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Reliability of δD and δ^{18}O Values of

Inclusion Fluids from Sulfides

by

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ABSTRACT

Experiments designed to measure isotope fractionation effects during the extraction of mineral inclusion fluid waters showed that water interacted with some samples displayed large heavy-isotope-depletions. The major factors responsible for these heavy-isotope-depletions are (1) organic contaminants present in or on the surfaces of the mineral; (2) physical adsorption of the water on the mineral or extraction apparatus surfaces; and (3) chemical adsorption of the water on the mineral surfaces. Factors 2 and 3 may vary with the crystallinity or trace element composition of the mineral.

INTRODUCTION

Analysis of the oxygen and hydrogen isotopic composition of the water trapped as inclusion fluids is a powerful tool in studies of mineral formation, particularly in studies of hydrothermal minerals, as a tracer of fluid source(s) and an indicator of depositional conditions. In the course of stable isotope studies of the fluids trapped in epigenetic sphalerite and pyrite of Middle Pennsylvanian age coals from Iowa, Illinois, Missouri, and Kansas, some samples produced fluids with δD and $\delta^{18}O$ values as low as -137 per mil and -12.3 per mil, respectively (Whelan, unpublished data). These values were anomalously low and inconsistent with those of any of the possible diagenetic or hydrothermal fluids suggested by the hydrogeologic history of the host coals. The unavoidable presence of an organic component in the sphalerite and pyrite samples, arising from solid coal inclusions and also (probably) from inclusions of liquid or gaseous organic compounds in the minerals, suggested that the heavy-isotope-depleted compositions of the inclusion fluids might be reflecting their exchange with or adsorption onto an organic contaminant. Natural organic compounds commonly have low δD values and many readily adsorb other compounds. Exhaustive but futile efforts to rid the samples of organic contaminants prior to inclusion fluid extraction reduced but did not eliminate the depletions (Whelan, unpublished data), supporting the hypothesis of organic contamination.

This communication reports the results of a series of experiments designed to explore the magnitude of and the factors responsible for the δD and $\delta^{18}O$ depletions of the inclusion fluids extracted from the coal-hosted sphalerite and pyrite, and from similar experiments using hydrothermal sulfide minerals from Creede, Colorado and Panasquiera, Portugal, and hydrothermal non-sulfide minerals from the Illinois-Kentucky fluorspar district. These experiments also imply that organic contamination is a critical factor in the heavy-isotope depletions of the inclusion fluids, but, suggest as well, that physical adsorption (physisorption) and (or) chemical adsorption (chemisorption) of inclusion fluid water onto the surfaces of the mineral or extraction apparatus during the extraction are also factors. In general, these experiments demonstrate that the measured δD and $\delta^{18}O$ values of inclusion fluids extracted from some sulfides and (or) minerals with an organic contaminant may not accurately reflect the isotopic composition of the fluids that deposited them.

SAMPLES USED IN THE EXPERIMENTS

Fourteen samples were used: 6 pyrite, 2 sphalerite, 2 barite, a chalcopyrite, an arsenopyrite, a calcite, and a quartz. Two samples each of coal-hosted sphalerite (A and B) and pyrite (A and B); two samples of latest-stage botryoidal pyrite from Creede, Colorado (courtesy of G. S. Plumlee); two samples of pyrite and one each of chalcopyrite and arsenopyrite from Panasquiera, Portugal (courtesy of R. O. Rye); and two samples of barite and one each of calcite and quartz from the Illinois-Kentucky fluorspar district (courtesy of C. K. Richardson). Although most hydrothermal fluids contain organic components, sometimes in abundance, these locales are much poorer in organics than the coal environment.

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ANALYTICAL PROCEDURES

Techniques used in the extraction and analysis of the contents of fluid inclusions are discussed in detail in Chapter 5 of Roedder 1984. The procedures used in this laboratory for physical crushing of a mineral are essentially those described by Hall and Friedman (1963) and Rye and O'Neil (1968). The sample is placed in a stainless steel tube that has been crimped and welded shut at one end and ultrasonically cleaned prior to use. A high vacuum valve is attached to the open end of the tube so that the entire extraction vessel may be attached to a vacuum manifold for sample outgassing and extraction of the inclusion fluids. Five to twenty grams of the mineral is loaded, according to the size and anticipated abundance of inclusions, and outgassed for at least 12 hours at a temperature of 60 to 100°C. After outgassing, the stainless steel tube is placed in a hydraulic press and the mineral crushed. Crushing generally reduces the grain size to <8 mesh. Water and condensible gases released by crushing are vacuum distilled into a glass trap or sample tube at liquid N_2 temperatures. Distillation is hastened by warming the crushed material to ~105°C.

