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Petedunnite ($CaZnSi_2O_6$), a new zinc clinopyroxene from Franklin, New Jersey, and phase equilibria for zincian pyroxenes*

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Abstract

A zinc clinopyroxene with the formula

$$(Ca_{0.92}Na_{0.06}Mn_{0.02})(Zn_{0.37}Mn_{0.18}Fe_{0.19}Fe_{0.12}Mg_{0.14})(Si_{1.94}Al_{0.06})O_6$$

has been found in the zinc deposit in Franklin, New Jersey. Because Zn is the dominant M1 cation, this phase is a new mineral species, and the endmember is considered to be $CaZnSi_2O_6$. It has been named for Dr. Pete J. Dunn of the Smithsonian Institution in recognition of his extensive work on Franklin minerals. The X-ray, chemical, and optical data are consistent with the interpretation of petedunnite as a clinopyroxene with space group *C2/c*. Unit-cell parameters are $a = 9.82(3)$, $b = 9.00(1)$, $c = 5.27(2)$ Å, $\beta = 105.6(2)°$, $V = 448(2)$ Å^3. Plots of available chemical analyses suggest extensive solid solution between petedunnite and diopside-hedenbergite-johannsenite. Petedunnite is dark green, has a calculated density of 3.68 g/cm^3 and has {110} cleavages. Optical properties are $\alpha = 1.68(1)$, $\beta = 1.69(1)$, $\gamma = 1.70(1)$, $2V_Z = 80(5)°$, $Z \wedge \mathbf{c} = 40(5)°$, $Y \parallel b$, X, Y = light yellow, Z = light green, $r > v$ (strong).

Preliminary high-pressure experiments at 20 kbar and 900°C have yielded the phase $CaZnSi_2O_6$, with $a = 9.803(6)$, $b = 8.975(7)$, $c = 5.243(7)$ Å, $\beta = 105.75(7)°$, $V = 444.0(9)$ Å^3, $\rho_{calc} = 3.853(8)$ g/cm^3. The lower-pressure assemblage hardystonite ($Ca_2ZnSi_2O_7$) + willemite (Zn_2SiO_4) + quartz will buffer the $CaZnSi_2O_6$ content of a coexisting clinopyroxene solid-solution at a maximum for given *P-T* conditions. Petedunnite substitution is also buffered in clinopyroxene solid-solution as a function of the ratio f_{O_2}/f_{S_2} in the presence of wollastonite + sphalerite + quartz. Phase equilibria calculated from thermodynamic data collated for phases in the system Zn-Al-Si-O-S suggest that much of the Franklin area zinc ore formed at a relatively high fugacity ratio of f_{O_2}/f_{S_2} that was presumably inherited from a S-poor premetamorphic protore.

Introduction

Dr. Pete J. Dunn sent us a rather unusual-appearing hand specimen collected at Franklin, New Jersey, which he had tentatively identified as a Zn-rich clinopyroxene. Preliminary microprobe analysis suggested that the Zn content of the pyroxene is sufficiently high to define this material as a new mineral species. Although zincian clinopyroxenes (varieties jeffersonite and zinc-schefferite: Palache, 1935) are not unusual at Franklin and Sterling Hill, they are all rich in Mg and/or Mn and do not have Zn as the dominant M1 cation. We therefore carried out detailed studies of the Zn-rich pyroxene and confirmed that some portions of the specimen contain sufficient Zn in the M1 site to warrant species status. We have named this mineral *petedunnite* in honor of Dr. Pete J. Dunn of the Department of Mineral Sciences, Smithsonian Institution, Washington, D.C., in recognition of his many contributions to mineralogy, especially at Franklin and Sterling Hill, New Jersey. The name and mineral status have been approved by the IMA Commission on New Minerals and Mineral Names. The holotype specimen of petedunnite is in the collection of the Smithsonian Institution with catalogue number NMNH 162211, and fragments preserved during this study for preparation of thin sections and single-crystal mounts are stored in the Mineralogical Collections, Department of Geological Sciences, University of Michigan.

Occurrence

Petedunnite is known in a single unusual hand specimen from Franklin, New Jersey. The specimen is approximately 10 cm in diameter and consists largely of dark green, anhedral clinopyroxene surrounded by light green clinopyroxene and massive calcite. Although the pyroxene appears to be a homogeneous single crystal in hand specimen, in thin section it is seen to be a mosaic of 10–100-μm-sized, parallel to subparallel clinopyroxene subgrains containing inclusions of isotropic and anisotropic minerals with grain sizes on the order of 1–10 μm.

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Table 1. Mineral inclusions in petedunnite

Mineral	Chemistry*	Abundance	Luminescence**	Optical observation
Willemite	Zn, Si	common	brilliant green	scattered blebs and veins
Calcite	Ca, (Mn)	common	brilliant red	colorless
Genthelvite	Si, Zn, S	common	brilliant blue	isotropic, colorless
Garnet	Si, Ca, Fe, Al	common	none	isotropic, yellow
Gahnite	Al, Zn	common	blue	isotropic, faint green
Albite	Si, Al, Na	common	light blue	anisotropic, colorless
Quartz	Si	uncommon	faint violet	anisotropic, colorless
Galena	Pb, S	uncommon	none	opaque blebs
Sphalerite	Zn, S	rare	brilliant blue	micrometer-sized specks
Sphene	Ca, Ti, Si	rare	none	not found
Apatite	Ca, As, P	rare	none	not found
Allanite	Si, Al, Ca, Ce	rare	none	not found
Iron oxide	Fe, (Mn)	rare	none	veining garnet
Unidentified	Si, Zn, Na?†	rare	blue	not found
Unidentified‡	Si, Al, Ca, (Mn)	rare	pinkish orange	not found

* Listed in order of decreasing weight fraction for elements with $Z > 10$ as determined by EDA; parentheses mark minor elements (<1 wt%).

