

Minor elements – the middle child between petrochemistry and geochemistry

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<https://doi.org/10.70499/FJRP9154>

INTRODUCTION

Some 30 years ago I wrote an article for EXPLORE titled 'A Cry from the Heart', then four years later, 'Another Cry from the Heart', both concerned the application of statistical procedures to geochemical data. I cannot write 'Another another ...', but that is what this is, and this time the cry concerns the data and how they are reported.

The Data

A colleague had requested help in visualizing geochemical data for 194 analyses of the <63 µm fraction of glacial tills from the Northwest Territories, Canada. In the study, three analytical procedures were employed. An Aqua Regia attack was selected to generate data to support base metal and gold mineral resource potential estimation; that attack preferentially solubilizing elements held in sulphides and loosely held on weathering products. A four-acid dissolution (HF-HClO₄-HNO₃-HCl) was chosen to generate data to support till provenance studies. A 'Total' Li-metaborate fusion procedure was undertaken to generate reliable rare-earth, and other, elemental data where the elements were held in minerals resistant to four-acid dissolution. Subsequently, element concentrations were determined in the solutes by ICP-OES or ICP-MS.

For the 'Total' determinations, concentrations of both major and minor elements were reported as oxides by the laboratory, based on the assumption that these data were going to be used for petrochemical studies, and possibly the calculation of normative mineral compositions.

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Discussion

Figure 1 presents the data for the minor element manganese (Mn), the MnO results reported in the 'Total' (LBF) determinations having been converted to elemental concentrations. Firstly, differences in the amounts of Mn liberated by Aqua Regia versus four-acid dissolutions are apparent in the displacement of the data into opposite quadrants about their 1:1 diagonals (Figs. 1A & 1a), predictably, the four-acid dissolution solubilizes more Mn than Aqua Regia. Secondly, the close agreement of the four-acid dissolution and 'Total' Lithium Metaborate Fusion data is reflected by the alignment of data around the 1:1 diagonals of their plots (Figs. 1C & 1c). The similar relationship between Aqua Regia and Lithium Metaborate Fusion data (Figs. 1B & 1b) as for Aqua Regia and four-acid dissolution data (Figs. 1A & 1a) is also exemplified in comparing Figures 1A and 1B (similarly, Figs. 1a & 1b), with displacements on the same sides of the 1:1 diagonals.

Figure 1. Mn (mg/kg) determinations of the <63 μm fraction of glacial tills by Aqua Regia (Mn-AQ), four-acid (Mn-4Acid), and Li-metaborate (Mn-LBF) procedures.

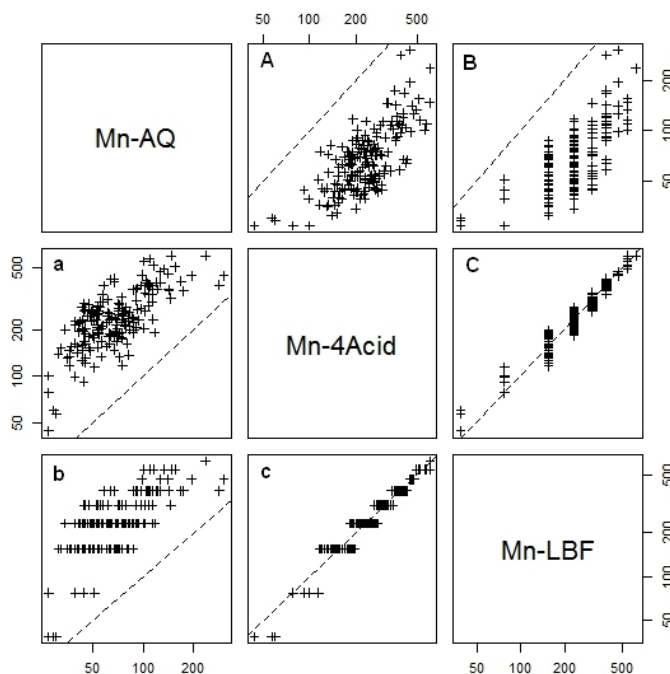
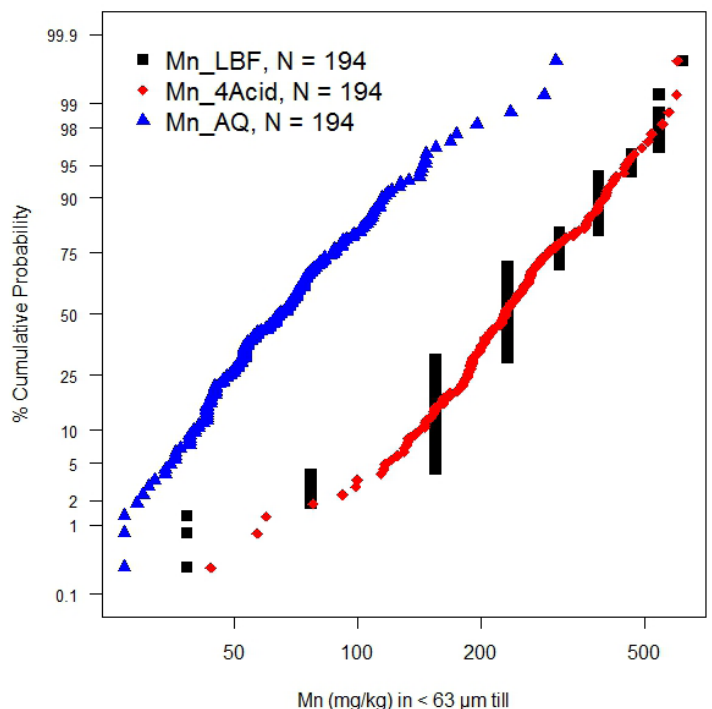


