



A Comparison of Shewhart, Thompson and Howarth, and Youden Plots – Advantages and Disadvantages

Robert G. Garrett, Emeritus Scientist, Natural Resources Canada, Geological Survey of Canada, 601 Booth Street, Ottawa, ON CANADA, K1A 0E8, Email: garrett@NRCan.gc.ca

INTRODUCTION

The need, in truth necessity, to monitor the abundant analytical data that applied geochemistry projects generate cannot be over stressed. If all the interpretation, mapping and statistical analysis is to be credible it requires sound sampling design and reliable geochemical analyses. Without a solid foundation later work is potentially at risk.

The most frequently used form of analytical quality control (QC) is the Shewhart plot, where data are displayed against date or time of acquisition, or the order in which the determinations being monitored were received back from the laboratory. The latter is based on the belief that data will be reported in the order they were generated, something that can only be ascertained by discussion with the laboratory. These control charts are named after Walter A. Shewhart, a statistician who worked for Bell Labs in the 1920s. He introduced them to meet the needs of engineers involved in the monitoring the reliability of telephony transmission systems (http://en.wikipedia.org/wiki/Control chart). In applied geochemistry, Shewhart charts can be employed for monitoring Control Reference Material (CRM) results for analytical drift or occasional excursions due to failure in the systemic analytical process, analogies being chronic and acute medical problems, respectively.

The use of routine duplicate determinations for QA/QC, and the associated estimation of analytical variability, was introduced by Youden (1951), a statistician employed by the National Institute of Standards and Technology. A form of Shewhart plot widely used by applied geochemists displays the absolute difference between duplicate determinations from a single laboratory against their order of accession, or their mean, to be viewed in the context of prior control criteria. In 1973 Thompson and Howarth (1973, 1978) introduced a variant, employing logarithmic scaling, that accommodated the large range, often several orders of magnitude, encountered in duplicate determinations from applied geochemistry projects. Youden's displays of determination-2 vs. determination-1, with equal x- and y-scaling, became known as Youden plots (http://www.medcalc.org/manual/youdenplot.php). In addition to estimating the precision of the analyses statistically from the duplicates, the plot permitted visual assessment of duplicate quality through the closeness of the plotted duplicates to the 1:1 line. When used for inter-laboratory

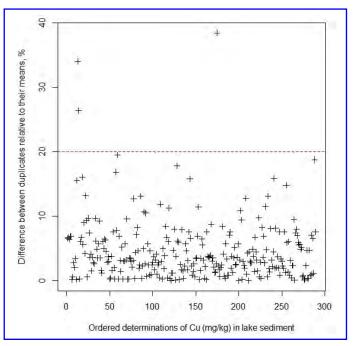


Figure 1. Shewhart plot for incoming laboratory Cu data in order of accession, the dashed line at 20% indicates the acceptance level, three duplicate pairs above the dashed line require investigation

comparisons the departures from the 1:1 relationship could be interpreted in terms of the different laboratories performance.

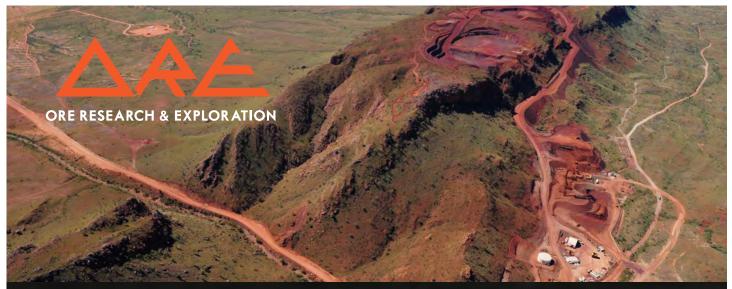
EXAMPLES

Several examples of Shewhart and Youden plots, and a Thompson-Howarth plot, are displayed in this article using duplicate determination data (N = 289) from a 2014 re-analysis program (McCurdy et al., in press) of samples retrieved from the Geological Survey of Canada (GSC) sample archive for two National Geochemical Reconnaissance lake sediment surveys undertaken in Northern Saskatchewan in 1977 and 1993. The graphics presented were prepared using the Open Source R Project for Statistical Computing software (R Core Team 2015) and 'rgr', 'The GSC Applied Geochemistry EDA Package' (Garrett 2013, 2015), that sits on top of R and provides the functionality required for many QA/QC tasks.

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Beth McClenaghan (beth.mcclenaghan@NRCan-RNCan.gc.ca) Business Manager: Pim van Geffen 1-604-681-6765 (explorenewsletter@gmail.com) Back Issues contact: Al Arseneault (office@appliedgeochemists.org)

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Notes from the Editor

The June 2015 issue of **EXPLORE** features one technical article comparing Shewhart, Thompson and Howarth, and Youden plots by GSC Emeritus Scientist Bob Garrett. **EXPLORE** thanks all contributors and reviewers for this second issue of 2015: Steve Amor, Al Arsenault, Lynda Bloom, Patrice de Caritat, Bob Garrett, Matt Leybourne, and Mike Parsons. It was great to see many of you in Tucson at the 27th IAGS. The September issue of **EXPLORE** will feature highlights from the Symposium, short course and field trips.

Beth McClenaghan *Editor*





President's Message

Greetings and I hope that 2015 is progressing well for everyone. I am writing this message having just returned from Tucson and the 27th

IAGS. Overall, the Symposium was a great success thanks to the hard work by Erick Weiland and his co-conveners, Rob Bowell and Sarah Lincoln, and the rest of the local organizing committee (some of whom were not very local). The meeting went off without a hitch; the only issue was the lower than ideal attendance due to the difficult times in the applied geochemistry field and mineral exploration industry. However, more than 250 attendees (not including the large number of partners) enjoyed an excellent mix of field trips, short courses, and technical sessions. Personally, the highlight of the field trip portion of the meeting was the eight days I spent on two rafts (with 22 other people) floating down the Colorado River through the Grand Canyon. The trip was outstanding not only for the incredible geology, but also the professionalism and enthusiasm of the boat handlers (CRATE, special thanks to Walker and McKenna), but also the amazing knowledge, patience, and ability to communicate the geology, flora, fauna, and natural and human history of the canyon provided by our guide, Wayne Ranney. There will be a more expansive review of this field trip as well as the other field trips and short courses in the next issue of EXPLORE.

The Symposium short courses were very well received and there was a good mix of topics from isotopes in mineral exploration through to the utility of indicator minerals. Technical Sessions included a wide variety of topics including exploration geochemistry, ore deposits, applied geochemistry, medical geology, and isotopes. Some of the best talks were presented by students, with the best student oral presentation awarded to Antonio Celis (University of British Columbia) and the best student poster (and 5 minute oral) to Stacie Jones (Queen's University).

