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Chemical Zoning in Wolframite from San Cristobal, Peru

A. Campbell[1] **and U. Petersen**

Department of Geology, Harvard University, 24 Oxford Street, Cambridge, MA 02138, USA

Abstract. Fifty wolframite crystals from San Cristobal (Peru) were analysed with the electron microprobe for Fe, Mn, and W. Detailed studies of several samples reveal complex compositional zoning within individual crystals. One sample contains two crystals with contrasting zoning: one crystal has a high-Fe core and an Fe-poor rim, whereas the other has an Fe-poor core and a high-Fe rim. This suggests that these two crystals formed at different moments and that the wolframite composition did not change monotonically with time. The full range of wolframite compositions measured is from 28 to 97 mol% ferberite ($FeWO_4$). Although a range of 59 mol% was determined for one sample, the average range for all fifty samples is 10 mol%. Samples with average compositions in the range of 84–92 mol% ferberite have relatively small compositional variations, whereas those with average compositions in the range of 61–84 mol% are quite variable. On a vertical longitudinal section of the Main Vein of San Cristobal it appears that the low ferberite values correspond spatially with high tungsten grades. The iron content of the wolframite goes through a minimum across its depositional interval. This may be due to a change in the Fe/Mn ratio of the mineralizing solution with either distance or time.

It is generally considered that different ore and gangue minerals are deposited as the chemistry of an ore solution evolves along its path due to changes in pressure, temperature or chemical exchange with wall rocks. Similarly, the compositions of those minerals that are capable of solid solution should also vary in response to changing environmental conditions.

The reasons for compositional zoning in wolframite have been a controversial subject for many years. Initially, many geologists argued that a *high* Mn/Fe ratio indicates a high temperature of deposition, whereas others contended that a *low* Mn/Fe ratio indicates a high temperature of deposition (Moore and Howie, 1978). More recently, the controversy has become more involved. Singh and Varma (1977) and Voyevodin (1981) reported that the intermediate members of the wolframite series have higher temperatures of deposition than the pure end members, huebnerite and ferberite. Amosse (1978) stated that the composition cannot be related directly to temperature and suggested that the Fe/Mn ratio of the solution is important. Most of the recent investigations into the compositional zoning of wolframite have determined the composition of this mineral with the electron microprobe and found that crystals of wolframite are often chemically zoned (Takla, 1976; Moore and Howie, 1978; Bird and Gair, 1976). Moore and Howie (1978) concluded that the huebnerite/ferberite ratio of wolframites from Cornwall, England varies too much (0.4 to 1.7) to have been a function of a uniform temperature gradient. Groves and Baker (1972) concluded that the regional variation of wolframite composition in Tasmania is controlled by the Fe/Mn ratio of the mineralizing solutions.

Other studies have attempted to correlate solid solution zoning with bulk metal ratio zoning. Birnie and Petersen (1977) reported that the As/Sb ratio in geochronite correlates with the bulk assay Pb/Zn ratio zoning in the limestone veins of the Huachocolpa district, Peru. Bushnell (1980) stated that the silver content of tetrahedrite and the iron content in the cores of sphalerite crystals roughly reflect the zoning pattern indicated by the bulk assay Ag/Cu ratio at the Cananea Duluth breccia pipe in Mexico. Hackbarth (1984) demonstrated that variations in the Ag/Cu of tetrahedrite correlates well with the bulk assay Ag/Cu ratio zoning and with the distribution of maximum silver and copper grades in three veins of the Silver Belt in the Coeur d'Alene mining district.

This study examines the variation of the Fe/Mn ratio in wolframite $(Fe,Mn)WO_4$, and compares its spatial distribution with that of the band of high grade tungsten ore in the Main Vein of San Cristobal (Peru). The distributions of tungsten, copper, lead, zinc and silver at San Cristobal have been described by Campbell (1983) and by Petersen and Campbell (1983). In general, they found that all five metals occur in undulating, subhorizontal bands that are geometrically similar and spatially coincident. From this they concluded that the hydrologic system responsible for mineralization was relatively stable throughout the period of mineralization.

