

Interactive comment on “Glaciochemical investigations on the subterranean ice deposit of Vukušić Ice Cave, Velebit Mountain, Croatia” by Z. Kern et al.

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Response to Dietmar Wagenbach and Michele Citterio

First of all we would like to say thanks to our Referees for their valuable comments and critics on the manuscript. We accept the Referees' critics that some basic information is still missing for a more secure interpretation of the stable water isotopes so we omit this part of the manuscript. Consequently, our reply will focus only on those comments relevant for the revised version. When almost both Reviewers addressed the same problem their comments are listed and the following response refers to both.

Comment from Dietmar Wagenbach: Information on the chemical (and isotope prop-
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erties) may either be used to infer processes which are related to the formation and dynamics of such ice bodies or to assess the environmental and climate significance of the archived signals. However, the introduction does not provide the purpose (or any main objective) of the study.

Authors' response:

A new paragraph is added to define the purpose of the study.

Comment from Dietmar Wagenbach: Instead the authors give here the a priori notation that: They (ice deposits)... "offer a unique alternative to decipher comparable palaeoenvironmental information (e.g. air pollution history) like Alpine glaciers" - which is by no means warranted at this stage.

Authors' response: Introduction is rewritten, taken also consideration Michele Citterio's comments. The focus of the introduction is changed.

Comment from Dietmar Wagenbach: The reader is lost since almost no setting of the cave environment relevant for the impurity sources and the expected governing ice formation processes are given (except, some scattered indications coming lately at the end of the paper). At least basic information on the sampled ice block (including a glaciological and stratigraphical characterisation) is essential here. For example, I wonder how (wind blown) snow and soil dust being trapped in the ice covered cave section might have influenced the results.

Authors' response:

Site description paragraph has been completed with the demanded information.

Comment from Dietmar Wagenbach: Supporting data which are needed to characterize the sampled ice core sequence remained largely inconclusive or blurred: (a) given radiocarbon date but not addressed at all, (b) lack of a statement, at least, on the assumed, characteristic time resolution of the depth profiles (estimated from the two tritium tie points and outstanding stable water isotope cycles)

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Comment from Michele Citterio I. 26-28: unfortunately these radiocarbon dates are pretty inconclusive

Authors' response:

The sole radiocarbon date is omitted and the estimated time resolution of the depth profile is discussed in the revised version.

Comment from Dietmar Wagenbach: The reliability of the minor trace element data is unclear: (a) What are the contribution of blanks, associated uncertainties and detection limits related to the whole analytical procedure (not just the ICP-MS one). In this context, the authors should be alarmed by the relatively high Zn level (sensitive to contamination), the generally high variability and the frequent disproportion among crustal elements (except Ca, Mg). Moreover, the operational defined restriction to the "non-filterable" fraction (at neutral conditions) is not addressed.

Authors' response:

Determination of the procedural blanks has been inserted into the relevant methodological section. The restriction to filtered fraction has been mentioned both in the relevant methodological section and at the Results section as well.

Comment from Dietmar Wagenbach: The comparison with other trace element data (precipitation, Alpine firn) is largely incomplete and not representative (refer among others to: Barbante et al. J. Anal. At. Spectrom., 1999, 14, 1433–1438; P. Gabrielli et al. Atmos. Chem. Phys. Discuss., 6, 8781–8815, 2006 and various precipitation networks).

Authors' response:

Data for the Eastern Italian Alps in Barbante et al. 1999 and in Gabrielli et al. 2006 is exactly the same as the Gabrielli et al. 2008 dataset and this latter has already been used in the original version. In addition a new glaciochemical data has been published from Mt. Ortles, a relatively near high elevation site (Gabrieli et al. 2011

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Atmos. Chem. Phys. Discuss 11, 6493–6530, 2011) we included also this dataset into the comparison. As Na and K have been added to the cave ice dataset we could include these species into the comparison to the Zavizan precipitation chemistry. We have found hydrochemical data for the soil solution from the North Velebit. In addition Iskrba (Slovenia) is also included as Iskrba is the nearest site where heavy metal measurements are available from the EMEP network.

Comment from Dietmar Wagenbach: Moreover, the formal PCA results appears to be strongly biased by the outstanding "dust horizons" at around 1.2-1.7m and the overall trends within the PC2 (Zn, Cu, Cr) group.