Finally, a comment about the Symposium venue. It was held at the Hilton El Conquistador in the Oro Valley of Tucson, Arizona. The resort has good meeting rooms and the staff and food were excellent. The setting was stunning; the desert of the American Southwest is beautiful in the spring, and teeming with a surprising array of flora and fauna – the only downside is looking for your golf balls in the rough, as there are plenty of snake holes and cactus to catch the unwary! All in all, it was another excellent IAGS, with great support from a number of key sponsors including Rio Tinto, Freeport-McMoRan, ALS Minerals, Ore Research and Exploration, Newmont, SRK, Simpleview, Turner Labs, Golder and Associates, Independent Mining Consultants, and Geosoft. The venue for the 28th IAGS is still in discussion, but looks to be in Canada in 2017.

Kurt Kyser from Queen's University in Kingston is now well ensconced as Editor-in-Chief of GEEA, so please send him (excellent) manuscripts so that he is not left with little to do. The Special Issue of GEEA in honour of Eion Cameron is almost completed, so look for that to be published early in 2016 (although papers will be available on-line as soon as they are ready). At the end of the year, Ryan Noble (CSIRO in Perth) will be taking over as the AAG President. At the IAGS in Tucson, Steve Cook (Teck, Vancouver) agreed to become the AAG Vice President in 2016-2017.

I wish you all the best for the next few months – hopefully a busy field season for all.

Matt Leybourne, President



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SHEWHART PLOTS

Figure 1 is a typical Shewhart plot as used for QA/QC in the GSC's regional geochemistry programs, where the absolute difference between duplicates is expressed as a percentage of their mean and plotted in the order of data acquisition. Data acceptability is assessed, as analytical batches are received back from the laboratory, against a criterion of difference between the duplicates relative to their means not exceeding some value, 20% in this instance.

For a formal report the percent relative differences can be plotted against their means. As the range of the 289 duplicate means, representing the range of Cu levels

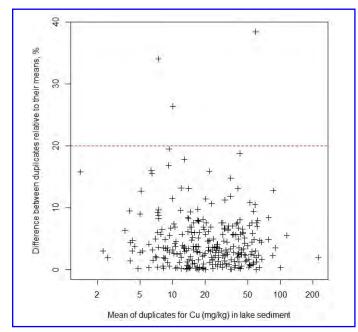


Figure 2. Shewhart plot where the percent relative differences are plotted vs. duplicate pair means for Cu, again with a 20% acceptance level indicated by the dashed line

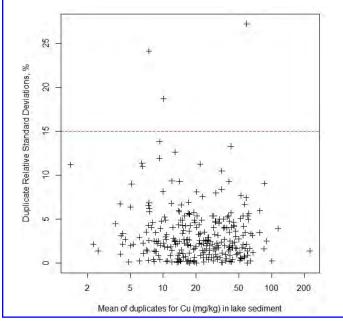


Figure 3. Relative Standard Deviations of individual duplicate pairs vs. duplicate pair means for Cu. An acceptable RSD of 15% is approximately equal to a 20% relative difference acceptance

encountered in the surveys, is in excess of two orders of magnitude it is appropriate to use logarithmic scaling for the x-axis, see Figure 2. A variation on this display is to plot the Relative Standard Deviations (RSDs) of the duplicate pairs rather than their absolute differences on the y-axis. For the case of a duplicate its RSD is the square root of the square of the difference divided by two, divided by the duplicate pair mean, i.e. $\sqrt{[(x_1 - x_2)^2/2]/(x_1 + x_2)^2}$, expressed as a percentage. This is essentially a linear transformation of the difference (x1 - x2) and explains the similarity of the point distributions in Figures 2 and 3. All that has changed is the y-axis scaling, and in the case of these Cu data Figure 3 offers no benefit over Figure 2. Where plotting the RSDs can be of benefit is when presenting data to illustrate the problems in acquiring precise analyses as the detection limit of an analytical procedure is approached. Figure 4 presents the data for the Cd duplicates from the same re-analysis program.

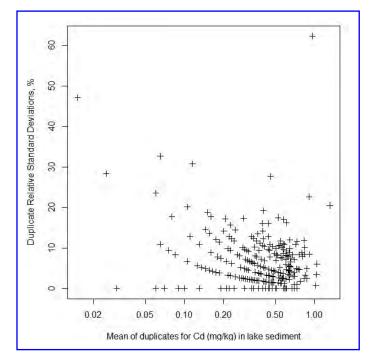


Figure 4. Plot of duplicate RSDs versus duplicate means for Cd demonstrating the effects of quantization and proximity to the lower detection limit of the analytical procedure

The eye-catching features are the trends of decreasing RSDs with increasing means, demonstrating the improvements in precision as levels increase above the method detection limit. These trends occur as discrete 'curves' due to quantization in the analytical data reporting. The detection limit for Cd is 0.02 mg/kg, with the one value below the limit, a non-detect, having been set to 0.01 to permit processing; between 0.02 and 0.09 there are only 9 possible reporting values, thus the number of possible differences is constrained. If the data were reported to an additional decimal place the discrete curves would not be apparent, and the 'curves' would merge into a 'band'. The line of points at zero RSD indicate instances where the duplicate

determinations were identical, and none of these were due to artifacts from setting non-detects to an arbitrary value of half the detection limit. The impact of proximity to the lower detection limit can be best illustrated by presenting the data on the x-axis as the ratio of the duplicate mean to the lower detection limit, see Figure 5. The single point with a ratio of less than one is the duplicate pair where one measurement was a non-detect. What is apparent from Figure 5 is that the combined effects of quantization in laboratory reporting and proximity to the lower detection limit for Cd are not lost until the duplicate means exceed the lower detection limit of 0.02 mg/kg by a factor of 30, i.e. reach 0.6 mg/kg. The distribution of the points in Figures 4 and 5 is identical and the extra insight is gained by choice of the axis scaling which is explicitly related to the detection limit.

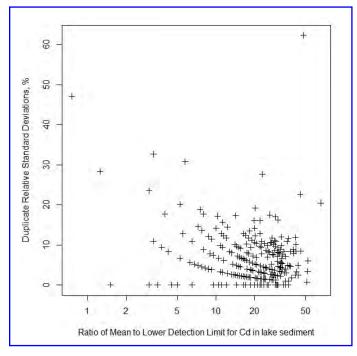


Figure 5. The Cd data of Figure 4, but with the duplicate means expressed as a multiplier of the lower detection limit

THE THOMPSON-HOWARTH PLOT

Figure 6 is the Thompson-Howarth plot for the Cu duplicate determinations displayed in Figures 1 to 3. A target precision for the analyses, expressed as a RSD of 10% was selected. The assumption that the differences are normally distributed permits the addition of the 95 percentile limit for that RSD to the plot and counting the number of duplicates that fall beyond the limit (Fletcher 1981, Garrett & Grunsky 2002, Garrett 2013). There are only two extreme points, and the probability that the data met the 10% RSD criterion exceeds the 0.9999 level. The difference between the 15% RSD acceptance level in Figure 3 and the acceptance that the RSD is better than 10% by the Thompson-Howarth procedure (Fig. 6) is that the Thompson-Howarth procedure is a population estimate, while in Figure 3 the RSDs apply to individual duplicates in the population.

