Supplemental Material for Scientific Notebook No. 084

E. PEARCY NOTES

What are the source rocks for the borehole sediments? What are the REE contents of the source rocks? How do those contents compare to the REE contents of the sediments?

What are the REE contents of the local groundwaters? How do they compare to the alluvium patterns? In Oasis Valley Johannesson et al. (1999) showed groundwater REE patterns that are the opposite of our alluvium patterns (e.g., the waters are enriched in HREEs).

During weathering and transport of the alluvial sediments, what happens to the original REE contents? REEs tend to be immobile during weathering. Some would be immobile because they are contained within resistant minerals like zircon, monazite, and sphene. Other REEs would be immobile because they sorb onto clays and iron oxides.

If the REEs we have measured in the fines from the alluvium are mainly on clays or iron oxides, can that be interpreted, in part perhaps, in terms of colloidal **transport** on clay or iron oxide particles in a fluvial, braided stream environment? - followed by **deposition** among the conglomerates of the system and **retention** within the deposited sediments.

What are the REE contents of the SZ waters in contact with the REE-containing clays and iron oxides? [it will be some very low number] Is the REE content of the waters consistent with the REE abundances in/on the clays and iron oxides?

Is there any correlation between LREEs and clays? Duddy, 1980; Olivera-Pastor et al., 1988 report adsorption of LREEs onto clays as a means of fixing LREEs during weathering.

Limited enrichment of MREEs were observed in Fe-rich nodules and Fe-Mn coatings in a marine environment (e.g. Palmer and Enderfield, 1986).

**Where are the REEs hosted in the unaltered source rocks?

During weathering of the source rocks, the REE undergo some degree of redistribution from their original minerals. The degree of redistribution of REEs that occurs during weathering may be considerable (e.g., Banfield and Eggleton, 1989) or somewhat less (REF??) depending on the composition of the original host minerals and the conditions under which weathering occurred.

- REEs are used for provenance studies for shales. So REEs are more or less quantitatively retained in the clays during transport and deposition, right?

- Need to do a heavy mineral separation on the fines to determine REEs in heavies vs REEs on clays and iron oxides?

** Use SEM/EDS to examine representative samples of our fine fraction to rule out significant heavy mineral contributions to REE contents.

Why normalize to PAAS?

Why normalize to chondrites?

** Check for correlations between LREE, MREE, and HREE variations and clay minerals (of various types), FeOx MnOx minerals, and any others. Use those correlations (if any) to interpret major modes of REE adsorption within the various horizons sampled in the well. Use REE adsorption patterns as analogs for what might occur with actinides.

Our measurements of REEs in the fines of the alluvial sediments include REEs (i) retained within minerals composing the sedimentary grains transported as suspended particles, (ii) sorbed onto surfaces of the suspended sedimentary particles, and (iii) transported as colloids and retained within the alluvium by filtration. We will not have measured those REEs transported in the dissolved load, but the abundance of REEs in the dissolved load is most likely to have been quite low compared to the abundance of REEs carried in the suspended and bed loads.

Our measured REE abundances in the fines will not have been strongly affected by post-depositional interactions with REEs in groundwater moving through the sediments because the concentrations in the sediments as deposited are large compared to the concentrations in the groudwaters.

Interpretations:
Our measured REE abundances are generally enriched in LREEs relative to HREEs. The La/Lu ratios for all samples are greater than 1.3. The highest La/Lu ratio is 2.19 and the lowest is 1.32. What is special about the samples with the greatest and least degree of enrichment? How do these observations compare to the experimental results of Benedict et al (1996)?

REEs in common rocks tend to occur as substitutions for Ca. In our samples, where is the Ca? Plagioclase appears to be the main mineral that would likely have a significant Ca concentration, but the measured REE concentrations are not well correlated with the abundance of plagioclase in the samples. What else has significant Ca? There is only trace calcite in the XRD data. Could the variability in calcite abundance at levels below XRD detection (e.g., less than about 5 volume percent) account for the REE abundances?

There is no correlation between REE abundances and the abundances of varioius clay minerals, so there may be no preference for accomodation of the REEs among the clay minerals measured.

Try normalizing to average chondritic values. Might be better to just normalize to shales though, if the differences between chondrite values and these samples is large.

Plot un-normalized concentrations to look for Oddo-Harkins rule (concentrations for even numbered elements greater than their odd numbered neighbors).

It is unlikely that the REE concentrations in these samples are dominated by the influence of heavy minerals. In these samples, Gd/Yb ratios vary from 1.08 to 1.40. This is consistent with most commonly observed post-Archean sediment values (McLennan, 1989). Addition of even minor amounts of monazite (0.005 % to sandstones and 0.02 % to shales) produces Gd/Yb values greater than 2.0. Even limited zircon abundances would give rise to Gd/Yb ratios less than 1.0. La/Yb ratios range from 1.34 to 2.22. This range is consistent with most post-Archean sedimentary rocks. This La/Yb range is inconsistent with the inclusion of significant allanite. Allanite abundances of 0.02 % and greater produce La/Yb ratios greater than 15 for low REE abundance sediments such as these. Further, there is essentially no correlation among Zr, Hf, Th, and Yb, suggesting minimal influence from zircon, allanite, or monazite in these samples.

Can quantify the Eu anomalies (McLennan chapter page 176)

Our measured samples (35 mesh??) may be just the fines from the original volcanic rock. The clay content from XRD is low and the other minerals are likely from the original volcanics. That is consistent with the REE patterns which make smoother curved when normalized against C1 chondrites (thought to be representative of igneous rocks??) than when normalized against PAAS. Trends are similar, though. Enriched in LREEs and have a negative Eu anomaly.

Are our REE measurements dominated by heavy minerals (zircon, monazite, sphene, and such)?
- check for correlations with Zr, Ti, ...

If not in heavies, where are they?

We have REE concentrations for <35 mesh fines. What is this fraction mineralogically?

Where are these REEs, on clays or iron oxides or in minerals/rock fragments, heavies?

Is there a correlation between REE abundances and lithology or clast size?

What about REEs and iron oxides? Do they tend to be associated? REEs and zeolites? REEs and clays?

If the REEs are mainly on clays or iron oxides, can that be interpreted, in part perhaps, in terms of colloidal **transport** on clay or iron oxide particles in a fluvial, braided stream environment? - followed by **deposition** among the conglomerates of the system and **retention** within the deposited sediments. What are the REE contents of the SZ waters in contact with the REE-containing clays and iron oxides? [it will be some very low number] Is the REE content of the waters consistent with the REE abundances in/on the clays and iron oxides?

In the alluvium, there is uncertainty in the abundance of iron oxides because they can be amorphous and not show on the XRDs.

Iron oxides could/should be more important to sorption than clays, yes?

What about anthropogenic REE inputs from "military activities"?

plutonium is in the same chemical family as the rare earth element samarium. Plutonium is similar to uranium, neptunium, and americium in that all of these elements have four possible oxidation (valence) states (i.e., +3, +4, +5, and +6).

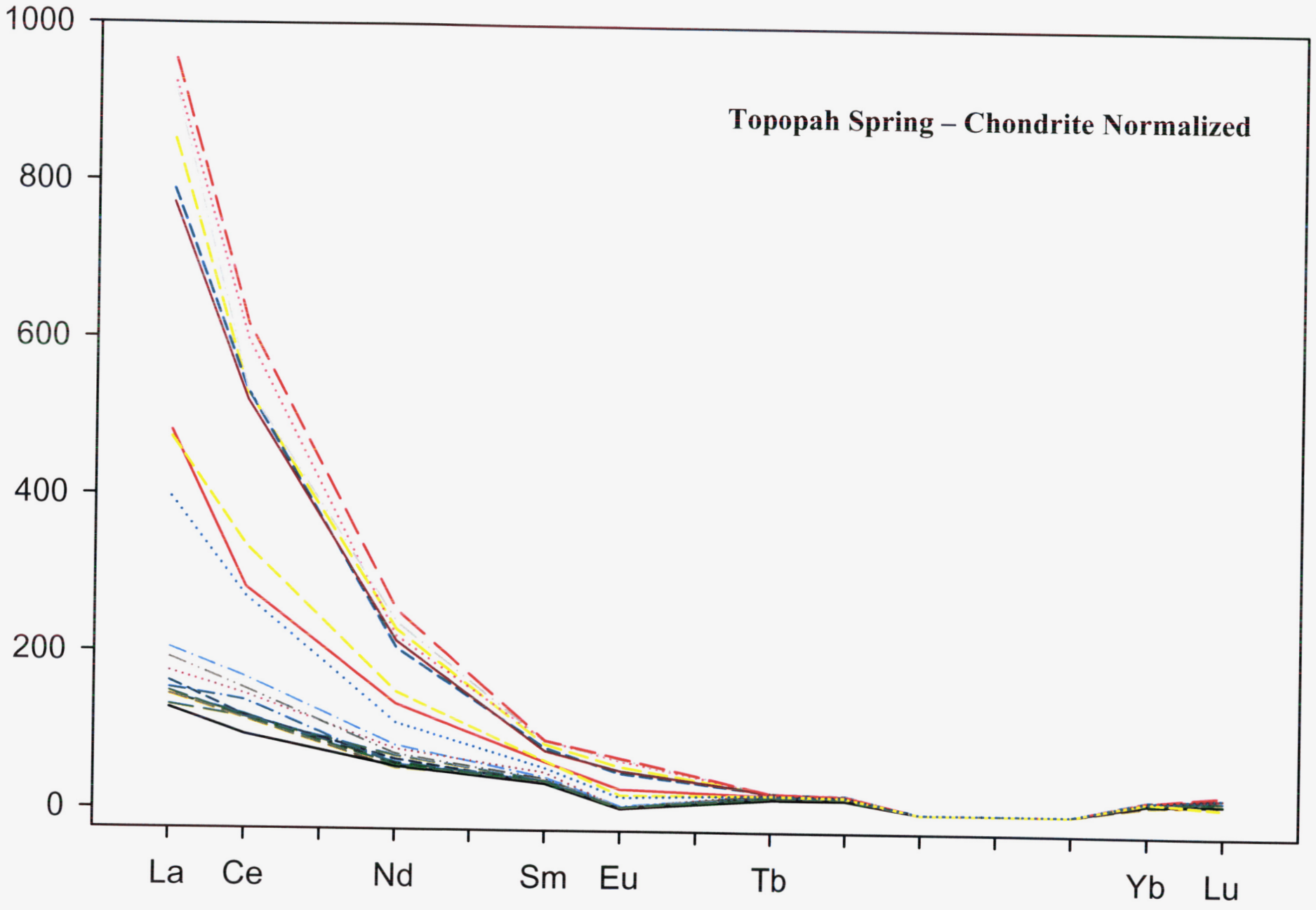
rare earth elements (REE) as analogues to the long-lived actinides is also evaluated in groundwater and rock samples at Olkiluoto (SW Finland).

