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Geochemistry of Fluid Inclusions of W, Cu and Au-Ag Ore Deposits in South Korea and Its Significance

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ABSTRACT: Limited geochemical components have been detected in fluid inclusions from ore deposits in south Korea by non-destructive and destructive analytical methods. Review of fluid inclusion studies display that the homogenization temperatures and salinities are in direct proportion. W and Cu ore deposits tend to show higher homogenization temperatures and salinities than Au ore deposits. Abundant halite-bearing fluid inclusions from the Eonyang Granite producing precious amethyst crystals may indicate that the initial fluid originated from magma is highly saline as shown by the quartz from the granite.

Raman Laser microprobe detected CO_2, N_2 and CH_4 in a gold deposit, while these components are hardly detected from other deposits, even though destrucive analysis has dectected CO_2, N_2, CH_4, H_2S, and SO_2 from most of ore deposits. Individual fluid inclusion shows quite different components. These results suggest that large numbers of fluid inclusions should be analysed by Raman Laser microprobe to gain reliable data.

Halite-bearing inclusion is hardly found in fluid inclusions from epithermal gold deposits in south Korea. Geochemistry, homogeinzation temperature and salinity of fluid inclusions may be useful to apply for exploration to find a concealed orebody.

INTRODUCTION

Fluid inclusion studies on ore deposits have been generally confined to the homogenization temperatures and salinities in south Korea. Geochemistry of fluid inclusions, therefore, is estimated only from observation of liquid CO_2 inclusion and solid daughter minerals such as halite or sylvite. Chances for using Raman laser microprobe in USA and gas-collection lines in Japan have revealed some geochemistry of fluid inclusions studied in Korea.

This study may be the first step of studying geochemistry of fluid inclusions. Since the results are obtained only representative specimen from individual ore deposit. However, it is interesting that the limited geochemistry of fluid inclusions is applicable to interpretation of genesis of studied ore deposits.

Selected ore deposits for this study (refers to Fig. 1) are as follows;

1) Okgye Au-Ag ore deposit (Kwangjin Report, 1987)

Gold and silver ouccur as minor elements in Pb-Zn dominant quartz veins. It had been mined for gold which is substantially associated with sulphide minerals in the quartz.

2) Sangdong W-Mo ore deposit

Tungsten skarn ore deposit, associated with swarms of quartz veins bearing scheelite, wolframite, or molybdenite. The skarn of this ore deposit is classified into three zones, quart-mica skarn with 3 to 6% of tungsten in the core, rimmed by quartz-hornblende skarn with about 1~2% of tungsten, and the rest of garnet-pyroxene skarn with about 0.3% of tungsten (Moon, 1983). Samples for this study were mainly taken from the quartz-mica zone and the garnet-pyroxene zone of the skarn orebody and from the quartz viens.

3) Yeonhwa Pb-Zn ore deposit (Chung, 1986)

Skarn type of Pb-Zn ore deposit. Galena and sphalerite occur in pyroxene-garnet skarn and in veins of limestone (Pungchon limestone). Samples for this study were taken from fine quartz viens which are rarely observed.

4) Daehwa W-Mo ore deposit (Park et al., 1974)

Quartz vein type ore deposit. Scheelite and molybdenite are main ore minerals associated with a little chalcopyrite. Geology is mainly composed of gneiss.

5) Seolhwa Au ore deposit (Kwangjin Report, 1987)

Quartz vein type of gold deposit, developed in biotite granite.

6) Sanbang Au ore deposit

Quartz vein type of gold deposit, developed in granite.