Geologic setting

The San Cristobal tungsten-base metal mine is located in the central Andes of Peru, about 120 km ENE of Lima.

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[1] *Present address:* Department of Geoscience, New Mexico Institute of Mining and Technology, Socorro, NM 87801, USA

The sedimentary rocks in the area consist of Devonian phyllites, Permian volcanic flows, Triassic-Jurassic limestones, and Cretaceous sandstones, limestones and shales. There are also several intrusive plugs of quartz porphyry with some related alaskite dikes. The Main Vein of San Cristobal is situated near the Chumpe quartz porphyry (Pastor 1970). The alaskite dikes are thought to be earlier than the ore mineralization because in the upper portions of the mine they are cut by the vein. A hydrothermally altered sample of the Chumpe quartz porphyry gave a K-Ar age of 5.4±0.3 m.y. (Bartlett 1984). We presume that this is also the age of the hydrothermal mineralization.

The main structural feature of the San Cristobal region is the Chumpe anticline. The San Cristobal Main Vein cuts perpendicularly across the core of the anticline and is hosted by both phyllites and volcanic rocks.

Alteration adjoining the vein within the phyllites can be separated into three types (Pastor 1970). Closest to the vein is a zone of silification (1–2 meters); next is a zone of sericitic and argillic alteration (3–5 meters); the outermost zone is characterized by abundant chloritization (7–14 meters). In the volcanic host rock the silicified zone is absent, and the sericitic and argillic zone is only 3 meters wide. However, the chloritic zone in the volcanic rocks is more than 30 meters wide.

Mineralization in the Main Vein comprises three paragenetic stages. They consist of: 1) pyrite, wolframite and quartz; 2) pyrite, chalcopyrite, sphalerite, galena and barite; and, 3) siderite with minor sphalerite and galena. Wolframite was deposited only during the first stage of mineralization. It occurs as euhedral crystals up to 8 cm long and twins are common. Wolframite occurs intermixed with pyrite and quartz, with the bulk of the pyrite being earlier and the bulk of the quartz later than the wolframite. Detailed descriptions of the mineralization and local geology can be found in Pastor (1970), Lepry (1981) and Campbell (1983).

Crystal zoning

For this compositional study, wolframite was sampled from 49 localities to achieve a good spatial distribution within the mine. Well formed crystals were collected wherever possible in order to obtain a record of all compositional variations. This, however, was not always successful and many samples consisted of brecciated and broken crystals. Fifty wolframite samples were analysed for Fe, Mn, and W on both ARL EMX-SM and CAMECA MBX electron microprobes. The analytical totals ranged from 99 to 102% with a precision of ± 1% and ±2% of the amount present for Fe and Mn, respectively. Energy dispersive analysis did not reveal the presence of any other elements in detectable amounts.

Individual samples were analysed in up to 78 spots to check for chemical zonation within single crystals and between crystals of a given hand sample. The results are summarized in Table 1, which is organized by decreasing average ferberite content.

The individual analyses range from 28 to 97 mole% ferberite although virtually all of the analyses (99%) are in a narrower range of 50 to 94 mole%. The compositional range within single crystals varies from 0 to 59 mole%. However, the average range per crystal is only 10 mole%.

