Elemental and Sr Isotope Investigations of Human Tooth Enamel by Laser Ablation-(MC)-ICP-MS: Successes and Pitfalls & Anthropological Applications

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Sr isotope investigations

- Tracing magma/mantle processes
- Tracing ancient civilization migrations in sites of Archaeological interest
- Hydrothermal activity/diagenetic processes
- Groundwater research

Radioactive Decay - The Basic Equations

Total number of daughter atoms in system undergoing decay is:

$$D = D_o + D^*$$

where D = total; D_o = original; D^* = number produced by decay

As $D^* = N\,(e^{\lambda t} - 1)$, then:

$$\boldsymbol{D = D_o + N\,(e^{\lambda t} - 1)}$$

$\boldsymbol{\lambda}$ = decay constant
t = age of rock, mineral

Basic equation for age determination of rocks & minerals.

Radioactive Decay - The Basic Equations

Writing decay equation using a ‘real” example, such as the decay of ^{87}Rb to ^{87}Sr:

$$^{87}Sr = {}^{87}Sr_o + {}^{87}Rb\ (e^{\lambda t} - 1)$$

However:

Much easier and more meaningful to measure the **ratio of two isotopes** rather than the **absolute abundance of one (using a MC-ICP-MS instrument)**.

Radioactive Decay - The Basic Equations

Therefore, ^{87}Sr is normalized to a non-radiogenic isotope, i.e. ^{86}Sr.

Thus, the useful form of the decay equation is:

$$\frac{^{87}Sr}{^{86}Sr} = \left(\frac{^{87}Sr}{^{86}Sr}\right)_{Initial} + \frac{^{87}Rb}{^{86}Sr}(e^{\lambda t} - 1)$$

BACKGROUND

- Water/sediments/rocks contain elements that have ***radiogenic isotopes*** that formed by the decay of their long-lived radioactive parent nuclides in the rocks of the continental crust.

- Thus, the ***isotopic composition*** of these elements (e.g., Sr) in water and soils depend on the **age** and **parent-daughter ratios** of the bedrock exposed to weathering in the drainage basins of the continents.

Sr isotope compositions – ***Soils/ SurfaceWater/ Upper crust***

- Depends upon:
  - the **$^{87}Sr/^{86}Sr$ ratios** and **Sr concentrations** of each rock type present in drainage basin;
  - the area of surface exposure of the different rock types;
  - the susceptibility to chemical weathering of the minerals contained within the rocks;
  - mixing of water derived from different rock types within streams entering the basin

$^{87}Sr/^{86}Sr$ compositions - **Advantages**

- Unlike chemical compositions, Sr isotope ratios are ***NOT*** fractionated/varied by:
  - Changes in temperature, pH, etc;
  - Biological activity
  - However, Sr isotopes can monitor effectively ***mixing*** between different components

Sr isotope compositions – ***terrestrial reservoirs***

$^{87}Sr/^{86}Sr$ isotope compositions of:

- Present-day MORB (**M**id-**O**cean **R**idge **B**asalt) = **0.7020 – 0.7025**
- Old (>2.7 billion year-old) granite = >**0.7200**
- **Present-day seawater** has a $^{87}Sr/^{86}Sr$ value of **0.7092**

$^{87}Sr/^{86}Sr$ compositions – Analytical Considerations

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CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

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Measuring $^{87}Sr/^{86}Sr$ variations in minerals and groundmass from basalts using LA-MC-ICPMS

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Outline

- Ramos et al. (2004) undertook a thorough evaluation of potential elemental and molecular interferences including Ca dimers and Ca argides, Fe dioxides, Ga and Zn oxides, doubly charged REEs and Hf, and singly charged Kr and Rb.
- Critical interferences include Kr, Rb, and doubly charged Er and Yb ions, while molecular species have only a limited impact on Sr isotope ratios.
- Demonstrate the accuracy with analyzed minerals, including marine carbonate, plagioclase, and clinopyroxene, which offer differing concentrations of interfering elements.
- Address potential complications and pitfalls associated with the technique and LA-MC-ICPMS in general.

Collector Configuration – Ramos et al. (2004)

Table 3
Collector block configuration of the ThermoFinnigan Neptune™ MC-ICPMS used for both solution and LA-MC-ICPMS Sr isotope analysis

Collector	L4	L3	L2	L1	C	H1	H2	H3	H4
Mass	83	83.5	84	85	85.5	86	86.5	87	88
Isotope of interest	$^{83}Kr_{11.5\%}$	$^{167}Er^{2+}$	$^{84}Sr_{0.56\%}$	$^{85}Rb_{72.2\%}$	$^{171}Yb^{2+}$	$^{86}Sr_{9.86\%}$	$^{173}Yb^{2+}$	$^{87}Sr_{7.00\%}$	$^{88}Sr_{82.6\%}$
Isobaric interferences			$^{84}Kr_{57.0\%}$			$^{86}Kr_{17.3\%}$		$^{87}Rb_{27.8\%}$	
Er^{2+}	$^{166}Er^{2+}$		$^{168}Er^{2+}$	$^{170}Er^{2+}$					
Yb^{2+}			$^{168}Yb^{2+}$	$^{170}Yb^{2+}$		$^{172}Yb^{2+}$		$^{174}Yb^{2+}$	$^{176}Yb^{2+}$

Monitored species and interferences affecting the Sr masses are also illustrated along with natural abundances for Sr, Rb and Kr.

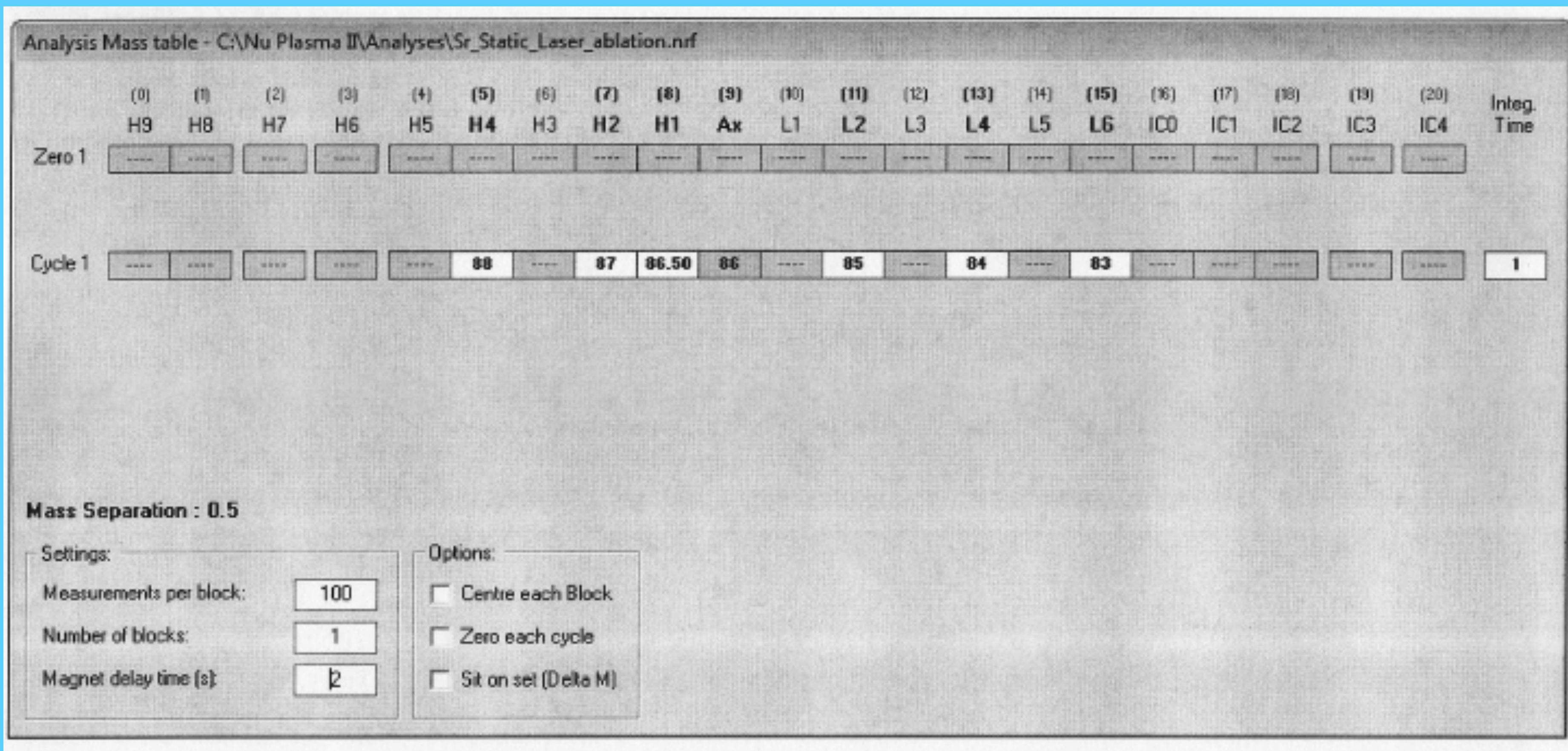
Collector Configuration – Paton et al. (2007)

Table 3.
Nu Plasma collector array, incorporating the distribution and magnitude of relevant elemental and molecular interferences (adapted from Ramos *et al.* 2004)

Collector	L3	L2	Axial	H2	H3	H4	H5
Mass	83	84	85	86	86.5	87	88
Double mass	166	168	170	172	173	174	176
Analyte isotopes	-	$Sr_{0.56\%}$	-	$Sr_{9.86\%}$	-	$Sr_{7.02\%}$	$Sr_{82.56\%}$
Singly-charged interferences	$Kr_{11.55\%}$	$Kr_{56.90\%}$	$Rb_{72.15\%}$	$Kr_{17.37\%}$	-	$Rb_{27.85\%}$	-
Doubly-charged interferences	$Er_{33.41\%}$	$Er_{27.07\%}$ $Yb_{0.14\%}$	$Er_{14.88\%}$ $Yb_{3.03\%}$	$Yb_{21.82\%}$	$Yb_{16.12\%}$	$Yb_{31.84\%}$	$Yb_{12.73\%}$
Molecular interferences[a]	$^{43}Ca^{40}Ar_{0.13\%}$	$^{44}Ca^{40}Ar_{2.13\%}$	-	$^{46}Ca^{40}Ar_{0.003\%}$	-	-	$^{48}Ca^{40}Ar_{0.179\%}$
	$^{43}Ca^{40}Ca$	$^{44}Ca^{40}Ca$	-	$^{46}Ca^{40}Ca$	-	-	$^{48}Ca^{40}Ca$

[a] Only molecules containing either ^{40}Ca or ^{40}Ar are considered of any influence, as such all other combinations are omitted. Percentages indicated are the combined abundances of Ca dimers and Ca argides.

Collector Configuration – *In-situ Sr*, University of Notre Dame



Methodology
(Ramos et al. 2004)

- UP213 nm laser ablation system coupled to Neptune MC-ICP-MS

- Employed rastering – troughs of 160 x 500 microns, or 80 x 500 microns (using a 80 micron spot size)

- Depth of penetration ~ 70 to 130 microns

- He gas was flushed into laser ablation cell at a rate of ~0.90 L/min

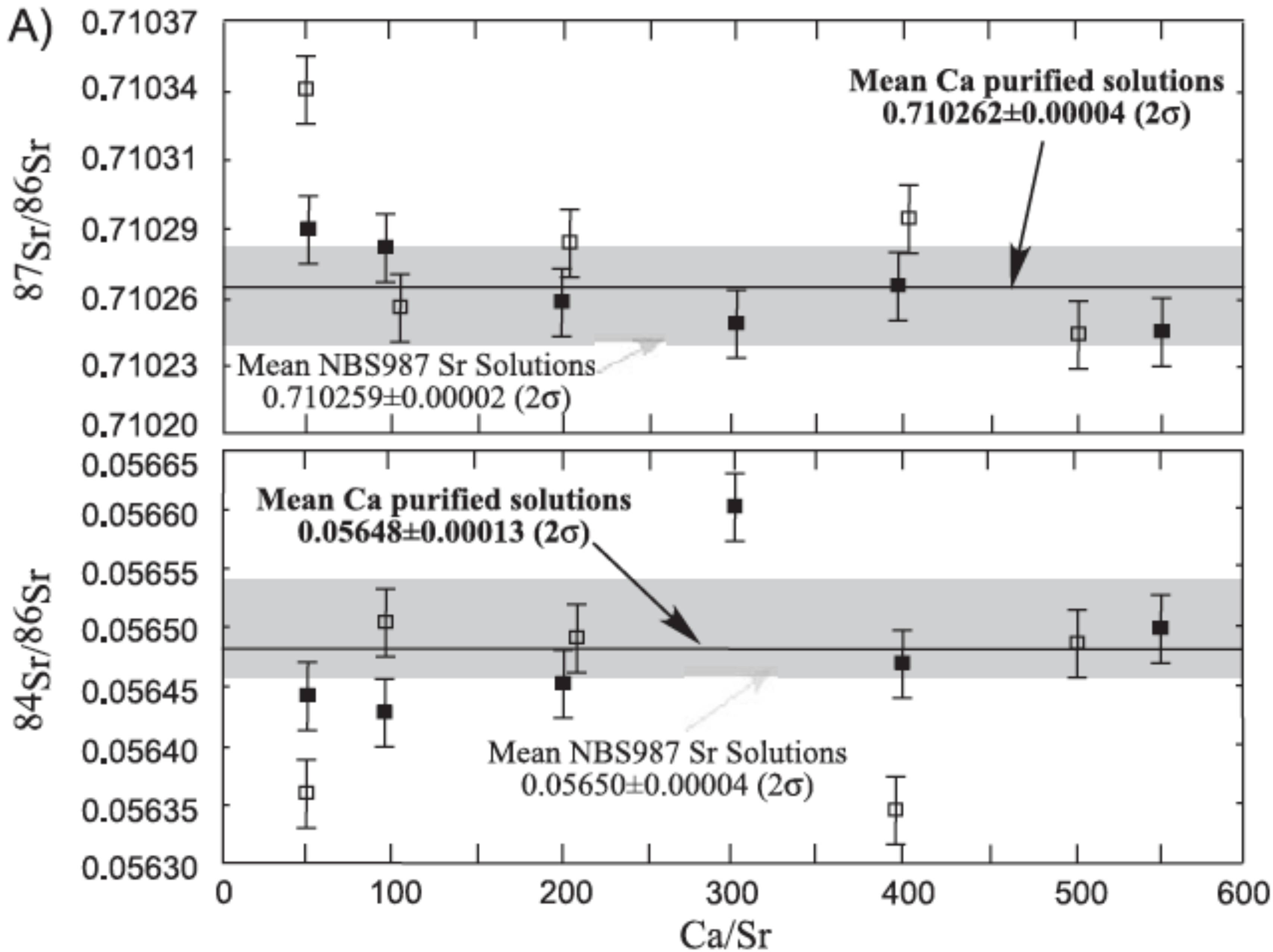
Methodology
(Ramos et al. 2004)

- Sample (Ar) gas flow rate was ~0.7 L/min
- ^{88}Sr ion signal – minimum value of ~1.0 volt
- Generate precision of <0.00005 – standard error 2 sigma level on the $^{87}Sr/^{86}Sr$ ratio
- Baseline measurements were conducted “on-peak” for 180 seconds

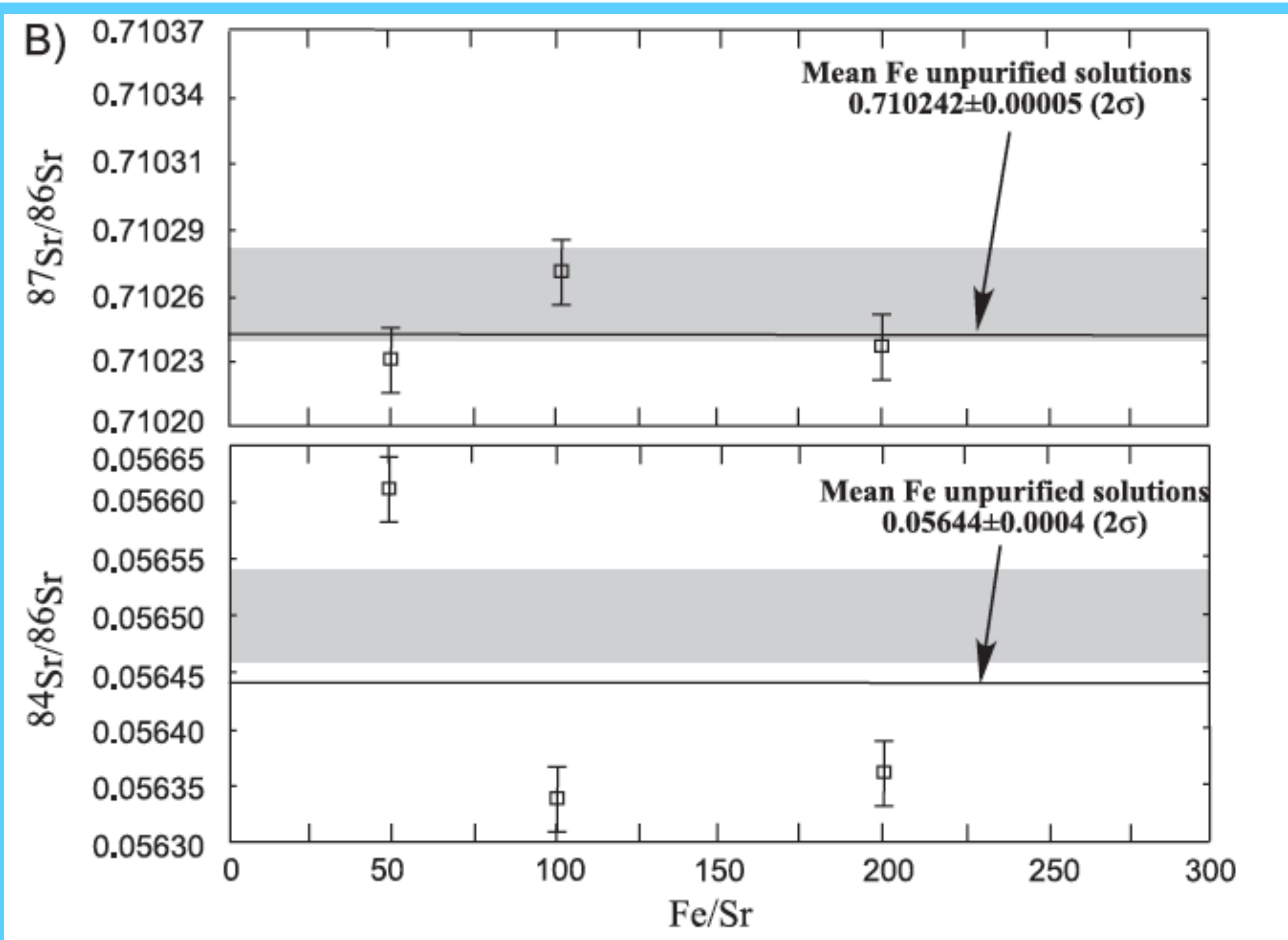
Interferences

- **Ca dimers (e.g., $^{44}Ca^{43}Ca^+$)** have been shown to interfere with Sr isotope masses during secondary ionization mass spectrometry (SIMS) measurements of carbonate and aragonite (Weber et al., 2004).

- Waight et al. (2002) suggest that **Ca argides (e.g., $^{44}Ca^{40}Ar^+$)**, present as a result of Ca ionization in the argon plasma, also interfere with Sr isotope masses when analyzing materials characterized by high Ca/Sr ratios such as carbonate (~500) and plagioclase (~50–200).