7) Sangweon Au-Ag ore deposit (Yun, 1991)

Quartz vein type of gold and silver deposit, develo-

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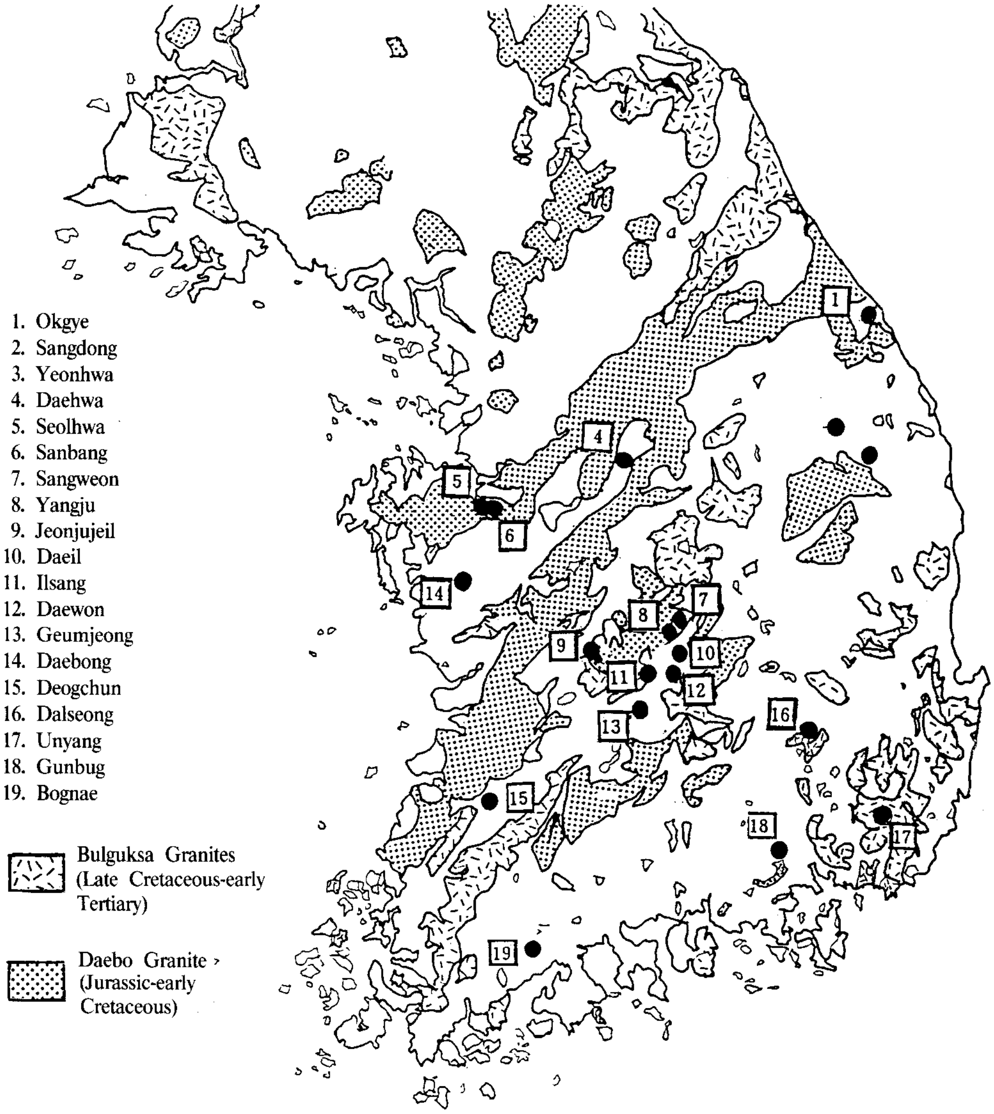


Fig. 1. Location map of sampled ore deposit.

ped in biotite gneiss.

8) Yangju Au ore deposit (Yun, 1991)

Quartz vein type of gold ore deposit, developed in biotite gneiss

9) Jeonjujeil Ag-Au ore deposit

Quartz vein type of silver ore deposit, developed in biotite gneiss.

10) Daeil Au ore deposit (Kwangjin Report, 1987)

Quartz vein type of gold ore deposit, developed in biotite gneiss.

11) Ilsang Au ore deposit

Quartz vein type of gold ore deposit. Developed in biotite gneiss.

12) Daewon Au ore deposit

Quartz vein type of gold deposit, developed in biotite gneiss.

13) Geumjeong Au ore deposit (Kwangjin Report, 1990)

Quartz vein type of gold ore deposit, developed in biotite gneiss.

14) Daebong (Cheongyang) Au ore deposit (Kwangjin Report, 1990)

Quartz vein type of gold ore deposit, developed in biotite gneiss.