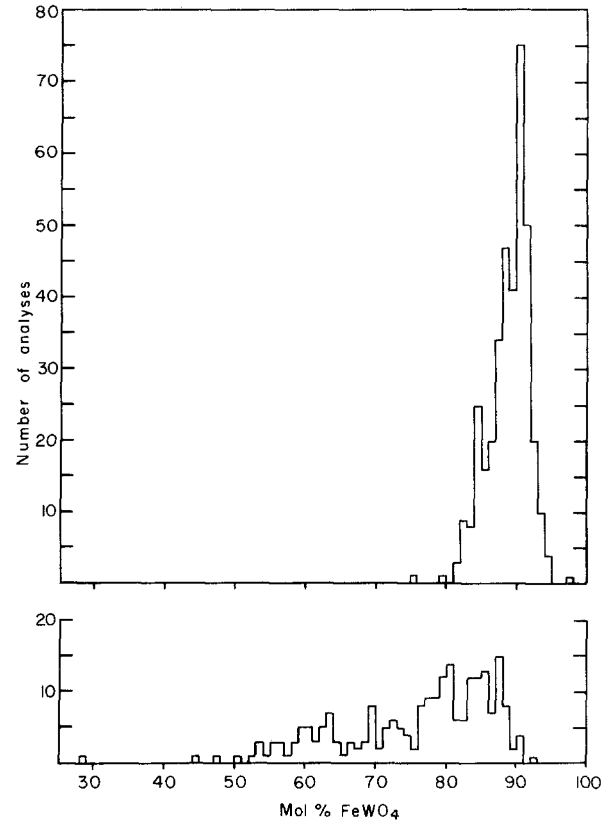

Fig. 1. Distribution of all wolframite analyses. Figure 1a (top) shows the analyses from samples with high average ferberite contents and Figure 1b (bottom) shows those for samples with low average ferberite contents

The data in Table 1 can be divided into two populations based on the compositional variation within a sample. The first population has average ferberite compositions from 84–92 mole% and has relatively minor compositional variations, resulting in small range differences (average 4.8) and small standard deviations (average 1.8). In contrast, the second population has average ferberite compositions of 61–84 mole% and has greater compositional variations, resulting in large range differences (average 17.5) and large standard deviations (average 6.4). The samples with average compositions of 84 mole% appear to be evenly split between the two populations. These two populations are termed the high average ferberite composition population and the low average ferberite composition population.

The two compositional populations also differ in the distribution of analytical values. Plotted in Fig. 1a are all analyses from samples with high ferberite average compositions. Virtually all of the analyses fall within the range 81–94 mole% ferberite. Figure 1b shows all of the analyses from samples with low ferberite average compositions. Although there is overlap between the compositional ranges of the two populations, there is a clear difference in their distributions. All analyses in the high average ferberite populations cluster very tightly whereas the analyses in the low average ferberite population show a large range. Also note that 55% of the analyses in 1a are equal to or greater than 98% of the analyses in 1b.

The contrasting characteristics of the two average ferberite composition population distributions appear to be real and not a function of the number of analyses per sample because there are samples in both populations with a large number of analyses. For example, in the group with high average values there are 78 analyses for sample SC-11, resulting in a standard deviation of 3, and 56 analyses for SC-25 with a standard deviation of only 1. On the other hand, in the second population the 52 analyses on SC-119 have a standard deviation of 10.

The detailed compositional zoning of wolframite was examined in two crystals of sample SC-119, where crystal morphology suggested that at least two entire crystals were present. Figure 2 illustrates the results of the two microprobe traverses that were made. Traverse 1 demonstrates that the edges of the first crystal are richer in Fe than the core, whereas traverse 2 demonstrates the opposite for the second crystal (i.e., the core is richer in Fe than the edges). The compositional variations along both traverses are roughly symmetrical, indicating that the crystal grew out from the center in both directions. The fact that the two crystals are compositionally zoned in opposite senses suggests that these crystals grew at different times and that the factor or factors which controlled the wolframite composition varied with time in a cyclic, not a monotonic, manner.

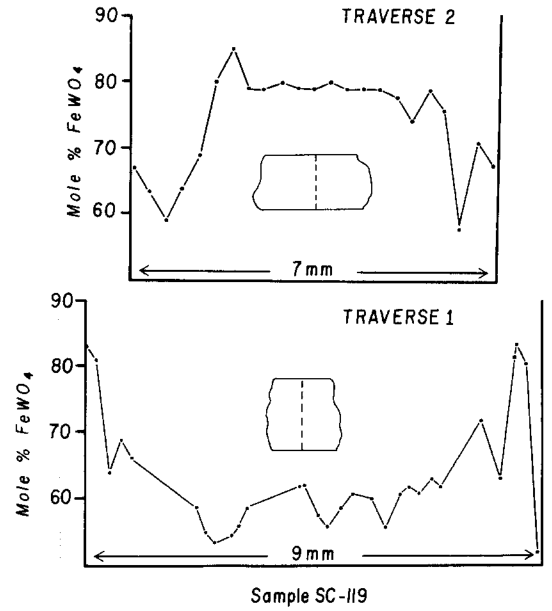

Fig. 2. Microprobe traverses of two wolframite crystals from sample SC-119. The sketches indicate the approximate shape of the crystals and the positions of the analytical traverses. Both traverses show relatively symmetric zoning

