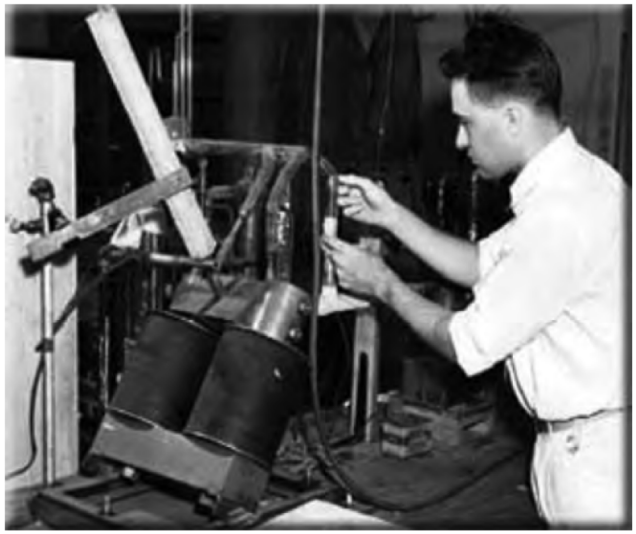
In Situ Laser-Laser carbon and oxygen isotopes measurements in carbonates: A step forward field isotopic characterization

Christophe Thomazo [*1], Pierre Sansjofre [2], Olivier Musset [3], Ivan Jovovic [1], Theophile Cocquerez [1], Stefan Lalonde [4].

[1] Biogéosciences, CNRS UMR 6282, Université Bourgogne Franche-Comté, France
[2] MNHN, Sorbonne Université, CNRS UMR 7590, France
[3] Laboratoire Interdisciplinaire CARNOT, CNRS UMR 6303, Université de Bourgogne Franche-Comté, France
[4] Institut Universitaire Européen de la Mer, CNRS UMR 6538, France



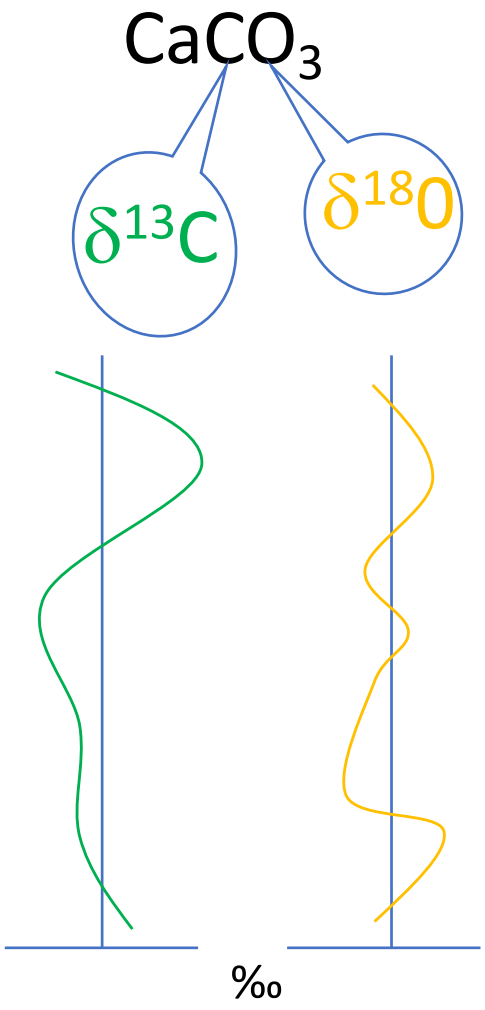
A.O. Nier "tuning" one of his early mass spectrometers. (Courtesy of IsoPrimeLtd.)

In Wieser, M. E., & Brand, W. A. (2013). Isotope ratio studies using mass spectrometry.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 18, NUMBER 6 JUNE, 1950

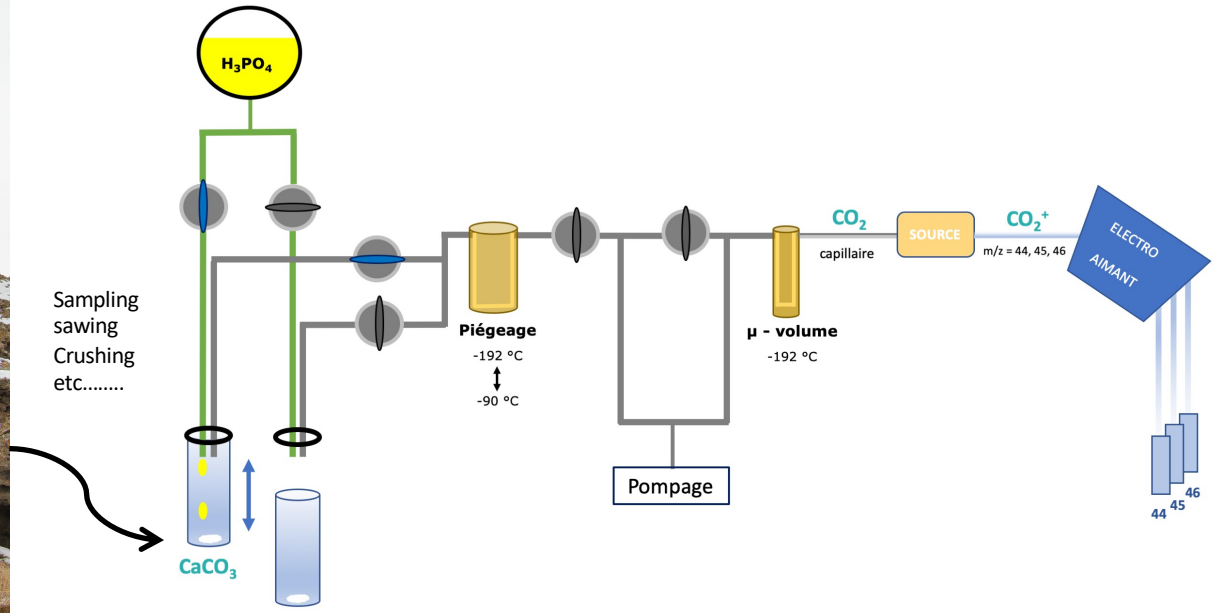
On the Isotopic Chemistry of Carbonates and a Paleotemperature Scale*

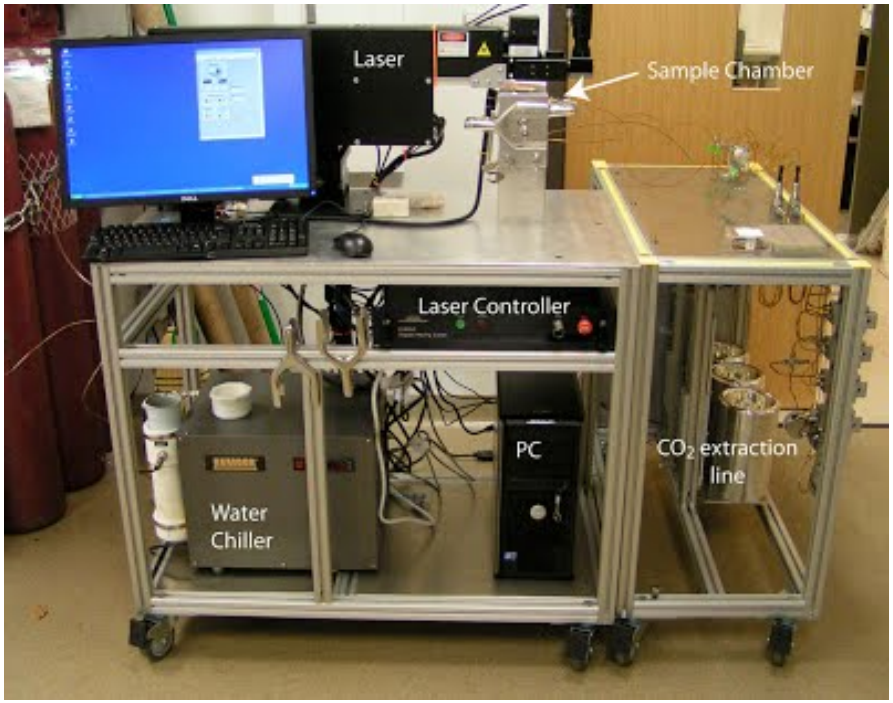
J. M. McCrea†
Kent Chemical Laboratory, University of Chicago, Chicago, Illinois
(Received January 30, 1950)