15) Deogchun (Jeongju) Au ore deposit

Quartz vein type of gold ore deposit, developed in granite.

16) Dalseong W-Cu ore deposit (Kwangjin Report, 1990)

Breccia pipe type. Quartz swarms filled in breccia of andesite, containing wolframite and chalcopyrite.

17) Unyang Amethyst deposit

Amethyst occurs in granite as euhedral crystals.

18) Gunbuk Cu ore deposit (Kwangjin Report, 1990)

Quartz vein type of copper ore deposit, developed in the Cretaceous sediments of the Kyeongsang basin. And sometimes calcite contains chalcopyrite. Gold was produced as by-product.

19) Bognae Au ore deposit (Kwangjin Report, 19 87)

Quartz vein type of gold ore deposit in fractures of gneiss Quartz veins contain mainly galena, pyrite, arsenopyrite and chalcopyrite with small amount of native gold.

Background of Fluid Inclusions Studies from Studied ore Deposits

Fluid inclusion studies in Korea have mainly dealt with the homogenization of fluid inclusion and the salinities. History of fluid inclusion study is not so long that only about 50 papers of fluid inclusion study are published in Korea since 1960. Following tables are all data of ore deposits in south Korea collected from published either domestic or foreign journals.

As Table 1, 2 and 3 show, some of ore deposits such as tungsten or copper deposits exhibit relatively high homogenization temperatures above 400℃ and highly saline fluid supersaturated with NaCl, but gold and silver deposits display comparatively low homo-

Table 1. Homogenization temperatures and salinities of fluid inclusions in quartz from trungsten ore deposits in south Korea.

Name of mine	Mineral	Homogenization temperature(℃)	Slinity (NaCl eq. wt%)	Reference
Buam (skarn)	quartz	162~363	0.9~12.9	K.J. Moon (1984)
Cheongyang	quartz	210~350	6.7~10.1	H.I. Park et al. (1981)
Chongyang	quartz	280~340	6.7~10.0	H.I. Park et al. (982)
〃	fluorite	210~230	3.0	
Daewha	quartz	205~314		H.I. Park et al. (1981)
	fluorite	170~295		
Daewha	quartz	232~357	0.3~ 7.9	H.I. Park et al. (1985)
Dalseong	quartz	154~335		J.M. Chi et al. (1974)
Dongbo	quartz	205~365	16.9~17.2	H.I. Park et al. (1985)
	sphalerite	195~295	13.0~15.7	
	calcite	190~270	9.7~12.4	
Ilkwang	quartz	305~435	4.9~12.0	C.S. So et al. (1983)
Ilkwang	quartz	250~400	15.0~47	J.M. Chi ( )
Jungbo	quartz	260~330	4.0~ 9.0	H.I. Park et al. (1981)
Sangdong (skarn)	quartz	120~410	1.4~48	K.J. Moon (1983) (1985)
	pyroxene & garnet	320~580		
	fluorite	134~267		
Sannae	quarz	300~470	5.5~23	C.S. So (1984)
Ssangjeon	quartz	397~441	5.1~ 6.0	S.T. Youn & H.I. Park (1982)
Suri	quartz	245~345	5.0~ 9.0	H.I. Park et al. (1981)
Susan	quartz	235~335	4.0~ 9.7	H.I. Park et al. (1981)
fluorite	225~305	5.0~7.7		
Ulsan	quartz	230~360	3.7~16.8	K.H. Park & H.I. Park (1980)
Useok	quartz	310~365		H.I. Park (1980)
Useog	quartz	315~360		H.I. Park et al. (1981)
Wolak	quartz	239~360	3.9~ 9.6	I.S. Lee & H.I. Park (1982)
	fluorite	224~332	2.7~ 6.9	
Weolag	quartz	234~394	3.7~11.7	C.S. So et al. (1983)
Youngha	quartz	270~360		H.I. Park et al. (1981)

Table 2. Homogenization temperatures and salinities of fluid inclusions in minerals from Cu ore deposits in south Korea.