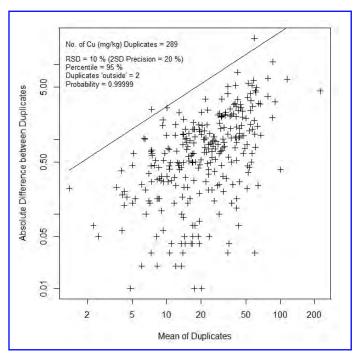


Figure 6. Thompson-Howarth plot of the Cu data with a target RSD of 10%. The diagonal line indicates the expected 95th percentile of the duplicates achieving a 10% RSD

From the point of view of making statements concerning the population statistics the Thompson-Howarth procedure is superior as a QC procedure. But for illustrating duplicate analysis behavior in reports plotting the individual RSDs in various ways has demonstrable advantages, as shown above.

YOUDEN PLOTS

Frequently geochemical reports present duplicate data as Youden plots, where the values for the duplicate determinations are plotted against the values for the sample from which the duplicate was split during sample preparation. In the instance of field duplicates, the analyses would be for two samples closely co-located on the scale of the survey. Figure 7 is the Youden plot for the Cu duplicate determinations in Figures 1 to 3, with the two axes equally logarithmically scaled, as the data span in excess of two orders of magnitude, and the 1:1 line plotted. Adequacy of the data is estimated by proximity to the 1:1 line. In some reports the correlation of the duplicates across the range of the data is presented. However, one could still have a good correlation between the duplicates and a systematic drift of greater divergence between the duplicates with increasing or decreasing levels. The correlation coefficient is not an informative statistic in the QA/QC context. Additionally, a regression line is sometimes estimated, and the gradient tested to determine if it is statistically equal to one, and the intercept is statistically equal to zero. As the determinations plotted against each other are independent of each other ordinary least squares regression is inappropriate, and orthogonal regression, a.k.a. the reduced major axis, should be used to quantify the interrelationship between the two sets of determinations (Garrett, 2013). In fact, the correct

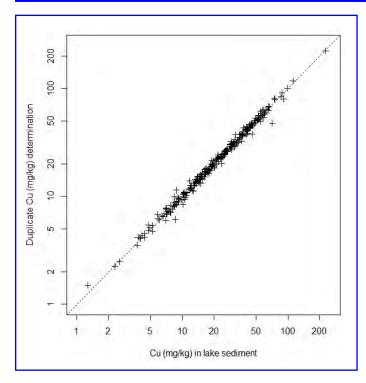


Figure 7. Traditional Youden plot for the duplicate Cu data. The diagonal line indicates the 1:1 relationship along which all data would ideally plot

statistical test does not involve regression modeling and is for the average difference between all the pairs of determinations being zero, the paired t-test (Reimann et al. 2008).

When the difference between two determinations is zero it follows that the ratio of their values will be one. This suggests an alternative plot, where the ratios between the determinations are plotted against the means of the duplicates on the y- and x-axes, respectively, see Figure 8.

Logarithmic scaling is used on both axes, firstly, for the x-axis as the data span more than two orders of magnitude, and secondly, and more importantly, for the y-axis so that similar-fold differences from unity plot the same linear distance above and below unity. Thus a value of 2 will plot the same distance above the unity dashed line as a value of 0.5 will plot below.

The mean ratio and its standard deviation may be estimated and the standard error of the mean computed. If the difference between the mean ratio and unity is within the 95% two-sided confidence interval on the mean there is no statistically significant difference between the duplicate determinations at the 95% confidence level. The 'rgr' function that prepares Figure 8 displays the result of this test, the equivalent of a paired t-test. The 95% confidence interval on the ratios is estimated and plotted, and optionally the information placed as a text block on the plot at a position of the user's choice (see Fig.8). Both classical and robust estimates of the 95% confidence interval on the range of the ratios are made, the latter using the median and Median Absolute Deviation (MAD) rather than the mean and standard deviation. For Cu in Figure 8, there are 13 duplicates that fall outside the classical 95% limits, as

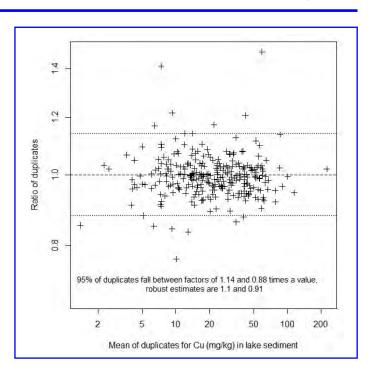


Figure 8. Plot of duplicate pairs as ratios vs. the duplicate mean. The dotted horizontal lines indicate the upper and lower 95% confidence bounds for the duplicates

would be expected for a data set of size 289 with normally distributed data.

Figures 9 to 11 display the Youden and ratios plots for the Mn data. The data span in excess of three orders of magnitude, making plotting with log-log scaling essential; four duplicates require follow-up, with the duplicates reporting uncharacteristically low levels relative to the routine determinations (Fig. 9).

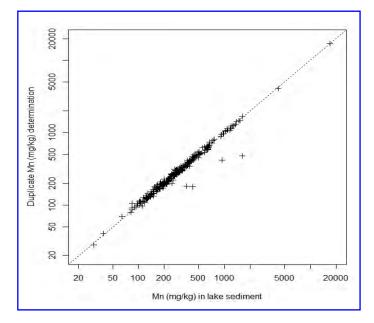


Figure 9. Traditional Youden plot for the duplicate Mn data, with the 1:1 line indicated

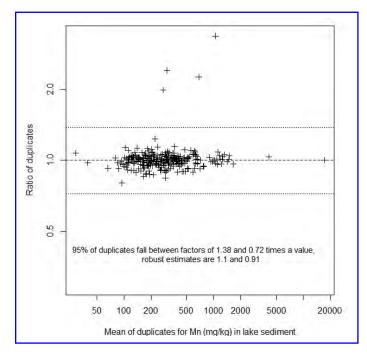


Figure 10. Ratio plot for the Mn duplicates. The dotted horizontal lines indicate the upper and lower 95% confidence bounds for the duplicates

Figure 10 is the equivalent ratios plot, where the ratios are computed as determination-1 divided by determination-2. The routine determination precedes the duplicate in the data file, and as a result the four errant duplicates plot above the unity line. It is not known whether the duplicate

determinations were relatively low, or the routine determinations relatively high, or even some combination of these two situations. It is worth noting the effect of the four 'outliers' in both Figures 10 and 11. In Figure 10 they exert a major effect on the estimated 95% limits for the range of ratios, for a value of 100 mg/kg there is a 95% chance the duplicates were in the range of 138 to 72 mg/kg. The robust estimates of the expected range, which have 'ignored' the 'outliers' by using the median and MAD, are 110 and 91 mg/kg, indicating the benefits of following-up on the four duplicate determinations and rectifying whatever problems may have occurred in the batches of analyses where they occurred. Finally, Figure 11 presents a probability plot of the ratios in addition to the ratio plot. This confirms that, as one would hope, that the ratios approximate a normal distribution and the four errant duplicates are true 'outliers' requiring attention.

