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Assemblages with titanite (CaTiOSiO₄), Ca-Mg-Fe olivine and pyroxenes, Fe-Mg-Ti oxides, and quartz: Part I. Theory

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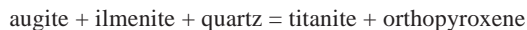
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ABSTRACT

Critical evaluation of the thermodynamic data for titanite, in conjunction with a heat capacity equation that takes into account the $P_{21/a} \leftrightarrow A_{2/a}$ transition and a more complete P - V - T data set for titanite, indicates that: (1) enthalpy of formation values greater than -2600 kJ/mol are not supported by calorimetry; (2) calculated internally consistent feasible solutions converge to enthalpy of formation from the elements values between -2608 and -2600 kJ/mol and 113 to 121 J/mol·K for the entropy; (3) the practice of adjusting the enthalpy of formation to fit phase equilibrium experiments may be erroneous, in contrast, it is the currently accepted entropy of 129.20 ± 0.84 J/mol·K that may need revision to a smaller value. Consequently, we optimize standard-state properties for end-member titanite ($P_{21/a}$ structure) consistent with the thermodynamic data in the program QUILF. In addition, we use a modified version of the program to calibrate equilibria among titanite (CaTiOSiO₄), Fe-Mg-Ti ilmenite and spinel, Ca-Mg-Fe pyroxenes and olivine, and quartz. Calculations at 1 and 3 kbar, and 650, 850, and 1100 °C, in the system CaO-MgO-FeO-Fe₂O₃-TiO₂-SiO₂, suggest that the reactions:



and



impose well defined f_{O_2} , a_{SiO_2} , and $X_{\text{Fe}}^{\text{Opx}}$ restrictions to the assemblages (1) titanite + spinel phase + quartz, (2) titanite + orthopyroxene, (3) augite + ilmenite, and consequently titanite stability. The absence of quartz ($a_{\text{SiO}_2} < 1$ with respect to Qz) favors the sub-assemblage Fe-Mg-Ti spinel + titanite over augite + ilmenite, and the latter over titanite + orthopyroxene. Nonetheless, in the absence of quartz, no titanite-bearing assemblage is stable relative to olivine + orthopyroxene + augite + ilmenite + Fe-Mg-Ti spinel. From the phase relations, we can also infer that in quartz-saturated rocks: (1) titanite can coexist with orthopyroxene only at low $X_{\text{Fe}}^{\text{Opx}}$ values, regardless of f_{O_2} conditions, whereas the assemblage titanite + orthopyroxene + spinel phase requires high f_{O_2} , relative Mg-enrichment (from high to moderate $X_{\text{Fe}}^{\text{Opx}}$), and temperatures ≤ 650 °C. (2) The association of titanite with a spinel phase is generally indicative of relatively oxidizing conditions. (3) The assemblage titanite + olivine requires f_{O_2} condition close to FMQ and relative Fe-enrichment (from moderate to high $X_{\text{Fe}}^{\text{Opx}}$), and temperatures ≤ 650 °C.

INTRODUCTION

Titanite can participate in reactions among silicates, oxides, and carbonates. Moreover, it has been shown that such reactions can constrain intensive parameters and place limits on the stability of major rock-forming phases (e.g., Hunt and Kerrick 1977; Wones 1989; Manning and Bohlen 1991). In this paper, we discuss the petrological significance of reactions among end-member titanite, Ca-Fe-Mg pyroxenes and olivine, Fe-Mg-Ti ilmenite and spinel, and quartz.

Titanite-bearing, oxide-silicate equilibria have been long considered to indicate relatively oxidizing conditions (Verhoo-

gen 1962; Carmichael and Nichols 1967). More important, the assemblage titanite + magnetite + quartz is also generally thought to mark a fundamental boundary between relatively reducing and oxidizing conditions (Wones 1989). The Wones (1989) predictions were confirmed experimentally in the system CaO-FeO-Fe₂O₃-TiO₂-SiO₂ (Xirouchakis 1997; Xirouchakis and Lindsley 1998). The phase relations, however, are more complex than originally proposed (Wones 1989), with the presence of titanite placing tight limits on the stability of hendenbergite_{ss} (CaFeSi₂O₆-Fe₂Si₂O₆), fayalite_{ss} (Fe₂SiO₄-CaFeSiO₄), ilmenite_{ss} (FeTiO₃-Fe₂O₃), magnetite_{ss} (Fe₃O₄-Fe₂TiO₄), and quartz (Xirouchakis and Lindsley 1998).

We expand upon these results by considering the stability of the assemblage titanite + spinel phase + quartz in the model

