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MONATOMIC METAL VAPOR PRESSURES FROM MINERALS

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ABSTRACT

Relative concentrations of monatomic metal vapors emitted from minerals at geologically significant temperatures can be measured by using flameless atomic absorption spectrophotometry. Essentially, the method involves enclosing the mineral in an evacuated heated quartz cylinder, and measuring the absorbed portion of a suitable resonance line as it passes through the mineral vapor. Measurements of monatomic zinc vapors from franklinite ((Fe, Zn) Fe_2O_4), zincite (ZnO), and willemite (Zn_2SiO_4), are used to establish their paragenesis.

The method is directly applicable to phase equilibria studies involving elements with measurable monatomic vapors.

The basis for using flameless atomic absorption spectrophotometric mineral vapor pressure measurements in phase equilibria studies lies in the nature of the measurements and in the consequences of chemical equilibrium. Briefly stated these are as follows:

1) The chemical potential (μ) of an element is identical in all stable coexisting phases at equilibrium.

2) For an ideal gas the relation between chemical potential (μ) and vapor pressure is as follows:

$$\mu = \mu^0 + RT \ln \frac{P}{P^0}$$

where μ and μ^0 are the chemical potentials of a pure gas at pressures P and P^0 respectively, and at the same temperature T. If P^0 is chosen as unity in the same system of units as P, then the above equation becomes as follows:

$$\mu = \mu^0 + RT \ln P$$

It should be noted that P in this equation is dimensionless.

3) Vapor pressures measured by this method are extremely low and can be treated as "ideal" gases.

4) If more than one vapor component is present, the proportion of each vapor component is specified at a constant temperature. If this distribution holds over the temperature interval measured, by monitoring one vapor substance it is possible to get a relative comparison of

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the chemical potential of the species in several minerals at various temperatures. All but the alkali elements listed in Table 1 have essentially monatomic vapors. For example, Mann and Tichner (1960) showed by mass spectrometric measurements that zinc vapor at 520°C contains less than 2×10^{-4} percent diatomic molecules. At the pressures and temperatures of the zinc vapor measurements made by the writer, the percent of diatomic zinc is even less. Nesmeyanov (1963), in summarizing the vapor pressure data of the alkali metals, indicates that for Li, Na, K, Rb, and Cs, the diatomic species are very subordinate (10^{-4} for Li to 10^{-3} for K and Rb), and that these ratios hold over large temperature intervals.

5) Monatomic vapors of geologically important elements exist at geologically significant temperatures, and are usable for absorption measurements (Table 1).

6) The proportion of vapor is so small relative to the solid that the composition of the solid can be regarded as constant over the measured temperature interval. I have experimentally determined the tempera-

TABLE 1

Monatomic Vapor Pressures of Selected Elements at 227°C (Nesmeyanov, 1963)

Element	mm Hg	
Zn	$2.61 \cdot 10^{-5}$	
Cd	$1.51 \cdot 10^{-3}$	
Hg	44.2	
Tl	$1.66 \cdot 10^{-10}$	
Mg	$3.17 \cdot 10^{-7}$	
Ca	$2.28 \cdot 10^{-10}$	
Sr	$4.13 \cdot 10^{-9}$	
Ba	$1.29 \cdot 10^{-10}$	
Li	$5.89 \cdot 10^{-9}$	(Li_2 $9.87 \cdot 10^{-13}$)
Na	$6.56 \cdot 10^{-4}$	(Na_2 $2.50 \cdot 10^{-6}$)
K	$2.06 \cdot 10^{-2}$	(K_2 $2.71 \cdot 10^{-5}$)
Rb	$1.10 \cdot 10^{-1}$	(Rb_2 $3.06 \cdot 10^{-4}$)
Cs	$2.40 \cdot 10^{-1}$	(Cs_2 $6.50 \cdot 10^{-4}$)

ture at which the percent adsorption of solid zinc (99.999 percent purity) equaled the percent absorption of zincite measured at 457°C, with identical optical instrumental settings. The vapor concentrations can be assumed to be similar. The data of McKinley and Vance (1954) for the absolute vapor pressure of solid zinc as a function of temperature can be used to estimate the zinc vapor pressure of zincite at 457°C. This value is approximately 10^{-7} mm of mercury. The zinc vapor pressure, the cell volume, and the temperature are all known. Ideal gas conditions can be assumed, and the amount of zinc present as vapor relative to that present in zincite can be approximately calculated (stoichiometric zincite is assumed). The ratio of zinc present as vapor relative to solid zinc in zincite (0.100 gm sample) is between $1{:}10^5$ and $1{:}10^6$. It is only because of the extreme sensitivity in measuring changes in the vapor concentrations that any variation from stoichiometry can be sensed.