Vein wide zoning of wolframite composition

It is difficult to interpret the spatial variation of the wolframite composition at San Cristobal because of the large compositional changes within some samples relative to the overall compositional range in the vein. This is further complicated because many samples contain only broken crystals and thus only part of the original compositional variation. Nevertheless, the observations and arguments presented in the previous section indicate that there are real differences between the high- and low-ferberite samples. If vein wide zoning is actually present, it should be possible to document a systematic spatial distribution of high- versus low-ferberite values.

Assuming that the wolframite population has been sampled more or less adequately, a dividing criterion of 84 mole% seems appropriate. Averages of less than 84 mole% ferberite are labeled "low-ferberite," whereas averages of 84 or greater mole% are called "high-ferberite." This results in 19 low-ferberite and 31 high-ferberite samples. It is possible that some samples with average composition close to the dividing criterion may be misclassified.

The first step was to investigate whether the low-ferberite samples are from below, above, or coincide with the high grade tungsten band outlined on the basis of channel sample averages. Initially, we studied the location of the samples from the two wolframite compositional groups relative to the high tungsten grade band as interpreted by Campbell (1983) and Petersen and Campbell (1983). This indicated that 14 (=74%) of the 19 low-ferberite samples coincide with the high tungsten grades and that 15 (=55%) of the 27 high-ferberite samples correspond to areas of low tungsten grade. Four wolframite samples could not be used in this context because they are located outside the area for which tungsten grades are available. The alternative interpretations (i.e., that the low-ferberite samples are either above or below the tungsten ore band) were not convincing.

It then became evident that the initial interpretation of the high grade tungsten band could be modified somewhat to achieve a better correlation of the low-ferberite samples with the tungsten ore zone. This was done with the aid of a set of eight longitudinal sections prepared by G. Murdock (pers. commun.) for different tungsten cut-off grades. In Fig. 3 the higher tungsten grade areas are outlined for three of his cut-offs (0.40, 0.35 and 0.30% WO_3). At the highest of these cut-offs the tungsten ore appears to be localized in six ore shoots. At the intermediate cut-off two pairs of ore shoots have merged, so that the remaining four ore shoots start to outline an ore band. At the lowest cut-off only one (or at most two) small gaps remain and the ore band is clearly visible. The contours outlining these ore bands are well constrained over considerable lengths (solid lines). Elsewhere, the outline of the ore band was interpreted (dashed and dotted lines) using as additional input the mined out areas, the explored areas that have not been mined and for which no ore has been blocked, and the expected parallelism of the upper and lower boundaries of the ore band. Only in a couple of places was it necessary to further guide the position of the dotted outlines such as to conform with known wolframite compositions. The resulting three outlines of the high-grade tungsten ore zone are reproduced in Fig. 4 together with the wolframite compositions. Evidently, there is quite a satisfactory correlation of the low-ferberite samples (black dots) with the tungsten ore band; 18 (=95%) of the 19 low-ferberite samples can thus be interpreted to correspond to the high-grade ore band, whereas 24 (=89%) of the 27 high-ferberite samples are located in the adjoining low-grade areas (above and below the tungsten ore band).

