

## Oxygen isotope study on the hydrothermal alteration in the Wolf River Batholith, Wisconsin in U.S.A.

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**ABSTRACT:** Oxygen isotope compositions of whole rock and/or mineral separates (quartz and feldspar) have been determined for the granitic and related rocks from the Wolf River Batholith, Wisconsin. Hydrothermal alteration resulting in the decrease of  $\Delta_{Q-F}$  values was observed locally throughout the batholith. Feldspars of different colors (pink, gray and red) were separated whenever feasible and analyzed. Most red feldspars ( $An_{10-30}$ ) show the highest and constant  $\delta^{18}O$  values (9.3~10.0 permil) suggesting nearly complete isotope exchange with hydrothermal fluid. Based on  $\delta^{18}O$  values and the alteration temperatures (260~350°C) estimated from fluid inclusion study,  $\delta^{18}O$  of fluid is calculated to be  $5.0 \pm 1.4$  permil. Phanerozoic sedimentary formation water in Wisconsin is most likely the source of the fluid.

**Key Words:** Isotopic fractionation, hydrothermal alteration

### INTRODUCTION

The oxygen isotopic fractionation between coexisting minerals at equilibrium provides us with measures of the temperature of equilibration and composition of the fluid (Taylor, 1978). Also, if isotopic disequilibrium is found in the coexisting minerals, it is possible to infer the degree of isotopic interaction between the mineral phases and the aqueous fluid derived from outside of the system (Wenner and Taylor, 1976).

In this research an oxygen isotope study was carried out on the Wolf River Batholith in Wisconsin, one of the main exposed Precambrian anorogenic granitic bodies, to determine the nature of hydrothermal alteration in mineral phases and to characterize oxygen isotope composition of the batholith.

### SAMPLE COLLECTION AND OXYGEN ISOTOPE ANALYSIS

Ninty-two samples were collected from the Wolf River Batholith and whole rock samples and mineral separates were prepared for the deter-

mination of oxygen isotope composition.

Mineral separations of quartz and feldspar were made by hand-picking. Cold hydrofluoric acid was used to dissolve away feldspars for fine-grained.

The extraction of oxygen from silicates was performed by reacting with  $BrF_5$  at 650-670°C in nickel reaction vessels (Clayton and Mayeda, 1963).  $CO_2$  gas was obtained from oxygen by combustion with a resistance-heated graphite rod (Taylor and Epstein, 1962). The mass spectrometer used was a 60°, single-focusing, double collecting Nuclide 3~60 RMS.

### GEOLOGICAL SETTING

The Wolf River Batholith belongs to Proterozoic anorogenic granitic rocks (*c.a.* 1.46 Ga) (Medaris *et al.*, 1973; Van Schmus, 1973). Rock types intruded by the Wolf River Batholith are various and most are not older than 1.85 Ga (Anderson, 1975). Most of the western and northern part of the batholith consist of calc-alkaline plutonic rocks representing Penokean Orogeny (1.80~1.90 Ga). Along the southern margin, an Archean migmatite-gneiss terrain is intruded by the batholith in

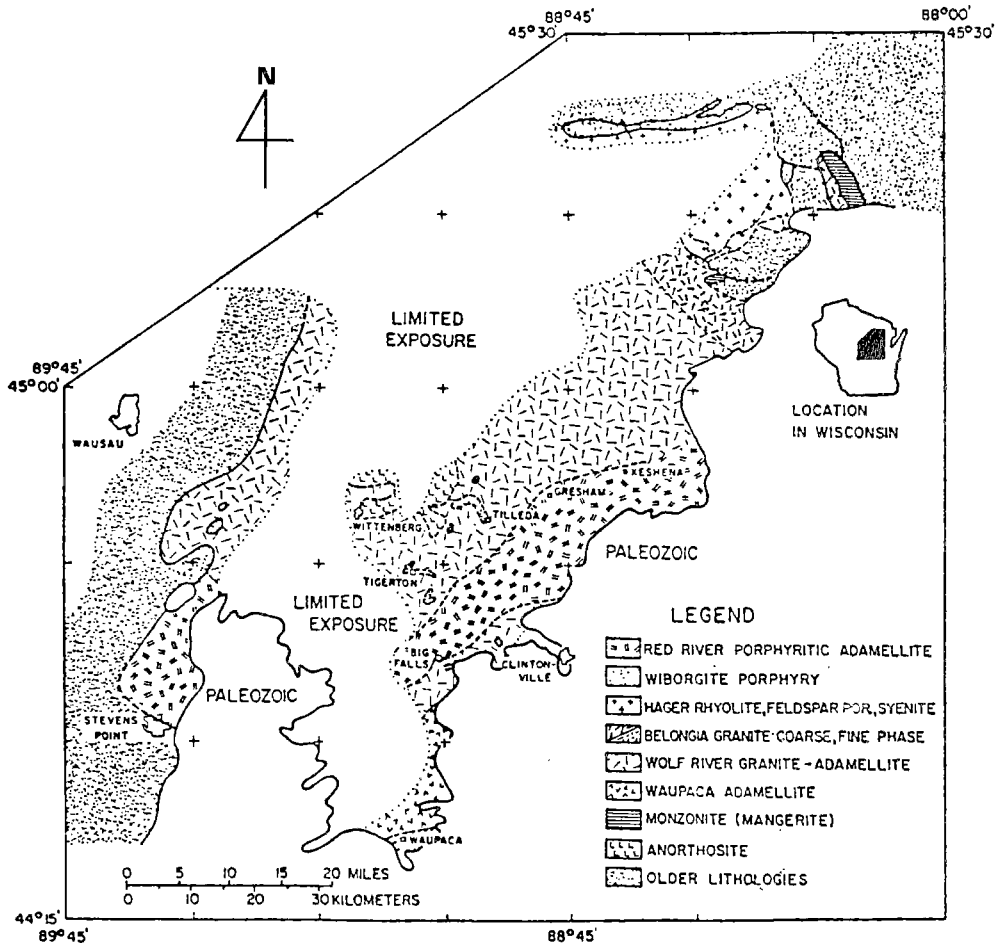


Fig. 1. Geologic map of the Wolf River Batholith.

restricted areas (Van Schmus and Anderson, 1977). The eastern and southern parts are composed of undifferentiated Paleozoic rocks, Cambrian sandstones, and Ordovician limestones, dolomite, sandstone and shale (Dutton and Bradly, 1970).