- C cycle
- PaleoT°C
- …

Wet chem. Acid digestion + cryogenic purification



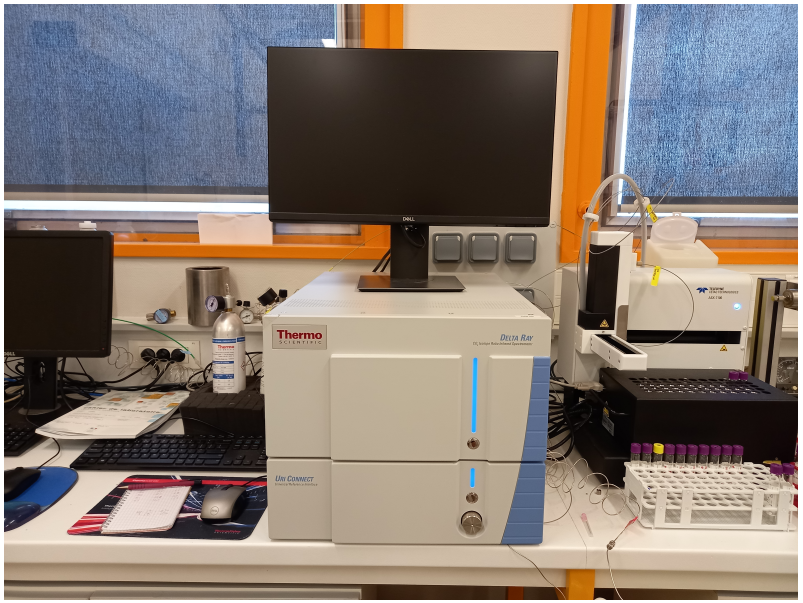


(e.g. Sharp 1992; Sharp and Cerling 1996)

Laser ablation + GC or Cryogenic purification

e.g. 20W CO_2 laser (beam size >80mm) with a pulse generator

New generation



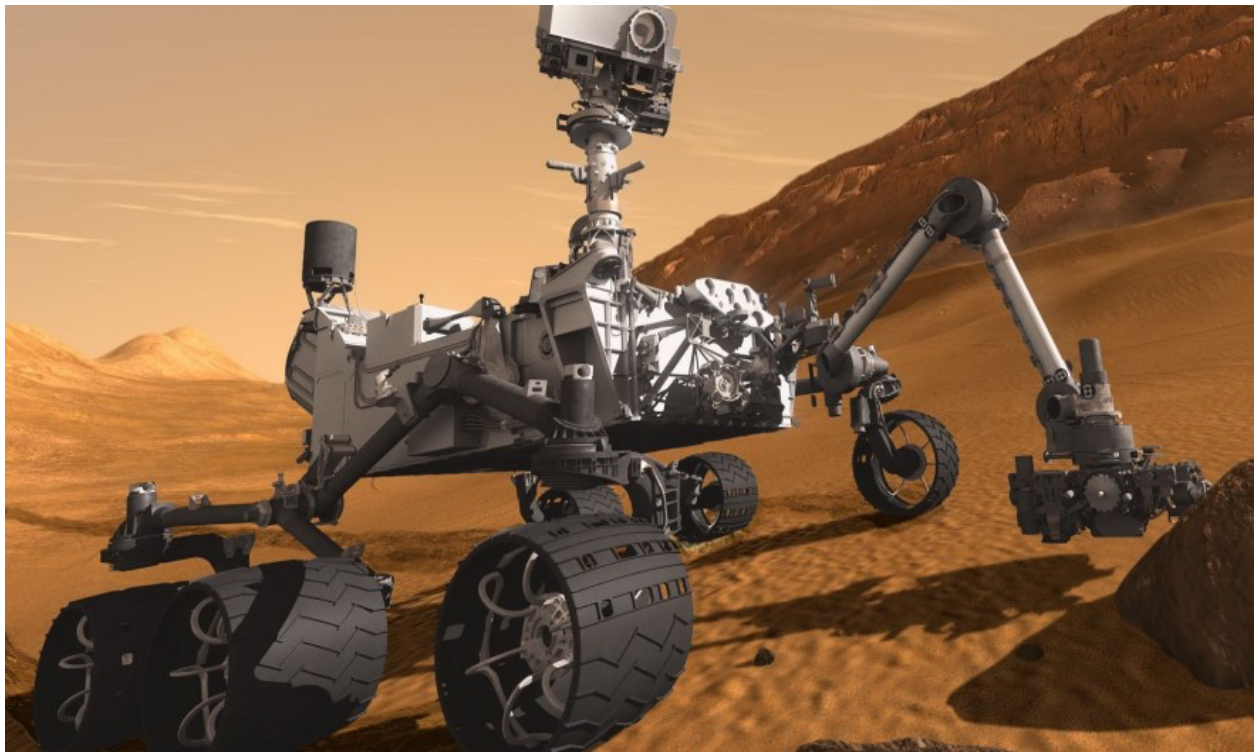
IRMS : m/Z separation = 300Kg

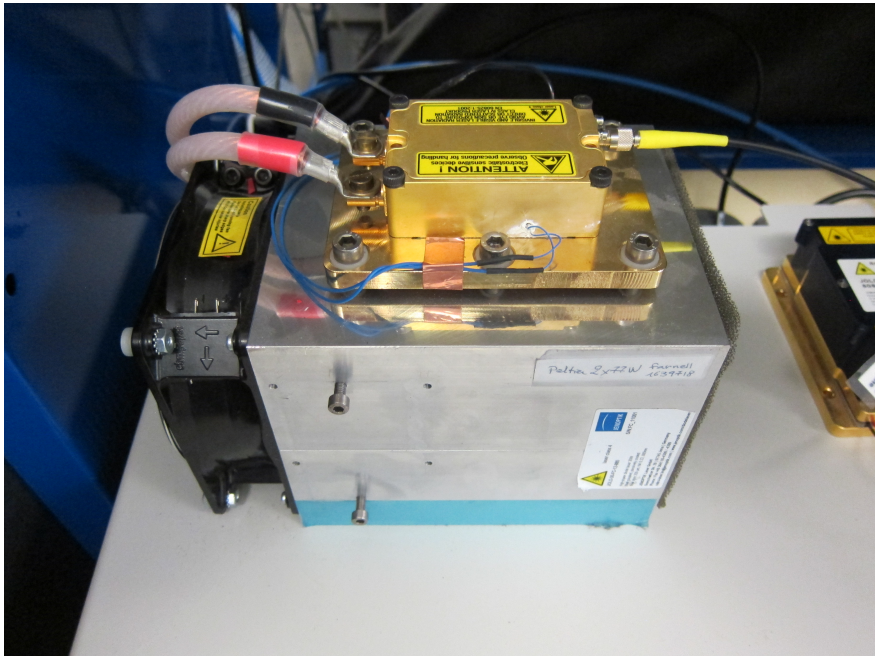
IRIS/CRDS : Optical measurement = 30Kg

OBJECTIVES

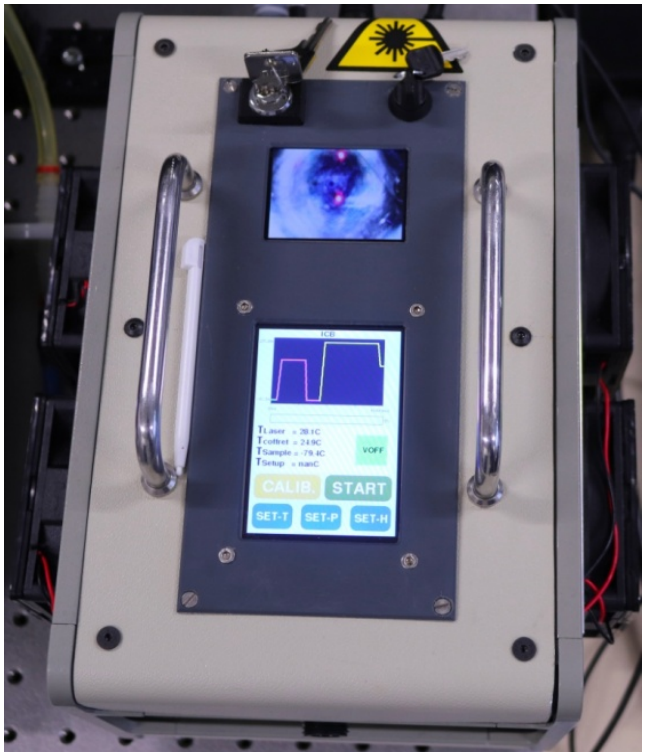
1/ Punctual analyses system coupled to CRDS/IRS?

2/ Field deployable?