** As observed at 15 kV and 0.3 a beam current; similar luminescent colors were observed in the luminoscope at 10–15 kV.

† The presence or absence of Na cannot be resolved by EDA in the presence of major Zn.

‡ Possibly a zeolite.

Mineral identifications were made with qualitative energy-dispersive analytical X-ray data obtained on the University of Michigan ARL-EMX microprobe, supplemented by optical and luminoscopic observations. Mineral inclusions in the pyroxene were identified as shown in Table 1. Fifteen different phases were identified, including eight luminescent minerals and three transparent, isotropic minerals. It is difficult to confirm equilibrium phase assemblages in this sample, but the genthelvite is closely associated with gahnite in a manner suggesting an equilibrium relationship.

The clinopyroxene is variable in composition with replacement of Zn by Mg and Mn. The areas with dominant Zn (petedunnite) may have formed by exchange of original diopside-hedenbergite-johannsenite solid solutions with the Zn-rich fluids that also caused precipitation of willemite, gahnite, genthelvite, and sphalerite. Because of the variable chemistry of the clinopyroxene, it was necessary to obtain analytical, optical, and X-ray data on only those portions of pyroxene with the highest Zn concentrations as established in thin section by prior electron-microprobe analysis.

X-ray crystallography

Weissenberg and precession photographs were obtained on a cleavage fragment of Zn-rich clinopyroxene separated from a polished thin section. The photographs have extinctions and symmetry consistent with space groups *C*2/*c* and *Cc*; the former is assumed to be the true space group by analogy with other clinopyroxenes. The lattice parameters of natural petedunnite were refined by least squares using powder data obtained with a polycrystalline sample with a 114.6-mm-diameter Gandolfi camera and Cu$K\alpha$ radiation with Si as internal standard. The lattice parameters of synthetic $CaZnSi_2O_6$ were refined from data collected on an X-ray powder diffractometer with a graphite monochromator using Cu$K\alpha$ radiation and fluorite as an internal standard. The powder data are listed in Table 2, and the refined lattice parameters from uniquely indexed reflections are given in Table 3. Ribbe and Prunier (1977) showed how the parameters *a*, *b*, and $c \sin \beta$ vary as a function of the radii of the M1 and M2 cations in pyroxenes of space group *C*2/*c*. Using their regression equations and assuming the site occupancies given below, we calculate values $a = 9.82$, $b = 8.99$, and $c \sin \beta = 5.09$ Å for natural petedunnite. These are very similar to the observed values (Table 3) and support the occupancies inferred from the electron-microprobe analyses.

Chemistry

Natural petedunnite was analyzed by Dr. P. J. Dunn with an ARL-SEMQ electron microprobe using an operating voltage of 15 kV and a sample current of 0.025 μa. Standards were Kakanui hornblende (Si, Ca, Mg, Al, Fe, Na), manganite (Mn), and synthetic ZnO (Zn). Data were corrected using the procedures of Bence and Albee (1968) and are given in Table 4. The derived formula, when normalized to four cations and six oxygens, is $(Ca_{0.92}Na_{0.06}Mn_{0.02})(Zn_{0.37}Mn_{0.18}Mg_{0.14}Fe^{2+}_{0.19}Fe^{3+}_{0.12})(Si_{1.94}Al_{0.06})O_6$. This formula and the X-ray observations are consistent with a diopside-like structure having an eight-fold-coordinated M2 site (largely occupied by Ca), and an octahedrally coordinated M1 site (with Zn as the dominant cation). Assigning of some of the Fe into the ferric state provides a charge balance for Na in the M2 site and Al in the tetrahedral site. The ideal end-member composition for petedunnite is $CaZnSi_2O_6$.

The petedunnite analysis is compared to the analyses of zincian diopside (variety jeffersonite) of Palache (1935) in Table 4. Petedunnite is lower in Mn + Mg and higher in Zn than these diopsides. The analyses in Palache appear somewhat questionable as they have poor totals (for wet-chemical analyses), low Si (in the first analysis) and low

Table 2. X-ray powder-diffraction data for natural and synthetic petedunnite

Natural petedunnite				Synthetic $CaZnSi_2O_6$		
I/I_0	d_{obs}	d_{calc}	*hkl*	d_{calc}	d_{obs}	I/I_0
10	6.49	6.52	110	6.50	6.52	40
5	4.76	4.73	200	4.72	4.72	18
2	4.50	4.50	020	4.49	4.48	9
—	—	4.42	$11\bar{1}$	4.41	4.40	3
1	3.36	3.36	021	3.35	3.34	2
2	3.25	3.26	220	3.25	3.25	10
100	3.02	3.01	$22\bar{1}$	3.001	3.001	100
40	2.96	2.95	310	2.968	2.966	45
2	2.906	2.909	$31\bar{1}$	2.904	2.904	7
30	2.589	2.583	$13\bar{1}$	2.575	2.573	40
		2.537	221	2.526	—	—
80	2.537	2.536	$20\bar{2}$	2.529	2.525b	90
		2.536	002	2.523	—	—
—	—	2.364	400	2.359	2.357	3
1	2.324	2.322	311	2.315	2.313	4
10	2.227	2.229	$31\bar{2}$	2.224	2.217	13
		2.228	112	2.217	—	—
—	—	2.208	$22\bar{2}$	2.199	2.202	2
—	—	2.172	330	2.168	2.167	6
10	2.137	2.147	$33\bar{1}$	2.142	2.141	20
—	—	2.123	$42\bar{1}$	2.117	2.116	13
2	2.060	2.057	041	2.050	2.049	3
30	2.022	2.022	$40\bar{2}$	2.018	2.019	9
—	—	2.018	202	2.010	2.011	9
2	1.979	1.979	$13\bar{2}$	1.972	1.971	2
					1.958	2
5	1.910				1.907	1
10	1.874				1.869	6
					1.788	2
10	1.770				1.764	14
					1.719	1
					1.679	3
					1.661	1
					1.632	10
					1.625	15
					1.573	3
					1.559	5
					1.535	6
					1.530	5
					1.506	6
					1.495	6
					1.450	1
					1.430	8
					1.414	6
					1.413	4

Note: For natural petedunnite, intensities are visually estimated using Cu*Kα*, Ni-filtered radiation, Gandolfi camera with D = 114.6 mm, and Si as internal standard. For synthetic $CaZnSi_2O_6$, Cu*Kα* radiation; powder X-ray diffractometer with graphite monochromator; fluorite as internal standard.