V Marcos, N., 2002. *Low-temperature mobility of rare earth elements, U and Th at the Olkiluoto site, SW Finland.* Mat. Res. Soc. Symp. Proc. **713**, 825-832.

Johannesson K.H., Farnham I.M., Guo C., and Stetzenbach K.J., 1999. Rare earth element fractionation and concentration variations along a groundwater flow path within a shallow, basin-fill aquifer, southern Nevada, USA. Geochim. Cosmochim. Acta, **63**, 2697–2708.

Krauskopf, K.B., 1986. Thorium and rare-earth metals as analogues for actinide elements. Chemical Geology, **55**, 323–335.

9 Figures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800
600
400
200
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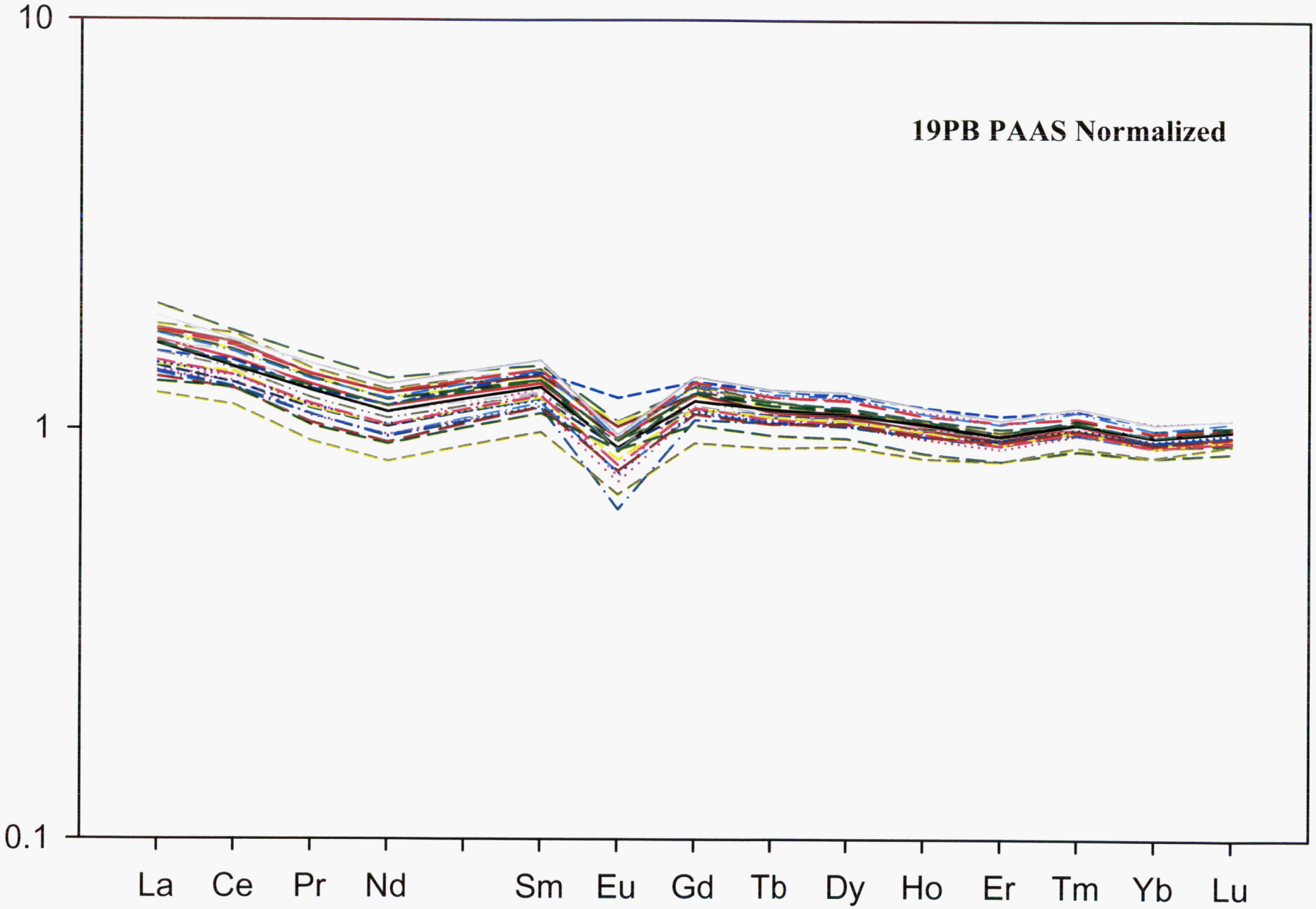
La
Ce
Nd
Sm
Eu
Tb
Yb
Lu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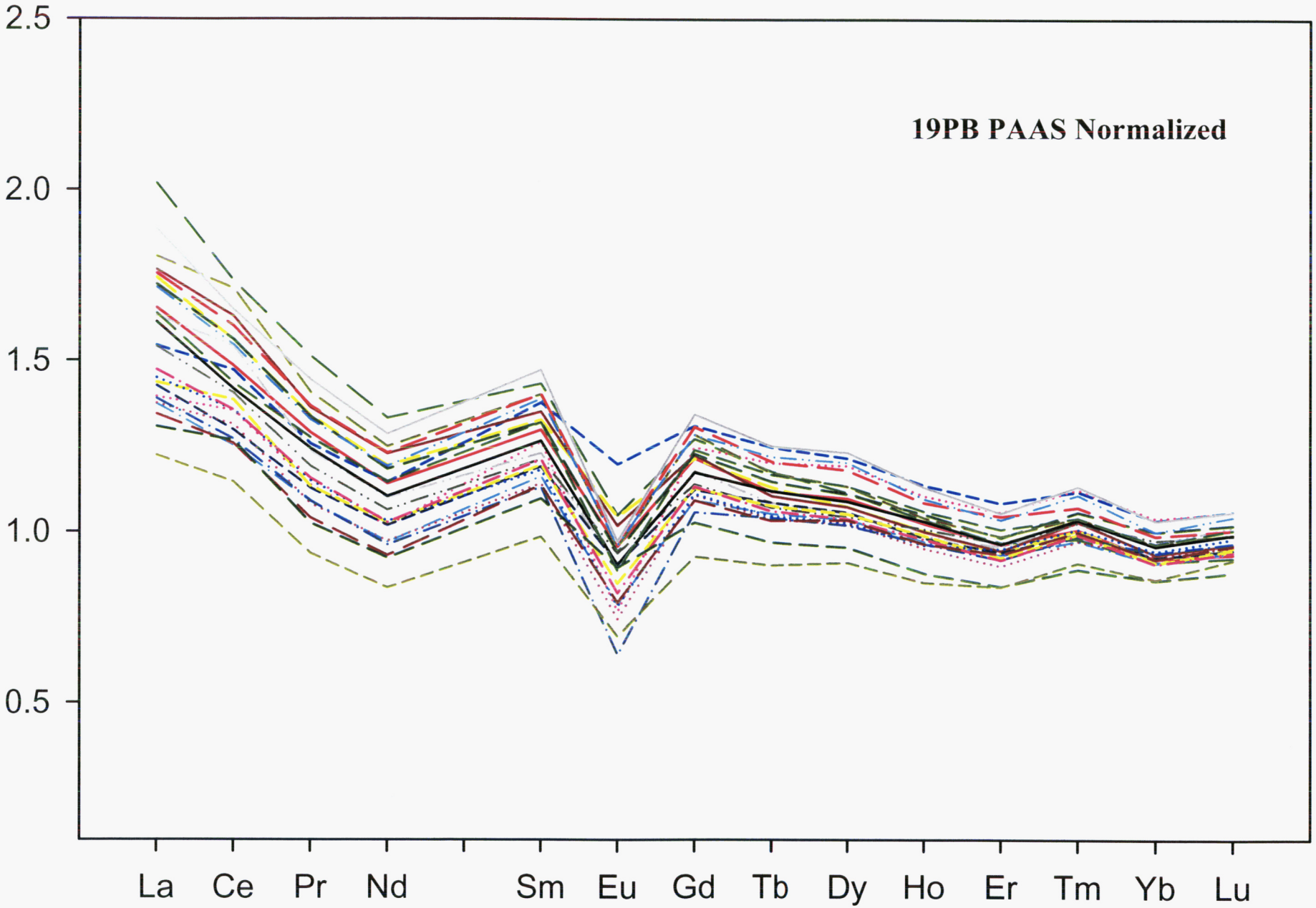
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu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2.5
2.0
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Ce
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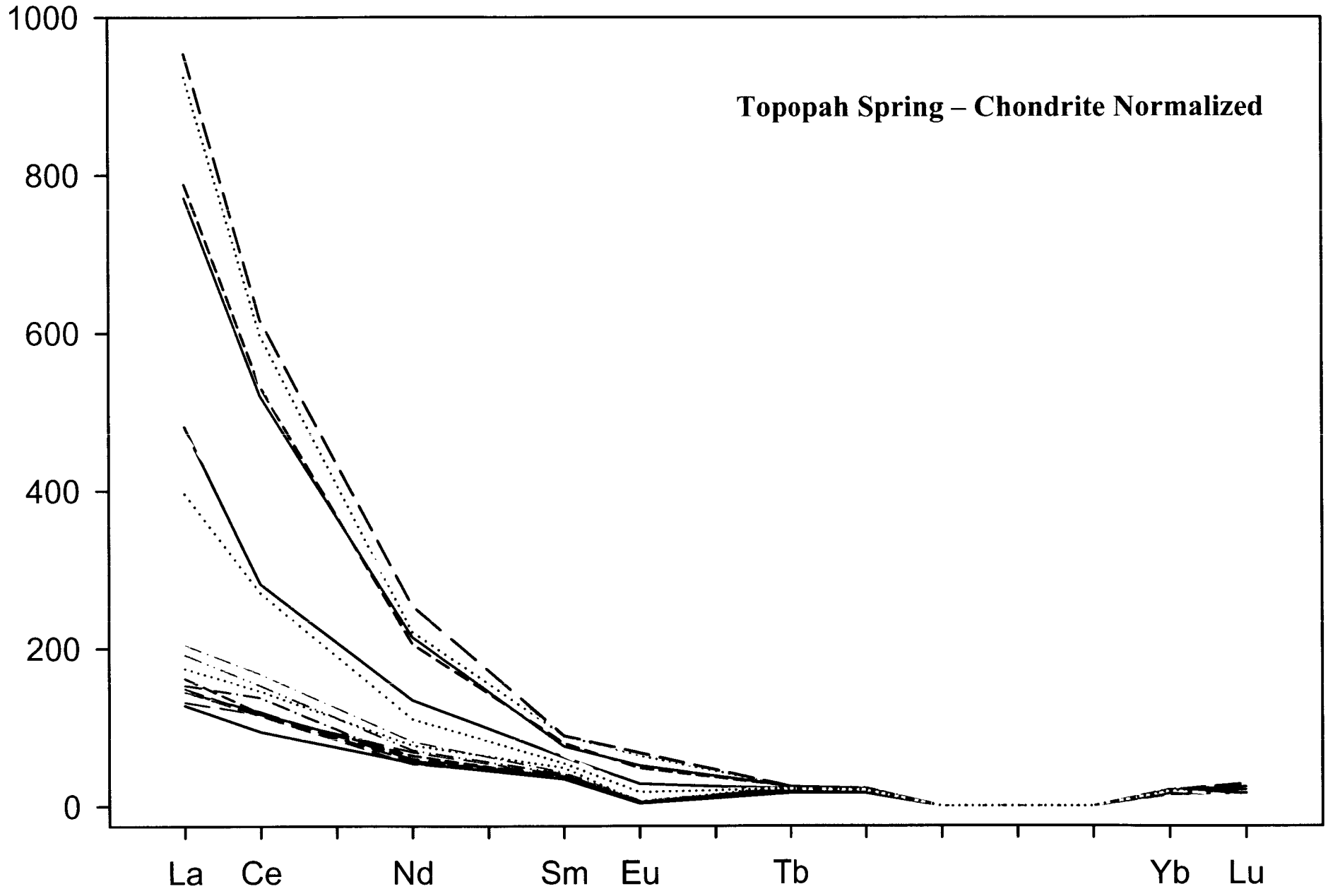
Tm
Yb
Lu