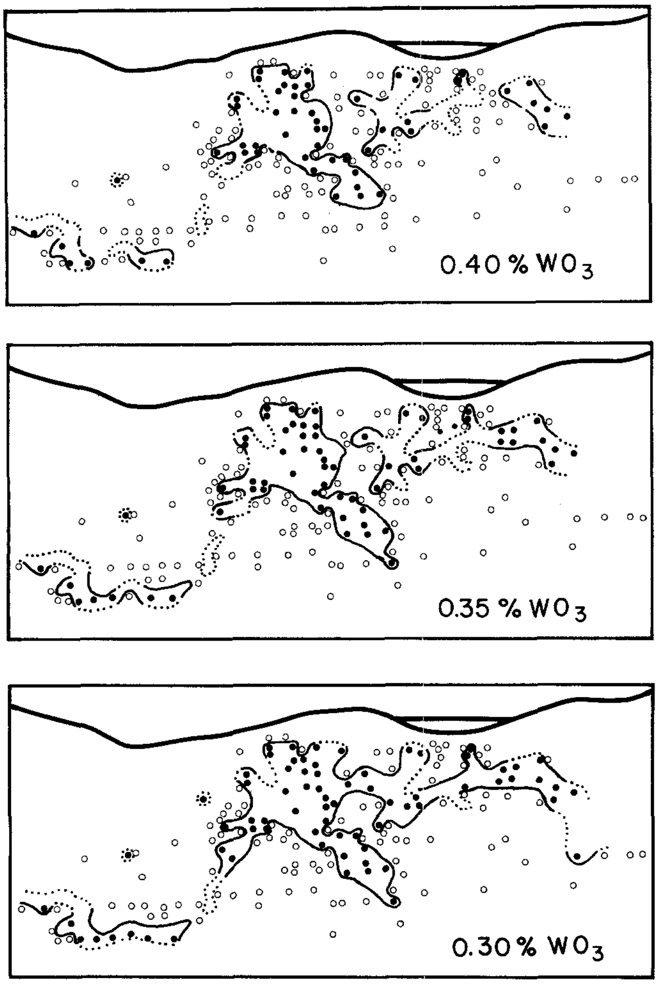

Fig. 3. Longitudinal section of the San Cristobal Main Vein showing the distribution of tungsten grades and the interpreted high grade tungsten band for cut-off values of 0.40, 0.35, and 0.30% WO_3

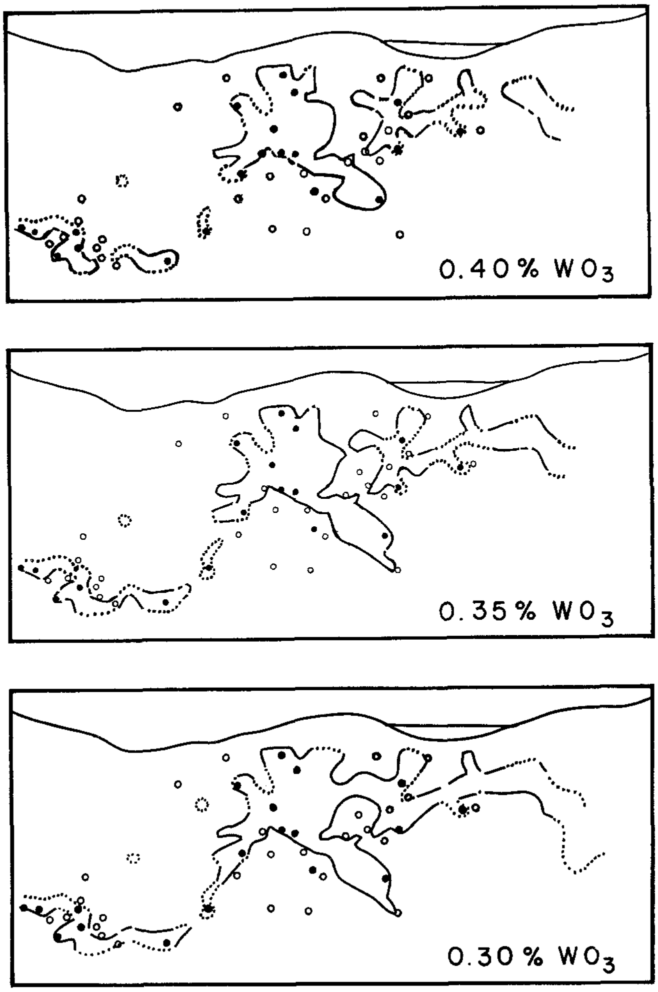

Fig. 4. Correlation of tungsten metal grade distribution (from Figure 3) with average ferberite composition of wolframite crystals. Black dots equal less than 84 mole % ferberite. Open circles equal 84 or greater mole % ferberite

The preceding comparison suggests that the average iron content of the wolframite goes through a minimum across the depositional interval of tungsten. This could be related to either: 1) variations in solution composition with time, or 2) variation in the solution composition with distance.