Table 3. Refined unit-cell parameters for natural petedunnite and synthetic $CaZnSi_2O_6$

	Natural petedunnite	Synthetic $CaZnSi_2O_6$
a (Å)	9.82(2)	9.803(6)
b (Å)	9.00(1)	8.975(7)
c (Å)	5.27(2)	5.243(7)
β (°)	105.6(2)	105.75(7)
$c \sin \beta$ (Å)	5.08(3)	5.046(8)
V (Å³)	448.(2)	440.0(9)

Ca (in the second analysis). Nevertheless, there are clear affinities between zincian diopside and petedunnite.

The petedunnite analysis is plotted in the composition space $CaZnSi_2O_6$-$CaMnSi_2O_6$-$Ca(Mg,Fe)Si_2O_6$ and compared with other analyses available for zincian pyroxenes (Fig. 1). Data from the literature indicate that solid solution is extensive among diopside, hedenbergite, and johannsenite. Few clinopyroxenes have been analyzed for Zn. Smith (1966) reported levels of 0.01–0.09 wt% ZnO for analyses of 17 diopside-hedenbergite solid solutions. Burton et al. (1982) have given analyses of 30 hedenbergites with 0.03–0.21 wt% ZnO. However, pyroxenes from the Franklin–Sterling Hill area may contain more significant solid solution of $CaZnSi_2O_6$ (Palache, 1935; Frondel and Ito, 1966; P. Dunn, written comm., 1984). Although there appears to be complete solid solution between natural impure petedunnite and diopside-hedenbergite-johannsenite, there is no indication of solid solution extending to ideal $CaZnSi_2O_6$ in natural parageneses.

Physical properties

In hand specimen, petedunnite is dark green in color and translucent. Its hardness and density could not be accurately measured because of the abundance of foreign inclusions. A density of 3.68 g/cm³ was calculated from the unit-cell volume and the chemical analysis of natural petedunnite. Petedunnite exhibits {110} cleavages and has a vitreous luster. It does not luminesce either in short- or long-wavelength ultraviolet radiation or under the electron-microprobe beam at 15-kV operating voltage.

The optical properties of petedunnite are difficult to measure owing to the turbid nature of the sample and its strong dispersion. Attempts were made to measure the refractive index of the petedunnite crystal that was mounted for single-crystal study on a fiber using a spindle stage. However, this yielded poor results owing to the turbid nature of the crystal and its tabular shape. Approximate

Table 4. Chemical analysis for petedunnite compared with zincian diopsides from Franklin

	Petedunnite (this study)	Jeffersonite (Palache, 1935)		
SiO_2	48.4	45.95	49.03	
Al_2O_3	1.2	0.85	0.86	
Fe_2O_3*	3.8	9.47	0.00	
FeO*	5.7	0.38	7.75	
MnO	5.8	10.20	7.91	
MgO	2.4	3.61	5.81	
CaO	21.3	21.55	19.88	
ZnO	12.6	10.15	7.14	
Na_2O	0.7	—	—	
Sum	101.9	102.16	98.38	
Si	1.944	1.865	1.992	IV
Al	0.057	0.040	0.041	IV
Fe^{3+}*	0.116	0.288	0.000	M1
Fe^{2+}*	0.190	0.013	0.263	M1
Mg	0.144	0.217	0.352	M1
Zn	0.374	0.303	0.214	M1
Mn	0.197	0.349	0.272	M2
Ca	0.917	0.933	0.865	M2
Na	0.061	—	—	M2

* Mole fractions of Fe^{2+} and Fe^{3+} and equivalent wt% FeO and Fe_2O_3 calculated to yield six oxygens when normalized to four cations.

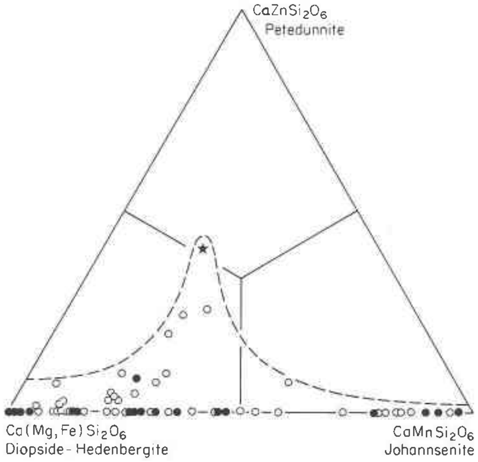

Fig. 1. Compositions of natural clinopyroxenes plotted in the space $CaZnSi_2O_6$-$CaMnSi_2O_6$-$Ca(Mg,Fe)Si_2O_6$. Only pyroxenes with <4 wt% Al_2O_3, Fe_2O_3, or Na_2O are plotted. All zinciferous pyroxenes are from the Franklin area (Palache, 1935; Frondel and Ito, 1966; Dunn, written comm., 1984). Pyroxenes with Fe > Mg are shown as solid circles, and those with Fe < Mg as open circles. The type petedunnite (Table 4) is the starred point. The dashed line shows the observed limit of natural pyroxene solid solutions in this system.

refractive indices, measured on cleavage fragments from the same area on the thin section as was used for single-crystal studies, using white light, a gelatin slide, and Cargille refractive index oils, are $\alpha = 1.68(1)$, $\beta = 1.69(1)$, $\gamma = 1.70(1)$. The optical angle, sign, and orientations, measured using a universal stage with 1.65 R.I. hemispheres and making no correction for tilts, are $2V_Z = 80(10)°$, $Z \wedge c = 40(5)°$, $Y \parallel b$, $r > v$ (strong). These measurements are approximate owing to the strong dispersion of X, Z, and both optic axes in the (010) plane. Considering the relatively large errors in the measured refractive indices and optic axial angles, the two sets of optical data are considered to be in agreement. Flat-stage observations reveal weak pleochroism with X, Y = light yellow, Z = light green, $X = Y < Z$. These data may be compared with preliminary data on synthetic $CaZnSi_2O_6$, which has $\beta = 1.72(1)$, $Z \wedge c$ is large, and no pleochroism and dispersion were observed.