Name of Mine	Mineral	Homogenization temperatures(℃)	Salinity (NaCl eq.wt%)	Reference
Geoje	quartz	213~262	6.6~10.9	C.J. Kim & H.I. Park (1984)
	sphalerite	186~301	7.1~14.4	
Goseong	quartz	240~353	8.5~13.6	H.I. Park (1983)
Haman	quartz	289~489	11.7~54.9	H.I. Park et al. (1985)
	calcite	182~287		
Jeilgunbuk	quartz	290~316	18.3~48.2	
Sambong	quartz	284~351	6.1~11.6	H.I. Park (1983)
	calcite	144~157		
Seongji	quartz	276~350	6.2~11.6	

Table 3. Homogenization temperatures and saliaities of fluid inclusions in minerals from Au-Ag ore deposits in south Korea.

Name of mine	Mineral	Homogenization temperature(℃)	Slinity (NaCl eq. wt%)	Reference
Bobong	quartz	90~350	3.2~8.9	C.S. So et al. (1989)
Bolgok	〃	223~360	3.2~4.9	S.F. Choi et al. (1989)
Cheolam	〃	225~270	4.0~10.0	H.I. Park et al. (1987)
Chungil	quartz	154~336		T.Y. Chang & J.M. Chi (1989)
Chungnam	〃	120~335	3.0~9.0	C.S. So & K.L. Shelton (1987)
Dadeok	〃	206~310	5.8~12.8	H.I. Park et al. (1988)
	sphalerite	267~310	0.9~11.5	〃
	calcite	232~253	4.5~5.5	〃
Daeheung	quartz	120~372	2.0~11.2	
Daejang	〃	130~365	5.0~13.0	H.I. Park & D.L. Kim (1988)
	calcite	90~295	2.0~14.0	
Dunjeon	quartz	180~405	0.5~5.1	H.I. Park et al. (1987)
	calcite	149~233	0.4~4.5	
Gaekum	quartz	145~340	5.8~7.3	C.S. So et al. (1989)
Geojae (Myeongjin)	qrartz	244~370	2.9~8.1	S.G. Choi et al. (1983)
Geumyong	quartz	210~350	1.0~7.1	S.J. Chi et al. (1987)
	quartz	120~340	2.5~10.0	C.S. So et al. (1983)
	calcite	150~286	5.0~6.5	
	fluorite	90~275	1.5~6.0	
Ilbo	quartz	110~361	5.5~12.0	C.S. So & K.L. Shelton (1987)
Jangheung	quartz	135~315	6.7~7.3	C.S. So et al. (1989)
Jinsan	quartz	125~370	0.5~3.0	C.S. So et al. (1988)
	calcite	110~180	0.0~1.5	
	fluorite	135~370	00.0~3.0	
Mugeug	quartz	137~287	0.8~7.9	H.I. Park & S.J. Kang (1988)
	calcite	141~228		
Namseong	quartz	225~335		H.K. Lee et al. (19870
Palbo	quartz	140~321	3.1~8.3	C.S. So et al. (1989)
Samkwang	〃	159~274	1.2~7.4	K.J. Moon (1986)
Samgwang	〃	164~400	1.2~7.9	C.S. So et al. (1988)
Samsong	〃	75~340	2.6~7.9	C.S. So et al. (1989)
Seonggeo	〃	105~340	5.5~11.2	C.S. So & K.L. Shelton (1987)
Sobo		135~365		C.S. Co et al. (1988)
	sapalerite	158~278	4.6~5.4	
Tongyeong	quartz	130~225	1.0~4.0	H.I. Park (1983)
Yangpyeong	〃	130~350	7.0~8.3	C.S. So et al. (1989)
Yeosu	〃	121~335	3.4~7.6	

genization temperatures with low salinities.

Author has developed a exploration technique by using a tendency of homogenization temperatures, assuming that the homogenization temperatures obtained from one quartz vein may indicate a flowing direction of fluid (Moon. 1983).

The highly saline fluid derived from magma is frequently observed as abundant halite crystals in fluid inclusions. The assumption from the presence of halite crystals have led to find a granitoid as a source rock underneath the Sangdong tungsten skarn ore deposit (Moon, 1991) in the Sangdong mine area.

