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Significance of the assemblage titanite + magnetite + quartz in granitic rocks*

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ABSTRACT

The equilibrium hedenbergite + ilmenite + oxygen = titanite + magnetite + quartz is important in distinguishing relatively oxidized from relatively reduced granitic rocks. The equilibrium expression is

$$\log f_{O_2} = -30930/T + 14.98 + 0.142(P - 1)/T,$$

where T is the temperature (in kelvins) and P is the pressure (in bars). Occurrences of hedenbergite-rich clinopyroxene and ilmenite in granitic plutons imply oxygen fugacities similar to those required for the stability of fayalite. When the assemblage titanite + magnetite + quartz occurs with clinopyroxene or amphibole with intermediate or higher Mg/(Mg + Fe) ratios, relatively high oxygen fugacities are implied. Mesozoic batholiths of the circum-Pacific, such as the Sierra Nevada batholith, crystallized under much higher oxygen fugacities than did alkaline batholiths of continental affinities, such as the Pikes Peak batholith.

INTRODUCTION

Determination of the important variable f_{O_2} at the P and T of crystallization of granitoid rocks is often hampered by subsolidus re-equilibration and/or alteration. Late-stage re-equilibration in granitic plutons commonly changes the compositions of primary magnetite and ilmenite, so that ilmenite-magnetite geothermometry cannot be applied to ascertain oxygen fugacities during crystallization of the magmas (Buddington and Lindsley, 1964; Haggerty, 1976). Oxygen fugacity is also difficult to estimate in silicic volcanic rocks that contain only one Fe-Ti oxide phase. As a consequence, one must seek other equilibria that constrain f_{O_2}.

The titanite + magnetite + quartz assemblage indicates relatively high oxygen fugacities in siliceous magmas (Verhoogen, 1962; Wones, 1966, 1981; Carmichael and Nicholls, 1967; Lipman, 1971; Czamanske and Wones, 1973). Definition of the phase-assemblage boundary between titanite + magnetite + quartz and hedenbergite + ilmenite assemblages, as discussed herein, is based on investigations of the stability of hedenbergite (Gustavson, 1974; Liou, 1974), titanite (Hunt and Kerrick, 1977), and magnetite (Chou, 1978; Hewitt, 1978). Bohlen and Essene (1978), Helgeson et al. (1978), and Robie et al. (1978) have published summaries of the thermodynamic properties of some of these pertinent phases.

METHODS OF DERIVING FREE ENERGIES

The experimental data of Gustavson (1974), Liou (1974), Chou (1978), and Hewitt (1978) were recalculated at 1 bar (0.1 MPa), using additional data from the compilations of Robie et al. (1967, 1978). These data are summarized in Table 1.

From Gustavson's (1974) determination of the equilibrium

$$\underset{\text{andradite}}{6Ca_3Fe_2Si_3O_{12}} = \underset{\text{wollastonite}}{18CaSiO_3} + \underset{\text{magnetite}}{4Fe_3O_4} + O_2, \qquad (1)$$

a free-energy value for andradite can be extracted using selected data as follows. The entropy and free energy of wollastonite and oxygen are from Robie et al. (1978). Data for magnetite are from Hewitt (1978), as determined for the equilibrium (FMQ)

$$\underset{\text{magnetite}}{2Fe_3O_4} + \underset{\text{quartz}}{3SiO_2} = \underset{\text{fayalite}}{3Fe_2SiO_4} + O_2, \qquad (2)$$

where the data for fayalite and quartz are from Robie et al. (1978). Hewitt's data are favored for Equilibrium 2 over those of Chou (1978) because of the near-proximity of Chou's result to the Ni-NiO buffer as determined by

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* *Editor's note:* This short contribution by David Wones has circulated in manuscript form in the hands of a privileged few since 1981. For some reason, it was not published before his untimely death in 1984. In "formalizing" some of Dave's earlier thoughts on the importance of titanite stability, its omission in the citable literature has been regrettable. With the approval of his wife Connie and the faculty at Virginia Polytechnic Institute and State University, it has been reviewed and prepared for publication by Gerald K. Czamanske and Steven R. Bohlen of the U.S. Geological Survey, Menlo Park, California. The sense of the manuscript is unaltered; however, G.K.C. and S.R.B. have imposed minor changes in line with common manuscript review procedures. S.R.B. recalculated the equilibria, using more recent thermodynamic data (see review by Berman, 1988); these calculations do not differ significantly from Dave's, so no adjustments have been made to his values.

