Discussion

More than just a convoluted table? Discussion of "Mediterranean tephra stratigraphy revisited: Results from a long terrestrial sequence on Lesvos Island, Greece" by Margari et al.
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Margari et al. (2007) recently published a range of major and trace element geochemical data (EPMA, bulk tephra solution ICP–MS) as part of a study of a series of tephras from a lake sediment core on Lesvos Island, Greece. In their paper they propose correlations for some of their deposits with more widespread tephra deposits in the Mediterranean. However, some issues stemming from their sample preparation methods, a confused table of data, an incorrect statement about the incomparability of analytical methods, and a possible miscorrelation in the paper by Margari et al. led us to the decision to write this comment.

In their discussion of trace element analysis and correlation of tephras from their core, Margari et al. (2007) state that published tephra data obtained by neutron activation analysis cannot be directly compared with their ICP–MS analyses (bottom of p. 46). This is a somewhat traditional misconception i.e. that concentration data produced by different methods are not comparable. It is true however that, depending on the elements' concentrations, different methods produce data of differing quality, largely as a consequence of different detection limits. Independent of the method applied however, a value for an element's concentration has to be valid (within the given analytical error for that technique) and should thus be comparable with data acquired by other methods, provided standard analytical protocols are followed. Several papers specifically compare tephra compositional data obtained by different analytical methods and show the validity of this approach (e.g. Westgate et al., 1994; Pearce et al., 2002, 2004; Steinhauser et al., 2006).

To check the alleged incomparability of the ICP–MS data from Margari et al. with neutron activation analysis (NAA) from other studies, we decided to plot the tephra data from Margari et al. against data from our extensive data base of Mediterranean tephras (obtained by NAA, see Peltz et al., 1999; Steinhauser et al., 2006). After overcoming several problems with the data presented by Margari et al. (discussed later), we found a perfect agreement between samples ML-3 and ML-4 from Margari et al. and the chemical fingerprint of the Giali main eruption ("Yali D" of Bond, 1976) from our database. This comparison is presented in Fig. 1, where the concentrations of elements present in both data sets were normalised to mean upper crust (from Taylor and McLennan, 1985), and plotted according to their atomic number. The data from Margari et al. show high concentrations of Cr, Fe and Co, which can be explained as contamination of their sample by sediment derived from the local, peridotitic basement, or even of the coring tools, but all other elements show a near perfect agreement with the Giali lower pumice (i.e. the Giali main eruption). Had Margari et al. compared these data sets, they would have undoubtedly observed this agreement immediately.

Margari et al. (2007) assigned the ML-3/ML-4 tephras to the caldera-forming eruptions of Nisyros (upper and lower caldera pumice), a correlation which can easily be excluded by the presence of the distinct Eu-anomaly observed in ML-3 and ML-4. However, had
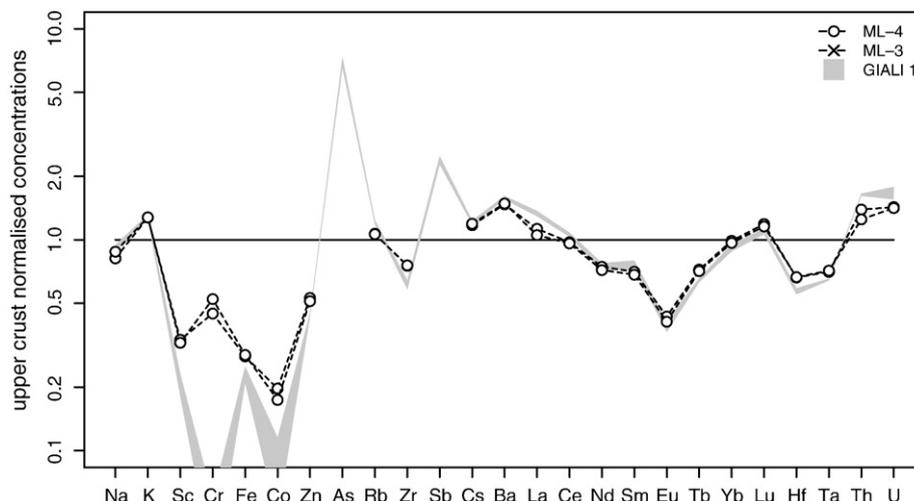
Fig. 1. Element concentrations of the Giali (Yali) lower pumice (Peltz et al., 1999; Steinhauser et al., 2006) compared to ML-3 and ML-4 (Margari et al., 2007). All analyses normalised to average upper continental crust (Taylor and McLennan, 1985). The shaded area shows the variation range of six pumice samples from Giali lower pumice.