In spite of the strong contrast between the massive unmetamorphosed anorogenic nature of the batholith and synorogenic metamorphosed character of the older surrounding rocks on the western and northern borders of the batholith, the intrusion has had no interaction with the surrounding rocks in the form of migmatization or hydrothermal activity. Inclusions of these older rocks are uncommon and are largely restricted to the margins (Anderson and Cullers, 1979).

The batholith consists of plutons which are

largely composed of biotite-granite and biotite-hornblende adamellite with minor occurrences of quartz syenite, older anorthosite and iron-rich pyroxene-olivine monzonite.

Granitic plutons include the Waupaca Adamellite, the Wolf River Granite, the Wiborgite Porphyry, the Red River Adamellite, the Belongia Granite, the Hager Granite, the Hager Feldspar Porphyry, and the Hager Syenite. The spatial distribution of the plutons are shown in Fig. 1.

### OXYGEN ISOTOPE COMPOSITIONS OF PLUTONS

Whole rock samples and/or mineral separates from eighty-four granitic rocks, four anorthosites

**Table 1.** Oxygen isotope composition of the Wolf River Batholith

Pluton	Sample	WR	Q	F	Sample	WR	Q	F	
Wolf River Granite	1		7.3	6.3	25		8.0	5.3	
	2	7.6	7.8	7.1	26	6.9			
	3		8.2	7.3	27	6.9			
	5		7.3		28	7.2			
	6	7.2	8.1	7.4	29	7.1			
	8		7.4	6.6	30		8.2	7.6	
	9		8.3	7.1	31		7.5	7.1	
	13		8.5	7.4	32	6.8	7.4	6.6	
	14		7.8	8.6	33	7.0	7.5	6.7	
	15	7.0	7.2	6.0	34		8.8	7.7	
	17		8.3	6.6	35		7.7	6.5	
	18		7.9	7.5	36		8.3	6.2	
	19	7.2	8.0		37		8.0	5.8	
	20		8.1		38		7.6	6.5	
	21		8.2	6.8	39		7.9		
	22		8.1	6.1	40		7.6	6.4	
	23		7.2	6.8	41		8.1	6.8	
	24		8.5	7.3					
	Wiborgite Porphyry	4		8.2		42		7.7	6.0
		10		8.6	6.8	43	7.1		
		11		7.3	6.8	12		8.0	6.7
		16	7.0	7.6	6.2				
	Red River Adamellite	7	6.6	7.2	6.0	54		8.4	6.6
		44		8.0	7.0	55		8.1	
45		7.8	8.8		56		7.5		
46		7.6			57		8.3	8.1	
47		6.8			58		7.4	6.3	
48			8.2	8.0	59		7.9	6.4	
49			8.5	8.4	60		8.7	6.8	
50			8.5	7.2	107		7.2	5.0	
51			8.3		108		8.0	7.4	
52			8.3	7.9	109		8.4		
53			7.5	6.9					
Waupaca Adamellite		61	7.0	6.7		65		6.6	5.7
		62	5.7	6.4		66	7.4	7.9	6.7
	63	6.4	7.0		67	5.7	7.4		
	64		7.0	6.0	68	6.4			
Belongia Granite (Fine)	69	6.5	7.9	6.5	72	6.4	7.5	5.7	
	70	7.7			73		8.4		
	71		7.5	6.2	74		7.3		
	(Coarse)	75	8.0	8.9	7.4	78		8.6	8.0
		76	7.1	7.4		79		8.3	7.3
		77		7.9					
	Hager Granite	80	7.7		81	6.9			
Monzonite	90	6.8		92	6.3				
	91	5.8		94	7.5				
Anorthosite	102	7.0		104	7.5				
	103	6.5		105	6.9				

WR: whole rock, Q: quartz, F: feldspar.

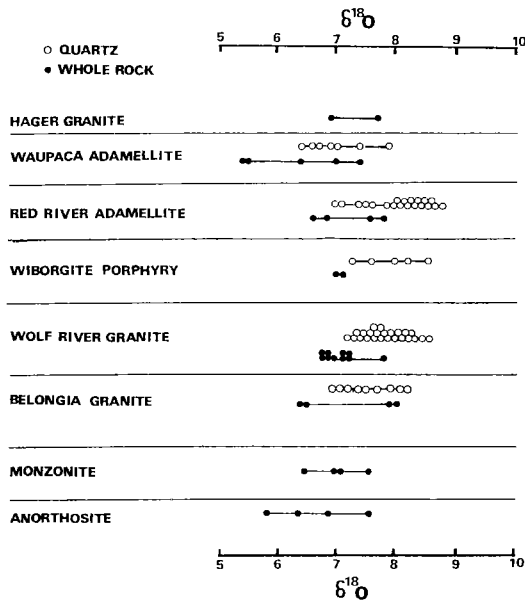


Fig. 2. Oxygen isotope composition of the Wolf River Batholith.

and four monzonites were analyzed for their oxygen isotope compositions (Table 1).  $\delta^{18}\text{O}_Q$  and  $\delta^{18}\text{O}_{WR}$  values throughout the entire batholith are fairly uniform and vary within 3 permil (Fig. 2).  $\delta^{18}\text{O}_Q$  ranges from 6.4~8.9 permil with average being 7.9 for 73 samples. The  $\delta^{18}\text{O}_{WR}$  ranges from 5.7~8.0 permil with average being 7.0 for 37 samples. All the granitic rocks, except the Waupaca Adamellite and the monzonite, show an even narrower range of about two permil (6.9~9.0 for quartz and 6.4~8.0 for whole rock). The Waupaca Adamellite is lower than others by about one permil (6.4~7.4 for quartz and 5.7~7.4 for whole rock). According to the oxygen isotope composition, the Wolf River Batholith belongs to the low end of so-called normal granite (Taylor, 1978).