Extraction of inclusion fluid water by decrepitation is done by loading the sample into a glass tube, evacuating and outgassing, and heating until the fluid inclusions burst. For sulfides, the maximum heating temperature is ~350°C; above that temperature, many sulfides begin to decompose. Carbonates, silicates, barite, and fluorite may be heated to somewhat higher temperatures. Decrepitation has the advantage that the glass vessel is less apt to react with the evolved gases and liquids than the stainless steel crush-tube, and provides less surface area for adsorption. The higher temperatures, however, greatly increase the likelihood of reaction between the host mineral and evolved volatiles.

All of the experiments reported here were performed by adding three microliters of Standard Mean Ocean Water (SMOW; δD and δ^{18}O = 0 ^{o}/oo) to an evacuated extraction vessel containing the residue of a sample from which the inclusion fluids had already been removed. The SMOW was vacuum distilled into the extraction vessel (crush-tube or glass vessel) at liquid N_2 temperature and allowed to equilibrate with the mineral residue. The time of equilibration varied, but was generally about 15 minutes, which is comparable to the time that elapses between sample crushing and the beginning of inclusion fluid water recovery during a routine inclusion fluid extraction. The SMOW was then vacuum distilled out of the sample and its isotopic composition determined. Although these experiments were not strictly equivalent to an extraction of inclusion fluids, they do permit a qualitative evaluation of how well the extraction procedures work and the recognition of troublesome samples. Table 1 lists the details of the experiments, and the isotopic shift, if any, in the δD (or δ^{18}O) of the SMOW.

EXPERIMENTAL RESULTS

Blanks run using empty crush-tube extraction vessels have shown that, when the amount of recoverable water decreases below ~1 microliter, the recovered water may display large negative shifts in its δD value (J. F. Whelan, unpub. data). Seven blank runs using 5 microliter aliquots of SMOW displayed small and reproducible shifts; the average δD shift was -7.4 ± 1.4 per mil (Table 1). The SMOW was transferred into clean crush-tube

extraction vessels at liquid N_2 temperature and then recovered at about 105°C. Recoveries of the injected SMOW were always near 100 percent.

Experiments I-V were performed on sphalerites A & B and pyrites A & B from Illinois basin coals.

Experiment I

This first experiment tested the effect of the coal-hosted sulfides on the isotopic composition of the water in contact with them. The samples were outgassed at ~100°C, then the SMOW was vacuum distilled into the crush-tubes and allowed to equilibrate with the sample for 12 to 16 hours. Recovery of the SMOW from the sphalerite samples at ~105°C was slightly in excess of 100 percent. Excess yields were common until pre-experiment outgassing temperatures were elevated to 300 to 350°C to drive off adsorbed water and to decrepitate any inclusions still intact after crushing (see experiment V). Several succeeding experiments were invalidated by yields in excess of 100 percent and are not discussed here. Equilibration with sph A produced a δD shift of -13 per mil. This shift was negligible in comparison to the -65 per mil δD shift of the SMOW recovered from sph B (Table 1).

Only 33 percent of the SMOW added to pys A was recovered in the initial extraction of 40 minutes, a routine recovery time. This very low recovery was accompanied by an extremely large δD shift of -98 per mil. An additional 2 hours of extraction yielded an additional 18 percent, which was an insufficient quantity for isotope analysis. SMOW added to pys B had a higher initial recovery of 65 percent but still shifted by -92 per mil. An additional 2.5 hours of extraction produced an additional 51 percent (i.e., for the combined extraction, an excess yield equivalent to 114 percent), with a δD shift of -99 per mil.

Experiment II

Experiment II sought to test whether significant δD shifts could occur during a time comparable to that which routinely elapses between sample crushing and extraction of the inclusion fluids, ~15 minutes. Although the isotope shifts produced by the pyrite samples were somewhat smaller than in experiment I, (in fact, the shifts produced by the two coal-hosted pyrite samples decreased steadily during these experiments), the results were essentially the same as in experiment I (Table 1). The decrease in the shifts that accompanied repeated cycling through the extraction procedure suggested gradual removal of a source of the shifting. Experiment II demonstrated that large negative δD-shifts could occur within the time span of a routine extraction.