Margari et al. undertaken a suitable sample preparation to separate the pure glass fraction from the tephra deposits in their core (see below), only then would a correlation with the pure glass from the Nisyros caldera pumices be valid. The compositional differences between bulk samples and pure glass separates are already well documented for these Mediterranean tephras (Saminger et al., 2000), and as the samples analysed by Margari et al. are unlikely to be pure glass (see below), their proposed correlation with Nisyros remains problematic. Fig. 2 shows the distribution range of elements in the Nisyros caldera pumice (our data) compared with the ML-3 and ML-4 tephra (Margari et al., 2007), and significant differences are evident in the concentrations of Zr, Eu, Hf and Ta. Samples from the Nisyros upper and lower caldera pumices collected and analysed by Margari et al. (2007) however, again, show an acceptable agreement between data obtained by NAA and ICP–MS (see Fig. 3) and further dispel any doubts about the comparability of data produced by different methods. Further, a thorough literature search would have led to the information that a clear distinction between the lower and upper caldera pumice of Nisyros can be accomplished by comparing the concentration ratios of Eu/Ta versus Th/Hf (Sterba et al., 2006), see Fig. 4. Unfortunately, this means of discrimination does not work for

the three samples NUP a, NUP b and NLP presented in Margari et al. (2007), because of the large variation in their Hf values (see Fig. 3), which is not further explained by Margari et al. (2007). The variation in the Hf data from NUP a, NUP b and NLP correlates with the variation in Zr in these samples and is probably a result of the incomplete dissolution of zircons by the acid digestion method used.

Margari et al. (2007) describe their sample preparation methods on p. 36, using the terms "pure tephra" and "pure glass" to describe the samples and products. It is highly unlikely that the 0.1 g of sample digested for ICP–MS analysis was "pure glass" as this would require some form of separation of the glass from other phases within the tephra, typically achieved using heavy liquids (or other methods of density separation) and/or magnetic separation (see Schmid et al., 2000; Mackie et al., 2002; Pearce et al., 2004). Only sieving and the application of deionised water will not yield a pure glass fraction. Even the treatment of the samples with H_2O_2, $Na_4P_2O_7$ and HCl will only oxidise organics, disperse clays and dissolve carbonate (and possibly some apatite and Fe oxide) phases, but will leave silicate and some oxide minerals (both juvenile and detrital), as well as glass, within the products. At best, the material analysed by Margari et al. was a cleaned (i.e. clay, carbonate and organic free) "bulk tephra", although the high
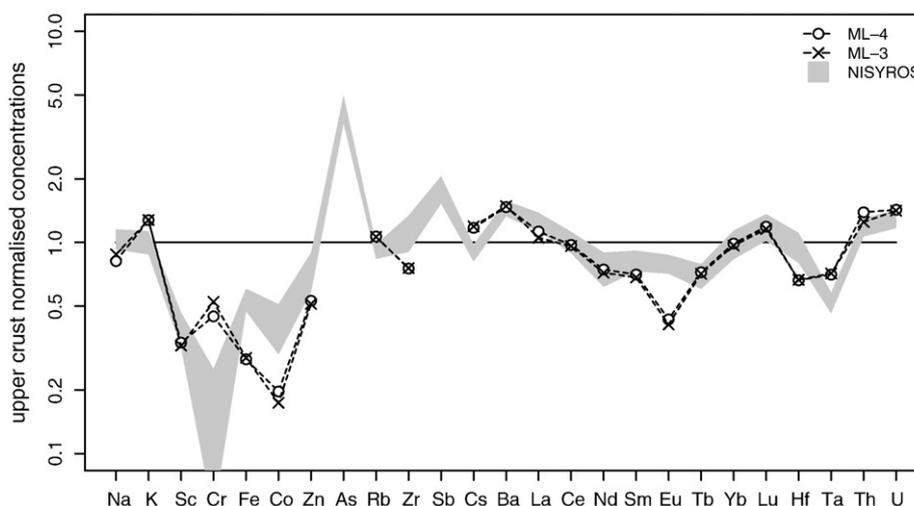

