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GEO SCIENCES MAINZ

# Elementi in traccia e isotopi di Ca, Sr in denti di dinosauro

Centro Interdipartimentale Grandi Strumenti CINQUANTA

UNIMORE UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

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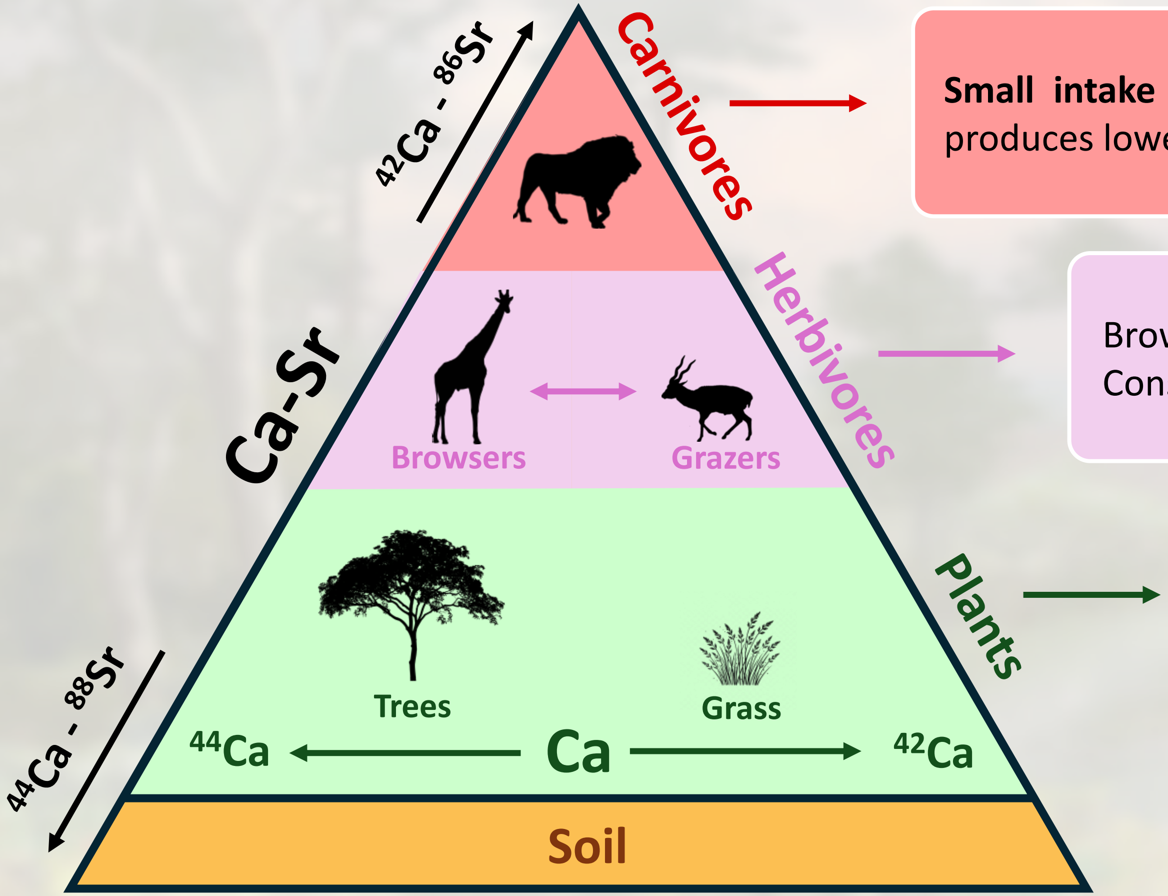
# Ca and Sr stable isotopes as trophic tracers

Food is the main Ca source for vertebrates. **Bones and teeth serve as essential Ca storage** and show lower $\delta^{44/42}Ca$ values than dietary calcium due to isotope fractionation during physiological processes such as the mineralization of hard tissues. Stable Sr follows similar pathways to Ca.




**Small intake of about 1–2% of mineralized tissue** (bone enriched in $^{42}Ca$) from prey produces lower Ca isotope composition in bones and teeth of the predator.

Browsers eat high-growing plants, grazers eat grass and low-growing vegetation. Consumed plant type affects **Ca isotopic variations that move up the food chain.**

Fractionation processes that produce **intra-plant differences**. Leaves in trees are more $^{44}Ca$ enriched than roots and low growing plants.

Black animal silhouettes are from phylopic.org.

Heuser A., Tütken T., Gussone N. and Galer S. J. G. (2011) Calcium isotopes in fossil bones and teeth — Diagenetic versus biogenic origin. Geochimica et Cosmochimica Acta 75, 3419–3433.

Moynier F. and Fujii T. (2017) Calcium isotope fractionation between aqueous compounds relevant to low-temperature geochemistry, biology and medicine. Sci Rep 7, 44255.

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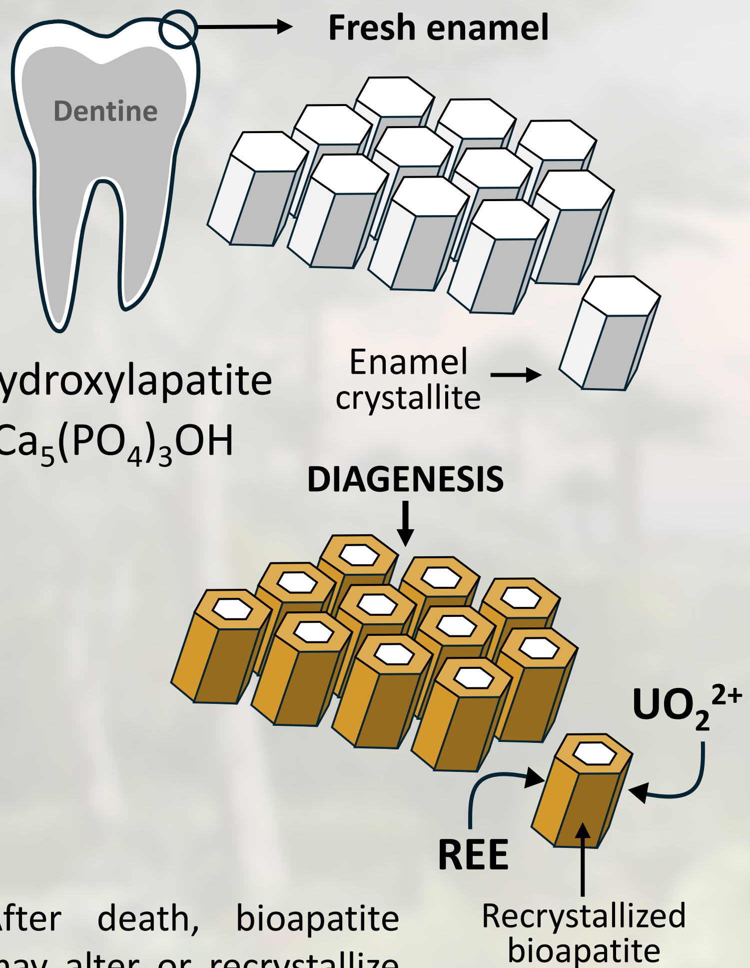
# Diagenesis, trace elements and radiogenic Sr

