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Fluid inclusion studies of the copper-bearing quartz veins in Gowuch Formation, Drosh-Shishi area, Chitral, northern Pakistan

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ABSTRACT: *Copper mineralization, generally confined to the Gowuch Formation, in Drosh-Shishi area is a part of the upper crust of Kohistan arc terrain in Chitral, northern Pakistan. It is related to the hydrothermal activity and is mainly associated with altered diorites and quartz veins. It occurs in different forms; within quartz veins, along foliation planes, in dissemination and as supergene enrichment. Fluid inclusion studies indicate that the salinity of the hydrothermal solution is 12.28–13.40 equivalent wt% NaCl and the homogenization temperature ranges from 160 to 350°C. This suggests that the copper mineralization is related to the late stage vein formation as a result of diorite and granodiorite intrusion.*

INTRODUCTION

The classic hypothesis for derivation of magmatic ore deposits (Lindgren, 1933; Halland, 1972) has come under increasing scrutiny in recent years. The genetic concept that involves aqueous fluids, containing metals, are released from crystallizing magma and these fluids move upward and outward from their source to deposit metals in suitable structures and chemical sites. Fluid inclusion and stable isotope studies are of major importance in the assessment of the relative role played by primary magmatic water with or without other water in the formation of specific hydrothermal ore deposits. Fluid trapped during the growth of host crystals in an ore (i.e. primary inclusions) are the samples of the ore fluids, and hence may reveal much about the conditions of ore transport and deposition. There are secondary fluid inclusions which also develop due to shearing and reheeling of fractures, and provide information on fluids that were present around the host crystal at some unspecified time after the original growth (Roedder, 1977).

The present fluid inclusion study has been conducted on the copper-bearing quartz veins which transact the diorites of the Gowuch Formation in Drosh area, Chitral (Fig. 1). The main aim of this study is to find out the homogenization temperature and the composition of the ore forming fluid.

COPPER MINERALIZATION

Copper mineralization in Gowuch Formation at Drosh-Shishi area occurs within a belt which is considered to be the extreme north part of the Kohistan complex. Gowuch Formation is mainly comprising of Mesozoic sediments and volcanic rocks intruded by diorite and quartz veins. Copper mineralization is mostly confined to the quartz veins and diorites. Porphyritic andesites crop out in the south of the melange sequence in Gowuch

Formation, and it extends north-east south-west along the regional strike of the enclosing rocks. These rocks dip steeply to the north and are underlain by red shale, sandstone and conglomerates of Purit Formation (Pudsey et al., 1985). The Purit Formation has faulted contact with the lower lying Gowuch Formation. The latter is faulted against the diorites of the Lowari plutons, exposed further south of the Gowuch Formation (Fig. 1).

Based on field observation, four types of copper mineralization are observed in the area:

1. Copper mineralization along quartz veins;
2. Copper mineralization along foliation planes;
3. Disseminated Copper mineralization;
4. Supergene enrichment of Copper.

Copper mineralization along quartz veins

In Gowuch Formation the altered diorite sills are intruded by a large number of quartz veins. These veins are milky white in colour, 2-3 cm wide and 10 to 20 m long. Tetrahedrite, chalcopyrite and bornite are the main copper-bearing phases with lesser amount of sphalerite, galena, pyrite and magnetite in the quartz veins. These phases occur as coarse grained irregular masses within the interstices of quartz.

Copper mineralization along foliation planes

Copper mineralization in the form of tetrahedrite and chalcopyrite along with other ore phases (i.e. galena, sphalerite and pyrite) are generally present along foliation planes in the zones of intense shearing. These ore phases are usually precipitated along foliation planes in the form of microveins or thin bands of carbonates and quartz. Supergene enrichment in the form of azurite and chalcocite is present along foliation plane.