Experiment III

This experiment measured the $\delta^{18}O$ values of the fluids recovered from the coal-hosted sulfides. The $\delta^{18}O$ values of the SMOW recovered from the pyrite samples, however, displayed $\delta^{18}O$ decreases of -13.6 and -12.5 per mil. The differences of the δD and $\delta^{18}O$ shifts produced by interaction between sphalerite and pyrite and the SMOW requires at least two independent mechanisms to produce the isotope shifts. Some factor unique to the pyrite samples caused them to produce a $\delta^{18}O$ shift as well as the δD shift.

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Experiment IV

For this experiment, the samples were outgassed at 350°C overnight in an attempt to absolutely eliminate any possible contribution from natural fluid inclusions. The outgassing provided a clue to a possible cause of the shifts because it produced a semi-opaque ring of a coal-tar-like material above the heating jacket on the inside of the glass vessel that contained sph B. Heating of sph A to 350°C did not produce such a ring nor did heating of the pyrite samples. It seemed likely that the large negative δD-shift of the SMOW equilibrated with sph B reflected an unusually high organic matter content. Total organic carbon determinations verified this (Table 1). Gas chromatographic studies of the hydrocarbons in the coal-hosted sulfides are in progress (Whelan, Hofstra, and Landis - unpublished data). Outgassing did not substantially affect the negative δD-shifts of the SMOW added to sph A and pys A and B (Table 1). Sph B was no longer used for fear of seriously contaminating the vacuum manifold and the mass spectrometer.

Experiment V

This experiment sought to determine whether recovery of the SMOW at ~300°C from a glass-tube decrepitation vessel, instead of stainless steel crush-tubes, would eliminate the shifts of the SMOW δD and $δ^{18}O$ values. Recoveries were much higher and initially exceeded the quantity of water than had been added by injection. This excess apparently represented either residual water from the incomplete recoveries of the earlier experiments or water from the continued bursting of natural inclusions in the pyrite samples. Recoveries were a believable 90 to 100 percent on the second run of pys A and third run of pys B. The trend toward smaller shifts continued with δD shifts of only -28 per mil from both pyrite samples on their final runs!

Experiments VI, VII, and VIII were performed on sulfide samples from the Creede district, Colorado, and from the Panasquiera Sn-W deposit, Portugal. Natural inclusion fluids were thoroughly removed from these samples by first crushing and then outgassing at 350°C. In general, the procedures of experiments I through V were duplicated to determine whether "cleaner" sulfides from higher temperature hydrothermal systems could also produce the isotope shifts.

Experiment VI

This experiment measured the shifts produced by two samples of botryoidal, finely-interbanded pyrite and marcasite from Creede and one sample each of pyrite and chalcopyrite from Panasquiera. The SMOW was equilibrated for about 15 minutes with the sample in a crush-tube extraction vessel and then recovered at about 105°C. Five runs were made using the Creede samples. Recoveries ranged from 82 to 103 percent and δD shifts were -17 to -12 per mil, with no apparent correlation between yield and shift (Table 1). The Panasquiera pyrite and chalcopyrite samples produced recoveries and shifts of 100 percent and -21 per mil, and 90 percent and -46 per mil, respectively (Table 1). This experiment demonstrated that the fractionation effects were not restricted to samples from coals.

Experiments VII and VIII

These experiments tested for a correlation between the amount of surface area exposed to the added SMOW and the magnitude of isotope shifts. In both experiments, equilibration took place in crush-tube extraction vessels and the SMOW was recovered at about 105°C. In experiment VII, only several coarse chunks (about 1 cc) of pyrite and arsenopyrite from Panasquiera were used; experiment VIII used the same material but after crushing and decrepitation at 350°C. All runs on these samples resulted in recoveries near 100 percent and negligible negative δD-shifts, comparable to shifts measured during the blank runs. At least for these two samples, the amount of surface area did not affect the magnitude of the isotope shift.

Experiment IX

This experiment tested the effects of non-sulfide minerals on the isotopic composition of SMOW equilibrated with them. SMOW was equilibrated overnight in crush-tube extraction vessels with a calcite, a quartz, and two barite samples from the Illinois-Kentucky fluorspar district. The SMOW was recovered at about 105 C. The δD shifts were uniform, ranging from -8 to -5 per mil, again comparable to shifts measured during blank runs.