One way to explain the first alternative is to postulate two pulses of mineralization: one depositing Fe-poor wolframite over a narrow interval and another depositing Fe-rich wolframite over a broader interval, spanning the narrow Fe-poor depositional interval. The average composition of wolframite in the narrow interval would be more Fe-poor than in the areas that received only the Fe-rich wolframite. This hypothesis is supported by the division of the samples in Table 1 into two populations, each possibly representing pulses of different solutions. Furthermore, the deposition of both Fe-poor and Fe-rich wolframite would account for higher tungsten grades in a central zone. The upper and lower margins would be lower grade because only Fe-rich wolframite was deposited there.

In order to explain the second alternative, one might postulate that the Fe/Mn ratio of the solution could be affected by increased coprecipitation of some Fe-bearing minerals (such as pyrite) over a part of the depositional interval of wolframite. In the region in which more pyrite deposited, the Fe/Mn ratio of the solution would decrease. If one makes the likely assumption that the Fe/Mn ratio of the solution affects the chemical composition of the precipitating wolframite, then the Fe/Mn ratio of the wolframite would decrease under these conditions. Unfortunately, the amount of pyrite deposited at San Cristobal has not been quantified.

A fluctuation with time in the position of the zone of increased pyrite co-deposition postulated in the foregoing paragraph could account for the reversals of the compositional zoning in the crystals of sample SC-119. This is schematically illustrated in Fig. 5. The crystals of wolframite will be zoned if, for some reason (such as the deposition of pyrite), the composition of the wolframite being deposited goes through a minimum in mole% ferberite across the depositional interval (Fig. 5a) and if the position of this minimum fluctuates with time. If the minimum moves from 1 to 2 to 1 to 3 in Fig. 5a, the zoning of crystals at those places will be as shown in Figs. 5b–d.

Table 1. Chemical composition of wolframite from San Cristobal (mole % $FeWO_4$)

Sample number	Average	Range Low	Range High	Range difference	Number of analyses	Standard deviation
SC-28	92	90	93	3	7	1
SC-25	91	87	93	6	56	1
SC-105	90	90	92	2	11	3
SC-108	90	82	94	12	12	4
SC-116	90	89	90	1	8	1
SC-118	90	90	90	0	9	0
SC-123	90	88	92	4	10	1
SC-124	90	89	91	3	10	1
SC-11	89	75	97	22	78	3
SC-115	89	85	92	7	12	2
SC-122	89	88	90	2	9	1
SC-1	88	86	89	3	5	1
SC-2	88	87	89	2	5	1
SC-4	88	87	90	3	6	1
SC-5	88	84	90	6	14	2
SC-106	88	81	92	11	11	3
SC-109	88	87	90	3	10	1
SC-114	88	85	91	6	8	2
SC-8	87	85	89	4	6	1
SC-18	87	82	89	7	11	2
SC-111	87	85	88	3	9	1
SC-6	87	84	89	5	8	2
SC-112	86	81	88	7	10	2
SC-107	85	84	87	3	11	1
SC-128	85	83	87	4	11	1
SC-17	84	82	86	4	6	1
SC-101	84	83	84	1	10	0
SC-104	84	82	87	5	5	2
SC-102	84	75	89	14	11	4
SC-111	84	76	88	12	8	5
SC-126	84	77	88	11	12	4
SC-103	83	78	88	10	10	3
SC-120	83	73	88	15	10	4
SC-13	83	70	88	18	6	7
SC-7	83	69	90	21	7	7
SC-3	82	78	84	6	6	3
SC-110	81	69	87	18	13	6
SC-117	81	55	92	37	9	14
SC-125	80	72	90	18	12	6
SC-12	79	73	86	13	6	5
SC-27	79	77	80	3	6	1
SC-16	78	72	80	8	4	4
SC-9	74	69	77	8	7	3
SC-19	73	63	80	17	7	6
SC-26	69	66	71	5	2	4
SC-119	68	52	85	33	52	10
SC-121	66	28	87	59	9	21
SC-14	65	53	77	24	9	9
SC-127	65	57	72	15	14	4
SC-10	61	50	71	21	4	11