GEOCHEMICAL ANALYSIS OF FLUID INCLUSIONS

Geochemistry of Fluid Inclusions Analysed by Laser Raman Microprobe (LRM)

It is found that non-destructive analysis of fluid inclusions is confined to limited components. 35 thin sections from 7 ore deposits such as Sangdong tungsten, Daehwa tungsten, Donsan tungsten, Gunbuk copper, Jangkun Pb-Zn, Eonyang quartz and Geumpo Au-Ag ore deposits are attempted to be analysed by the laser Raman microprobe (Moon, 1990). It is proved that all elements are not always analysed by LRM, since the content of carbon dioxide was not detected by LRM in a specimen from the Sangdong ore deposit, even if liquid CO_2 bearing fluid inclusion is observed in the same specimen. It may suggest that LRM analysis of fluid inclusions demand to analyses a number of fluid inclusions with tedious works, since individual fluid inclusion could have different composition. N_2 CH_4 and CO_2 contents are detected from only the Keumpo Au-Ag ore deposit among the seven ore deposits. This result may have supported an assumption that the fluid involved in glod mineralization in south Korea was either derived from the latest stage of magma after substantially cooled or travelled quite a long distance through country rocks from a deeply emplaced magma (Moon, 1990).

Gas-chromatographic Analysis of Fluid Inclusions

Quartz samples from 14 ore deposits are crushed and sieved to collect grains between 0.2 mm and 0.5 mm in diameter and finally collected about 3 mg from individual sample. Table 4 shows results of the gas-chromatographic analysis of fluid inclusions. Since this destructive analysis also was confined to several elements, contents of H_2O, N_2, CH_4 and CO_2 only are compared in the results. As we already understand, most of fluid inclusions have water as major component.

Table 4. Mole % of gas content analysed from fluid inclusions.

Ore deposit	Sample No.	Name of Mire	H_2O	CO_2	CH_4	N_2
Au-Ag	K-3	Samwon	97.2	2.3	0.4	0.2
	K-4	Samwon	97.9	1.6	0.4	0.2
	K-8	Bognae	34.5	11.7	3.6	50.2
Au	K-1	Yangju	97.6	2.1	0.3	0
	K-2	Daewon	99.1	0.5	0.2	0.2
	K-5	Daeil	88	1	0.5	10.5
	K-9	Ilsang	99.6	4.8	0.3	0
	K-10	Sanbang	95.8	3.3	0.7	0.2
	K-1	Seolhwa	92.4	7.3	0.3	0
Pb-Zn	G-1	Okgye	94.5	0	4.2	1.3
	G-2	Jeonjujeil	99.4	0.5	0	0
Cu	C-1	Gunbug	98.4	1.3	0.3	0
Amethyat	A-1	Unyang	97.4	2.1	0.2	0.3
W	W-1	Sangdong(Mo)	98.6	1.3	0.1	0
	W-1	Daehwa	84.6	1.2	0.2	12.4
	W-3	Sangdong(Qt)	96.6	1.9	0.4	1.1
	C-2	Dalseong	77,.3	17.4	2.2	3.1
	X-1	Sangdong(Px)	89.6	2.0	0	8.4
	W-5	Sangdong(Qt)	97.2	2.5	0	0 .1

W-1 (MoS_2 bearing quartz vein), W-3 (Scheelite bearing quartz vein), Px-1 (Pyroxene from skarn), W-5 (Quartz from skarn, quartz- mica zone).

Relatively high content of N_2 is detected from Daeil Au, Bognae Au-Ag and Daehwa W-Mo ore deposits as shown in Fig. 2. It is significant that over 50 mol% of N_2 content with 35 mol% of H_2O in fluid inclusions was detected from the Bognae Au-Ag deposit. More detailed study on this deposit is essentially required. In fact, fluids of quartz from the Sangdong W-Mo ore deposit contain about 1 mol% of N_2, whilst the fluid inclusions of clinopyroxene contain remarkably higher content of N_2 than those of quartz at the Sangdong W-Mo ore deposit. The content of N_2 detected from quartz in the quartz-mica skarn is relatively similar with that from quartz in the quartz veins. This result may suggest that the geochemical environment of forming the pyroxene crystal was quite different from that of quartz at the Sangdong ore deposit, showing a trend of decreasing the nitrogen content with time for evolution of skarn zones to late quartz vein system.