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system CaO-MgO-FeO-Fe₂O₃-TiO₂-SiO₂. This is facilitated by the lack of affinity shown by titanite for Mg (e.g., Deer et al. 1982). Furthermore, in the system CaO-FeO-Fe₂O₃-TiO₂-SiO₂, and in the range 600–1000 °C, <1 bar –3.8 kbar, *f*_{O₂} between IFQ and FMQ, and in the presence of fayalite_{ss}, ilmenite_{ss}, magnetite_{ss}, and hedenbergite_{ss}, titanite did not appear to contain any Fe (Xirouchakis 1997). Thus, as a first approximation, titanite can be treated as a pure phase in equilibria with Fe-Mg-Ti ilmenite and spinel (Andersen et al. 1991), Ca-Mg-Fe pyroxenes and olivine (Davidson and Lindsley 1989), quartz, rutile, and iron. A complete list of titanite-bearing, oxide-silicate equilibria are included in the latest version of the QUILF program (file quilf.rct), which can be downloaded from <http://pbisotopes.ess.sunysb.edu/geo/general/faculty/lindsley.html>. The addition of titanite does not alter QUILF (Lindsley et al. 1990; Lindsley and Frost, 1992; Frost and Lindsley, 1992; Andersen et al. 1993), it simply expands it. In this study, we discuss (1) the thermodynamic properties of titanite, albeit briefly, and (2) the factors controlling titanite stability, primarily, in the presence of Fe-Mg-Ti ilmenite and spinel, Ca-Mg-Fe pyroxenes and olivine, and quartz.

TITANITE (CaTiOSiO₄) THERMODYNAMIC MODEL

Xirouchakis and Lindsley (1998) derived $\Delta H_{\text{bar},298\text{K}}^0$ and $S_{\text{bar},298\text{K}}^0$, and a $C_p(T)$ equation for titanite (A2/a structure) that is internally consistent with the thermodynamic data in QUILF (Andersen et al. 1993), and with the Xirouchakis et al. (1997) calorimetry data and their own phase equilibrium experiments. Xirouchakis and Lindsley (1998) stated that their heat capacity equation (1) does not account for the P2₁/a ↔ A2/a transition, and (2) may overestimate the heat capacity of titanite at high temperatures. But they also demonstrated that, regardless of the heat capacity equation accepted (Xirouchakis and Lindsley 1998; King et al. 1954), an enthalpy of formation value of -2610 ± 2.9 kJ/mol is consistent with entropy values smaller than the currently accepted value of 129 J/mol·K (King et al. 1954). They also showed that entropy values close to 129.20 J/

mol·K are consistent with enthalpy of formation values greater than -2597 kJ/mol (Holland and Powell 1990; Berman 1991; Xirouchakis and Lindsley 1995) or -2602 kJ/mol (Holland and Powell 1985). Independent support to these conclusions comes from the recent work of Holland and Powell (1998), Chatterjee et al. (1998), and Tangeman and Xirouchakis (2000).

In this study, we derive standard-state properties for end-member titanite (P2₁/a structure) that are internally consistent with the Xirouchakis and Lindsley (1998) experimental data, the Andersen et al. (1993) database, the Tangeman and Xirouchakis (2000) heat capacity equation, the Xirouchakis et al. (1997) enthalpy of formation, and a more complete *P-V-T* data set (Taylor and Brown 1976; Kunz et al. 1996; Angel et al. 1999; Kunz et al. 2000). Note that Kunz et al. (1996, 2000), Angel et al. (1999), Xirouchakis et al. (1997), and Tangeman and Xirouchakis (2000) used the same samples without phase impurities of stoichiometric titanite (CaTiOSiO₄).

In the optimization of the thermodynamic data, we also explored the effect of different enthalpy of formation values on the entropy. The optimization results (Table 1) are in good agreement with the Xirouchakis and Lindsley (1998) conclusions regarding the internally consistent range of $\Delta H_{\text{bar},298\text{K}}^0$ and $S_{\text{bar},298\text{K}}^0$ values for titanite. The enthalpy of formation constraints (Table 1) were calculated from two different sets of calorimeter calibrations (Al₂O₃ vs. Pt: Xirouchakis et al. 1997, Xirouchakis unpublished data). [Calibration of the calorimeter with Al₂O₃ (corundum) disks, of equal weight to the sample, results in a calibration factor different from that obtained when Pt spheres are used. The latter are generally heavier than the sample. Consequently, the different calibration factors result in different $\Delta H_{\text{bar},298\text{K}}^0$ values. The Al₂O₃ (corundum) calibration of the calorimeter is generally preferred because it is not always possible to correct for heat pick-up from the Pt spheres or wire during drop (A. Navrotsky, personal communication; Müller and Kleppa 1973)]. We did so because, although the two sets of enthalpy of formation values do not overlap, they define a range of permissible enthalpy values from -2615 to -2600 kJ/mol

TABLE 1. Thermodynamic data for titanite

	max	avg	min	Preferred	Enthalpy constraints
$\Delta_f H^0$ (J/mol)	-2 610 123.97	-2 607 339.12	-2 607 223.50	-2 607 339.12	2 610 124 ± 2900, Al ₂ O ₃ calibration
S^0 (J/mol·K)	102.45	111.75	111.37	111.75	"
$\Delta_f G^0$ (J/mol)	-2 460 603.59	-2 460 592.25	-2 460 363.40	-2 460 592.25	"
$\Delta_f H^0$ (J/mol)	-2 605 690.00	-2 602 170.22	-2 601 136.68	-2 601 136.68	-2 602 850 ± 2840, Pt calibration
S^0 (J/mol·K)	106.93	117.36	117.96	117.96	"
$\Delta_f G^0$ (J/mol)	-2 457 503.52	-2 457 095.33	-2 456 241.23	-2 456 241.23	"
$\Delta_f H^0$ (J/mol)	-2 610 123.97	-2 605 690.00	-2 600 155.99	-2 600 155.99	none
S^0 (J/mol·K)	102.45	113.44	119.75	119.75	"
$\Delta_f G^0$ (J/mol)	-2 460 603.59	-2 459 446.90	-2 455 793.25	-2 455 793.25	"

Note: The values incorporated in QUILF are in bold; max, avg, and min refer to input *T*, *P*, and mineral compositions.