Fig. 2. Element concentrations in ML-3 and ML-4 tephra layers compared to the natural distribution range of the elements in Nisyros caldera pumice (taken from Steinhauser et al. (2006), Peltz et al. (1999), 25 samples) All analyses normalised to average upper continental crust (Taylor and McLennan, 1985).
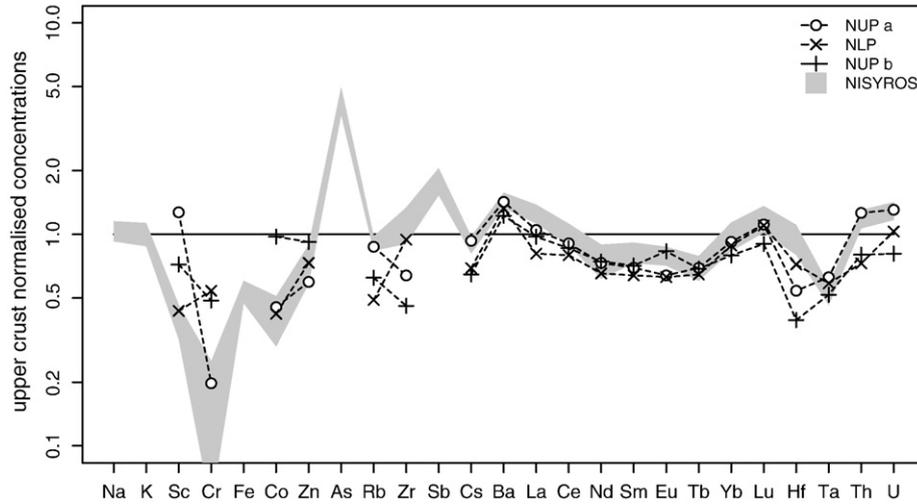
Fig. 3. Element concentrations in Nisyros caldera pumice according to Margari et al. (2007) compared to the natural distribution range of the elements in Nisyros caldera pumice (taken from Steinhauser et al. (2006); Peltz et al. (1999), 25 samples). All analyses normalised to average upper continental crust (Taylor and McLennan, 1985).

Cr, Fe and Co in their analyses compared with the Giali tephras attests to the presence of at least some detrital contamination which could have been removed if a thorough separation of the glass had been attempted. The use of the term "pure" in any context here is however misleading. The sample preparation method used has implications for the comparability of their analytical data with other studies.