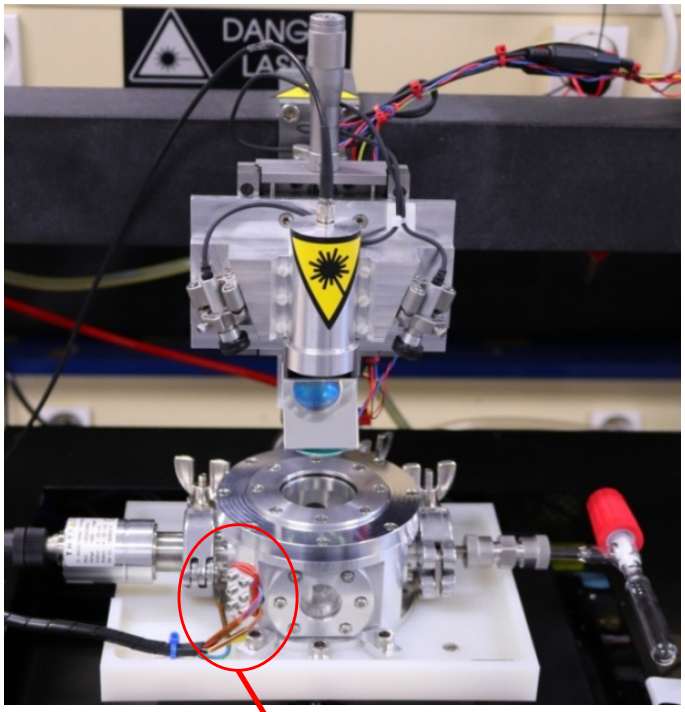
Laser diode (25 W- emission at 880 nm) - connected to an optical fiber of 200 μm.
- high optical / electrical efficiency (≥30%)
- inexpensive (<2k€)

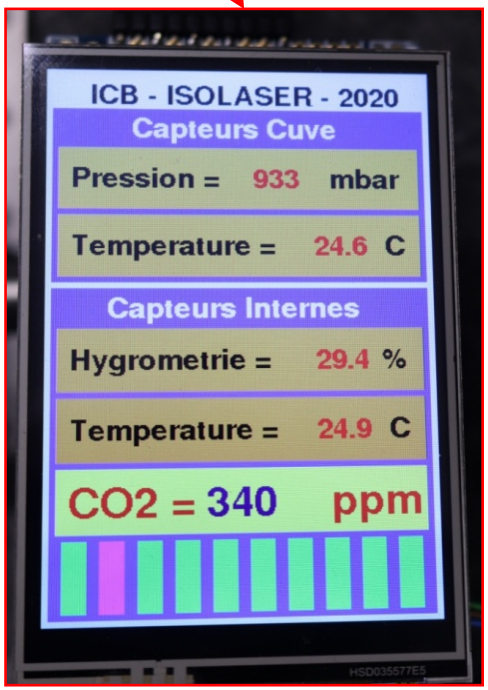


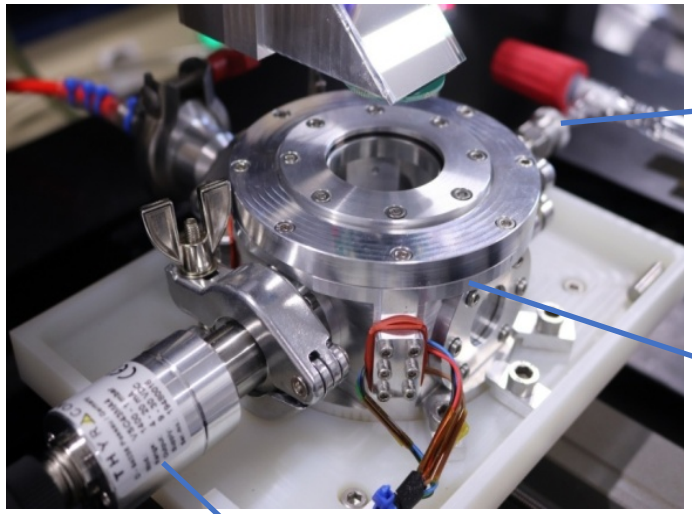
Control Box (color screen data display)
- Laser parameters (time, energy, etc…)
- Sample vizualistaion

$$CaCO_3 \Rightarrow CaO + CO_2$$

→ calcination reaction at « low - 900°C » temperature (NO PLASMA)







No purification step! - direct gas collection by pressure equilibration in sample tubes…. Or direct connection to IRIS/CRDS …

→ 8 different types of carbonate minerals

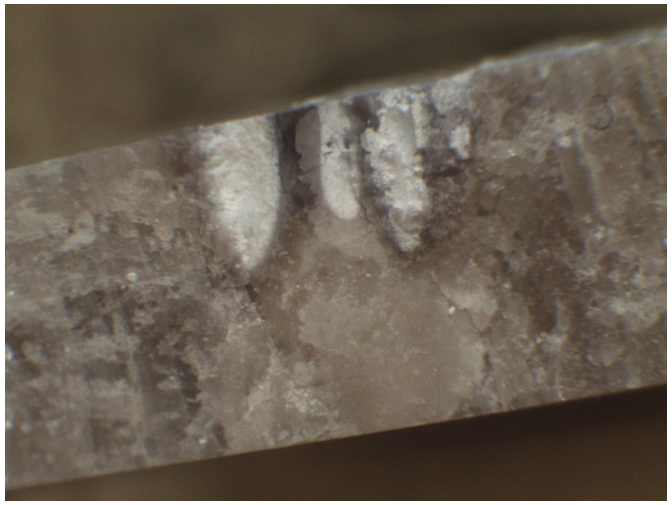
	Sample	Description	Formula	Origin	ID number
1	Calcite 1	Speleothem	$CaCO_3$	DMC	nd
2	Calcite 2	Ferroancalcite	$CaCO_3$	DMC	nd
3	Dolomite 1	Micrite	$(Ca\text{-}Mg)CO_3$	DMC	76-5
4	Dolomite 2	Saccharoïd	$(Ca\text{-}Mg)CO_3$	Saxony (DMC)	912
5	Siderite	Macrocrystal	$FeCO_3$	DMC	nd
6	Malachite	Macrocrystal	$Cu_2CO_3(OH)_2$	Siberia (DMC)	472
7	Rhodocrosite	Macrocrystal	$MnCO_3$	Rothenberg Mine (DMC)	985
8	SDV	Dolomicrite	$(Ca\text{-}Mg)CO_3$	Noonday Fm. (USA)	nd

