DANGERS OF DETERMINING ISOTOPE RATIOS USING MEANS OF INDIVIDUAL RATIOS. G. R. Huss, R. C. Ogliore, K. Nagashima, M. Telus and C. E. Jilly, HIGP, Univ. of Hawaiʻi at Mānoa, 1680 East-West Road, Honolulu, HI 96822 (ghuss@higp.hawaii.edu)

Introduction: During the last year, our research group discovered that the method of data reduction that we have used for decades to process ion microprobe data introduces a positive bias in some of the isotope ratios. This has been known in other communities for many decades. This bias and its statistical origin are discussed in a companion abstract by Ogliore et al. [1] and in a paper submitted to *Nuclear Instruments and Methods in Physics B* [2]. In brief, the problem is that the expectation value of the mean of individual ratios (of sample counts drawn from two Poisson distributions) is always larger than the ratio of the means of the two distributions. The bias is larger as the number of counts in the individual ratio decreases. This is particularly insidious when studying short-lived radionuclides, because the size of the isotopic effect typically scales inversely with the abundance of the daughter element, as does the bias from reducing data as the mean of the ratios. A much-less-biased way to calculate isotopic ratios from mass spectrometric data is to sum the counts over the entire measurement and calculate the ratio from the total counts [1,2]. The purpose of this abstract is to review some important data sets that we have published over the years and to evaluate the extent to which the bias introduced by inappropriate data reduction affected the results. Additional discussion of this problem as it relates to our current study of ^{60}Fe can be found in [3].

Studies of ^{60}Fe: This bias problem first came to light during our work on the Fe-Ni system. Thus, it seems appropriate to revisit the first chondrule for which we reported an excess of ^{60}Ni*, Semarkona chondrule SMK 1-4 [4]. We reanalyzed the data set collected for this chondrule at ASU using both the means of the ratios and the ratios of total counts. We also remeasured this chondrule as part of our study of UOC chondrules [3]. The results are shown in Table 1. In all cases, data are corrected internally for mass fractionation, and the UH data are corrected for detector drift. Notice first of all that we reproduce the published result when the data are reduced and normalized as in the original publication [4]. When normalizing to ^{62}Ni, the inferred initial ratio is lower and has a larger error, primarily because the uncertainty on ^{61}Ni is included twice due to the mass fractionation correction. When the data are reduced as ratios of total counts, the value of the inferred initial ratio drops significantly and is no longer resolved from zero. The two normalizations give precisely the same result, as they should. The new data collected by [3] have smaller uncertainties because the counting statistics are better, but the inferred initial ratio is also lower and is not resolved from zero. Because of higher count rates (= lower bias), the UH data obtained from the means of the ratios also fail to show evidence of ^{60}Fe. Based on these results, we would not have reported the detection of ^{60}Fe in this chondrule. However, other chondrules do show clear excesses of ^{60}Ni*, and the inferred initial ratios are in the same range as those we initially reported [cf, 3,4]. We will re-analyze all of our previously reported data and will report them in a future publication.

Table 1. $(^{60}Fe/^{56}Fe)_0$ ratios for SMK 1-4 calculated by two methods and normalized to two different isotopes.

ASU data reduced as mean of measured ratios	
^{61}Ni normalized	^{62}Ni normalized
$(2.89\pm1.44)\times10^{-7}$	$(0.74\pm3.07)\times10^{-7}$
ASU data reduced as ratio of total counts	
^{61}Ni normalized	^{62}Ni normalized
$(0.77\pm2.06)\times10^{-7}$	$(0.58\pm3.10)\times10^{-7}$
UH multicollection data reduced as mean of ratios	
^{61}Ni normalized	^{62}Ni normalized
$(1.8\pm1.2)\times10^{-7}$	$(-3.3\pm8.4)\times10^{-8}$
UH multicollection data reduced as ratio of total cts	
^{61}Ni normalized	^{62}Ni normalized
$(4.8\pm9.5)\times10^{-8}$	$(-2.8\pm8.5)\times10^{-8}$

Studies of ^{10}Be: McKeegan et al. [5] first showed the ^{10}Be was present in CAIs when they formed. Shortly thereafter, the ASU ion probe group showed that ^{10}Be was present in seven type-A CAIs and that $(^{10}Be/^{9}Be)_0$ did not correlate with $(^{26}Al/^{27}Al)_0$ in these samples [6]. The count rates for beryllium and boron in these CAIs were very low, so low that we could not use our standard data reduction techniques. The ^{10}B/^{11}B and ^{9}Be/^{11}B ratios were calculated from the total counts because many of the individual measurement cycles did not have any counts of one or more isotopes. However, the total counts for the denominator were >500, so the bias produced by the total counts method is <2‰, much less than the tens of percent effects that were observed. We therefore conclude that the data reported in [6] are reliable and are not subject to significant bias due to inappropriate data reduction.

Studies of ^{26}Al: Because it was very difficult originally to find clear evidence for ^{26}Al in chondrules, we checked some of our earliest data for chondrules from unequilibrated ordinary chondrites. In that work, we reported $(^{26}Al/^{27}Al)_0$ ratios for chondrules from Inman (L3.3) and Chainpur (LL3.4) of $(1.1\pm0.7)\times10^{-5}$ and $(0.92\pm0.24)\times10^{-5}$, respectively [7, 8]. Recalculation of those results using total counts instead of the mean of the ratios gave a slightly lower value of $(1.0\pm0.7)\times10^{-5}$ for the Inman chondrule, but the result for the Chainpur chondrule was unchanged. Counts per cycle for ^{24}Mg were ~10,000 for Chainpur and from ~1000 to ~7500 cps for Inman. The expected bias is thus <0.1‰, so the change in the Inman result is likely a random statistical effect.