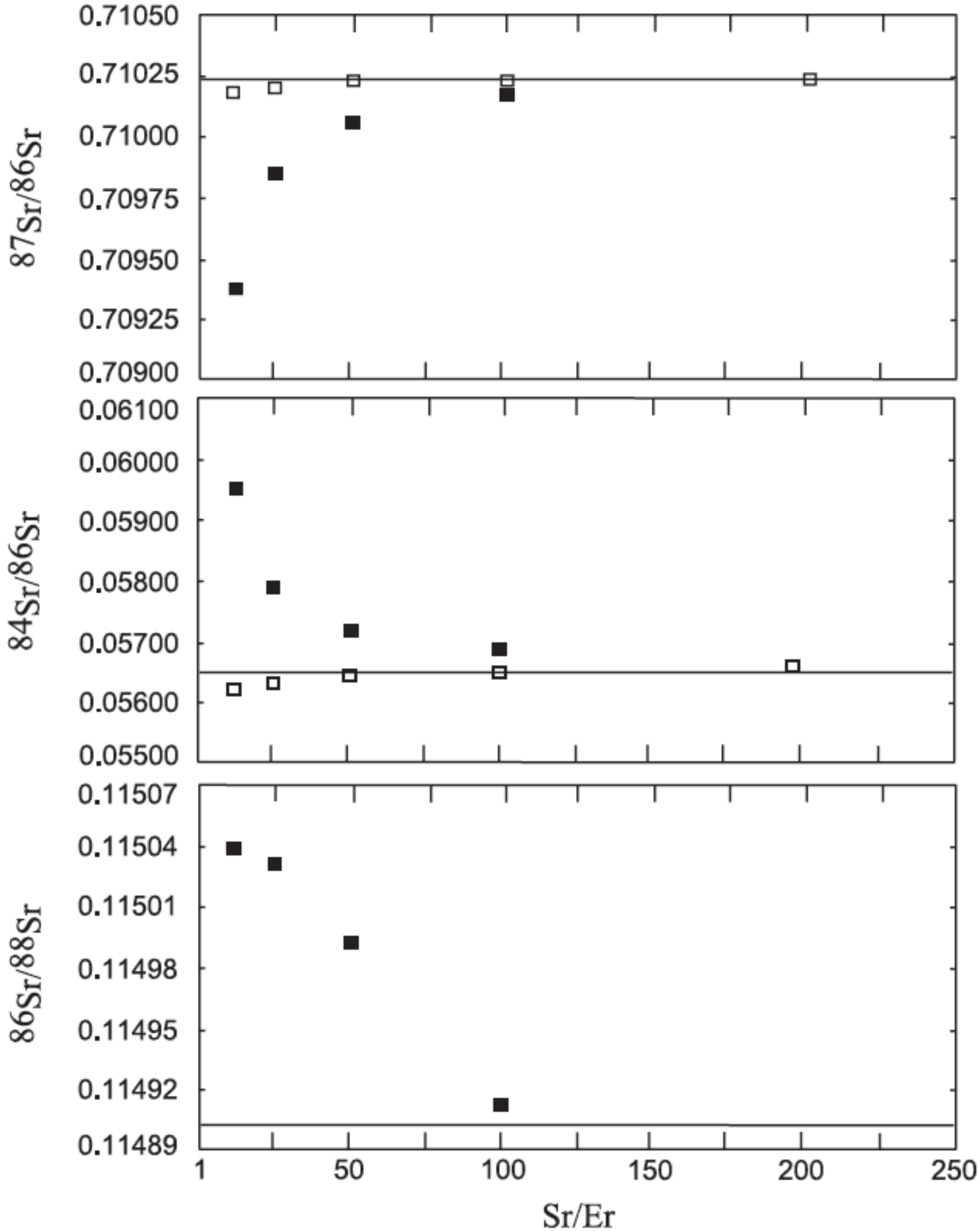
Ramos et al. (2004)



Ramos et al. (2004)

Interferences

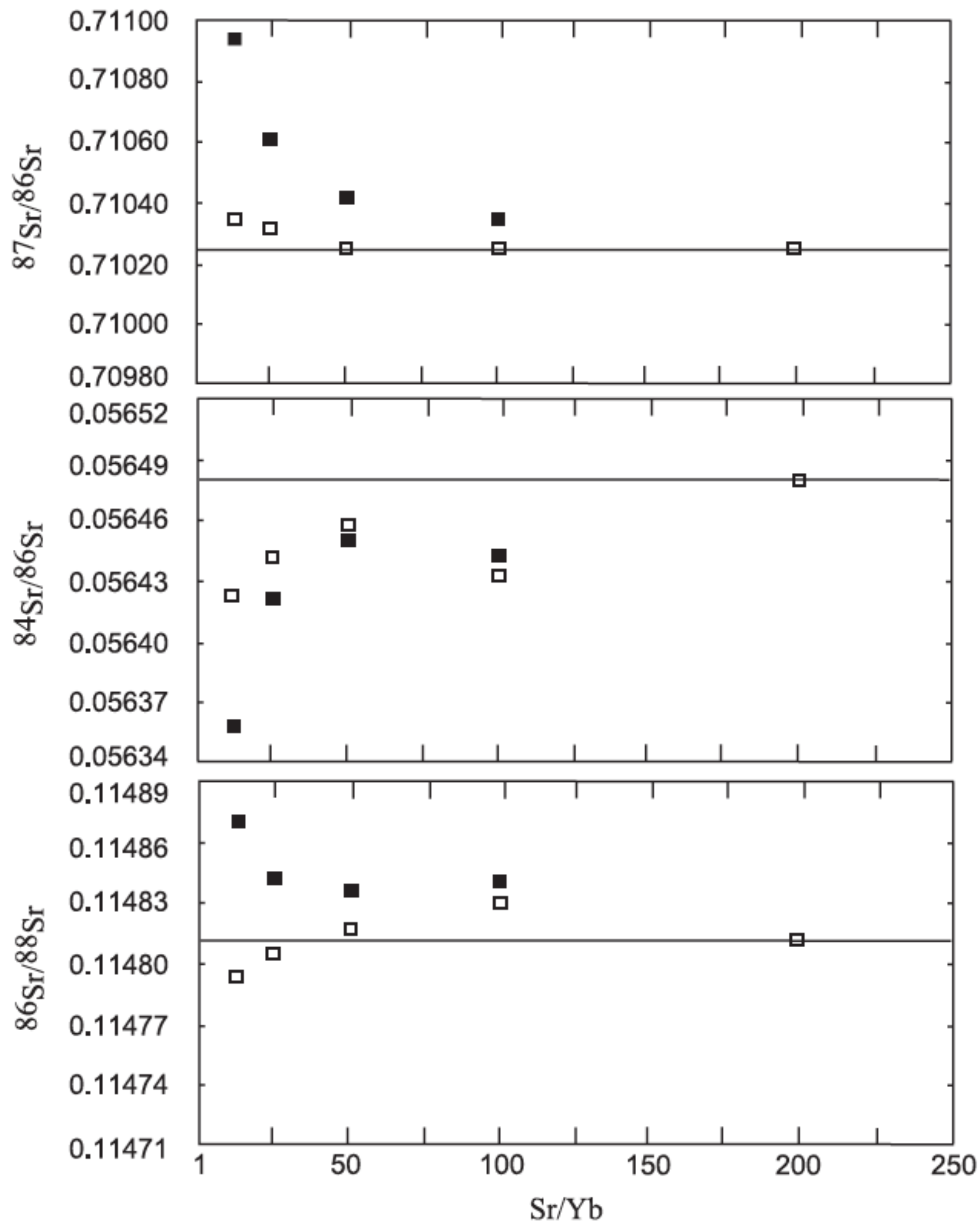
- **Erbium (Er):**
- Forms singly- (Er^{+}) and doubly-charged (Er^{2+}) ions in plasma; the latter are problematic since mass (m)/charge (z) of Er^{2+} ions overlaps that of Rb, Sr and Kr
- $^{168}Er^{2+}$ overlaps ^{84}Sr and $^{170}Er^{2+}$ overlaps ^{85}Rb



Ramos et al. (2004)

Interferences

- **Ytterbium (Yb):**



Ramos et al. (2004)

Anthropological Investigations

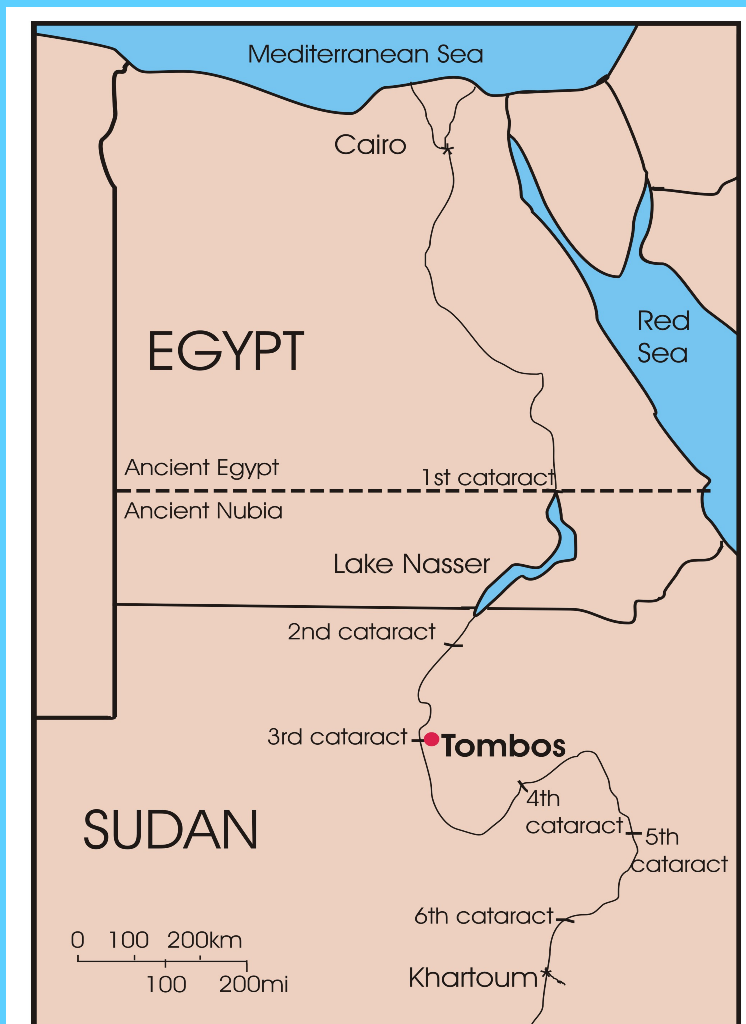
Sr isotope analysis of tooth enamel – why?

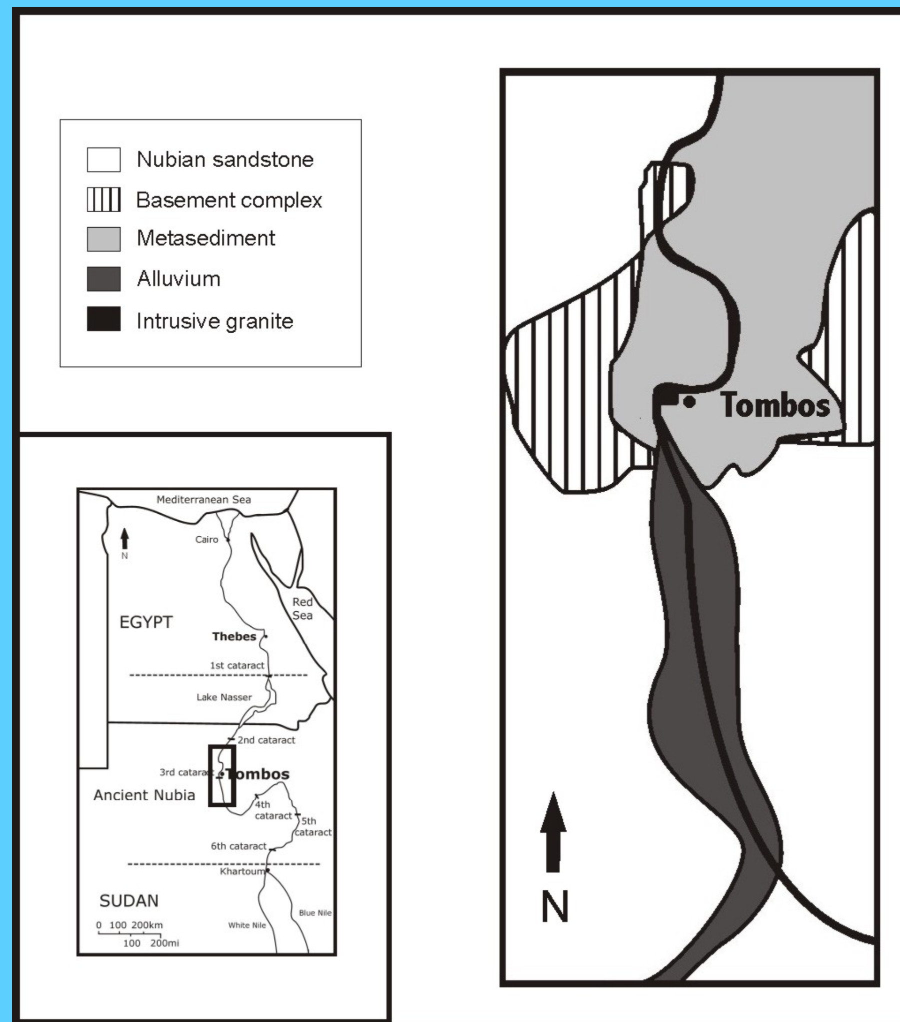
- Mature dental enamel is substantially denser and less porous than other skeletal tissues- stable and more resistant to structural and chemical change;

- Sr isotope ratios measured in dental enamel reflect various periods of life dependent on the tooth type sampled, ranging from the time in utero to approximately sixteen years of age;

- Sr incorporated is more likely an average of several months or years of strontium ingestion due to the long residence time in the body;

Study Area & Regional Geology





Buzon et al. (2007, *J. Archaeol. Sci.,* **34**:1391-1401)

Advantages of (MC)-ICP-MS instrumentation

- Typical Sr isotope analysis by TIMS (Thermal Ionization Mass Spectrometry) takes **~1.5 to 2 hours** to complete

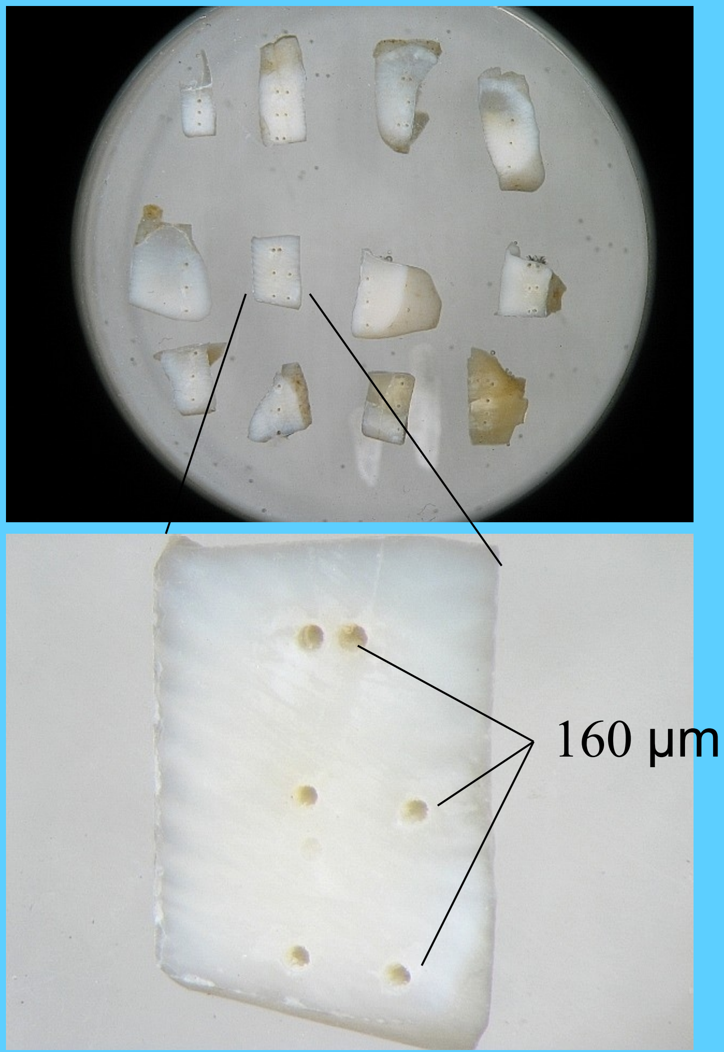
- Typical Sr isotope analysis by solution-mode MC-ICP-MS takes ~**15 minutes** (up to 8 times faster) with little (if any) detriment to the quality of the individual measurements

- Trace element analyses conducted either by solution- or laser ablation modes using a quadrupole ICP-MS instrument also consist of relatively rapid measurements (few minutes)

- Sr isotope measurements by LA-MC-ICP-MS are also extremely rapid (minutes); however are they **accurate**??

Analytical Methods
(details in Simonetti et al., 2008. *Archaeometry*)

- Quadrupole-ICP-MS (Perkin Elmer ELAN6000):
  - Trace element abundances via both solution mode & laser ablation analysis
- Multi-collector-ICP-MS (NuPlasma Instrument):
  - Sr isotope measurements via both solution mode & laser ablation analysis
- New Wave Research UP213 laser ablation system



Laser Ablation Trace Element Analysis – Brief Outline

- NIST SRM 612 international glass standard used for external calibration – with normalization of intensities to ^{43}Ca
- GLITTER® laser ablation software – data reduction, concentration determinations, detection limits, internal uncertainties
- Validation of elemental abundances verified with 'internal' standard – Durango Apatite
- Similar analytical protocol and internal standard as described by **Trotter & Eggins (2006, Chem. Geol.)**

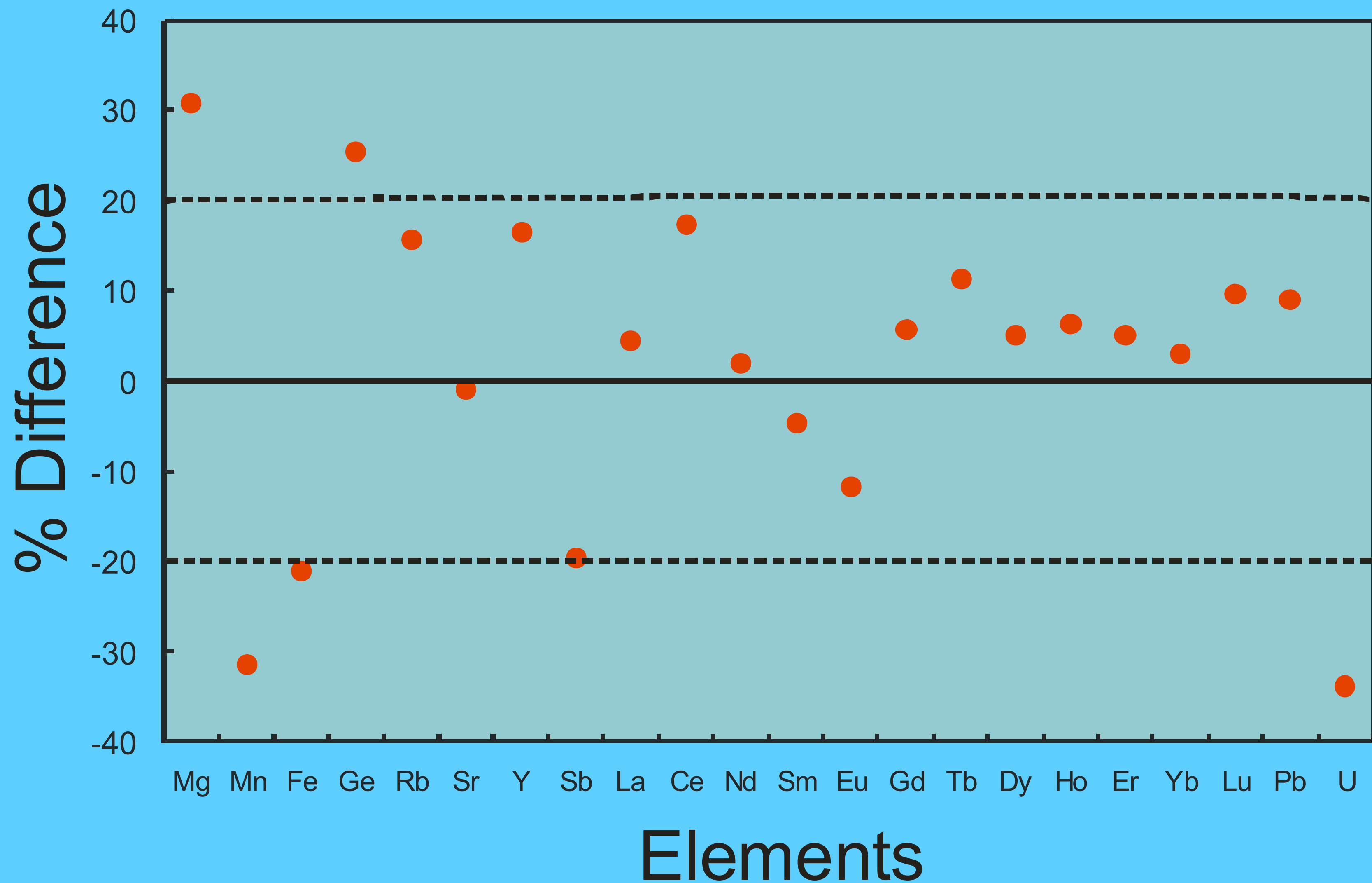
- Durango Apatite:

  $Ca_5(PO_4)_3(F, Cl, OH)$

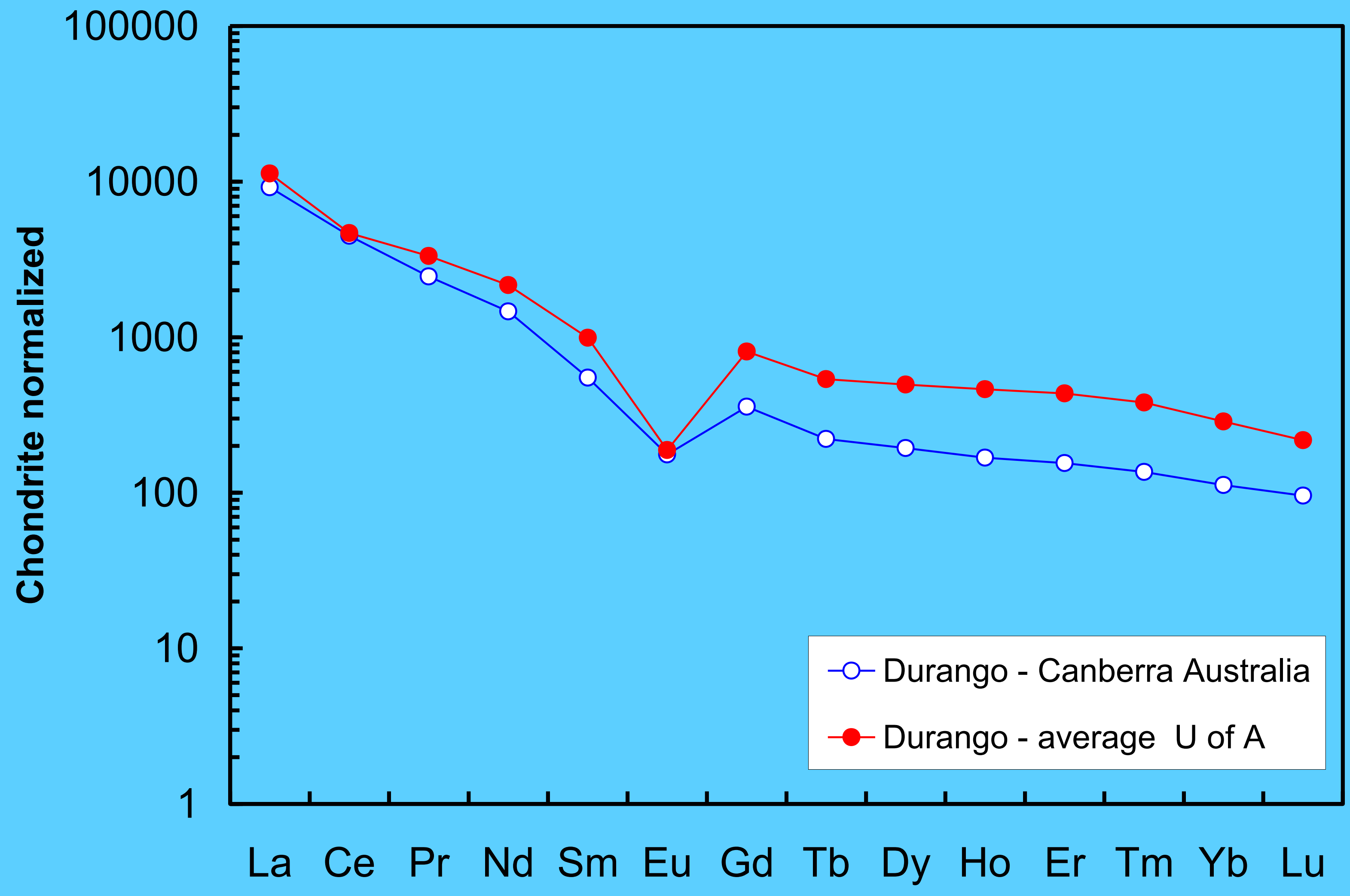
- Enamel - hydroxyapatite:

  $3Ca_3(PO_4)_2.CaX$; where $X = F, Cl, CO_2, OH$

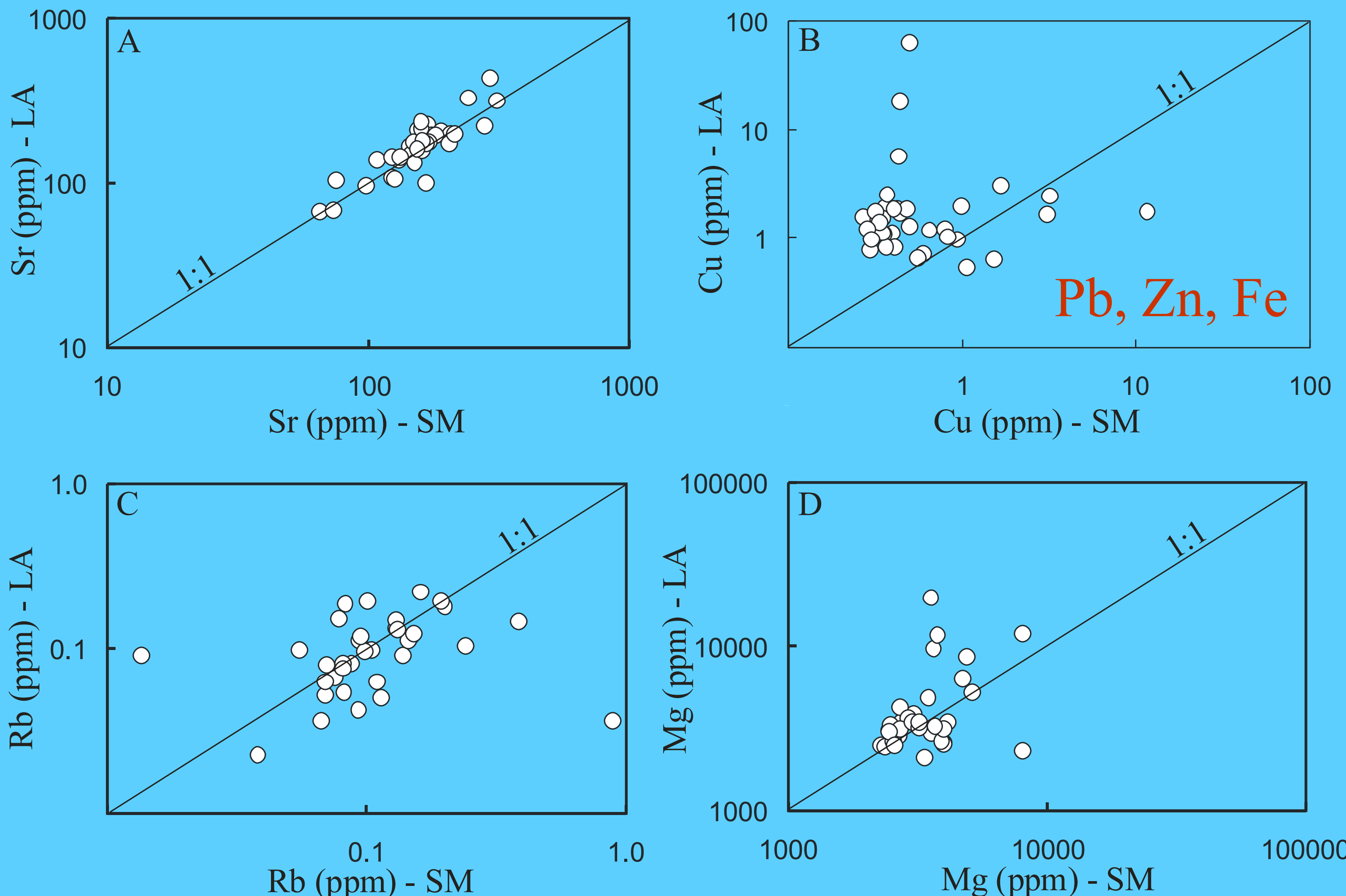
Comparison ***laser ablation*** vs. ***solution mode*** – Durango Apatite



Durango Apatite –
This study *vs*. Trotter & Eggins (2006)



Comparison trace element abundances – Laser ablation (LA) vs Solution Mode (SM) for enamel

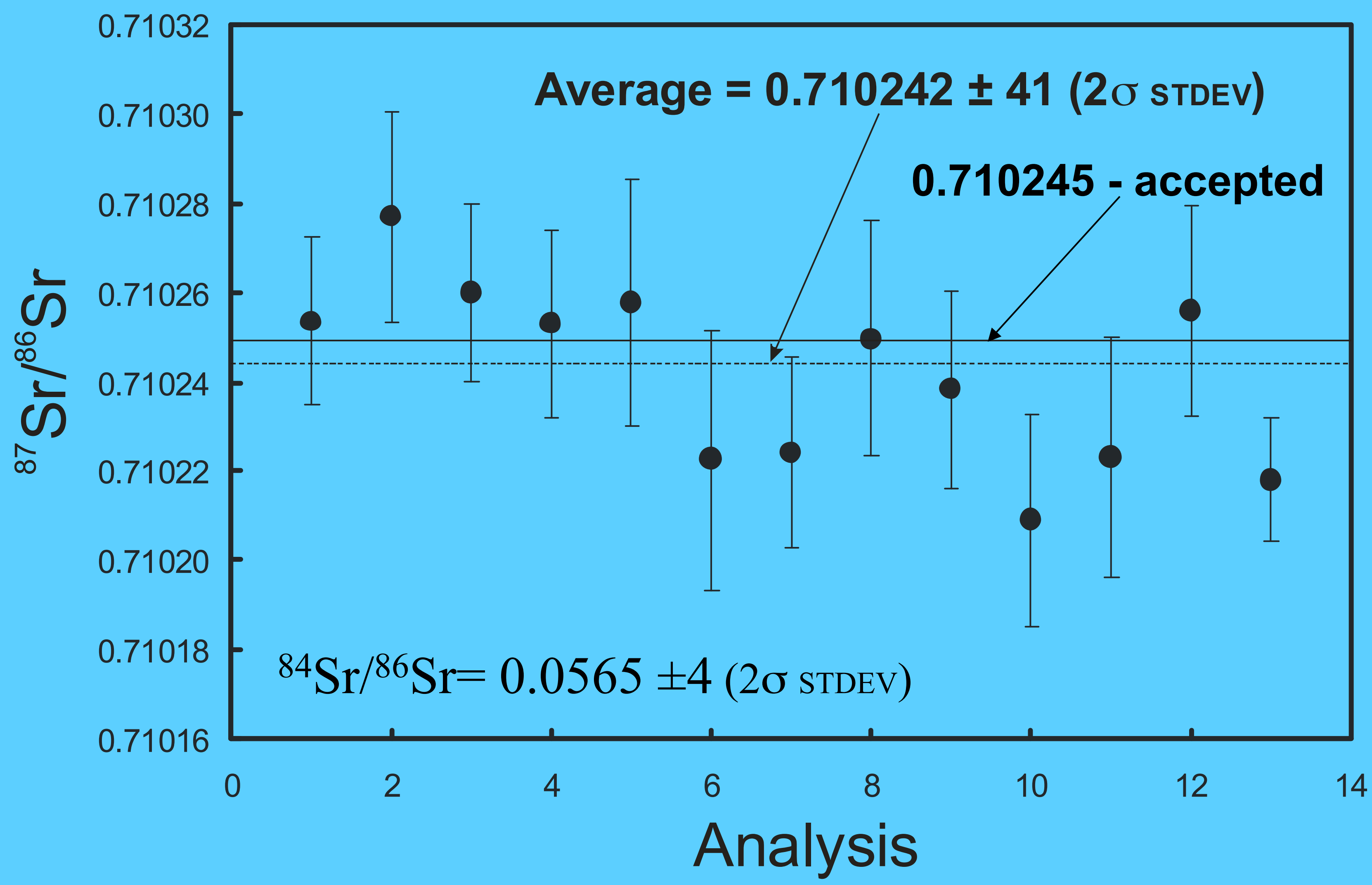


Simonetti et al. (2008)

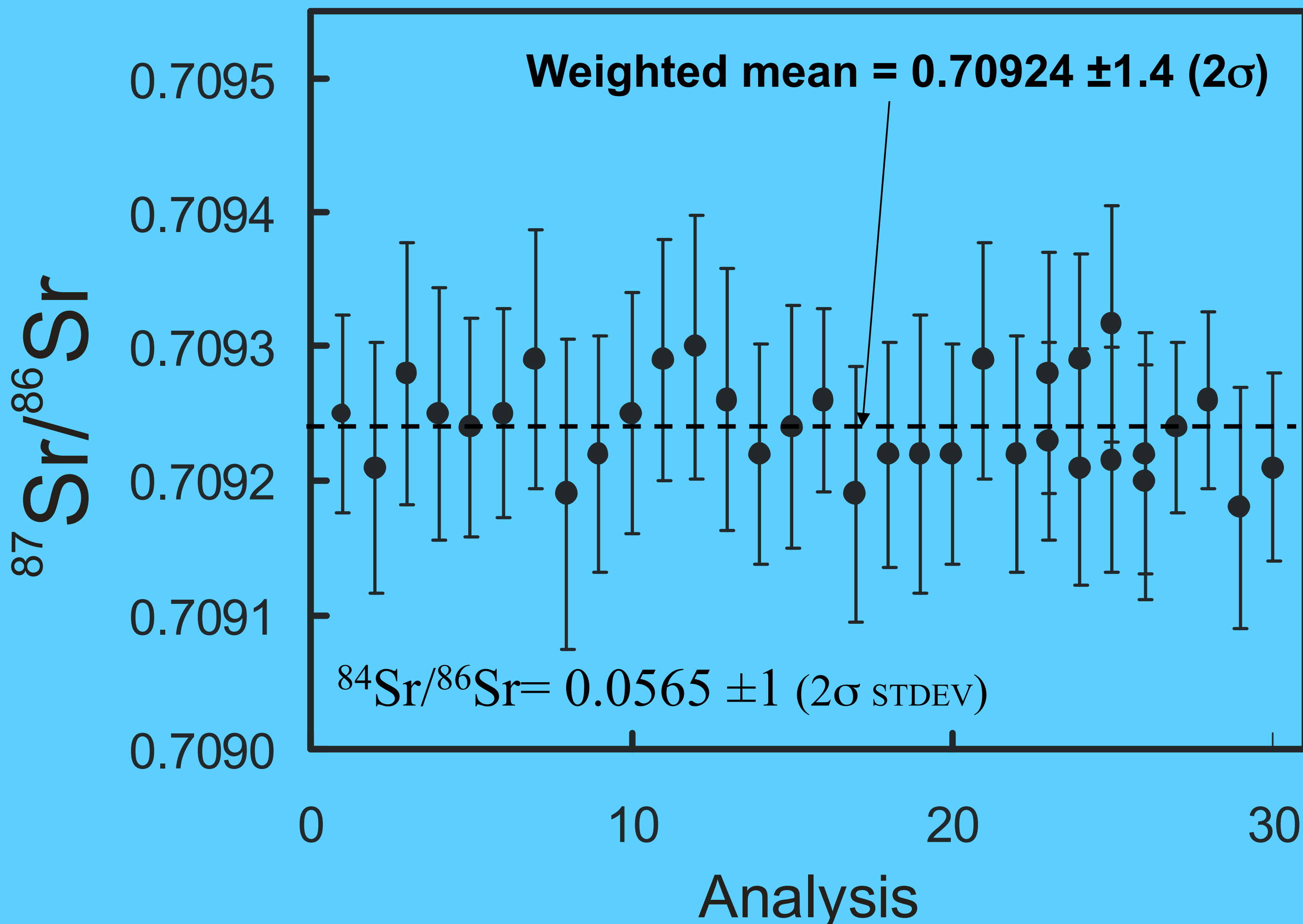
MC-ICP-MS Sr Isotope Analyses

- Monitor isobaric interferences: ^{84}Kr, ^{86}Kr, $^{85}Rb \rightarrow ^{87}Rb$, $^{40}Ar+(^{16}O)_3 \rightarrow ^{88}O$
- Monitor invariant $^{84}Sr/^{86}Sr$ values → 0.0565 in nature
  - Schmidberger et al. (2003, Chem. Geol.); Bizzarro et al. (2003, Geochem. Cosmochim. Acta)
- Laser spot size used was 160 microns

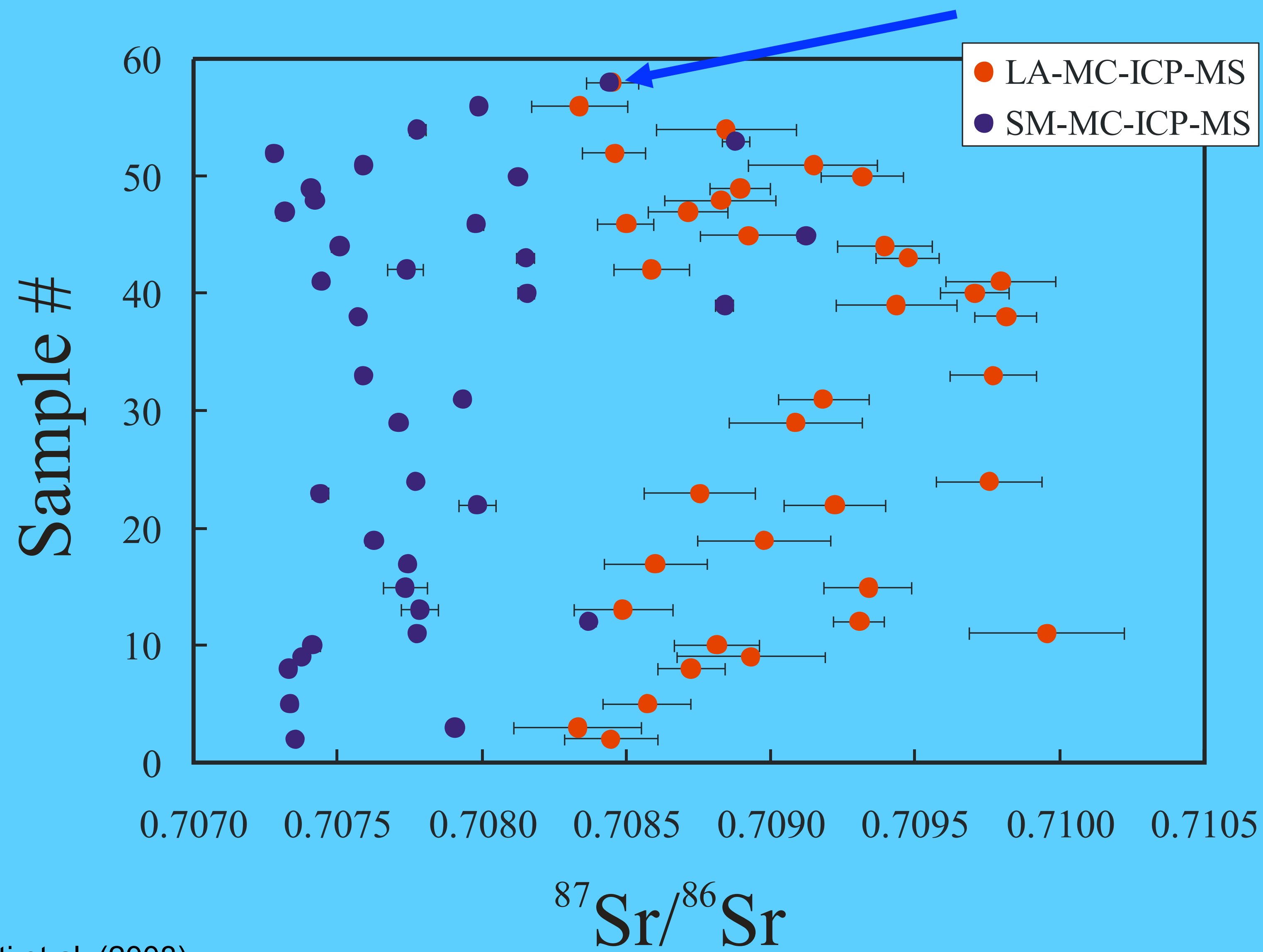
NIST SRM 987 Sr isotope standard solution-mode - 100 ppb solution