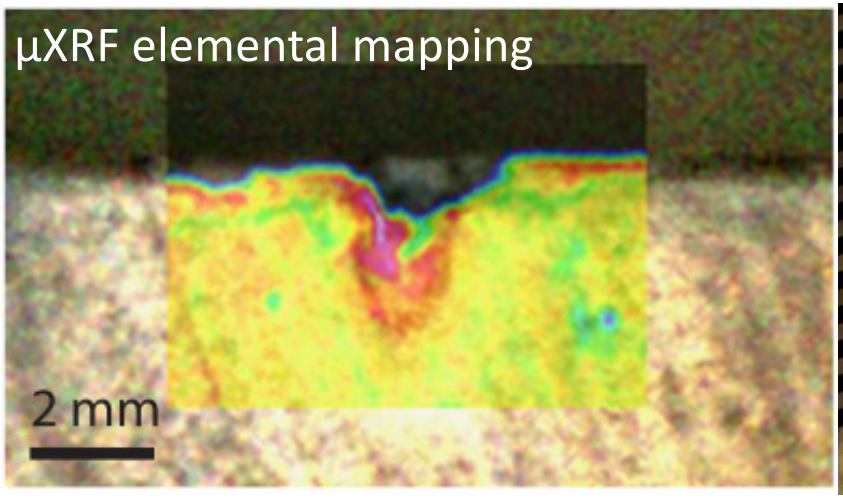
$\delta^{13}C$ from -18.2 to +3.3 ‰

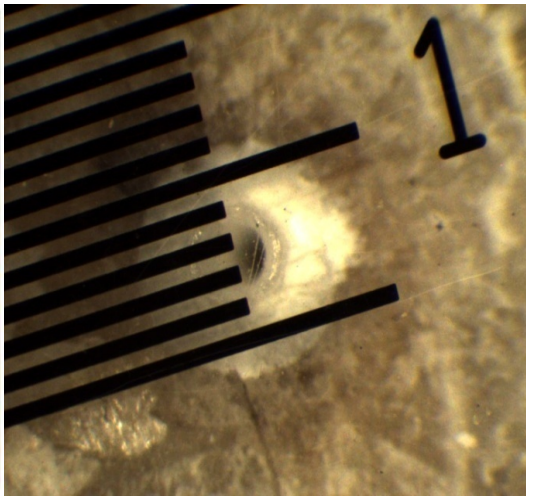
$\delta^{18}O$ from -14.6 to -1.7 ‰

$$CaCO_3 => CaO + CO_2$$

- Heat affected zone = 300µm to 1mm

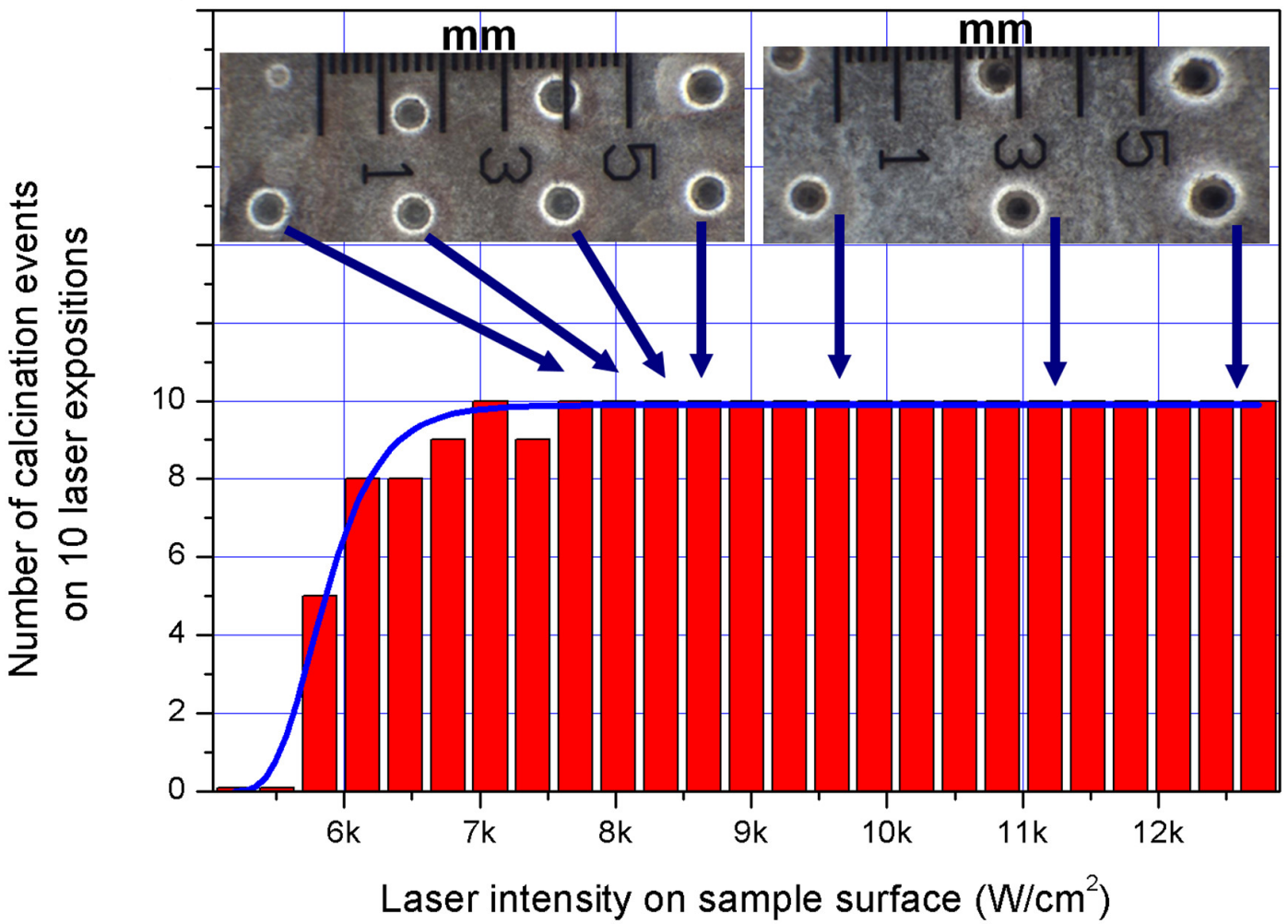




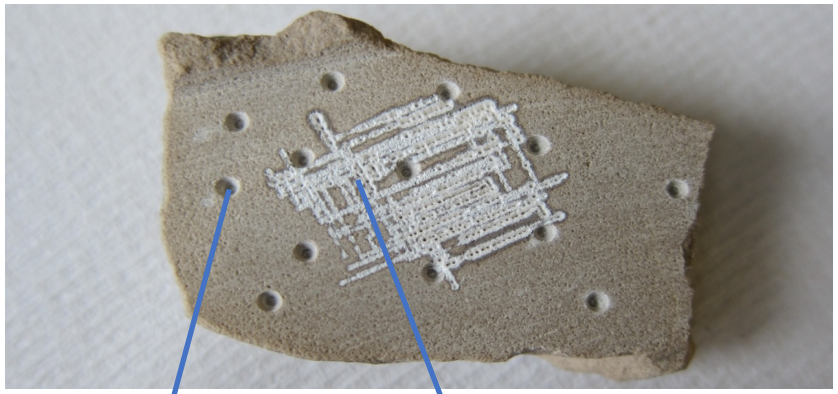


- Locally increased Ca intensities (µXRF) reveal the presence of CaO

Histogram of calcinations events as a function of laser intensity at a constant exposure time of 5 s



- above the specific threshold of a given type of carbonate the probability of triggering calcinations is 100% and does not depend on impurities, grain boundaries, inclusion or cracks.



Laser calcination rastering

Microdrill subsamples

Inter-calibration work flow:

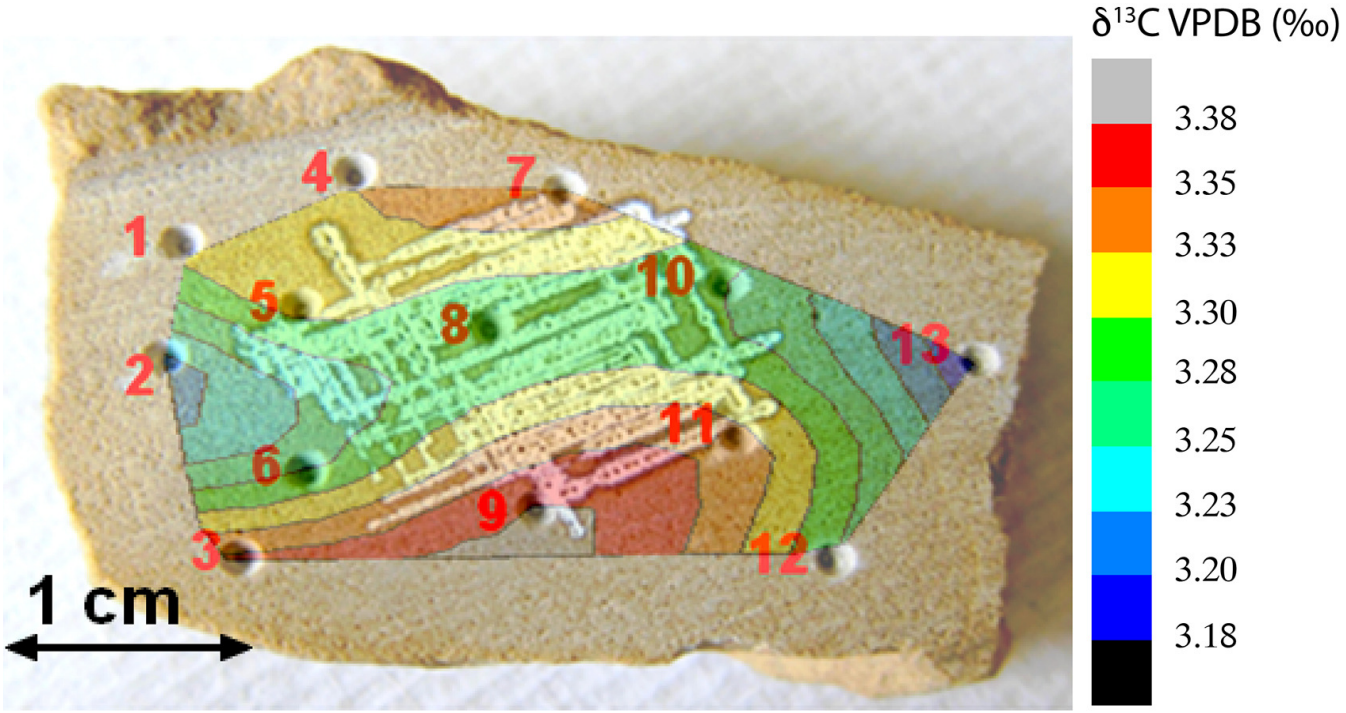
Micro-drilling

Kiel IV-IRMS measurements

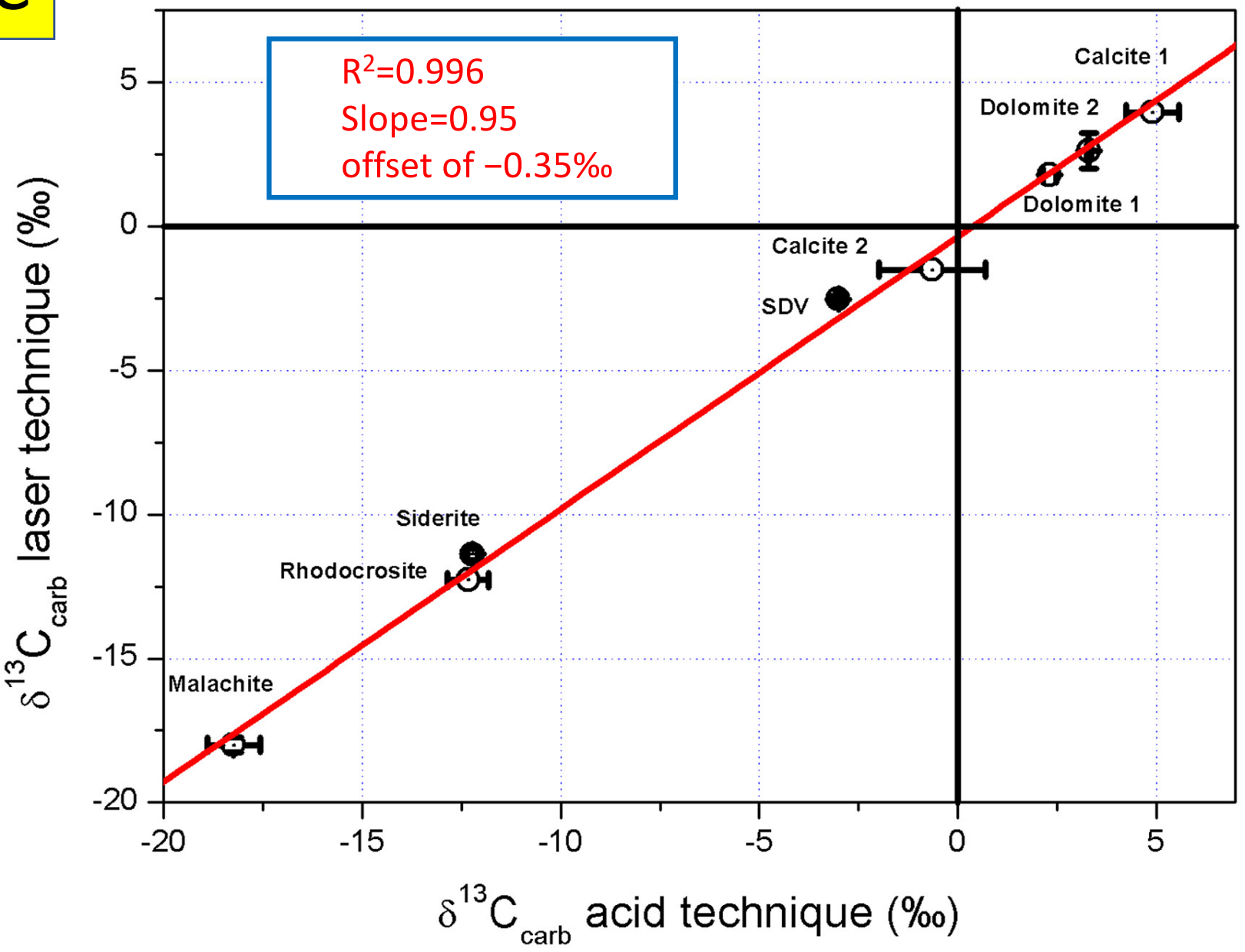
Check isotopic spatial distribution (e.g. maps)