Topopah Spring – Chondrite Normalized
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Tb
Yb
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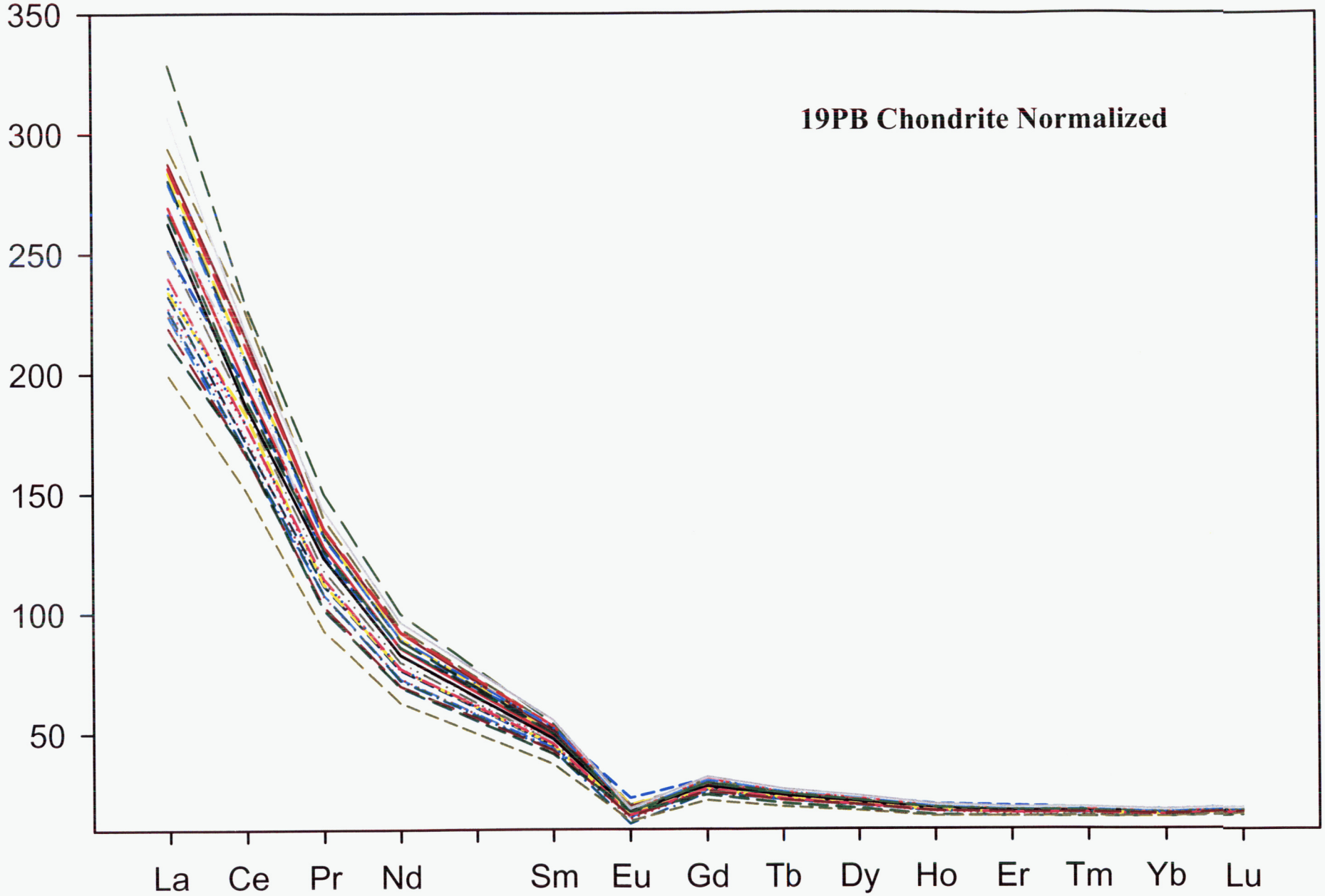
19PB Chondrite Normalized
350
300
250
200
150
100
50
La
Ce
Pr
Nd
Sm
Eu
Gd
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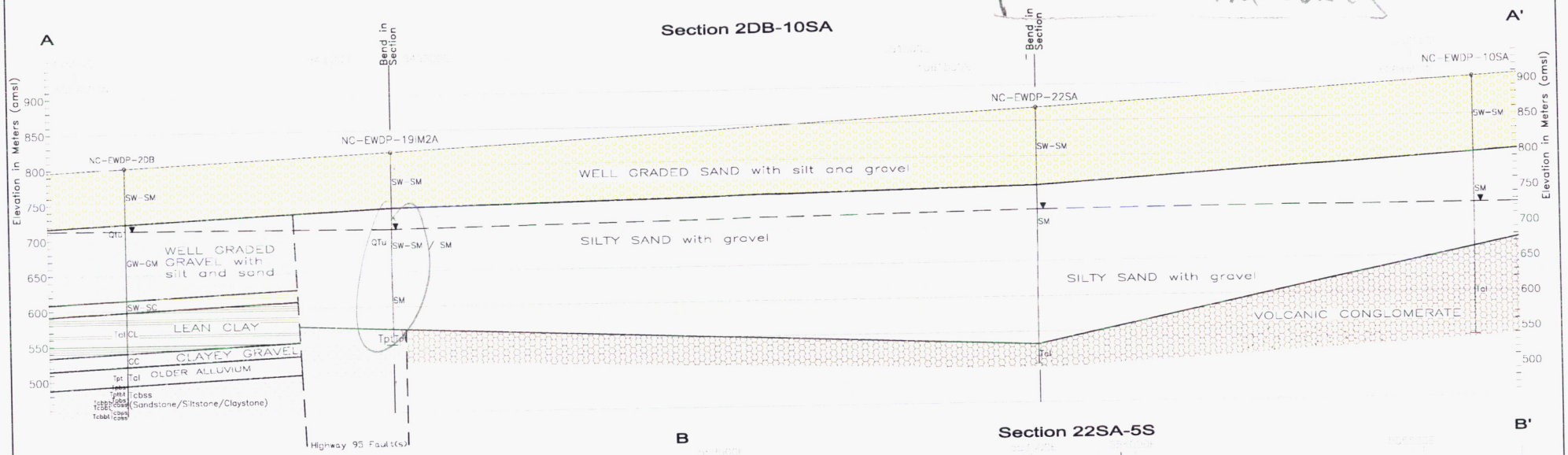
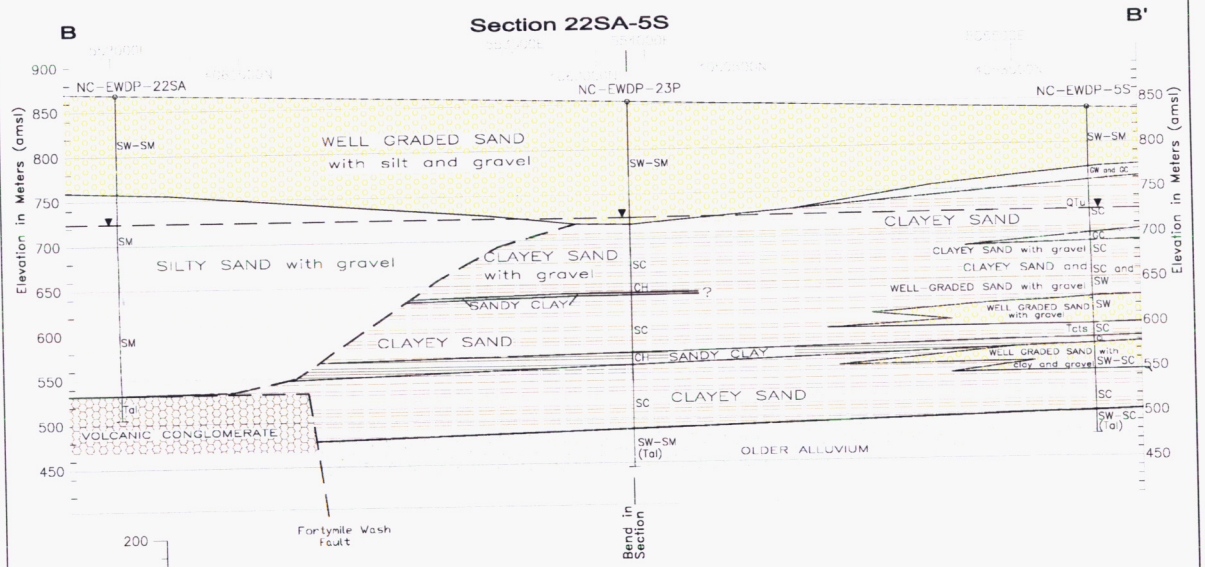
Ho
Er
Tm
Yb
Lu