Laser ablation Sr isotope measurements – Modern-day Coral

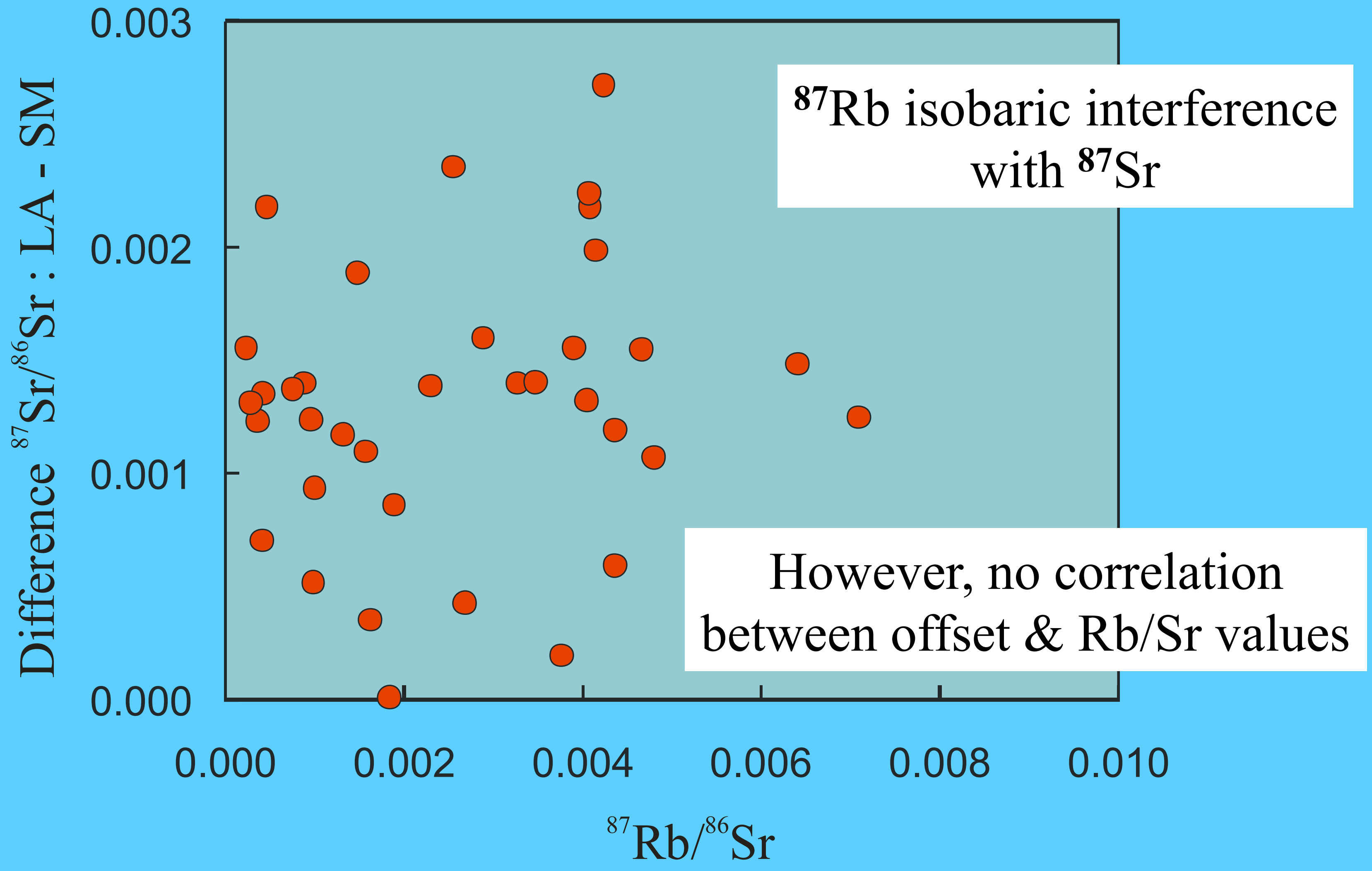


Comparison $^{87}Sr/^{86}Sr$ isotope values – LA- *vs* SM-MC-ICP-MS



Simonetti et al. (2008)

What is the cause of the offset? Rb?



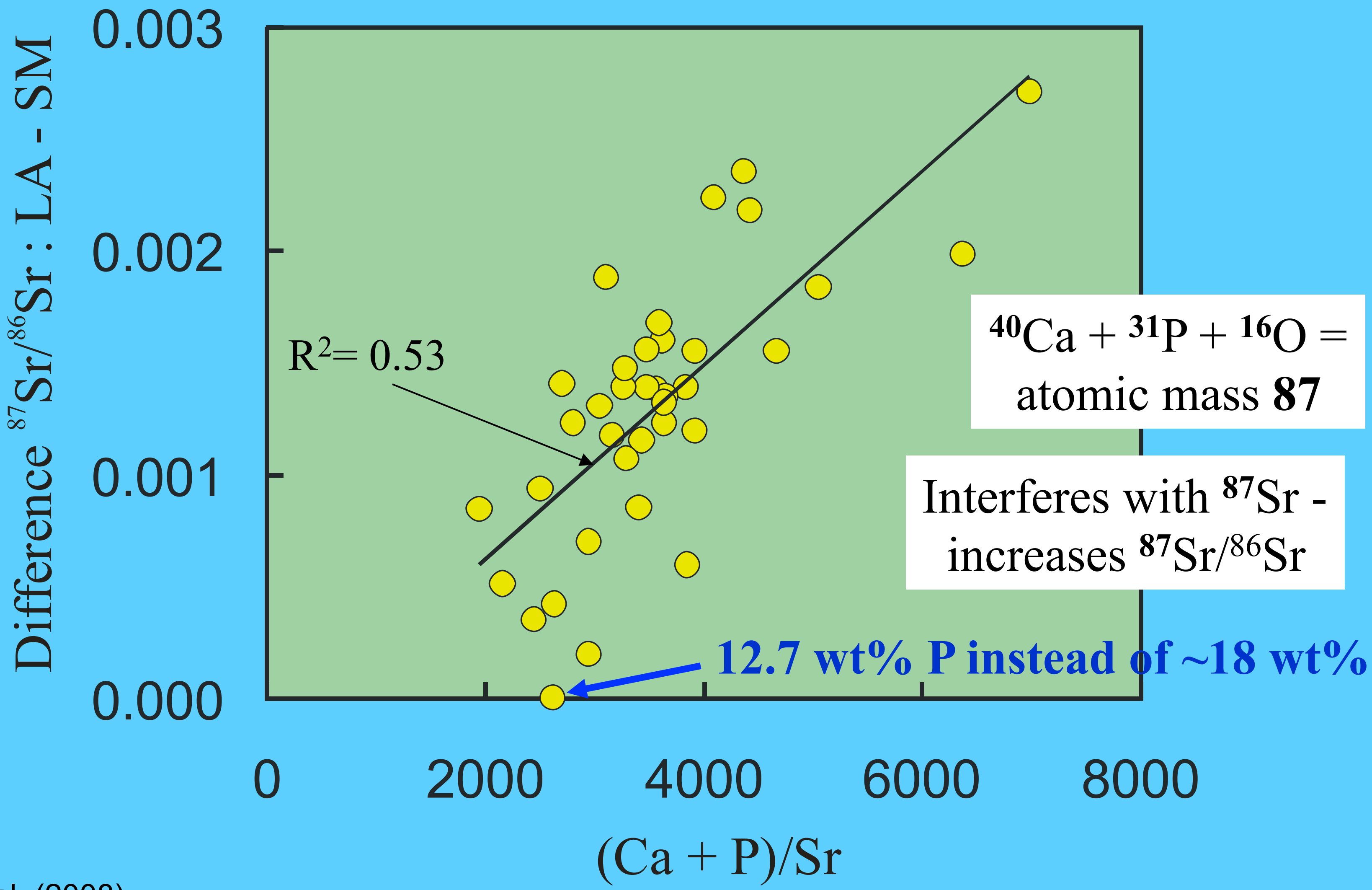
What is the cause of the offset?? REEs + Y?

- Solution mode-ICP-MS analysis of all of the enamel samples investigated in this study indicate extremely low concentrations of REEs and Y
- These extremely low concentrations were confirmed by subsequent laser ablation analyses (i.e. all below detection limit)

Average values (n= 37 samples)

	ppm
Y	0.02
La	0.008
Ce	0.012
Nd	0.007
Sm	<b.d.
Eu	0.002
Gd	0.003
Tb	0.002
Dy	0.001
Ho	0.0003
Er	0.001
Yb	0.0008
Lu	0.001

What is the cause of the offset?



Simonetti et al. (2008)

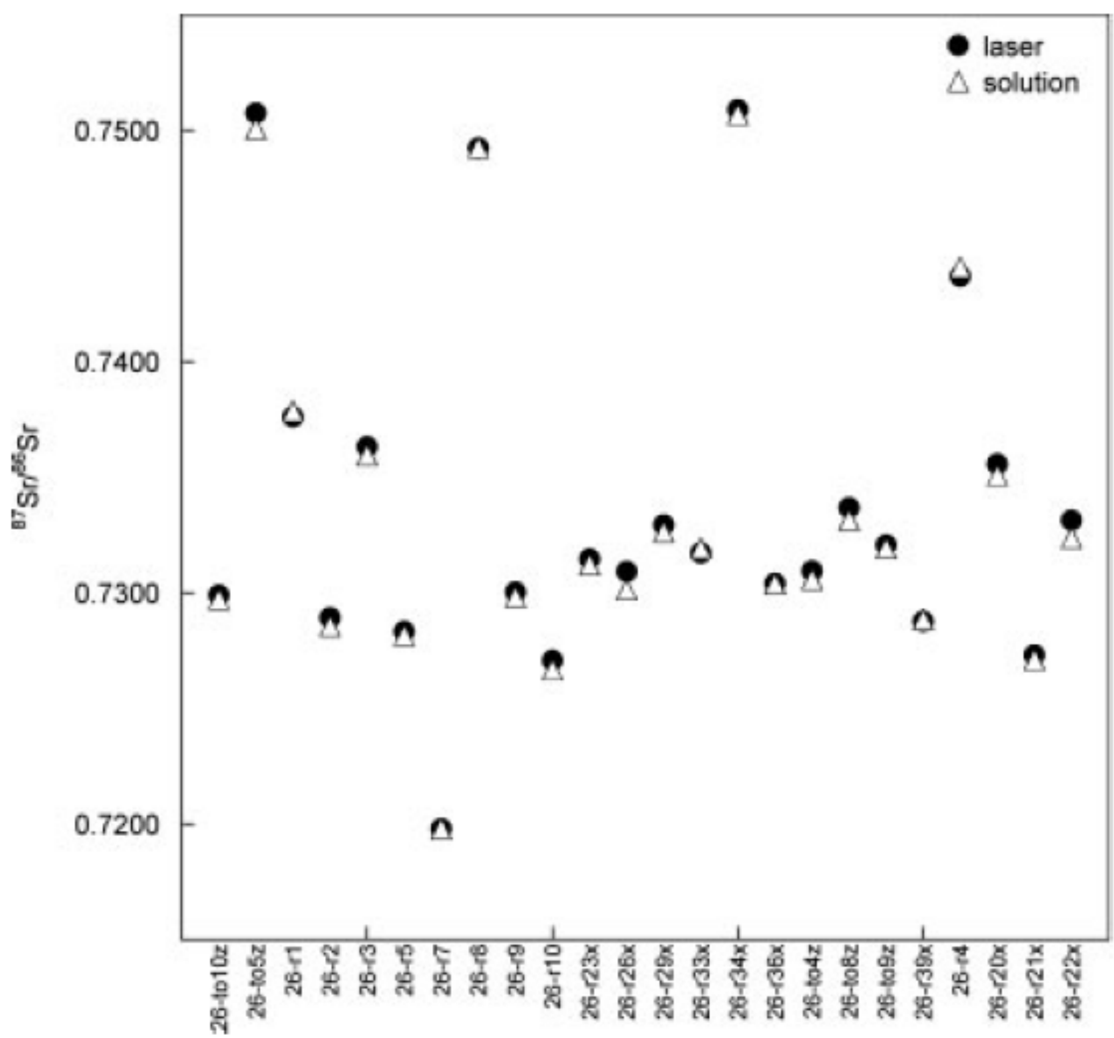
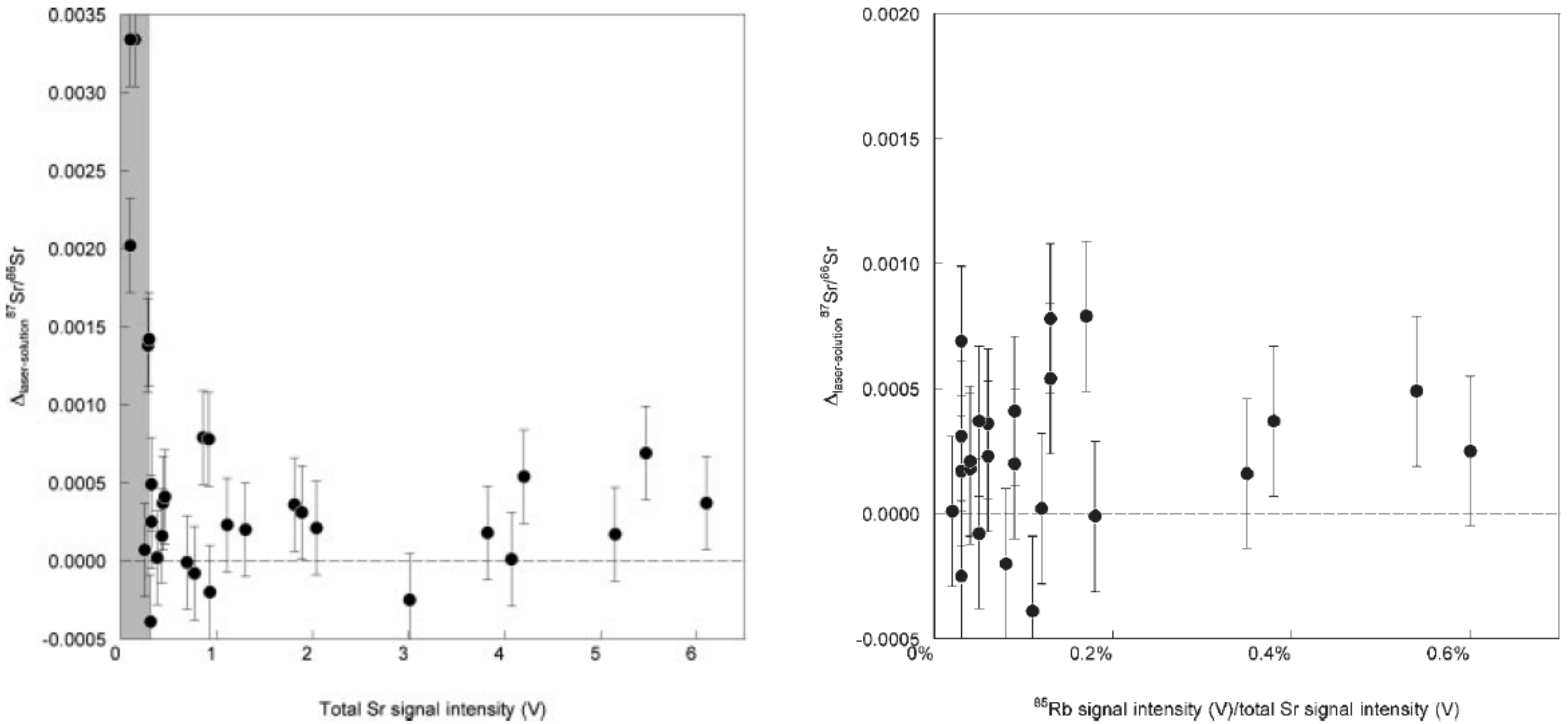
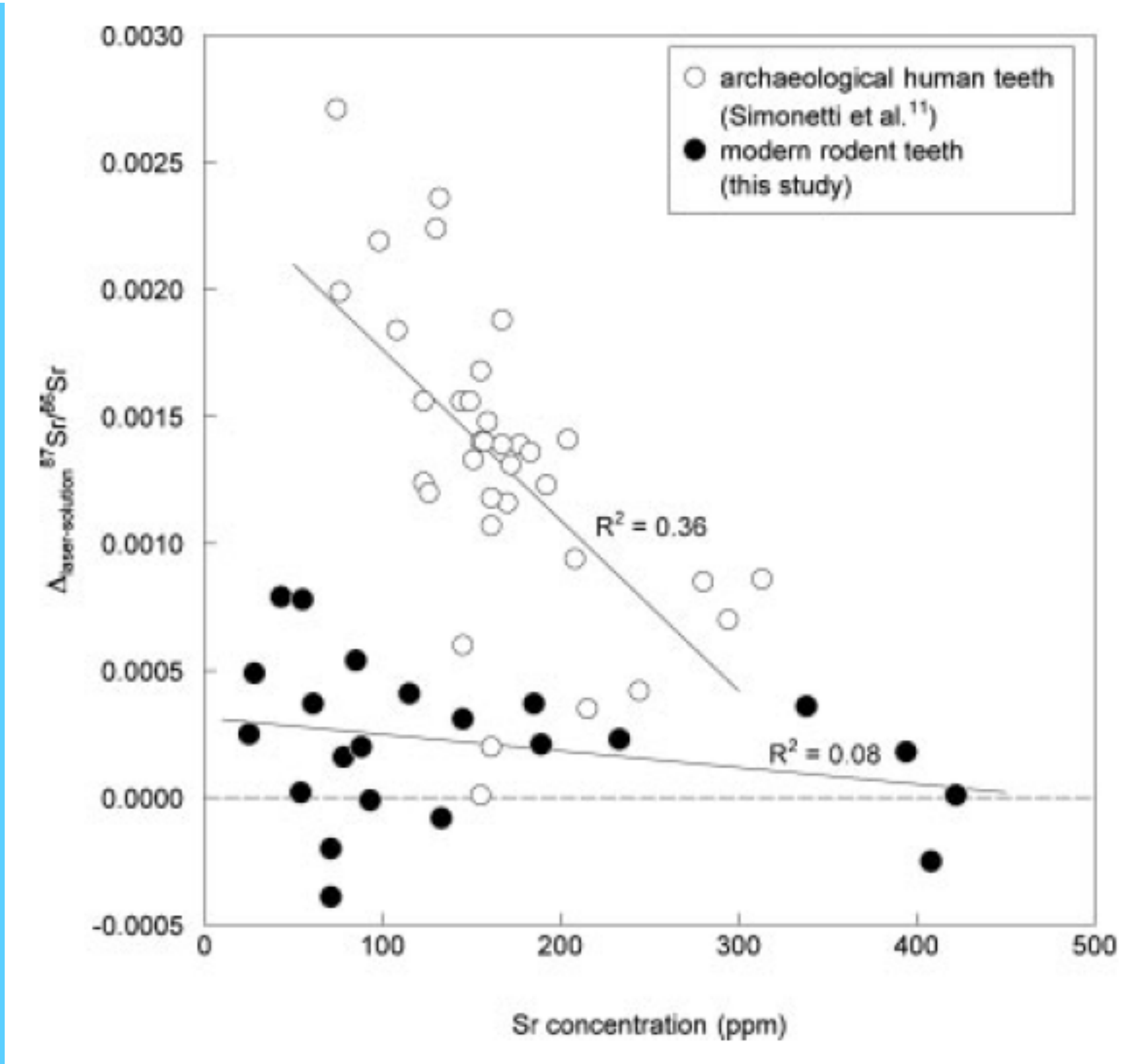


Figure 1. $^{87}Sr/^{86}Sr$ of modern rodent teeth from Gladysvale Cave, South Africa, measured by solution and laser ablation MC-ICP-MS. The external errors for the laser values (2σ, ±0.0003) and the solution values (<0.0001) are smaller than the symbols.

