

## Sulfur Isotope Study on the Wolf River Batholith, Wisconsin in U.S.A.

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**ABSTRACT:** Sulfur isotope compositions have been determined for the granitic and related rocks from the Wolf River Batholith, Wisconsin in U.S.A. Sulfur content and isotope composition of granitic rocks of the Wolf River Batholith range from 30 to 140 ppm and from 1.1 to 6.5 permil respectively, and are considered to be magmatic. Sulfur content and isotope composition of the Penokean plutonic rocks, surrounding country rocks, range from 31 to 381 ppm and from -1.7 to 7.2 permil respectively. The positive correlation observed between sulfur and oxygen isotope data of granitic rocks and the Penokean plutonic rocks may be due to the assimilation of the Penokean plutonic rocks by a primary magma of deep-crustal origin, or to mixing, at depth, of a primary magma with another magma having higher  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$ .

**Key words:** granitic rocks, sulfur isotope, sulfur content

### INTRODUCTION

There exist only a few studies related to the sulfur isotope composition of granites and the possibility of using sulfur isotope for the discrimination of source materials between primary igneous and sedimentary origin has been under debate (Shima *et al.*, 1963; Hoefs, 1973; Coleman, 1977, 1979). The applications of sulfur isotopes for distinguishing between ilmenite- and magnetite-series of granites (Sasaki and Ishihara, 1979, Czamanske *et al.*, 1981, Ishihara and Sasaki, 1989), and between I- and S-type granites in Australia (Coleman, 1979) have indicated the potential utility of sulfur isotopes in studying granitic rocks.

Sulfur isotope compositions of the Wolf River Batholith has been analyzed in this study, and combined with the oxygen isotope data presented by Kim and Shieh (this volume), the genetic relationship between the batholith and older surrounding country rocks was examined. Since

the geological background on the Wolf River Batholith are presented by Kim and Shieh (this volume), it is omitted in this paper.

### ANALYTICAL METHODS

#### Sulfur Content

To determine the whole rock sulfur contents, samples were processed using a ball mill grinder. After grinding, the powders were manually ground in a porcelain mortar to -200 mesh. Whole rock sulfur contents were determined in two ways: 1) analysis on 1 gram of powdered rock using the LECO Sulfur Analyser and 2) analysis on 1-50 grams of powdered rock using Kiba reagent. Ideally the LECO is capable of measuring whole rock sulfur with an accuracy of 1 ppm and a precision of 1%. Replicated analyses of most samples, however, indicate a reproducibility of 10 ppm or about 15%. This relatively poor reproducibility may be due to the

sample inhomogeneity, or it may be due to problems inherent in the application of the LECO technique to silicate rocks. For instance, halogens contained within a sample can cause erroneously low sulfur values during fusion of rocks.

### Sulfur Extraction and Isotope Analysis

Extraction of total sulfur for isotope analysis was carried out using a tin-strong phosphoric acid (Kiba reagent), a mixture of stannous chloride and dehydrated phosphoric acid (Sasaki *et al.*, 1979). Kiba reagent dissolves silicates and reduces sulfides and sulfates to H<sub>2</sub>S. H<sub>2</sub>S was introduced into zinc acetate solution to be converted into ZnS. Then ZnS was converted to Ag<sub>2</sub>S by adding 0.1 mole AgNO<sub>3</sub> solution. The final product, Ag<sub>2</sub>S, was filtered and dried. The sulfur recovered by Kiba reagent is about 35 to 120% of sulfur content determined by LECO sulfur analyzer but generally slightly lower (70~90% of LECO analysis). The reason for lower recovery by Kiba than LECO might be due to the loss of sulfur in the form of ZnS and/or Ag<sub>2</sub>S during the process.

For the interpretation of data involving sulfur content in later sections, the concentrations given by the LECO analysis were used, because more samples were processed through the LECO and loss of sulfur must be less than by the Kiba process. Sulfur extracted from samples by the Kiba process was converted to SO<sub>2</sub> by reaction with CuO in vacuo at 900 to 1000°C (Fritz *et al.*, 1974). The mass spectrometer used was a 60°C, single-focusing, double collecting Nuclide 3-60 RMS. The sample preparation and the analysis were carried out in the stable isotope lab. in Purdue University.