water @ ~ 368 | 107 meters to 193 meters depth | Depth 351 634 feet. full sonic core interval





EXPLANATION

Symbols

- Geologic contact (Alluvium based on USCS)
- Geologic contact – inferred
- Geologic contact – facies boundary
- Subsurface fault – dashed where inferred
- Approximate water table

Borehole Name

Lithostratigraphic Unit (USGS) | USCS Unit (Nye County)

Lithologies

- Well graded sand with silt and gravel (SW-SM)
  Well graded sand with clay and gravel (SW-SC)
  Well graded sand and gravel (SW)
- Well graded gravel with sand (GW)
  Well-graded gravel with sand and silt (GW-GM)
  Well-graded gravel with sand (GW)
  Clayey gravel with sand (GC)
- Silty sand with gravel (SM)
  locally includes some SW-SM
- Clayey sand (SC)
  Clayey sand with gravel (SC)
- Sandy lean clay (CL)
  Sandy fat clay (CH)
- Older alluvium (Tal)
- Volcanic conglomerate (Tal)
- Volcanic units (Tpt, Tcbss)

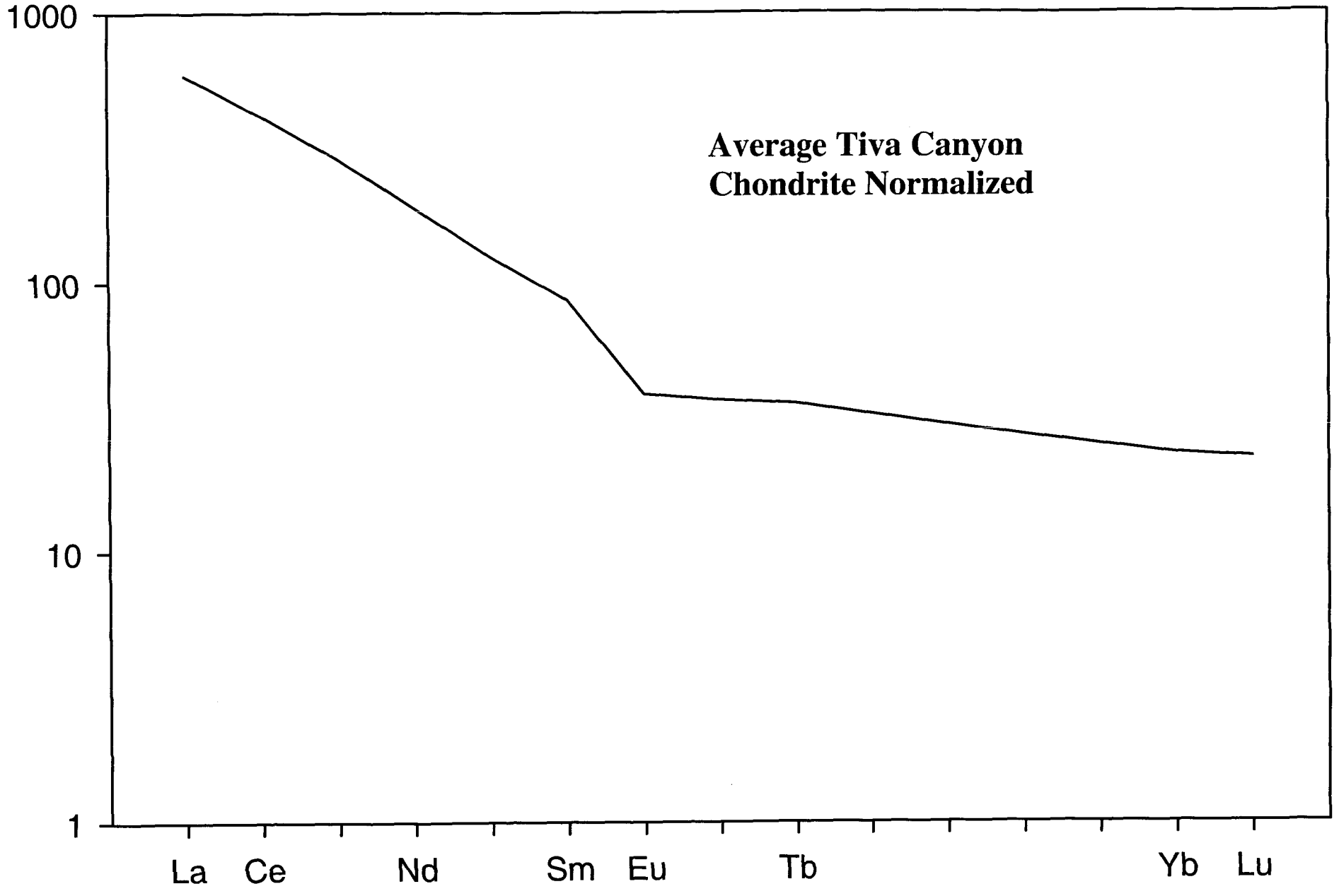
Notes:

1) Vertical exaggeration = 5x
2) Boreholes NC-EWDP-2DB and -5S alluvium descriptions based on non-quantitative methods.
3) Topographic profile is generalized.

Scale: 0, 100, 200 Meters; 0, 500, 1000, 1500, 2000 Meters

Nye County, Nevada
Nuclear Waste Repository Project Office
Early Warning Drilling Program
Alluvium Cross Sections
2DB - 10SA (A-A') and 22SA - 5S (B-B')
Base Map in NAD27 UTM Coordinate System