Copeland et al. (2008)

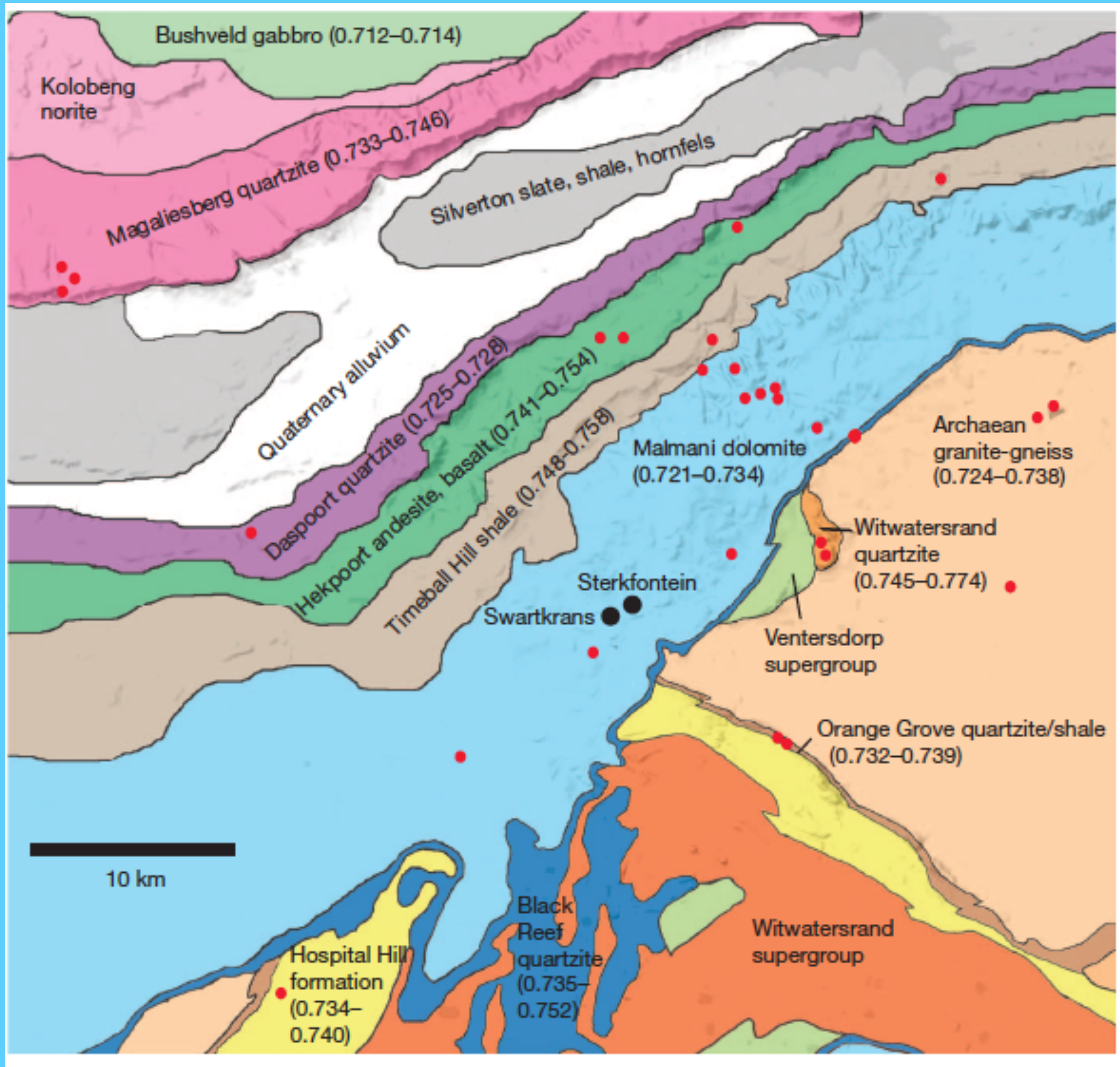


Copeland et al. (2008)

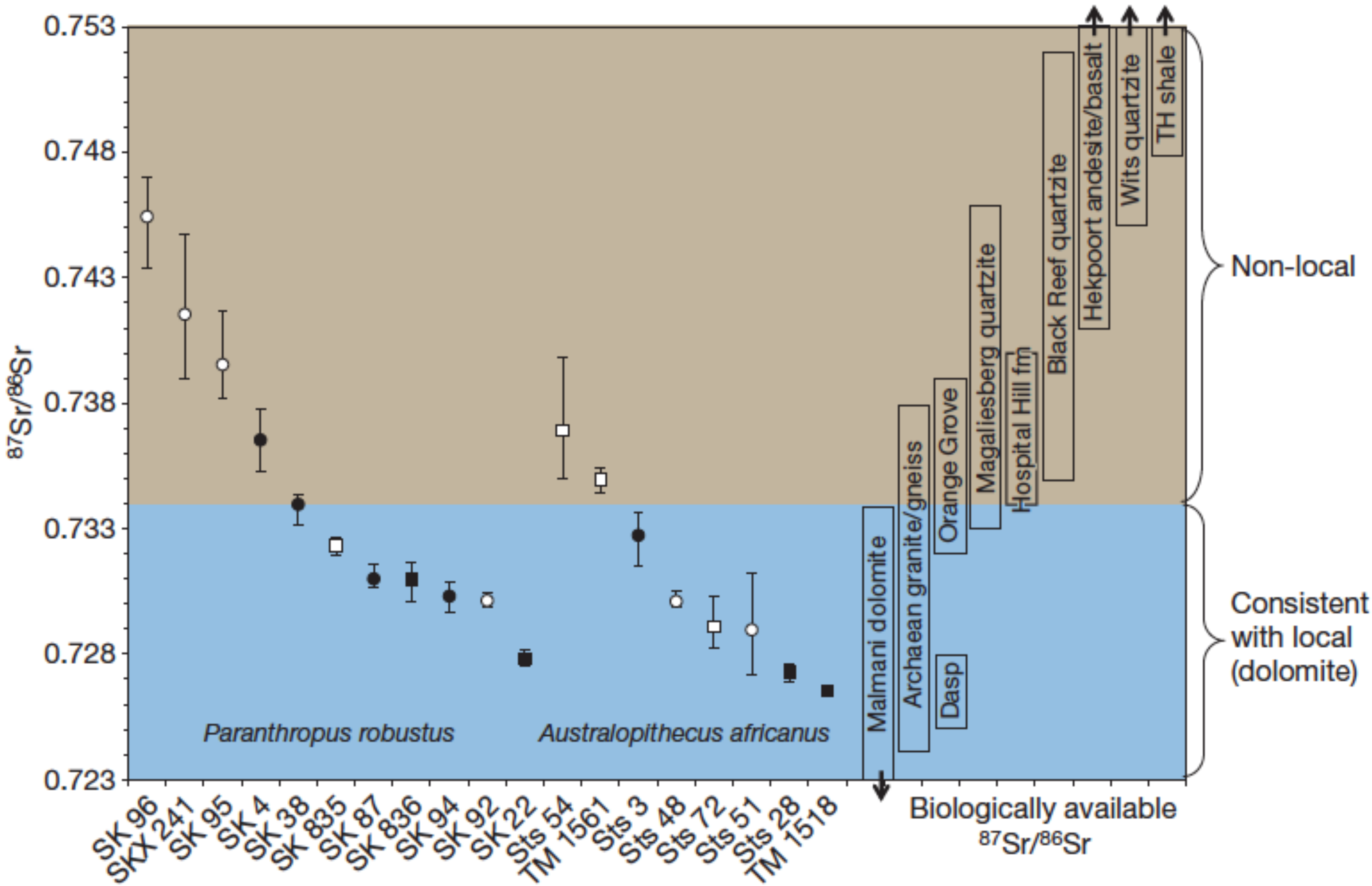


Copeland et al. (2008)

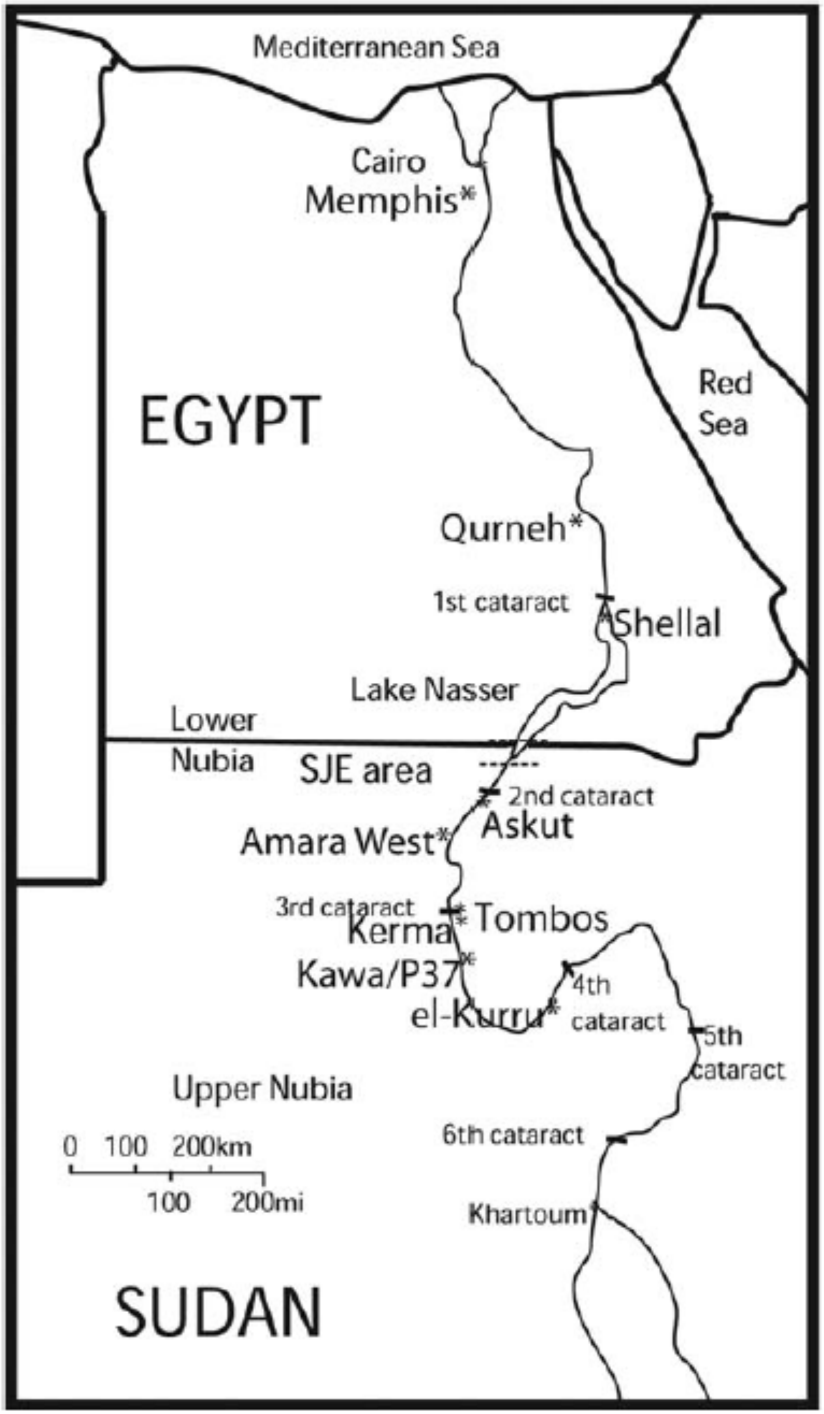
Geological Map of Sterkfontein Valley, South Africa



Copeland et al. (2011)



Copeland et al. (2011)



Buzon & Simonetti (2013)

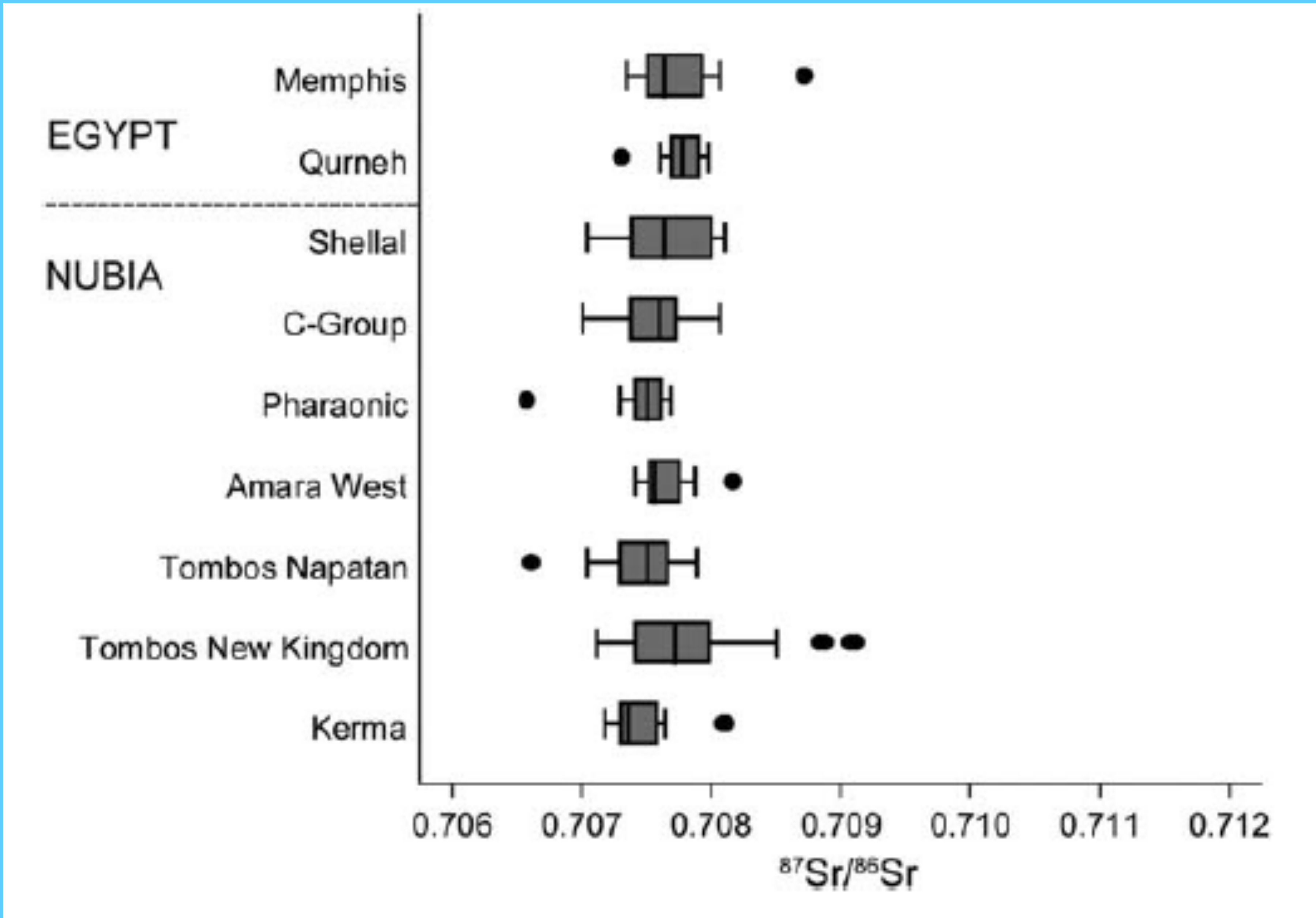
TABLE 1. Summary $^{87}Sr/^{86}Sr$ statistics for faunal samples

Site	Mean	Median	Standard deviation	Range
Askut	0.70900	0.70724	0.00153	0.70679–0.71248
C-Group	0.70790	0.70761	0.00114	0.70666–0.71086
Amara West	0.70723	0.70715	0.00030	0.70699–0.70802
Tombos (modern)	0.70746	0.70745	0.00018	0.70724–0.70773
NDR P37	0.70708	0.70692	0.00041	0.70678–0.70755
Kawa	0.70881	0.70910	0.00097	0.70740–0.71006
el-Kurru	0.70852	0.70869	0.00195	0.70649–0.71037

TABLE 2. Summary $^{87}Sr/^{86}Sr$ statistics for human samples

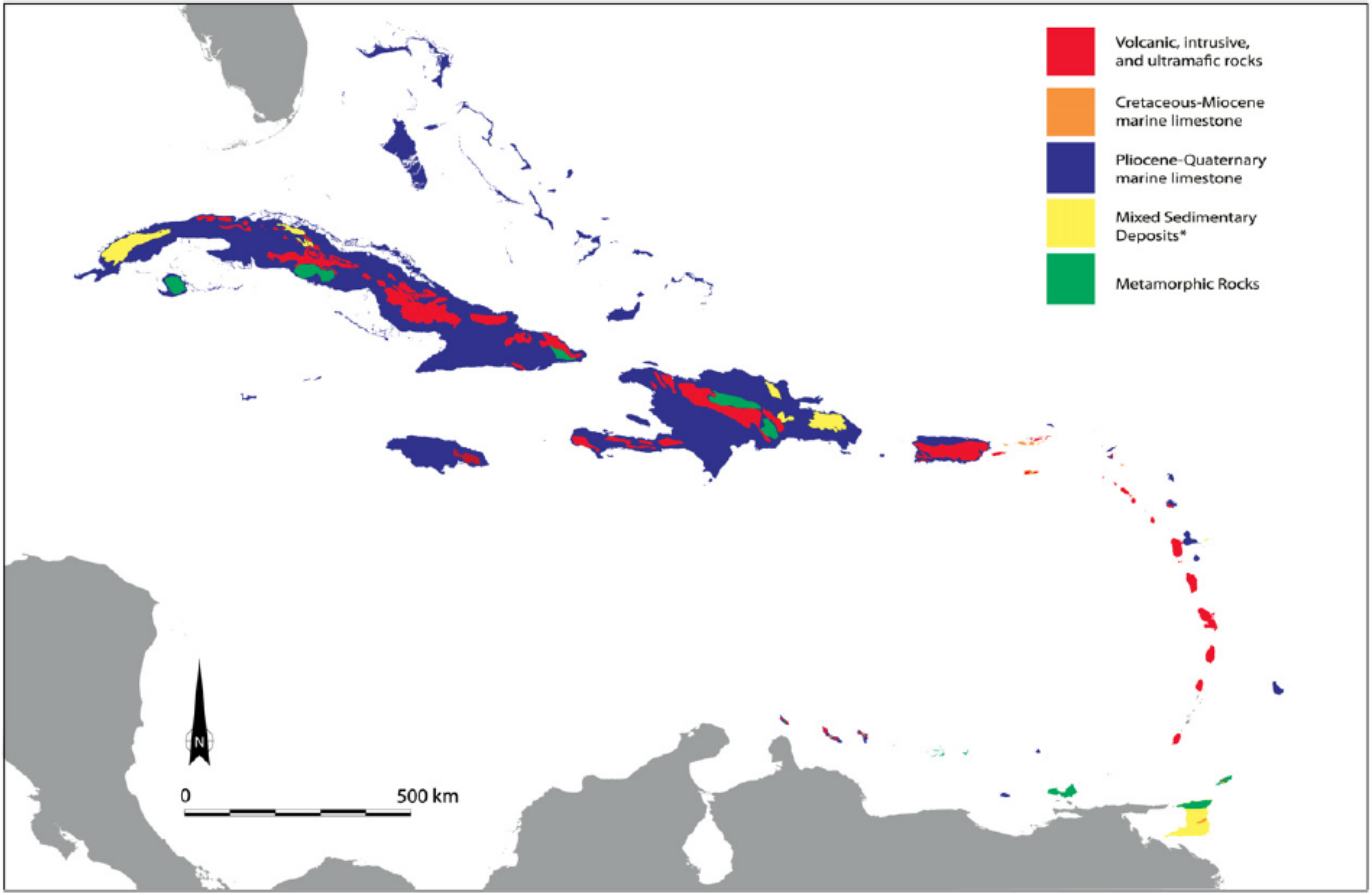
Site	Mean	Median	Standard deviation	Range
Memphis	0.70777	0.70764	0.00034	0.70735–0.70872
Qurneh	0.70777	0.70778	0.00017	0.70731–0.70798
Shellal	0.70765	0.70764	0.00031	0.70705–0.70811
C-Group	0.70758	0.70760	0.00026	0.70701–0.70807
Pharaonic	0.70746	0.70751	0.00027	0.70658–0.70769
Amara West	0.70763	0.70756	0.00018	0.70733–0.70817
Tombos Napatan	0.70747	0.70751	0.00026	0.70661–0.70789
Tombos New Kingdom	0.70779	0.70772	0.00047	0.70712–0.70912
Kerma	0.70748	0.70736	0.00029	0.70718–0.70812

