Nitrite isotope characteristics in ^{15}N-labelled and non-labelled agricultural soil

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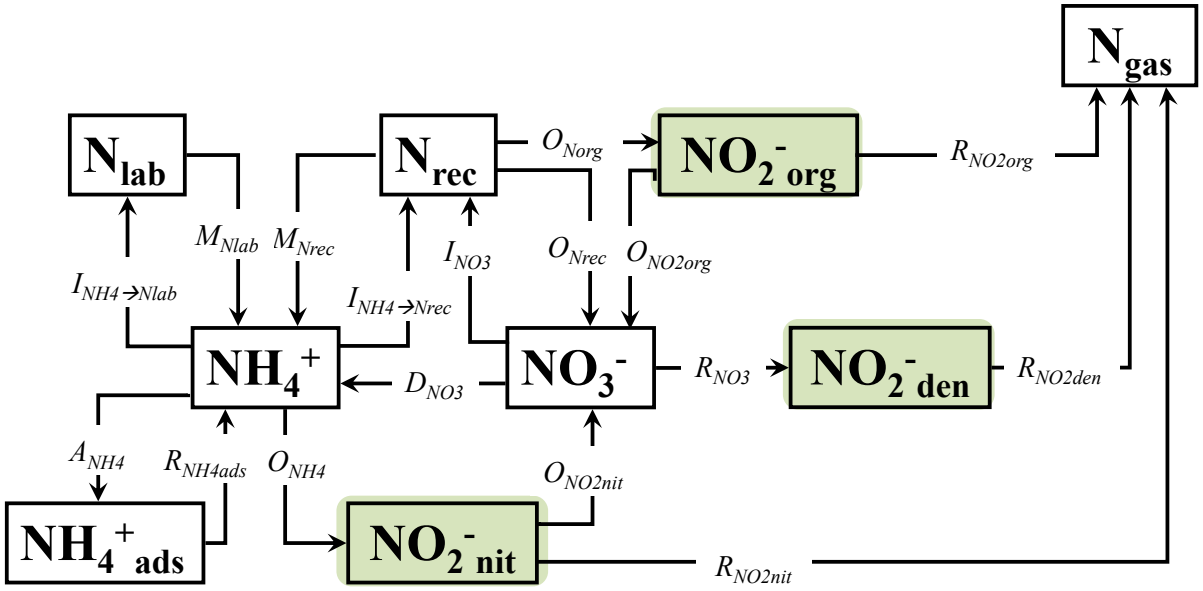
Nitrite (NO_2^-) is a crucial compound in the complex N soil cycle.
As an intermediate of nearly all N transformations, its isotopic signature may provide precious information on the active pathways and processes. NO_2^- analyses have been already applied in ^{15}N tracing studies increasing their interpretation perspectives (*Müller et al., 2014*).



(*Müller et al., 2014*)

3 main sources:
- **orgN oxidation (*org*)**
- **nitrate reduction (*den*)**
- **ammonium oxidation (*nit*)**

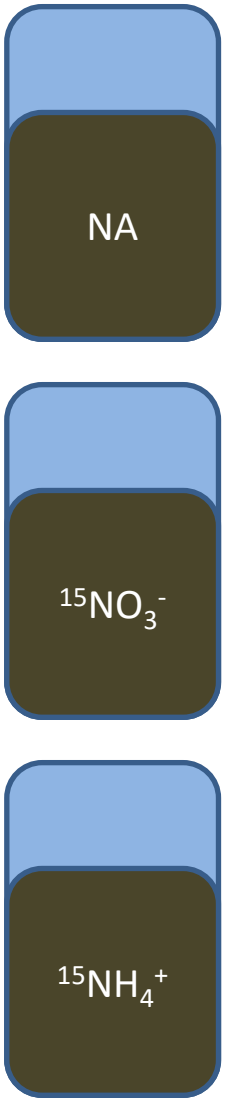
2 main sinks:
- **reduction to NO, N_2O (*R*)**
- **oxidation to nitrate (*O*)**

Natural abundance NO_2^- isotope studies in ocean waters are already used as important tool in tracing N transformations (*Buchwald & Casciotti, 2013*).
Natural abundance NO_2^- isotope studies in soils were so far not applied and this study aims at testing if such analyses are also useful in tracing the soil N cycle.