Date: 03/2003	Geologist: BW/JSW
	Drawn by: JSW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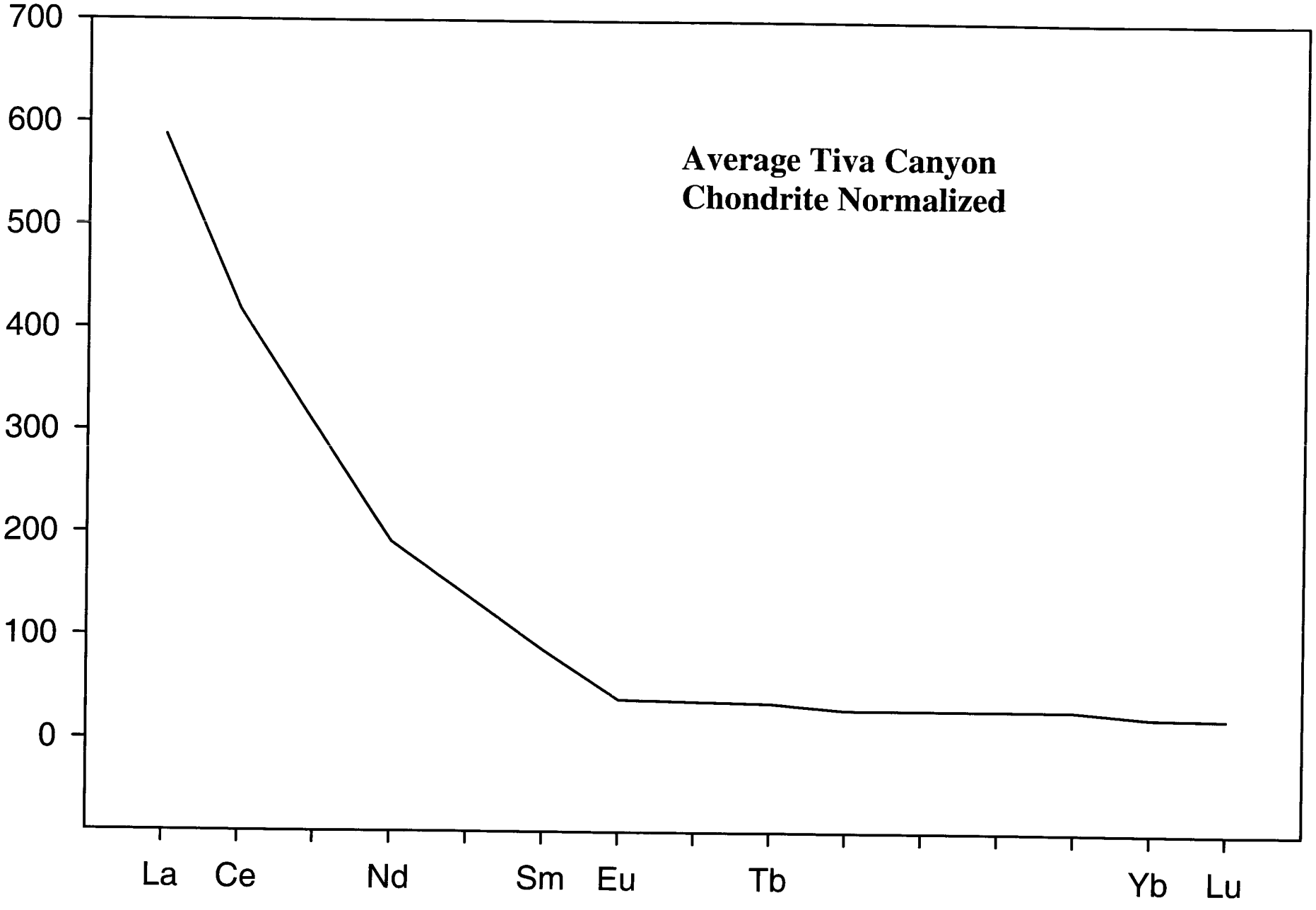
Chondrite Normalized
1000
100
10
1
La
Ce
Nd
Sm
Eu
Tb
Yb
Lu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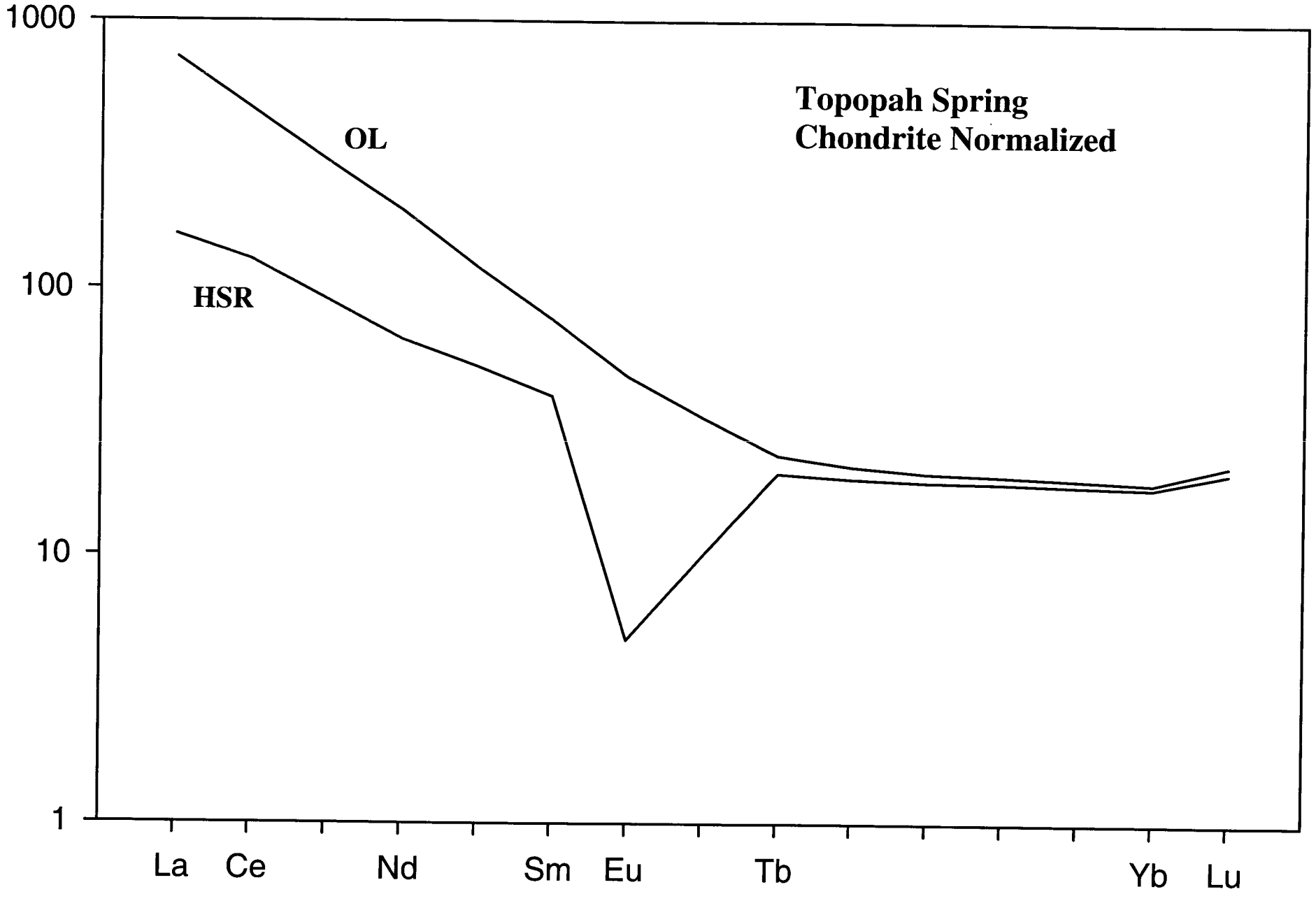
Topopah Spring
Chondrite Normalized
OL
HSR
1000
100
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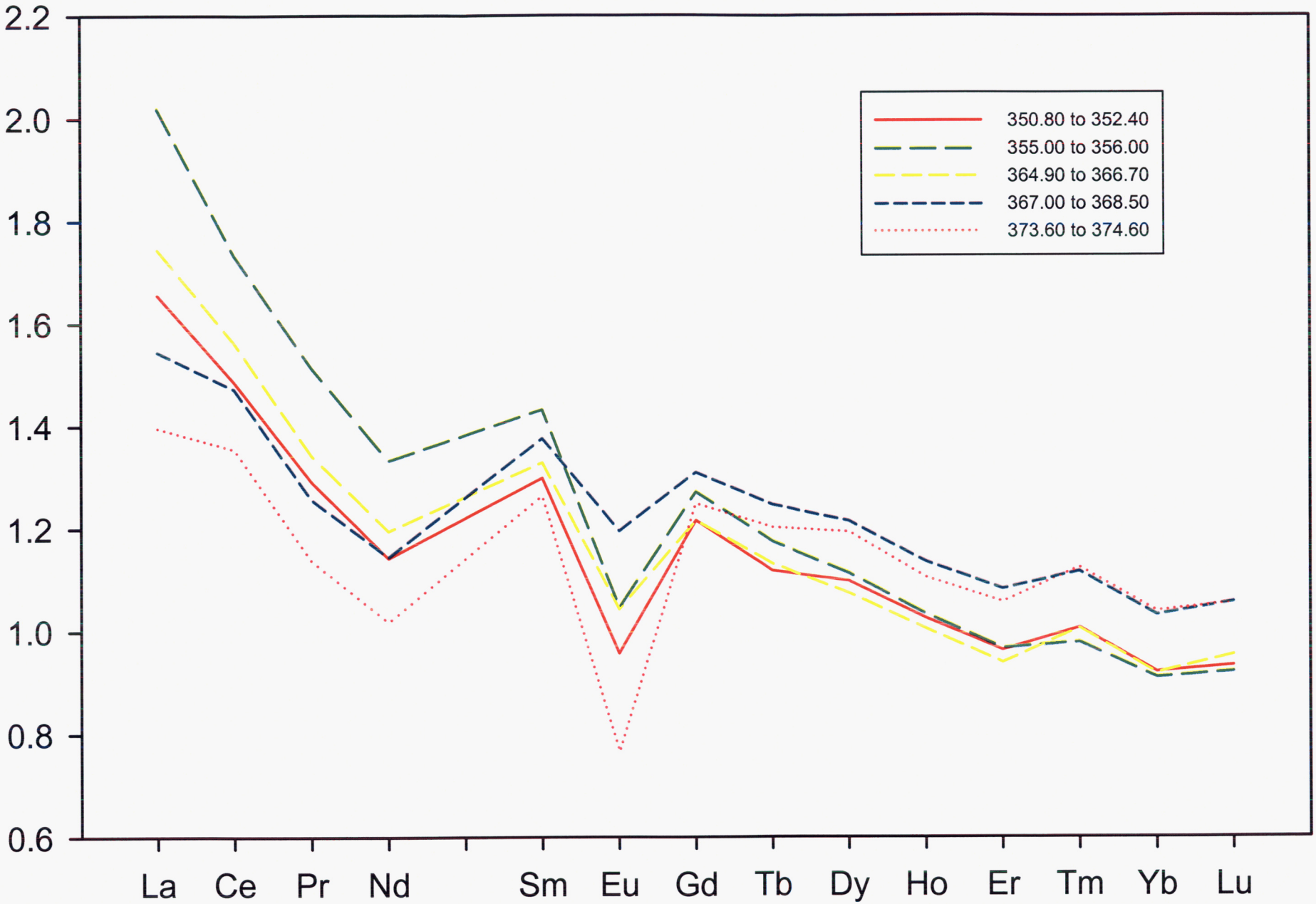
La
Ce
Nd
Sm
Eu
Tb
Yb
Lu