Buzon & Simonetti (2013)



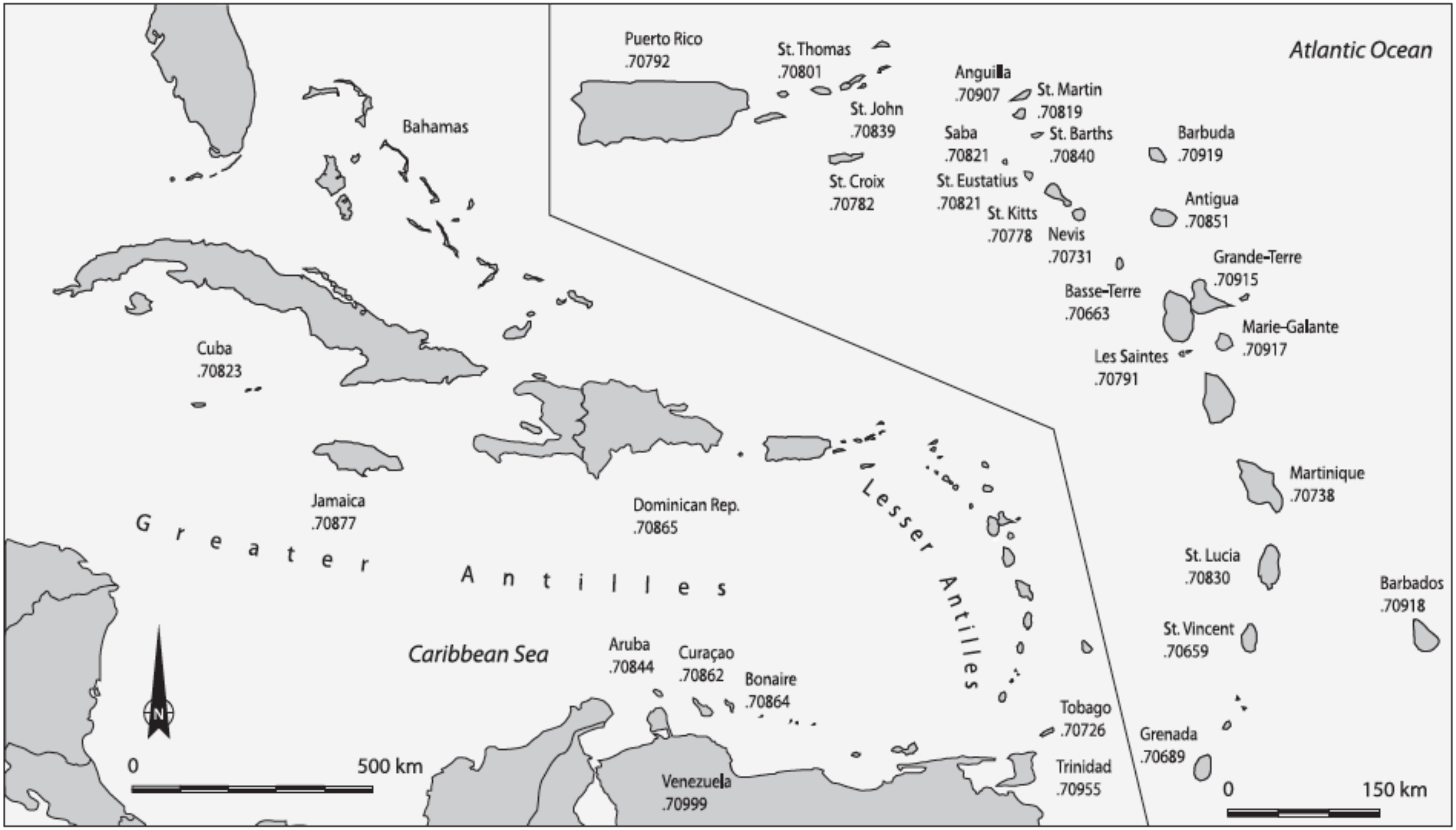
Buzon & Simonetti (2013)

Bioavailable Sr – Carribean Region



Laffoon et al. (2012)

Bioavailable Sr – Carribean Region



Laffoon et al. (2012)

Geological Map of Puerto Rico

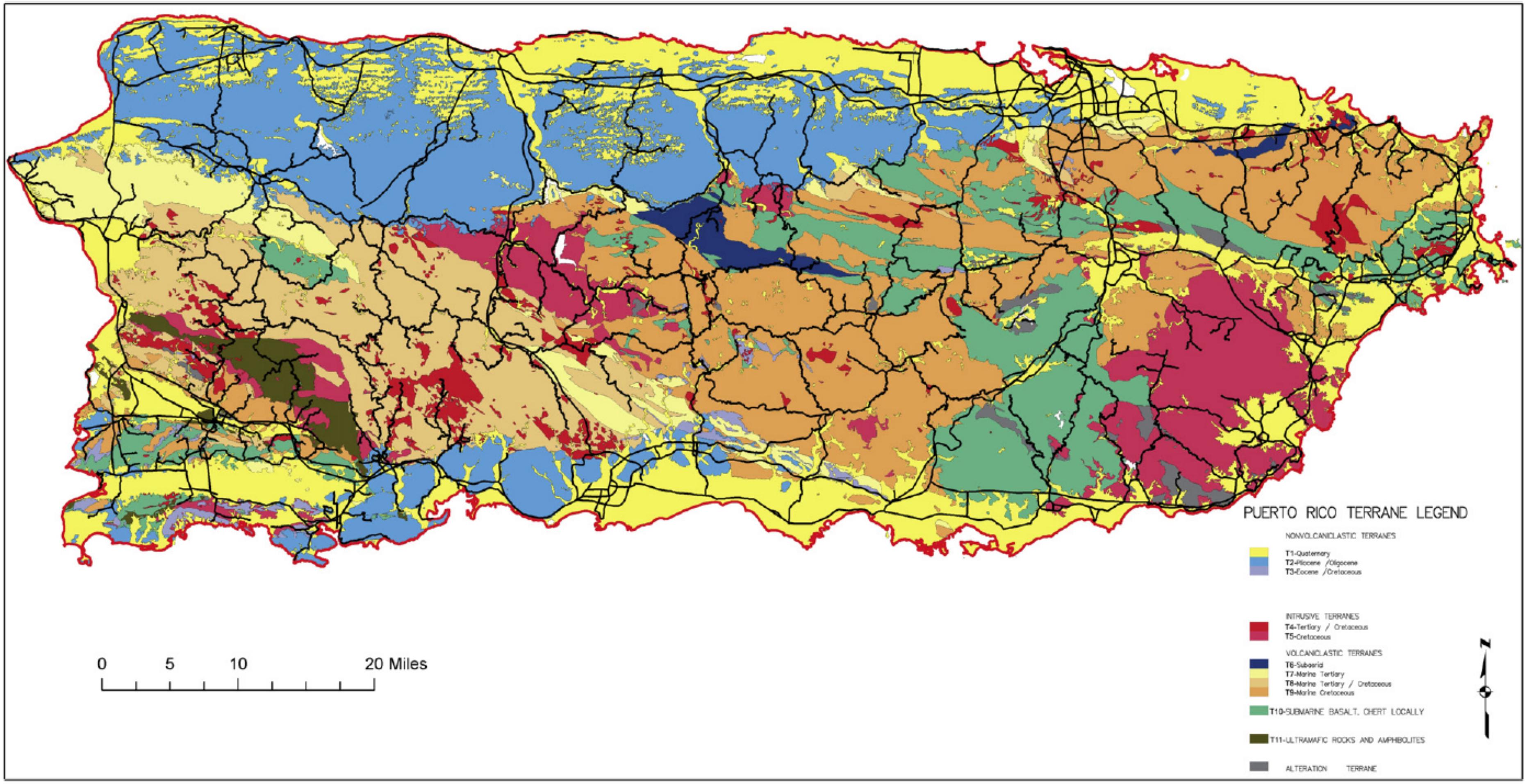


Fig. 1. Geological terrane map of Puerto Rico, adapted from Bawiec (1998).

Pestle et al. (2013)

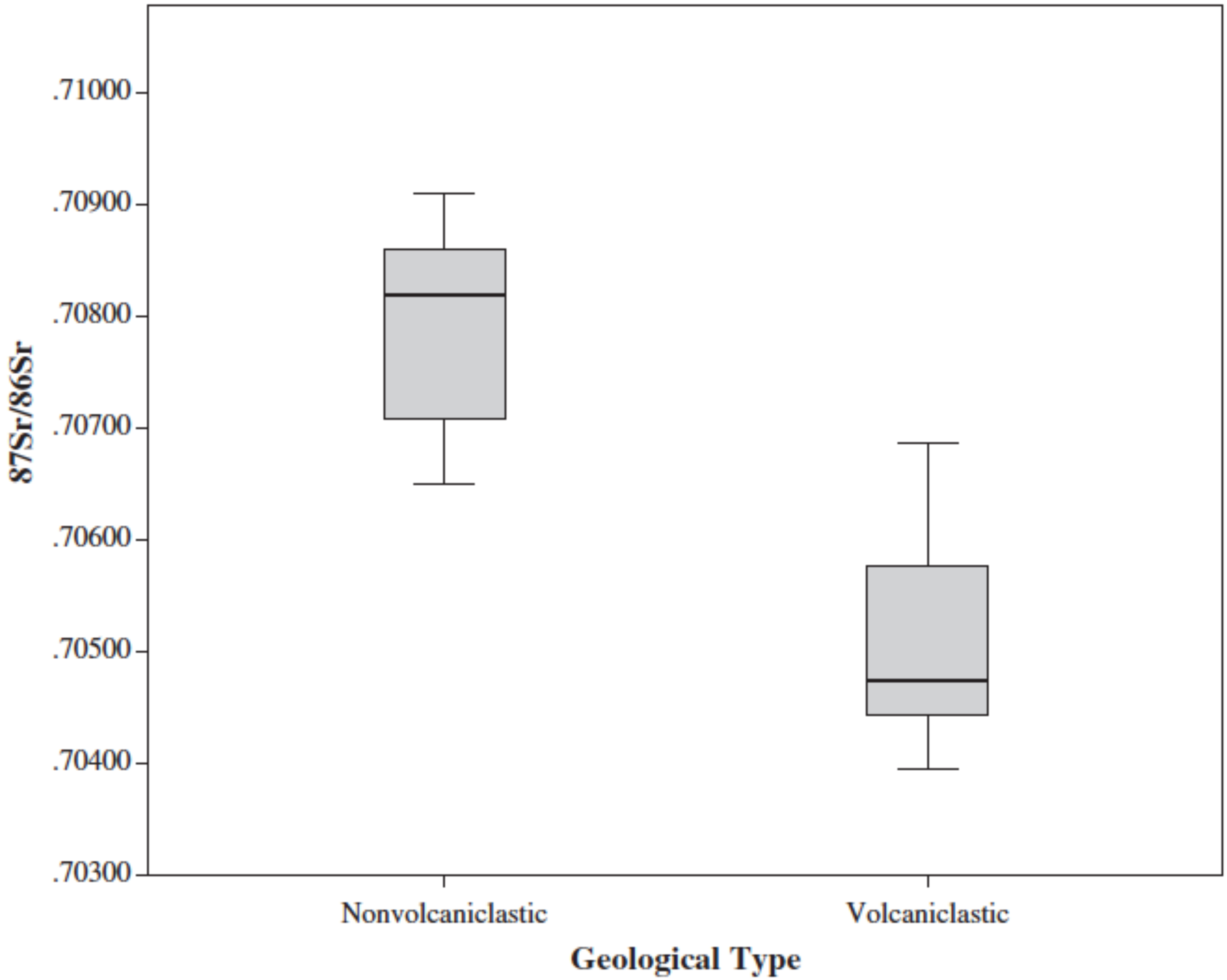


Fig. 2. $^{87}Sr/^{86}Sr$ values of Puerto Rican geological samples grouped by broad geological type.

Pestle et al. (2013)

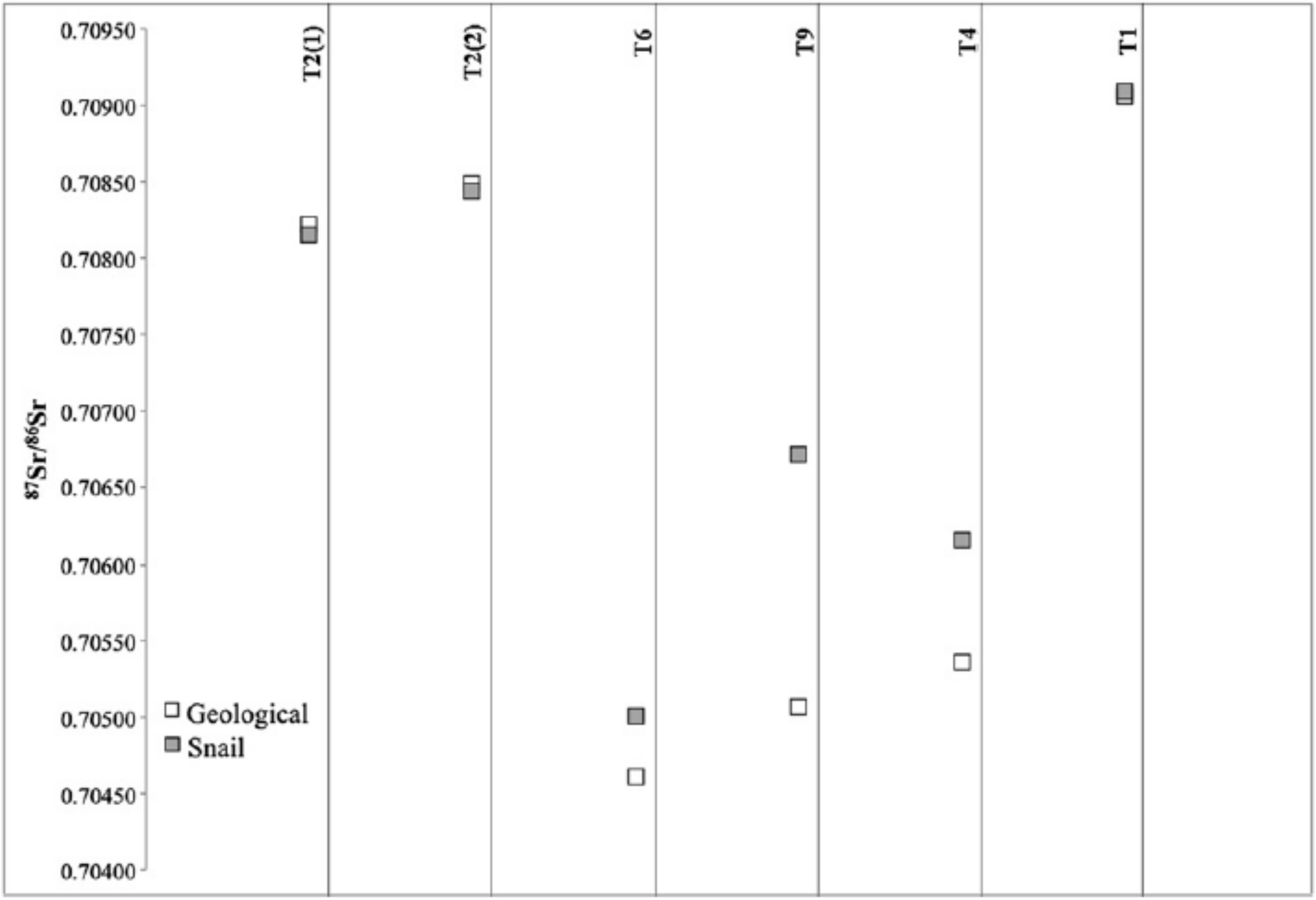
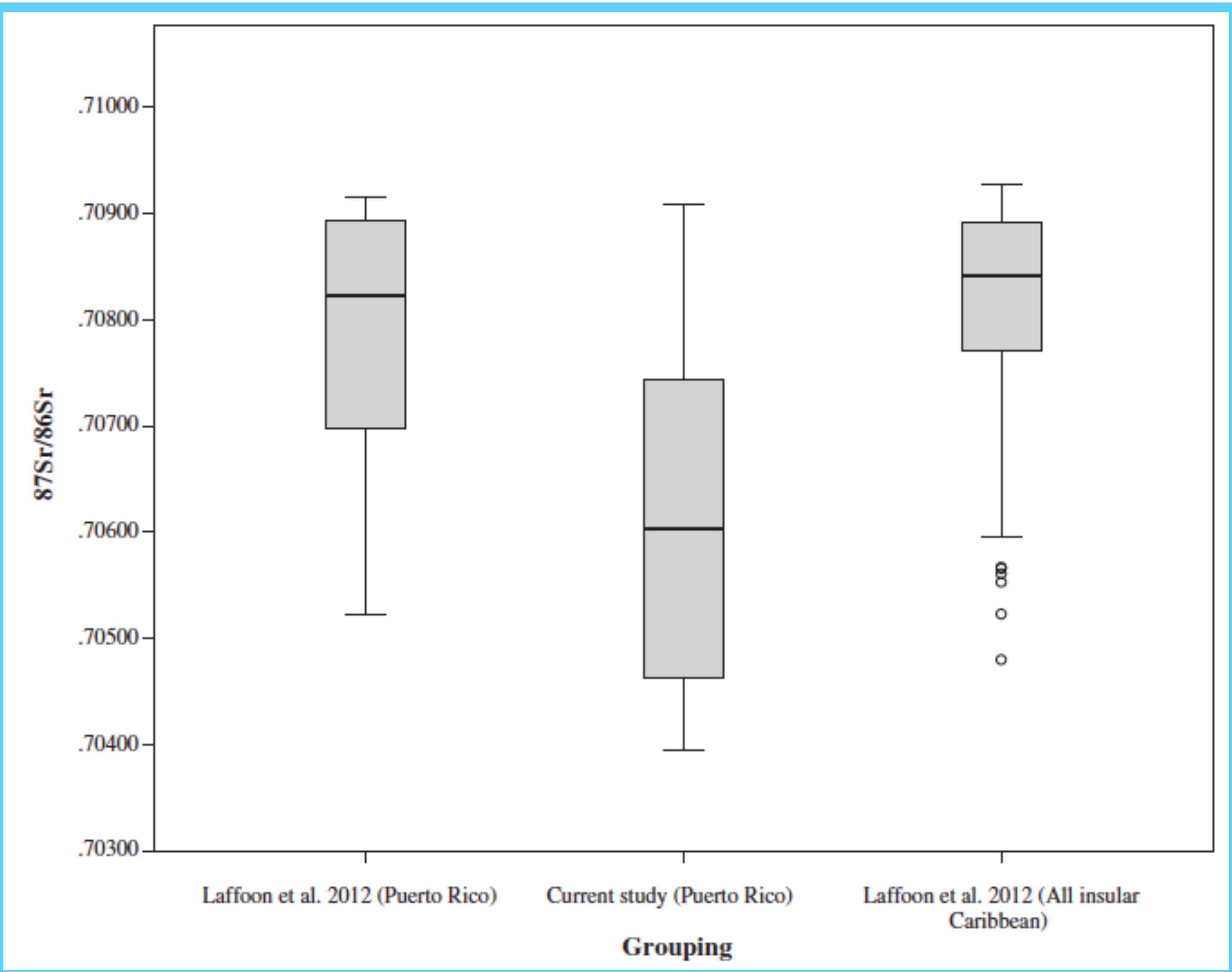


Fig. 3. $^{87}Sr/^{86}Sr$ values of paired geological-malacological (snail shell) samples.

