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Anomalous low-density wolframite and fluid inclusion control of density, evidence from fluid inclusion content of water and carbon dioxide

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ABSTRACT

Anomalous low-density wolframite occurs at Pasto Bueno, northern Peru. Density varies between 5.78 g/cm^3 and 7.35 g/cm^3, and bears no relation to the MnO/FeO ratio of the wolframite. The "light wolframite" density is a function of the total volume of fluid inclusions in a given sample. This relation of "apparent" mineral density to fluid inclusion population is quantified by a measure of extractable water and carbon dioxide contained in fluid inclusions.

INTRODUCTION

Wolframite has a nominal density of 7.3 g/cm^3, with the density of the iron-bearing end member of the Mn-Fe solid solution series, ferberite, being 7.51 g/cm^3, and that of the manganese-bearing end member, huebnerite, being 7.12 g/cm^3. A ferberite sample from Liquinaste, Jujuy, Argentina was shown to have a low specific gravity of 5.17 (Kittl, 1951). Chemical analyses indicated this was normal ferberite containing additional water. Kittl and Kittl (1965) suggested that water was substituting in cation sites with about 30 percent of the unit cell FeO containing water as necessary to explain the chemical composition and low specific gravity. Escobar and others (1971) examined the crystallography of this low-density wolframite to determine the effects of included structural water on the crystal structure. Low specific gravity ferberite would be expected to exhibit differences in bond lengths and bond angles distorting the crystal structure. Escobar and others (1971) concluded that low densities measured were not due to water substituting for cations in the structure, but that the simplest explanation was the existence of "pores" in the crystals. This study provides direct confirming evidence for their conclusions.

FLUID INCLUSION DATA

Epithermal vein deposits of Pasto Bueno, Peru (Landis and Rye, 1974) have long been a source of high quality wolframite crystals. Pasto Bueno samples of low specific gravity wolframite of both intermediate composition (75 percent MnO) and ferberite (<5 percent MnO) were used in this report. The density of these samples varies from 5.78 g/cm^3 to 7.35 g/cm^3 (table 1). Primary fluid inclusions in wolframite contain fluids rich in water and carbon dioxide as documented by fluid inclusion methods and stable isotope vacuum extraction techniques. Water and carbon dioxide content extracted from fluid inclusions during a crushing procedure in vacuum shows that the abundance of water and carbon dioxide released from fluid inclusions in the wolframite varies with the apparent mineral density (fig. 1). Density measurements were made using standard pycnometer methods on millimeter-sized grains.

Though the size range and number of fluid inclusions are not known for each sample used in the density measurements, the content of water and carbon dioxide in fluid inclusions is a direct measure of the total inclusion volume in a given sample. The small variations in the CO_2/H_2O ratio and in the chemistry of fluids present during wolframite precipitation in the Pasto Bueno deposit permit comparison of these data with samples selected throughout the deposit. The amount of water and carbon dioxide per gram of host mineral is related to apparent mineral density, with a high correlation coefficient of -.96 for carbon dioxide and of -0.93 for water. The release of water and carbon dioxide by crushing in a vacuum without heating indicates that the water was not bonded to the structure in cation sites.

Fluid inclusions are common in the crystals studied and generally are elongated in planes parallel to (010) and aligned with the C-axis. The inclusions are commonly much less than 1 micrometer in maximum length. Figure 2A illustrates a larger (approximately 1 micrometer two-phase inclusion in wolframite with a vapor bubble and liquid plainly visible. Figure 2B shows