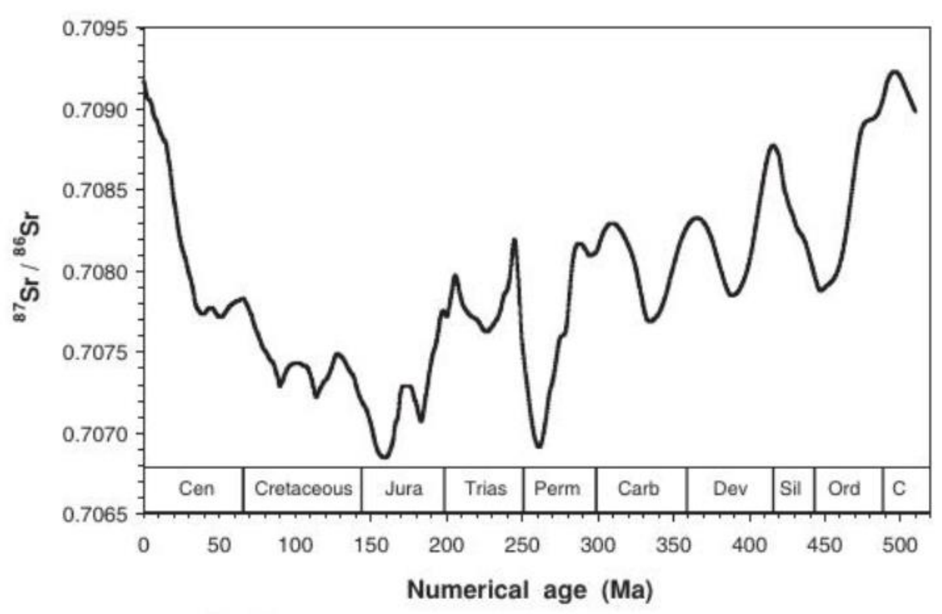


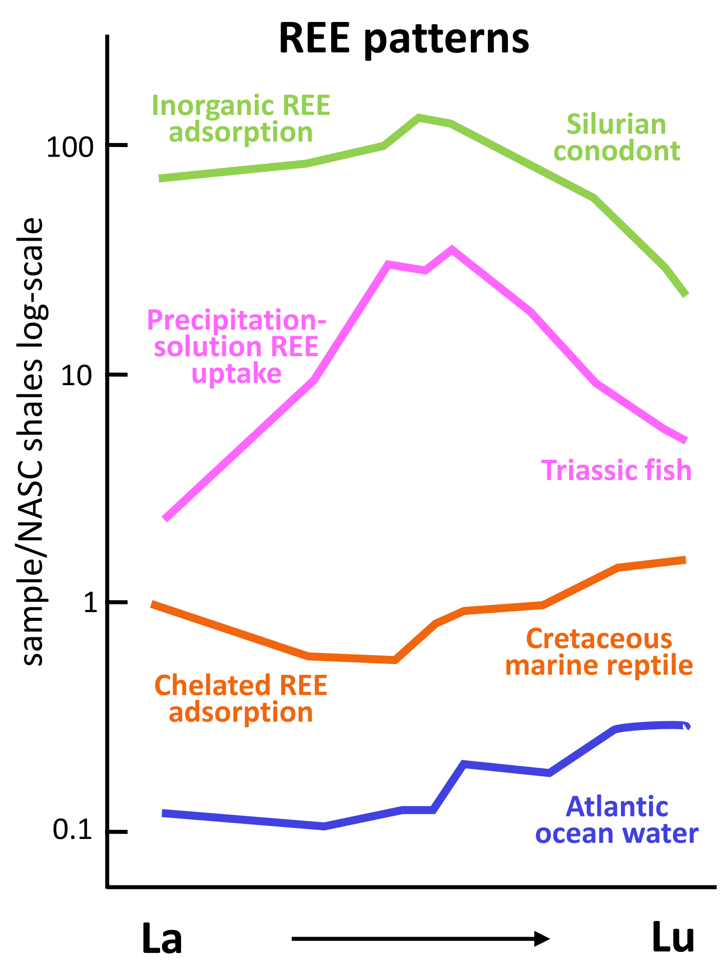

Hydroxylapatite
$Ca_5(PO_4)_3OH$

After death, bioapatite may alter or recrystallize **absorbing trace elements from the environment.**

Reconstruct taphonomic conditions based on the **normalized rare earth element (REE) distribution patterns**, anomalies and trace element correlations.

In seawater influenced environments $^{87}Sr/^{86}Sr$ can be used as a diagenetic tracker (McArthur's global $^{87}Sr/^{86}Sr$ curve).





Reynard B. and Balter V. (2014) Trace elements and their isotopes in bones and teeth: Diet, environments, diagenesis, and dating of archeological and paleontological samples. Palaeogeography, Palaeoclimatology, Palaeoecology 416, 4–16.

McArthur J. M., Howarth R. J. and Shields G. A. (2012) Strontium Isotope Stratigraphy. In The Geologic Time Scale Elsevier. pp. 127–144.



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# Case study – Dinosaur teeth

Better **constrain the diagenetic history of fossil teeth**, enabling stronger reconstructions of feeding behavior and habitat in ancient ecosystems through preserved diet-related isotope signatures.

**Quantify the degree of diagenetic alteration of the teeth** and whether they still preserve diet-related Sr and Ca isotope information.