Pestle et al. (2013)



Pestle et al. (2013)

CONCLUSIONS

- Accurate quantification of abundances for a variety of trace elements present within tooth enamel is achieved by laser ablation-ICP-MS with NIST SRM 612 glass standard as external calibration
- Sr isotope compositions of tooth enamel obtained by solution mode-MC-ICP-MS analysis are both accurate and precise, and greatly increases sample volume throughput without detriment to the quality of analysis (relative TIMS)
- $^{87}Sr/^{86}Sr$ determinations by laser ablation-MC-ICP-MS yield inaccurate (much higher) values and is principally related to a co-variance between Ca+P+O isobaric interference *vs*. absolute Sr abundances

Simonetti et al. (2008, *Archaeometry*)

CONCLUSIONS

- Sr isotope compositions obtained by LA-MC-ICP-MS for anthropological studies should be treated with caution………..best applied for studies with large Sr isotope variations in surrounding bedrock geology

- Careful and detailed investigation of Sr isotope composition of bedrock geology is highly recommended for accurate interpretation of results

Application of Sr isotope geochemistry to groundwater issues

Case Study: Bénin, Africa

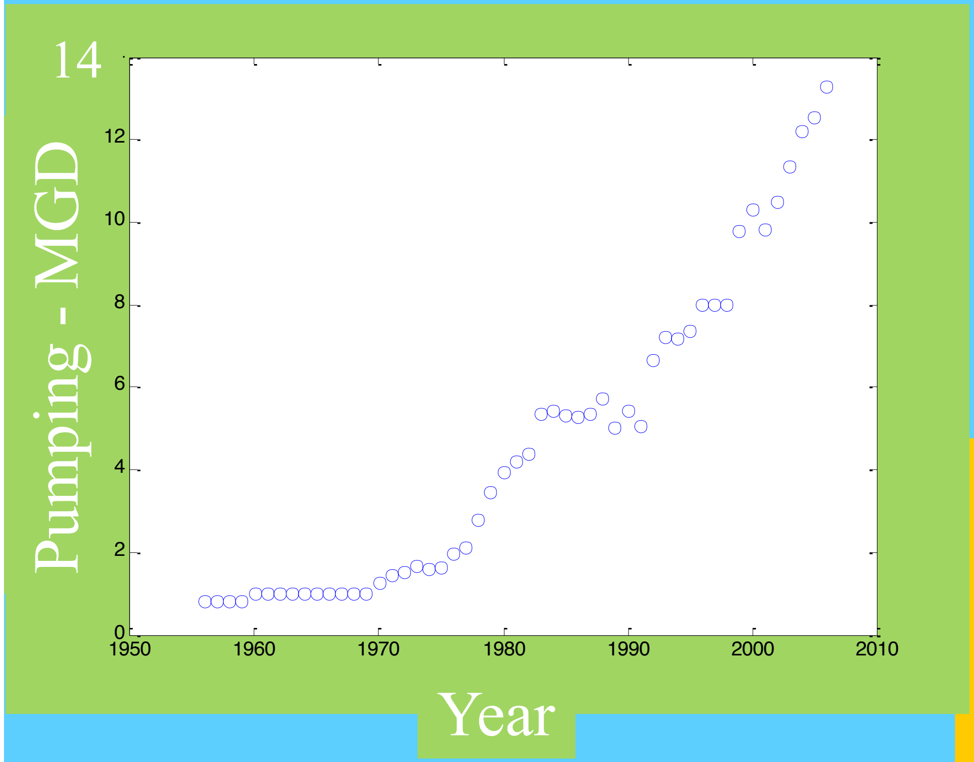
Collaboration with Dr. Steve Silliman

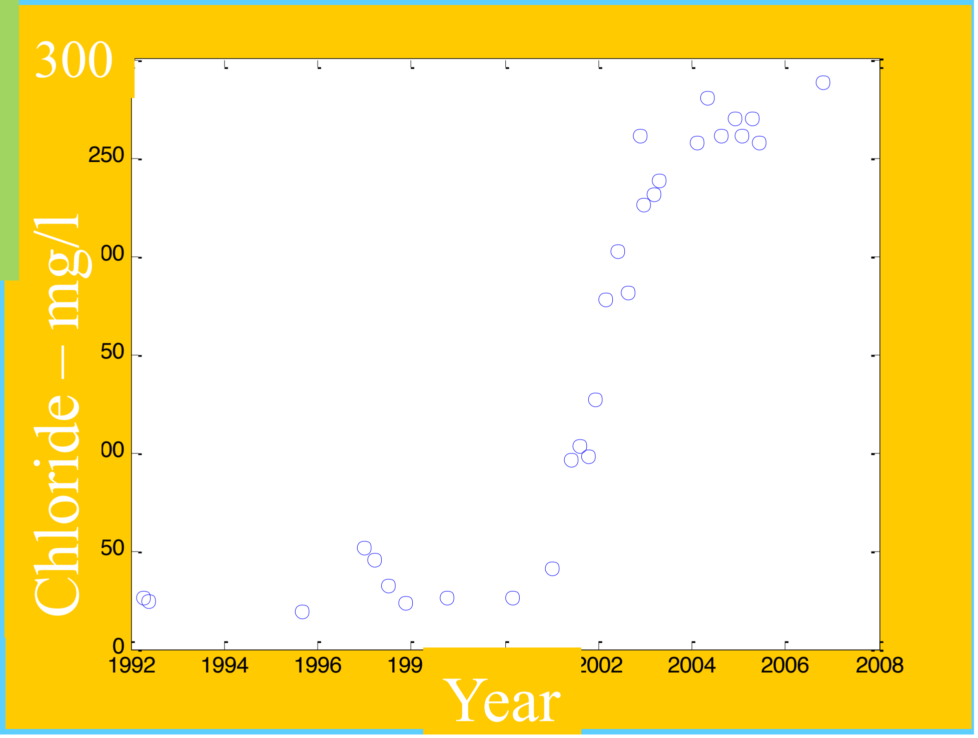

Mauritania
Mali
Niger
Senegal
The Gambia
Guinea-Bissau
Burkina Faso
Guinea
benin
Nigeria
Togo
Sierra Leone
Côte d'Ivoire
Ghana
Liberia
Cameroon
Equatorial Guinea
São Tomé and Principe
Gabon
Bénin, Africa


Godomey
Well
Field
9.93 km
Image © 2010 TerraMetrics
US Dept of State Geographer
Data SIO, NOAA, U.S. Navy, NGA, GEBCO
Image © 2010 DigitalGlobe
Google
lat 6.412651° lon 2.294109° elev 5 m
Eye alt 34.33 km

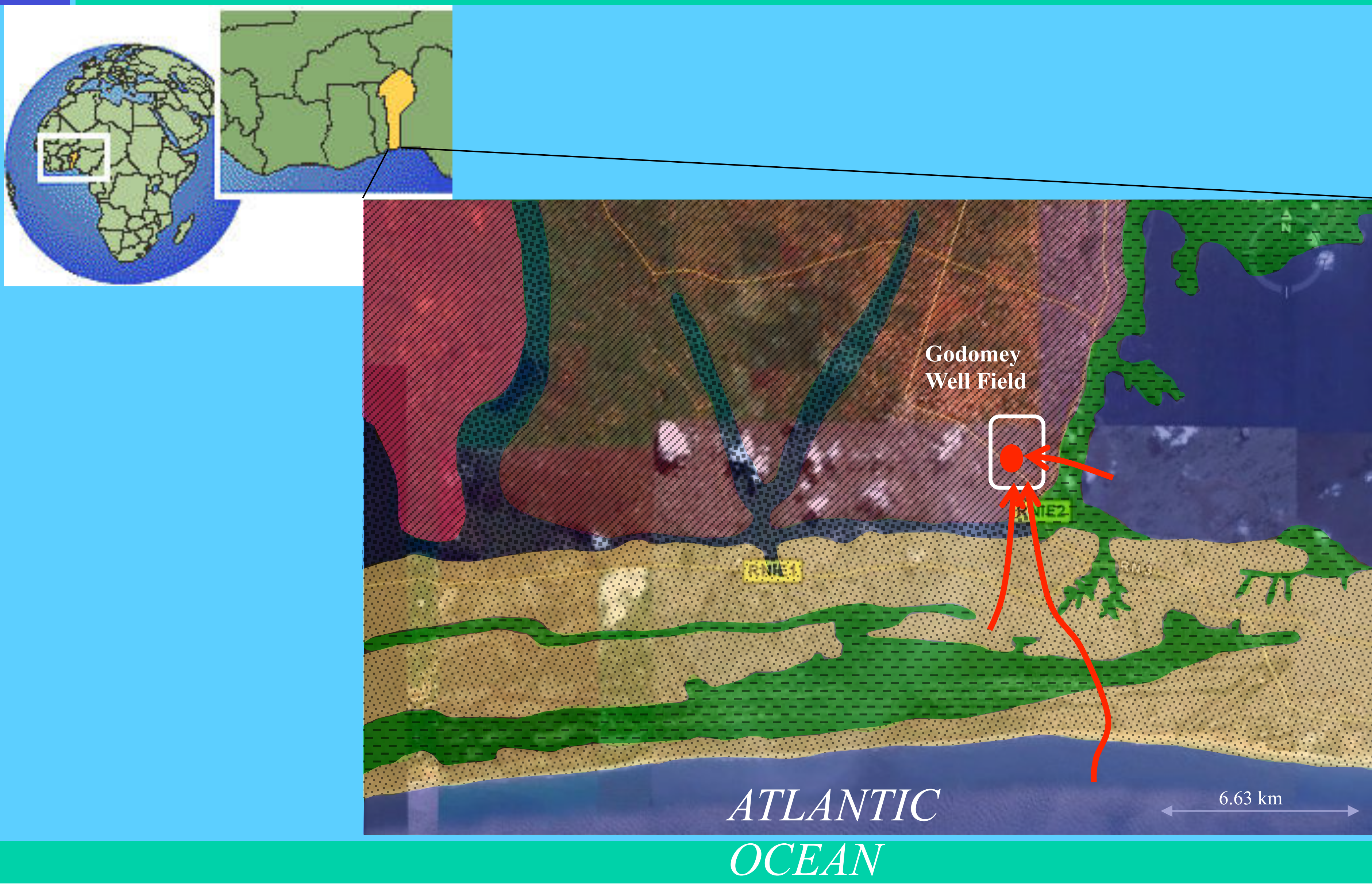

Benin
Togo
© 2010 Europa Technologies
US Dept of State Geographer
© 2010 Cnes/Spot Image
Image © 2010 TerraMetrics
Google
lat 8.870649° lon 2.418787° elev 286 m Eye alt 373.58