Methods

Flow-through laboratory incubations in N_2-reduced atmosphere (He with 2% N_2, 21% O_2)
Water content varied from 55 to 86% water-filled pore space

3 treatments:



for NA treatments

→ gas analyses: N_2O flux, N_2O isotopes ($\delta^{15}N$, $\delta^{15}N^{SP}$, $\delta^{18}O$)

→ soil analyses: NO_3^-, NO_2^-, NH_4^+ content
isotopes NO_3^- ($\delta^{15}N$, $\delta^{18}O$), **NO_2^- ($\delta^{15}N$, $\delta^{18}O$),** NH_4^+ ($\delta^{15}N$)

for ^{15}N treatments

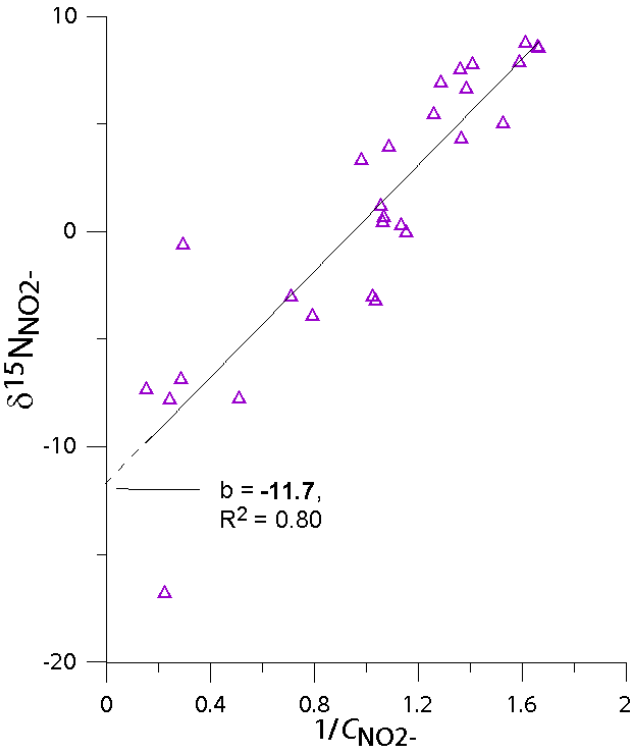
→ gas analyses: N_2O flux,
N_2 flux (determined with ^{15}N gas flux method)
^{15}N abundance in N_2O and N_2 ($a^{15}N_{N2O}$, $a^{15}N_{N2}$)

→ soil analyses: NO_3^-, NO_2^-, NH_4^+ content
^{15}N abundance in NO_3^-, NO_2^-, NH_4^+
($a^{15}N_{NO3-}$, $a^{15}N_{NO2-}$, $a^{15}N_{NH4+}$)

First NA nirite isotopic analyses in soil studies

immediate alkaline extraction
isotopic analysis with the denitrifier method for selective nitrite reduction with *Stenotrophomonas nitritireducens*

Keeling plot applied to identify the dominant NO_2^- source



Based on the intercept (b) the **dominant NO_2^- input** is characterised with $\delta^{15}N_{NO2-}$ of -11.7 ‰

when related to NO_3^- (with mean $\delta^{15}N_{NO3-}$ of 4.5 ‰):

ε (NO_2^-/ NO_3^-) = -11.7 ‰ – 4.5 ‰ = -16.2‰

value within the literature data
for NO_3^- to NO_2^- reduction step of denitrification