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TABLE 1. Molar volumes and entropies at 298.16 °K and free energies of formation at 1000 °K for selected phases

Phase	Formula	V_{298} (cm³)	S_{298} (J/K)	G_{1000} (J)	Uncertainty (J)
Andradite	$Ca_3Fe_2Si_3O_{12}$	131.65 (a)	293.42 (c) 291.48 (g)	−4 676 197 (f) −4 624 625 (c) −4 633 965 (h)	1900
Fayalite	Fe_2SiO_4	46.39 (a)	148.32 (b)	−1 150 821 (b)	
Hedenbergite	$CaFeSi_2O_6$	68.3 (a)	170.29 (c) 169.66 (d)	−2 318 567 (f) −2 295 192 (c) −2 305 659 (i) −2 308 191 (j) −2 299 555 (h)	1900
Ilmenite	$FeTiO_3$	31.69 (a)	105.86 (b)	−982 744 (b)	
Magnetite	Fe_3O_4	44.52 (a)	146.14 (b)	−789 434 (b) −793 040 (f) −787 661 (e)	2300
Quartz	SiO_2	23.72* (a)	41.46 (b)	−729 982 (b)	
Titanite	$CaTiSiO_5$	55.65 (a)	129.20 (b)	−2 132 072 (b) −2 129 175 (f) −2 128 467 (h)	2500
Wollastonite	$CaSiO_3$	39.93 (a)	82.01 (b)	−1 352 174 (b)	

Note: References are as follows: (a) Robie et al. (1967). (b) Robie et al. (1978). (c) Helgeson et al. (1978), Bird and Helgeson (1980). (d) This study, using method of Bohlen and Essene (1978). (e) This study, using data of Hewitt (1978). (f) Bohlen and Essene (1978). (g) This study, using data of grossularite, hematite, and corundum from Robie et al. (1978). (h) This study. (i) Kurchakova and Avetisyan (1974). (j) Navrotsky and Coons (1976).
* Volume taken for high quartz.

Huebner and Sato (1970). The result of Chou's seems unlikely because the data of Ernst (1960, 1962, 1966), Eugster and Wones (1962), Buddington and Lindsley (1964), Wones and Eugster (1965), and Gilbert (1966), as well as those of Gustavson (1974) and Liou (1974), all require significant separation of the Ni-NiO and FMQ buffer curves in terms of oxygen fugacity and temperature. The free energy for andradite determined from Gustavson's data is listed in Table 1, along with values determined by Bohlen and Essene (1978) and Helgeson et al. (1978).

Liou (1974) established the position of the equilibrium

$$\underset{\text{andradite}}{2Ca_3Fe_2Si_3O_{12}} + \underset{\text{quartz}}{4SiO_2} = \underset{\text{hedenbergite}}{4CaFeSi_2O_6} + \underset{\text{wollastonite}}{2CaSiO_3} + O_2. \qquad (3)$$

Using the free energy for andradite determined from Equilibrium 1, the free energy of hedenbergite was calculated (see Table 1). This value is comparable to the estimates by Kurchakova and Avetisyan (1974), Navrotsky and Coons (1976), and Helgeson et al. (1978), but is higher than the value determined by Bohlen and Essene (1978). Such a result is directly related to the lower free energy established by the latter authors for andradite, owing to their use of the data for FMQ of Wones and Gilbert (1969), which have been superseded by those of Hewitt (1978).

The free energy for titanite was determined from the experimental work of Hunt and Kerrick (1977), as outlined by Bohlen and Essene (1978). The equilibrium

$$\underset{\text{calcite}}{CaCO_3} + \underset{\text{rutile}}{TiO_2} + \underset{\text{quartz}}{SiO_2} = \underset{\text{titanite}}{CaTiSiO_5} + CO_2 \qquad (4)$$

was determined in an H_2O-bearing system, and so the derivation of thermodynamic data for titanite requires knowledge of the free energy of CO_2 in CO_2-H_2O mixtures. In this study, the values of Shmonov and Shmulovich (1974) were used.

There are three sources of uncertainty in the free energies calculated by these procedures, including uncertainties in the calorimetric determinations of the heat capacities and heats of formation as quoted by Robie et al. (1978), uncertainties in the calibration of temperature among the laboratories in which the phase equilibria were determined, and uncertainties in the data for the particular oxygen-fugacity buffers used in the experiments. Anderson (1977) has demonstrated that some of the errors in calorimetry, although important in the determination of the absolute value of free energy for an isolated phase, cancel each other in reactions. Thus, a simple estimate of the sum of the errors may overestimate the actual error.