5 Figures

350 to 374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2.0
1.8
1.6
1.4
1.2
1.0
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Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
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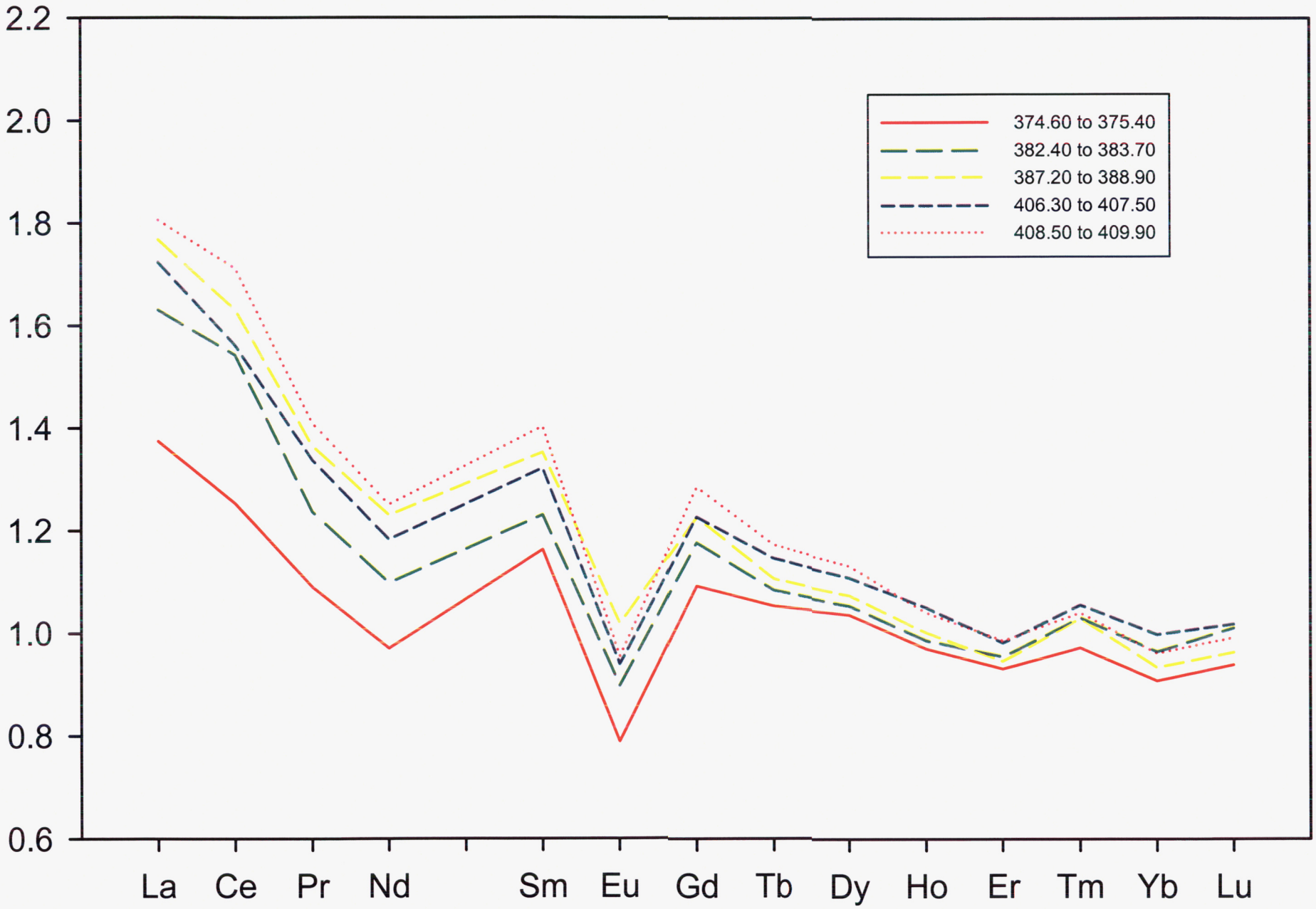
355.00 to 356.00
364.90 to 366.70
367.00 to 368.50
373.60 to 374.60

374 to 409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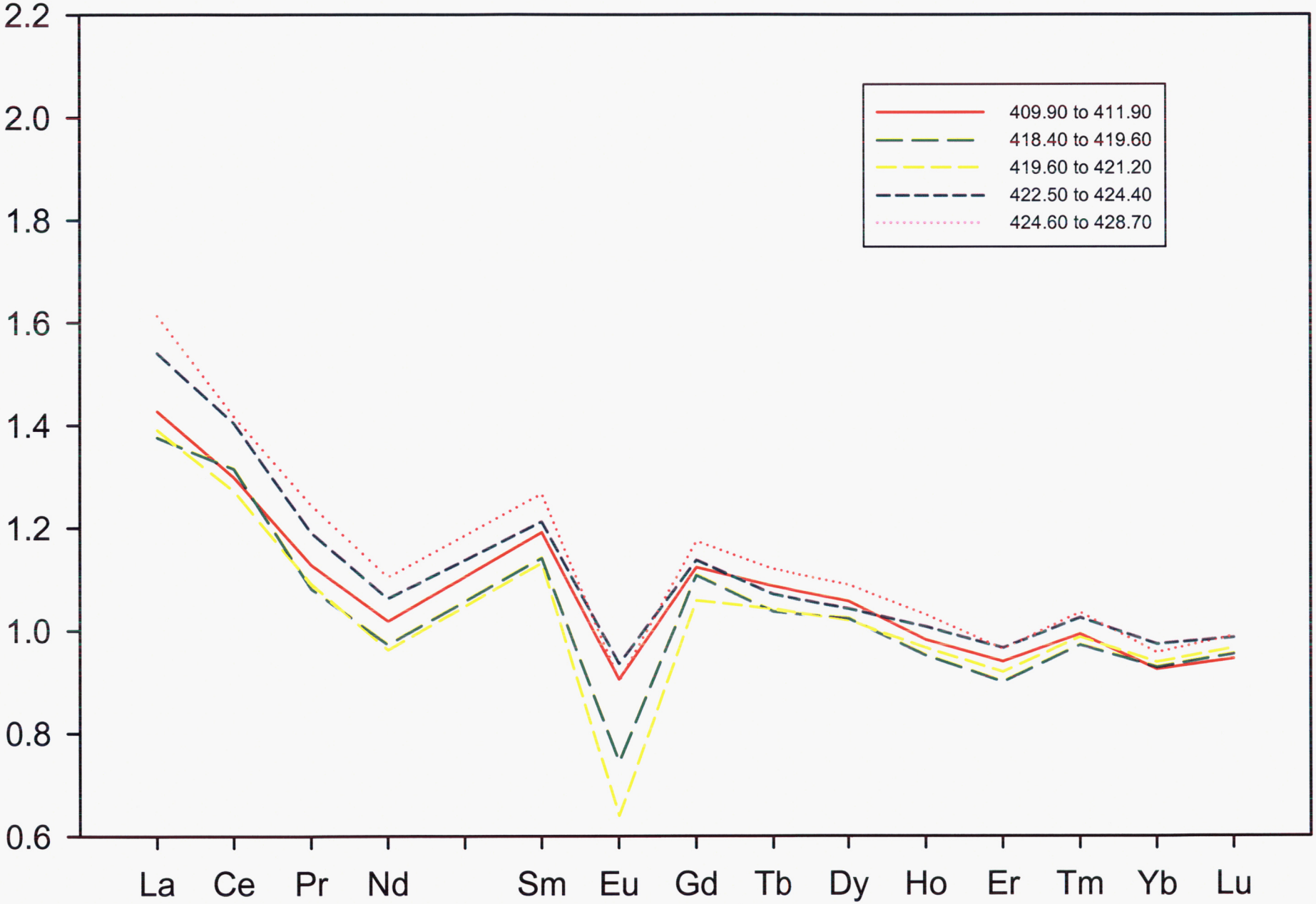
Yb
Lu
374.60 to 375.40
382.40 to 383.70
387.20 to 388.90
406.30 to 407.50
408.50 to 409.90