## HYDROTHERMAL ALTERATION

### Oxygen Isotope Fractionation between Quartz and Feldspar

The oxygen isotope fractionation between quartz and feldspar at magmatic temperature is approximately 1 to 2 permil. Fractionation of less than

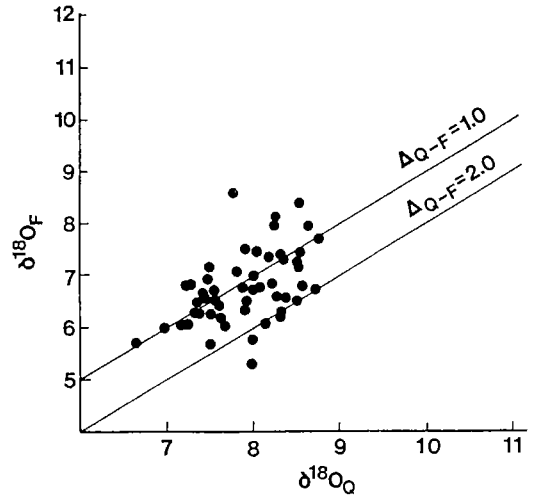


Fig. 3.  $\delta^{18}\text{O}_F$  vs.  $\delta^{18}\text{O}_Q$  of granitic rocks of the Wolf River Batholith:  $\Delta_{Q-F}$  values between 1 and 2 permil indicate isotopic fractionation at magmatic temperature.  $\Delta_{Q-F}$  values less than 1 permil indicate low temperature hydrothermal alteration.

1 between quartz and feldspar are ubiquitous in the entire batholith.  $\Delta_{Q-F}$  values range from -0.8 to 2.7 (55 pairs) (Fig. 3); about 60% of them (36 out of 55) are between 1.0 and 2.5, while the rest are less than 1.0 with one sample having a negative value (-0.8). Such an isotopic disequilibrium developed locally without any observable geographical pattern throughout the batholith.

Since quartz is the most resistant among common rock-forming minerals to isotopic exchange, isotopic disequilibrium between quartz and feldspar must be caused by a shift of isotope composition of the feldspar.

About 50% of samples contain brick-red feldspar. The proportion of red to pink and/or gray feldspar varies in each sample, but no sample has 100% of red feldspar. In samples containing red feldspar, only some grains and/or parts of individual grains are red-colored. In porphyritic rocks, red feldspar occurs less frequently in phenocryst than in the groundmass. The proportion of the red feldspar in coarse-grained samples is relatively less than that of fine-grained samples. In thin section a fracture is not necessarily observed in the red-colored part of phenocryst or coarse-grained feldspar. Therefore in most grains the boundary

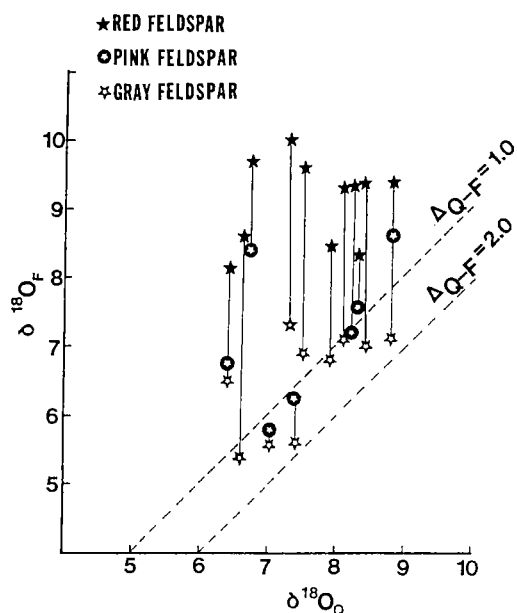


Fig. 4.  $\delta^{18}\text{O}_F$  vs.  $\delta^{18}\text{O}_Q$  for samples having feldspar of different colors.

between red and non red feldspar is not clear.

Since granitic rocks containing the brick-red feldspar were reported as being hydrothermally altered in many areas (*e.g.*, Wenner and Taylor,

1976), the possibility that red feldspar might be the product of hydrothermal alteration was anticipated before the analysis, and an effort was made to separate representative feldspar grains.

#### Isotopic Disequilibrium between Coexisting Feldspars

The colors of feldspar in the Wolf River Batholith are gray, pink and red. Some samples contain all of these, while others contain two of three varieties. Although efforts were made to separate the red feldspar from the gray and/or pink feldspar whenever feasible, only eleven samples were separated successfully due to their indiscrete boundary.

All the red feldspars show distinct isotopic disequilibrium with coexisting quartz.  $\Delta_{Q-F(R)}$  ranges from  $-0.6$  to  $-2.7$  for 11 samples (Table 2 and Fig. 4).  $\Delta_{Q-F(G)}$  ranges from  $-0.1$  to  $1.8$  permil for 10 samples with seven of them lying within the magmatic range of  $1.0\sim 1.9$ .  $\Delta_{Q-F(P)}$  ranges from  $-1.7$  to  $1.2$  in seven samples; among them three are within  $1.0$  and  $1.3$ . Samples having small  $\Delta_{Q-F(G)}$  and  $\Delta_{Q-F(P)}$  also show the most negative  $\Delta_{Q-F(R)}$