The data are presented in terms of the  $\delta$  notation and values are reported in permil (parts per thousand).

$$\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 10^3 \text{ permil}$$

In this expression R is the ratio of <sup>34</sup>S/<sup>32</sup>S. The standard used for reporting isotope compositions is CDT (Canyon Diablo Troilite) and

**Table 1.** Comparison of sulfur isotope composition between direct combustion and combustion after Kiba processing (sample RN-5)

Kiba Process	Direct Combustion
$\delta^{34}\text{S}$ (CDT, permil)	$\delta^{34}\text{S}$ (CDT, permil)
23.02	23.49
23.77	23.14
average 23.04 $\pm$ 0.38	23.32 $\pm$ 0.18

the analytical error in this research is 0.5 permil. The isotope composition relationship between two phases (A and B) is expressed as a fractionation factor,

$$\alpha_{A-B} = R_A/R_B$$

and the symbol  $\Delta$  is defined as

$$\Delta_{A-B} = 1000 \ln \alpha_{A-B}$$

For relatively small fractionations

$$\Delta_{A-B} \cong \delta^{34}\text{O}_A - \delta^{34}\text{O}_B$$

To check the procedure of sulfur extraction, a pure pyrite (RN-5) was analyzed both directly and indirectly. The RN-5 was converted to Ag<sub>2</sub>S following the same procedure used for rock samples by Kiba reagent. The  $\delta^{34}\text{S}$  of this RN-5 was compared to the  $\delta^{34}\text{S}$  of the RN-5 which was burned directly. The difference is less than 0.1 permil which is within the experimental error (Table 1).

## RESULTS AND DISCUSSION

### Analytical Results

Thirty-eight granitic rocks, four monzonite, four anorthosite and seven Penokean plutonic rocks were analyzed by LECO analyzer. Thirty granitic rocks, four monzonite rocks, four anorthosite and six Penokean plutonic rocks were analyzed by Kiba process. Sulfur contents and isotope compositions of the Wolf River Batholith and the Penokean plutonic rocks are shown in Table 2 and Fig. 1. Sulfur content of the granitic rocks ranges from 30 to 140 ppm

**Table 2.** Sulfur Content and Isotopic Composition of the Wolf River Batholith and the Penokean plutonic rocks

	LECO (ppm)	KIBA (ppm)	Ag <sub>2</sub> S (mg)	(Kiba/LECO) (%)	$\delta^{34}\text{S}$ (permil)
<b>Wolf River Batholith</b>					
<b>Wolf River</b>					
<b>Granite</b>					
CL3A	54				
DR8	117	88	6.9	75	2.2
		90	2.4	77	
1016	77	59	3.4	77	2.4
1017	45	15	4.2		4.0
1204	49	6	2.1	16	
1214	62	57	4.8	92	
1215	78	69	4.6	88	5.7
1306	50				
1506	36				
1507	61				
1516	87				
1517	80				
<b>Wolf River</b>					
<b>Granite</b>					
<b>(cumulate)</b>					
GR4A	50	45	3.1	90	4.0
GR6	55	34	2.1	62	4.8
GR24A	61	76	8.1	125	3.3
GR34	89	82	11.3	92	2.7
HT30	109	107	8.1	98	3.6
		37	2.8	34	
TG11A	49	42	2.1	86	3.8
<b>Red River</b>					
<b>Adamellite</b>					
CL16	65	42	2.4	65	4.9
GR3	76	30	2.7	39	6.5
TG11	79				
1001	45				
1002	49				
1115	76	60	7.0	79	4.4
1232	61	50	3.1	82	4.8
1301	65				
1319	49	36	2.9	74	
<b>Wiborgite</b>					
<b>Porphyry</b>					
CL30	49	33	3.0	67	5.1
GR36B	64	51	3.0	80	4.6
TG17B	36	30	1.8	83	
1210		46	6.2		4.3