409 to 428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419.60 to 421.20
422.50 to 424.40
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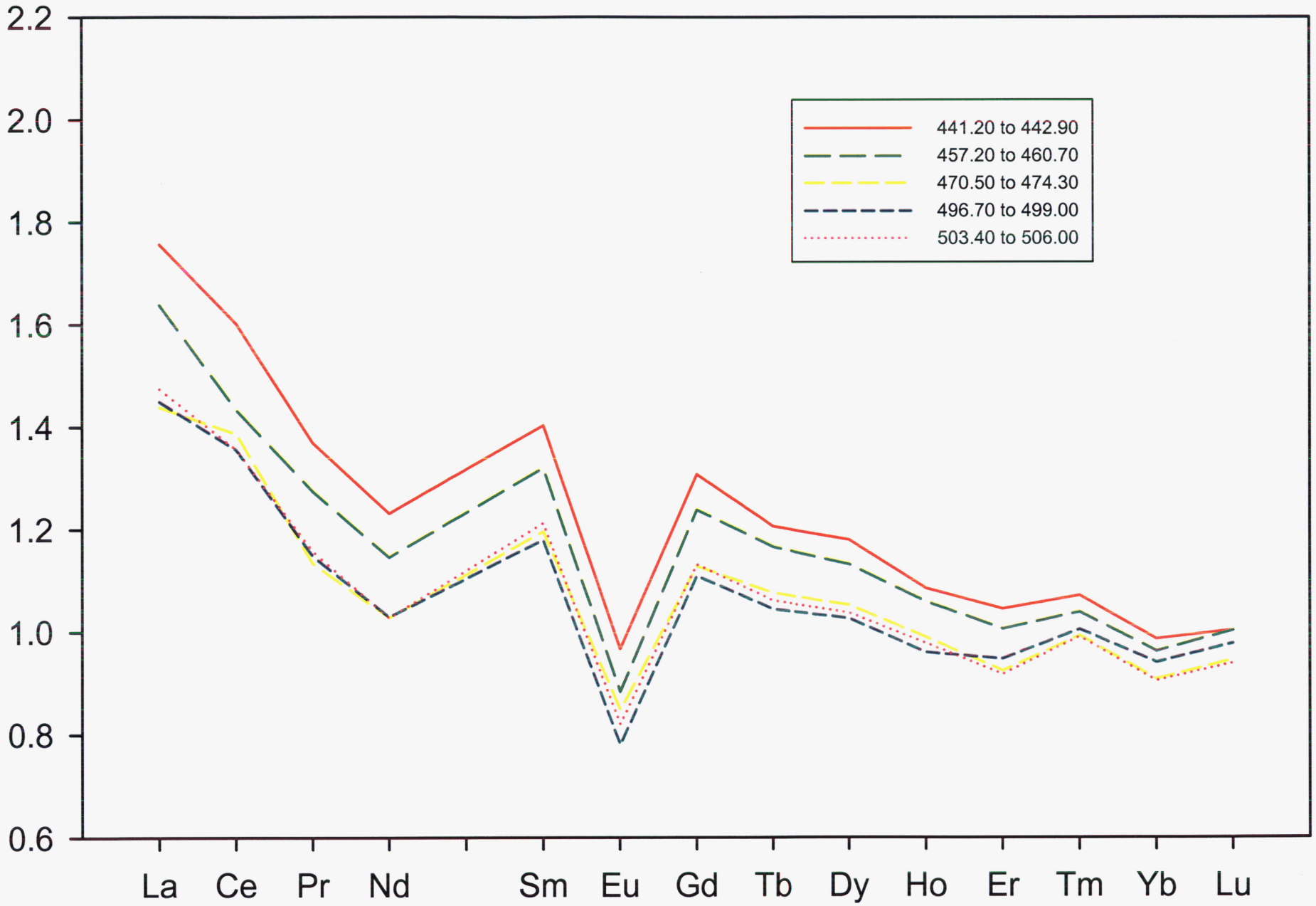
441 to 506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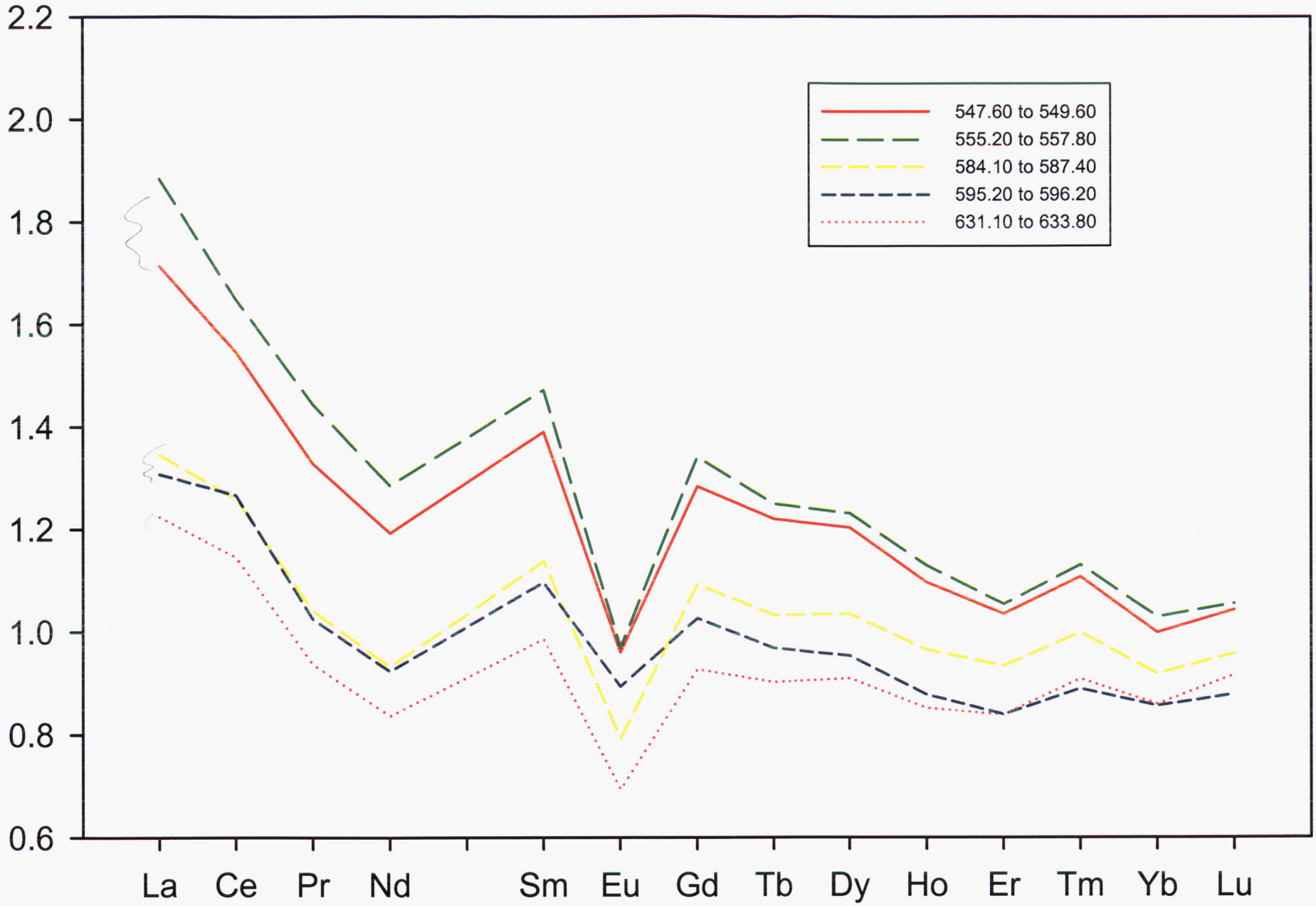
547 to 633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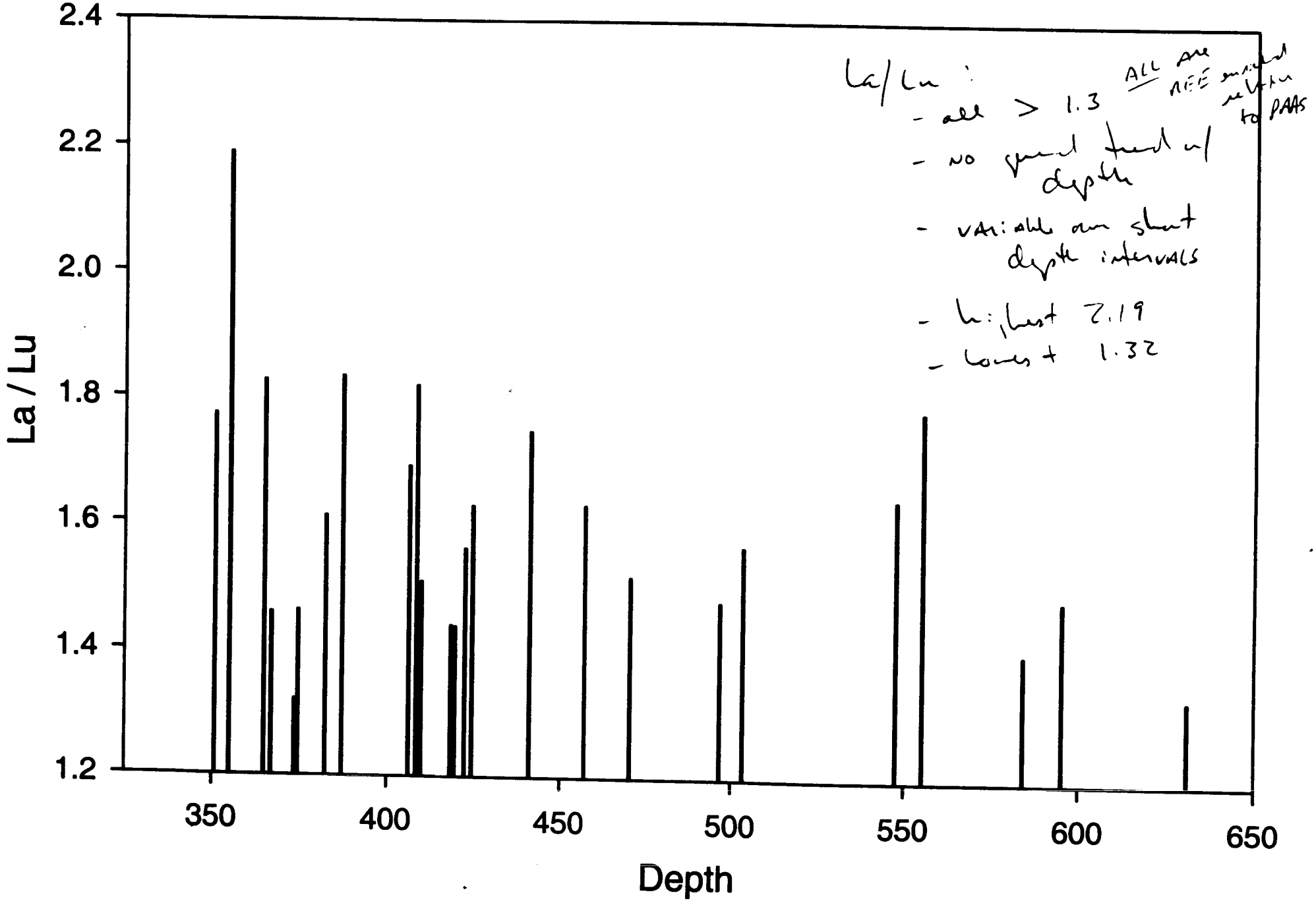
1 Figure


La/Lu
2.4
2.2
2.0
1.8
1.6
1.4
1.2
350
400
450
500
550
600
650
Depth
La/Lu:
- all > 1.3
ALL are REE enriched relative to PAAS
- no general trend w/ depth
- variable over short depth intervals
- highest 2.19
- lowest 1.32

PB REE Data

English,

100% Recycled Paper

As I clean up & close up Scientific Notebook here is final REE #s and summary figures, note highlighted #s are the correct values for those samples which underwent chemical separation. Originally sample 11.9/7.9 had >26,000 ppm U, clean $Al(OH)_3$ had 31 ppm U pretty good separation. All is documented in Scientific Notebook # 084

What's it all mean?

1) Figure Nopal Tuff is comparison of Aniel vs Us (sample Nop-ECP-1 Nopal formation)

Good!

2) Fig 2 Slightly Altered again comparison between Aniel (1991) Table 1 sample E & US

Good... no mobility according to her ... looks that way at least 2 m away from edge of deposit.

Fig 3 Strongly Altered

1) There is mobility in REE

a) Sample 11.9/7.9 is hottest ring sample along E-W traverse perhaps HREE slightly enriched (seen better in Fig 4)

b) Sample 17.0/7.5 is acid leached hole ALL REE were leached? seen in Fig 4

c) Sample 8.45/13.82 is in fracture 2.5 m from edge perhaps only LREE low & rest okay

Final Fig.