Interlaboratory temperature calibrations are not routine, and the habits of individual experimentalists even within the same laboratory differ sufficiently that the maximum error resulting from temperature differences is difficult to assess. Most hydrothermal investigators are confident of ±5 °C in their quoted values. The data used here were all collected using either Ni-NiO or FMQ as the buffer assemblage. Both Huebner and Sato (1970) and Hewitt (1978) quoted uncertainties for their expressions of oxygen-fugacity variations with temperature.

The estimated uncertainties, listed in Table 1, are maxima because no attempt was made to evaluate the com-

TABLE 2. Constants relating oxygen fugacity (bars) to temperature (K) for particular mineral assemblages

Assemblage	*A*	*B*	*C*	Reference
$Fe_3O_4 + Fe_2O_3$	26629*	15.29*	0.018*	Chou (1798)
$Ni + NiO$	24930	9.36	0.046	Huebner and Sato (1970)
$CaFeSi_2O_6 + FeTiO_3 + CaTiSiO_5 + Fe_3O_4 + SiO_2$	30939	14.98	0.142	This study
$Fe_2SiO_4 + Fe_3O_4 + SiO_2$	25287	8.95	0.110	Hewitt (1978)
$CaSiO_3 + FeTiO_3 + CaTiSiO_5 + Fe_3O_4$	30096	11.43	−0.035	This study

$$\log f_{O_2} = -(A/T) + B + [C(P-1)/T]$$

* These coefficients are not valid below 1073 K. Between 873 K and 1073 K, the expression is

$$\log f_{O_2} = 0.026 + (4381/T) - (0.1572 \times 10^4)/T^2$$

(after Chou, 1978).

pensating errors discussed by Anderson (1977). Note, however, that the positions in f_{O_2}-T space of the equilibria discussed below are insensitive to relatively small uncertainties in the free energies of the phases; uncertainties of 3 to 5 kJ in the ΔG^0_T values of the phases change the positions of the equilibria by only 0.2 units of $\log f_{O_2}$.

STABILITY OF THE ASSEMBLAGE TITANITE + MAGNETITE + QUARTZ

Verhoogen (1962) demonstrated that the equilibrium

$$\underset{\text{titanite}}{6CaTiSiO_5} + \underset{\text{magnetite}}{2Fe_3O_4} = \underset{\text{wollastonite}}{6CaSiO_3} + \underset{\text{ilmenite}}{6FeTiO_3} + O_2 \qquad (5)$$

separates an oxidized titanite + magnetite assemblage from a reduced wollastonite + ilmenite assemblage. The latter assemblage is uncommon, but the reaction serves as a basis for exploring pyroxene- and amphibole-bearing assemblages.

By adding SiO_2, one can write the equilibrium

$$\underset{\text{titanite}}{3CaTiSiO_5} + \underset{\text{magnetite}}{2Fe_3O_4} + \underset{\text{quartz}}{3SiO_2} = \underset{\text{hedenbergite}}{3CaFeSi_2O_6} + \underset{\text{ilmenite}}{3FeTiO_3} + O_2, \qquad (6)$$

in which hedenbergite and ilmenite now represent the reduced assemblage.

The curve for Equilibrium 6 intersects that for Equilibrium 2 at about 660 °C and generates an equilibrium that is independent of oxygen fugacity (Fig. 1):

$$\underset{\text{titanite}}{CaTiSiO_5} + \underset{\text{fayalite}}{Fe_2SiO_4} = \underset{\text{hedenbergite}}{CaFeSi_2O_6} + \underset{\text{ilmenite}}{FeTiO_3}. \qquad (7)$$

Rocks in which hedenbergite and ilmenite coexist can have oxygen fugacities greater than FMQ only at temperatures above 660 °C.

An equilibrium comparable to 6 but involving amphibole can be written:

$$\underset{\text{titanite}}{12CaTiSiO_5} + \underset{\text{magnetite}}{14Fe_3O_4} + \underset{\text{quartz}}{36SiO_2} + 6H_2O = \underset{\text{ferrotremolite}}{6Ca_2Fe_5Si_8O_{22}(OH)_2} + \underset{\text{ilmenite}}{12FeTiO_3} + 7O_2. \qquad (8)$$

Equilibrium 8 can be applied to distinguish relatively oxidized granitoids containing titanite + magnetite + quartz from those that are more reduced and contain amphibole + ilmenite.