**Table 2.** continued.

	LECO (ppm)	KIBA (ppm)	Ag <sub>2</sub> S (mg)	(Kiba/LECO) (%)	$\delta^{34}\text{S}$ (permil)
<b>Waupaca A-</b>					
<b>damellite</b>					
TG38	113	50	3.5	44	3.2
WP5A	81	61	5.8	75	1.1
XW4B	59	46	5.8	78	
1107	140	129	17.8	92	4.2
<b>Belongia</b>					
<b>Granites</b>					
11M	53				
58M	30	18	2.6	60	
83AT	33	18	2.2	53	5.7
1633	35	30	2.8	86	2.8
<b>Monzonite</b>					
GR17B	22	28	3.9	127	3.9
GR26A	477	450	3.8	94	3.5
TM3	770	734	2.8	95	3.1
<b>Anorthosite</b>					
XS2	150	43	113	13.8	75
W5	25	16	1.7	70	3.6
W22	125	10	1.4	40	
1502		131	19.8	105	3.0
<b>Penokean plutonic rocks</b>					
<b>Northeast</b>					
1533	49	34	4.2	69	6.5
1534	125	131	8.6	105	4.2
1537	205	179	9.4	87	7.2
<b>Southwest</b>					
1005	61	41	2.7	67	6.2
1009	43				
1012	31	12	2.4	45	-1.7

(LECO) with an average of 66 ppm. Only four samples (DR8, HT30, TG38, 1107) show sulfur contents higher than 100 ppm, which were collected near the contact zone with country rocks. However, the  $\delta^{34}\text{S}$  of these are similar to other samples and other samples collected near the contact zone are similar in sulfur content.

The Waupaca Adamellite has the highest sulfur content (59~140, with an average of 98 ppm) among granitic plutons. This may be a distinct feature of the Waupaca Adamellite or may arise from the small number of samples (four)

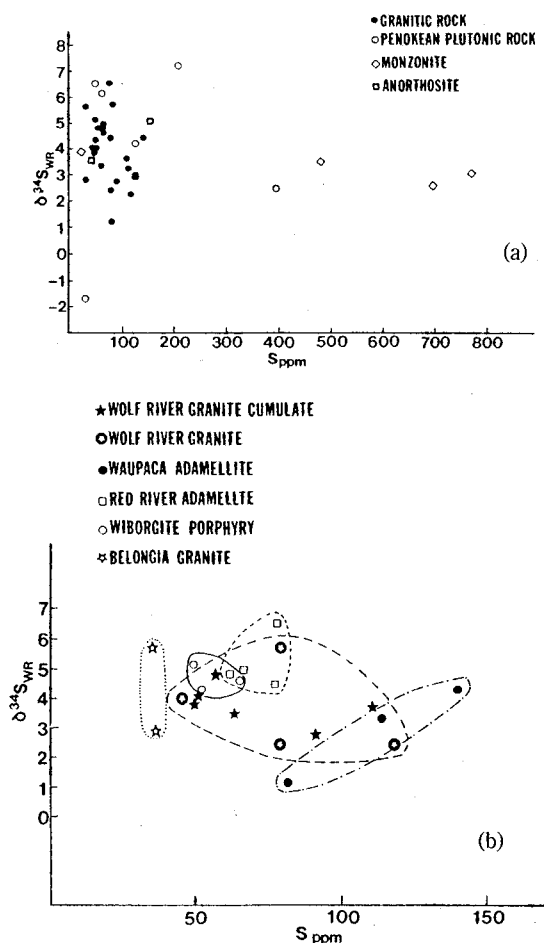


Fig. 1. Sulfur content vs.  $\delta^{34}\text{S}_{\text{WR}}$ . (a) the Wolf River Batholith and the Penokean plutonic rocks, (b) granitic rocks of the Wolf River Batholith

among all the granitic plutons. The Wolf River Granite (36~117, average 67 ppm) and the Red River Adamellite (45~79, average 63 ppm) are similar in sulfur content. The Wiborgite Porphyry shows lower values (36~64 average 50 ppm), and the Belongia Granites (30~53, average 38 ppm) displays the lowest values.

Sulfur contents of the monzonite and the anorthosite are generally higher than granitic rocks and show wider variations. Three (GR 26A(477 ppm), TM3(770), 1706(630)) of the four monzonite samples analyzed show much higher sulfur contents, but GR17B (22 ppm) displays a value lower than those of the granitic

rocks. Samples TM3 and 1706 are from relatively large bodies located in the northeastern part of the batholith, and samples GR17B and GR26A are from small bodies exposed in the center of the batholith near the anorthosite.

Sulfur content of the anorthosite ranges from 25 to 150 ppm. Sample XS2 and 1502 are higher than 125 ppm, but W5 and W22 are lower than 43 ppm. There is no apparent relationship between the sulfur content and sample distance from the contact zone with the Wolf River Granite, which surrounds the anorthosite body.