$T_{\text{transition}}^{\text{latm}} = 483 \pm 5\text{K}$ and $T_{\text{transition}}^{\text{P}} = T_{\text{transition}}^{\text{latm}} - 0.0053 \cdot (P - 1.01325)$, *P* is in bars. Taken from Tangeman and Xirouchakis (2000) are the transition temperature, heat capacity, and volume equations:

$$C_p = \frac{(-2.3952 \cdot 10^6)}{T^3} + \frac{(-5.8601 \cdot 10^{-3})}{T^2} + \frac{0.2239 \cdot 10^5}{T} + \frac{(-0.5913 \cdot 10^4)}{\sqrt{T}}$$

$$+ 0.4277 \cdot 10^3 + (-7.772 \cdot 10^{-2}) \cdot T + 1.3751 \cdot 10^{-5} \cdot T^2$$

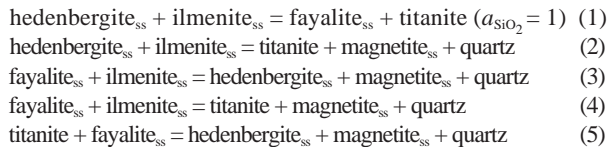
$$+ 3.0877 \cdot \sum_{k=1}^{k=2} \frac{\tau^{3(2k-1)}}{2k-1} \text{ for } \tau = \frac{T}{T_r} \leq 1, \text{ or } 2.3034 \cdot \sum_{k=1}^{k=2} \frac{\tau^{-5(2k-1)}}{2k-1} \text{ for } \tau = \frac{T}{T_r} \geq 1.$$

$$V_{PT} = 5.3799 + 1.5434 \cdot 10^{-4} \cdot T + 9.0737 \cdot 10^{-2} \cdot e^{(-7/200)} + (-2.9392 \cdot 10^{-6}) \cdot P + 1.0633 \cdot 10^{-1} \cdot e^{(-P/35000)}.$$

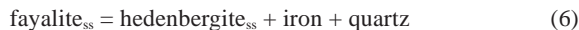
(Fig. 1). This range covers all calorimetrically determined $\Delta H_{\text{1bar,298 K}}^{\circ}$ from the elements for titanite (Todd and Kelley 1956; Robie et al. 1978; Xirouchakis et al. 1997). The apparent agreement between the optimizations using (1) no enthalpy constraints and (2) enthalpy constraints based on the Pt calibration factor cannot be used to argue for or against one or the other of the calibration methods. All the enthalpy and entropy values labeled as preferred in Table 1 reproduce the Xirouchakis and Lindsley (1998) experimental data in the system CaO-FeO-Fe₂O₃-TiO₂-SiO₂ within experimental T , P , f_{O_2} , and compositional uncertainties. Finally, a set of enthalpy and entropy values, specific to this version of QUILF (Lindsley and Frost 1992), was accepted because it affords a relatively more precise representation of the experimental data. The assessment of available phase equilibrium and thermochemistry data (Fig. 1) indicates that: (1) enthalpy of formation values greater than -2600 kJ/mol are not supported by calorimetry; (2) although the degree of overlap is small, the calculated internally consistent feasible solutions converge to enthalpy of formation values between -2608 and -2600 kJ/mol and 113 to 121 J/mol·K for the entropy; and finally (3) the practice of adjusting the enthalpy of formation to fit phase-equilibrium data may be erroneous; in contrast, it is the currently accepted entropy of 129.20 ± 0.84 J/mol·K that may need revision to a smaller value. Of course, the actual value depends on the thermodynamic database of choice (i.e., Berman 1988, 1991; Andersen et al. 1993; Berman and Aranovich 1996; Holland and Powell 1990, 1998; Chatterjee et al. 1998).

TOPOLOGIC RELATIONS

We used QUILF to calculate the reactions among iron, hedenbergite_{ss} (CaFeSi₂O₆-Fe₂Si₂O₆), fayalite_{ss} (Fe₂SiO₄-CaFeSiO₄), ilmenite_{ss} (FeTiO₃-Fe₂O₃), magnetite_{ss} (Fe₃O₄-Fe₂TiO₄), and quartz. The phase relations were originally explored theoretically by Xirouchakis and Lindsley (1998). In Figure 2, we show the results of the calculations at 1 bar where it can be seen that the reactions:



generate an invariant point (I) at 619 °C and 0.2 log f_{O_2} units below FMQ. Reaction 1 terminates at invariant point (II), located at 658 °C and 6.04 log f_{O_2} units below FMQ, by its intersection with the reaction



where fayalite_{ss} is Ca-saturated with respect to hedenbergite_{ss}. At 1052 °C and 4.6 log f_{O_2} units below FMQ, the intersection of the titanite-absent reaction 3 with the reaction:



generates a third invariant point (III). Finally, the intersection of the fayalite_{ss}-absent reaction 2 with reaction 7 generates a