**Multi-proxy geochemical study** combining radiogenic Sr ($^{87}Sr/^{86}Sr$), stable Sr ($\delta^{88/86}Sr$), Ca ($\delta^{44/42}Ca$) isotopes and trace elements.

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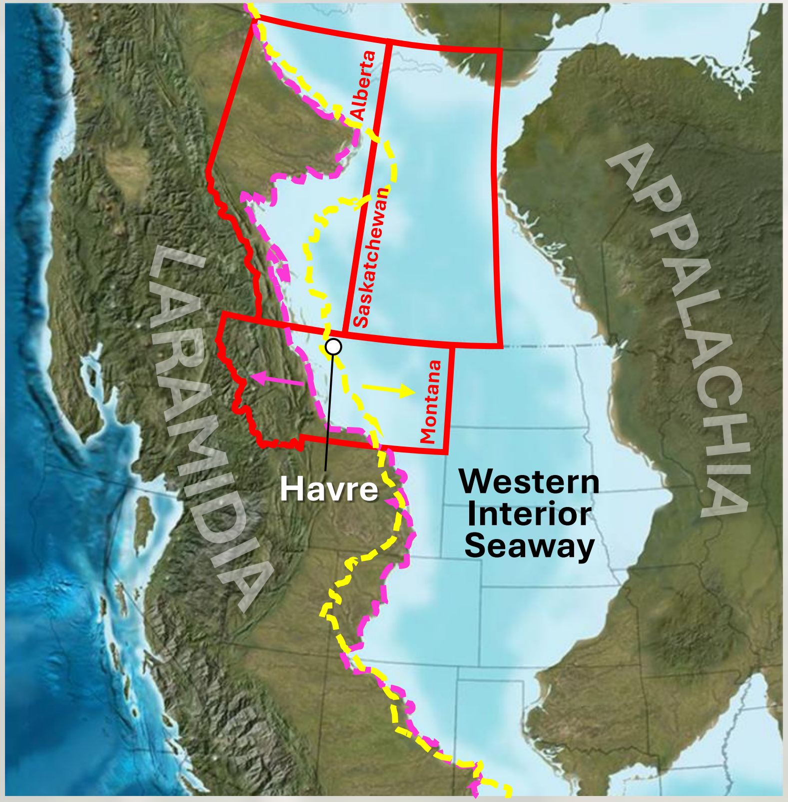
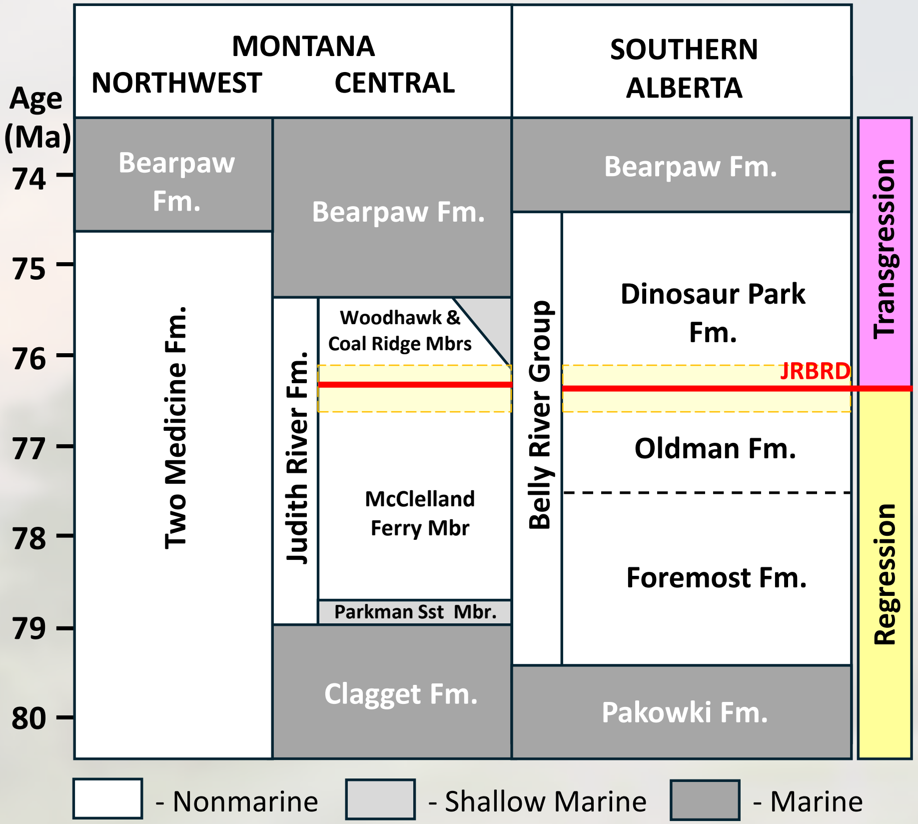
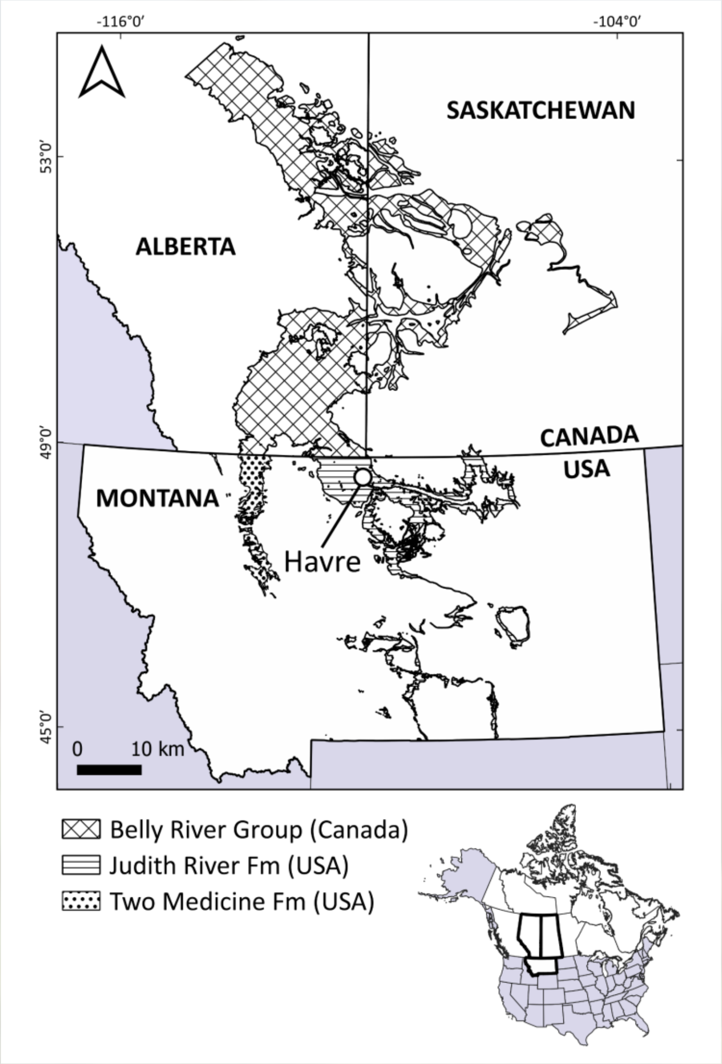
# Where – Judith River Formation