The temperature dependency of oxygen fugacity in Equilibria 5 and 6 can be approximated by

$$\log f_{O_2} = -A/T + B + C(P-1)/T.$$

Values of *A*, *B*, and *C* for Equilibria 5 and 6 and for three of the more common f_{O_2}-buffer curves are listed in Table 1. Equilibrium curves for Equilibria 5, 6, and 7, along with the FMQ and HM buffer curves, are shown in Figure 1.

The effect of the diopsidic component in the clinopyroxene is graphically displayed in Figure 1, where the two light curves represent the calculated displacement of Equilibrium 6 as the result of the reduction of the activity of hedenbergite. The equilibria are also affected by impurities in ilmenite, magnetite, and titanite. Natural ilmenites contain both Fe_2O_3 and $MnTiO_3$ components, which dilute the concentration and the activity of $FeTiO_3$, so that ilmenite will coexist with clinopyroxene at higher oxygen fugacities than those inferred for the pure components. This effect with be partly offset by the Fe_2TiO_4 component in magnetite, and Fe^{3+}-, Al-, and F-bearing components in titanite.

APPLICATION TO NATURAL ASSEMBLAGES

The intrinsic oxygen fugacity of a magma is related to its source material. The assemblage titanite + magnetite + quartz in volcanic or granitic rocks permits an estimate of relative oxygen fugacity. Lipman (1971) found a sequence of clinopyroxene-bearing ash-flow tuffs in which titanite was alternately present and absent. The presence of both ilmenite and magnetite in these flows (although ilmenite is sparse in titanite-bearing tuffs) allowed Lipman to estimate temperature and oxygen fugacity for the titanite-bearing and titanite-free assemblages. His data, plotted in Figure 1, demonstrate that the titanite-bearing tuffs were indeed more oxidized at a given temperature. Because the tuff sequence is a natural analogue of Equilibrium 6, that equilibrium was recalculated using the Fe-Ti oxide compositions reported by Lipman (1971) and his unreported clinopyroxene composition (approximately Hd_{33}). As shown by the dashes in Figure 1, this calculated equilibrium agrees well with the f_{O_2}-T relations determined by Lipman from Fe-Ti oxide analyses.