Disseminated Copper mineralization

Copper mineralization in the form of chalcopyrite and tetrahedrite is disseminated mainly in the diorites. Both chalcopyrite and tetrahedrite occur as fine-to medium-grained and are usually present in association with each other. Cubic grains of pyrite are also found in association with chalcopyrite and tetrahedrite.

Supergene enrichment of copper

Azurite and malachite along with limonite are the secondary minerals formed due to oxidation of sulfide minerals. These phases generally occur along fractures and the margins of sulfide minerals.

PREPARATION/PROCEDURES AND TYPES OF FLUID INCLUSIONS

The analytical work for the fluid inclusion research has been carried out in the Geological Survey of Japan, Tsukuba, Japan. A total of 8 samples of copper-bearing quartz veins were selected for the preparation of doubly polished sections of 100-150 μm thickness. These polished sections were studied under the petrographic microscope to observe the morphology of the inclusions and to select them for microthermometry measurements.

Fluid inclusions are classified as primary, secondary or pseudo-secondary depending upon when the inclusions were trapped relative to the formation of bulk of the enclosing minerals. All the quartz veins examined during this study experienced repeated fracturing in the presence of aqueous fluids as is evidenced by the abundant planes of secondary inclusions observed at low magnification. Generally, high density of randomly oriented fractures decorated with fluid inclusions made it difficult to determine with confidence whether a given inclusion was along one of these fractures (secondary or pseudosecondary) or was trapped during crystal growth (primary). Therefore, it is avoided to classify the fluid inclusion as primary, secondary or pseudo-secondary but, rather, have related