Late Campanian 73.5 Ma (Transgression)
Middle Campanian 80.0 Ma (Regression)




Eberth D. A. (2024) Stratigraphic architecture of the Belly River Group (Campanian, Cretaceous) in the plains of southern Alberta: Revisions and updates to an existing model and implications for correlating dinosaur-rich strata ed. J. Kriwet. PLoS ONE 19, e0292318.

Ramezani J., Beveridge T. L., Rogers R. R., Eberth D. A. and Roberts E. M. (2022) Calibrating the zenith of dinosaur diversity in the Campanian of the Western Interior Basin by CA-ID-TIMS U–Pb geochronology. Sci Rep 12, 16026.

Rogers R. R., Eberth D. A. and Ramezani J. (2023) The "Judith River–Belly River problem" revisited (Montana-Alberta-Saskatchewan): New perspectives on the correlation of Campanian dinosaur-bearing strata based on a revised stratigraphic model updated with CA-ID-TIMS U-Pb geochronology. Geological Society of America Bulletin.

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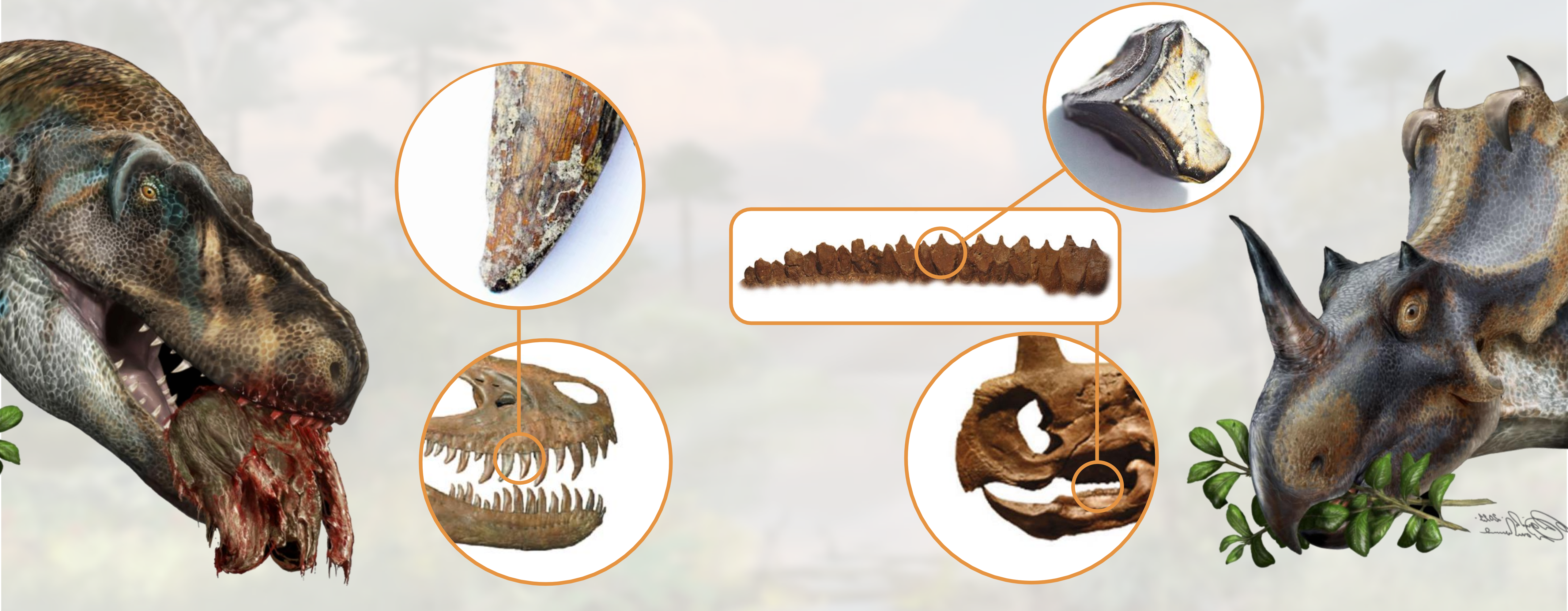
# Materials – Teeth fragments

53 Dinosaur tooth fragments from unidentified **tyrannosaurids** (n = 29) and **ceratopsids** (n = 24), from 15 different microsites located in Cottonwood Coulee, Fresno Reservoir, Havre (Montana, USA), a small area of US public lands administered by the US Bureau of Land Management.



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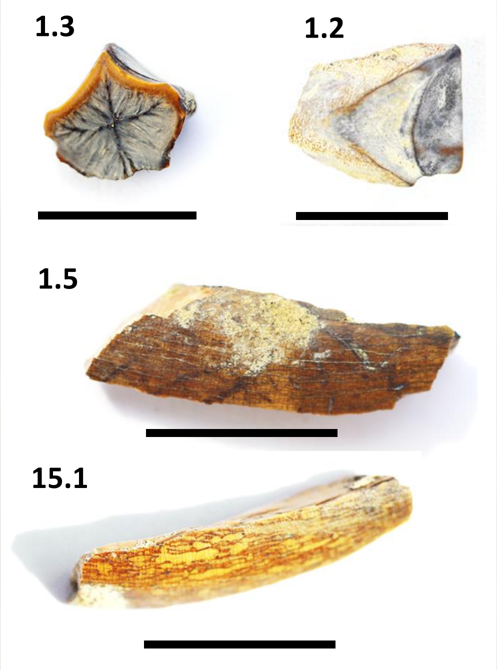
# How – Trace elements

In-situ analyses on a **subsample set of 15** previously cut and polished **teeth fragments** (5 dentine and 5 enamel samples for ceratopsids and 2 dentine and 3 enamel samples for tyrannosaurids).


