

# Comment on “Determination of Total Sulfur at Microgram-per-Gram Levels in Geological Materials by Oxidation of Sulfur into Sulfate with in Situ Generation of Bromine Using Isotope Dilution High Resolution ICPMS”

This comment concerns the general lack of agreement among sulfur determinations on the U.S. Geological Survey (USGS) whole rock standard BCR-1 and the recent report by Makishima and Nakamura<sup>1</sup> (M&N) on the determination of sulfur in geological materials by isotope dilution utilizing an enriched <sup>34</sup>S spike, bomb digestion of the sample, and measurement of the <sup>32</sup>S/<sup>34</sup>S ratio by high resolution ICPMS. Although ICPMS can measure a great number of elements extremely well, sulfur is one of the more important elements that is particularly difficult to measure accurately on this type of instrumentation. This is because of the large interference from <sup>16</sup>O<sup>16</sup>O<sup>+</sup> on <sup>32</sup>S<sup>+</sup>, the major isotope of sulfur (~95%), and the index isotope that yields the most precise data for <sup>32</sup>S/<sup>34</sup>S ratio. The instrument used by the authors operating at a resolution of ~3000 resolves these two species and permits, in principle, the direct measurement of the <sup>32</sup>S<sup>+</sup> and <sup>34</sup>S<sup>+</sup> ion currents. Other approaches have been tried in an effort to eliminate the oxygen interference problem. Yu et al.<sup>2</sup> recently used electrothermal vaporization to generate water-free vapor for introduction to a quadrupole ICPMS, but this approach has fundamental limitations. The approach of M&N is direct and should be relatively robust.

The authors report sulfur concentrations on 10 geochemical reference standards, including the well-known and important BCR-1. This standard is a whole rock powder made from material collected from a single flow of the Columbia River Basalt in Oregon. Although it was issued by the USGS in 1964 and went out of stock in 1982, a great many geochemical laboratories around the world still possess and use it, and there is a continuing interest in cataloging its chemical constituents. In a 1992 compilation of data on BCR-1, Gladney et al.<sup>3</sup> surveyed 77 journals and found 1395 references containing 9464 original

data on this material. The chemical determinations in this data base increased by 33% in the first decade after it went out of stock.

The most common technique used by geochemists for determining sulfur in rocks is by inductive heating of a powdered sample followed by IR detection of the liberated SO<sub>2</sub>. To be accurate, such instruments require accurate standards for calibration, and in many cases, the standards must match the matrix of the unknown to obtain data free of bias. Thus, a wide range of accurately characterized reference materials are needed. High resolution ICPMS offers the promise of measuring sulfur and many other major, minor, and trace elements from a single dissolution, the most time-intensive step in isotope dilution, but this capability must be rigorously demonstrated for each analyte.

We have used an isotope dilution thermal ionization procedure for the determination of sulfur in a variety of matrixes since 1984.<sup>4,5</sup> In this procedure, samples are combusted in a Carius tube using nitric acid or a mixture of nitric and hydrochloric acids. This procedure completely oxidizes and destroys organic matrixes and completely dissolves all metallic matrixes. We applied this technique to the determination of sulfur in BCR-1 in 1991 and again in 2001. In the first experiment, three samples ranging in size from 0.31 to 0.38 g were combusted in Carius tubes with an enriched <sup>34</sup>S spike, 10 g of NIST nitric, and 4 g of NIST hydrochloric acid at 240 °C for three significantly different time intervals of 14, 33, and 57 h. At this temperature, nitric acid is a powerful oxidizing agent, and in addition, free chlorine gas is produced from the decomposition of nitrosyl chloride formed by reaction of hydrochloric and nitric acids. Although this combination of acids does not dissolve the silicate portion, it does attack it, and appears to be sufficiently invasive to liberate sulfur from the silicate matrix. It will also react with, dissolve, and convert all sulfides to sulfate. The sulfur in BCR-1 probably exists as discrete sulfide phases, and therefore, this dissolution procedure is sufficient to equilibrate the spike with all sulfur atoms in the sample. The sulfur isotopic composition in BCR-1 was also determined on a separate sample and used in the calculation of the concentration.

In the second experiment, three samples ranging in mass from 0.11 to 0.31 g were combusted for the same time interval using the same procedure as above. But in this case, four separate samples were dried for 2 h in a dry N<sub>2</sub> atmosphere<sup>6</sup> to determine the mass losses, which were 0.97, 1.49, 1.17, and 1.20%. The mean value was 1.21%, with a standard deviation of 0.12%. This mass loss is assumed to be water from the atmosphere. This correction is significant and means that chemical determinations on all powdered geologic samples should be reported on a dry mass basis. This could account

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Table 1. Comparison of Isotope Dilution Results for Sulfur in BCR-1