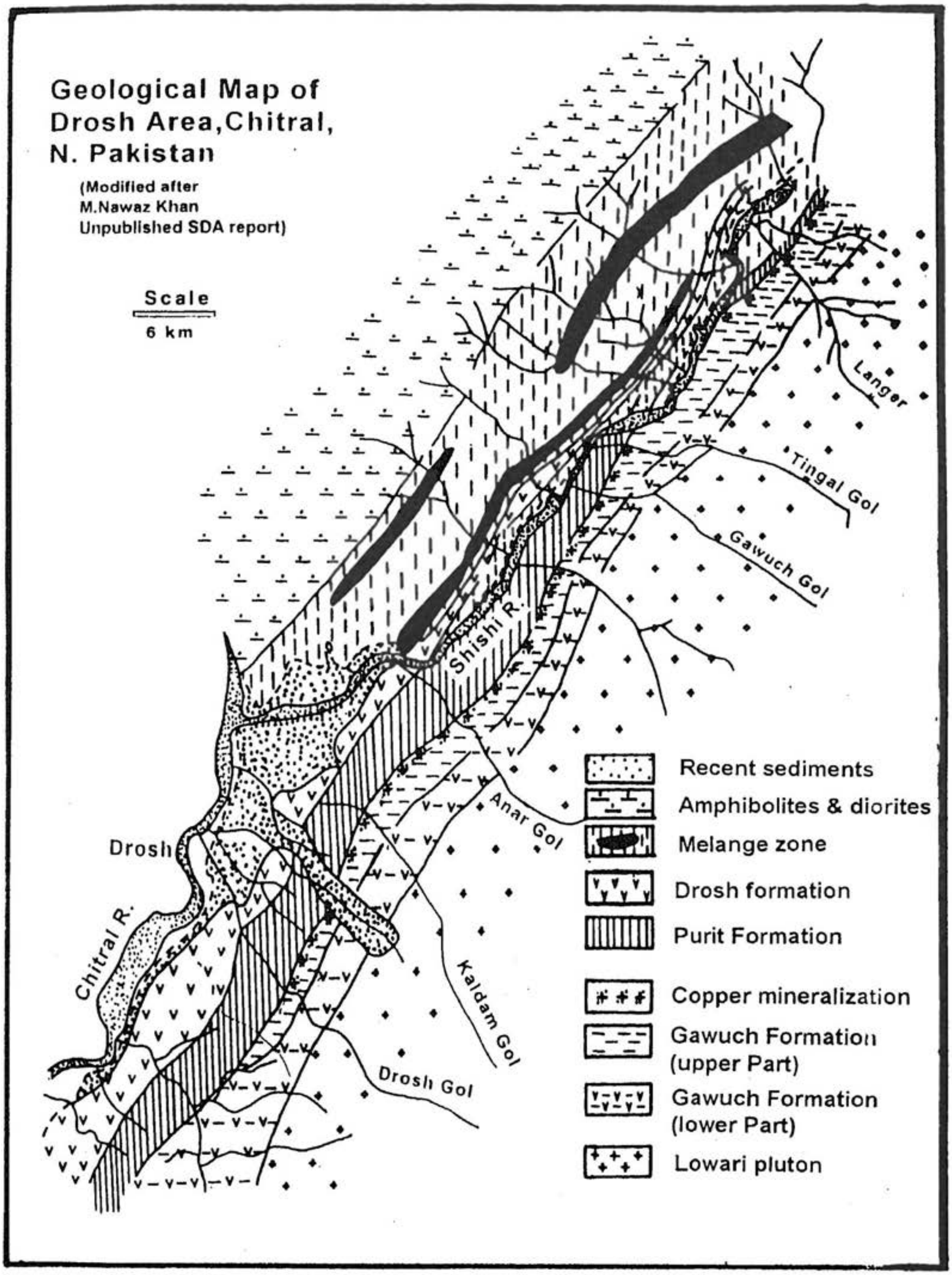

Fig. 1. Geological map of Drosh–Shishi area, Chitral, N. Pakistan.

groups of inclusions to various stages of vein filling.

These fluid inclusions are mainly two-phase (liquid + vapour), but too small, i.e. <5 μm, and make trails occurring across the quartz grain boundaries. It may be noted that the quartz grains are the fine-grained aggregated stuff containing these minute fluid inclusions. Only one sample could be selected for the measurement. The fluid inclusions present in this sample are fairly large > 10 μm. Two phase (liquid + vapour) liquid-rich inclusions and poly-phase (liquid + CO_2 + vapour) liquid-rich inclusions are identified. They commonly occur together in quartz. No daughter crystals are noticed. The co-existence of these two types of inclusion is the strong evidence for the presence of two or more immiscible phases (i.e. liquid, vapour and CO_2) due to boiling at the time of the formation of inclusions .

A USGS - type Gas-flow Heating/Freezing Stage was used for the measurement of homogenization temperature (Th) and melting temperature (Tm). This equipment includes i) Heating/Freezing Stage, ii) Electric Gas Heating Element, iii) Doric Trendicator, and iv) Microscopic objectives. Air compressor, thermocouple, cylinder containing dry nitrogen and Dewar containing liquid nitrogen are also included in the Heating/Freezing Stage.

Calibration of the thermocouple and the whole system has been done. For the thermocouple calibration pure water and pure ice was used. The thermocouple and the system was also calibrated to 0°C. A number of inorganic, organic and pure metals were used for the calibration of the instrument (Table 1). In this way accuracy and precision for the instrument was obtained. During the operation the gas flow rate was maintained as 20 SCFH at T > 0°C and 10 SCFH at T< 0°C.

TABLE 1. STANDARD MATERIALS FOR THE CALIBRATION OF THE USGS-TYPE GAS-FLOW HEATING/FREEZING SYSTEM

Materials	Melting Point (°C)
Hg	-38.9
Pure Water	0.00
Phnoexybenzen (NPL tripple-point cell)	26.867
In	156.5
Sn	231.97
Bi	271.3
Pb	327.43
Zn	419.58
$NaNO_3$	306.8
KNO_3	333
$K_2Cr_2O_7$	398
Organic Materials (e.g., anthraquinone etc.)	various
Synthetic fluid inclusions (e.g., NaCl-H_2O etc.)	various

The metals used in the calibration are 99.9999% pure. For the organic materials capillaries of 0.5 mm diameter are used.