See leaching in hole & LREE low in fracture

HREE high in ring

So Long

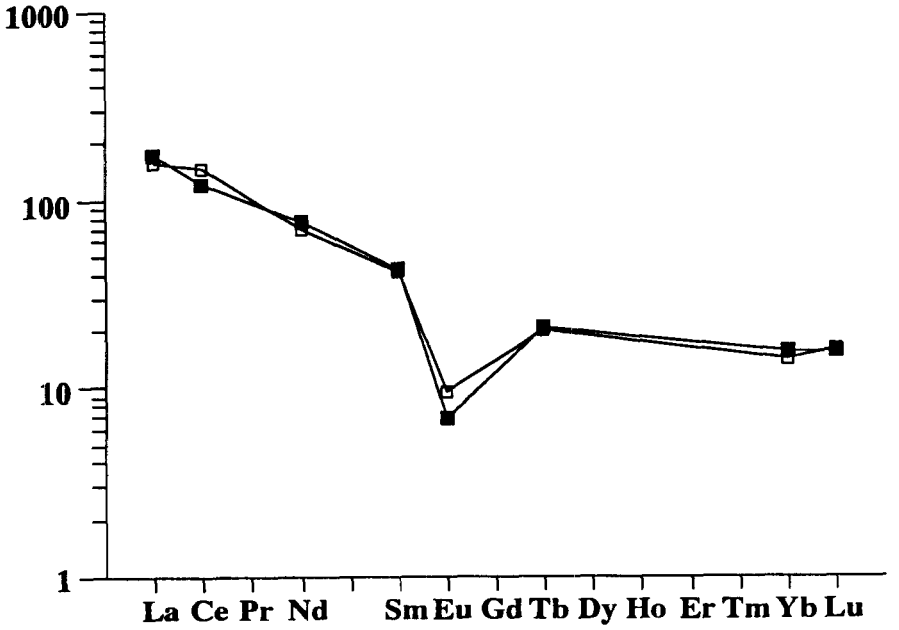
Bill

revised Nopal REE summa

Sample	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Hf	Ta	Th	U	Sc	ICP-Sc
Nopal Tuff	48.3	96.2	37.8	6.97	0.66		3.2	0.49	7.6	3.83	39.2	5.53	2.92	2.5
Aniel Nopal (f)	46	91		9.1	0.57	1.11	4.4	0.61	6.6	2.74	34.4	9.7		
An. N. (e)80 m	51	127	43	8.2	0.72	0.95	3.1	0.55	8.4	2.26	34.1	9.7		
9.7/7.35	57.5	107	49	8.67	0.67		3.38	0.53	8.19	3.59	42.8	15.7	3.16	3.1
11.9/7.9	48	153	47	13.3	1.2	2.42	9.9	1.36	9.3	0.74	56.7	49	6.94	4.4
mass corr 11.9	25.17	80.22	24.64	6.973	0.629	1.269	5.191	0.713	4.876	0.388	29.73	25.69	3.639	
yield corr 11.9	**30.359**	**96.768**	**29.726**	**8.4119**	**0.759**	**1.5306**	**6.2615**	**0.8602**	**5.882**	**0.468**	**35.861**	**30.991**	**4.3894**	**0.82699**
17.0/7.5	59.2	94	25	4.04	0.2	1.9	3.1	0.48	9.5	0.58	45.8		16.3	9.4
corr 17.0	21.4	33.9	9.02	1.46	0.07	0.69	1.12	0.17	3.43	0.21	16.5		5.88	
yield corr 17.0	**34.138**	**54.205**	**14.416**	**2.3297**	**0.1153**	**1.0956**	**1.7876**	**0.2785**	**5.4781**	**0.3345**	**26.41**		**9.3993**	**0.62556**
8.45/13.82	39.1	77	33	12.6	1.45	5	5.7	0.74	7.7	0.75	214		24.6	
corr8.45	15.4	30.3	13	4.95	0.57	1.96	2.24	0.29	3.03	0.29	84.1		9.67	
avg yield corr	**21.341**	**42.026**	**18.011**	**6.877**	**0.7914**	**2.729**	**3.111**	**0.4039**	**4.2026**	**0.4093**	**116.8**		**13.427**	**0.72**

Bret Leslie 12/8/93

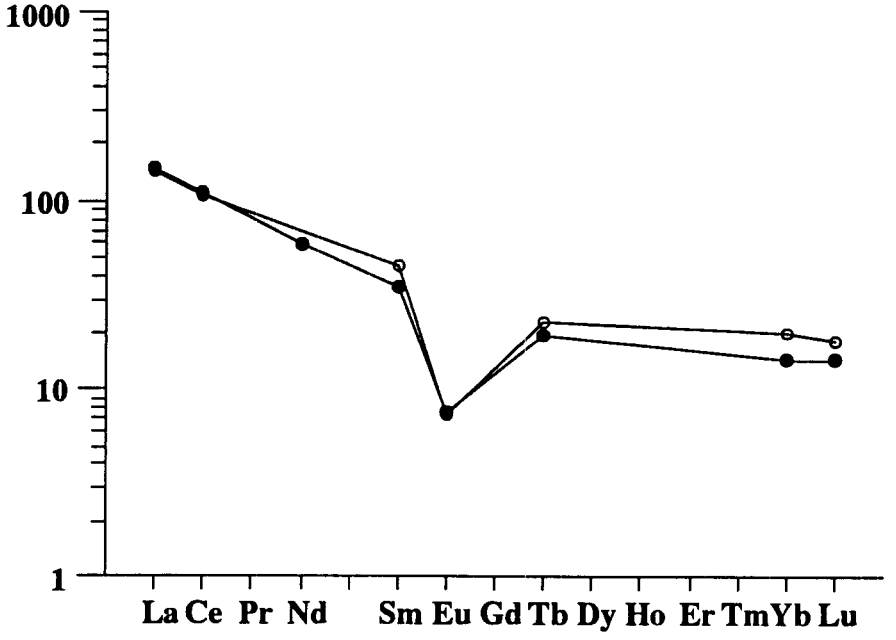
Chondrite-normalized REE (Nakamura 1974) for Slightly Altered Nopal Tuff



Legend

- ▫ Aniel Nopal Sample (e) 80 m away
- ■ NOPI-94 9.7/7.35

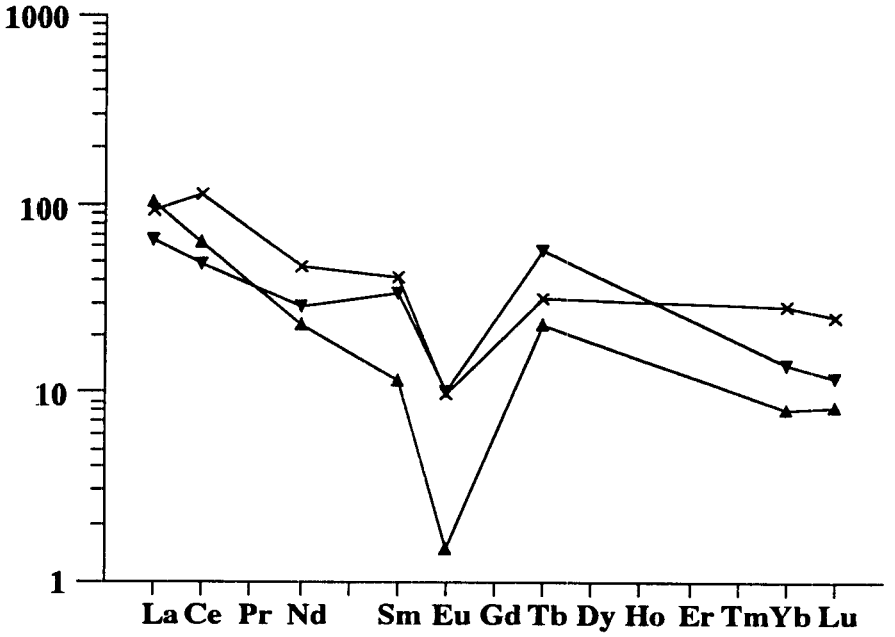
Chondrite-normalized REE (Nakamura 1974) for Nopal Tuff



Legend

- ● Nopal Tuff
- ○ Aniel Nopal Sample (f)

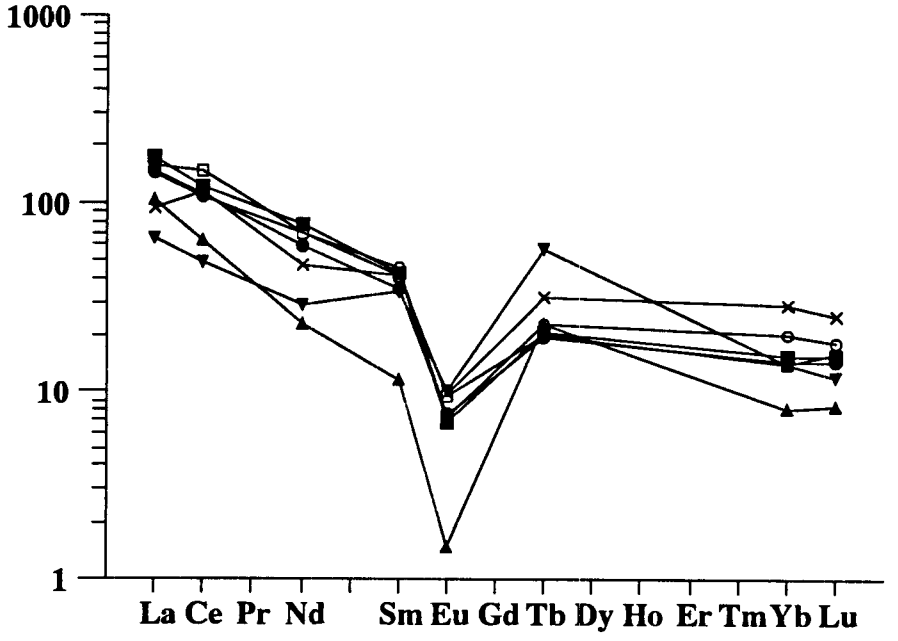
Chondrite-normalized REE (Nakamura 1974) for Strongly Altered Nopal Tuff



Legend

×	NOPI-90	11.9/7.9
▲	NOPI-81	17.0/7.5
▼	NOPI-140	8.45/13.82

Chondrite-normalized REE (Nakamura 1974) for All Nopal Samples



Legend

- ● Nopal Tuff
- ○ Aniel Nopal Sample (f)
- □ Aniel Nopal Sample (e) 80 m away
- ■ NOPI-94 9.7/7.35
- × NOPI-90 11.9/7.9
- ▲ NOPI-81 17.0/7.5
- ▼ NOPI-140 8.45/13.82

ADDITIONAL INFORMATION FOR SCIENTIFIC NOTEBOOK NO. 084

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