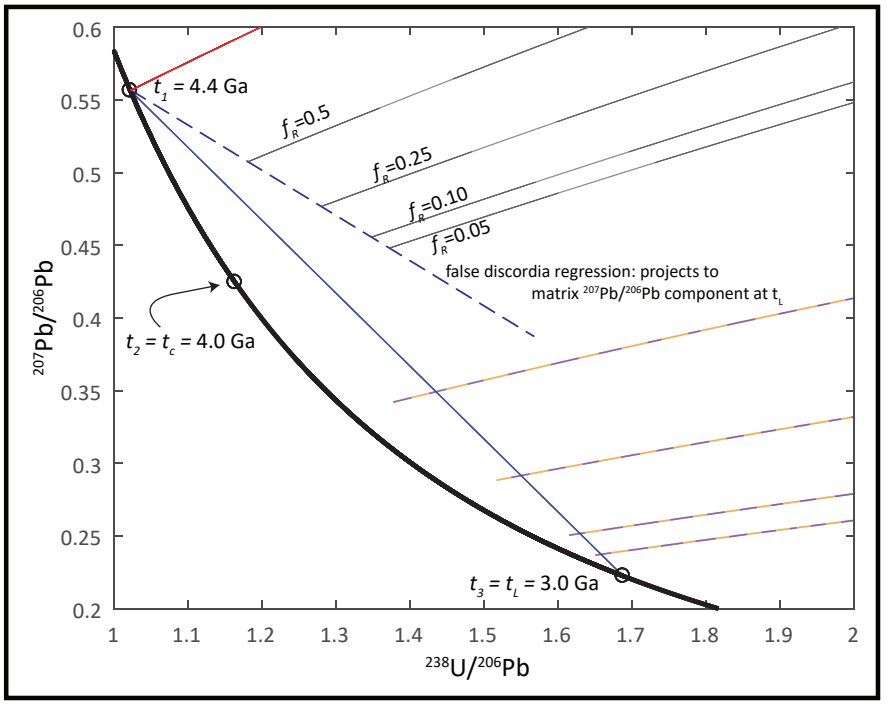


Figure 7: (Top, Right) U-Pb decay and isotope evolution of a zircon having a crystallization age of t_1 = 4.4 Ga, and experiencing first clustering of Pb at $t_2 = t_c$ = 4.0 Ga, followed by Pb loss from the matrix at $t_3 = t_L$ = 3.0 Ga. Early Pb is driven into clusters, increasing their $^{238}U/^{206}Pb$ ratio. There is no net loss of Pb at $t = t_c$, thus, the bulk isotope evolution continues to evolve in a closed system manner until $t = t_L$. Pb within clusters is considered immobile, and thus Pb is lost from the matrix, having a lower $^{207}Pb/^{206}Pb$ composition. The magnitude of the isotopic shift at the time of Pb loss, as well as the final bulk ratio, is determined by the fraction of (mobile) Pb retained (f_R).

This model highlights the impact of multi-domain element (Pb) mobility and its potential influence on Pb loss systematics. The final (bulk) isotope ratios resulting from this behavior are, primarily, function of zircon crystallization (t_1), the timing of cluster formation (t_c), the timing of Pb loss (t_L), and the fraction of Pb lost/retained. For simple discordant regressions, this model would suggest that nanoscale phenomena can potentially distort Pb loss trends and the temporal significance of discordant regressions (Figure 7).

This modeling also forms predictions regarding unique behavior: the formation of discordant regressions with positive slopes in inverse concordia space (Figure 8). This phenomenon is observed for a subset of (t_1, t_c, t_L) histories that mobilize a low-$^{207}Pb/^{206}Pb$ component. For otherwise well-behaved zircon, positive slopes are difficult to explain, and may be particularly indicative of this type of differential mobility.

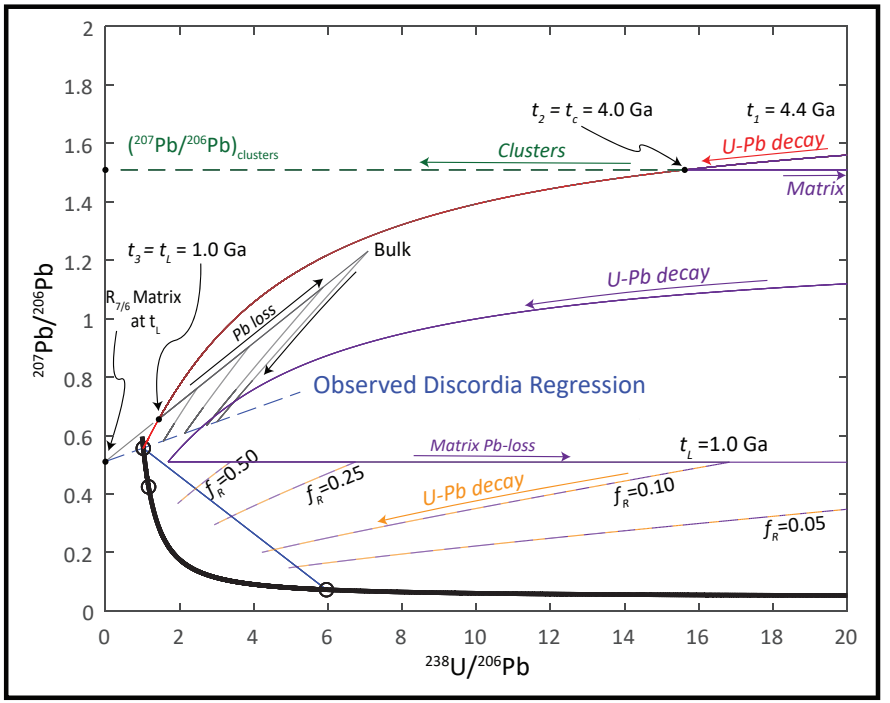


Figure 8: (Top, Right) U-Pb decay and isotope evolution of a zircon having a crystallization age of t_1 = 4.4 Ga, and experiencing first clustering of Pb at $t_2 = t_c$ = 4.0 Ga, followed by Pb loss from the matrix at $t_3 = t_L$ = 1.0 Ga. The blue dashed line indicates the discordia regression of bulk data having lost different amounts of matrix Pb at time $t = t_L$.

Pairing atom probe tomography with U-Pb microanalysis represents a novel means to understand scale-dependent chemical phenomena, as well as their temporal and structural associations.

With its combination of isotope sensitivity, spatial resolution and detection limits, APT is the only technique capable of resolving isotopically distinct nanodomains. Understanding their stability and behavaior is critical to understanding discordant phenomena, particularly in Archean and Hadean geochronology.

Acknowledgements: The authors would like to acknowledge the continued training and collaboration with CAMECA, Inc. and the Max-Planck-Institut fur Eisenforschung. This work was supported by a U.S. National Science Foundation Postdoctoral Fellowship (EAR-1806924).

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