Table 2. Oxygen isotope composition of quartz and feldspars of different colors

Sample	$\delta^{18}\text{O}$ (permil)				$\Delta$ (permil)		
	Quartz	F(P)	F(G)	F(R)	Q-F(P)	Q-F(G)	Q-F(R)
Wolf River Granite							
5	7.3		7.3	10.0		0.0	$-2.7$
39	7.9		6.4	8.4		1.5	$-0.5$
Wiborgite Porphyry							
4	8.2	7.2		9.3	1.0		$-1.1$
Red River Adamellite							
45	8.8	8.6	7.1	9.4	0.2	1.7	$-0.6$
51	8.3	7.6		8.8	0.7		$-0.5$
55	8.1		7.1	9.3		1.0	$-1.2$
56	7.5		6.9	9.6		0.6	$-2.1$
109	8.4		7.0	9.4		1.4	$-1.0$
Waupaca Adamellite							
61	6.7	8.4		9.4	$-1.7$		$-2.7$
62	6.4	6.7	6.5	8.1	$-0.3$	$-0.1$	$-1.7$
63	7.0	5.8	5.6		1.2	1.4	
65	6.6		5.4	8.6		1.2	$-2.0$
67	7.4	6.3	5.6		1.1	1.8	

F(P), F(G), F(R):pink, gray and red feldspar.

values. Generally  $\Delta_{Q-F(P)}$  values lie between the values of  $\Delta_{Q-F(G)}$  and  $\Delta_{Q-F(R)}$ . Isotopic fractionations between quartz and feldspars of different color indicate that red feldspar have undergone more extensive isotopic exchange with hydrothermal fluid than gray and pink feldspars.

$\delta^{18}O$  of red feldspar ranges from 8.1 to 10.0. It is noteworthy that seven out of eleven samples approach a maximum  $\delta^{18}O$  value, that is, 9.3 to 10.0.

Since red feldspar must have undergone the most extensive isotopic exchange with hydrothermal fluids and most of them approach a common  $\delta^{18}O$  value, it is likely that they have experienced nearly complete oxygen isotope exchange with hydrothermal fluids. If the red feldspar represents a close approach to the isotopic equilibrium with the fluid and if the isotope composition of the fluid is known, then the temperature of the hydrothermal alteration can be calculated. Alternatively, if we know the temperature of alteration, we can infer the isotope composition of the fluid involved. In the present work the temperature of hydrothermal alteration was obtained through fluid inclusion studies.

### Fluid Inclusion

Six samples were selected for fluid inclusion study (Table 3), of which four samples (4, 55, 56, 61) contained red feldspar.  $\Delta_{Q-F}$  values of these samples are negative, thereby indicating hydrothermal alteration. Two samples (16, 54) contained no red feldspar and  $\Delta_{Q-F}$  values are magmatic, ranging from 1.2~1.8 permil. Since feldspars are not suitable for fluid inclusion studies because of their cleavage development (Roedder, 1984), and the surface of red feldspars were turbid due to their alteration to sericites and disseminated iron oxides, fluid inclusions in quartz were studied as an alternative.

Temperatures of the eutectic point, melting of ice and homogenization were measured on a total of seventy fluid inclusions in six samples. Since the exact temperature of eutectic point could not be measured, only  $T_m$  (temperature of melting of ice) and  $T_h$  (temperature of homogenization) are

reported in Table 3.

The inclusions are mostly trapped along healed fractures. Irregular and round shapes are most common, and only a few, isolated, short prism-shaped inclusions are found. In many cases, the gas to liquid volume ratio of irregular-shaped inclusions vary widely, from 0 to 100%. A wide variation of gas to liquid ratios of adjacent inclusions in the same plane are also common. With this variation of ratios, the shape and configuration of irregular-shaped fluid inclusion clearly indicated 'necking'. Although similar situations are frequently observed in many round-shaped inclusions, the variation of ratios is smaller (10 to 80%) and the gas to liquid ratios of 20 to 40% are most common.

The gas to liquid ratios of observed fluid inclusions ranged from 10 to 70% but, regardless of the ratio, all inclusions homogenized to liquid. The abundance and size of fluid inclusions differ between hydrothermally altered and unaltered samples. The population of fluid inclusions in unaltered samples is generally less than one fifth of that of altered samples. The size of fluid is small (less than 10  $\mu m$ ) and only a few are larger than 5  $\mu m$ ; in unaltered samples only a few are larger than 3  $\mu m$ .

Two distinct types of fluid inclusion were observed based on the eutectic point of melting in freezing runs, even though precise measurements of temperature could not be made. The Type-I has much lower eutectic point (lower than about  $-46^\circ C$ ) than that of NaCl ( $-20.8^\circ C$ ). The Type-II has a eutectic point close to that of NaCl. The Type-I occurs in both altered and unaltered samples and was predominant (about 80% of inclusions observed) over the Type-II. The Type-II also occurred in both samples with almost even proportion. Such low eutectic temperatures of the Type-I must be attributed to its compositional effects other than those of NaCl and/or KCl. Adding KCl to an NaCl-H<sub>2</sub>O brine lowers the eutectic point by only 2.1 $^\circ C$ , to  $-22.9^\circ C$ . In contrast, the addition of CaCl<sub>2</sub> or MgCl<sub>2</sub> results in a much greater depression of eutectic point, to lower than  $-49.8^\circ C$  and  $-33.6^\circ C$ , respectively

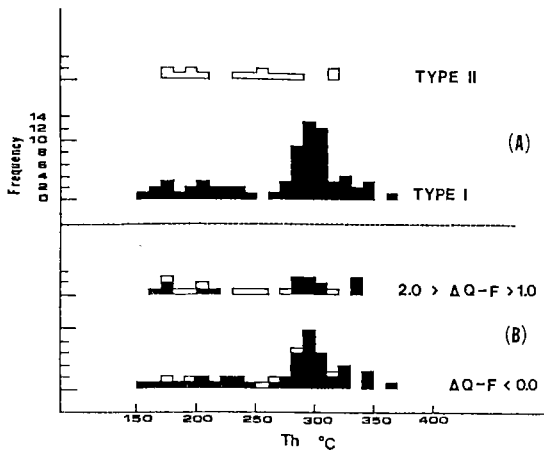
**Table 3.** Melting and homogenization temperatures of fluid inclusion  
(a) Unaltered Samples