The total range of  $\delta^{34}\text{S}$  in the granitic rocks is from 1.1 to 6.5 permil with an average of 4.0 permil. The Waupaca Adamellite is the lowest with an average of 2.8 permil (1.1~4.2). The Wolf River Granite is next lowest with an average of 3.7 permil (2.2~5.7). The Red River Adamellite (4.4~6.5, average 5.2 permil) and the Wiborgite Porphyry (4.3~5.1, average 4.7 permil) are similar but the Red River Adamellite is slightly higher, by 0.5 permil on average.

Sulfur content of the Penokean plutonic rocks ranges from 31 to 381 ppm with the average of 128 ppm, and  $\delta^{34}\text{S}_{\text{WR}}$  ranges from -1.7 to 7.2 permil, which are wider than those of the Wolf River Batholith

### Origin of Sulfur

To understand the significance of sulfur isotope composition, the question about the source of sulfur should be answered: is sulfur magmatic or from hydrothermal fluid or from country rock during or after the emplacement of the batholith? Or is the source of sulfur a combination of these rather than a single source? In order to answer this question, sulfur contents, sulfide mineralogy and texture, and sulfur solubility in silicate melt of the Wolf River Batholith must be considered.

### Sulfide Mineralogy and Texture

The size of most sulfide grains is usually less than  $3\ \mu\text{m}$ . Since many grains are barely large

enough to be resolved by the microscope, it is easy to imagine that many more are not large enough for microscopic examination. The only sulfide mineral identified under the microscope is pyrite.

Pyrite shows a strong affinity with biotite, both on the surface and as inclusion. It also is included in quartz, rarely feldspar, and may also occur interstitial to other minerals. Pyrite is observed in several habits, usually with euhedral crystal faces. However, a euhedral crystal of pyrite does not necessarily indicate crystallization at the magmatic stage, because pyrite has a strong tendency to form secondary euhedral crystals. About fifty percent of the pyrite grains are located on the rims of biotite flakes. This indicates that the bulk of sulfide deposition took place after the completion of biotite crystal growth.

However the timing of deposition, whether during crystallization of magma or from an extraneous source after emplacement, is ambiguous. On the one hand, the sulfides could have nucleated on biotite phenocrysts suspended in the melt during magmatic stage; on the other hand, hydrothermal fluids circulating through a solidified batholith could have deposited sulfides on the surface of biotite grains. Hence the most common sulfide texture reveals little about the timing of deposition. Some pyrite grains enclosed by biotite, quartz and feldspar may represent early formed phenocrysts. However, sulfide developed interstitially to biotite, feldspar and quartz is suggestive of late crystallization. In conclusion most grains could have been deposited either during the magmatic stage or the hydrothermal stage. Or some of them might have originated from an extraneous source and were precipitated onto the sulfur of the magma origin.

#### Speciations and Solubilities of Sulfur in Felsic Magmas

The solubility of sulfur depends on various factors such as  $P_t$ ,  $f_{O_2}$ ,  $f_{S_2}$  and the activities of

$H_2O$  and  $Fe^{2+}$  in the melt. The difficulty in quantifying the effects of these variables arises from the fact that some variables are interdependent (Ohmoto, 1986).

One approach to estimation of maximum solubility of sulfur in silicate melts is to study natural igneous rocks which contain sulfide-bleb inclusions in major silicate minerals (e.g. feldspar, hornblende, biotite). These sulfides indicate that such melts were saturated with sulfur as sulfide minerals or a sulfide liquid during crystallization of the silicate melts. The reported solubility of sulfur is less than 50 ppm for the I-type granitoids in Arizona (Banks, 1982), less than 60 ppm for the Japanese dacites (Ueda and Itaya, 1981; Ueda and Sakai, 1984), less than 100 ppm for the I- and S-type granitoids in Japan (Ishihara *et al.*, 1985), and less than 50 ppm for the S-type granitoids in Nova Scotia (Kubilius, 1983).