Authors' response:

PCA analysis has been repeated excluding the samples (VS4.6, VS6.1, VS6.2) showed unusually high concentration. The results showed the same pattern as before proving that the PCA results are robust. The PCA pattern from this repeated analysis will be also included into the revised figure to support the interpretation.

Comment from Dietmar Wagenbach: There is no observational evidence presented warranting the statements that, among others: (a) changes of non local bedrock species are related to atmospheric ones, (b) long term Zn and Cu agree with respective deposition trends (c) the level of various trace species are consistent in with those observed at other sites.

Authors' response:

Discussion is expanded taking into consideration the newly added data.

Comment from Dietmar Wagenbach: Reduce the given numbers to their significant digits, particularly in Table 1. In view of the strongly skewed data distribution the arithmetic mean and SD presented in Table 1 are not appropriate entries. Add some information from descriptive data statistics (e.g median, quantiles, min./max, etc.).

Authors' response:

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Mean, median and min/max are presented in the revised table to better characterize the distribution of the glaciochemical data. See revised Table 1 below

Comment from Dietmar Wagenbach: indicate meaning of grey areas in figure 1

Authors' response:

The grey shading is Croatia. It is indicated in the figure. See revised Fig 1 below.

Comment from Dietmar Wagenbach: Revise figure 2 as providing a more useful picture on the cave topography and the immediate environment of the sampled ice block (among others, indicate the vertical scale and address the displayed contour lines in the present sketch)

Comment from Michele Citterio: Fig. 2: please add some detail topography of the cave surroundings

Authors' response:

This figure has been completed. See revised Fig 2 below

Comment from Dietmar Wagenbach: Figure 5 illustrating the formal ^{14}C date calibration is obsolete here.

Comment from Michele Citterio: Fig. 5 is not necessary

Authors' response:

This figure is left from the revised version.

Comment from Dietmar Wagenbach: In illustrating the depth variability of selected trace elements, the logarithmic concentration scale deployed in figure 9 is not useful. Display the data on a linear scale e.g. normalized to the overall mean (again, preferentially as histograms). There is an obvious imbalance between the amount of external (supplementary) data shown in figures to the ice related ones. Thus, strictly reduce these figures to those really needed (a good deal of relevant findings displayed in the

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external material may be certainly replaced by a concise sentence).

Authors' response:

The number of plotted element profiles has been reduced. Linear scale is applied in the revised version.

Comment from Dietmar Wagenbach: The presented Supplementary Material made up by an uncommented exel file (even lacking units) is anything else than a useful addendum.

Authors' response:

Unit is $\mu\text{g g}^{-1}$ in the Supplement, too. This information is given in the revised file.

Comment from Michele Citterio p.1563 l.3-7: These sentences can be misleading to a majority of TC readers who may not be familiar with cave climate. Air temperature in caves does not track the surface climate in a simple way. The most obvious effect is the delay and damping of the surface temperature signal due to the thermal inertia of the rockmass. However what is most important here is that the underground air circulation (the very reason perennial cave ice can exist at much lower elevations than the regional glacier equilibrium line) also makes cave ice respond in a different way to surface climate, so making comparison of cave ice and surface glaciers is not straightforward. Typical cave ice deposits are found either at the bottom of single-entrance descending caves ("cold traps") or close to the lower entrance of multi-entrance caves or cave systems. In both settings, the hypogean air circulation makes for colder cave temperatures than the mean annual air temperature at the same elevation outside the cave. For cold traps in particular, the cave temperature is mostly dependent on winter surface ice temperatures and is largely unaffected by summer air temperatures, which instead affect glacier mass balance the most.

Authors' response:

The Introduction is rewritten, taken also consideration Dietmar Wagenbach's com-

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ments.