We also checked more-recent Al-Mg data on chondrules that we reported at the Tucson Meteoritical Society Meeting [9]. Although there were slight differences in the final numbers, none of the initial ratios reported in [9] changed by more than 10% (well within quoted errors) and the changes were random. Count rates were sufficiently high to avoid bias.

Studies of ^{53}Mn: *Mn-Cr in CV fayalite:* Mn-Cr data were reported for Kaba fayalites by [10]. The resulting $(^{53}Mn/^{55}Mn)_0$ ratio was in good agreement with that measured previously in fayalites from Mokoia by [11]. Count rates for chromium isotopes in these measurements were typically <1 cps, and even with long counting times, some cycles had zero counts. This precluded us from reducing the data as the mean of individual ratios; we had to use total counts. The total counts in a measurement ranged from ~80 to ~800. There is still a residual bias of 2.5–25‰ even when using total counts [1,2]. However, the $^{53}Cr/^{52}Cr$ ratios were between 0.2 and 2.8, compared to a standard value of ~0.1134, so the residual bias is not important.

Mn-Cr in pallasites: In the mid 1990s, Mn-Cr measurements of phosphates and zoned olivines in pallasites by ion probe indicated that pallasites formed early with $(^{53}Mn/^{55}Mn)_0$ ratios as high as $\sim1\times10^{-5}$ [12,13]. Later measurements by thermal ionization mass spectrometry did not confirm these results [e.g., 14]. Nor did later ion probe measurements at ASU and UH [15]. We can now state with confidence that the initial ion probe results were experimental artifacts due to reducing the data as means of individual ratios rather than as ratios of the total counts. Table 1 compares the originally inferred initial ratios (tabulated in an unpublished preprint) with initial ratios determined using ratios of the total counts. Using total counts, we find no effects in any of the meteorites studied. Counts per cycle for ^{52}Cr were in the range of a 30 to 250 for 150 cycles, and the predicted bias using the mean of the ratios is 4–30‰ [1,2]. A slight residual positive bias of <0.2‰ thus remains in some of the data.

Table 1: $(^{53}Mn/^{55}Mn)_0$ ratios for pallasites

Meteorite	Mean of Ratios*	Ratios of Total Cts
Albin	$(1.3\pm1.1)\times10^{-5}$	$\mathbf{(-0.2\pm9.3)\times10^{-6}}$
Brenham	$(1.9\pm1.3)\times10^{-5}$	$\mathbf{(0.2\pm1.3)\times10^{-5}}$
Eagle Stn.	$(5.9\pm8.1)\times10^{-6}$	$\mathbf{(-1.3\pm10.0)\times10^{-6}}$
Glor. Mtn.	$(1.5\pm1.0)\times10^{-5}$	$\mathbf{(3.7\pm10.6)\times10^{-6}}$
Imilac	$(8.0\pm8.1)\times10^{-6}$	$\mathbf{(-3.1\pm8.5)\times10^{-6}}$
Springwater	$(8.7\pm5.7)\times10^{-6}$	$\mathbf{(2.7\pm5.3)\times10^{-6}}$

* Data from unpublished preprint.

More-recent measurements of the Mn-Cr system in pallasite olivines using the much-more-sensitive UH ims 1280 did not encounter as much bias because count rates were much higher, ~10,000 cps for ^{52}Cr.

Summary and Conclusions: There is a clear problem with systematic *positive* bias in isotope ratios when data are collected as a series of ratios and final results are calculated as the mean of those ratios [1,2]. We have reviewed a variety of data sets obtained over the years and have found that 1) some were reduced properly, even if we did not have a full understanding of the bias problem (e.g., Be-B data, Kaba fayalite Mn-Cr data), 2) some were reduced incorrectly and the reported results were biased to varying degrees (some Fe-Ni data, early Mn-Cr data for pallasite olivines), and 3) some data were obtained at high enough count rates that the bias was relatively minor (Al-Mg in chondrules). The cosmochemistry and geochemistry communities must come to grips with this problem. It will be important in any application where ratios are calculated from random samples of Poisson distributions and then averaged. The count rate at which the bias become significant depends on the precision and accuracy required in the measurements. It is relatively easy to address the problem by simply calculating the ratios from the sum of the total counts. The data can still be gathered in cycles to address problems of noise and signal stability, and time interpolation can still be utilized to avoid errors from a changing source signal. But instead of averaging the ratios, the time-interpolated counts should be summed before calculating the final ratio.

References: [1] Ogliore R. C. et al. (2011) *LPS XLII*, #1592. [2] Ogliore R. C. et al. (2011) *Nuc. Instr. Meth. Phys. Res. B.*, submitted. [3] Telus M. et al. (2011) *LPS XLII*, #2559. [4] Tachibana et al. (2006) *Ap. J. 639*, L87-L90. [5] McKeegan K. D. et al. (2000) *Science 289*, 1334-1337. [6] MacPherson G. J. et al. (2003) *GCA 67*, 3165-3179. [7] Russell et al. (1996) *Science 273*, 757-762. [8] Huss G. R. et al. (2001) *MAPS 36*, 975-997. [9] Huss G. R. et al. (2007) *MAPS 42*, A57. [10] Hua X. et al. (2005) *GCA 69*, 1333-1348. [11] Hutcheon et al. (1998) *Science 282*, 1865-1867. [12] Hutcheon I. and Olsen E. (1991) *LPS XXII*, 605-606. [13] Hsu et al. (1997) *LPS XXVII*, 609-610. [14] Lugmair G. and Shukolyukov A. (1998) *GCA 62*, 2863-2886. [15] Tomiyama T. et al. (2007) *LPS XXXVIII*, Abstract #2007. Supported by NASA grant NNX08AG58G to GRH.