DISCUSSION

Organic contamination is strongly implicated as a cause of the heavy-isotope depletions that occurred when 3 microliter aliquots of SMOW were added to the coal-hosted sphalerite samples in these experiments. The tarry substance driven from sph B during outgassing at 350°C was not produced during heating of sph A and sph B produced much greater than did D-depletions sph A. In addition, the δD values of inclusion fluids tend to decrease (i.e. D-depletions may be increasing) as the organic carbon contaminant content increases in sphalerites sampled from the closely related Springfield (No. 5), Herrin (No. 6), and Danville (No. 7) coals (Whelan, Cobb, and Rye, unpublished data). Small solid coal inclusions, and, quite possibly, inclusions of liquid and gaseous hydrocarbon, are sources of organic contamination in the coal-hosted sphalerite.

Repeated cycling through the outgassing and extraction procedures produced a progressive decrease in the D-shift measured on the SMOW equilibrated with pys A and B. It is possible that some contaminant of limited volatility, such as many organic compounds, was progressively being eliminated. Progressive saturation of available adsorption sites on the mineral surfaces is also a possibility, although careful outgassing between experiments had sought to eliminate this possibility. Pys A and B differed from sphs A and B in that they also caused a negative shift in the SMOW $\delta^{18}O$ values. This difference in behavior may simply reflect mineralogy, or, it may reflect that the pyrite precipitated in the coal before the sphalerite, and is probably not hydrothermal (Whelan, Cobb, and Rye, unpublished data). The pyrite may have, therefore, been exposed to a different suite of organic contaminants during precipitation.

Not all samples that caused heavy-isotope depletions had high total organic carbon contents (Table 1). The Creede pyrite samples and PGL-230 (cpy) and PGL-289 (py) from Panasquiera are examples of minerals with low

total organic carbon contents that caused negative δD shifts. Physisorption or chemisorption of water molecules onto the surfaces of these minerals are likely causes of these shifts.

Physisorption is energetically comparable to van der Waals bonding (Hawley, 1977). The concentration of physisorbed molecules on a surface increases with increasing partial pressure of the adsorbate and decreases with increasing temperature. Physisorption is a completely reversible process. That is, all inclusion fluid water molecules physically adsorbed to mineral or extraction apparatus surfaces are, theoretically, recoverable, as long as the liquid N_2 distillation is continued for a sufficient time, and particularly if the sample and apparatus are warmed sufficiently.

Although the isotopic fractionation between physisorbed water molecules and water vapor may be large, physisorption should result in relatively small negative δD-shifts providing recoveries are near 100 percent. The tendency for recoveries from the blank runs and from sph A and from experiments VII, VIII, and IX to approach 100 percent with time, but still produce small negative δD-shifts suggests physisorption of the water molecules on the mineral and apparatus surfaces. The similarity between the negative δD-shifts measured on the blank runs and those of the SMOW recovered from the Illinois-Kentucky samples and PGL-27 (py) and PGL-303 (aspy) from Panasquiera indicates that physisorption on these well-behaved samples was minimal.

Chemisorption of water is energetically equivalent to a chemical reaction between the water molecule and a surface, and resulted in the formation of new species from the adsorbate molecule (for a discussion of chemisorption, see Chapter 15 in Adamson, 1976). For instance, rust results from the chemisorption of water onto iron with the resulting formation of iron oxide and hydroxyl ion. Chemisorption is not completely reversible. The rate of chemisorption increases with the partial pressure of the adsorbate and with temperature. Because of the strong bonds formed, chemisorption should result in large isotopic fractionations between the adsorbed and gaseous components, and recoveries less than 100 percent.

The much less than quantitative recoveries from pys A and B and from the samples used in experiment VI at temperatures of 105°C, in spite of total extraction times of several hours, suggest chemisorption of SMOW onto the sulfide surfaces. Near-quantitative recoveries were possible with these samples only at temperatures >300°C. The large negative δD-shifts of some of these runs are also consistent with chemisorption. Why don't all pyrite samples cause a negative δD-shift? Possibly because the extent of physisorption or chemisorption is positively correlated with the surface energy of the adsorbent, and surface energy increases as the number of defects in the crystal increase (Adamson, 1976). A poorly crystalline pyrite (formed at low temperatures?) might, therefore, adsorb much more strongly and extensively than a well-crystallized pyrite (formed at higher temperatures). Differences between the trace element contents of two pyrites might also cause greatly different adsorption properties.

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SUMMARY

These experiments demonstrate that the isotopic compositions of the inclusion fluids extracted from some sulfides may deviate significantly from that of the fluid actually trapped in the inclusions. Isotope studies of inclusion fluids should, therefore, (1) include several experiments of the type reported here to evaluate the effect of the samples on the isotopic compositions of the water extracted from them; and (2) extract inclusion fluids from sulfide minerals by first crushing, to open as many inclusions as possible, and then heating to temperatures of at least 300°C to speed the recovery of the released fluids. This heating should be as rapid as is feasible to limit reaction between the released fluids and the sample or extraction vessel.