As noted above, the optimal parametric statistical test for the equivalence of duplicate determinations is the paired t-test, which compares the mean difference for the duplicates to zero in the context of the spread of the duplicate differences about their mean. If a confidence band, at some stated level, around the mean difference includes zero one accepts the hypothesis that the mean difference is zero and that the duplicates are 'identical' in the context of the study. If zero falls outside the confidence bounds, there are serious problems that need to be understood before proceeding further with data interpretation.

For three reasons the paired t-test for duplicate geo-

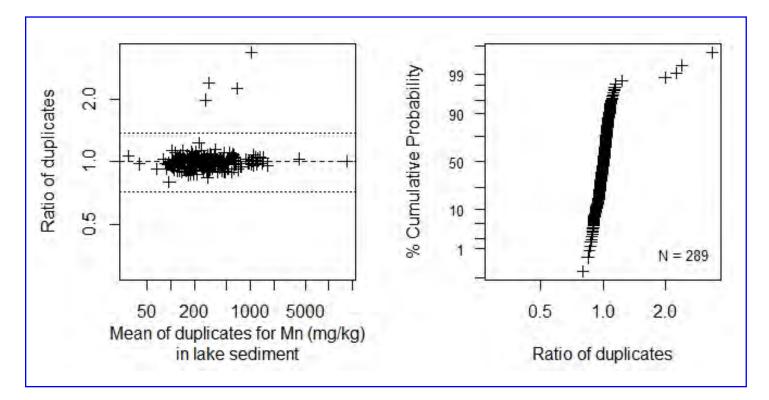


Figure 11. Combined ratio plot and cumulative normal probability plot of the ratios for Mn. The dotted horizontal lines indicate the upper and lower 95% confidence bounds for the duplicates

chemical analyses should be carried out with a logarithmic transform. Firstly, the data often span more than an order of magnitude which induces a property known as heteroscedasticity, implying that variances of groups of data across the data range are not constant. Constant variance is a critical assumption for parametric statistical tests like the t-test, in fact it is arguably more important than the requirement for normality. The standard solution to this problem is a logarithmic transform, see Bartlett (1947) and many statistical texts since. Secondly, and equally important, geochemical data are compositions and are constrained in the values they can take, i.e. they cannot be less than zero, if such could ever be determined, or greater than 1 million mg/kg or 100% (Aitchison 1986). The situation with univariate data has been discussed by Filzmoser et al. (2009), and at trace element levels, and in fact up to 10%, a logarithmic transform will 'open' the data satisfactorily. Finally, geochemists tend to think in ratios, levels are 'twice average background', or 'three times threshold'. Working after a logarithmic transform simply treats the data the way geochemists think about them, as ratios.

With logarithms a subtraction is a division, thus taking the difference of the logarithms of the duplicates, or computing their ratios is equivalent, and a paired t-test on the 'logs' of the data is equivalent to a t-test on the ratios. Table 1 presents the screen output when ratio plots are generated (Figs. 8, 10 and 11). The paired t-test results are in the second 'paragraph' for the plot results, they include the absolute difference from unity, the standard error of the mean of the ratios, and the 95% confidence interval. The software tests to see whether unity falls within the confidence interval, and if it is the following line is displayed informing the user that there is no statistical difference from unity, and thus there is no systematic bias. Should the test fail an appropriate line is displayed.

DISCUSSION

Several variations have been presented for Shewhart plots of analytical duplicate data from a regional geochemical survey. Each display has its own particular advantage. For monitoring incoming laboratory data plotting in acquisition sequence assists in detecting if a laboratory procedure has gone out of control for a short period of time, or in a single or series of batches - the GSC procedure is to insert a duplicate in each batch of 20 samples for analysis. The Thompson-Howarth plot is also well suited to monitoring data as it is acquired and assessing its acceptability. For summarizing the results for a report it is more informative to plot the duplicate means on the x-axis. It is a matter of choice whether the y-axis is scaled for the absolute differences between the duplicates, or their Relative Standard Deviations – it is the mean of all variances behind the individual RSDs that estimates the overall precision for the duplicate data being presented. As shown for Cd (Fig. 5), plotting the duplicate means as their ratios to the procedure detection limit can assist to displaying the relationship of analytical precision to proximity to the detection limit. If for some element or compound this relationship is unacceptable the display helps justify the need for an alternative procedure. In the case of nugget effects due to a missmatch between particulate/mineral grain size and aliquot

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Table 1. Text display associated with the ratio plots for Cu and Mn
> ad.plot4(Cu, "Cu (mg/kg) in lake sediment", ifalt = T, if.order = F)
Range of ratios of the 289 duplicates: 0.767 1.48 Median ratio = 0.9961 MAD of ratios = 0.04919 Mean ratio = 0.9989 SD of ratios = 0.06956 95% CI for ratios = 0.1369
Absolute ratio difference from $1 = 0.001091$ SE of Mean of ratios = 0.00409 95% CI = 0.00805 Mean ratio is not different from 1 at the 95% level, no bias
95% of duplicates will fall between factors of 1.14 and 0.88 times a value Robust factor estimates based on the MAD are 1.1 and 0.91
> ad.plot4(Mn, "Mn (mg/kg) in lake sediment", ifalt = T, if.order = F)
Range of ratios of the 289 duplicates: 0.8 3.37 Median ratio = 1 MAD of ratios = 0.05031 Mean ratio = 1.019 SD of ratios = 0.195 95% CI for ratios = 0.3837
Absolute ratio difference from $1 = 0.01917$ SE of Mean of ratios = 0.0115 95% CI = 0.0226 Mean ratio is not different from 1 at the 95% level, no bias
95% of duplicates will fall between factors of 1.38 and 0.72 times a value Robust factor estimates based on the MAD are 1.1 and 0.91

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weight the solution could be as simple as scaling-up the procedure to accommodate an increased aliquot weight.

The traditional Youden plot is well established as a report display for duplicate data. However, it is extremely wasteful of plot space, especially when the data range over several orders of magnitude (see Figs. 7 and 9). Furthermore, it encourages the use of the correlation coefficient, and even a regression model, implicitly accepting either the initial determination or duplicate as the dependent variable. As noted previously, the correlation coefficient is not an informative statistic in terms of assessing all the aspects of bias between the duplicate analyses. Furthermore, a simple linear regression is not the appropriate regression model, the question being, which is the independent variable and which the dependent? There is no answer. The appropriate regression model is one for orthogonal regression (the reduced major axis), which accepts both variables as independent. This model minimizes the sums of the error squares at right angles to the regression line, and not parallel to either the routine or duplicate determination axis. The optimal statistical test is the paired t-test that directly tests for the average difference between the duplicates being zero.