Petrology

The mineral petedunnite may well be unique to the Franklin area as clinopyroxenes examined so far from other areas contain little or no Zn (Fig. 1). Even at Franklin Furnace, petedunnite is likely to be very rare because most clinopyroxenes have Zn subordinate to Mg (Fig. 1). Other Franklin pyroxenes coexisting with hardystonite and/or willemite + quartz should be analyzed to evaluate Zn-Mg exchange among pyroxene, melilite, and willemite. In addition, other Zn deposits such as Långban, Sweden, or Broken Hill, Australia, may eventually yield pyroxenes with significant contents of petedunnite component because of locally similar chemical environments. At Långban, an assemblage containing willemite + franklinite + awaruite (Nysten, 1984) requires low f_{S_2} to stabilize awaruite and willemite and relatively high f_{O_2} to allow significant Mn^{3+} in the franklinite. These conditions are similar to those of the Franklin area (see below). At Broken Hill, V. J. Wall and coworkers of Monash University have found ilmenite rich in $ZnTiO_3$, which requires low-f_{S_2} conditions similar to those stabilizing zincite and willemite at Franklin (Wall, pers. comm., 1978). Zincian clinopyroxenes should also be sought in these and related assemblages to further evaluate the importance of petedunnite solid solutions.

The find of genthelvite at Franklin is of interest, first because it is a newly reported mineral for this area (Palache, 1935; Frondel, 1972; P. J. Dunn, written comm., 1983). Its presence in the petedunnite-bearing rock also suggests that the willemite in the rock could have significant solid solution of Be_2SiO_4, or that phenakite (Be_2SiO_4, willemite structure) could also occur at Franklin. Experiments on the Zn_2SiO_4-Be_2SiO_4 join (Hahn and Eysel, 1970; Chatterjee and Ganguli, 1975) show that ~20–30 mol% Be_2SiO_4 may substitute into Zn_2SiO_4 coexisting with nearly pure Be_2SiO_4 at high T (1200–1300°C). Although the maximum solid solution of Be_2SiO_4 in Zn_2SiO_4 will decrease with decreasing T, several mole percent may possibly still persist in willemite that formed at moderate T (700–800°C). The reaction

$$\underset{\text{genthelvite}}{2Zn_4Be_3(SiO_4)_3S} = \underset{\text{willemite}}{3Zn_2SiO_4} + \underset{\text{phenakite}}{3Be_2SiO_4} + \underset{\text{sphalerite}}{2ZnS}, \quad (1)$$

which may govern a stability limit of genthelvite, also suggests that activity of $(Be_2SiO_4)_{ss}$ is buffered at a significant level in willemite from the genthelvite + sphalerite + petedunnite rock. Gurvich (1963) reported willemite associated with phenakite, genthelvite, gahnite, quartz, and other minerals from a mylonite zone in the USSR. Analysis of the willemite yielded 0.53 wt% BeO, equivalent to 1.5 mol% Be_2SiO_4. Marchenko et al. (1976) reported 0.25 wt% BeO or 0.7 mol% Be_2SiO_4 in a willemite from a granite. Palache (1935) noted that Be was detected in qualitative spectroscopic analyses of Franklin willemite. Franklin willemites (and hardystonites) should be analyzed for Be and for phenakite as well as chrysoberyl ($BeAl_2O_4$, olivine structure), and gugiaite ($Ca_2BeSi_2O_7$, melilite structure) should be sought in Franklin rocks that contain some Be. In the petedunnite-bearing rock, the Be_2SiO_4 content of willemite coexisting with genthelvite and sphalerite could serve as a thermometer following calibration of Reaction 1.

Phase equilibria

No subsolidus experiments are available that are applicable to the system $CaZnSi_2O_6$-$Ca(Mg,Mn,Fe)Si_2O_6$, so it is difficult to evaluate the stability of natural petedunnite. A few experiments available at high temperatures and pressures in simple systems and assemblages reported at Franklin provide some information on limits that will buffer $CaZnSi_2O_6$ in pyroxene solid solutions.

The system ZnO-SiO_2

High-temperature experiments on this system at 1 atm reveal the assemblages zincite + willemite and willemite + tridymite (Segnit, 1954). At pressures greater than approximately 30 kbar, Zn_2SiO_4 + SiO_2 react to form $ZnSiO_3$ pyroxenes (Doroshev et al., 1982; Olesch et al., 1982), which in turn invert to Zn_2SiO_4 (spinel structure) + stishovite or to $ZnSiO_3$ (ilmenite structure) at still higher pressures (Hayashi et al., 1965a, 1965b; Ringwood and Major, 1967; Syono et al., 1971; Akimoto et al., 1974; Ito and Matsui, 1974; Doroshev et al., 1982, 1983). Contrary to the assertions of Doroshev et al. (1982, 1983), these reactions provide poor analogues to mantle phase equilibria because of the different crystal-chemical behavior of Zn vs. Mg. In any case, the high-pressure reactions have little applicability to crustal rocks such as those at Franklin.