Vapor pressure measurements of solid phases can be used to determine metastable relations between solids, especially in systems with low reaction rates—the vapor pressure of a metastable univariant system is always greater than that of the stable univariant system at the same temperature. Because small variations in vapor pressure can be sensitively measured by absorption, the measurements offer a means of determining phase boundaries quite precisely. Just as a discontinuity in a cooling curve indicates a change in the system, a discontinuity in the vapor pressure curve indicates a change in the system. If two contemporaneously formed phases contain a mutual element, assumed to represent an independent component, the chemical potential of that element must be equal in both phases at the formational temperature. Because vapor pressures are proportional to chemical potentials, the temperature at which the vapor pressure of the mutual element is equal should, if the formational relations are preserved, indicate the last equilibrium temperature. The data presented here for franklinite ($(Fe, Zn)Fe_2O_4$)/zincite (ZnO)/willemite (Zn_2SiO_4) illustrate this potential use.

A custom-built, highly sensitive atomic absorption spectrophotometer (Salotti, 1967) was used to measure the monatomic zinc vapor released during heating from franklinite, willemite, and zincite from Sterling Hill, New Jersey. Electron probe analysis of all three minerals showed them to be homogeneous with respect to zinc and iron. A tubular furnace with quartz end plates contained the sample. The mineral was enclosed in a quartz cylinder, flushed with argon, evacuated, and sealed at approximately 10^{-6} atm. A schematic diagram of the system is shown in Figure 1.

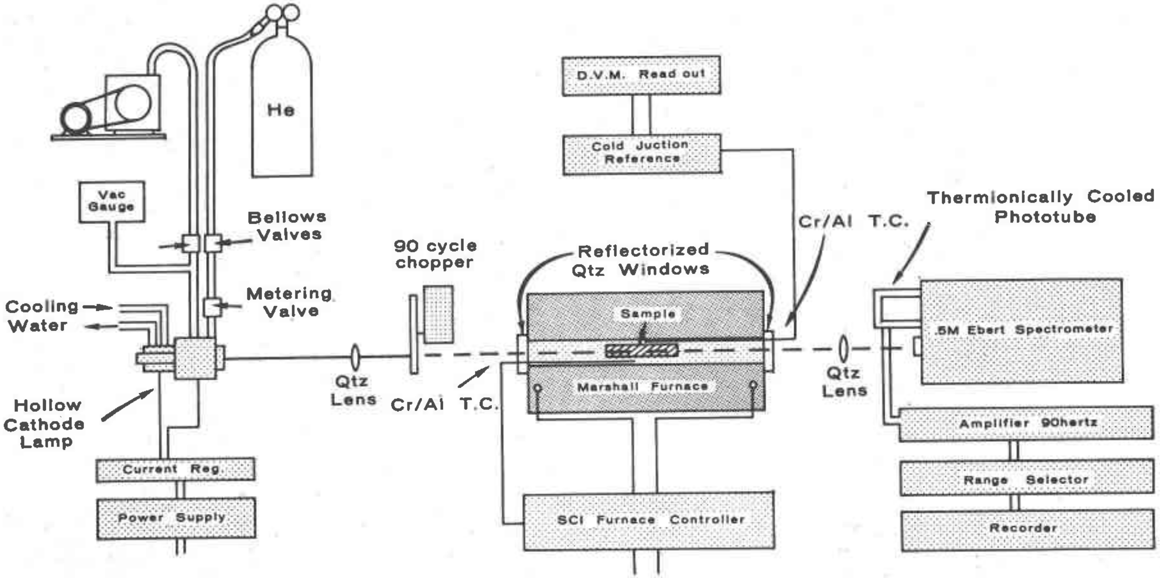

FIG. 1. Schematic drawing of apparatus used in measuring monatomic mineral vapor concentrations.

Using the 2138A zinc line, readings were taken in percent absorption of the base signal for all three minerals between 176°C and 464°C. Percent absorption of the base signal is converted to absorbance (2 — log $(I/I^{0}) \times 100$). If measurements are made under similar conditions, the value of the absorbance is dependent upon the concentration of monatomic zinc in the absorption cell. The data obtained from these measurements are presented in Table 2. Each temperature datum point in Table 2 is obtained by approaching the listed temperature from two directions at least twice. The readings so obtained agree well within the tolerances imposed by the experimental system.