The ratio plot, a Youden variant, is a far more efficient use of plot space. Only one axis (x) spans the whole range of the duplicate data and the other (y) focuses of the differences from the 1:1 line always plotted on the traditional Youden plot, and the real subject of interest. To give equal graphical 'weight' to ratios above and below unity it is necessary to employ logarithmic scaling. Due to the nature of the ratio it implicitly leads to a statistical test equivalent to a paired t-test on the logarithms of the duplicates – an appropriate test for acceptability of the duplicates, assuming they satisfy any initial prior quality control criteria. Furthermore, this approach leads to the estimation of 95% limits on the expected range of the duplicates across the range of the data, a useful way of presenting the analytical precision.

The importance of the graphical inspection of QA/ QC data cannot be overstressed. In the examples provided any outliers can be readily recognized (Figs. 1-3, 6, 9-11). Simply calculating precisions from duplicate data can easily hide unpleasant truths. If outliers exist they need to be explained, they could be due to procedural errors in the analytical process, in which case they need to be understood and appropriate action undertaken. Alternately they could be due to sample inhomogeneity arising from the particulate nature of the mineral(s) containing the element being monitored. If the latter is the case it has to be accepted as a reflection of the geochemical/mineralogical reality and precision can only be rectified by adopting a different analytical procedure. If sample heterogeneity has to be accepted, robust estimators may be used to calculate precision which down-weight or remove the influence of outliers. In effect, a precision is estimated that applies to the main mass of the data, ignoring the outliers, see for example Table 1 and Figures 8 and 10. This may be comforting, but can also be misleading as to the realities of the analyses.

CONCLUSION

It is proposed that ratio plots are a useful addition to the displays available to the applied geochemist for displaying analytical duplicate data, noting that it could also be used for field sampling duplicates. Ratio plots are graphically efficient and provide for a rapid appraisal of duplicate quality across the data's range. While software is available in 'rgr' (Garrett 2013, 2015) to prepare all the plots and carry out the statistical computations presented here, the procedures can be implemented in other software packages.

ACKNOWLEDGEMENTS

The author thanks Martin McCurdy for drawing the author's attention to the issues around the graphical presentation of duplicate data and appropriate statistical expressions of analytical precision. He also provided the data set used here from one of his current projects. The author also thanks Eric Grunsky and Martin McCurdy, both of the Geological Survey of Canada, Ottawa, for their comments on a draft of this article for **EXPLORE**, and to the Editor of **EXPLORE** and Lynda Bloom for their constructive reviews. ESS Contribution No.: 20140496

REFERENCES

Aitchison, J. 1986. The statistical analysis of compositional data. Chapman and Hall, London, 416 p.

Bartlett, M.S. 1947. The use of transformations. *Biometrics*, 3(1), 38-51.

Filzmoser, P., Hron, K. & Reimann, C. 2009. Univariate statistical analysis of environmental (compositional) data: Problems and possibilities. *Science of the Total Environment*, **407**(2009), 6100-6108.

Fletcher, W.K. 1981. Analytical methods in geochemical prospecting. In: G.J.S. Govett (Ed.), *Handbook of Exploration Geochemistry, Vol. 1,* Elsevier, Amsterdam, 255 p.

Garrett, R.G. 2013. The 'rgr' package for the R Open Source statistical computing and graphics environment - a tool to support geochemical data interpretation. *Geochemistry: Exploration, Environment, Analysis,* **13**(4), 355-378. doi 10.1144/geochem2011-106.

Garrett, R.G. 2015. rgr: The GSC Applied Geochemistry EDA Package. http://cran.r-project.org/web/packages/rgr/ index.html

Garrett, R.G. & Grunsky, E.C. 2002. S and R functions for the display of Thompson-Howarth plots. *Computers & Geosciences*, **29**(2), 239-242.

McCurdy, M.W., Pehrsson, S.J. & Campbell, J.E. in press. Regional lake sediment and water geochemical data, North-

ern Saskatchewan (NTS 64L, 64P, 74N, 74O and 74P). *Geological Survey of Canada*, Open File 7746.

R Core Team, 2015. The R Project for Statistical Computing. http://www.r-project.org/

Reimann, C., Filzmoser, P., Garrett, R. & Dutter, R. 2008. Statistical Data Analysis Explained: Applied Environmental Statistics with R. John Wiley & Sons Ltd., Chichester, 343 p. Thompson, M. & Howarth, R.J. 1973. The rapid estimation and control of precision by duplicate determinations. *Analyst*, **98**(1164), 153-160.

Thompson, M. & Howarth, R.J. 1978. The rapid estimation and control of precision by duplicate determinations. *Journal of Geochemical Exploration*, **9**(1), 23-30.

Youden, W.J., 1951. Statistical methods for chemists. John Wiley & Sons Ltd., New York, 126 p.





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Please let us know of your events by sending details to: Steve Amor Geological Survey of Newfoundland and Labrador P.O. Box 8700, St. John's, NL, Canada, A1B 4J6 Email: StephenAmor@gov.nl.ca Tel: +1-709-729-1161

earthscience.conferenceseries.com22-26 JUNE30th European Conference of the Society for Environmental Geochemistry and Health. Bratislava Slovakia. Website: www.geology.sk/ geohealth/segh-conference-2015/10-12./22 JUNE-2 JULY26th International Union of Geodesy and Geophysics General Assembly. Prague Czech Republic. Website: www.iugg2015prague.com/ 10-12./10-12./21-26-JUNEIsotopes 2015. Jerusalem Israel. Website: tinyurl.com/kmu8sxe16-21./26-28 JUNEECROFI23 - The Sorby Conference on Fluid and Melt Inclusions. Leeds UK. Website: www.see.leeds.ac.uk/ecrofi17-20./29 JUNE-2 JULYConference on Mathematical and Computational Issues in the Geosciences. Stanford CA USA. Website: www.siam.org/meetings/gs15/23-28./12-16 JULY13th International Conference on the Biogeochemistry of Trace Elements. Fukuoka Japan. Website: www.icobte2015.org24-2715-17 JULY5th International Conference on Environmental Pollution and Remediation. Barcelona Spain. Website: icepr.org/24-3125-29 JULYAnnual Meeting of the American Crystallographic Association. Philadelphia PA USA. Website: tinyurl.com/3dfn8lu5-13.8126-29 JULYGranulites & Granulites 2015. Windhoek5-13.81	rg.
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26-31 JULY Gordon Research Conference — Chemical Oceanography 2015. Holderness NH USA. Website: tinyurl.com/os2gc35	
26 JULY-6th International Conference on Medical1 AUGUSTGeology. Aveiro Portugal. Website: medgeo15.web.ua.pt/	SEPTEM SEPTEN
27-28 JULY Urban Geochemistry: The impact of legacy infrastructure and contaminants. Detroit MI USA. Website: www.iagc-society.org/UG.html	