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TABLE 1

1. δD and δ^{18}O data collected to test the reliability of crush-tube and decrepitation procedures for the extraction of mineral inclusion fluids.

SAMPLE	EXPERIMENT NO.	EQ. TIME (hrs)	EXT'N. TEMP (° C)	EXT'N. TIME (mins)	RCV'Y (%)	δD SHIFT (°/oo)	δ^{18}O SHIFT (°/oo)	TOTAL ORGANIC C (%)
COAL-HOSTED SULFIDES								
sph A-I	I	12	105	40	110	-13		0.11
" -II	II	12	105	30	105	-18		
" -III	II	0.2	105	35	108	-13		
" -IV	III	17	105	30	103	-4	-0.4	
" -V(HT)	IV	0.25	105	30	98	-18		
				70				
sph B-I	I	12	105	70	112	-65		4.2,3.1
" -II	II	0.2	105	33	100	-88		
" -III	II	15	105	48	103	-78	-1.2	
py A-I	I	12	105	40	33	-98		0.41,0.61
"	"		105	120	18	--		
" -II	I	12	105	50	59	-65		
"		12	105	210	13	-116		
" -III	II	0.25	105	30	90	-75		
" -IV	III	14	105	53	97	-46	-13.6	
" -V(HT)	IV	0.2	105	30	64	-38		
" -VI(HT)	V	0.25	105	120	117	-27		
" -VII(HT)	V	0.33	105	45	91	-28		
py B-I	I	12	105	30	65	-92		0.22,0.34
"	"		105	150	51	-99		
" -II	I	12	105	40	64	-81		
"	"		105	135	44	-87		
" -III	II	0.2	105	35	71	-64		
" -IV	III	15	105	36	82	-62	-12.5	
" -V(HT)	IV	0.2	105	32	63	-46		
" -VI(HT)	V	0.25	255	68	158	-27		
" -VII(HT)	V	0.25	290	72	123	-35		
" -VIII(HT)	V	0.25	310	79	100	-28		
CREEDE AND PANASQUIERA SAMPLES								
Creede py A-I(HT)	VI	0.25	105	40	89	-13		0.12
" " -II(HT)	VI	0.4	105	31	82	-12		
" " -III(HT)	VI	12	105	45	88	-13		
" B-I(HT)	VI	0.33	105	60	93	-17		0.1
" " -II(HT)	VI	0.33	105	30	103	-15		
PGL-289 py	VI	0.25	105	36	100	-21		0.03
PGL-230 cpy	VI	0.5	105	70	90	-46		0.04
PGL-27 py-I	VII	0.25	105	33	100	-4		0.14
" " -II	VII	0.25	105	36	100	-5		
" " -III	VIII	0.3	260	35	103	-2		
PGL-303 aspy-I	VII	0.25	105	70	100	-9		0.04
" " -II	VII	0.25	105	33	100	-9		
" " -III	VIII	0.33	300	36	103	-3		
ILLINOIS-KENTUCKY DISTRICT SAMPLES								
calcite-I	IX	12	105	35	130	-6		
" -II	IX	13	105	30	107	-8		
barite A-I	IX	12	105	33	105	-6		0.07
" -II	IX	15	105	25	109	-8		
barite B-I	IX	12	105	30	103	-8		0.05
" -II	IX	13	105	31	103	-5		
quartz-I	IX	12	105	30	105	-7		0.03
" -II	IX	14	105	30	105	-7		
CRUSH-TUBE EXTRACTION BLANK RUNS								
BLANK (5ul SMOW)		2	105	30	~100	-6		
"		"	"	"	"	"	-7		
"		"	"	"	"	"	-6		
"		"	"	"	"	"	-7		
"		"	"	"	"	"	-10		
"		"	"	"	"	"	-8		
"		"	"	"	"	"	-8		

From left to right, these columns list: the number of the experiment as discussed in the text; the period of time that the SMOW was allowed to equilibrate with the mineral residue; the temperature to which the reaction vessel was heated during the reextraction of the SMOW; the period of time allowed for recovery of the SMOW; the percentage of the three microliter aliquot that was recovered; and, the shifts in the δD and δ^{18}O values of the recovered SMOW. Sources of the samples are briefly described in the text. Blank runs were performed on five microliter aliquots.