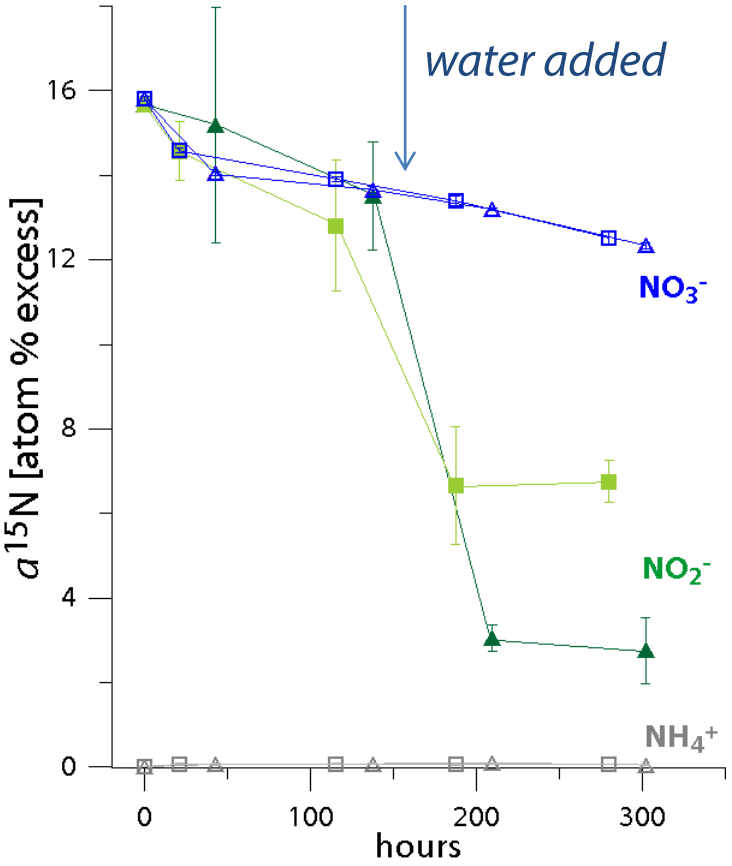
Nitrate reduction N isotope effect ~ - 15 ‰
(Granger et al., 2008)

Results – nitrite and nitrate - ^{15}N treatment

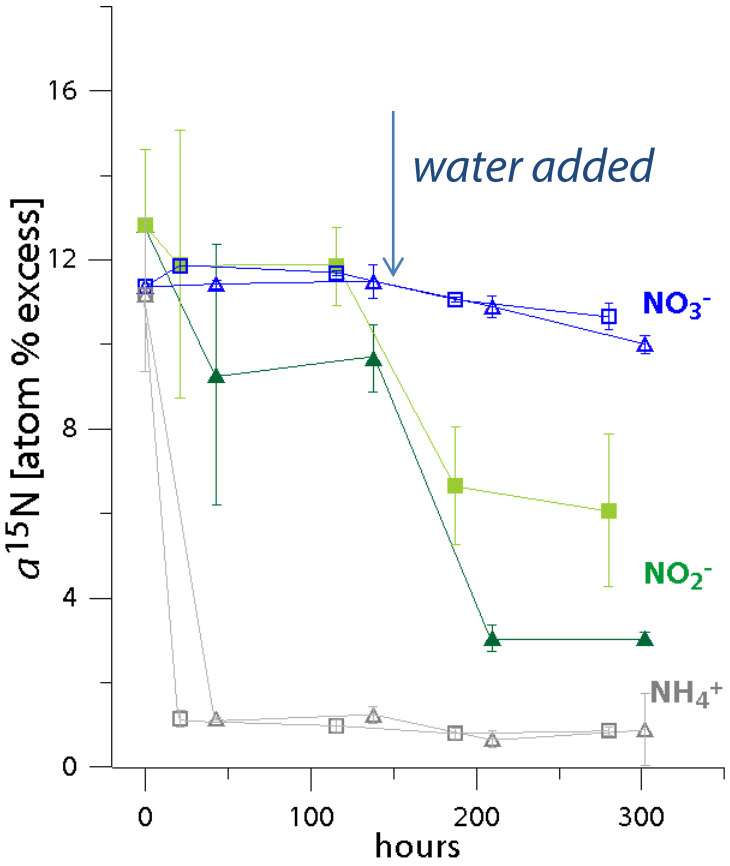
Sudden drop in ^{15}N abundance in NO_2^- ($a^{15}N_{NO2-}$) after water addition to the soil

$a^{15}N_{NO2-}$ decreases of ca. 5 to 10 atom %, and $a^{15}N_{NO3-}$ only slightly of ca. 1 atom %.