27 JULY- 2 AUGUST	19th INQUA Congress (Quaternary Perspectives on Climate Change, Natural Hazards and Civilization). Nagoya, Japan. Website: inqua2015.jp
8-14 AUGUST	Geoanalysis 2015. Leoben, Austria. Website: geoanalysis.info
10-12 AUGUST	12th International Congress of Applied Mineralogy. Istanbul Turkey. Website: icam2015.org/
10-12 AUGUST	Microscopy & Microanalysis 2015. Portland OR USA . Website: tinyurl.com/qewvuz3
10-12 AUGUST	SGA 2015. Nancy France. Website: sga2015.blog.univ-lorraine.fr/
16-21 AUGUST	Goldschmidt 2015. Prague Czech Republic. Website: goldschmidt.info/2015/
17-20 AUGUST	CANQUA 2015 Meeting. St. John>s NL Canada. Website: www.canqua.com/meetings
23-28 AUGUST	29th Meeting of European Crystallographic Association. Rovinj, Croatia. Website: ecm29.ecanews.org/
24- 27 AUGUST	13th SGA Biennial Meeting "Mineral Resources in a Sustainable World". Nancy France. Website: sga2015.blog.univ-lorraine.fr/
24- 31 AUGUST	International Conference on Gas Geochemistry 2015. Chengdu China. Website: conf13.ic-gg.org/dct/page/70002
5-13 SEPTEMBER	17th Annual Conference of the International Association for Mathematical Geosciences. Freiberg Germany. Website: tinyurl.com/nyovly9
9-11 SEPTEMBER	8th European Conference on Mineralogy and Spectroscopy (ECMS 2015). Rome Italy. Website: www.ecms2015.eu/
13-18 SEPTEMBER	27th International Meeting on Organic Geochemistry. Prague Czech Republic. Website: www.imog2015.org/
16-19 SEPTEMBEF	a 13th International Symposium on Biomineralization. Granada Spain. Website: granada-en.congresoseci.com/biominXIII

CALENDAR OF CVENTS continued from page 13
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20-25 SEPTEMBER	8th Hutton Symposium on Granites and Related Rocks. Florianopolis Brazil. Website: www.hutton8.com.br	9-13 NC
21-25 SEPTEMBER	11th meeting on Applied Isotope Geochemistry. Orléans France. Website: aig11.brgm.fr	
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27-30 SEPTEMBER	Society of Economic Geologists 2015 Conference: World-Class Ore Deposits:	4 DECE
	Discovery to Recovery. Hobart Australia.	2016
	Website: www.seg2015.org/	
20 CEDTEMBED	International Society for Environmental	10-16 JA
28 SEPTEMBER- 2-OCTOBER	International Society for Environmental Biogeochemistry 22nd Symposium. Piran Slovenia. Website: www.iseb22.ijs.si	
	510venia. website. www.ise622.ijs.si	18-19 JA
5-6 OCTOBER	4th Annual International Conference on Geological & Earth Sciences. Singapore. Website: www.geoearth.org/	10-17 37
		27 AUG
6-9 OCTOBER	3rd International Workshop on Antimony in the Environment. Leipzig Germany.	4 SEPTI
	www.ufz.de/index.php?de=33277	11-15 SE
18-21 OCTOBER	4th International Conference on Selenium in the Environment and Human Health. Sao Paulo Brazil. Website: tinyurl.com/knrujup	16- 21 C

	NUMBER 167 EXPLORE
1-5 NOVEMBER	GSA 2014 Annual Meeting. Baltimore MD USA. Website:
	www.geosociety.org/meetings/2015
3-5 NOVEMBER	10th Fennoscandian Exploration and Mining. Levi Finland. Website: 10times.com/fem-levi
9-13 NOVEMBER	Introduction to Secondary Ion Mass Spectrometry in the Earth Sciences. Potsdam Germany. Website: www.gfz-potsdam.de/SIMS/short-course
30 NOVEMBER– 4 DECEMBER	American Exploration and Mining Association Annual Meeting. Spokane WA USA. Website: tinyurl.com/papq5jx
2016	
10-16 JANUARY	Winter Conference on Plasma Spectrochemistry. Tucson AZ USA. Website: icpinformation.org/Winter_Conference.html
18-19 JANUARY	10th International Symposium on Environmental Geochemistry. Perth Australia. Website: www.iseg10.com/
27 AUGUST – 4 SEPTEMBER	35th International Geological Congress. Cape Town South Africa. Website: www.35igc.org
11-15 SEPTEMBER	2nd European Mineralogical Conference. Rimini Italy. Website: emc2016.socminpet.it/
16 21 OCTORER	Water Rock Interaction 15 Évora Portugal

16-21 OCTOBER Water Rock Interaction 15. Évora Portugal. Website (pdf): tinyurl.com/lch75x8

Geochemistry Meetings in 2015 and 2016

Applied Isotope Geochemistry 11 (AIG-11)

Date: September 21-25, 2015 Location: Orleans, France Website: <u>http://aig11.brgm.fr</u>

The purpose of this international conference is to bring together specialists in the different fields related to applied isotope geochemistry, to present state-of-the-art developments as well as key examples of application and to promote exchange of ideas between scientists. The aim of the 11th Applied Isotope Geochemistry conference is to provide a forum where a wide range of applications of isotope analyses in geosciences and related fields are presented. A special focus will be put on water resources, as the downstream Loire River is scheduled to become a Unesco World Heritage site and to join the Natura 2000 network.

AIG-11 conference welcomes contributions on a wide range of the related topics including:

• Technological achievements and their applications, isotope techniques in environmental geochemistry

- Isotope hydrology as a tool for water supply policy, paleoclimatology and paleoenvironmental changes, recent applications and developments in dendroisotopes
- Biogeochemistry and ecological applications, isotopic tools applied to degradation of organic contaminants
- Applied gas isotope geochemistry
- Isotope geochemistry of sedimentary to high temperature geological processes, ore genesis and hydrocarbon exploration
- Non-geoscience applications (e.g. archeometry, forensic studies, food authenticity, medical studies, doping investigations).

Geoanalysis 2015

Date: 8-14 August 2015 Location: Leoben, Austria Website: geoanalysis.info

This conference offers the opportunity to young scientists to get international exposure to the leading scientists in the field of geoanalysis. Special care is being taken to provide

Geochemistry Meetings in 2015 and 2016... continued from page 14

inexpensive accomodation and low conference fees for students from all over the world. Topics of interest include:

Instrumental:

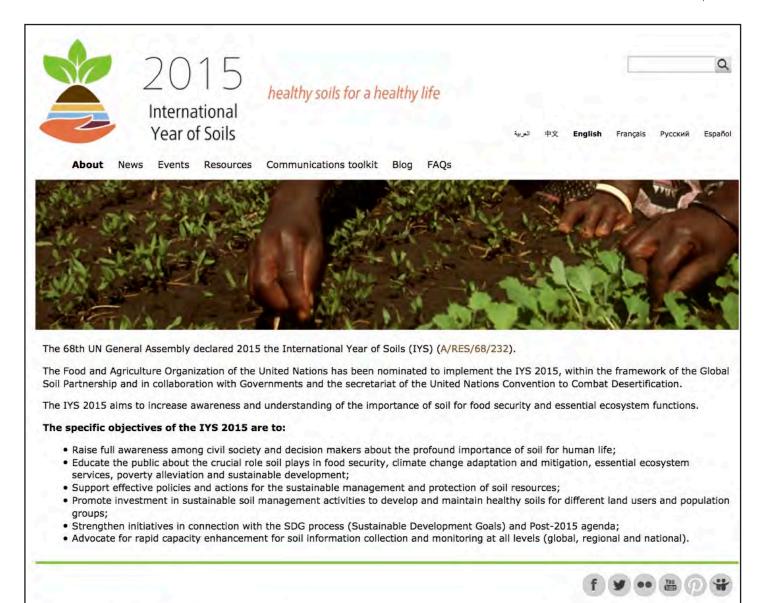
- XRF/XRD
- ICP-MS (LA-ICP-MS, ICP-QMS, MC-ICP-MS)
- EPMA
- SIMS
- MLA and QEMSCAN
- SEM and TEM
- · Any other analytical technique related to geoanalysis