DISCUSSION

A total number of 6 two-phase (liquid + vapour) fluid inclusions were subjected for freezing measurement. The freezing temperature was measured up to –70°C and the melting temperature (Tm) was recorded from –9.5 to –8.5°C. Salinites have been calculated from final melting measurements (Fig. 2; Table 2) and are reported as equivalent concentrations of NaCl. The low Tm affinity advocates 12.28 to 13.40 equivalents wt.% NaCl within the inclusions (Bondar, 1992;

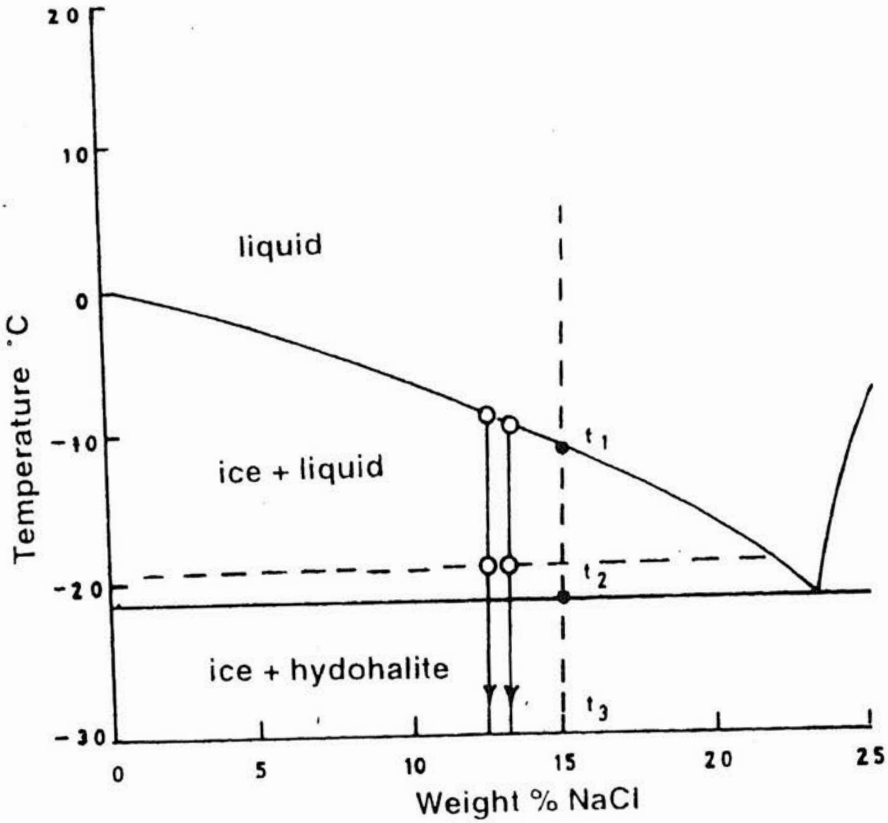

Fig. 2. Portion of the NaCl-H_2O phase diagram to show which phase changes occur in an inclusion containing 15 wt.% NaCl (modified after Shepherd et al., 1985). t_1 = –10°C (ice forms and continues to crystallize), t_2 = –21.2°C (eutectic), t_3 = –20°C (supercooled temperature). On warming the inclusion follows the same path as taken upon freezing until at t_2 the first liquid forms from melting of solid phases. For 13.40 to 12.28 equivalent wt.% NaCl; t_1 = –9.5 to –8.5°C, t_2 = –19.2°C (eutectic), t_3 = –45°C (supercooled temperature).