Laser calcination & gas collection

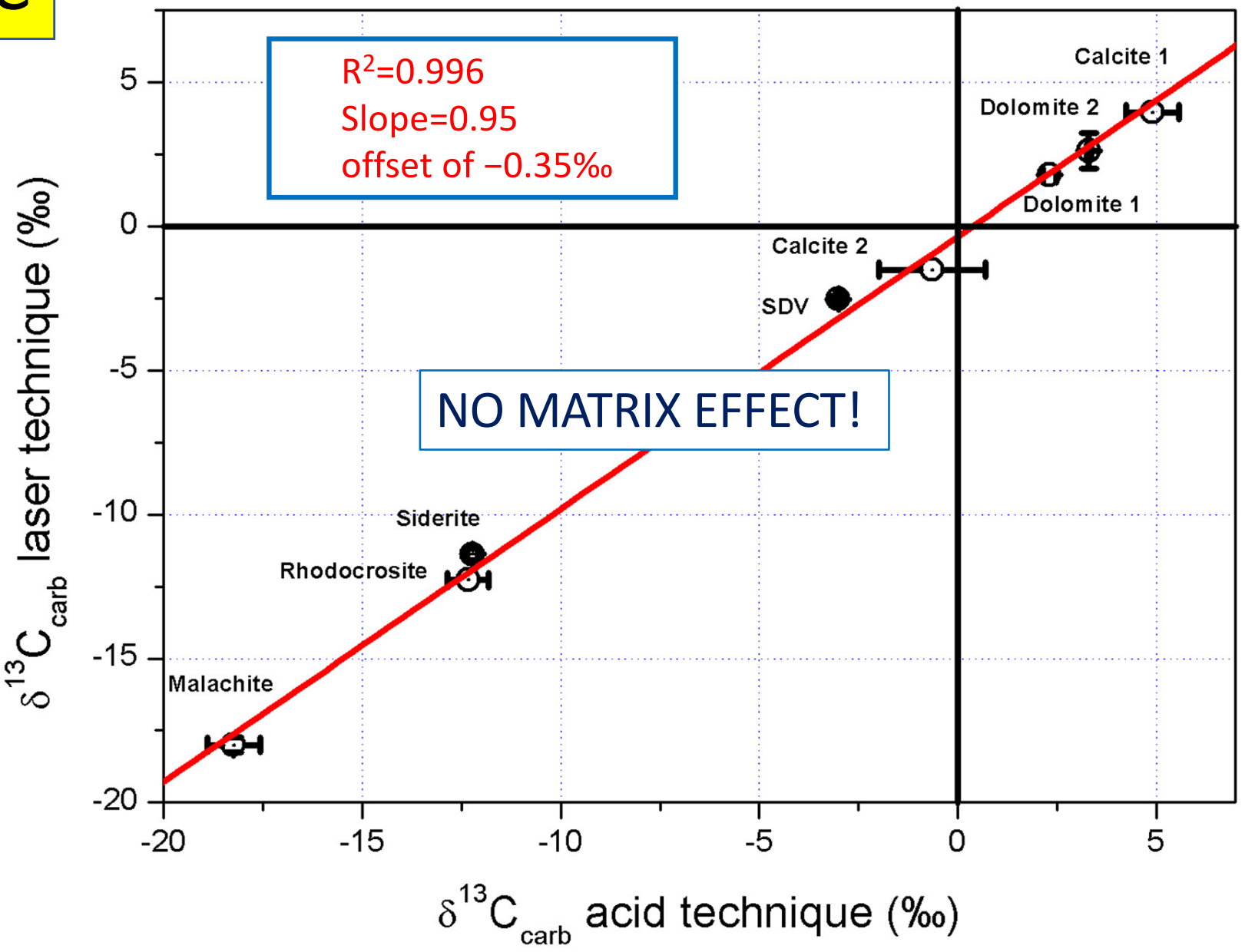
Dual inlet IRMS & IRIS



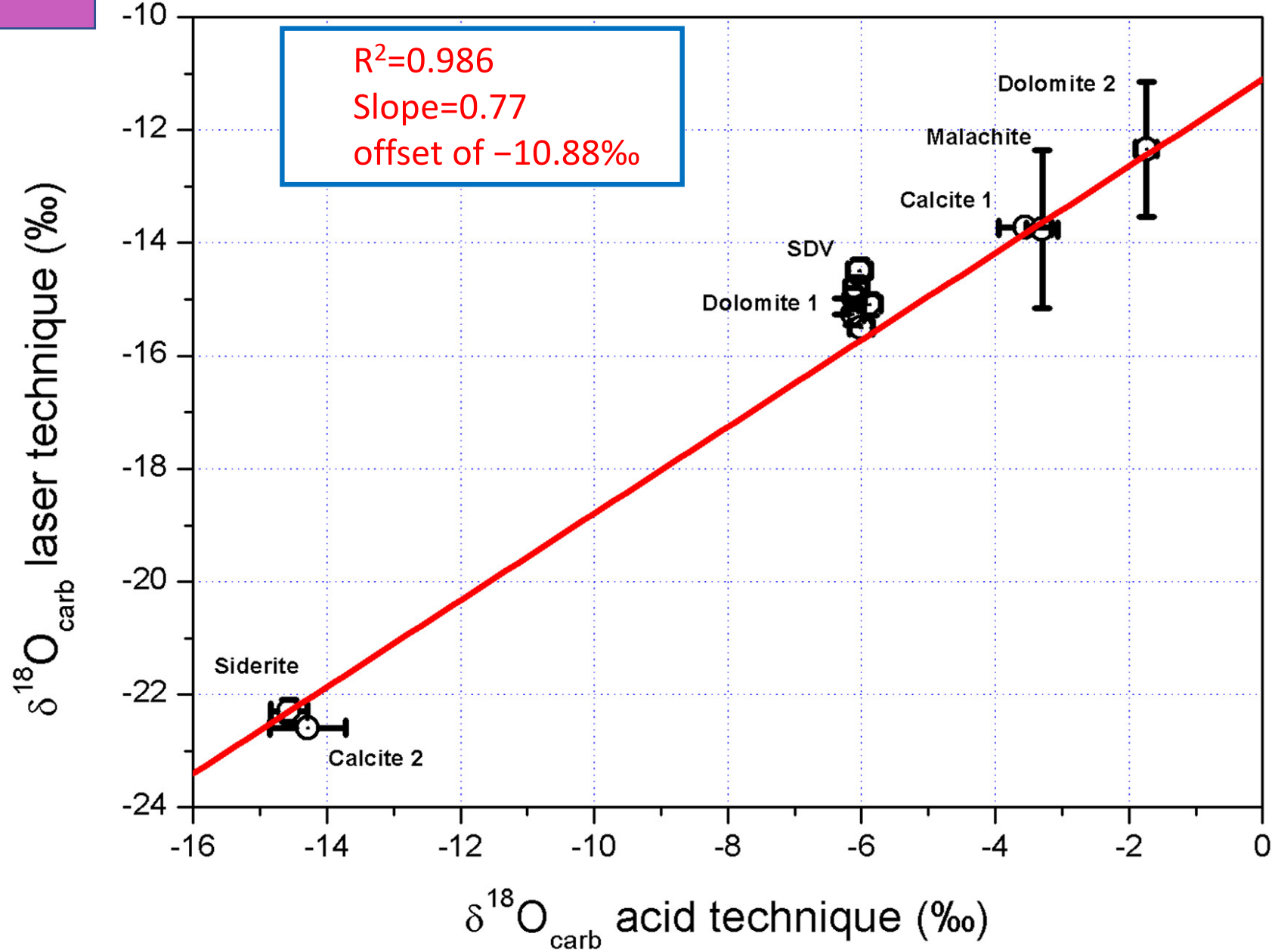
$\delta^{13}C$


R2=0.996
Slope=0.95
offset of −0.35‰
Calcite 1
Dolomite 2
Dolomite 1
Calcite 2
SDV
Siderite
Rhodocrosite
Malachite
δ13Ccarb laser technique (‰)
δ13Ccarb acid technique (‰)
5
0
-5
-10
-15
-20
-20
-15
-10
-5
0
5

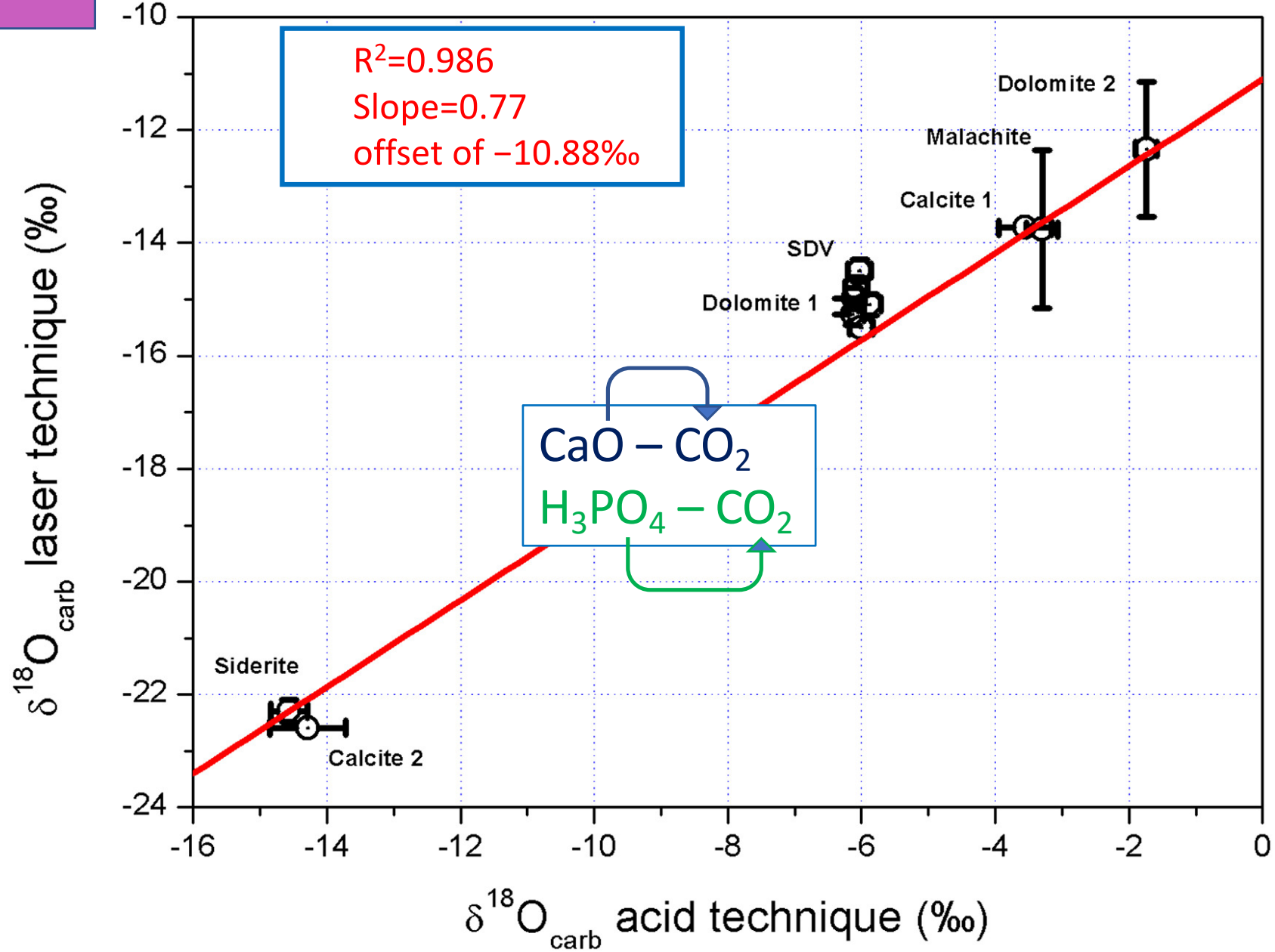
$\delta^{13}C$

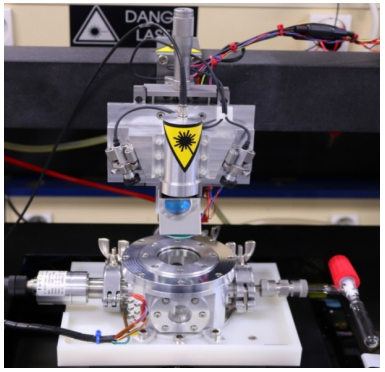

R²=0.996
Slope=0.95
offset of −0.35‰
NO MATRIX EFFECT!
Calcite 1
Dolomite 2
Dolomite 1
Calcite 2
SDV
Siderite
Rhodocrosite
Malachite
δ13Ccarb laser technique (‰)
δ13Ccarb acid technique (‰)
5
0
-5
-10
-15
-20
-20
-15
-10
-5
0
5

$\delta^{18}O$


R2=0.986
Slope=0.77
offset of −10.88‰
Dolomite 2
Malachite
Calcite 1
SDV
Dolomite 1
Siderite
Calcite 2
δ18Ocarb laser technique (‰)
δ18Ocarb acid technique (‰)
-10
-12
-14
-16
-18
-20
-22
-24
-16
-14
-12
-10
-8
-6
-4
-2
0

$\delta^{18}O$


R²=0.986
Slope=0.77
offset of −10.88‰
Dolomite 2
Malachite
Calcite 1
SDV
Dolomite 1
CaO – CO2
H3PO4 – CO2
Siderite
Calcite 2
δ18Ocarb laser technique (‰)
δ18Ocarb acid technique (‰)
-10
-12
-14
-16
-18
-20
-22
-24
-16
-14
-12
-10
-8
-6
-4
-2
0