As shown in Fig. 3, most of studied ore deposits

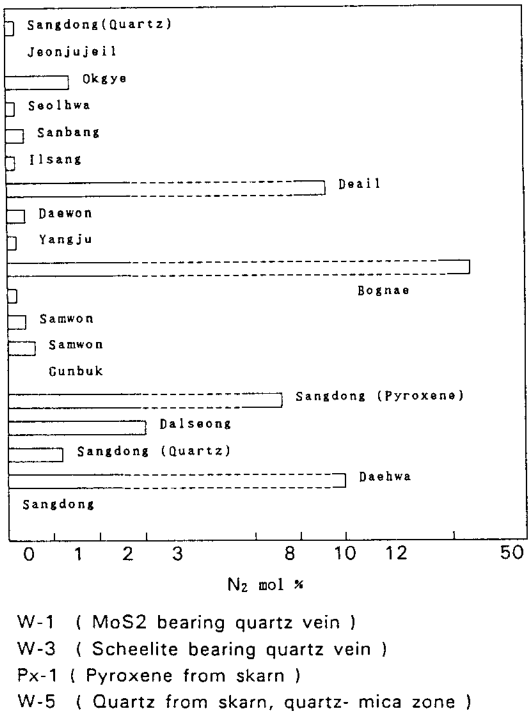


Fig. 2. Comparative diagrams of N_2 content in the fluid inclusions from different places.

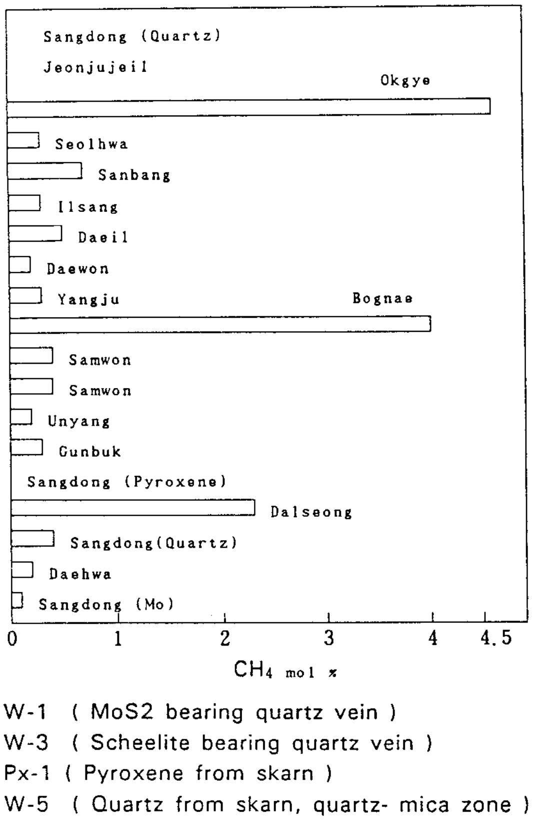


Fig. 3. Comparative diagrams of CH_4 content in the fluid inclusions from different places.

except the Jeonjujeil and the Sangdong skarn (pyroxene) show content of CH_4 in their fluid inclusions. Particularly, the Okgye, the Bognae and the Dalseong display higher content of CH_4 than others. Under assumption of methane's organic origin, CH_4 content seems to be derived from meteroic water which have passedthrough country rock containing graphitic or carbonaceous materials. The location of the Okgye near coal mines and thick Cretaceous sediments at the Dalseong may be a cause to increase the CH_4 in the fluids from these ore deposits. As mentioned before, it should be checked again about the anomalous content of CH_4 in fluid inclusions from the Bognae. It is interesting that the pyroxene of the Sangdong which is believed to have formed during early mineralization by fluid contains litte methane, while the vein quartz tends to increase CH_4 in the fluid at the Sangdong W-Mo ore deposit. This result also depicts the geochemical environment of fluid at the early stage was different form that at the late stage.