Polished teeth section used in the laser ablation ICP-MS analysis.




Some of the teeth fragments (unpolished). Scale bar = 1cm

Thermo Fisher Scientific ICP-MS X series II equipped with the 213 nm laser ablation device UP-213 from New Wave Research housed at the **Centro Interdipartimentale Grandi Strumenti (CIGS)-UNIMORE.**

Tuning using the NIST 610 and NIST 612 glasses measuring the intensity of U and Th signals ($^{238}U/^{232}Th$ vs. $^{238}U$). Oxide production below 1%.

| | Pre-ablation | Ablation |
|---|---|---|
| Spot-size | 65 µm | 55 µm |
| Energy Intensity | 30% | 80% |
| Hz frequency | 10 Hz | 10 Hz |
| Dwell time | 5 s | 45 s |
| He flux | 600 ml/min | 600 ml/min |

Data reduction was performed following Longerich [2].

1. External standard: NIST 612
2. Internal standard: Ca (37% m/m)
3. Quality control standards: NIST SRM 1400 and NFHS-2-NP [1].

1. Boer W., Nordstad S., Weber M., Mertz-Kraus R., Hönisch B., Bijma J., Raitzsch M., Wilhelms-Dick D., Foster G. L., Goring-Harford H., Nürnberg D., Hauff F., Kuhnert H., Lugli F., Spero H., Rosner M., van Gaever P., de Nooijer L. J. and Reichart G. (2022) New Calcium Carbonate Nano-particulate Pressed Powder Pellet (NFHS-2-NP) for LA-ICP-OES, LA-(MC)-ICP-MS and µXRF. Geostandard Geoanalytic Res 46, 411–432.
2. Longerich H. and Jackson S. (1996) Laser Ablation Inductively Coupled Plasma Mass Spectrometric Transient Signal Data Acquisition and Analyte Concentration Calculation. Journal of Analytical Atomic Spectrometry - J ANAL ATOM SPECTROM 11.

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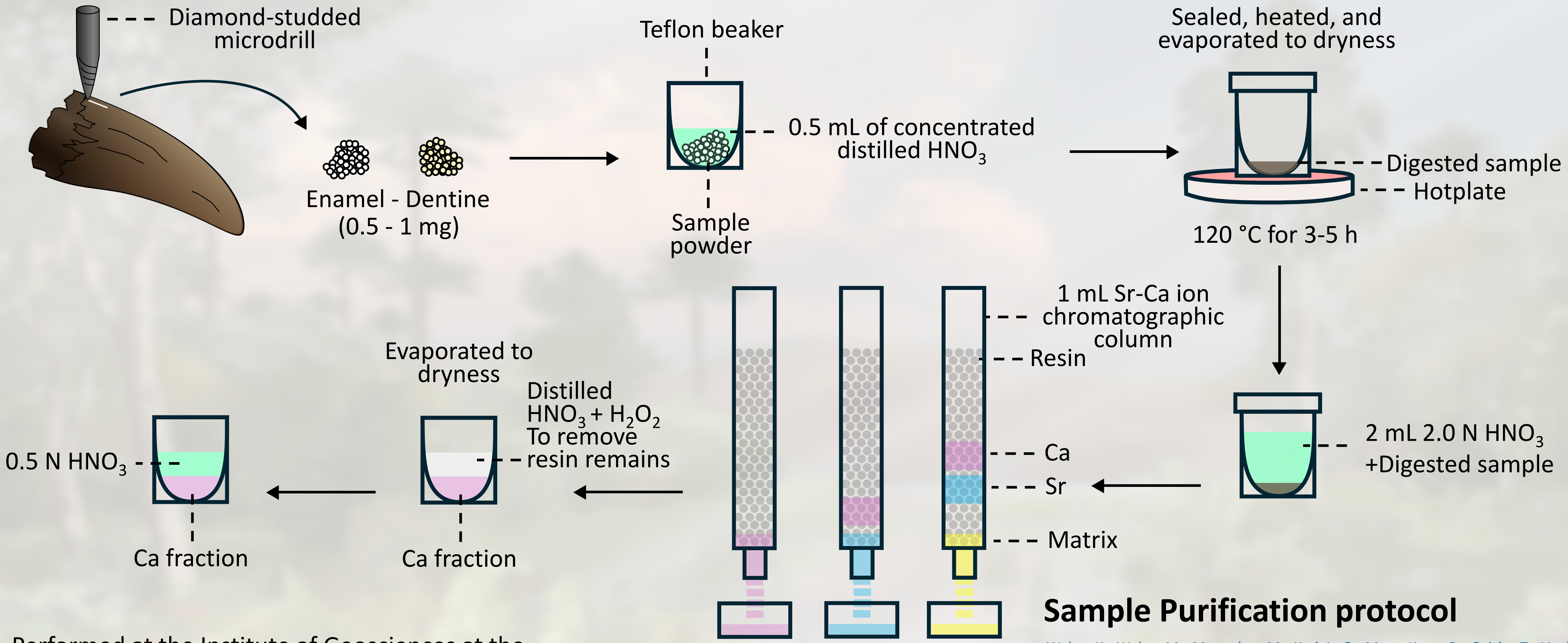
# How – Ca and Sr isotopes




Purification - prepFAST MC
(ESI Elemental Scientific)

Performed at the Institute of Geosciences at the University of Mainz (Germany).

## Sample Purification protocol


Weber K., Weber M., Menneken M., Kral A. G., Mertz-Kraus R., Geisler T., Vogl J. and Tütken T. (2021) Diagenetic stability of non-traditional stable isotope systems (Ca, Sr, Mg, Zn) in teeth – An in-vitro alteration experiment of biogenic apatite in isotopically enriched tracer solution. Chemical Geology 572, 120196.