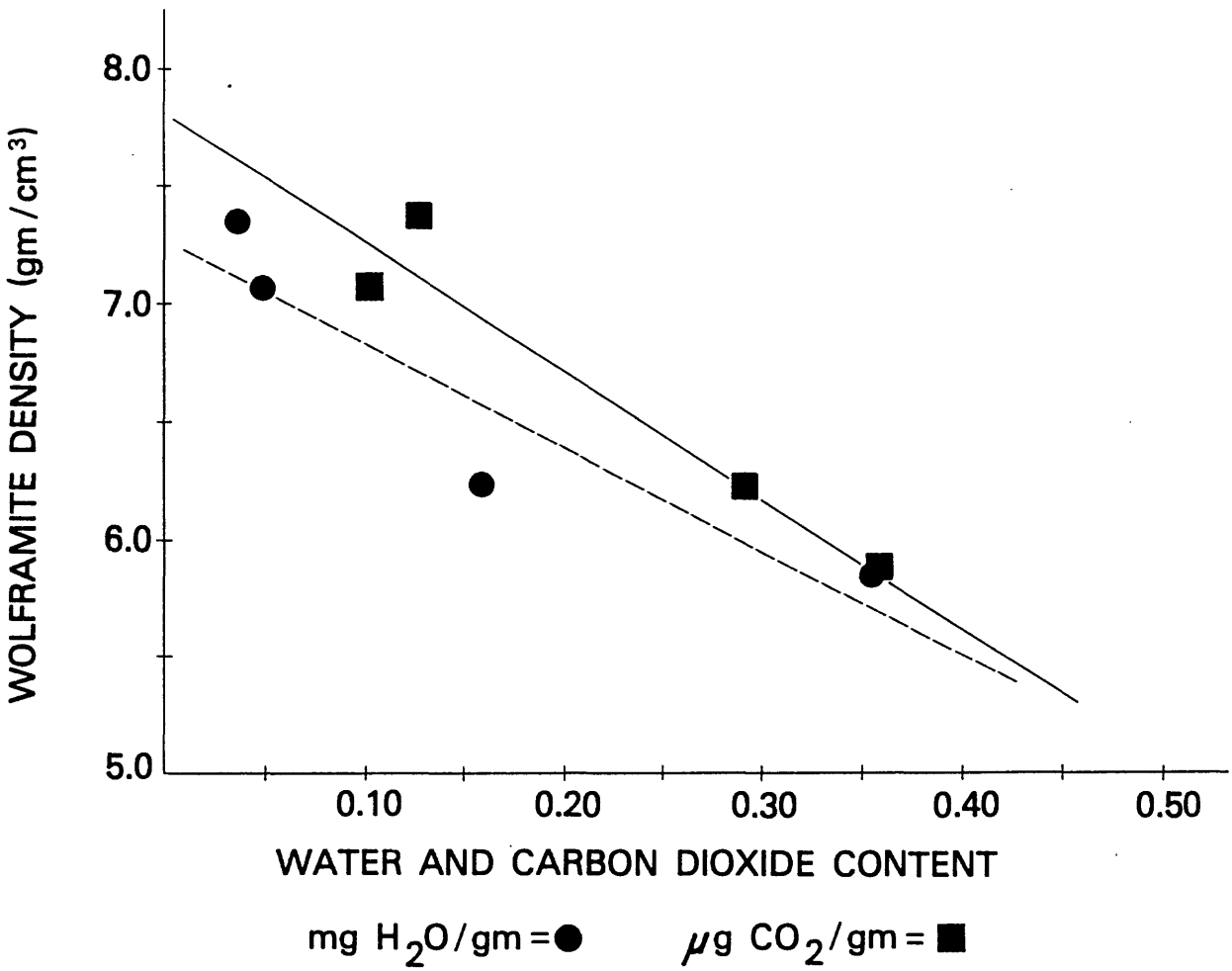

Figure 1.--Wolframite density plotted against water and carbon dioxide content from fluid inclusions.

Table 1.--Density, composition, and water and carbon dioxide content extracted from fluid inclusions in wolframite

Sample No. and Composition*		Wolframite Density (gm/cm^3)	mg H_2O/gm	Micromole CO_2/gm
7Mn-WO4				
1.	M	7.04	0.0475	0.101
2.	M	7.09	---	---
3.	M	6.22	0.1580	0.290
4.	M	5.78	---	---
5.	M	7.07	---	---
9H-164	M	7.35	0.0357	0.126
7H-Blk-WO4	F	5.85	0.3540	0.352
9H-Blk-WO4	F	6.94	---	---

Linear least squares Equation for data:

Density = f (fluid inclusion content) Correlation (probability)

density = 7.81 - 5.48 (micromole CO_2/gm) R = -0.96 $p<0.035$

density = 7.27 - 4.40 (milligram H_2O/gm) R = -0.93 $p<0.072$

*Composition: M = MnO rich wolframite (approx. 75 percent MnO)

F = FeO rich wolframite (<5 percent MnO)

ferberite crystals containing sub-micron size, spherical fluid inclusions similar to those described by Escobar and others (1971) as "pores" in the wolframite. No attempt has been made to relate the size and number of these fluid inclusions directly to the apparent density of the host mineral.

CONCLUSIONS

Escobar and others (1971) correctly concluded that the low density of "light wolframite" is not the result of structural differences and the incorporation of water into the wolframite structure. Variable size and number of fluid inclusions and their content of largely water and carbon dioxide produce the aberrant wolframite density. This effect is greatest for determinations on high-density minerals and those minerals that host large volumes of fluid inclusion "pores".

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Figure 2A.--Photomicrograph of two-phase liquid-vapor inclusions in (010) plane of wolframite crystal. Scale bar is approximately one micron.

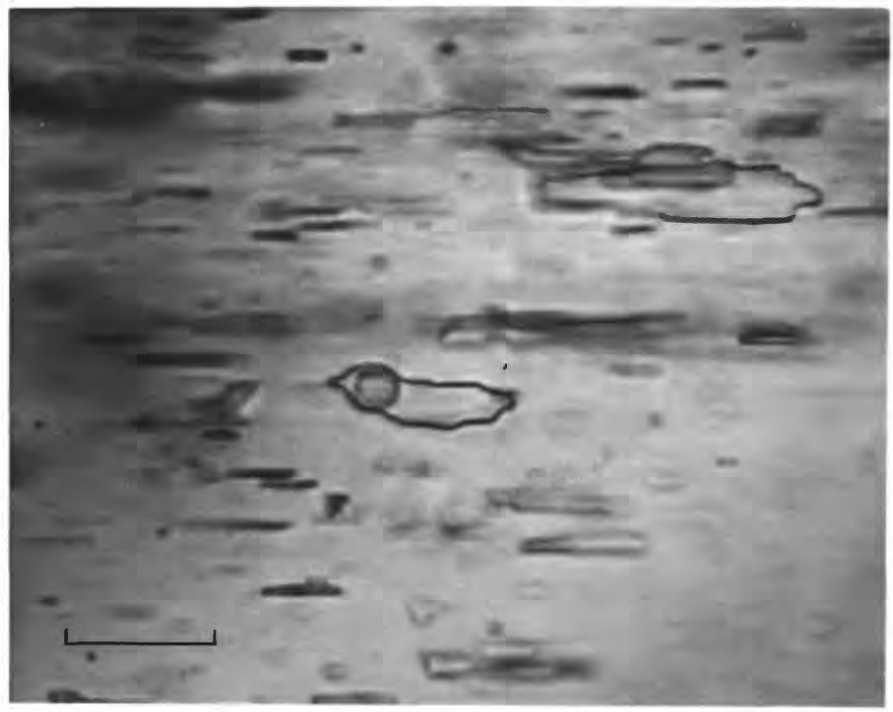

Figure 2B.--Photomicrograph of wolframite crystals containing sub-micron elongate and spherical fluid inclusions. The wolframite crystals are localized along an internal former growth surface within an enclosing host quartz crystal. Scale bar is approximately 10 microns.