Sample	T <sub>m</sub>	T <sub>h</sub>	Type	G/L Ratio	Sample	T <sub>m</sub>	T <sub>h</sub>	Type	G/L Ratio
16	-11.1	338.2	I	25	54	-8.0	288.7	I	40
	-11.3	308.0	I	30		-1.8	162.3	II	70
	-25.4	156.5	I	50		-18.6	278.6	I	30
	-15.0	172.6	I	25		-2.4	157.5	II	45
	-4.4	294.3	II	50		-11.2	310.5	I	25
	-2.0	224.5	II	75		-18.5	306.4	I	70
	-22.4	238.3	I	25		-5.5	248.9	I	30
	-16.0	315.0	I	30		-16.9	215.4	I	25
	-15.4	349.4	I	40		-4.8	244.3	I	15
	-15.0	321.1	I	30		-19.2	156.4	I	25
	-3.5	189.4	II	25		-14.9	238.9	I	40
	-2.4	271.2	II	25		-17.5	302.4	I	40

## (b) Altered Samples

Sample	T <sub>m</sub>	T <sub>h</sub>	Type	G/L Ratio	Sample	T <sub>m</sub>	T <sub>h</sub>	Type	G/L Ratio	
56	-1.6	274.4	I	30	61	-20.4	349.3	I	20	
	-14.9	148.5	II	70		-18.4	281.2	I	25	
	-1.6	326.4	II	20		-20.3	266.8	I	20	
	-16.4	365.0	I	25		-21.2	276.5	I	50	
	-17.6	314.8	II	50		-20.6	299.5	I	40	
	-13.0	294.3	I	15		-1.6	159.1	II	15	
	-18.2	300.2	I	15		-15.4	160.5	I	25	
	-16.3	310.1	I	15		-15.5	290.9	I	25	
	-22.7	282.6	I	45		-18.9	310.2	I	25	
	-19.4	284.6	I	30		-19.1	296.3	I	40	
	-14.4	305.0	I	25		-18.4	281.5	I	35	
	-15.4	306.4	I	40		-19.6	284.8	I	70	
	-11.2	340.1	I	30						
Sample	T <sub>m</sub>	T <sub>h</sub>	Type	G/L Ratio	Sample	T <sub>m</sub>	T <sub>h</sub>	Type	G/L Ratio	
4	-19.4	284.6	I	20	55	-23.7	127.8	I	45	
	-17.2	294.3	I	30		-19.5	155.5	I	25	
	-1.3	168.6	II	5		-15.3	216.5	I	30	
	-11.4	152.4	I	15		-10.8	221.5	I	20	
	-9.5	208.2	I	10		-23.4	200.9	I	15	
	-9.5	221.0	I	10		-24.0	220.5	I	10	
	-9.2	204.5	I	20		-4.6	245.0	II	30	
	-20.6	279.5	I	20		-19.2	299.3	II	15	
	-5.4	255.5	I	25		-18.6	192.6	I	30	
	-15.2	320.3	I	50		-24.1	184.3	I	75	
	-22.0	283.2	I	20		-24.8	196.3	I	50	
	-15.2	169.8	I	25		-24.3	235.8	I	45	
	-18.4	356.4	I	45		-24.2	284.1	I	30	
	-21.8	338.0	I	40		-8.4	192.6	I	45	
	-14.5	278.2	I	20		-19.6	158.4	I	25	
	-20.3	284.1	I	30		-14.3	178.4	I	30	
-21.2	306.4	I	25							
-15.1	171.9	I	50							

T<sub>m</sub> and T<sub>h</sub> are in °C. G/L Ratio is volume ratio.

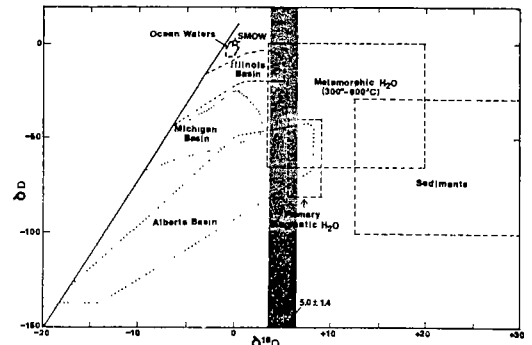


**Fig. 5.** Histogram of homogenization temperature ( $T_h$ ) of the Type-I and the Type-II inclusions: (A) Population of the Type-I and the Type-II fluid inclusions in all samples regardless of  $\Delta Q-F$  values. (B) Samples having  $\Delta Q-F$  values less than 0 contain much more fluid inclusions than those having magmatic  $\Delta Q-F$  values.

(Crawford, 1981). Therefore a eutectic point observed at lower than  $-46^\circ\text{C}$  indicates the existence of  $\text{CaCl}_2$  in a fluid inclusion. Also, depressions of melting temperature of ice ( $T_m$ ) are quite different between two types.  $T_m$  of the Type-I ranged from  $-6$  to  $-26^\circ\text{C}$ , mostly lies between  $-11$  and  $-22^\circ\text{C}$ .  $T_m$  of the Type-II is between  $-2$  and  $-4^\circ\text{C}$ .

No naturally occurring brine consisting of only one of the chloride species such as  $\text{KCl}$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$  (other than  $\text{NaCl}$ ) has been observed (Crawford, 1981). Therefore considering their low eutectic points, the Type-I inclusions must be multi-component fluids containing  $\text{CaCl}_2$ . Although, the exact composition of the fluid and the ratios of salts are unknown, the existence of  $\text{CaCl}_2$  provides very important constraints on the source of the hydrothermal fluid. Salinities equivalent to  $\text{NaCl}$  is calculated as 11.4~25.4 wt.% using Clynne and Potter's equation (1977).

The homogenization temperature range of the Type-I is 150~360°C and that of the Type-II is 160~315°C (Fig. 5). The mode of homogenization temperature of the type-I is 295°C and the average temperature is 265°C. The Type-I is believed to represent the hydrothermal fluid responsible for



**Fig. 6.** Oxygen isotope composition of hydrothermal fluid in the Wolf River Batholith compared with those of various other natural waters and sedimentary basinal waters of North America.

main hydrothermal alteration event based on its population and distinct mode of  $T_h$ .