Comment from Michele Citterio p.1563 l. 17- p. 1564 l.16: In this section there are two fundamental misconceptions that are reiterated and come into play later and undermine most of the discussion and conclusion sections: 1) while cave ice may be impermeable to surface meltwater (and even this could not be entirely true, as I have observed many times that hydraulically connected water films do form at crystal boundaries, at least in coarse grained cave lake ice) the water that reaches inside a cave and freezes can not be assumed to have the same composition of the meteoric water. This is one reason cold snow and firn from high altitude Alpine glaciers are so much more desirable. The manuscript doesn't take this problem into any consideration. There is no mention of what kind and how extensive the soil cover is in the cave surroundings, no information on groundwater, on the amount and seasonality of infiltration and dripping in the cave, and so on. Indeed, the high Ca and Mg reported later on demonstrate just how large the contamination from the carbonatic environment can be. Many other ions discussed throughout the manuscript may be either enriched or depleted by a soil horizon above the cave. 2) the other reason why this cave ice can not be assumed to be of similar use (and by no means can be interpreted along the same lines) as cold Alpine firn is that there seem to be no knowledge of the stratigraphy of the ice deposit. Firn layers high in the accumulation zone of a glacier may be expected to be reasonably continuous laterally, while cave ice of the type described here is typically very discontinuous laterally, because it forms from the freezing of thin water films flowing along the steepest gradient on the previous year's ice and typically resulting in lenses and "onion like" structures. The only type of cave ice that could be suitable is lake ice, where the original layer surface is known to have been flat and level. Here no information of the ice structure and stratigraphy is provided, not even generic descriptive terms. This makes very problematic to attach any stratigraphic or temporal meaning to depth below the surface, and consequently to interpret the ice core data in any meaningful way.

Author's response:

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Referee is right inasmuch as cave ice deposit formed from lake ice has much simple stratigraphy. However, we cannot agree with the Referee's statement: "The only type of cave ice that could be suitable is lake ice" as a nice recent example see: Stoffel et al. 2009 Quaternary Research 72: 16-26. From our viewpoint cave ice from non-lake origin with "onion like" structures" could also be suitable for environmental studies however much more dated levels and more complex age-models should be employed to infer a reliable chronological constraint. Nevertheless the criticised paragraphs have been rewritten or partially deleted from the new version.

Comment from Michele Citterio I. 10-13 the description does not match the field survey in Fig. 2, as in the figure it is clear that the ice in 1962 was not in contact with the rock on one side (and it wasn't in 2008 as well). The only reason for this can be active air circulation, as this gap between rock and ice is otherwise in the lowest part of the cave and most removed from the surface, which should be the coldest part and the favourite place for water to flow and freeze. Therefore I do not believe this to be a static cave as stated in the manuscript.

Authors' response:

The cave description is improved. In addition, we have never observed outward summer ventilation at the lower entrance in Vukušić Ice Cave and no any other speleologists mentioned that whom we could contacted. This is the reason why we had written in the manuscript that "There has not been available year-round ventilation data yet, however the system is thought to be classified as static cave." To further clarify this situation we will put in the text that: "Vukušić Ice Cave seems to be static cave because we did not notice any outward air circulation in summer during our explorations but we can not completely exclude dynamic ventilation."

Comment from Michele Citterio I. 14-15: here is another misconception: even assuming the 1962 survey of the ice surface was really this accurate (also, in which month was the 1962 survey carried out?), there is no information of the seasonal variability

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of the ice surface, so the -20 cm 1962-2007 and further -6 cm 2008-late autumn 2008 are very impossible to interpret. The deposit may have fluctuated by much more than those 20 cm since 1962 and there would still be no stratigraphic evidence that the ice exposed in 2008 at a lower level than the 1962 surface is indeed older. It may well have melted one meter below the 1962 level and then accumulated again, with no way to tell until some stratigraphic work is done. As a bare minimum, is there any visual stratigraphy info from the ice core? When several such fluctuations could have occurred, the tiny evidences of the tritium activity are too little to support any further conclusion

Authors' response:

The date of the 1962 survey is late summer, of the 2007 and 2008 surveys is October. So the interannual ice dynamics unlikely to have severe impact. In addition, there is some additional information about the cave glaciation. Another cave survey is available from 1996 where higher ice level is indicated however we have considered that those survey must documented an earlier stage of the interannual ice surface cycle as extensive ice ornaments are also reported from the cave wall which is typical during (late) spring. Hence we omitted this cave map (see also Kern et al. 2008). In addition, we have some personal communication from Croatian cavers that cave ice in the Vukušić Ice Cave has not shown any large fluctuations during the past decades.