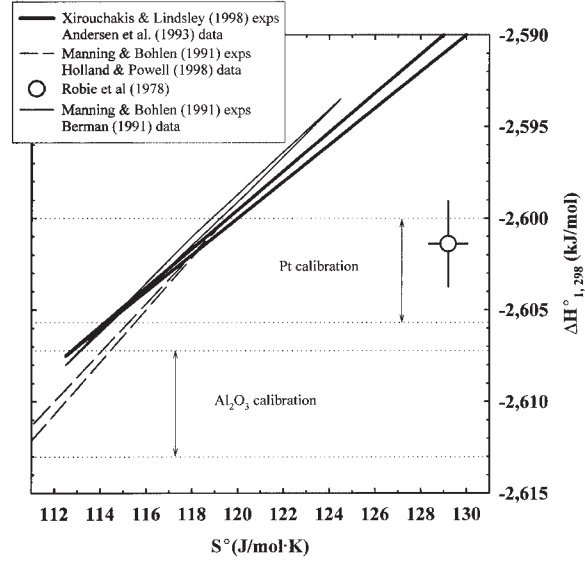


FIGURE 1. A plot of $H_{\text{1bar,298 K}}^0$ vs. S^0 showing feasible solutions for titanite ($P2_1/a$ structure) constructed using phase-equilibrium constraints from Xirouchakis and Lindsley (1998) and Manning and Bohlen (1991). Details for the calculations using the Manning and Bohlen (1991) data are given in Tangeman and Xirouchakis (2000). Note (1) that calorimetry does not support enthalpy of formation values greater than -2600 kJ/mol, and (2) the convergence with some overlap in the range -2608 and -2600 kJ/mol for the enthalpy of formation from the elements but only if we adopt entropy values between 113 to 121 J/mol·K.

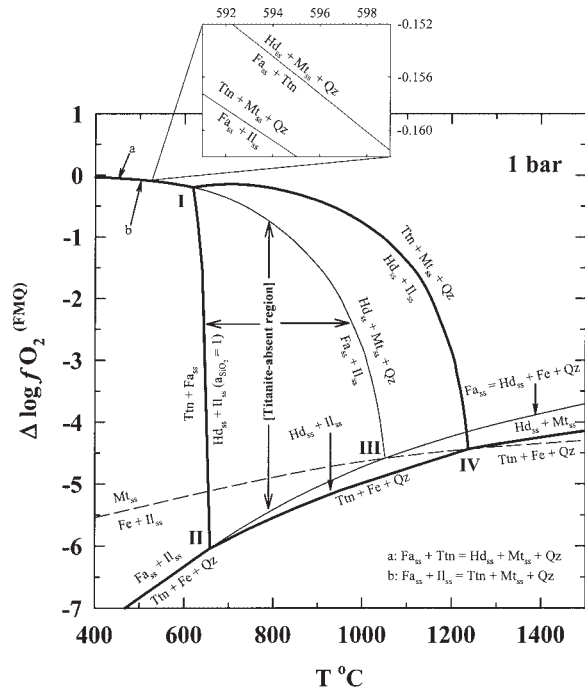


FIGURE 2. Calculated titanite-bearing reactions in the system CaO-FeO-Fe₂O₃-TiO₂-SiO₂ among iron, ilmenite_{ss} (FeTiO₃-Fe₂O₃), magnetite_{ss} (Fe₃O₄-Fe₂TiO₄), fayalite_{ss} (Fe₂SiO₄-CaFeSiO₄), hedenbergite_{ss} (CaFeSi₂O₆-Fe₂Si₂O₆), and quartz at 1 bar. Reactions labeled a and b are different but practically unresolvable at the large scale.

fourth invariant point (IV) at 1238 °C and 4.44 $\log f_{\text{O}_2}$ units below FMQ. At point (IV), magnetite_{ss} and ilmenite_{ss} approach the Fe_2TiO_4 and FeTiO_3 end-member compositions, respectively. At 1 bar, invariant point (IV) is not stable with respect to liquid and ferrobustamite (Xirouchakis and Lindsley 1998). It is, however, stable wherever hedenbergite_{ss} is stable (Lindsley and Munoz 1969). At <600 °C, the hedenbergite_{ss}- and ilmenite_{ss}-absent reactions 4 and 5, respectively, merge asymptotically with the FMQ buffer curve as the fayalite_{ss} loses Ca, and the magnetite_{ss} loses Ti with decreasing temperature.

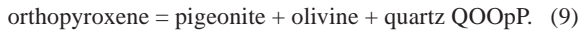
The invariant points I–V are also characterized by the absence of rutile, pigeonite ($\text{CaFeSi}_2\text{O}_6\text{-Fe}_2\text{Si}_2\text{O}_6$), and ferrosilite_{ss} ($\text{CaFeSi}_2\text{O}_6\text{-Fe}_2\text{Si}_2\text{O}_6$). In general, assemblages with titanite and rutile are metastable with respect to assemblages with titanite and Fe-Ti oxides. Whether titanite will coexist with either ferrosilite_{ss} or pigeonite instead of hedenbergite_{ss} is controlled by the reactions described by Davidson and Lindsley (1989) in the CaO-FeO-SiO_2 subsystem. For instance, at >8 kbar, coexisting $\text{Hd}_{\text{ss}} + \text{Fa}_{\text{ss}} + \text{Qz}$ will be replaced either by Ca-saturated ferrosilite or pigeonite depending upon the temperature (see Fig. 2 of Davidson and Lindsley 1989). Obviously, this places an upper pressure limit to the topology shown in Figure 2.