Carroll and Rutherford (1985) observed a maximum sulfur solubility of 200~300 ppm for granodiorite and granite compositions ( $FeO=1-8$  wt.%,  $P=2$  kb,  $T=1000^\circ C$ ,  $f_{O_2}=\text{below NNO buffer}$ ). A similar value of about 100 ppm was observed by Bradburry (1983) in an experiment using albite glass and pyrrhotite as starting materials at  $T=900^\circ C$ ,  $P=5$  Kbar and  $f_{O_2}$  near the QFM buffer. The sulfur content (30~140 ppm, average 66) of granitic rocks in the Wolf River Batholith is within the sulfur solubility range estimated by these experiments. However it is marginal when compared to that obtained by studies of natural rocks. Since Burnham (1979) first suggested the dominant role of  $HS^-$  in hydrous silicate melts as a sulfur species, studies (Ueda and Sakai, 1984; Rye *et al.*, 1984; Carroll and Rutherford, 1988) have suggested the importance of the oxidized form of sulfur ( $SO_4^{2-}$  and/or  $SO_3^{2-}$ ) in high  $f_{O_2}$  magmas. The most quantitative estimation of the ratio of sulfate to sulfide is from Carroll and Rutherford (1988). They showed that  $H_2S$  is the dominant sulfur species in low  $f_{O_2}$  region (lower than QFM buffer) and an abrupt increase of the ratio occurs between QFM buffer and QFM buffer plus two

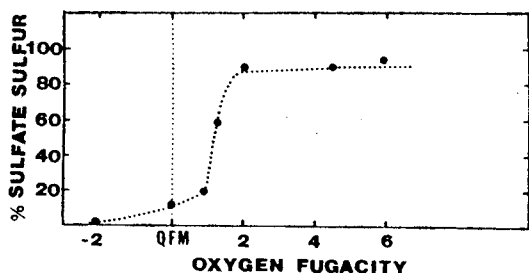


Fig. 2 The ratio of sulfate sulfur and sulfide sulfur in the silicate melt (from Carroll and Rutherford, 1988):  $f_{O_2}$  values are reported relative to the QFM buffer. Therefore QFM<sup>+2</sup>, for example, means 2log $f_{O_2}$  units above QFM buffer. Dashed line indicates the maximum  $f_{O_2}$  for

orders of  $f_{O_2}$  range (Fig. 2). The estimated  $f_{O_2}$  of the magma of the undifferentiated plutons in the Wolf River Batholith is parallel to, and slightly lower than, QFM buffer (Anderson, 1980). Considering the data presented in Fig. 2, the absence of sulfate in granitic rocks (as observed under the microscope) is not surprising, because the percentage of oxidized sulfur in the magma should be less than 10% at the  $f_{O_2}$  conditions of the batholith. If sulfur originated from the magma, the absence of sulfate agrees with the oxygen fugacity of the Wolf River Batholith, but this does not necessarily exclude the possibility of a hydrothermal solution source. At low  $f_{O_2}$  conditions, hydrothermal solutions can precipitate only sulfide sulfur.

#### Effect of Fractional Crystallization

If sulfur content exceeded the solubility of sulfur in magma, sulfide would be separated with the melt. As fractional crystallization proceeded, sulfide would be precipitated with the early crystallized portion, and the remaining melt would contain less sulfur than the original magma. This would result in the continuous decrease of sulfur content with increasing differentiation trend. However, if the magma was undersaturated with sulfur, sulfur contents of the early crystallized portion, the original magma and the final melt would be similar. But in a shallow environment, a different situation might exist. As differentiation proce-

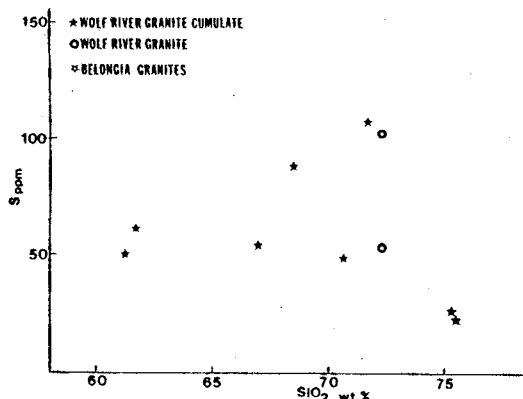


Fig. 3 Sulfur content vs. SiO<sub>2</sub> content of plutons belonging to the differentiation trend.

eded,  $f_{H_2O}$ , with other volatiles in the melt would increase. Under a favorable environment such as shallow depth, degassing of volatiles could occur. Then the sulfur content of the final melt would be lower than that of the original magma and early precipitated portion (cumulate) due to volatile degassing, while that of the cumulate and the original magma would be similar. The sulfur contents of the plutons of the differentiated sequence—the Wolf River Granite, the Wolf River Granite cumulate and the Belongia Granites—suggested by Anderson (1980) are plotted in Fig. 3. There is no clear difference between the sulfur content of the Wolf River Granite cumulate and that of the Wolf River Granite, but the Belongia Granites are lower than the former two. This trend and the epizonal character (emplacement depth of 3 to 4 km) of the Wolf River Batholith agree well with the sulfur-undersaturated magma model. Such a low sulfur content of the Belongia Granites is difficult to explain if sulfur was introduced to the batholith by a hydrothermal solution. A possible explanation is that hydrothermal fluid did not affect that particular portion of the batholith (the Belongia Granites).