Comment from Michele Citterio p. 1565: the cleaning of the core should preferably be performed in the lab, unless transporting the ice frozen is unfeasible. Here it should have been cleaned again once arrived in the lab to provide the best assurance.

Authors' response:

There was no possibility to clean the frozen cores in cold room conditions. So we have to agree with the Reviewer that transporting ice in frozen was pointless. As I had been afraid of this situation we decided to make the potentially most cautious field cleaning (precleaned one used plastic knives, precleaned sample holders, large volume ultrapure water transported into the cave and washing down the plastic glove between

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each sample)

Comment from Michele Citterio p. 1566-1568: shorten these

Autors' response:

We have shortened this part.

Comment from Michele Citterio p. 1567: it's a pity that some major ions have not been measured: at least Na⁺, K⁺, Cl⁻, NH₄⁺, SO₄⁻ should have been included to allow better interpretation of the trace elements. E.g. are the enriched U samples associated to higher clay silicates or to organic matter? K may have helped, as the association with Al values suggests contrasting evidences here (could it be that the filtering of the water altered some results?). Na⁺, Cl⁻ and SO₄⁻ would have allowed better analysis of the marine signal, and so on. If these data are available but were not included here, please consider including them in any future re-elaboration of this manuscript.

Authors' response

We have measured and included Na and K. Cl cannot be measured with ICP-MS. Ion chromatography should be applied to measure Cl⁻ and the other two mentioned complex anions (ammonium, sulphate). As regard the potential contamination due to filtering. We prepared comparative blank pairs. For the first series we measured milliQ water+acid, for the second series the milliQ water was filtered and after acidified. Compared the pairs it can be seen that filtering introduced some contamination for Ca, Na, Mg, Zn. However the latter blank series were employed as procedural blank and the corresponding blank values have been subtracted from the measured cave ice values to determine the final concentration.

Comment from Michele Citterio p. 1570 l. 8-16: This is all very much speculative and not really supported by data, furthermore any consideration based on the 6 cm/yr (mm/yr?) is very shaky as this loss rate is based on nothing more than the two points in time 1962 and 2007, and everything may have happened in between (see my other

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comment above).

Authors' response:

See the response above.

Comment from Michele Citterio p. 1573 l. 15-16: Ca and Mg are not trace elements in the carbonatic environment, and the reference is both useless and misplaced.

Authors' response:

The sentence is corrected.

Comment from Michele Citterio: p. 1574 l.6: yes, the very high Ca (and Mg) contents are indeed a clear signal from the local carbonatic bedrock, and both the finding of elevated values in cave ice and the very same interpretation suggested here have previously been published in Citterio et al. 2004b, so please fix this entire sentence.

Authors' response:

It is true that the high enrichment of Ca and Mg in cave ice has been observed by Citterio et al. 2004 already. We have mentioned this and cited the paper properly. However, they have not regarded Sr and have not compared the cave ice Ca/Mg ratio to the ratio derived from precipitation.

Comment from Michele Citterio: p. 1574 l. 8- : these affinity associations would require much better discussion. I understand these seem to be the empirical evidences, but somewhat unusual findings such as Ti, B and U behaving as a chalcophile elements deserve some discussion. Also, even though I believe most carbonate-hosted sulphide mineralizations in the region are Triassic, small concentrations of sulphides can normally be associated with most carbonates, so Fe, Cu and Zn and other metals may also have a very local natural origin.

Authors' response:

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Discussion is improved combining also the newly added Na, K and Pb. According to main geological sources there is no any known sulphide mineralization in the region.

Comment from Michele Citterio: Pb would also have been a useful measurement but I don't find it in the supplement data.

Authors' response:

Pb have been included in the revised version.

Comment from Michele Citterio: p.1575 : as stated above most of these conclusions are not adequately supported by data and proper interpretation.

Authors' response:

The conclusions have been rewritten.

Comment from Michele Citterio: Tab. 1 : Please note that Colle Gnifetti core is much higher elevation so chemical content is also different.

Authors' response:

We are do so.

Interactive comment on The Cryosphere Discuss., 4, 1561, 2010.

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Table 1. Basic statistics of elemental concentrations measured in the samples of Vukušić ice core. If concentration of particular element was below Limit of Detection (LOD) in particular sample then LOD/2 was used in calculation of the mean concentration. However, to avoid major bias due to this artificial substitution only those elements are presented for that no more than four samples were below LOD. Each value is in ng g^{-1} .