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# How – Ca and Sr isotopes

Calcium isotopes were measured at the **Institute of Geosciences at the University of Mainz (Germany)**.

1. Neptune Plus Multicollector-Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS).
2. Sample introduction was performed in 0.5 N $HNO_3$ using an Apex Omega HF (ESI Elemental Scientific) desolvator system.
3. A standard - sample bracketing approach was applied using an Alfa Aesar plasma standard solution as internal Ca isotope standard.
4. The $\delta^{44/42}$Ca values measured against the in-house standard were converted to NIST SRM 915a.

Weber K., Weber M., Menneken M., Kral A. G., Mertz-Kraus R., Geisler T., Vogl J. and Tütken T. (2021) Diagenetic stability of non-traditional stable isotope systems (Ca, Sr, Mg, Zn) in teeth – An in-vitro alteration experiment of biogenic apatite in isotopically enriched tracer solution. Chemical Geology 572, 120196.

Strontium isotopes were measured at **CIGS-UNIMORE (Italy).**

1. Neptune Multicollector-Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS).
2. Sr solutions from the prepFAST separation were diluted to 50 ppb with 4% $HNO_3$.
3. Selected samples were measured for $\delta^{88/86}$Sr. Samples were spiked with Zr to correct for mass bias fractionation.
4. All $\delta^{88/86}$Sr and $^{87}$Sr/$^{86}$Sr ratios were then expressed relative to NIST SRM 987.

Argentino C., Lugli F., Cipriani A. and Panieri G. (2021) Testing miniaturized extraction chromatography protocols for combined $^{87}$Sr/$^{86}$Sr and $^{88/86}$Sr analyses of pore water by MC-ICP-MS. Limnol Oceanogr Methods 19, 431–440.

Lugli F., Cipriani A., Tavaglione V., Traversari M. and Benazzi S. (2018) Transhumance pastoralism of Roccapelago (Modena, Italy) Early-Modern individuals: inferences from Sr isotopes of hair strands. American Journal of Physical Anthropology 167.

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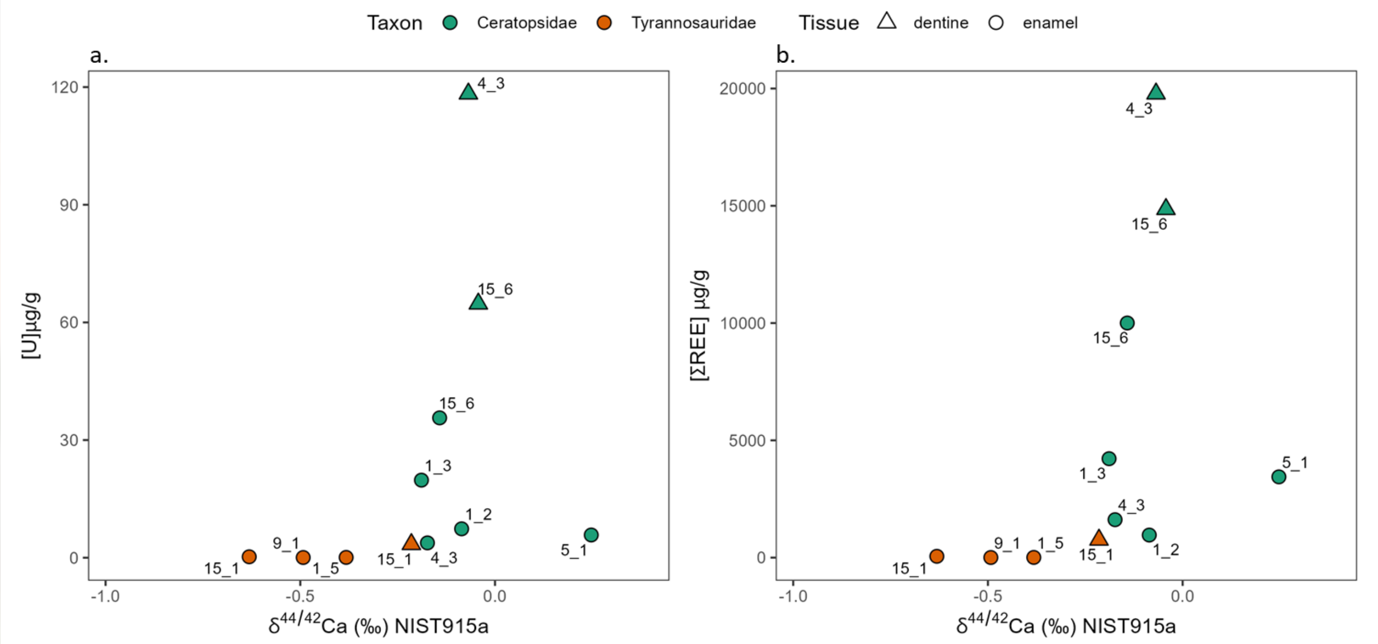
# Teeth diagenesis


Normalized REE profiles have similar patterns with LREE convex downward and MREE to HREE convex upward. **Enrichments are quite different when considering taxon and tissue.**




Most of the tooth samples (both enamel and dentine) exhibit a **high REE and U content caused by postmortem diagenetic uptake**.

Modern bones and teeth typically contain less than 1 µg/g of total REE; in fresh bioapatite, U occurs in very low concentrations (< 1 µg/g).


Kohn M. J. and Moses R. J. (2013) Trace element diffusivities in bone rule out simple diffusive uptake during fossilization but explain in vivo uptake and release. Proc. Natl. Acad. Sci. U.S.A. 110, 419–424.

Kohn M. J., Schoeninger M. J. and Barker W. W. (1999) Altered states: effects of diagenesis on fossil tooth chemistry. Geochimica et Cosmochimica Acta 63, 2737–2747.