Unfortunately, for the comparisons we have described above, trace element data could not easily be extracted from Table 4 in Margari et al. (2007). The values for the lanthanides had to be un-normalised as, contrary to the caption, not concentrations but the chondrite-normalised values are tabulated. Fortunately, Margari et al. (2007) declared the source of the normalisation factors (McDonough and Sun, 1995) and this enabled the deconvolution of the data. Additional difficulties arose in deciding which of the two listed values for Ba should be chosen for the comparisons we attempted, as they vary considerably, but not reproducibly. The same is true for Pb. Even more confusing is the presence in Table 4 of a value for the short-lived radioactive rare earth element promethium (Pm), which simply does not exist naturally. The most irritating fact is that a normalisation factor must have been invented (by interpolation of the normalised data) to enable Pm to be listed in Table 4. In addition, in compiling Table 4, Margari et al. (2007) imply a high analytical precision by

quoting up to five significant figures for their analyses which is contrary to their statements on page 36 where they claim a typical precision of 0.5–5% relative. The implied precision is much greater than can be routinely achieved by ICP–MS (typically around 1%, see Pearce et al., 2004). One has to ask how much thought went into the production of Table 4, if almost all the numbers are quoted to two decimal places, regardless of the order of magnitude, and when some elements are listed twice?

In conclusion, whilst the presentation of their data is problematic, Margari et al. (2007) did produce a valuable set of analyses on Mediterranean tephras. They suggest a correlation for some samples in their core with the Nisyros caldera pumices, but this is problematic and they have missed a more likely correlation (with the Giali lower pumice) because of a lack of appreciation of the comparability of different analytical methods. The ease with which geochemical data can now be generated means that it is widely available across the Earth sciences and is being employed in new disciplines by academics who often hail from non geochemical backgrounds. Oftentimes, as here, however, the geochemical data are simply used as another set of parameters, employed without a full appreciation of the analytical quality, the information they contain and, not just in this case, the extent to which various data sets can or cannot be compared. To
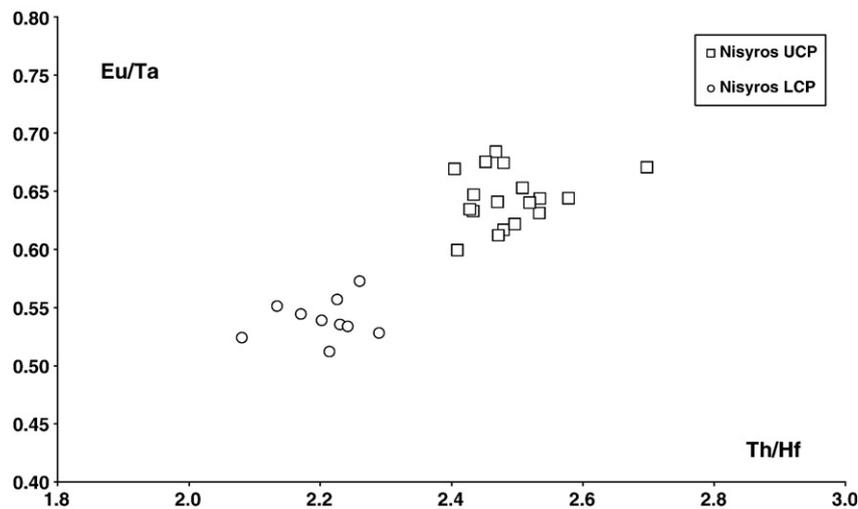

Fig. 4. Element concentration ratios in lower and upper Nisyros caldera pumice from Sterba et al. (2006).

analysts who have striven to produce high quality data sets (often by different methods), such misconceptions and the simple, avoidable errors, such as those present in the tables of data described above, are extremely galling. It is incumbent on the editing and refereeing process to ensure that these errors are not allowed into press. If they go unnoticed, the data, and the interpretations derived from them, run the risk of becoming embedded in the literature as facts. On this point, we note with some concern that Aksu et al. (2008) have already cited the work by Margari et al. (2007), stating that *"the Lower Pumice and Upper Pumice eruptions of Nisyros …… have been identified in a 40 m-long lake core from the Island of Lesbos"* and that *"in a long core from Megali Limni on the Island of Lesbos, the Nisyros tephra occurs stratigraphically below the Y5 tephra"* before continuing to discuss the age implications of these occurrences and correlations. Is this problematic correlation with the Nisyros Upper and Lower pumices already becoming an established fact?

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