	Mean	median	Min	Max
Na	374.71	259.04	54.18	1993.50
Mg	173.51	64.09	27.84	1632.37
Al	70.42	50.07	9.19	231.48
K	261.40	210.30	<LOD	1252.88
Ca	7313.91	3664.22	2588.19	47476.04
Ti	43.07	22.63	14.70	271.01
Cr	0.27	0.21	0.03	1.52
Mn	19.48	5.75	0.76	323.80
Fe	31.46	26.08	3.82	88.33
Co	43.49	23.05	15.12	271.42
Cu	0.26	0.14	<LOD	2.25
Zn	42.53	32.68	5.49	147.76
As	0.49	0.20	0.05	3.37
Rb	1.08	0.28	0.07	13.42
Sr	6.84	3.11	1.80	45.67
Ce	0.04	0.03	<LOD	0.12
Pb	0.24	0.20	0.06	0.56
U	0.09	0.03	<LOD	0.77

Fig. 1. revised Table 1

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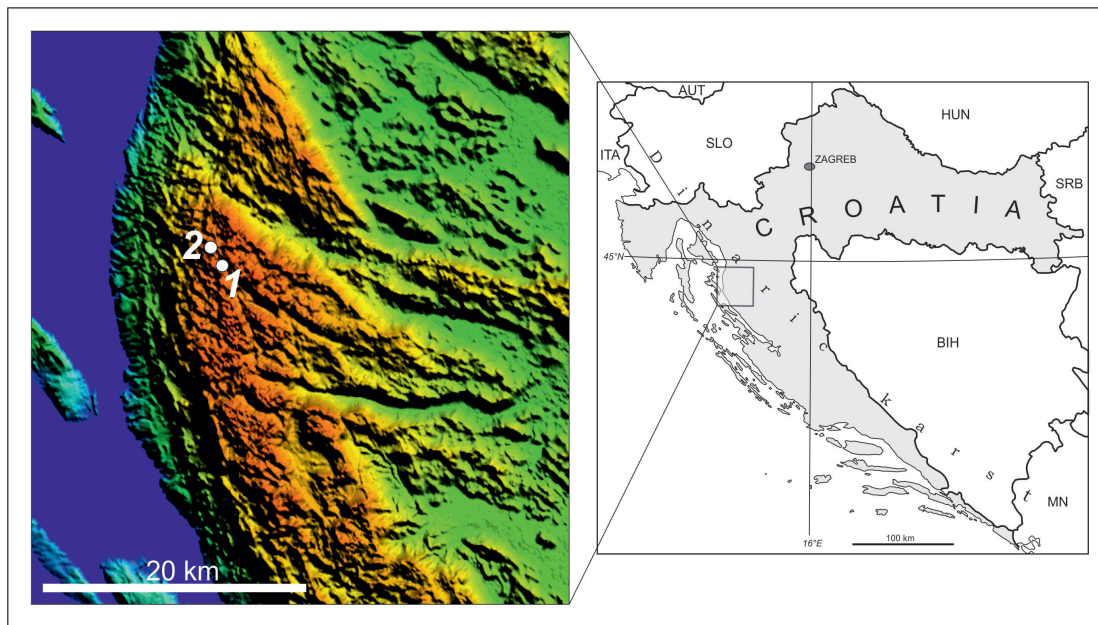