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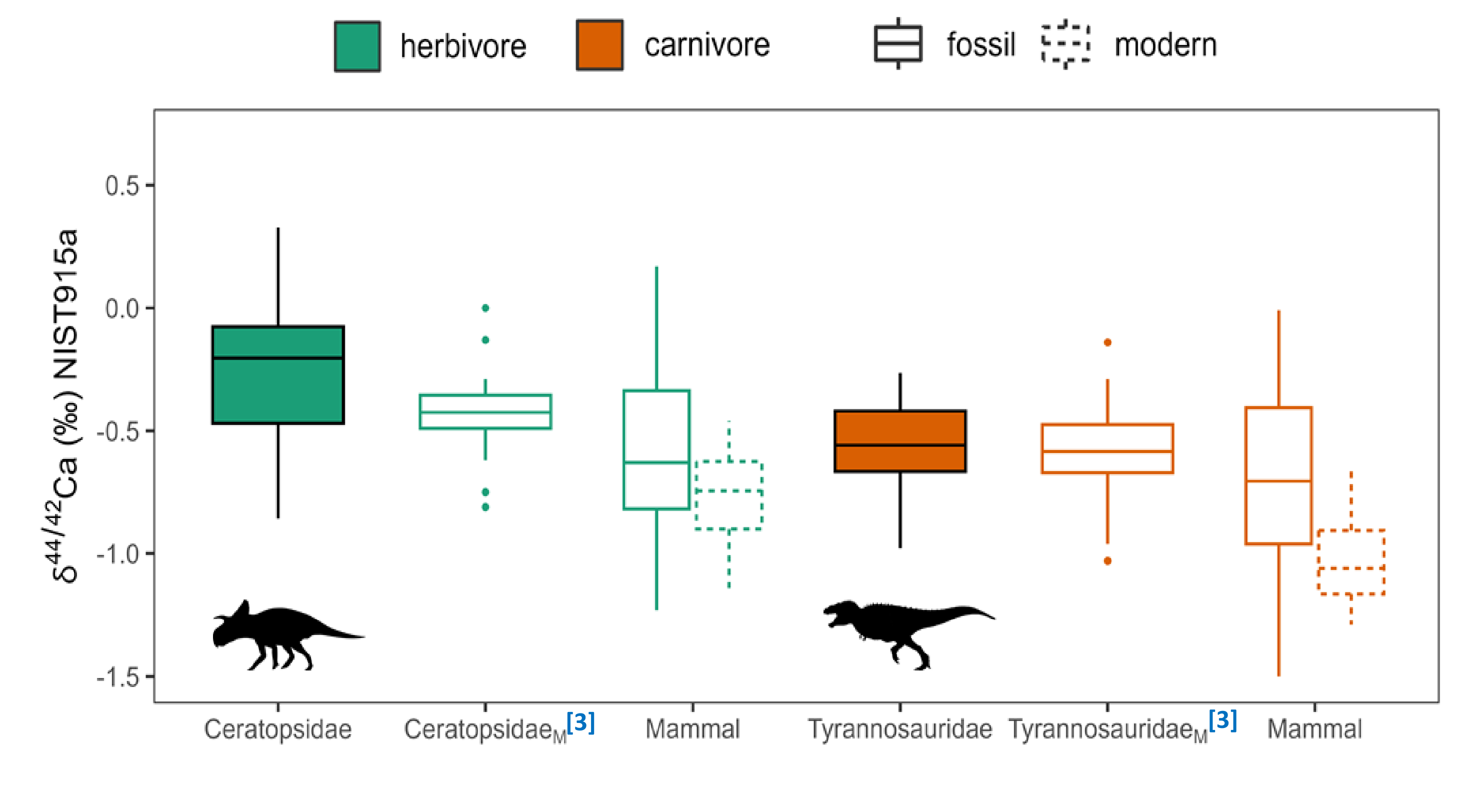
# Throphic Ca reconstruction in dinosaurs




Black animal silhouettes are from phylopic.org.

Ca isotope composition of tyrannosaurid and ceratopsid enamel shows **diet-related inter-taxon spacing**, with tyrannosaurids being the most $^{44}$Ca-depleted taxon.

This offset is consistent with the trophic level effect between modern herbivores and carnivores.

The trophic $\delta^{44/42}$Ca difference between the two taxa is comparable to previous Jurassic and Cretaceous dinosaur studies [1,2,3].

The $\Delta^{44/42}Ca_{carnivore\text{-}herbivore}$ in our dataset is -0.29‰.

The $\Delta^{44/42}Ca_{carnivore\text{-}herbivore}$ of enamel from modern African terrestrial mammals is ~0.30‰.

1. Hassler A., Martin J. E., Amiot R., Tacail T., Godet F. A., Allain R. and Balter V. (2018) Calcium isotopes offer clues on resource partitioning among Cretaceous predatory dinosaurs. Proc. R. Soc. B. 285, 20180197.
2. Heuser A., Tütken T., Gussone N. and Galer S. J. G. (2011) Calcium isotopes in fossil bones and teeth — Diagenetic versus biogenic origin. Geochimica et Cosmochimica Acta 75, 3419–3433.
3. Martin J. E., Hassler A., Montagnac G., Therrien F. and Balter V. (2022) The stability of dinosaur communities before the Cretaceous–Paleogene (K–Pg) boundary: A perspective from southern Alberta using calcium isotopes as a dietary proxy. GSA Bulletin 134, 2548–2560.

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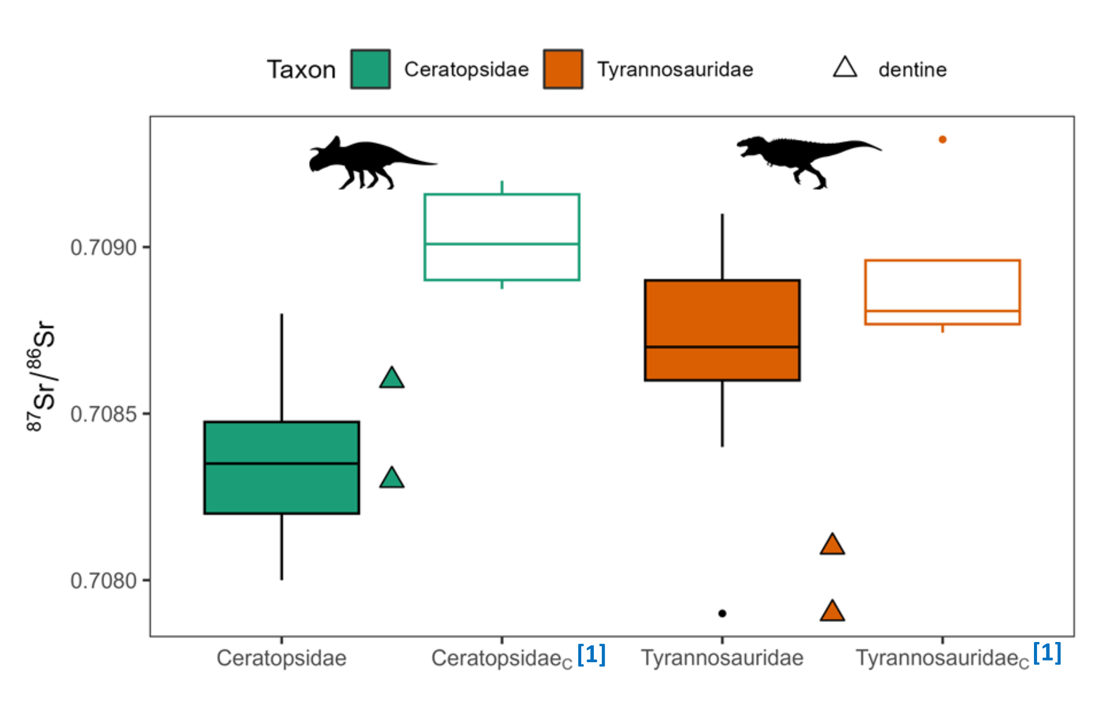
# Diet vs Diagenesis