The important conclusions to be drawn from Figure 2 are: (1) the stable coexistence of titanite with iron at low f_{O_2} conditions regardless of temperature; and (2) the existence of a titanite-absent field, defined by the reactions 1 and 3, where the isobarically divariant assemblages $\text{Fa}_{\text{ss}} + \text{Hd}_{\text{ss}} + \text{Il}_{\text{ss}} + \text{Mt}_{\text{ss}}$, $\text{Fa}_{\text{ss}} + \text{Il}_{\text{ss}} + \text{Mt}_{\text{ss}} + \text{Qz}$, and $\text{Fa}_{\text{ss}} + \text{Hd}_{\text{ss}} + \text{Il}_{\text{ss}} + \text{Qz}$ are stable. Clearly, higher-variance assemblages such as $\text{Hd}_{\text{ss}} + \text{Il}_{\text{ss}} + \text{Ttn}$ are not precluded in this field (Fig. 2).

It is the titanite-absent field in Figure 2 that we explore in the system $\text{CaO-MgO-FeO-Fe}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$. First, the addition of MgO displaces the redox reactions of interest to higher f_{O_2} conditions relative to their MgO-free counterparts at the same T and P . Second, it eventually causes olivine to react out and form orthopyroxene through the reactions:



and



Consequently, the olivine in the MgO-free reactions 1, 3, 4, and 5 will be replaced by orthopyroxene. Note also that in the subsystem CaO-MgO-FeO-SiO_2 , the phase relations among augite, orthopyroxene, and pigeonite are controlled by the reactions:



and



[For a detailed description, the reader is referred to Lindsley and Frost (1992).]

The phase relations with titanite can be explored in isobaric and isothermal plots of $\Delta \log f_{\text{O}_2}$ vs. μFeMg_{-1} (Fig. 3). Except for Figure 3, we compromise and use $X_{\text{Fe}}^{\text{Opx}} = \text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ in orthopyroxene as a monitor for μFeMg_{-1} . We do so by calculating the orthopyroxene that would have been in Fe-Mg exchange equilibrium with at least one of the ferromagnesian

phases that is present (see also Lindsley and Frost 1992; Lindsley et al. 1990). We do not examine assemblages with titanite, rutile, and either Ca-Fe-Mg pyroxenes or olivine because they are of high variance. Nevertheless, such assemblages are useful because, even in the absence of rutile, they constrain the activity of TiO_2 with respect to rutile during metamorphic or igneous processes. Note that the Fe-Mg-Ti ilmenite and spinel (also hereafter ilmenite and spinel phase) thermodynamic models have been calibrated for up to 2 $\log f_{\text{O}_2}$ units above FMQ. Consequently, the calculations above this range involving ilmenite ($\text{FeTiO}_3\text{-MgTiO}_3\text{-Fe}_2\text{O}_3$) and spinel phase ($\text{Fe}_3\text{O}_4\text{-Fe}_2\text{TiO}_4\text{-MgFe}_2\text{O}_4$) may become increasingly less precise although the topological arguments remain valid. The Ca-Mg-Fe pyroxenes and olivine thermodynamic models and the relative sequence of curves are not affected.

The calculations in the model system $\text{CaO-MgO-FeO-Fe}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$, at 1 and 3 kbar and 650, 850, and 1100 °C (Figs. 4–6) indicate that the reaction:



always places upper f_{O_2} and $X_{\text{Fe}}^{\text{Opx}}$ limits to the stable coexistence of augite and ilmenite. The curvature shown by reaction 12 under isobaric and isothermal conditions is the result of increasingly greater fractions of Fe_2O_3 in ilmenite and Fe_3O_4 in spinel phase with increasingly more oxidizing conditions. How-

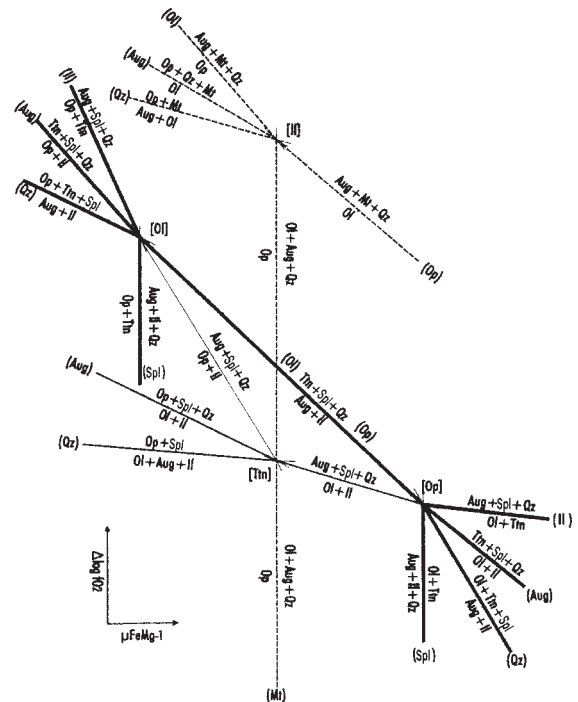


FIGURE 3. Schematic isothermal and isobaric μMgFe_{-1} vs. $\Delta \log f_{\text{O}_2}^{\text{FMQ}}$ projection of the phase relations among titanite (Ttn), orthopyroxene (Op), augite (Aug), olivine (Ol), Fe-Mg-Ti spinel (Spl), ilmenite (Il), and quartz (Qz) in the system $\text{CaO-FeO-MgO-Fe}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$. Heavy solid lines denote reactions with titanite whereas light solid lines represent reactions without titanite. Dashed light lines represent reactions among augite (Aug), orthopyroxene (Op), olivine (Ol), quartz (Qz), and pure magnetite (Mt) in the system $\text{CaO-FeO-MgO-Fe}_2\text{O}_3\text{-SiO}_2$.