The system CaO-ZnO-SiO_2

Segnit (1954) performed experiments on this system at 1 atm and high temperatures and found instead of $CaZnSi_2O_6$ the assemblage willemite + tridymite + hardystonite (melilite structure, $Ca_2ZnSi_2O_7$). Ideal petedunnite could form at higher pressures (P) and/or lower temperatures (T) by the reaction

$$\underset{\text{hardystonite}}{2Ca_2ZnSi_2O_7} + \underset{\text{willemite}}{Zn_2SiO_4} + \underset{\text{quartz}}{3SiO_2} = \underset{\text{petedunnite}}{4CaZnSi_2O_6}. \quad (2)$$

Although ideal petedunnite may not be stable at Franklin P-T conditions, the assemblage hardystonite + willemite + quartz would buffer the substitution of $CaZnSi_2O_6$ at a maximum in coexisting clinopyroxene solid solutions for a given P and T. Although this assemblage is as yet unknown at Franklin, it would provide a link between high-T experiments and natural systems.

To evaluate the possibility that $CaZnSi_2O_6$ is stable at higher pressures, reconnaissance experiments were conducted with a three-quarters-inch piston-cylinder device at State University of New York, Stony Brook. A clear glass of $CaZnSi_2O_6$ was prepared from fired $CaCO_3$, ZnO, and SiO_2 fused at 1400°C. This glass was crushed, sealed in a Pt capsule, and run at 20 kbar, 900°C for 6 d using a NaCl pressure medium. The run product was >98% clinopyroxene with only minor amounts of ZnO and a material of low refractive index (SiO_2 and/or unreacted glass) detected optically. The X-ray pattern yielded peaks attributable only to clinopyroxene and closely comparable to natural petedunnite (Table 2). Its unit cell was refined and is given in comparison with that for natural petedunnite (Table 3). This synthesis of $CaZnSi_2O_6$ clinopyroxene is taken as *prima facie* evidence of its stability at high pressures relative to the more abundant assemblage hardystonite + willemite + quartz (Reaction 2).

The system MgO-ZnO-SiO_2

Segnit and Holland (1965) and West and Glasser (1972) experimented on this system and placed limits of <20% $ZnSiO_3$ solid solution in $MgSiO_3$ pyroxene at high T and low P. Ghose et al. (1974) characterized a synthetic zincian orthopyroxene as $(Zn_{0.38}Mg_{0.62})(Zn_{0.07}Mg_{0.93})Si_2O_6$, and Morimoto et al. (1975) measured site occupancies as $(Zn_{0.64}Mg_{0.36})(Zn_{0.36}Mg_{0.64})Si_2O_6$ in a synthetic $ZnMgSi_2O_6$ orthopyroxene. Because $ZnSiO_3$ is favored as orthopyroxene at high pressures, increase of P should also extend the solid solution of $ZnSiO_3$ in orthopyroxene buffered by Zn_2SiO_4 + SiO_2. Given the observed intersite partitioning of Zn vs. Mg in orthopyroxene, a zincian enstatite would be expected to have Zn dominant in the M2 site for $X_{Zn} \geq 0.33 \pm 0.04$. This would be a new zincian pyroxene, and it may eventually be found in magnesian rocks from the Franklin area.

The system CaO-ZnO-Al_2O_3-SiO_2

Bunting (1932) experimented on the subsystem ZnO-Al_2O_3-SiO_2 and found the assemblages willemite + gahnite + tridymite and willemite + gahnite + zincite, which are also reported from the Franklin area. Segnit (1962) gave data for three planes in the quaternary system CaO-ZnO-Al_2O_3-SiO_2 and reported assemblages including hardystonite + willemite + tridymite + anorthite and hardystonite + willemite + gahnite + zincite. The latter assemblage has been reported in zinciferous ores of the Franklin area (Segnit, 1962). Although not evaluated by Segnit, the phase relations may be complicated by a continuous reaction involving melilite solid solutions:

$$\underset{\text{hardystonite}}{Ca_2ZnSi_2O_7} + \underset{\text{gahnite}}{ZnAl_2O_4} = \underset{\text{gehlenite}}{Ca_2Al_2SiO_7} + \underset{\text{willemite}}{Zn_2SiO_4}. \quad (3)$$

Hardystonite may also react with gahnite at higher pressures to form grossular and zincite:

$$\underset{\text{hardystonite}}{3Ca_2ZnSi_2O_7} + \underset{\text{gahnite}}{2ZnAl_2O_4} = \underset{\text{grossular}}{2Ca_3Al_2Si_3O_{12}} + \underset{\text{zincite}}{5ZnO}. \quad (4)$$

Related reactions may form with $CaZnSi_2O_6$:

$$\underset{\text{petedunnite}}{CaZnSi_2O_6} + \underset{\text{gahnite}}{ZnAl_2O_4} = \underset{\text{Ca-Tschermaks}}{CaAl_2SiO_6} + \underset{\text{willemite}}{Zn_2SiO_4}, \quad (5)$$

and

$$\underset{\text{petedunnite}}{3CaZnSi_2O_6} + \underset{\text{gahnite}}{ZnAl_2O_4} = \underset{\text{grossular}}{Ca_3Al_2Si_3O_{12}} + \underset{\text{willemite}}{2Zn_2SiO_4} + \underset{\text{quartz}}{SiO_2}. \quad (6)$$

In the petedunnite-bearing rock, gahnite, garnet, willemite, and quartz would buffer Reactions 5 and 6 if they