#### Effect of Hydrothermal Alteration

If sulfur was introduced by hydrothermal fluid and juxtaposed onto original sulfide in gran-

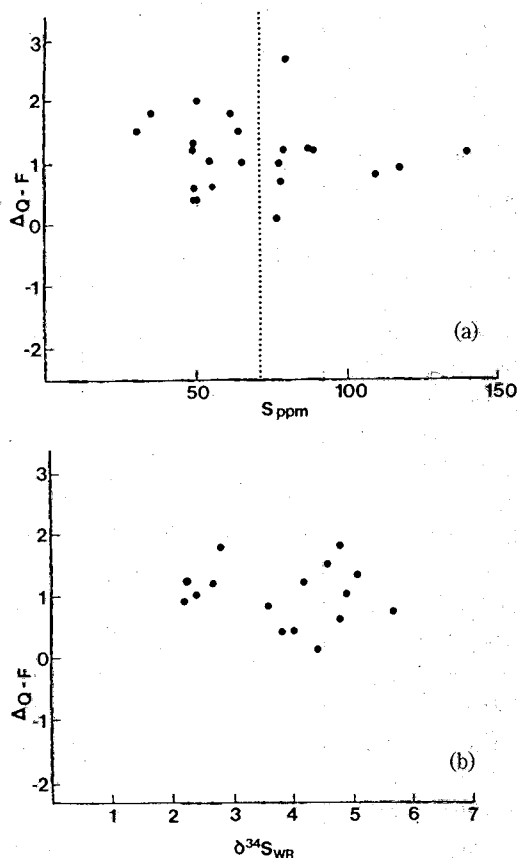


Fig. 4. (a) Q-F vs. sulfur content of granitic rocks of the Wolf River Batholith: The dashed line (70 ppm) indicates approximately the maximum solubility of sulfur in silicate melt based on the natural rock studies. Data of  $\Delta Q-F$  values are from Kim (1993), (b)  $\Delta Q-F$  vs.  $\delta^{34}S_{WR}$  of gran-

ite, the sulfur content of the granitic rocks would not be the same as their original content. Or, in the reverse case, interaction of a very sulfur depleted hydrothermal fluid with the batholith would leach the sulfur from the rocks. In both cases, sulfur contents should be different between hydrothermally altered samples and unaltered samples. If the sulfur originated from a hydrothermal solution, altered samples would show different  $\delta^{34}S$  from unaltered samples. But as is shown in Fig. 1b, no appreciable correlation is observed between the sulfur content and the isotope composition. The only possible way to explain this poor correlation is to say that  $\delta^{34}S$  of the hydrothermal solution is similar to the  $\delta^{34}S$  of the magma.

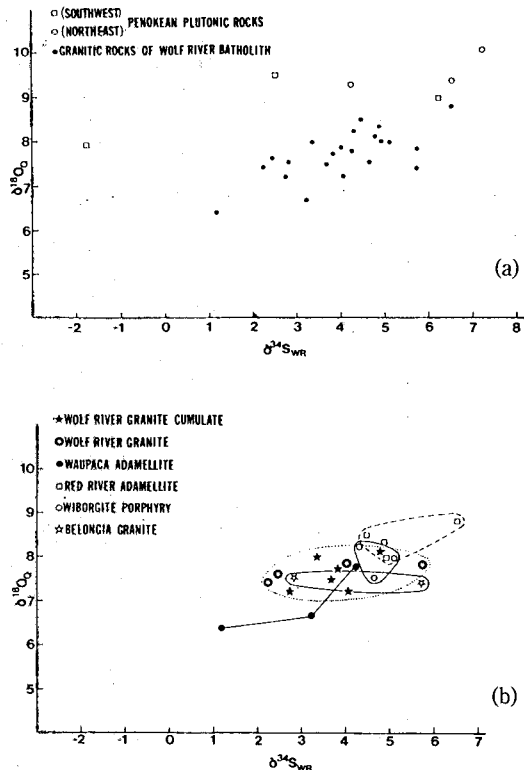


Fig. 5  $\delta^{18}O_Q$  vs.  $\delta^{34}S_{WR}$ . (a) granitic rocks of the Wolf River Batholith and the Penokean plutonic rocks, (b) each granitic plutons of the Wolf River Batholith.