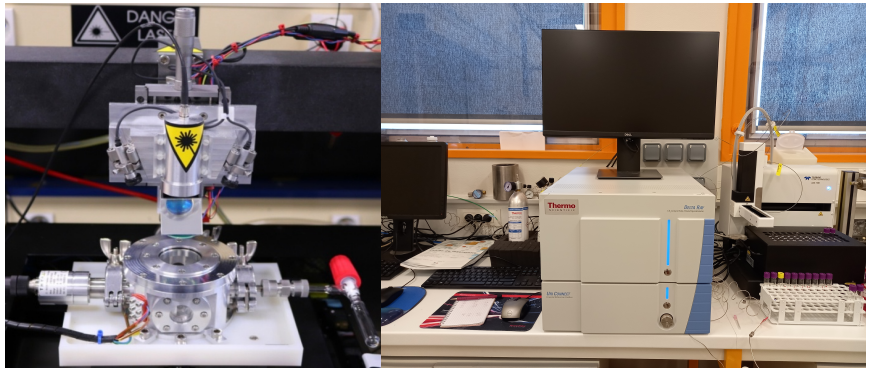


Isotopic differences between laser and classical technique

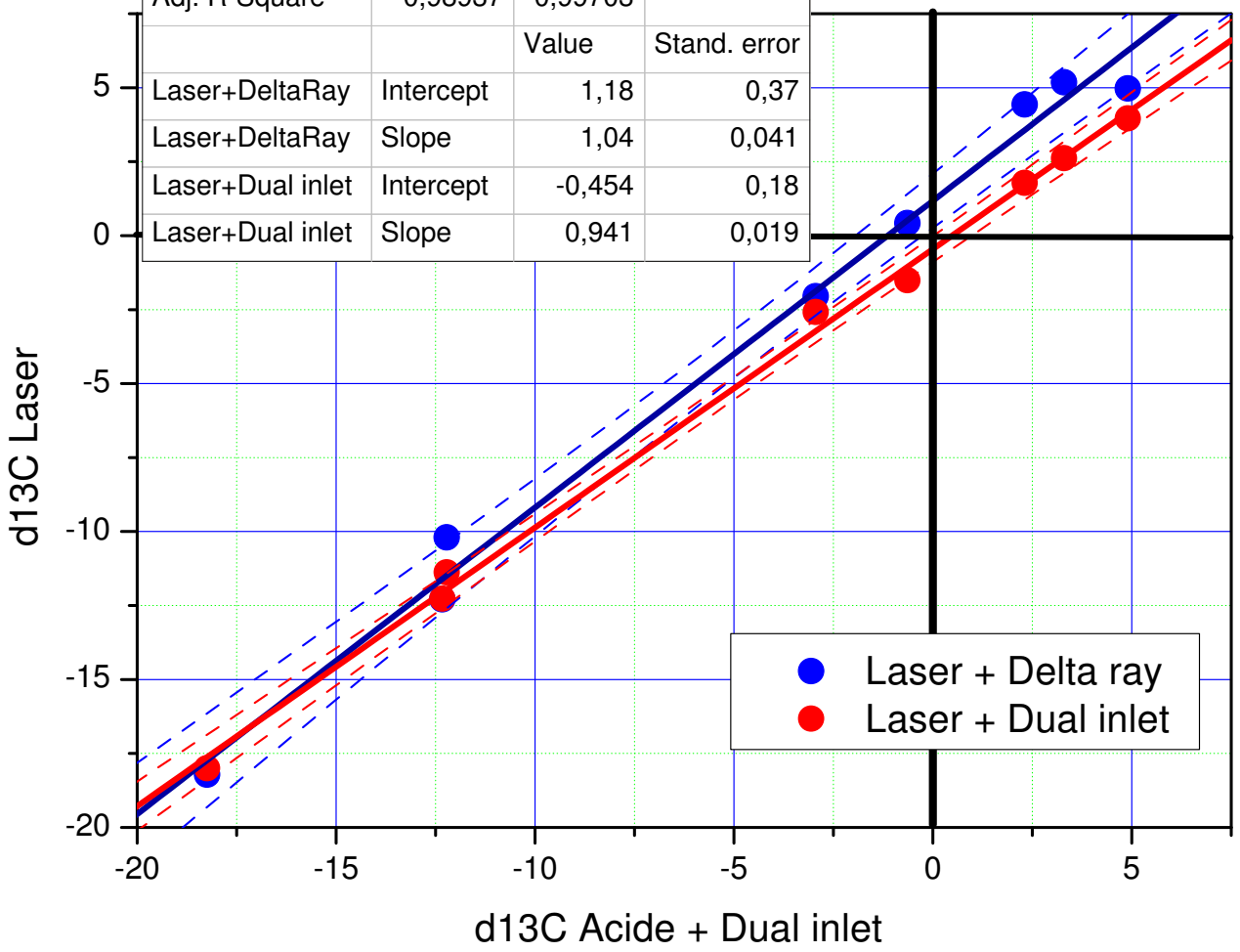
$\delta^{13}C$ = 0.17 ± 0.67‰
$\delta^{18}O$ = 9.38 ± 1.12 ‰

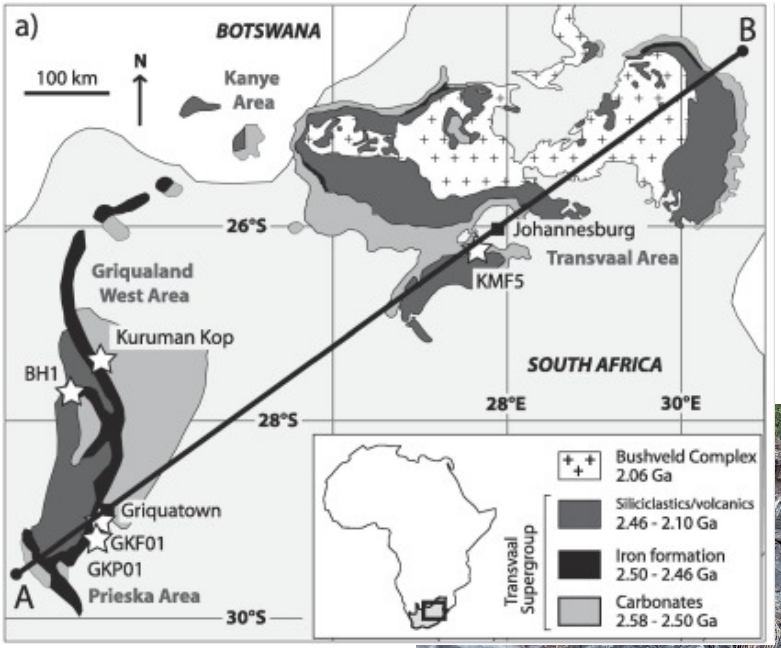
Reproducibility comparison between wet chem-IRMS and Laser-IRMS

	Number of microdrilling analyses	$\delta^{13}C$ ‰ VPDB	Standard deviation (1σ)	$\delta^{18}O$ ‰ VPDB	Standard deviation (1σ)	Number of laser calcination repeats	$\delta^{13}C$ ‰ VPDB	Standard deviation (1s)	$\delta^{18}O$ ‰ VPDB	Standard deviation (1σ)
Dolomite 2	13	3.30	0.05	-1.74	0.16	2	2.62	0.61	-12.34	1.19
Sidérite	9	-12.22	0.14	-14.57	0.27	2	-11.38	0.21	-22.29	0.20
Malachite	13	-18.24	0.66	-3.30	0.23	3	-18.00	0.27	-13.76	1.40



Equation	y = a + b*x		
Adj. R-Square	0,98937	0,99703	
		Value	Stand. error
Laser+DeltaRay	Intercept	1,18	0,37
Laser+DeltaRay	Slope	1,04	0,041
Laser+Dual inlet	Intercept	-0,454	0,18
Laser+Dual inlet	Slope	0,941	0,019





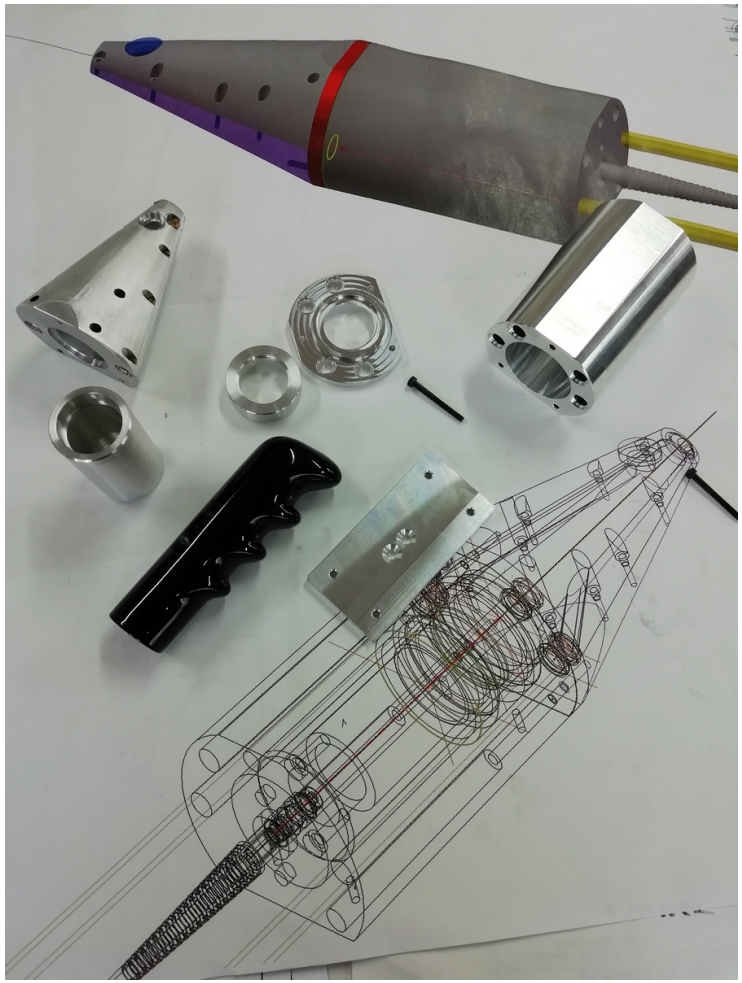
$\delta^{13}C$ ‰ VPDB	Standard deviation (1s)	$\delta^{18}O$ ‰ VPDB	Standard deviation (1σ)	**number of analyses**
-0,49	0,07	-14,74	0,12	**24**