	BCR-1	mean <sup>a</sup>	1s <sup>a</sup>	95% C.I. <sup>a</sup>
this study	N = 3 <sup>b</sup>	446.8	±2.6	±4.1
	N = 3 <sup>c</sup>	438.7	±2.0	±3.4 <sup>d</sup>
Watanabe <sup>7</sup>	N = 3	441	±1.5	±3.7
Makishima and Nakamura <sup>1</sup>	N = 5	474	±14	±18
consensus value <sup>3</sup>	N = 22	410	±50	

<sup>a</sup> Concentration and uncertainties are in units of  $\mu\text{g/g}$ . <sup>b</sup> The three different samples from a single bottle (split no. 27, position no. 8) were heated for three different time intervals, 14, 33, and 57 h, yielding concentrations of 449.7, 444.4, and 446.4  $\mu\text{g/g}$ , respectively. <sup>c</sup> The three different samples were from the same bottle as previously; a moisture loss of 1.21% was determined, and the correction was applied. <sup>d</sup> Expanded uncertainty; see ref 8.

for some of the discrepancies observed among laboratories.

Selected sulfur determinations are presented in Table 1. Our results are the first two sets of data. Both sets of our data are in good agreement, but we consider the second set to be superior because the moisture<sup>6</sup> content of the standard was determined and a correction applied. Our values are in good agreement with those of Watanabe<sup>7</sup> who used a mixture of nitric and hydrofluoric acids in PTFE decomposition vessels, a procedure that would completely dissolve the silicate portion as well as the sulfide phases. Our mean value is lower than that of M&N by 35  $\mu\text{g/g}$  or ~8% (compared to our data). They state that their "... large deviation for BCR-1 is not understood ..." and suggest that Watanabe's result is low as a result of "incomplete sulfur recovery." We believe that the excellent agreement between our results and those of Watanabe, obtained using two different dissolution and mass spectrometric methods, suggests that the lower values are accurate and that those of M&N are higher than the true value. A high result would suggest a positive interference at mass 32 or a deficiency at mass 34. Sulfur blanks were sufficiently small in their work that they can be excluded as the cause of high values.

A plot of all 26 sulfur determinations on BCR-1 compiled by Gladney et al.<sup>3</sup> is shown to the left of the dashed line in Figure 1. Three determinations were beyond the ordinate of the graph, as noted by the arrows. To the right is plotted the consensus value,  $410 \pm 50$   $\mu\text{g/g}$  sulfur, that was determined by data selection and analysis by Gladney et al.<sup>3</sup> The values of Watanabe (W) and our values (KVM) are also plotted on this figure. The small circles represent the mean, and the error bars represent a 95% confidence interval (C.I.). The data of M&N are to the far right. Their 1s uncertainty was converted to a 95% C.I. This figure illustrates three important points: (1) the wide dispersion of the data suggests that sulfur determinations on basaltic rocks could be subject to large biases and

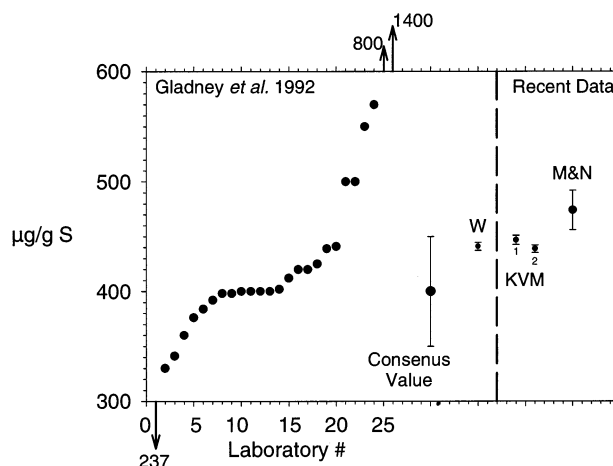


Figure 1. Comparison of individual laboratory determinations of the sulfur concentration in BCR-1 from sources compiled by Gladney et al.<sup>3</sup> To the right of these are the consensus value determined by Gladney et al.<sup>3</sup> and the value of Watanabe<sup>7</sup> (W). To the right of the dash line are the two values from this study (KVM), and the value of Makishima and Nakamura<sup>1</sup> (M&N). The last four data are plotted as means and their associated 95% C.I.

that accurate sulfur determinations in homogeneous whole rock basaltic matrixes are difficult to achieve; (2) assigning a value to materials by the consensus approach is necessarily imprecise due to multiple sources of biases that may not cancel; and (3) despite the differences in the three recent independent determinations, they are in much better agreement than the consensus data set.

Although BCR-1 has been shown to be homogeneous for many elements, this may not be the case for sulfur, which is a phase-forming element. Furthermore, M&N used sample sizes of 13–40 mg which are more than a factor of 3 smaller than those in this study. It is possible that BCR-1 is not homogeneous for these relatively small sample sizes. The relatively large moisture content of our BCR-1 sample suggests that discrepancies of several percent or more among laboratories could result from the lack of or improper moisture corrections. It is possible that a combination of the last two factors could account for the differences observed.

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