As an alternative approach, even though it is an indirect one, oxygen isotope fractionations between quartz and feldspar (Kim, 1993) versus sulfur content are plotted in Fig. 4a. Considering the studies of natural igneous rocks mentioned earlier, 60 to 70 ppm seems the maximum solubility of sulfur for felsic silicate melt. Since solubility estimated by experiments has a large error range, solubility values obtained from natural rocks were used here. The samples containing less than 70 ppm of sulfur (left side of dashed line) have slightly larger  $\Delta Q-F$  values than those containing more than 70 ppm. But correlation ( $r = -0.08$ ) is very poor. Even exclusion of two samples (upper and right extreme ends), does not improve the correlation much ( $r = -0.25$ ).  $\Delta Q-F$  versus  $\delta^{34}S$  also exhibits random distribution (Fig. 4b).

In conclusion, even though there is no strong evidence supporting the magmatic origin of sul-

fur in the Wolf River Batholith, the comparison of sulfur contents between hydrothermally altered samples and unaltered samples, and the sulfur contents of plutons belonging to the differentiation trend suggest a magmatic origin. These evidences are hardly explainable by the sole influence of hydrothermal solution.

## PETROGENESIS

Sulfur content of the Penokean plutonic rocks ranges from 31 to 381 ppm with the average of 128, and  $\delta^{34}\text{S}_{\text{WR}}$  ranges from -1.7 to 7.2 permil, which are wider than those of the Wolf River Batholith: sulfur content ranges from 30 to 140 ppm with the average of 66 and  $\delta^{34}\text{S}_{\text{WR}}$  ranges from 1.1 to 6.5 permil with the average of 4.0. Interestingly, samples from the southeastern part have scattered values and have a wider range in both sulfur content and isotope composition (31~381 ppm, -1.7~6.2 permil) than samples from the northeastern part (49~210 ppm, 4.2~7.2 permil).

Based on only the sulfur content and isotope composition, the Penokean plutonic rocks can be a possible source material of the Wolf River Batholith. However, the consideration of oxygen isotope data (Kim and Shieh, same volume) and wide variations of sulfur content and isotope composition makes them an improbable source.

As shown in Fig. 5a,  $\delta^{18}\text{O}_\text{Q}$  and  $\delta^{34}\text{S}_{\text{WR}}$  values of granitic rocks of the Wolf River Batholith show a positive correlation ( $r=0.69$ ) and increase toward the values of samples from the northeastern part of the Penokean plutonic rocks. If original values of the parent magma were similar to or lower than the present values of the batholith,  $\delta^{18}\text{O}_\text{Q}$  and  $\delta^{34}\text{S}_{\text{WR}}$  values of the batholith are intermediate between the original parental magma and those of the Penokean plutonic rocks. The possible explanations for this trend are that 1) sulfur was introduced from the Penokean plutonic rocks by hydrothermal fluid, 2) the Penokean plutonic rocks were assimilated by the parent magma of

granitic rocks, 3) the magma from deep source was mixed with another magma having higher  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$  values, at depth, and produced the granitic rocks of the batholith or 4) the source material was inhomogeneous and produced magma which is slightly different in  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$  values as a result of successive partial fusion.

The possibility of hydrothermal alteration was investigated and was considered implausible in the earlier discussion. Also, the oxygen isotope composition of quartz can not change more than one permil considering its resistance to isotopic exchange at temperature below 300°C.