Applications:

- Reference Materials
- · Metrology applied to chemical analysis

- Proficieny testing
- Sample preparation
- · Geochronology including for crude oils and oil deposits
- Isotope fractionation studies, including heavy elements
- · Environmental studies
- Mapping and regional geochemistry
- · Industrial processes and ore beneficiation
- Quality control
- Representative sampling
- Forensics
- Geochemical exploration
- On site analysis
- Education

continued on page 16



International Year of Soils 2015 Food and Agriculture Organization of the United Nations Viale delle Terme di Caracalla 00153, Rome Italy soils-2015@fao.org

Geochemistry Meetings in 2015 and 2016... continued from page 15

6th International Conference on Medical Geology (MEDGEO 2015)

Date: July 26-August 1, 2015 Location: Aveiro University, Aveiro, Portugal. Website: http://medgeo15.web.ua.pt/

The MEDGEO 2015 conference bring together researchers and decision makers from the physical sciences and the medical sciences who are interested in solving health problems caused by natural processes and materials. The participants of the conference will convey expertise in a range of scientific fields, such as geochemistry, biology, engineering, geology, hydrology, epidemiology, chemistry, medicine, nutrition and toxicology. Symposium themes:

- Environmental contaminants in health and disease
- Environmental toxicology, pathology and epidemiology
- *Climate change and human health*
- Therapeutic properties of minerals and waters
- Urban medical geology
- Modeling, mapping and monitoring of environmental • hazards and diseases
- Advances in analytical methods
- Environmental risk assessment and remediation technologies



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10th International Symposium on Environmental Geochemistry (ISEG10)

Date: January 19-21, 2016 Location: Perth, Western Australia Website: http://www.iseg10.com

ISEG-10 provides a forum for presenting the results of original and innovative studies across a very broad spectrum of environmental geochemistry. The Symposium aims to promote awareness and enable recognition of the transboundary nature of environmental issues and to assist in environmental understanding and management through the application of appropriate techniques and strategies. We encourage scientists, public and environmental health professionals, environmental managers, consultants, and regulatory officers with an interest in the behaviour that chemicals have on the environment and their affects on human health and natural ecosystems to meet, discuss and share their research findings and experience. ISEG-10 is relevant to international academics and researchers working in the broad field of environmental geochemistry, but is also of interest to consultants, regulatory authorities and public managers. The Perth symposium will bring together geochemists, environmental scientists, biologists, geologists, soil scientists, aquatic scientists and medical specialists. Symposium themes:

- Environmental Impacts of Small Scale Mining and Industry in the Developing World
- Geochemistry of Acidic and Alkaline Environments
- Geochemical Aspects of Climate Change
- Emerging Contaminants
- Mercury and the Metalloids in the Environment
- Urban Geochemistry
- Water Resources and Aquatic Environments
- Analytical Environmental Geochemistry

Water Rock Interaction 15 (WRI-15)

Date: October 16-21, 2016 Location: Évora, Portugal Website: <u>http://wri15portugal.org</u>

The WRI-15 Symposia represents an exceptional opportunity to update knowledge about each WRI core research activity, with Earth Scientists from National and International Institutions who have already been involved in research & development projects focused on related WRI research. The three Main Scientific Topics of the Symposium will be:

- Essentials of water-rock interaction
- Particular environments
- Case studies and applications



Recent Issues of Elements

Elements Volume 11, No.1 Mineralogy of Mars The Mars Science Laboratory (MSL) rover

Curiosity was designed and built to explore the surface of Mars and characterize its modern environment. Its primary objective was to search for ancient habitable environments. During its nominal one-Mars-year mission (23 Earth months),

Curiosity drilled and scooped samples, made mineralogical, isotopic, and compositional measurements, took hundreds of thousands of images that provided geologic context for samples, and acquired millions of observations of the modern environment.

Curiosity is the most advanced mobile geochemistry laboratory to have ever roved another planet, and it has been very productive. Within 8 months of landing, scientists were able to confirm mission success with evidence of an ancient habitable environment on Mars. This issue presents the range of discoveries related to the investigations of the solid materials at Gale Crater and elsewhere on Mars.

Elements Volume 11, No. 2 Arc Magmatic Tempos, Guest Editors: Scott Paterson and Mihai Ducea

The differentiation of our planet and formation of the continental crust, and its underlying mantle lithosphere, are in large part the result of magmatic processes at convergent margins. These magmatic processes are important to issues of societal interest such as the evolution of life, mineral and energy deposits, volcanic and fault hazards, and long-term climate change. Magmatism in oceanic and continental convergent arcs is not temporally or spatially steady-state, rather it occurs in pulses and lulls. The articles in the April 2015 issue of Elements explore the tempo of magmatism as recorded in the rock record, investigate the causes of high-volume events in subduction-related magmas, and provide an overview of recently developed models to explain episodic behavior in subduction magmatism.

AAG News Coordinator for Elements

Dennis Arne has kindly agreed to take over from Patrice de Caritat as the AAG's News Coordinator for *Elements*. Patrice and Dennis will work together through a transition period. From issue 11/5 onward, Dennis will be the principal contact between AAG and *Elements*. The Association thanks Patrice for his efforts as the News Coordinator for *Elements* for the past few years.