ever, neither spinel phase nor ilmenite approach end-member compositions because both oxides retain Ti and some Mg. At these high f_{O_2} conditions, titanite becomes effectively the most Ti-rich phase present. A lower X_{Fe}^{Opx} limit to the assemblage augite + ilmenite is placed by the reaction:

augite + ilmenite + quartz = orthopyroxene + titanite
 AIIQOpT (13).

At moderate to low X_{Fe}^{Opx} values where reaction 13 is stable, ilmenite is more Mg- than Fe^{3+} -rich. However, the incorporation of Fe^{3+} in its structure causes reaction 13 to show a small f_{O_2} dependency. Below 700 °C, reactions 12 and 13 generate an isobarically and isothermally invariant point, characterized by the absence of olivine, at moderate to low X_{Fe}^{Opx} values and high f_{O_2} conditions. Three additional titanite-bearing reactions, stable only at high f_{O_2} conditions, originate from this invariant point:

augite + ilmenite = orthopyroxene + titanite + spinel phase
 AIIOpTU (14),

orthopyroxene + ilmenite = titanite + spinel phase + quartz
 OpIIUQU (15)

and

orthopyroxene + titanite = augite + spinel phase + quartz
 OpTAUQ (16).

In Figure 4, this invariant point is shown at 650 °C, however, in reality reactions 14–16 intersect below 700 °C and slightly higher than 650 °C.

At isobaric and isothermal conditions, reactions 12 and 13 define a broad space in terms of a_{SiO_2} and X_{Fe}^{Opx} where titanite is not stable in the presence of orthopyroxene and/or Fe-Mg-Ti spinel + quartz ($a_{SiO_2} = 1$ with respect to Qz), because titanite will react with either orthopyroxene or Fe-Mg-Ti spinel + quartz to produce augite + ilmenite (Figs. 4–6). The absence of quartz ($a_{SiO_2} < 1$ with respect to Qz) increases the likelihood of observing titanite + spinel phase well within this space. Furthermore it decreases the stability field of orthopyroxene + titanite relative to augite + ilmenite. The calculations suggest that this titanite-absent field becomes larger with increasing temperature and pressure or, alternatively, smaller with decreasing temperature and pressure conditions (Figs. 4–6). Titanite can coexist stably with orthopyroxene, Fe-Mg-Ti spinel, and quartz after relative Mg-enrichment, decreasing temperatures, and increasing f_{O_2} (i.e., higher than FMQ) as the Ol-absent invariant point of Figures 3 and 4 is approached along the path defined by the assemblage orthopyroxene + ilmenite + augite + spinel phase + quartz, i.e., OpIIAUQ curve in Figure 4. In contrast, titanite can crystallize and coexist with olivine after relative Fe-enrichment with concomitant decrease in temperature and f_{O_2} approaching FMQ toward the Opx-absent invariant point of Figure 3 along the path defined by the assemblage olivine + ilmenite + augite + spinel phase + quartz, i.e., OIIAUQ curve in Figure 4. From Figures 4 and 5 it is clear that the quartz-absent assemblage orthopyroxene + augite + spinel phase + ilmenite + olivine (OpAUIIO curve) does not intersect a titanite-bearing reaction. Hence, titanite is probably precluded in quartz-absent rocks that contain this assemblage or its derivatives, i.e., OpPUIIO and APUIIO curves in Figure 6.