Fig. 2. Revised Fig1

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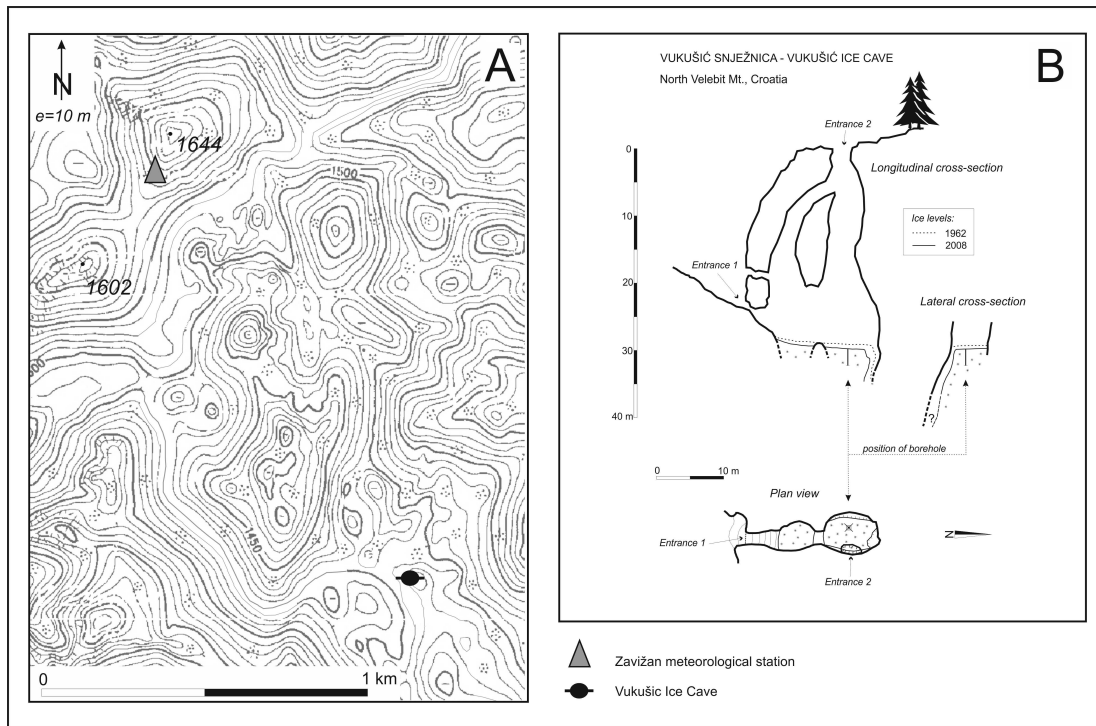


Fig. 3. Revised Fig2

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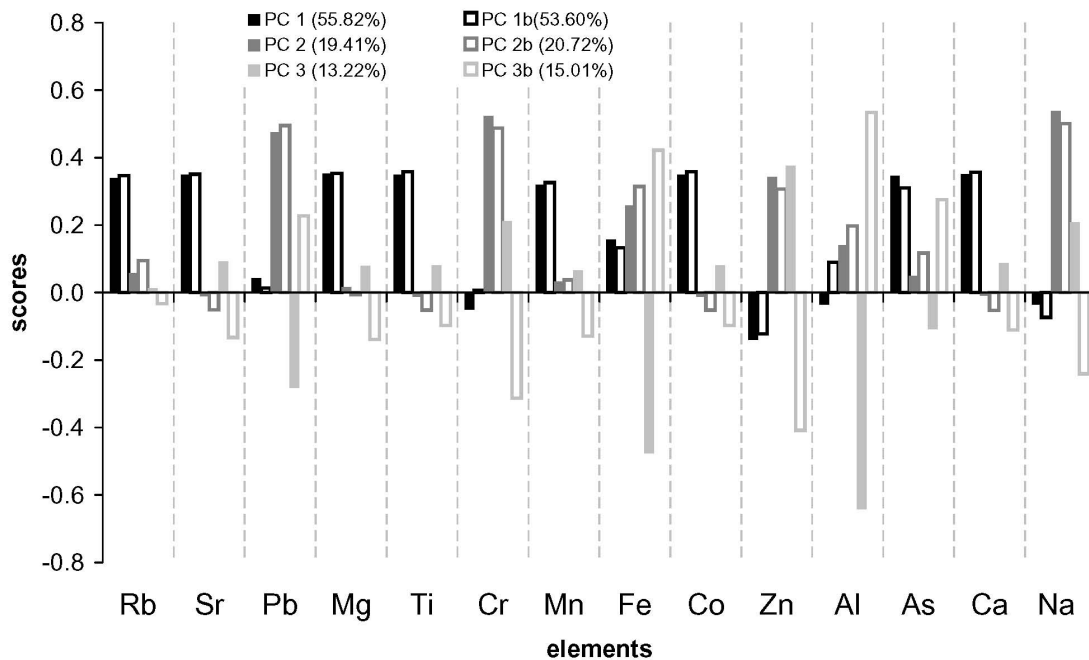
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Fig. 4. New Fig 5 (revised Fig 8)

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