Since the  $T_h$  of the Type-I clustered mostly between 260 and 350°C, this temperature range was used to calculate  $\delta^{18}\text{O}$  of hydrothermal fluid. And since seven out of eleven red feldspars approach common maximum  $\delta^{18}\text{O}$  value (9.3 to 10.0 permil), the average (9.5 permil) of these seven red feldspars was used for  $\delta^{18}\text{O}$  of the feldspars. Since isotopic fractionation of feldspar, especially plagioclase, depends on its composition as well as temperature (Matsuhisa *et al.*, 1979) the average composition of red feldspar ( $\text{Ab}_{0.8}\text{An}_{0.2}$ ) was used. The calculated  $\delta^{18}\text{O}$  of hydrothermal fluid was  $5.0 \pm 1.4$  permil using the feldspar-water curve of Matsuhisa *et al.* (1979). This range belongs to the range of metamorphic waters and is at the lower end of the primary magmatic water range (Fig. 6).

### Source of Hydrothermal Fluid

$\text{CaCl}_2$ -containing highly saline water (11.4 to 25.4  $\text{NaCl}$  equivalent wt.%), with a  $\delta^{18}\text{O}$  value of  $5.0 \pm 1.4$  permil, is deduced to be the hydrothermal fluid responsible for the alteration of the Wolf River Batholith. The possible sources of such a solution are: i) formation water from Paleozoic sedimentary rocks exposed to the east and south of the Wolf River Batholith, ii) Precambrian metamorphic water found in the Keweenaw of northern Michigan (Livnat, 1983), and iii) saline groundwater



in Precambrian crystalline rocks (e.g., Fritz and Frapé, 1982; Frapé *et al.*, 1984).

i) To the the east and south of the Wolf River Batholith, Phanerozoic sedimentary rocks are exposed. They are Cambrian sandstone, dolomite and shale, and Ordovician dolomite, sandstone, shale and limestone (Dutton and Bradly, 1970).  $\delta^{18}\text{O}$  of sedimentary rocks in Wisconsin is not known, but formation water from these sedimentary rocks can be a candidate in that they can supply enough Ca, and should fall into a suitable range of  $\delta^{18}\text{O}$  values, that for formation water of sedimentary basins in North America (Fig. 6). But other than these possibilities, there is no evidence that these formation waters possessed the other characteristics of the hydrothermal fluid of the Wolf River Batholith.

ii) In the Keweenaw copper province of northern Michigan, metamorphic/hydrothermal fluid having  $\delta^{18}\text{O}$  of  $6 \pm 1.5$  permil was reported (Livnat, 1983). This fluid is a  $\text{CaCl}_2$ -dominated brine with 3 to 20 NaCl equivalent wt.%. These properties are very similar to the characteristics of the fluid in the Wolf River Batholith. The source of this metamorphic fluid was suggested to have been seawater.

iii) Saline waters, stagnant pockets of Ca-Na-Cl brine at depth, are known to be widespread in the Canadian Shield. Total salinity ranges up to 30 NaCl equivalent wt.%, and Ca/Na ratio ranges from 0.1 to 10.0, but is typically between 1.0 and 10.0. These properties are also very similar to those of the hydrothermal fluid of the Wolf River Batholith. However, their oxygen isotope compositions are much lower than  $5.0 \pm 1.4$  permil observed in the Wolf River Batholith.

Kelly *et al.* (1986) proposed a basinal water model involving several stages. In this model the most important aspect concerns the latitudinal dependence of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of basinal water (Fig. 7). All the highly saline Precambrian-hosted mine waters plot to the left of the meteoric water line and at the same time these waters show latitudinal dependence with light waters occurring in more northerly regions. These positions were suggested to represent original basinal brines. Since we do not know the original brine

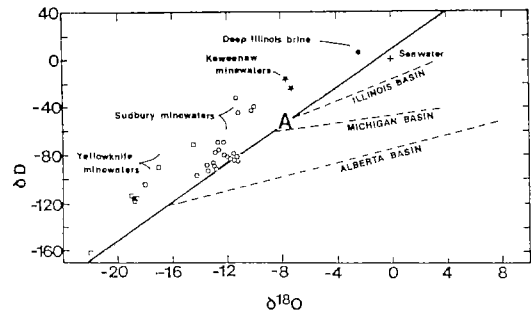


Fig. 7. Comparison of O and H isotope compositions of various Paleozoic-hosted and Precambrian-hosted subsurface waters (modified from Kelly *et al.*, 1986): A-isotope composition of hydrothermal fluid responsible for the alteration of the Wolf River Batholith according to the approximate latitude of the batholith.

composition responsible for the hydrothermal alteration of the Wolf River Batholith, we have to assume the position by approximating the latitude of the Wolf River Batholith. The schematic diagram explaining the model is shown in Fig. 8. Point A (also in Fig. 7) indicates the assumed original composition of basinal brine at the approximate latitude of the Wolf River Batholith. Stage 1 portrays the increasing salinity,  $\delta\text{D}$  values and  $\delta^{18}\text{O}$  of sedimentary formation water up to the point B ( $\delta^{18}\text{O}_\text{W} = 5.0 \pm 1.4$ ). If this water then penetrated the basement rocks, it would react with basement rock and produce the alteration product whose composition is represented along the line C. Red feldspar ( $\delta^{18}\text{O} = 9.3$  to  $10.0$ ) in the Wolf River Batholith are considered as alteration products whose compositions are around C. This line was drawn at a temperature  $290^\circ\text{C}$ , the mode of homogenization temperature of the fluid inclusion (therefore  $\Delta_{\text{F-W}} = 4.4$ ). During this stage it is assumed that the basement rocks become strongly grouted, if not sealed off entirely. In stage 2, the Paleozoic cover has been removed, and the brines trapped in the basement rocks underwent the retrograde exchange with the alteration products being depleted in  $\delta^{18}\text{O}$  and possibly enriched to a small degree in deuterium under conditions of low temperature and low W/R ratios. If this model is valid, the formation water responsible must have an isotope composition around D. Clearly a position