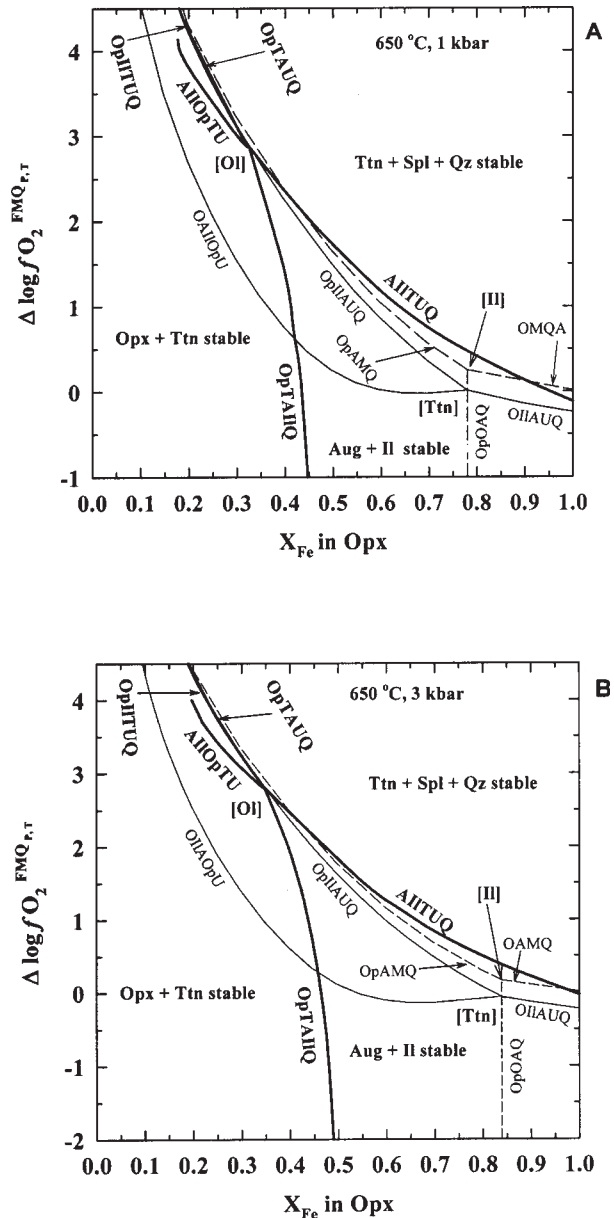


FIGURE 4. Calculated X_{Fe}^{Opx} vs. $\Delta \log f_{O_2}^{FMQ,T}$ projection of the phase relations among titanite (T), orthopyroxene (Op), augite (A), olivine (O), spinel phase (U), ilmenite (Il), and quartz (Q) in the system CaO-FeO-MgO-Fe₂O₃-TiO₂-SiO₂ at 650 °C, 1 and 3 kbar. Heavy solid lines: reactions with titanite. Light solid lines: reactions without titanite. The titanite-absent reactions, although not part of the discussion, are shown for completeness and to demonstrate the limits imposed by titanite on the stability of pyroxenes, olivine, and oxides. The olivine-, titanite-, and ilmenite-absent invariant points are shown as [OI], [Ttn], and [III], respectively. Reactions OpIIUQU and OpTAUQ are different but also unresolvable at this scale. The AIIOpTU curve is terminated at $X_{Fe}^{Opx} \sim 0.2$ for clarity. The crossing of curves labeled OpTAIIQ and OIIAOpU is indifferent. Dashed light lines represent reactions among augite (A), orthopyroxene (Op), olivine (O), quartz (Q), and pure magnetite (M) in the system CaO-FeO-MgO-Fe₂O₃-SiO₂.