Goldstein & Reynolds, 1994). This salinity (<26 equivalent wt.% NaCl) is inferred from the absence of cubic salt daughter minerals (Nash & Cunningham, 1973). The homogenizing (Th) temperature recorded ranges from 160 to 350°C. However, it is assumed that the mean temperature (255°C) represents true trapping temperature. Bodnar (1978) and Ahmad and Rose (1980) have proposed various reasons for this kind of wide range of homogenization temperature. The important one are as follows:

a. Leakage: This could be natural or at the time of heating measurement.

b. Trapping of both steam and liquid: This would give anomalously high homogenization temperature.

c. Low homogenization temperature: These might result from inadvertent examination of secondary and/or pseudo-secondary inclusions.

TABLE 2. VALUES FOR SALINITIES (WT.% NACL) THAT CORRESPOND TO FREEZING POINT DEPRESSIONS (TM ICE) FOR FLUID INCLUSIONS MELTING IN THE PRESENCE OF VAPOUR BUBBLE (DATA FROM BODNAR, 1992: ADOPTED FROM GOLDSTEIN AND REYNOLDS, 1994).

FPD	0	1	2	3	4	5	6	7	8	9
0	0	0.18	0.35	0.53	0.71	0.88	1.05	1.23	1.4	1.57
1	1.74	1.91	2.07	2.24	2.41	2.57	2.74	2.9	3.06	3.23
2	3.39	3.55	3.71	3.87	4.03	4.18	4.34	4.49	4.65	4.9
3	4.96	5.11	5.26	5.41	5.56	5.71	5.86	6.01	6.16	6.3
4	6.45	6.59	6.74	6.88	7.02	7.17	7.31	7.45	7.59	7.73
5	7.86	8	8.14	8.28	8.41	8.55	8.68	8.81	8.95	9.08
6	9.21	9.34	9.47	9.6	9.73	9.86	9.98	10.11	10.24	10.36
7	10.49	10.61	10.73	10.86	10.98	11.1	11.22	11.34	11.46	11.58
8	11.7	11.81	11.93	12.05	12.16	12.28	12.39	12.51	12.62	12.73
9	12.85	12.96	13.07	13.18	13.29	13.40	13.51	13.62	13.72	13.83
10	13.94	14.04	14.15	14.25	14.36	14.46	14.57	14.67	14.77	14.87
11	14.97	15.07	15.17	15.27	15.37	15.47	15.57	15.67	15.76	15.86
12	15.96	16.05	16.15	16.24	16.34	16.43	16.53	16.62	16.71	16.8
13	16.89	16.99	19.08	17.17	19.26	17.34	17.43	17.52	17.61	17.7
14	17.79	17.87	17.96	19.04	18.13	18.22	18.3	18.38	18.47	18.55
15	18.63	18.72	18.8	18.88	18.96	19.05	19.13	19.21	19.29	19.37
16	19.45	19.53	19.6	19.68	19.76	19.84	19.92	19.99	20.07	20.15
17	20.22	20.3	20.37	20.45	20.52	20.6	20.67	20.75	20.82	20.89
18	20.97	21.04	21.11	21.19	21.26	21.33	21.4	21.47	21.54	21.61
19	21.68	21.75	21.82	21.89	21.96	22.03	22.1	22.17	22.24	22.31
20	22.38	22.44	22.51	22.58	22.65	22.71	22.78	22.85	22.91	22.98
1	23.05	23.11	23.18							

d. Fluctuations in both pressure and salinity at the time of fluid trapping: These would affect the filling temperature.

The wide range in temperature, as observed in the studied samples, could be resulted from any or all of the above reasons. It is, therefore, very difficult to draw conclusion about the nature of the mineralizing fluid at this stage, however, we can at least know the high temperature range of mineralizing fluid which will be helpful in determining the composition of fluid during isotopic studies. The quartz veins hosting the copper-bearing minerals and the fluid inclusions are the late stage hydrothermal veins formed as a result of diorite or granodioritic intrusions. The evidences such as the daughter minerals (NaCl) in the fluid inclusions, high homogenization temperature (Th) and high salinity (>50 equiv. wt.% NaCl) as commonly reported in the porphyry copper deposits are, however, absent in the copper-bearing quartz veins of Drosh area.

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