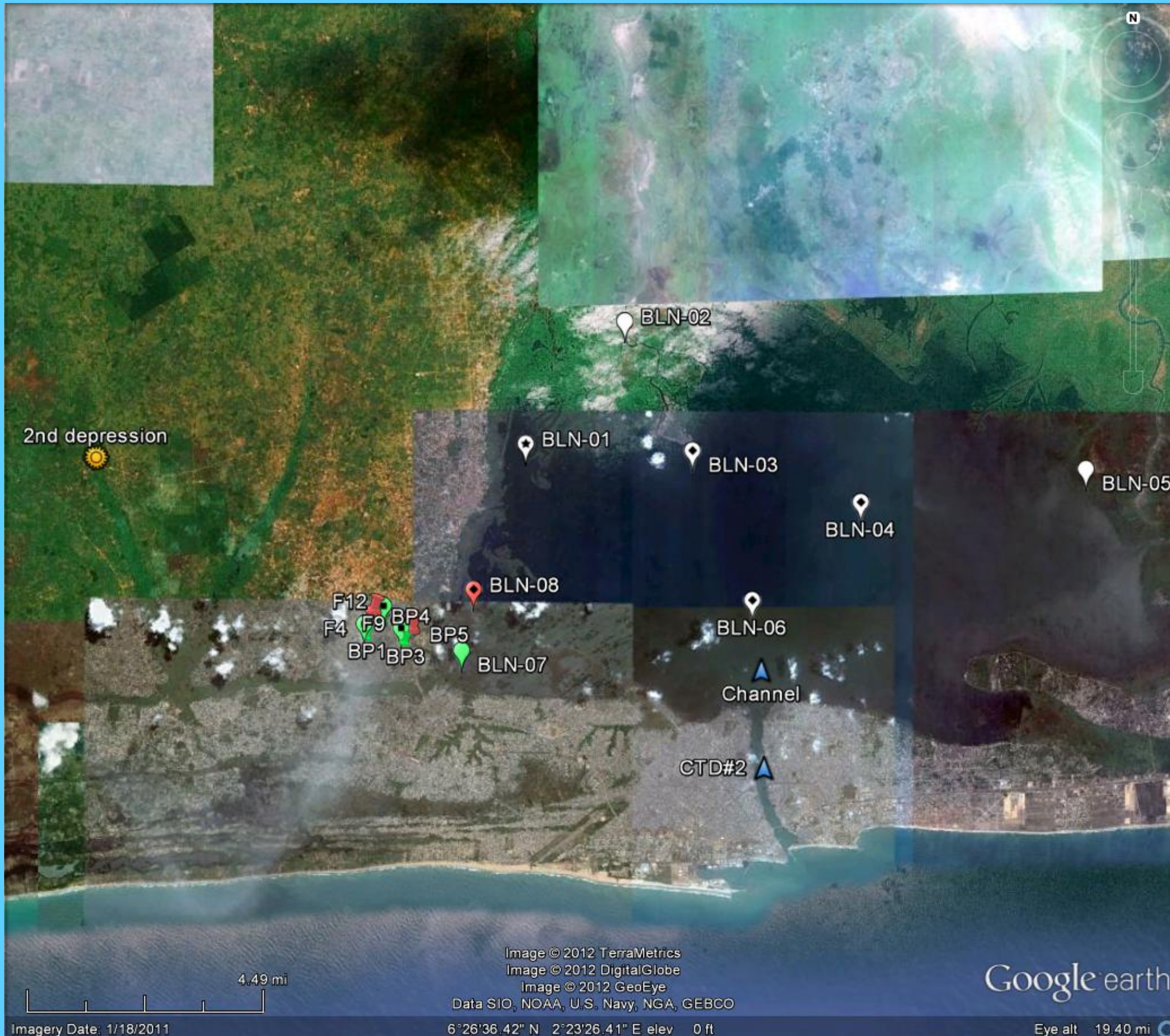
History of Pumping and Water Quality

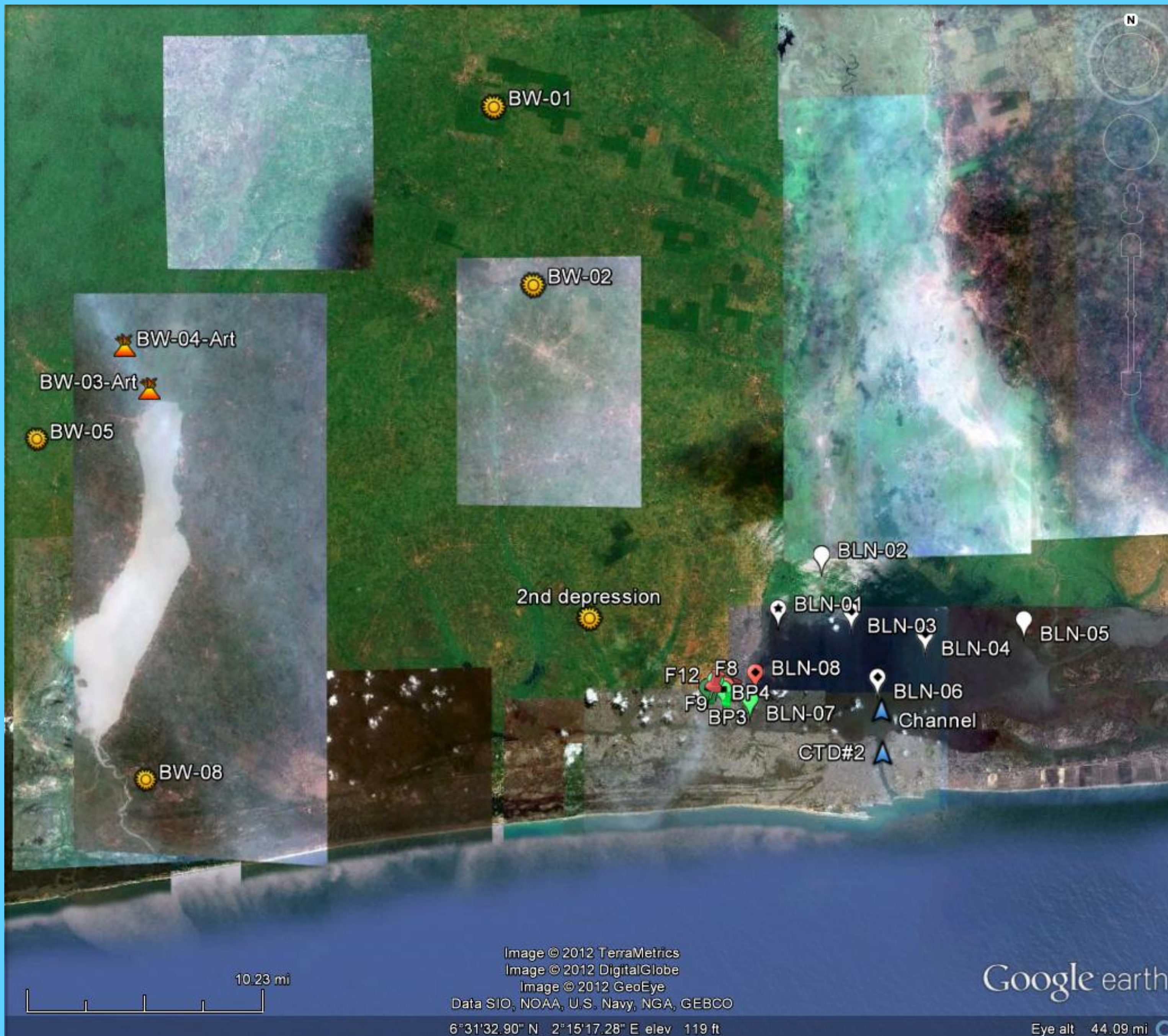


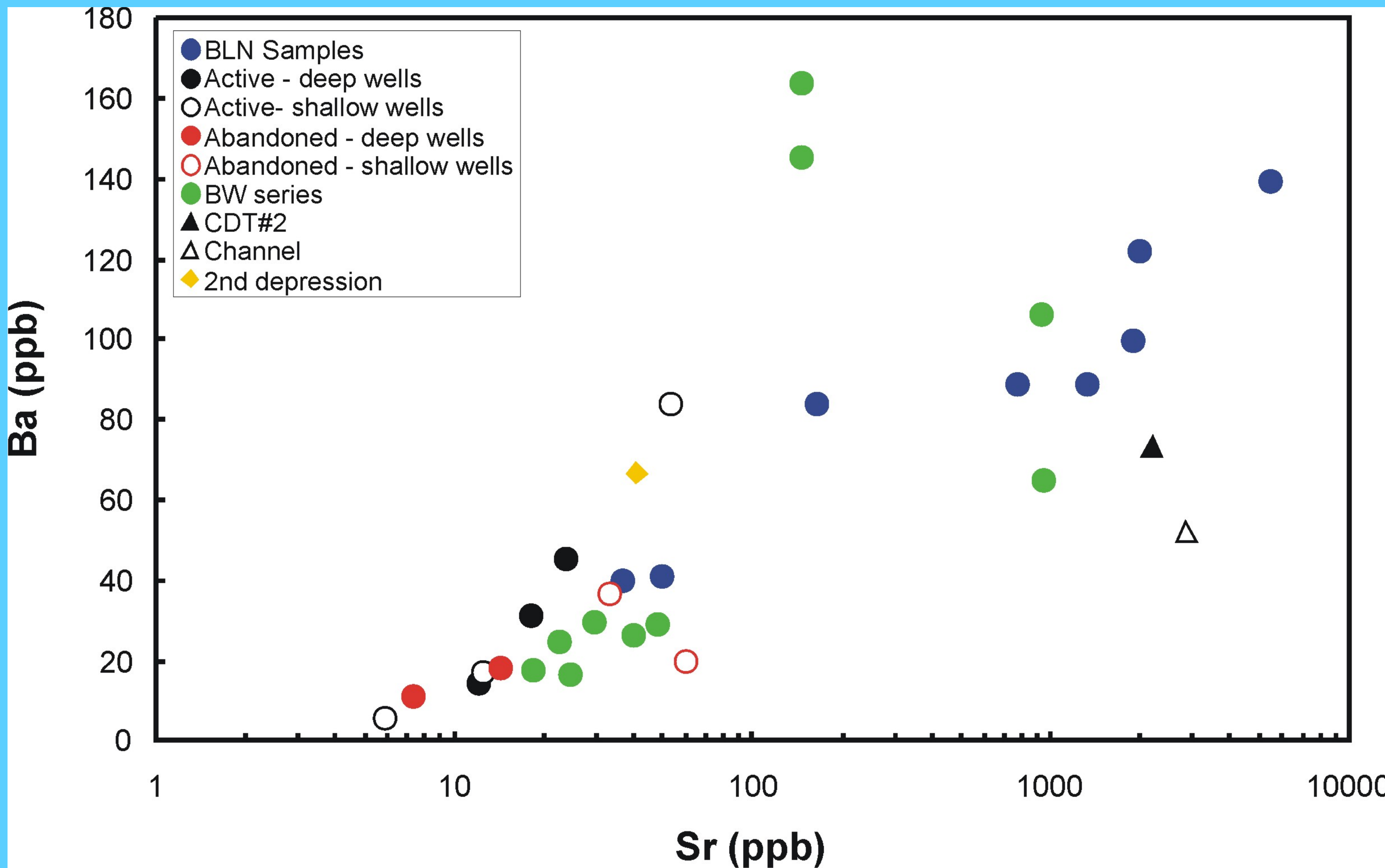


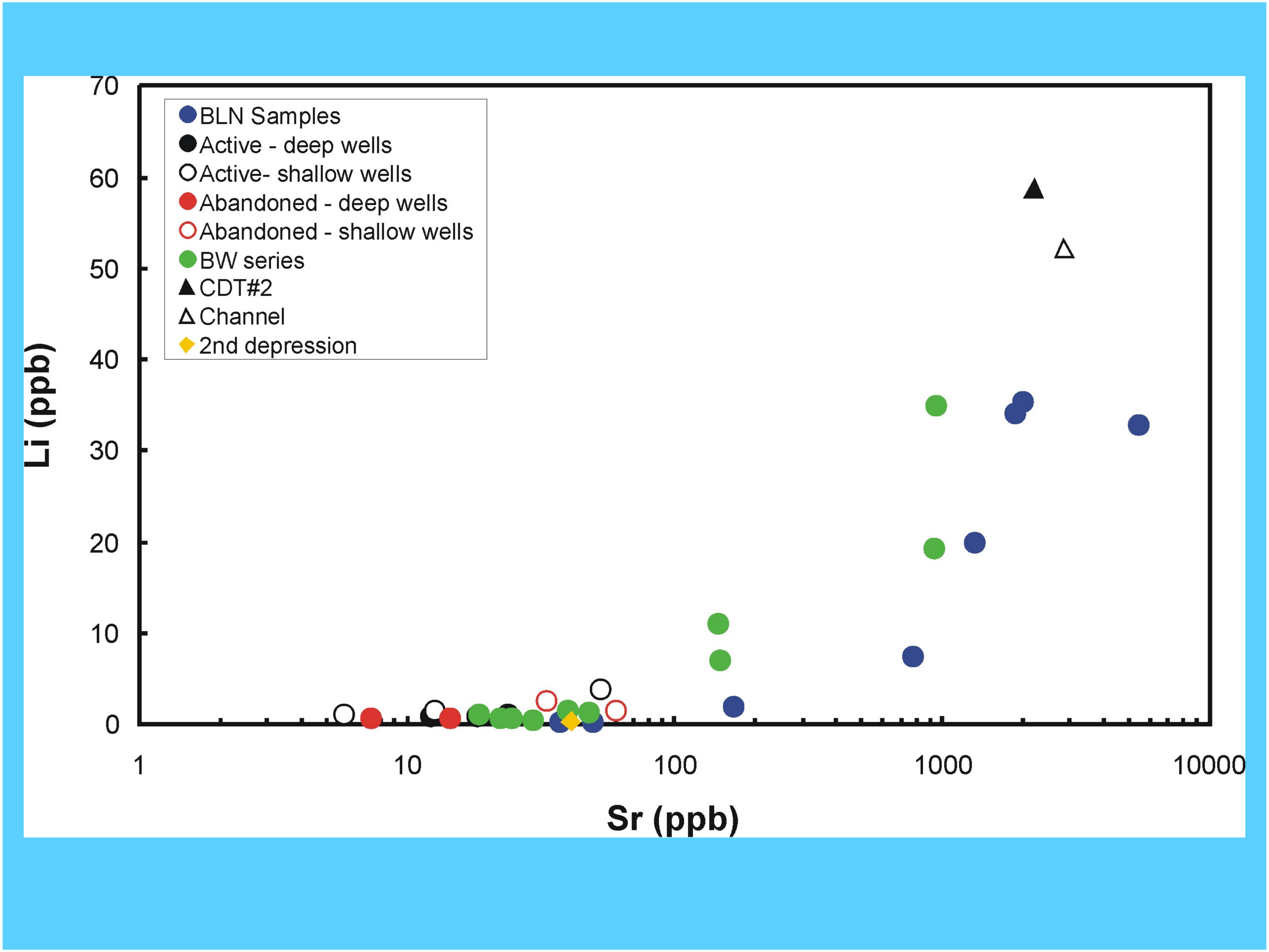
Coastal Near Surface Geology



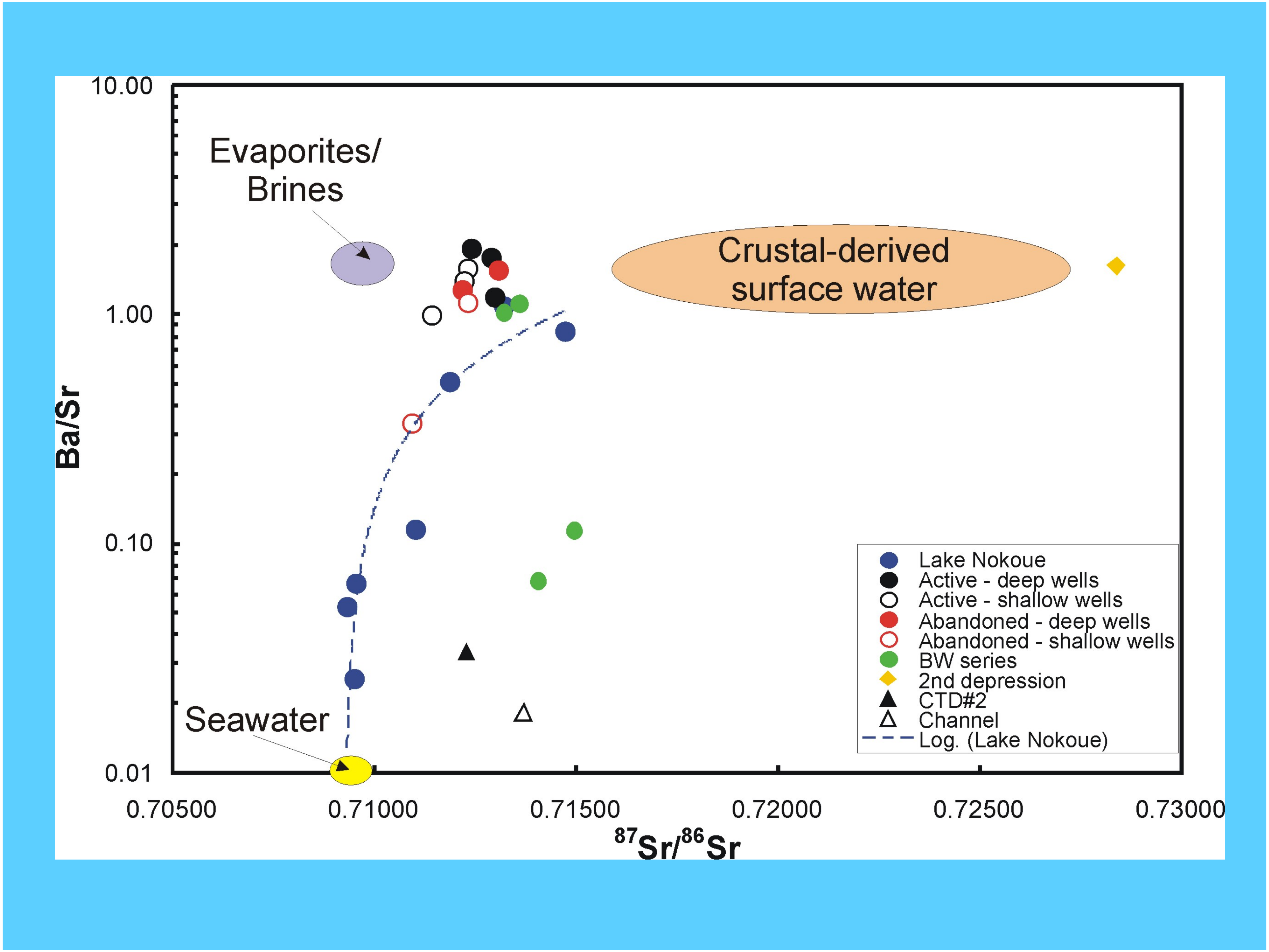

BLN-02
2nd depression
BLN-01
BLN-03
BLN-05
BLN-04
BLN-08
F12
BP4
F4
F9
BP5
BP1
BP3
BLN-07
BLN-06
Channel
CTD#2
4.49 mi
Image © 2012 TerraMetrics
Image © 2012 DigitalGlobe
Image © 2012 GeoEye
Data SIO, NOAA, U.S. Navy, NGA, GEBCO
Google earth
Imagery Date: 1/18/2011
6°26'36.42" N 2°23'26.41" E elev 0 ft
Eye alt 19.40 mi

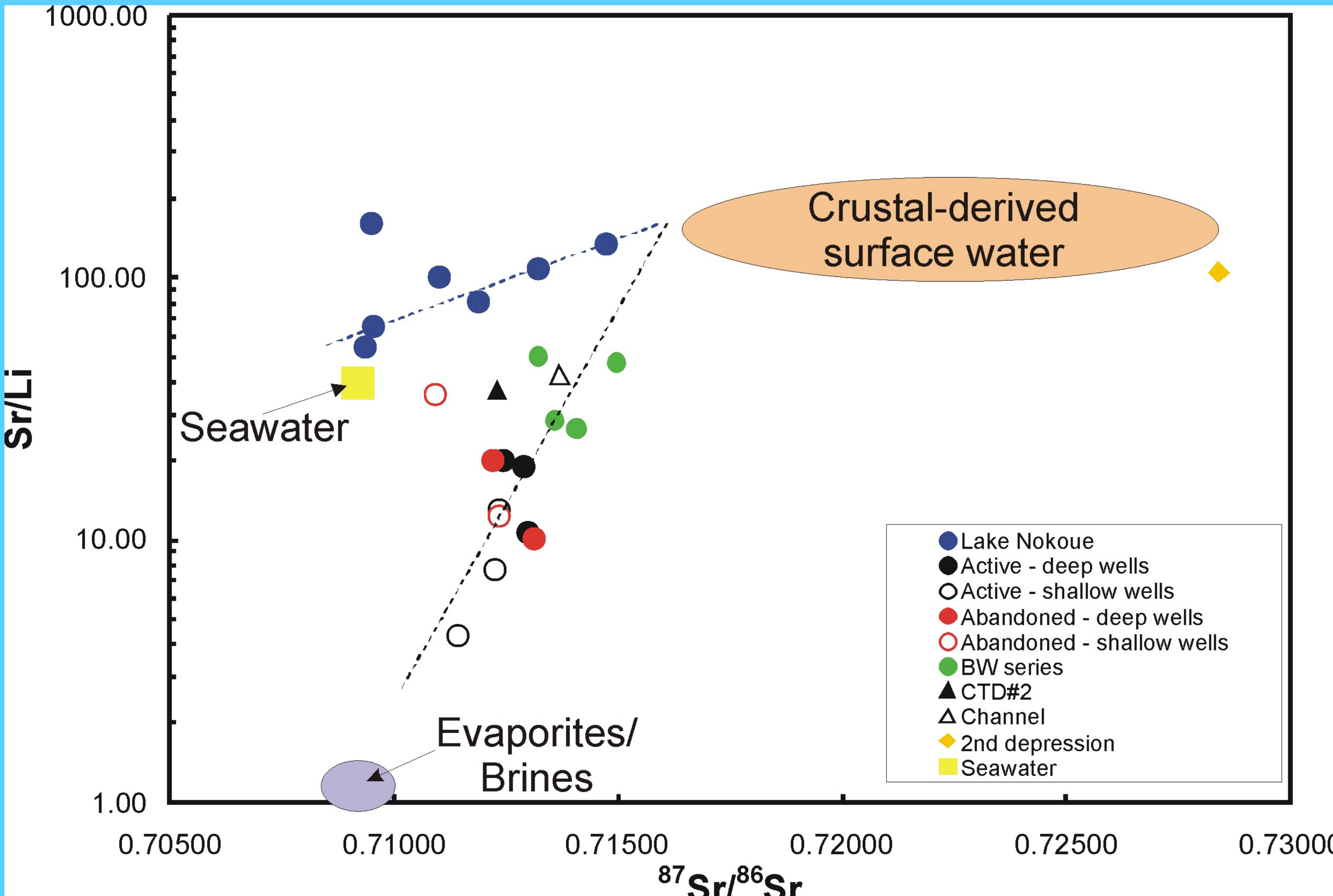

BW-01
BW-02
BW-04-Art
BW-03-Art
BW-05
BW-08
2nd depression
BLN-02
BLN-01
BLN-03
BLN-04
BLN-05
BLN-08
BLN-06
BLN-07
F12
F8
F9
BP4
BP3
Channel
CTD#2
N
10.23 mi
Image © 2012 TerraMetrics
Image © 2012 DigitalGlobe
Image © 2012 GeoEye
Data SIO, NOAA, U.S. Navy, NGA, GEBCO
Google earth
6°31'32.90" N 2°15'17.28" E elev 119 ft
Eye alt 44.09 mi


BLN Samples
Active - deep wells
Active- shallow wells
Abandoned - deep wells
Abandoned - shallow wells
BW series
CDT#2
Channel
2nd depression
Ba (ppb)
Sr (ppb)
0
20
40
60
80
100
120
140
160
180
1
10
100
1000
10000



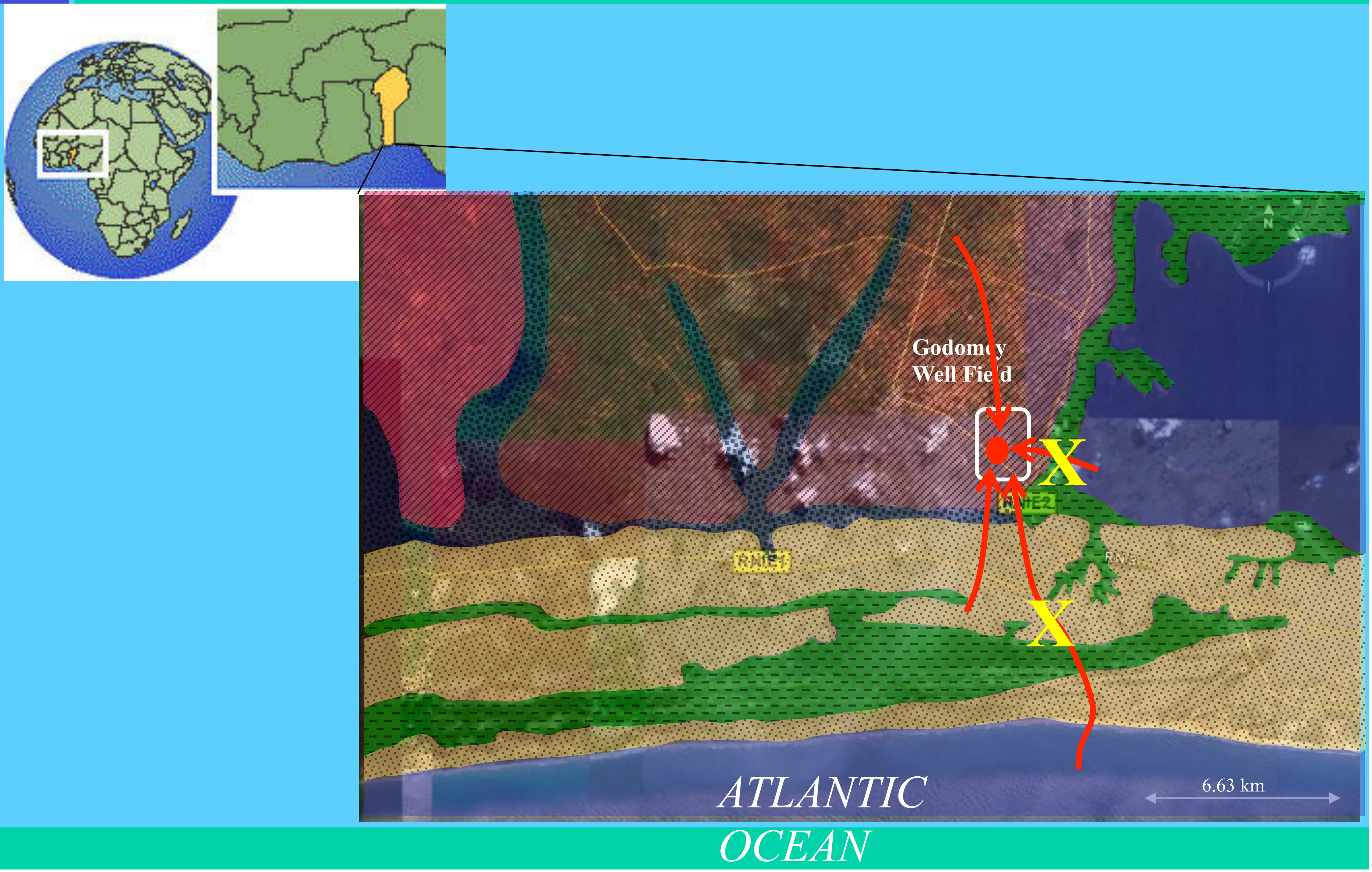
BLN Samples
Active - deep wells
Active- shallow wells
Abandoned - deep wells
Abandoned - shallow wells
BW series
CDT#2
Channel
2nd depression
Li (ppb)
70
60
50
40
30
20
10
0
1
10
100
1000
10000
Sr (ppb)


10.00
1.00
0.10
0.01
Ba/Sr
Evaporites/
Brines
Crustal-derived
surface water
Seawater
0.70500
0.71000
0.71500
0.72000
0.72500
0.73000
87Sr/86Sr
Lake Nokoue
Active - deep wells
Active - shallow wells
Abandoned - deep wells
Abandoned - shallow wells
BW series
2nd depression
CTD#2
Channel
Log. (Lake Nokoue)



1000.00
100.00
10.00
1.00
Sr/Li
0.70500
0.71000
0.71500
0.72000
0.72500
0.73000
87Sr/86Sr
Crustal-derived surface water
Seawater
Evaporites/ Brines
Lake Nokoue
Active - deep wells
Active - shallow wells
Abandoned - deep wells
Abandoned - shallow wells
BW series
CTD#2
Channel
2nd depression
Seawater

Coastal Near Surface Geology



CONCLUSIONS

- Elemental abundances and Sr isotope compositions for samples from Lake Nokoue are consistent with binary mixing between crustal-derived surface waters and seawater;

- The results reported here suggest that seawater is not a major component of subsurface water within the Godomey Well Field;

- The combined elemental and Sr isotope data require the presence of a third component- marine-derived evaporites/brines?