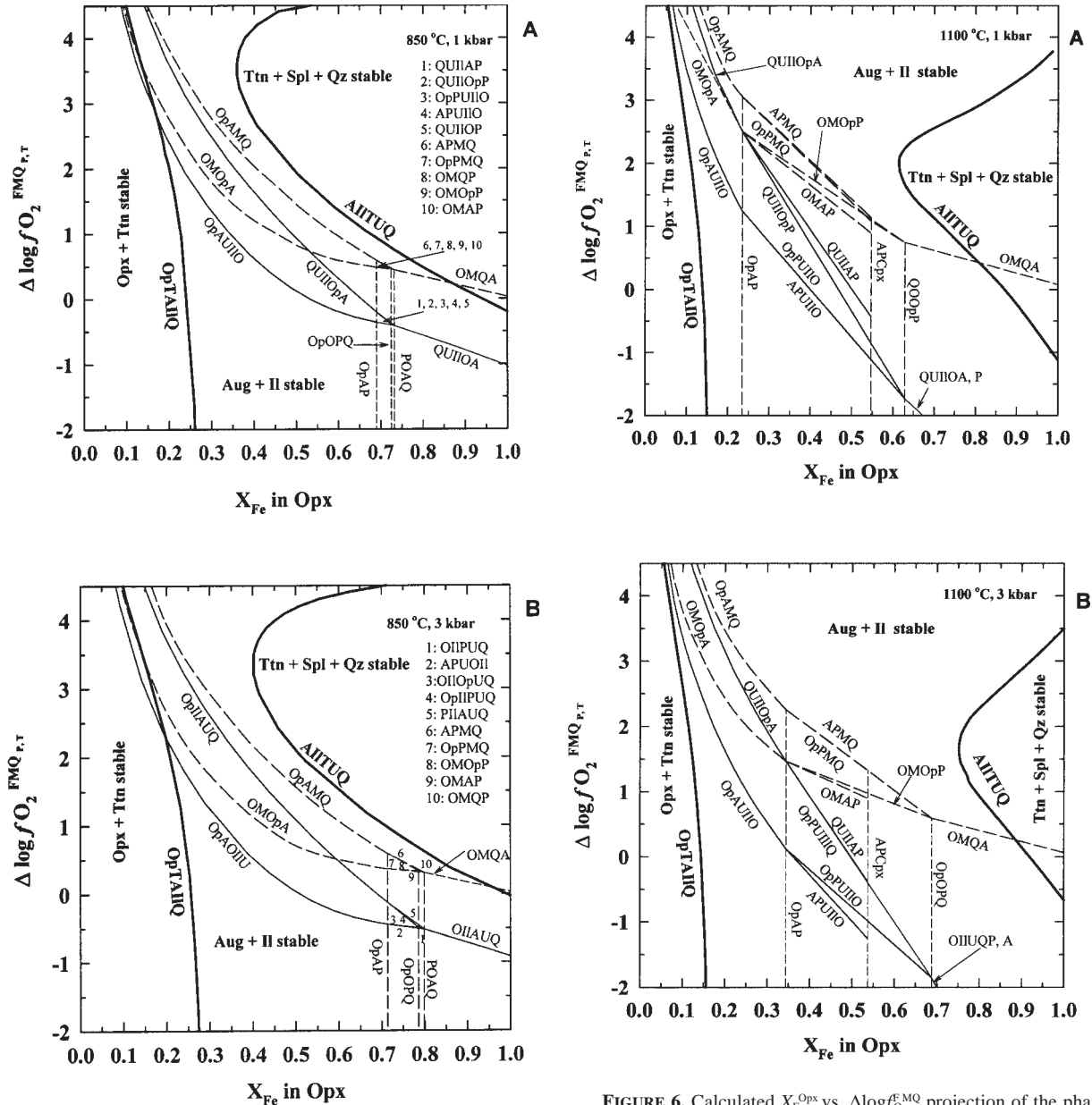


FIGURE 5. Calculated $X_{\text{Fe}}^{\text{Opx}}$ vs. $\Delta \log f_{\text{O}_2}^{\text{FMQ}}$ projection of the phase relations among titanite (T), orthopyroxene (Op), augite (A), olivine (O), spinel phase (U), ilmenite (Il), and quartz (Q) in the system CaO-FeO-MgO-Fe₂O₃-TiO₂-SiO₂ at 850 °C, 1100 °C, 1 and 3 kbar. Heavy solid lines = reactions with titanite. Light solid lines = reactions without titanite. Dashed light lines are as in Figure 4. Note the expansion of the augite + ilmenite stability field relative to titanite-bearing assemblages from 650 to 850 °C, and 1 to 3 kbar.

SUMMARY

The available calorimetry data do not support $\Delta H_{\text{bar}, 298}^{\circ}$ K values greater than -2600 kJ/mol from the elements for end-member titanite (CaTiOSiO₄). Moreover, internally consistent feasible solutions, constructed from selected phase-equilibrium experiments, converge with some overlap in the range -2608 and -2600 kJ/mol for the enthalpy of formation from the ele-

FIGURE 6. Calculated $X_{\text{Fe}}^{\text{Opx}}$ vs. $\Delta \log f_{\text{O}_2}^{\text{FMQ}}$ projection of the phase relations among titanite (T), orthopyroxene (Op), augite (A), olivine (O), spinel phase (U), ilmenite (Il), and quartz (Q) in the system CaO-FeO-MgO-Fe₂O₃-TiO₂-SiO₂ at 1100 °C, 1 and 3 kbar. Heavy solid lines = reactions with titanite. Light solid lines = reactions without titanite. Dashed light lines are as in Figure 4. Note the expansion of the augite + ilmenite stability field relative to titanite-bearing assemblages from 850 to 1100 °C, and 1 to 3 kbar.

ments but only if we adopt entropy values between 113 and 121 J/mol·K. The practice of adjusting the enthalpy of formation of titanite to fit phase-equilibrium data may be erroneous. It is probably the currently accepted entropy of 129.20 ± 0.84 J/mol·K that may need revision to a smaller value.

Equilibria among titanite, pyroxene(s), olivine, ilmenite, spinel phase, and quartz, extend the previously described oxide-silicate QUIIF equilibria in the model system CaO-MgO-

FeO-Fe₂O₃-TiO₂-SiO₂ (Lindsley and Frost 1992; Frost and Lindsley 1992; Lindsley et al. 1990; Frost et al. 1988). In addition, the presence of titanite places tight limits on the stability of the coexisting oxides and silicates. Based on the computed phase relations we draw the following general conclusions:

(1) In the CaO-FeO-Fe₂O₃-TiO₂-SiO₂ system, titanite can coexist with iron and/or Fe-Ti spinel with varying Ti content at low and high f_{O_2} conditions. Titanite-bearing assemblages are absent where the isobarically divariant assemblages $Fa_{ss} + Hd_{ss} + Il_{ss} + Mt_{ss}$, $Fa_{ss} + Il_{ss} + Mt_{ss} + Qz$, and $Fa_{ss} + Hd_{ss} + Il_{ss} + Qz$ are stable.

(2) In the system CaO-MgO-FeO-Fe₂O₃-TiO₂-SiO₂ and by extrapolation to more-complex natural systems, (a) the assemblage titanite + spinel phase + quartz is generally a good indicator of relatively high f_{O_2} , and it is likely more common in relatively Fe-rich bulk compositions and for decreasing temperature and pressure conditions. (b) At high temperatures, (≥ 650 °C) titanite is not stable in quartz-saturated rocks that contain ilmenite, spinel phase, and two pyroxenes, e.g., assemblages QUIIOPa, QUIIOPp, QUIIAP. (c) In quartz-saturated rocks, the coexistence of titanite and Fe-Mg-Ti spinel with either orthopyroxene or olivine requires a confluence of conditions relating bulk composition and f_{O_2} , and low temperatures (≤ 650 °C). Thus, such assemblages must be rare and probably to be encountered in plutonic rocks. (d) Regardless of T and f_{O_2} conditions, and bulk-composition, titanite is not stable in quartz-absent rocks that contain ilmenite, Fe-Mg-Ti spinel, olivine, and two pyroxenes, i.e., assemblages OpAUIIO, OpPUIIO, and APUIIO.

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