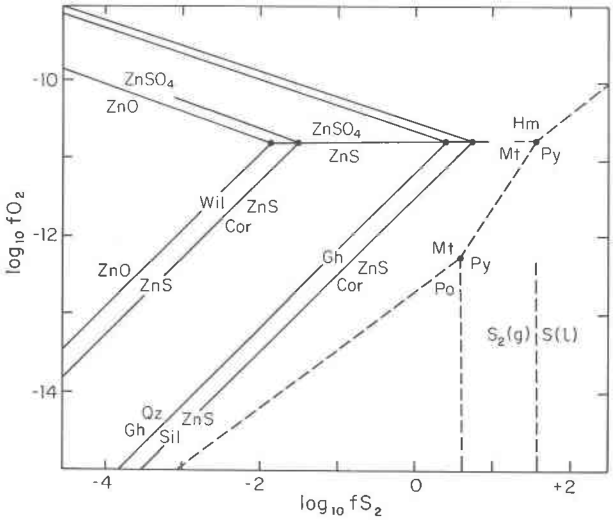

Fig. 2. Stability of phases in the system Zn-Al-Si-O-S as a function of f_{S_2}/f_{O_2} and comparison with reactions in the system Fe-O-S at 5 kbar and 1000 K. At high f_{O_2}, reactions involving ZnS are replaced with an analogous reaction with $ZnSO_4$ involving a slope change at the ZnS-$ZnSO_4$ boundary. Note the restriction of willemite (Zn_2SiO_4) and zincite (ZnO) to high f_{O_2}/f_{S_2} compared to the stability of pyrrhotite and pyrite. These reactions were calculated with the data in Table 4 and from Robie et al. (1978) for Fe-O-S phases at 5 kbar and 1000 K using $\Delta G^0_{1000K} = 0 = \Delta G^0_{298} + \Delta V \Delta P + RT\ln(f^n_{S_2} \cdot f^m_{O_2})$, where n and m are stoichiometric coefficients in an equation for a given reaction and T is in kelvins. Hm = hematite, Po = pyrrhotite, Py = pyrite, Mt = magnetite; see Table 5 for other abbreviations.

represent an equilibrium assemblage. Petedunnite and hardystonite contain little Al (Palache, 1935; Louisnathan, 1969; this work), and Reactions 3 and 5 are apparently driven far to the left during the formation of these minerals at Franklin.

The system Zn-O-S

This system contains limiting reactions among zinc oxides, sulfides, and sulfates. Ingraham and Kellogg (1963) experimentally desulfidized $ZnSO_4$ and $ZnO \cdot 2ZnSO_4$ at 950–1200 K and calculated phase equilibria with ZnS and ZnO for variable pressures of SO_2 and O_2. We have recalculated the same equilibria with respect to S_2 and O_2 fugacities (Fig. 2). Occurrences of zincite and sphalerite at Franklin will restrict ratios of f_{O_2}/f_{S_2} by the reaction:

$$\underset{\text{zincite}}{2ZnO} + S_2 = \underset{\text{sphalerite}}{2ZnS} + O_2. \quad (7)$$

Schaefer (1978) has investigated this reaction electrochemically at 950 to 1200 K. Recalculation of his results at 1000 K for f_{S_2} of 10^{-5} yields $f_{O_2} = 10^{-13.3}$, in good agreement with the calculated value of $10^{-13.0}$ using the data in Table 5. These f_{O_2} values are some four orders of magnitude higher than those indicated for the stability of iron sulfides (Fig. 2). Zinc sulfates would require higher f_{O_2} than ZnO and ZnS. However, the high solubilities of the zinc sulfates suggest that they would remain dissolved under most geologic conditions.

The system Ca-Zn-Si-O-S

The reaction

$$\underset{\text{petedunnite}}{2CaZnSi_2O_6} + S_2 = \underset{\text{wollastonite}}{2CaSiO_3} + \underset{\text{sphalerite}}{ZnS} + \underset{\text{quartz}}{SiO_2} + O_2 \quad (8)$$

will limit the solid solution of petedunnite component in clinopyroxene coexisting with wollastonite + sphalerite + quartz and should provide measurable Zn in such pyroxenes. Preliminary microprobe measurements of two skarn pyroxenes from sphalerite deposits yield 0.08 and 0.13 wt% ZnO, corresponding to 0.2 and 0.4% $CaZnSi_2O_6$. At lower f_{S_2}, these contents should increase, and Reaction 8 could be used to define a-X relations in pyroxene solid solutions with $CaZnSi_2O_6$. At higher f_{CO_2}, a pyroxene would have its $CaZnSi_2O_6$ content buffered by sphalerite + calcite + quartz instead. These and other reactions in P-T-f_{O_2}-f_{S_2}-f_{CO_2} space may be calculated once thermodynamic data are available for $CaZnSi_2O_6$.

Table 5. Molar volumes and free energies (from elements) for phases in the system Zn-Al-Si-O-S

Phase	Abbrev.	Formula	V^0_{298} (cm³)	Ref	$-\Delta G^0_{1000}$ (kJ)	Ref.
Sphalerite	ZnS	ZnS	23.83	(1)	170.7	(5, 11)
Corundum	Cor	Al_2O_3	25.58	(1)	1361.2	(6)
Quartz	Qz	SiO_2	22.69	(1)	730.0	(6)
Zincite	ZnO	ZnO	14.34	(1)	246.8	(7, 11)
Gahnite	Gh	$ZnAl_2O_4$	39.79	(2)	1646.7	(8, 11)
Zinc sulfate	$ZnSO_4$	$ZnSO_4$	41.57	(2)	590.9	(9, 11)
Zinc oxysulfate	$Zn_3O(SO_4)_2$	$Zn_3O(SO_4)_3$	103.59	(3)	1442.6	(9, 11)
Willemite	Wil	Zn_2SiO_4	52.51	(4)	1231.1	(10, 11)
Sillimanite	Sil	Al_2SiO_5	49.90	(1)	2095.0	(6)

Note: References are (1) Robie et al., 1978; (2) JCPDS, 1974; (3) Bald and Gruehn, 1981; (4) Klaska et al., 1978; (5) Mills, 1974; (6) Hemingway et al., 1982; (7) Wilder, 1969; Katayama et al., 1982; (8) Jacob, 1976; (9) Ingraham and Kellogg, 1963; (10) Kozlowska-Rog and Rog, 1979; (11) Appendix 1.