Arc Magmatic Tempos

Introduction to Arc Tempos High-Volume Magmatic Events Magma Production Rates for Intraoceanic Arcs Fractal Cadence of Arc Magmatism Continental Collision and Episodic Magmatism Subduction Zones and Climate Variability

SCOTT R. PATERSON and MIHAI N. DUCEA, Guest Editors



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Katherine Milidakis Analytical Chemist Newmont Mining 10101 E. Dry Creek Rd. Englewood, CO USA 80112 Membership # 4273

Jennifer Goldner Project Geologist Rio Tinto – Kennecott Exploration 4595 Wallace Lane Salt Lake City, UT USA 84117 Membership # 4275

Curtis Brett 354 – 200 Granville Street Vancouver, BC Canada V6C 1S4 Membership # 4276 Peter Muller Muller Geological Consulting 636 Burnham Road Philadelphia, PA USA 19119 Membership no. 4277

Andrew Mitchell Geological Consultant 37 Ravenstone Clifton Hill 51 Acutts Drive Hillcrest South Africa 3610 Membership no. 4280

Fred Block PhD retired 1710 Glenpark Drive Silver Spring, MD USA 20902 Membership no. 4281

Student Members

Steven Kramar Acadia University 9 Balcom Drive, Apt. 19 Wolfville, NS Canada B4P 2N8 Membership # 4272

Iwo Lojasiewicz California State University Long Beach P.O. Box 1581 Norwalk, CA USA 90651 Membership no. 4278

Thomas Bagley Acadia University P.O. Box 249 Canning, NS Canada B0P 1H0 Membership no. 4279

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Darwin B. Werthessen New Mexico Institute of Mining and Technology P.O. Box 4137 Socorro, NM USA 87801 Membership no. 4283

Book Review

Arsenic: Environmental Geochemistry, Mineralogy, and Microbiology. R.J. Bowell, C.N. Alpers, H.E. Jamieson, D.K. Nordstrom, and J. Majzlan (Editors), Reviews in Mineralogy and Geochemistry, Volume 79, 635 p. + 22 colour plates. Mineralogical Society of America and Geochemical Society, Chantilly, Virginia. ISBN 978-0-939950-94-2. Price: US\$45.00, US \$33.75 for MSA, Geochemical Society, and Clay Minerals Society members (www.minsocam.org).

This volume is the product of a two-day Arsenic (As) short course that was held in June 2014 in Nevada City, California following the Goldschmidt 2014 conference in Sacramento. I had the good fortune to participate in this course, as well as the preceding one-day field trip to Empire Mine State Historic Park, where several of the authors shared results from their ongoing research on the potential risks associated with high-As soils and gold mine wastes. The overall goal of the short course was to provide a thorough understanding of the mineralogy, thermodynamics, geochemistry, analysis, microbiology, and bioavailability of As in the near-surface environment, with a focus on implications for As toxicity, geochemistry in natural groundwaters, mine-associated impacts and possible mitigation options.

The short course volume contains 14 well-referenced chapters, written by many of the world's foremost As experts. The opening chapter, compiled by the editors, provides a brief overview of the distribution and cycling of As in the environment, including typical ranges of As in natural waters and earth materials. Chapter 2 (Majzlan et al.) provides an exhaustive review of the parageneses and crystal chemistry of As minerals, including two appendices summarizing the formulae of As minerals and other phases that commonly serve as hosts for As. The main focus of this 168-page chapter is on secondary As minerals in which As is bonded to oxyanions, given the importance of these minerals in controlling As mobility in the nearsurface. Chapter 3 (Campbell and Nordstrom) reviews the aqueous speciation of As, its sorption behaviour, and the redox cycling of As in natural environments. The following chapter (Nordstrom et al.) provides a critical evaluation of the thermodynamic properties of As minerals and aqueous species focusing on internal consistency, data quality, and knowledge gaps. For anyone interested in modeling the aqueous speciation of As, there are several key messages in this chapter: (i) there are no reliable stability constants available for thioarsenic species, which is a barrier to speciation modeling of As in sulfidic environments (e.g. geothermal waters); (ii) database errors can lead to inaccurate results when computing pe-pH diagrams using The Geochemist's Workbench® software; and (iii) updated As thermodynamic data should be added to geochemical databases to improve the accuracy and consistency of speciation calculations.

The next two chapters focus on the analysis of As in solids and other environmental media. Chapter 5 (Foster and Kim) is a comprehensive overview of molecular-scale As speciation measurements in solids using synchrotronbased X-ray absorption spectroscopy (XAS). This chapter provides an up-to-date review of the many As-XAS studies over the past two decades, and also includes practical tips on sample preparation, data collection, and processing and analysis of XAS results. The subsequent chapter by Leybourne et al. summarizes techniques for the field and laboratory measurement of total As and various As species, and highlights the challenges associated with sample preservation and low-level measurements in the field.

In Chapter 7, Amend et al. discuss the metabolism of As by microorganisms that transform arsenite or arsenate for the purposes of energy conservation or detoxification. The next two chapters describe the health risks associated with As exposure (Mitchell) and the various in vivo and in vitro methods for measuring and predicting the relative bioavailability of As in soils (Basta and Juhasz). These chapters clearly illustrate that recent collaborations between earth scientists, toxicologists, and public health professionals have led to significant advances in our understanding of the links between As mineralogy and bioaccessibility, improved risk assessments, and ultimately to more effective remediation of contaminated sites.

The final five chapters describe the cycling and management of As at both modern and historical mining sites. Chapter 10 (Craw and Bowell) discusses the occurrence of As in various types of mineral deposits, its geochemistry in mine wastes, and provides several excellent examples from studies of contrasting gold mineral deposits and mines in New Zealand. Management of As in the modern mining industry is reviewed in Chapter 11 (Bowell and Craw), including both active and passive methods for As removal. In Chapter 12, Jamieson describes recent studies of As contamination around the Giant Mine in Yellowknife, Canada, including the unique challenges associated with managing large quantities of arsenic trioxide and As-rich iron oxides that were produced during roasting of refractory gold ore. Chapter 13 (Alpers et al.) reviews the environmental legacy of historical gold mining in the Sierra Nevada Foothills of California and includes a summary of As mineralogy, bioaccessibility, and remediation work discussed during the aforementioned field trip to Empire Mine State Historic Park. The last chapter in this volume (Bowell) is an overview of the hydrogeochemistry of the Tsumeb base-metal deposit in Namibia, complemented by spectacular colour plates of some of the 76 different As minerals that have been identified in this As-rich deposit.

In summary, this short course volume is highly recommended to all applied geochemists with an interest in As. It is a well-written, thoroughly referenced, up-todate, and affordable resource that will be useful to anyone interested in As in the near-surface environment.

Michael B. Parsons

Geological Survey of Canada - Atlantic Dartmouth, Nova Scotia, Canada

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Matt Levbourne. President

Department of Earth Sciences and Mineral Exploration Research Laurentian University 935 Ramsey Lake Road Sudbury, ON P3E 2C6, Canada TEL: +1-705-675-1151 ext. 2263 email: mleybourne@laurentian.ca

David B. Smith, Secretary U.S. Geological Survey Box 25046, MS 973 Denver, CO 80225, USA TEL: (303) 236-1849 FAX: (303) 236-3200 email: dsmith@usgs.gov

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Symposia David Cohen, d.cohen@unsw.edu.au

AAG COORDINATORS

GEEA

Kurt Kyser, kyser@geol.gueensu.ca

EXPLORE Beth McClenaghan, beth.mcclenaghan@NRCan-RNCan.gc.ca ELEMENTS

Patrice de Caritat, Patrice.deCaritat@ga.gov.au AAG Regional Councillors

Ryan Noble, Ryan.Noble@csiro.au

P.O. Box 26099, 72 Robertson Road, Ottawa, ON K2H 9R0 CANADA, TEL: (613) 828-0199 FAX: (613) 828-9288, e-mail: office@appliedgeochemists.org



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