$^{15}NO_3^-$ treatment

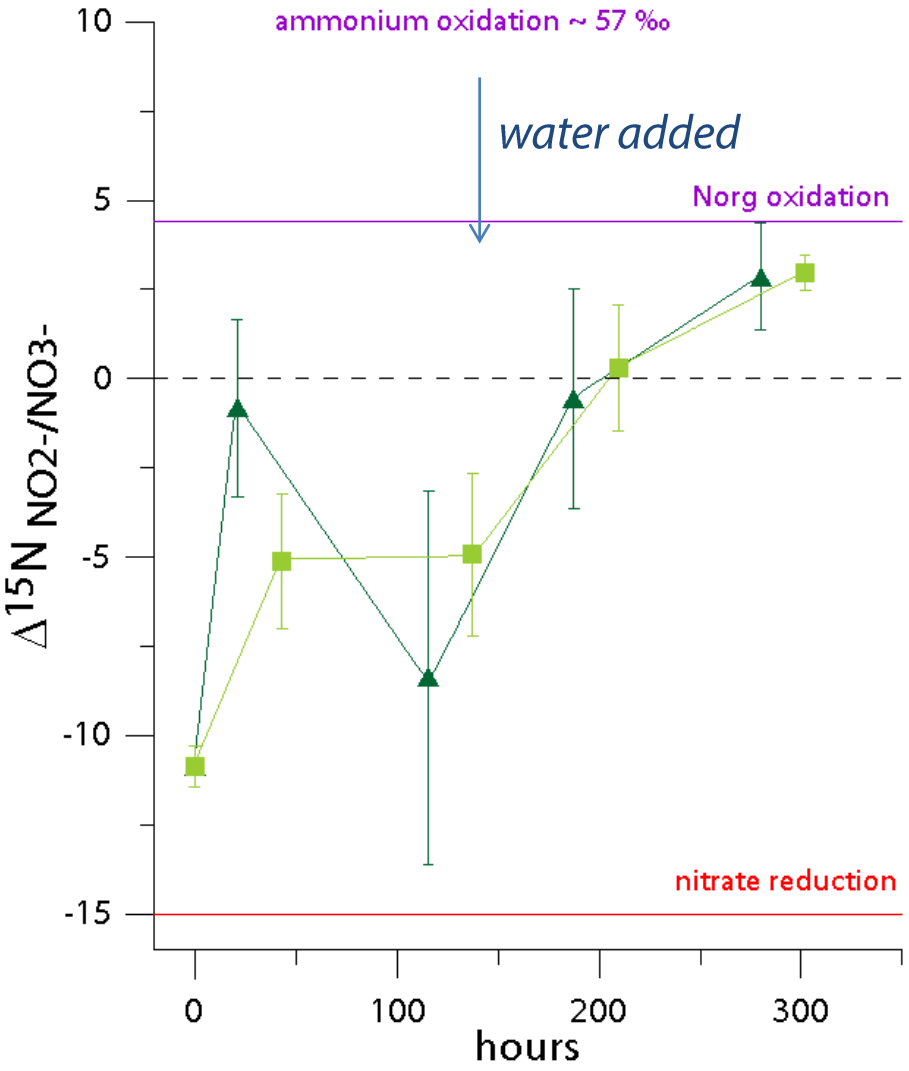


$^{15}NH_4^+$ treatment



This indicates an incorporation of **new source of unlabelled NO_2^-** for the wet part (two last samplings)