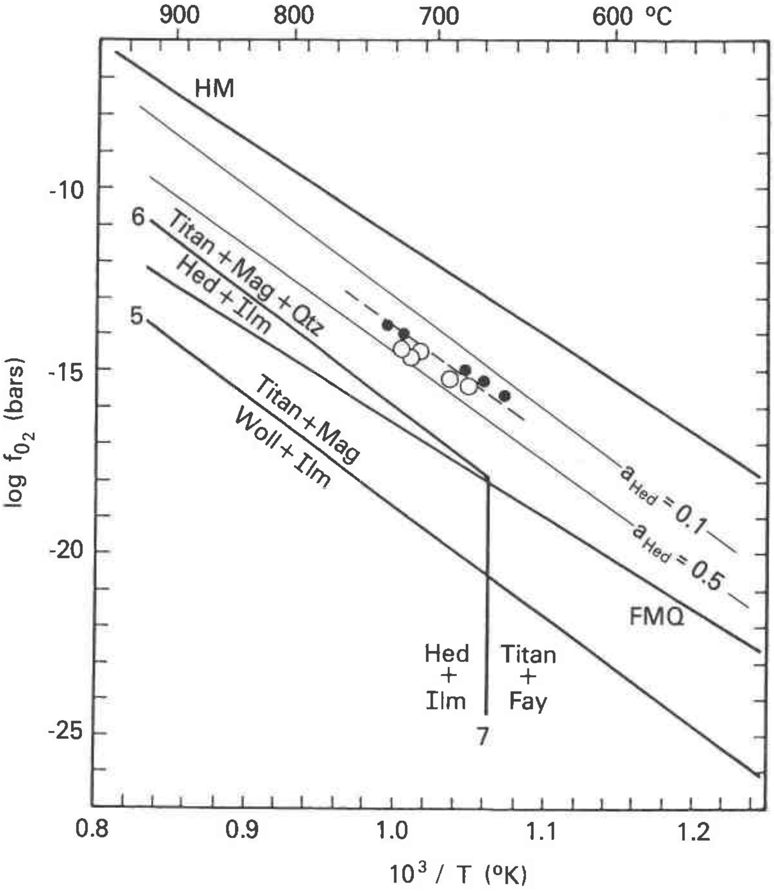

Fig. 1. Logarithmic plot of f_{O_2} versus T, showing stability of several mineral assemblages: FMQ, $Fe_2SiO_4 + Fe_3O_4 + SiO_2$; HM, $Fe_2O_3 + Fe_3O_4$; 5, $CaSiO_3 + FeTiO_3 + CaTiSiO_5 + Fe_3O_4$; 6, $CaFeSi_2O_6 + FeTiO_3 + CaTiSiO_5 + Fe_3O_4 + SiO_2$; 7, $CaTiSiO_5 + Fe_2SiO_4 + CaFeSi_2O_6 + FeTiO_3$. Light curves labeled $a_{Hed} = 0.5$ and 0.1 depict shift in Equilibrium 6 as a result of lowered activity of hedenbergite (greater diopside component) in clinopyroxene. Circles, f_{O_2}-T values determined by ilmenite-magnetite geothermometry for tuffs containing abundant clinopyroxene, ilmenite, and magnetite; dots, f_{O_2}-T values for tuffs from the same sequence that contain titanite, magnetite, and sparse ilmenite (Lipman, 1971); dashes, position of Equilibrium 6 calculated on the basis of the compositions of clinopyroxene, ilmenite, and magnetite in the tuffs ($a_{titanite}$ taken as 1).

It is difficult to establish the original oxygen fugacities of primary magmas from study of granitoid rocks. During slow cooling, magnetite typically cleanses itself of Ti, and ilmenite undergoes one or more stages of oxidation-exsolution (Buddington and Lindsley, 1964; Haggerty, 1976). The occurrence of euhedral titanite and magnetite as early-crystallizing phases in silicic rocks indicates that the magma was relatively oxidized. The more magnesian the pyroxene or amphibole occurring in the rock, the more oxidized was the magma. For rocks not containing quartz, Equilibrium 6 will be shifted to slightly lower values of f_{O_2}, depending on the activity of silica. Therefore, quartz-free rocks containing hedenbergite + titanite + ilmenite may represent f_{O_2} values as low as those defined by the FMQ buffer (see Fig. 1).

Prince (1945) demonstrated that the titanite component is soluble in intermediate to mafic magmas. In the system $CaTiSiO_5$-$NaAlSi_3O_8$-$CaAl_2Si_2O_8$, the eutectic between titanite and plagioclase is close to the plagioclase side only for albite-rich compositions. Thus, early titanite might be present only in more leucocratic magmas. Lipman (1971) and Johnson and Lipman (1988) have documented that titanite occurs as phenocrysts in volcanic rocks, Noyes (1978) showed that it is an early-crystallizing phase in granodioritic rocks of the central Sierra Nevada batholith, California, and Dillet and Czamanske (1987) found ubiquitous early titanite in all granitoids of the high-level Questa magmatic system, New Mexico. Czamanske and Wones (1973) found titanite to be a product of late-stage oxidation during crystallization of the Finnmarka complex, Norway.

Conversely, hedenbergitic pyroxene and ilmenite are primary phases during the crystallization of other granitic plutons. Barker et al. (1975) found these phases occurring with fayalite in the Pikes Peak batholith, Colorado. Rhyolites associated with bimodal volcanism (e.g., Lipman et al., 1972) also commonly contain Fe-rich pyroxenes and ilmenite as primary phases.

Takahashi et al. (1980) have compared Ishihara's (1975) classification of granites as magnetite- and ilmenite-bearing with the I and S classification of Chappell and White (1974; see also Hine et al., 1978). The absence of magnetite is often associated with S-type granites, because of the C content of the sedimentary source. However, as pointed out by Loiselle and Wones (1979), siliceous magmas formed by fractionation from mantle-derived magmas in rift zones are also reduced.

A summary treatment of volcanic rocks from various tectonic settings led Ewart (1979) to suggest that intrinsic oxygen fugacity is related to tectonic setting, with more highly oxidized magmas being associated with compressive tectonics and convergent plate boundaries. The

Questa magmatic system, however, is related to evolution of the Rio Grande Rift, and Czamanske and Wones (1973) demonstrated that granitoids associated with the Oslo graben became oxidized during crystallization. Recognition of the primary assemblage titanite + magnetite versus clinopyroxene (or amphibole) + ilmenite should aid in establishing the relative oxidation state of magmas that crystallized to form granites, commonly our only remaining record of magmatic activity in older terranes. However, it is doubtful whether oxidation state consistently depends on tectonic setting.

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