The system Zn-Al-Si-O-S

Important reactions in this system include

$$\underset{\text{willemite}}{Zn_2SiO_4} + S_2 = \underset{\text{sphalerite}}{2ZnS} + \underset{\text{quartz}}{SiO_2} + O_2, \quad (9)$$

$$\underset{\text{gahnite}}{2ZnAl_2O_4} + S_2 = \underset{\text{sphalerite}}{2ZnS} + \underset{\text{corundum}}{2Al_2O_3} + O_2, \quad (10)$$

$$\underset{\text{gahnite}}{2ZnAl_2O_4} + \underset{\text{quartz}}{2SiO_2} + S_2 = \underset{\text{sphalerite}}{2ZnS} + \underset{\text{sillimanite}}{2Al_2SiO_5} + O_2. \quad (11)$$

These reactions have also been identified by V. J. Wall (pers. comm., 1977) as being important during metamorphism of the Broken Hill zinc ore deposits. Experiments have been conducted only on Reaction 10 by Spry and Scott (1982), but their abstract does not contain sufficient information to use here. The locations of the reactions may also be calculated directly from the thermodynamic data available for the phases (Table 5). Similar reactions have been calculated by Winter et al. (1981) in the systems Mn-Si-Ti-O-S and Co-Ti-O-S, although recent improvements in the thermodynamics of some of the phases (e.g., Schaefer 1982; 1983; Robie et al., 1982; Robie and Hemingway, 1985) necessitate minor shifts in the placement of some of these equilibria. The phase equilibria in the system Zn-Al-Si-O-S were arbitrarily calculated at 5 kbar and 1000 K for this paper. Although this choice may be erroneous, the relative sequence of the reactions will be similar at other *P-T* combinations unless a solid-solid reaction intervenes.

Reaction 9 limits the stability of willemite vs. sphalerite + quartz. All three phases are found in the petedunnite-bearing sample, suggesting its equilibration at slightly more sulfidizing and/or less oxidizing conditions than the zincite-bearing assemblages that are elsewhere common in the zinc ores of the Franklin area (Fig. 2). Reactions 10 and 11 are important in limiting the stability of gahnite (± quartz) at Franklin and elsewhere, and calculations place the stability of pure gahnite (± quartz) much closer to the pyrrhotite field (Fig. 2), consistent with the much wider distribution of gahnite vs. zincite and willemite. Unfortunately, Reactions 7–11 do not uniquely fix f_{O_2} independently of f_{S_2} so that it is difficult to judge the relative importance of f_{S_2} vs. f_{O_2} in a given paragenesis of Zn minerals.

The system Zn-Mn-Fe-O

Solid solutions in franklinite may ultimately be useful in defining or limiting f_{O_2} by reactions such as

$$\underset{\text{franklinite solid solution}}{6ZnFe^{3+}_2O_4} = \underset{\text{magnetite solid solution}}{4Fe^{2+}Fe^{3+}_2O_4} + \underset{\text{zincite}}{6ZnO} + O_2, \quad (12)$$

for more reducing conditions, and

$$\underset{\text{hetaerolite solid solution}}{6ZnMn^{3+}_2O_4} = \underset{\text{hausmannite solid solution}}{4Mn^{2+}Mn^{3+}_2O_4} + \underset{\text{zincite}}{6ZnO} + O_2, \quad (13)$$

for more oxidizing conditions. Franklinites commonly contain significant Fe^{2+} or Mn^{3+} (e.g., Palache, 1935; Mason, 1946; Frondel and Klein, 1965; Burke and Kieft, 1972; Frondel and Baum, 1974; Vogel et al., 1976; Nysten, 1984), indicating the importance of these reactions and suggesting local gradients in f_{O_2}. Reaction 12 has been experimentally investigated at 1000 to 1400°C by Benner and Kenworthy (1966a), who found significant nonideality in the spinel solid solutions even at these high *T*. When extrapolated to lower *T* and f_{O_2}, their data suggest that franklinite equilibrated with zincite should contain little magnetite solid solution at metamorphic conditions (Benner and Kenworthy, 1966b). No experiments are available for franklinite-hetaerolite-hausmannite solid solutions coexisting with zincite. Quantitative application of Reactions 12 and 13 awaits adequate evaluation of nonideal activity-composition relations of complex spinels at high temperatures. Other more complex reactions may be obtained by adding iron, zinc, and manganese silicates to Reactions 12 and 13, but their use is limited until the thermodynamics of franklinite solid solutions are better understood.

Direct comparisons of the f_{O_2}/f_{S_2} conditions recorded by rocks in the Franklin area are hampered by formation and/or re-equilibration of many assemblages under varied *P-T-f* conditions. Nevertheless, most other metamorphosed base-metal sulfide deposits contain sphalerite and iron sulfides, indicating far lower f_{O_2}/f_{S_2} than Franklin (e.g., Nesbitt, 1979; Petersen, 1984). The unusually low sulfidizing capacity of the common Franklin–Sterling Hill zinc ores containing willemite or zincite was presumably inherited from a premetamorphic protore poor in sulfur. This condition will undoubtedly constrain the ultimate origin of the protore, and any model proposed for the formation of the Franklin area zinc ores must explain these observations.

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APPENDIX 1. THERMODYNAMIC DATA BASE FOR PHASES IN THE SYSTEM Zn-Al-Si-O-S

High-temperature thermodynamic data have not been systematically tabulated for most zinc phases in the compilations of Robie et al. (1978), Helgeson et al. (1978), and Chase et al. (1982). One of the difficulties relates to low-temperature heat-capacity data and their effects on free energy, which have not been properly evaluated. For calculations of high-temperature phase equilibria, this problem can be minimized by using free-energy data derived from emf or phase-equilibrium measurements at or near the temperatures of interest. Comments are given on individual phases below due to inconsistencies in thermodynamic properties among various sources.