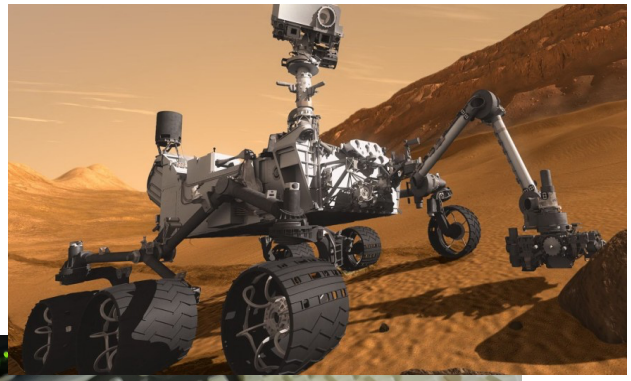
Conclusions

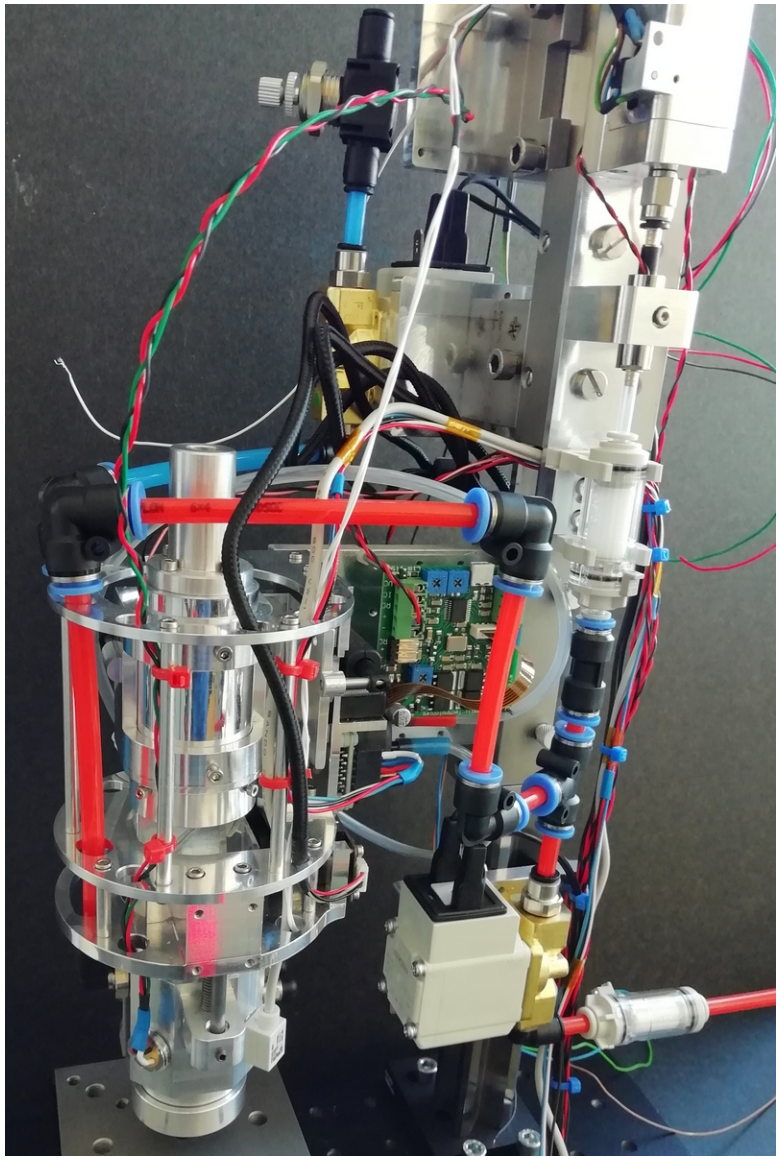
1/ Punctual analyses system coupled to CRDS/IRS?

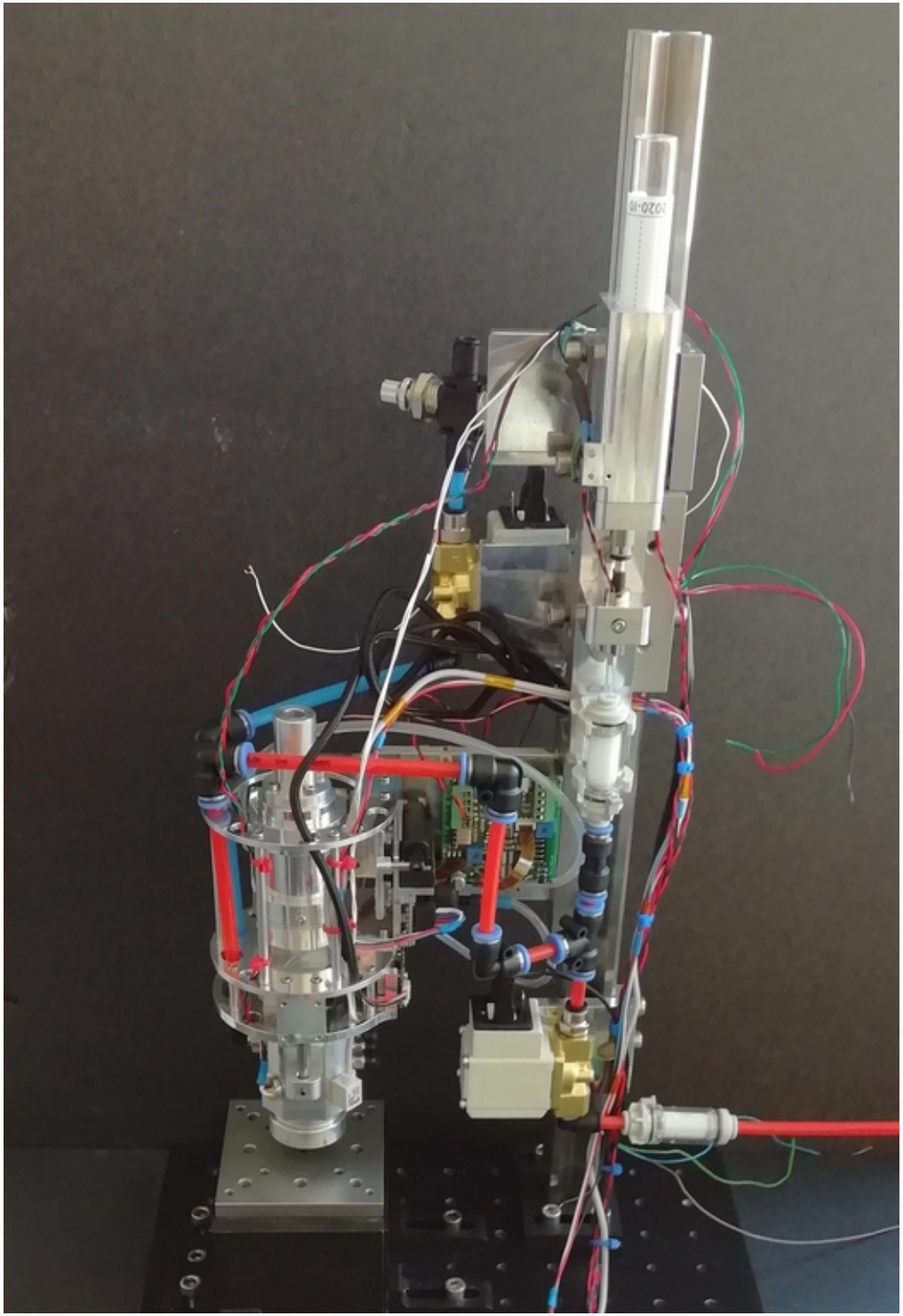
2/ Field deployable?

WORK IN PROGRESS









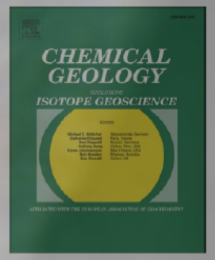
Thanks for your attention!

Chemical Geology 578 (2021) 120323

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo



Invited Research Article

In situ carbon and oxygen isotopes measurements in carbonates by fiber coupled laser diode-induced calcination: A step towards field isotopic characterization

Christophe Thomazo [a,b,*], Pierre Sansjofre [c], Olivier Musset [d], Theophile Cocquerez [a], Stefan Lalonde [e]