As shown in Fig. 3 and 4, abundances of CO_2 and CH_4 contents are similarly distributed in the studied ore deposits. It is strange that the Okgye which shows high content of CH_4 has not CO_2 content. It may be due to organic origin of CH_4 as assumed before. As we understand that the fluid of clinopyroxene containing CO_2 in the Sangdong was derived from the magma, it may be possible to assume that CO_2 content might be originated from the magma as well as derived from the meteoric water.

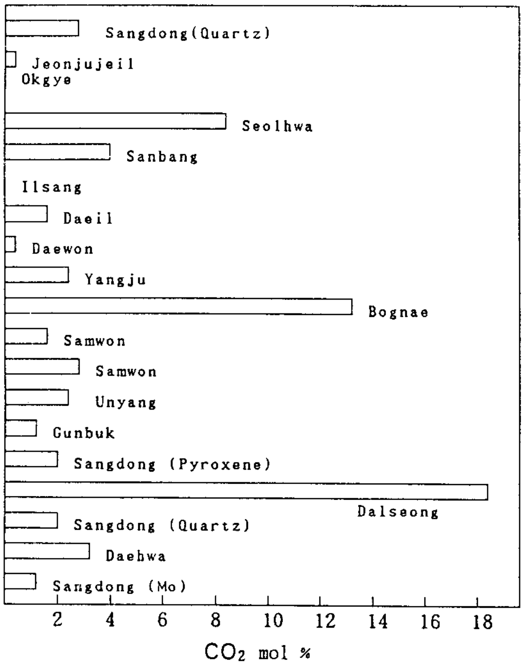
Relatively low content of H_2O in Daeil, Bognae, Sangdong, Dalseong and Daehwa may be a good clue depicting the magma origin, since it may be supported by the fact that the nitrogen which was assumed to have derived from the magma was more detected from these ore deposits as above than other deposits.

Experimental Analyses by Mass Spectrometer

Five samples from differnt ore deposits were analysed by mass spectrometer in geological survery of Japan. The results are as follows;

K-1 (Keumpo Au mine)=H_2O, CH_4, and CO_2 with other organic compounds are detected.

G-3 (Yeonhwa Pb-Zn mine)=CO_2 and CH_4 are



W-1 (MoS2 bearing quartz vein)
W-3 (Scheelite bearing quartz vein)
Px-1 (Pyroxene from skarn)
W-5 (Quartz from skarn, quartz- mica zone)

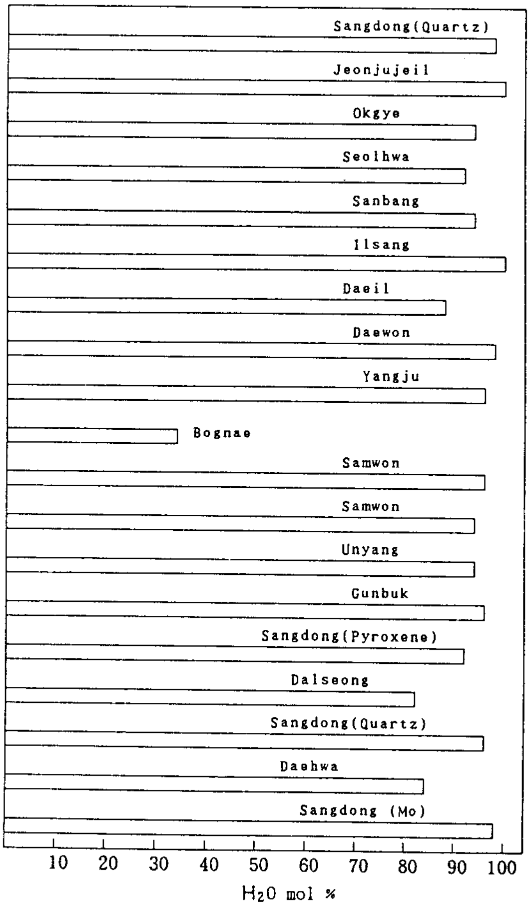
Fig. 4. Comparative diagrams of CO_2 content in the fluid inclusions from different places.

detected.

G-4 (Deogcheon Au mine)=CO_2 and CH_4 are detected.