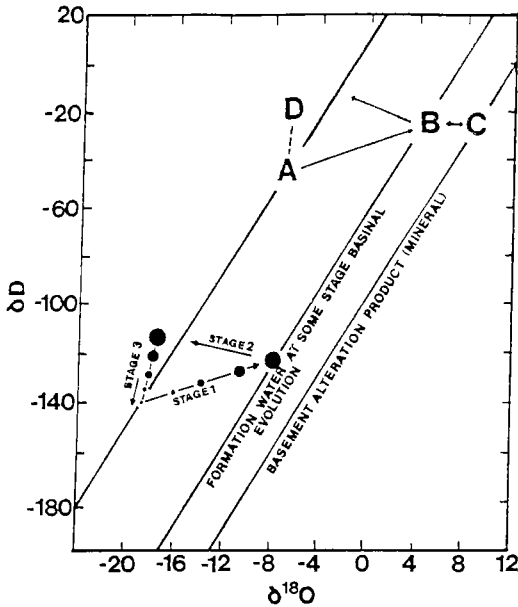


Fig. 8. Schematic illustration of isotopic evolution of the Precambrian-hosted brines according to the basinal water model.

other than A (different latitude) cannot produce the  $\delta^{18}\text{O}$  of feldspar (9.3~10.0 permil) and the estimated  $\delta^{18}\text{O}$  of fluid (4.5 permil at 290°C). Although there is no  $\delta\text{D}$  datum for the hydrothermal fluid in the Wolf River Batholith, which is important to follow the basinal water model, the basinal water model best explains the oxygen isotope composition of the fluid and feldspar with correct latitude.

The Basinal water model (iii) is remarkably different from the model involving Precambrian metamorphic water (ii). But basinal water model can include sedimentary formation water in Wisconsin (i), since this model intrinsically includes the Paleozoic sediments in each area. If mine water from Wisconsin can be sampled and analyzed, the effectiveness of this model can be tested.

#### Composition of feldspars

Since all red feldspars showed disequilibrium values of  $\Delta_{\text{Q-F}}$ , while pink and gray feldspars mostly retain their primary igneous values, it was

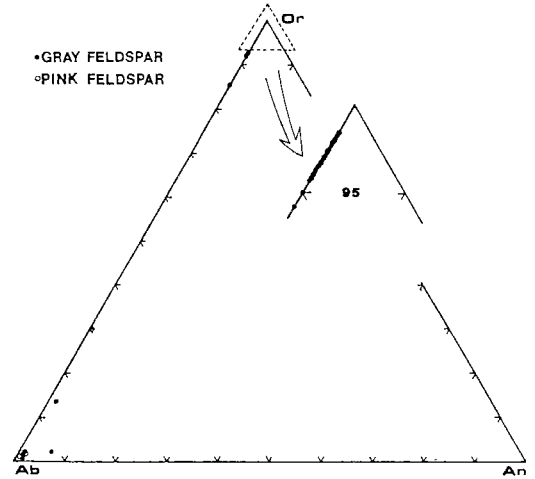


Fig. 9. Or-Ab-An triangular diagram of gray and pink feldspar from samples having no red feldspar.

suspected that the composition of the red feldspars might be different from the other feldspars, and its isotope composition be related to the composition of hydrothermal fluid.

In order to determine the chemical composition, coexisting feldspars with different colors (red, gray and pink) were analyzed by an electron microprobe. Eight samples containing not only red feldspars but also gray and/or pink feldspars were hand picked and analyzed. Gray and/or pink feldspars from four samples without red feldspars were analyzed for comparison.

Since most alkali feldspars were identified as perthite under the microscope, samples were probed on 10 points along a line with 100 m interval (Table 4). All the gray and pink feldspars are K-rich alkali feldspars with no An content (Fig. 9). The only exception was one gray feldspar (55), which showed an Na-rich plagioclase composition ( $\text{Ab}_{91.4}\text{Or}_{1.1}\text{An}_{7.5}$ ). In some gray and pink feldspars up to 3 points showed Na-rich composition ( $\text{An}_{0.7-3.4}$ ) except 55 ( $\text{Ab}_{5.7}\text{Or}_{0.5}\text{An}_{93.9}$ ). These Na-rich portions must be the lamellae of perthite. Red feldspars were all plagioclase of about oligoclase composition (Fig. 10). Similar to the alkali feldspar, some grains of plagioclase show lamellae of alkali feldspar composition (up to 3 out of 10 points).

Iron contents (FeO) of red feldspars (0.03~0.13 wt.%) are higher than those of gray and pink

**Table 4.** Normative and oxygen isotope composition of feldspars

No.	Q	F	F(P)	F(G)	F(R)	*	Ab	Or	An	Ab	Or	An	
4	8.2		7.2		9.3	P	2.34	97.66	0.00(8)	96.47	1.33	2.20(2)	
						G							
						R	94.25	3.00	2.75(7)	64.38	34.07	1.54(3)	
5	7.3			7.3	10.0	P							
						G	3.59	96.41	0.00(9)	99.08	0.56	3.36(1)	
						R	84.82	0.68	14.50(10)				
16	7.6	6.2				P	3.59	96.41	0.00(7)	92.24	3.44	2.32(3)	
						G							
						R							
33	7.5	6.7				P	3.29	96.72	0.00(7)	98.47	0.81	0.72(3)	
						G	4.87	95.13	0.00(9)	98.19	0.90	0.90(1)	
						R							
39	7.9			6.4	8.4	P	2.97	97.03	0.00(10)				
						G	2.82	97.18	0.00(10)				
						R	84.77	0.55	14.68(7)	22.72	75.03	2.25(3)	
45	8.0	6.7				P	3.34	96.66	0.00(9)	97.80	0.55	1.64(2)	
						G	3.90	96.10	0.00(10)				
						R							
55	8.1			7.1	9.3	P							
						G	91.40	1.12	7.48(9)	5.65	0.45	93.91(1)	
						R	83.26	0.51	16.23(10)				
56	7.5			6.9	9.6	P							
						G	3.69	96.31	0.00(8)	97.63	0.82	1.55(2)	
						R	76.2	1.02	22.79(8)	56.82	35.52	7.60(2)	
61	6.7		8.4		9.4	P	2.67	97.33	0.00(8)	75.40	22.50	2.10(2)	
						G							
						R	86.68	0.51	12.81(9)	40.70	53.21	6.09(1)	
62	6.4		6.7	6.5	8.1	P	3.15	96.85	0.00(7)	88.90	6.40	3.70(3)	
						G	4.31	95.69	0.00(9)	96.27	2.11	1.61(1)	
						R	84.31	0.34	15.35(10)				
64	7.0	6.0				P	3.53	96.47	0.00(7)	69.52	30.07	0.41(3)	
						G	3.82	96.18	0.00(10)				
						R							
106	8.4			8.0	9.4	P							
						G	3.86	96.14	0.00(10)				
						R	72.09	1.24	27.57(10)				