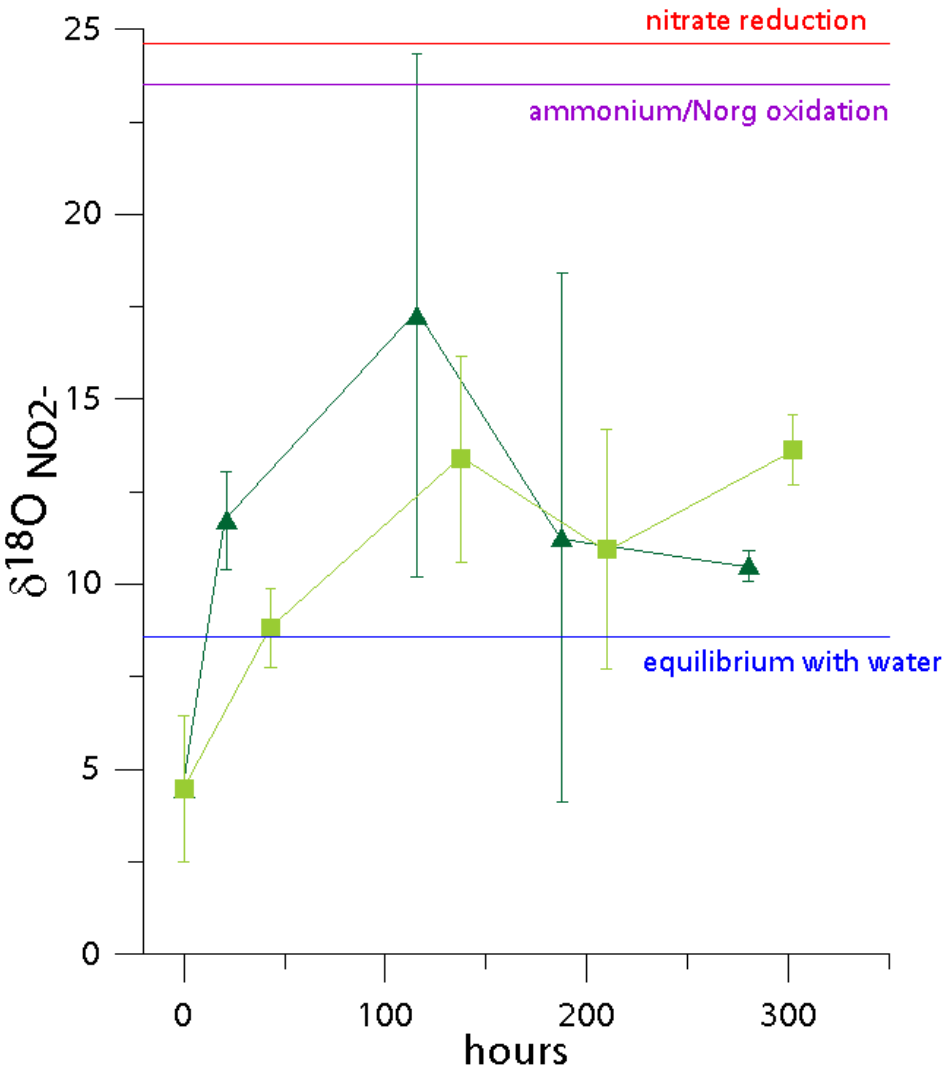
Results – nitrite – isotopic dynamics in NA treatment



In NA isotopes this change is reflected in higher $\Delta^{15}N(NO_2^-/NO_3^-)$;
for the wet part of the experiment
it was positive with mean of +1.6‰,
whereas for the dry part it was lower
with mean of -5.9‰.

Since for this case study $\delta^{15}N_{NH4+}$ is very high the new nitrite source noted for last two samplings (with ^{15}N treatment) can be rather Norg oxidation.

Results – nitrite – isotopic dynamics in NA treatment



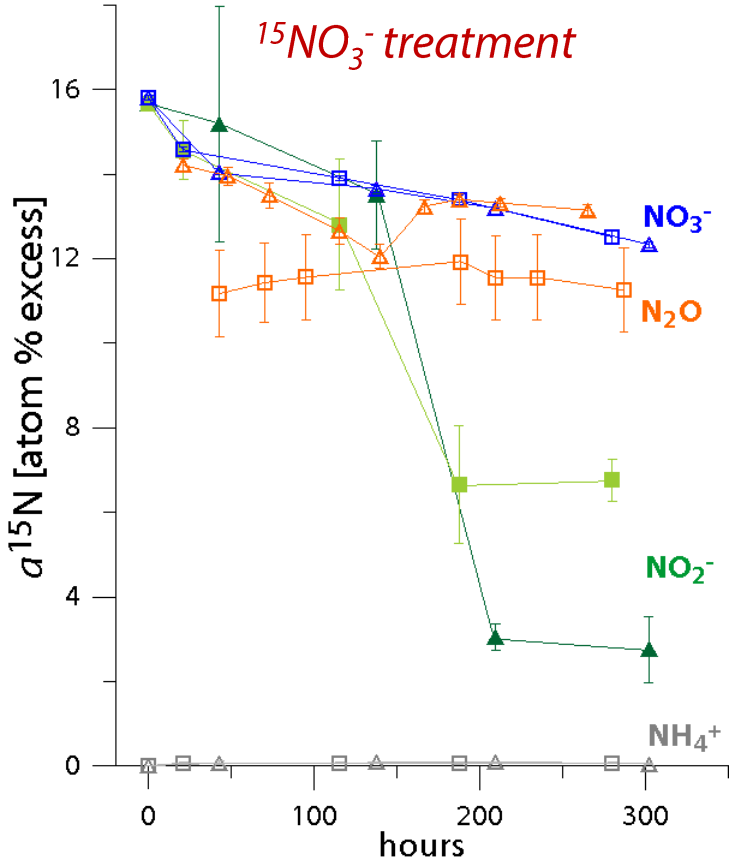
$\delta^{18}O_{NO2-}$ is very variable and complicated due to O-atoms equilibration with ambient water, since less informative.