G-5 (Daebong Au mine)=CO_2 and CH_4 are detected with H_2S, SO_2 and other organic compounds.

G-6 (Keumjeong Au gold)=CO_2 and CH_4 with other organic compound are detected.



W-1 (MoS2 bearing quartz vein)
W-3 (Scheelite bearing quartz vein)
Px-1 (Pyroxene from skarn)
W-5 (Quartz from skarn, quartz- mica zone)

Fig. 5. Comparative diagrams of H_2O content in the fluid inclusions from different places.

DISCUSSION

As we understand differences in chemical composition of individual fluid inclusions as shown in differences in homogenization temperatures, it is found that it is impossible to specify the causes of difference depending on different major ore element deposits. The significant different content of nitrogen from the Sangdong W-Mo ore deposit may have brought out a clue to identify the order of mineralizing fluid. More systemactic study on this matter is essentially required in order to prove that the earlier formed fluid inclusions such as contained in pyroxene should contain comparatively higher content of nitrogen than that in the late formed fluid inclusions in quartz. Besides, methane content hardly detected from pyroxene-fluid inclusions has supported the assumption of mixing fluid to the magmatic fluid by the meteoric water.

The origin of CO_2 in fluid inclusions is hardly defined, either magmatic or organic in sediments. It seems to cause more organic in fluid inclusions depending on country rock which accomodates the hydrothermal quartz veins, since quartz veins in the gneiss tend to contain comparatively abundant organic gases whilst a little detection of the organic gases in the granite, suggesting contamination of fluids.

CONCLUSION

The results of this study is summarized as follows;

Differnces in geochmistry of fluids depending on different major ore elements such as Au, Cu, Pb-Zn or W-Mo ore deposits in south Korea are hardly defined.

Nitrogen of fluid inclusions may be derived from early emanation from a magma.

Methane may be mainly derived from country rocks.

Carbon dioxide may be derived from magma and country rocks.

Highly salined fluid inclusions with high homogenization temperatures are hardly observed in the quartz from gold ore deposits in south Korea. Park and Lee (1991) have reported halite-bearing fluid inclusions from quartz in the Dunjeon gold deposit with high homogenization temperatures, which indicatea that this deposit is different from most of other epithermal gold ore deposits by showing high temperatures. Disregarding this unusal depoit, it may generalize either a long distance of fluid travelled from the source rock, or the latest fluid supplied from the magma, to form ephithermal gold deposit in south Korea.

More systematic study on geochemistry of fluid inclusions may bring a clue to interpret the origin of fluid and the genesis of the ore deposit.

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중석, 동, 금-은 광상 유체포유물의 지화학과 그 의의

문건주

요 약: 국내 광상의 유체포유물에 대한 지화학 조성이 제한적이나마 비파괴 방법과 파괴 방법을 이용하여 분석 탐지되었다. 그 동안의 유체포유물 연구 결과는 균질화온도와 염농도가 정비례함을 보여주고, 중석과 동 광상의 것이 금광상의 것 보다 좀더 높은 균질화온도와 염농도를 갖는 경향을 보여준다.

값진 보석 자수정을 산출하는 언양 화강암의 유체포유물은 많은 소금 결정을 딸광물로 가지고 있는데, 이 점에 있어서는 마그마로부터 근원한 최초의 유체는 아주 염도가 높았을 것을 잘 나타내 주고 있는 셈이다.

파괴분석에 의해 탄산깨스, 질소, 메탄, H_2S, SO_2가 대부분의 광상에서 검출됨에도 불구하고, 레이저 마이크로푸르브 (RLM) 분석에 의해서는 하나의 금광상에서 탄산깨스, 질소, 메탄이 검출되었을 뿐, 다른 광상의 유체포유물로부터 이들 성분이 분석되지 않았슴은 RLM 분석은 다수의 개별 유체포유물을 대상으로 분석해야 함을 암시해 주고 있다.

한국 금광상의 유체포유물은 소금 결정을 보이지 않는다. 유체포유물의 지화학, 균질화온도 및 염농도는 잠두광체 탐사에 응용 이용될 수 있다.