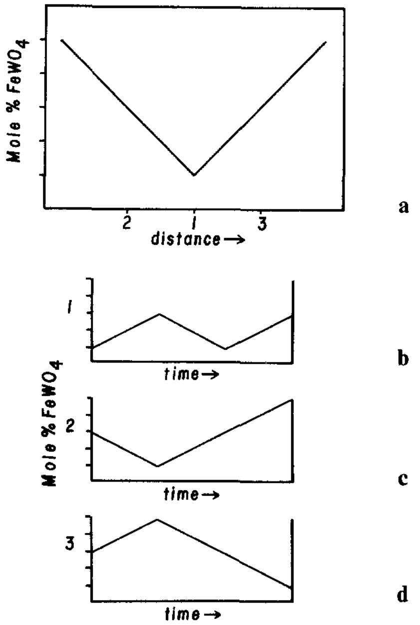

Fig. 5. Model for the compositional variation in wolframite at San Cristobal. If the wolframite composition varies across the depositional interval at a given time as shown in Figure 5a, and the minimum mole % ferberite moves in space, from 1 to 2 to 1 to 3 with time, then the crystals of wolframite growing at locations 1, 2 and 3 will be zoned as shown in 5b, 5c, and 5d, respectively

The above discussion is only meant to outline some possible explanations for the observed crystal and vein-wide zoning. Other, more minor affects, such as diffusion through a depleted boundary layer may also have played a role in the compositional zoning. Further work, beyond the scope of this investigation, is needed to determine the exact processes that were responsible for the intracrystalline and vein-wide variations in the Fe/Mn ratio of wolframite.

The most promising technique for future work appears to be the use of an infrared microscope. Wolframite, which is opaque to visible light, is transparent to near infrared radiation. Using growth banding in the wolframite (which is visible with an infrared microscope) it may be possible to establish a detailed paragenetic sequence within the wolframite that can be linked to compositional variations (Campbell et al., 1984) and then correlated spatially in the deposit.

Conclusions

The complex chemical zoning observed within individual crystals of wolframite at San Cristobal indicates that the chemical or physical factors responsible for controlling the wolframite composition during deposition must have varied with time in a cyclic manner. The complex cyclic nature of this variation makes it seem unlikely that temperature (which one would expect to go through a single maximum or to vary in a monotonic manner) is the sole factor controlling wolframite composition. Instead, variations in the Fe/Mn ratio of the solutions could have caused the changes in wolframite composition. The Fe/Mn ratio of the solutions may have varied at their source or changed along their path by co-deposition of Fe- (or Mn-) bearing minerals. These possibilities raise serious doubts about the claims of many authors (Amosse 1978; Moore and Howie 1978; Voyevodin 1981) that wolframite composition can be used as a geothermometer.

Past studies of the spatial distribution of wolframite composition have assumed models that are too simple for the spatial evolution and mineralogic zonation of an ore deposit (Amosse 1978; Taylor and Hosking 1970). Attempts have been made to correlate the Fe/Mn ratio in wolframite with depth, mine level, and distance from an intrusion. These parameters are not necessarily good zoning indicators, because they assume that fluid flow was uniformly vertical or perpendicular to an intrusive contact, without considering permeability variations which could channel the flow along irregular paths. More comprehensive studies of the zonation of vein deposits are necessary in order to interpret the spatial evolution of the mineralizing solutions. Then, together with studies of the compositional variation within wolframite crystals, it might be possible to separate the effects of time and space and to evaluate the changes in the Fe/Mn ratio of wolframite.

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