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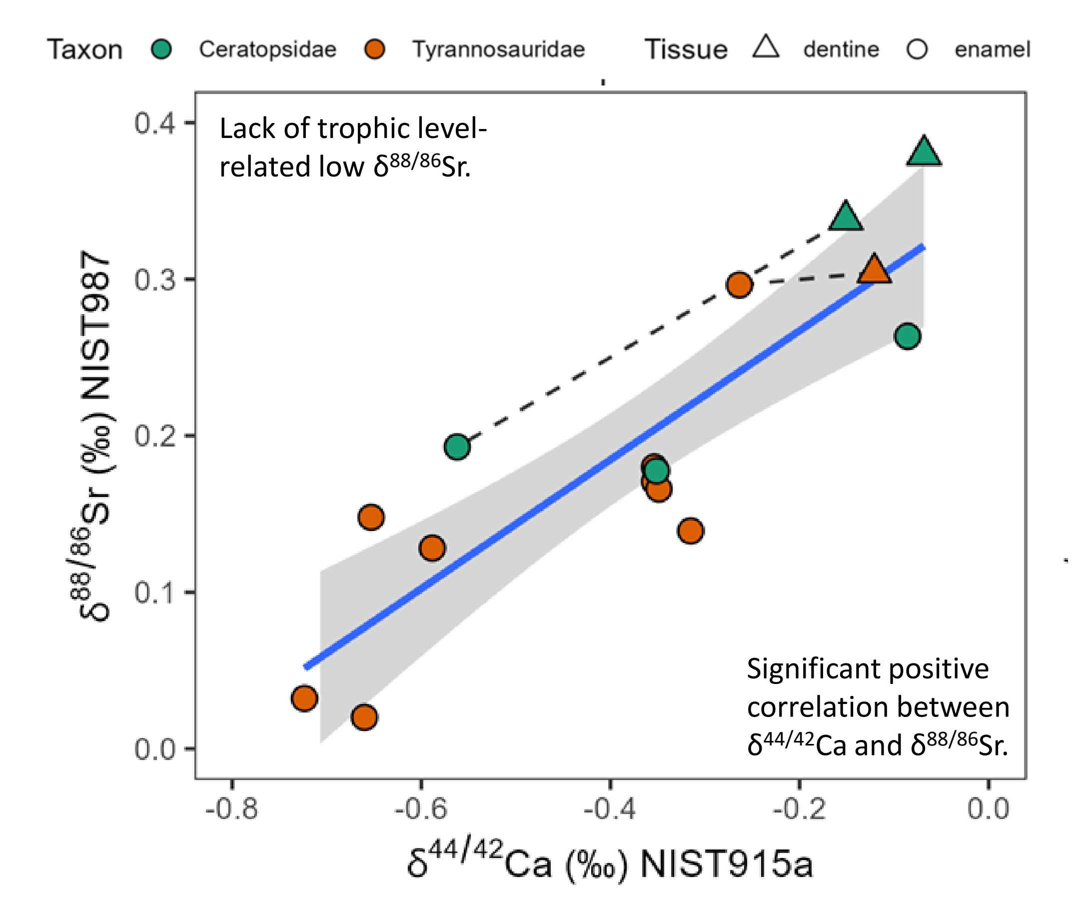


The $^{87}Sr/^{86}Sr$ of our teeth are more radiogenic than the seawater value at 75 Ma (0.7076 from McArthur[2]).

Ceratopsid enamel and dentine and tyrannosaurid dentine tend toward a less radiogenic end-member (possibly seawater), reconfirming a worse preservation status for these samples.


1. Cullen T. M., Zhang S., Spencer J. and Cousens B. (2022) Sr-O-C isotope signatures reveal herbivore niche-partitioning in a Cretaceous ecosystem. Palaeontology 65, e12591.
2. McArthur, J. M., Howarth, R. J., & Bailey, T. R. (2001). Strontium isotope stratigraphy: LOWESS version 3: best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up table for deriving numerical age. The Journal of Geology 109, 155–170.



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# Conclusions

Dentine is more enriched in trace elements (U, REE). Any trophic enrichment of $\delta^{44/42}$Ca is masked in dentine. **Enamel is overall less affected by post-burial diagenetic alterations.**

**Enamel $\delta^{44/42}$Ca values** are different between ceratopsids and tyrannosaurids reflecting a **trophic level effect** similar to modern mammals. Diet-related $\delta^{44/42}$Ca in enamel appears to be largely intact.

Significant alteration in Sr isotope composition ($\delta^{88/86}$Sr, $^{87}$Sr/$^{86}$Sr) coupled with Ca isotopes in fossil teeth can serve as a **sensitive diagenetic proxy**.

Soon to be published:

**Combined Ca, Sr isotope and trace element analyses of Late Cretaceous dinosaur teeth: assessing diet versus diagenesis**

Mateusz M. Michailow, Federico Lugli, Anna Cipriani, Francesco Della Giustina, Annalisa Ferretti, Daniele Malferrari, Denver Fowler, Elizabeth Freedman Fowler, Michael Weber, Thomas Tütken

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Thank you!

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