In the case of the assimilation of country rocks, the original composition of the primary magma is not known.  $\delta^{18}\text{O}_\text{Q}$  and  $\delta^{34}\text{S}_{\text{WR}}$  values of the mantle rocks have been considered to be 5~6 permil (e.g. Taylor and Sheppard, 1986) and  $0\pm 3$  permil (e.g. Coleman, 1977; Ohmoto, 1986) respectively. These values agree well to those measured for the lower end of the trend observed in the granitic rock of the Wolf River Batholith. Also,  $\delta^{18}\text{O}_\text{Q}$  and  $\delta^{34}\text{S}_{\text{WR}}$  values of the northeastern part of the Penokean plutonic rocks are in the higher end of the trend, suggesting assimilation of the Penokean plutonic rocks by the mantle derived magma. However, to produce the  $\delta^{18}\text{O}_\text{Q}$  and  $\delta^{34}\text{S}_{\text{WR}}$  of granitic rocks of the Wolf River Batholith, an almost 1 to 1 ratio between the primary magma and the country rock is required. In this assimilation model the primary magma is not necessarily of mantle origin. The assimilation model seems more likely if the primary magma originated from the lower crust, which had slightly higher  $\delta^{18}\text{O}_\text{Q}$  and  $\delta^{34}\text{S}_{\text{WR}}$  values than those from the mantle.

Another way to explain the trend is that, at depth, the primary magma was mixed with another magma of different isotope composition. As in Fig. 5b, each pluton appears to have its own domain in  $\delta^{18}\text{O}_\text{Q}$  and  $\delta^{34}\text{S}_{\text{WR}}$  space. Since the Belongia Granites are the differentiation product of the Wolf River Granite,  $\delta^{18}\text{O}_\text{Q}$  and  $\delta^{34}\text{S}_{\text{WR}}$  values of these plutons should be almost the same. If primary magma was mixed with another



er magma having higher  $\delta^{18}\text{O}_Q$  and  $\delta^{34}\text{S}_{\text{WR}}$  values, then, depending on the mixing ratio, slightly different isotope compositions in each pluton can be expected.

Alternatively, this trend can be explained by the heterogeneity of the source material. However, if only heterogeneity of the source material has caused the different  $\delta^{18}\text{O}_Q$  and  $\delta^{34}\text{S}_{\text{WR}}$  values of each pluton, then the positive correlation of those values is difficult to explain.

## CONCLUSIONS

1. Sulfur in the granitic rocks of the Wolf River Batholith is considered to be magmatic based on several lines of evidence: 1) when  $\Delta Q-F$  values, indications of hydrothermal alteration, are plotted against the sulfur content (30~140 ppm) and isotope composition (1.1~6.5 permil), no correlation is observed, 2)  $\delta^{34}\text{S}_{\text{WR}}$  of the Wolf River Granite cumulate and the Wolf River Granite and the Belongia Granites which belong to the differentiation trend are almost identical, 3) the sulfur contents of the Wolf River Granite cumulate and the Wolf River Granite are indistinguishable, while sulfur content of the Belongia Granite is lower (30~33 ppm). This must be due to volatile degassing from the differentiated melt of sulfur-undersaturated magma at shallow emplacement level.

2. The oxygen and sulfur isotope compositions as well as sulfur content suggest that the Penokean plutonic rocks are probably not suitable source material for the Wolf River Batholith.

3. There is a positive correlation between oxygen and sulfur isotope data of granitic rocks probably due to: 1) the assimilation of the Penokean plutonic rocks (country rocks) by magma of deep-seated source or 2) mixing of a primary magma with another magma having higher oxygen and sulfur isotope compositions.

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(책임편집 : 노진환)

## 미국 위스콘신주의 올프리버 저반에 대한 황동위원소 연구

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**요 약** : 올프리버 저반의 화강암질 심성암체의 황함량과 황동위원소는 각각, 30~140 ppm 및 1.1~6.5 permil의 조성범위를 보이며, 마그마 기원으로 판단된다. 주변 모암인 피노키안 심성암체의 황함량과 동위원소 조성은 각각, 31~381 ppm과 -1.7~7.2의 범위로서 올프리버 저반의 직접적인 근원 암이 될 수 없는 것으로 보인다. 피노키안 심성암체와 올프리버 저반의 화강암체들의 산소와 황동위원소 조성이 상당히 뚜렷한 선형의 경향을 보이는데, 이러한 경향은 심부 지하가 근원인 본원마그마에 의한 피노키안 심성암체의 동화작용, 또는 심부에서 본원 마그마와 좀 더 높은 산소 및 황동위원소 조성을 갖는 또 다른 마그마와의 혼합에 의한 것으로 볼 수 있다.

**핵심어** : 화강암, 황동위원소, 황함량