F(P), F(G), F(R): pink, gray and red feldspar. \*: color of feldspar. Number in parenthesis is the number of points analyzed.

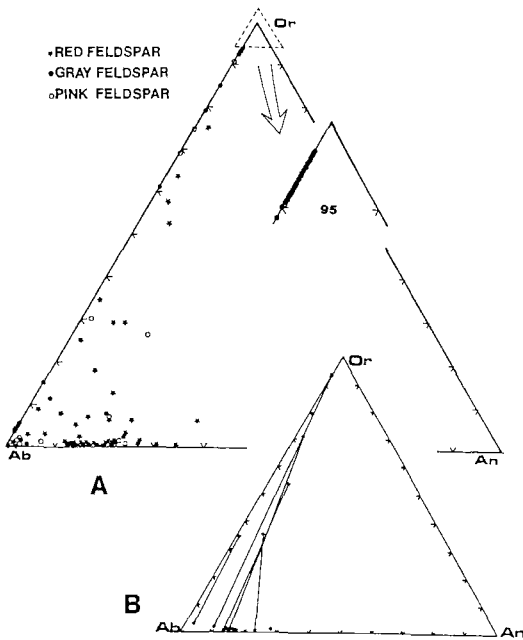


Fig. 10. Or-Ab-An triangular diagram of gray, pink and red feldspars: A-composition of each point, B-tie lines are drawn between the average compositions of hosts and lamellae.

feldspars (0.00~0.04 wt.%). The reason for the difference in iron content is not clear. The iron content in alkali feldspar of granites and pegmatites reported in the literature is generally lower than those in plagioclase (Smith, 1974, 1983), but there is no compelling data about the iron content of two feldspars when they coexist.

It is noteworthy that, regardless of altered or unaltered samples, all gray and pink feldspars are alkali feldspars, while the red feldspars are plagioclase of oligoclase composition, and oxygen isotope composition of plagioclase was affected by hydrothermal alteration, while alkali feldspars retained primary igneous composition. This may be related to the composition of hydrothermal fluid containing considerable amount of  $\text{CaCl}_2$ , but the specific reason of selective isotope exchange could not be drawn.

## CONCLUSIONS

1. Plutons of the Wolf River Batholith show

oxygen isotope compositions similar to each other.

2. Feldspars of different colors (gray, pink and red) exhibit different oxygen isotope compositions. The isotopic fractionation between quartz and gray and/or pink feldspars show mostly magmatic values (1~2 permil), while those between quartz and red feldspars show isotopic disequilibrium (less than 1 permil or even reversal).

3. Seven out of eleven red feldspars show  $\delta^{18}\text{O}$  values within a narrow range and with maximum values of 9.3~10.0 permil, which may indicate that the red feldspars underwent the most severe hydrothermal alteration and that nearly complete isotopic equilibrium with the hydrothermal fluid was achieved.

4. The temperature range of hydrothermal alteration determined by fluid inclusion study is mostly between 260 and 350°C with the mode of 290°C. The inferred hydrothermal fluid is a  $\text{CaCl}_2$ -containing brine with the salinity of 11.4~21.4 wt. % NaCl equivalent.

5. Based on  $\delta^{18}\text{O}$  of red feldspar and the temperature of hydrothermal alteration,  $\delta^{18}\text{O}$  of the hydrothermal fluid is calculated to be  $5.0 \pm 1.4$  permil.

6. The characteristics of the estimated hydrothermal fluid are similar to those of the Precambrian saline mine waters occurring in the Canadian Shield except in their oxygen isotope composition. However, if basal water model suggested by Kelly and others (1987) is adopted, oxygen isotope composition of the fluid matches well to that of basal water in Wisconsin, which once existed in sedimentary rock. Therefore a Phanerozoic basal water is considered to be a most plausible source of the hydrothermal fluid in the Wolf River Batholith.

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## 산소 동위원소 연구에 의한 미국 위스콘신주의 울프리버 화강암체의 열수변질 규명

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**요 약:** 미국 위스콘신주의 울프리버 화강암체의 산소 동위원소 조성을 분석(전암 또는 석영, 장석)한 결과 열수변질을 지시하는  $\Delta_{\text{Q-F}}$ 의 값이 전 암체에 걸쳐 분산되어 관찰되었다. 서로 다른 색의 장석(분홍, 회색, 붉은색)을 분리하여 분석한 결과, 붉은색의 장석( $\text{An}_{10-30}$ )이 거의 일정하면서 가장 높은  $\delta^{18}\text{O}$  값(9.3~10.0)을 보였다. 이는 붉은색의 장석이 열수용액과 거의 완전한 동위원소 교환반응을 한 결과로 믿어진다. 붉은색 장석의  $\delta^{18}\text{O}$ 과 유체포유물 연구에 의해 얻어진 변질온도(260~350°C)를 이용하여 열수용액의  $\delta^{18}\text{O}$ 을 추정하였으며(5.0±1.4 permil) 열수용액의 근원은 위스콘신주의 퇴적층간수인 것으로 생각된다.

**핵심어:** 동위원소 분별, 열수변질