Zincite, ZnO

Although the data of Robie et al. (1978) and Pankratz (1982) are in good agreement for zincite based on low-*T* heats of formation, the emf data of Wilder (1969) from 818 to 986 K give free energies that are 1 kJ less negative. The emf data of Kameda et al. (1980) are some 3 kJ less negative than those of Wilder, but Katayama et al. (1982) give emf data for the reduction of ZnO that are in good agreement with Wilder's (1969) data. The data of Wilder and Katayama et al. have been selected (Table 5).

Sphalerite, ZnS

The free energy of sphalerite (ΔG^0_{1000} = 170.7 kJ) is taken from the compilation of Mills (1974). It is 2.7 kJ less negative than that of Robie et al. (1978) and 0.8 kJ less negative than that of Helgeson et al. (1978). Schaefer (1978) calculated the ΔG^0_{1000} of sphalerite as −168.2 kJ from emf data on Reaction 7 using old data for the ΔG^0 of ZnO. Use of the data of Katayama et al. (1982) for ZnO yields $\Delta G^0_{1000} = -170.8$ kJ for Schaefer's data, close to the value of Mills.

Gahnite, $ZnAl_2O_4$

Jacob (1976) has determined the free energy of gahnite relative to ZnO and Al_2O_3 at 1000 to 1200 K with emf measurements. The result is 0.8 kJ more negative than that of Navrotsky and Kleppa (1968) at 973 K. The free energy of gahnite from the elements has been calculated from Jacob's data using the data of Hemingway et al. (1982) for Al_2O_3 and the data of Katayama et al. (1982) for ZnO.

Spry and Scott (1986) reported experiments and calculations on the stability of gahnite (ss) in the system Zn-Fe-Al-S-O. Although their data may be used to constrain *a-X* relations for spinel solid solutions, no new thermodynamic data were provided for gahnite.

Zinc sulfates, $ZnSO_4$ and $Zn_3O(SO_4)_2$

Ingraham and Kellogg (1963) measured fluid pressures over decomposing zinc sulfates at *T* = 950–1210 K. Hosmer and Krikorian (1980) used Ingraham and Kellogg's data in combination with their own measured enthalpy changes to calculate the thermodynamic properties of the zinc sulfates. Unfortunately, Hosmer and Krikorian's equation for ΔG vs. T appears to generate erroneous results. However, knowledge of the free energies of SO_3 (Robie et al., 1978) and ZnO (Katayama et al., 1982) allows direct calculation of the free energies of the zinc sulfates from the data of Ingraham and Kellogg. For $ZnSO_4$, the result is only 1 kJ less negative than that reported in Robie et al. (1978) based on low-T measurements. The data in Table 5 indicate that zinc oxysulfate is less stable than $ZnSO_4$ + ZnO, and thus it does not appear as a stable phase in Figure 2.

Willemite, Zn_2SiO_4

Only room-temperature data are given for willemite by Robie et al. (1978). Fedorov et al. (1978) attempted low-pressure experiments on the reaction

$$\underset{}{2Zn} + \underset{\text{quartz}}{SiO_2} + 2H_2O = \underset{\text{willemite}}{Zn_2SiO_4} + 2H_2 \quad (13)$$

at T = 773–973 K and calculated thermodynamic parameters for willemite. Calculations using their derived free energies indicate that willemite is less stable than ZnO and SiO_2. Fedorov et al. corrected for the partial pressure of Zn gas in Reaction 13, but this is erroneous if the experiments contained excess pure Zn liquid (a_{Zn} = 1) as described. Unfortunately, recalculation of the free energy of willemite from their data on P_{H_2}/P_{H_2O} without P_{Zn} does not improve the results, and their pressure measurements may be inaccurate. Alternatively, willemite may simply be unreactive at these relatively low temperatures, and Fedorov et al. may have measured the activities of O-H gases in liquid Zn instead. In any case, their thermodynamic data for willemite are erroneous.

Kozlowska-Rog and Rog (1979) obtained the free energy for the reaction

$$\underset{\text{zincite}}{2ZnO} + \underset{\text{silica}}{SiO_2} = \underset{\text{willemite}}{Zn_2SiO_4} \quad (14)$$

using emf measurements. Their data compare well with the 298 K values in Robie et al. (1978), are within 1.8 kJ of the heat of formation measured at 965 K by Navrotsky (1971), and are nearly identical to the free energies calculated from the early reduction data of Kitchener and Ignatowicz (1951). Combining the data of Kozlowska-Rog and Rog with the free energy of ZnO and SiO_2 allows calculation of the free energy of Zn_2SiO_4 (Table 5). The remaining uncertainty is in the choice of the silica polymorph, which was not specified by Kozlowska-Rog and Rog, but was assumed by us to be quartz. If tridymite or cristobalite was involved in the experiments instead, the free energy of willemite should be reduced by 0.3 or 0.9 kJ respectively, a small correction compared to remaining uncertainties derived from the free energy of ZnO.

Muan (1971) calculated the free energy of willemite from the oxides based on the partitioning of Zn/Co between ZnO (ss) and Zn_2SiO_4 (ss) using previously determined activity coefficients for ZnO-CoO (ss). His ΔG for willemite is ~10 kJ more negative than those of the other workers above. Muan's experiments are apparently unreversed, and his datum has been ignored for the purposes of this paper.

Estimated errors

Realistic estimates of errors in the free energies of the above Zn phases are still considered to be plus or minus several kilojoules per mole, approximately equivalent to half a log unit error in calculated f_{O_2} or f_{S_2}. Redetermination of the free energies by emf methods in one laboratory with similar cells should reduce the relative errors. Nevertheless, the data compiled in Table 5 are considered sufficiently accurate for calculations of the phase equilibria in Figure 2.