Figure 2. Cumulative probability plots for Mn (mg/kg) determined in the <63 μm fraction of glacial tills by Aqua Regia (Mn_AQ), four-acid (Mn_4Acid), and Li-metaborate (Mn_LBF) procedures.



These differences are clearly visualized in Figure 2, where the data are presented as probability plots. The displacement between Aqua Regia (blue triangles) and four-acid (red diamonds) reflects the different amounts of Mn liberated by the two acid-mixture dissolutions. The similar effectiveness of the 'Total' (black square) and four-acid (red diamonds) procedures in liberating Mn is exhibited by general overlap of the two cumulative probability plots. Comparison with the 'Total' analyses is complicated by the Mn data being restricted to only one of nine values by the reporting of the determinations as oxides to three decimal places – all of which have two leading zeroes! This carries little useful information for the geochemist, and prohibits any insightful data analysis.

Minor elements are defined as those with concentrations between 1,000 mg/kg (ppm) and one percent (10,000 mg/kg), a narrow one order of magnitude range (MINDAT 2020). In the instance of the 'Total' data discussed here, Ti, P, Mn and Cr were reported as percent oxides to two or three decimal places, often resulting in only one non-zero figure. Additionally, Ni and Sc were reported as elements with the major and minor elements. All the data for Ni were reported as less than a detection limit of 20 mg/kg, and the Sc to a useful two figures. The four-acid data for Ni show a range of 2.3 to 54.2 mg/kg, surely Ni could be determined in the Li-metaborate fusion solute by ICP-MS despite the dilution required to reduce the 'salt' content of the solute to workable levels.

The value of reporting high resolution in data, i.e. the absence of unnecessary rounding, is exemplified by studies such as Fabian *et al.* (2017) and Reimann *et al.* (2019a, b). They show that data reported with sufficient non-zero significant figures permits investigation of the relative roles of long-range diffuse contamination from industrial sources and local biogeochemical processes.

Some current data reporting practices, such as listing minor element concentrations as oxides in 'Total' analyses, can

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preclude any serious geochemical investigation. The conversion of elemental to oxide data, and *vice-versa*, is a trivial exercise, especially with 'spread sheet' software. Is there any purpose in retaining the way in which minor elements are currently reported in 'Total' analyses? They can be reported to the same standards as the trace elements resulting in no loss of information; then converted to oxides according to user requirements. Laboratories could even report the data in two tables, one for major and minor elements in percent oxides for petrochemical use, and the other for all data as mg/kg in up to four-figures for geochemical studies. The present practice of reporting minor elements as oxides is a failure.

Conclusions

It has been demonstrated that the reporting of minor element data in whole rock, 'Total', analyses is inadequate for geochemical studies. The frustration that this unnecessary inadequacy is the reason for this 'Cry', the 'Another another ...'. The minor elements are the awkward 'middle child' between the major and trace elements. Their reporting is torn between the needs of petrochemists and geochemists. This is unnecessary. There is no reason multiple reporting styles cannot be supported, and data not castrated by reporting with insufficient non-zero significant figures.

It is the hope of the author that this article will initiate a conversation between the scientists who use the data and the laboratories who provide them, so that no information is wasted.

Acknowledgements

The author thanks Clemens Reimann, Gwendy Hall and Paul Morris for their comments and suggestions on an earlier draft of this article, and Beth McClenaghan for editorial assistance.

Note: The plot preparation was undertaken with R 3.4.3 (R-Project, 2020) and package 'rgr' (Garrett, 2020).

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