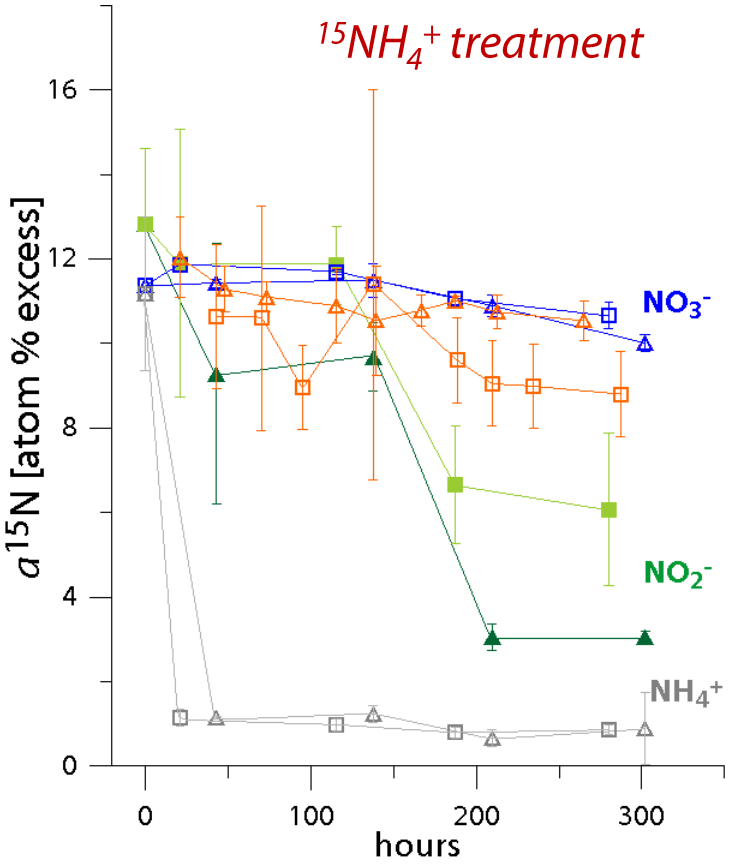
Possibly NO_2^- originating from both nitrate reduction and ammonium oxidation can be partially equilibrated with water. The final $\delta^{18}O_{NO2-}$ depends on the balance between nitrite abiotic equilibration and biological turnover (*Buchwald & Casciotti, 2013*). For soil pH of 6.8 equilibration processes will be more rapid than for ocean water of pH 8.

Results – nitrite and N_2O – ^{15}N treatment

Changes in nitrite isotopes are not reflected in N_2O. Whereas $a^{15}N_{NO2-}$ drops to 3 - 6 atom %, for $a^{15}N_{N2O}$ still 10 - 14 atom % are found.

This shows that NO_2^- pools originating from different pathways must be isolated and not the entire NO_2^- pool undergoes further reduction to N_2O.





Conclusions

• Natural abundance nitrite isotope studies may provide a new important tool in constraining the N soil cycling. Here we showed that based on $\delta^{15}N_{NO2-}$ Keeling plot the dominant NO_2^- source can be indicated and based on $\Delta^{15}N(NO_2^-/ NO_3^-)$ the changes in contribution of nitrate reduction and ammonium or organic N oxidation may be tracked;

• However, the pathways contribution for NO_2^- is not relevant for indication of N_2O sources, since not all NO_2^- pools are further reduced to N_2O;

• $\delta^{18}O_{NO2-}$ is probably not very useful in soil studies due to fast exchange of O-atoms in low pH; however for soils of neutral pH this may be an indicator of biological tranformation rates, similar as for ocean studies;

• Further experiments are needed to determine the characteristic isotope efects associated with particular NO_2^- inputs and sinks for soil studies.

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