The log of the absorbance plotted against the reciprocal of the absolute temperature defines a straight line for each mineral. The lines and their extensions defined for franklinite, willemite, and zincite

TABLE 2

Data Used in Construction of Figure 2

Zincite

#	% Abs	T°C	T°	10^4/T°	Absorbance	Log Abs.
1	3	311	584	17.1	0.0132	-1.88
2	4	316	589	17.0	0.0177	-1.75
3	28	408	681	14.7	0.1427	-0.85
4	27	409	682	14.7	0.1367	-0.84
5	29	411	684	14.6	0.1487	-0.83
6	65	457	730	13.7	0.4559	-0.36
7	68	458	731	13.7	0.4949	-0.31
8	80	464	737	13.6	0.6990	-0.16
				Franklinite		
1	5	176	449	22.3	0.0223	-1.65
2	12	234	507	19.7	0.0555	-1.26
3	21	281	554	18.1	0.1024	-1.00
4	34	341	614	16.3	0.1805	-0.74
				Willemite		
1	12	319	592	16.9	0.0555	-1.26
2	20	352	625	16.0	0.0969	-1.01
3	25	372	645	15.5	0.1249	-0.90
4	36	446	719	13.9	0.1938	-0.71

have dissimilar slopes and cross within the investigated temperature interval. These relations are shown in Figure 2.

The following interpretations are possible from these measurements:

1) Above 445°C, the stability sequence is willemite-franklinite-zincite.

2) At ~ 445°C, the chemical potential for zinc is similar in zincite and franklinite.

3) Between 400°C and 445°C the stability sequence is willemite-zincite-franklinite.

4) At ~ 400°C the chemical potential for zinc is similar in willemite and zincite.

5) Below 400°C the stability sequence is zincite-willemite-franklinite.

6) Disregarding pressure, the lowest temperature for zincite (Sterling Hill composition) and silica to react to form willemite (Sterling Hill composition) is ~400°C.

7) With available silica, willemite is stable relative to franklinite in the temperature interval investigated. The sequence of mineral

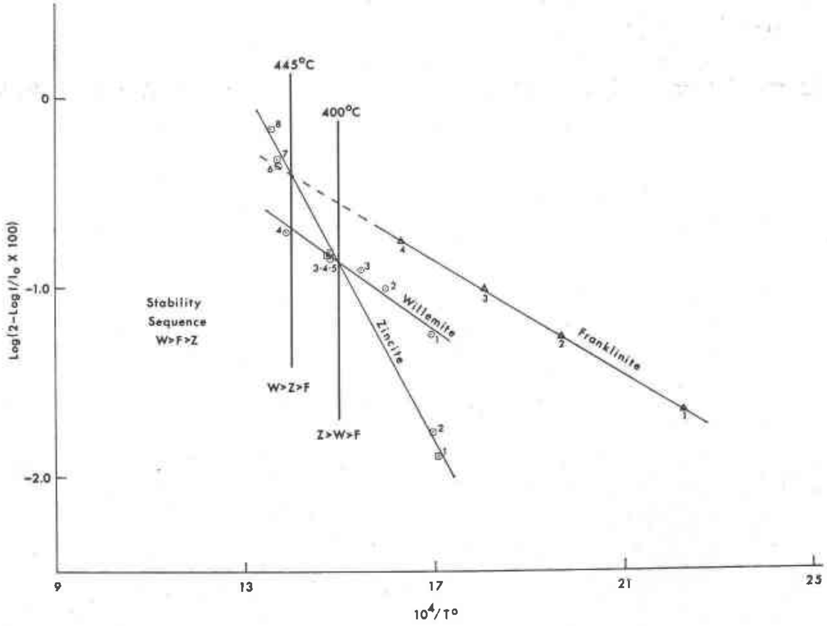

FIG. 2. Plot of the reciprocal absolute temperature against the log of the absorbance for franklinite, willemite, and zincite from Sterling Hill, New Jersey.

stabilities indicated by their vapor pressure curves is in agreement with the paragenetic scheme deduced by Ries and Bowen (1922) from a textural study of the Sussex County ores.

Flameless atomic absorption spectrophotometric mineral vapor pressure studies have an immediate use in geochemical investigations of ore deposits, igneous and metamorphic rocks. Applications also exist in the fields of ceramics and metallurgy.

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