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QUILF: A PASCAL PROGRAM TO ASSESS EQUILIBRIA AMONG Fe–Mg–Mn–Ti OXIDES, PYROXENES, OLIVINE, AND QUARTZ

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Abstract—Program QUILF assesses equilibria among Ti-magnetite, ilmenite, augite, pigeonite, orthopyroxene, olivine, and quartz (or subassemblages thereof). Oxide and silicate equilibria are related through the QUIlF equilibrium:

$$\begin{array}{ccccccc} SiO_2 & + & 2Fe_2TiO_4 & = & 2FeTiO_3 & + & Fe_2SiO_4 \\ \text{\underline{Q}uartz} & & \text{\underline{U}lvöspinel} & & \text{\underline{I}lmenite} & & \text{\underline{F}ayalite.} \end{array}$$

Depending on the assemblage, QUILF can provide information on temperature, pressure, oxygen fugacity, and the activities of SiO_2, TiO_2, and Fe° at which the phases were last in equilibrium. For many low-variance assemblages, the system is overdetermined; thus quantitative information can be extracted even if one phase is altered or has reequilibrated. QUIlF equilibria can reduce the uncertainties in temperature and oxygen fugacity as determined from coexisting ilmenite and Ti-magnetite alone.

QUILF is written in Turbo Pascal for IBM PC and compatibles. The compiled program is approximately 210 kbyte; it also requires two data files that total approximately 10 kbyte. The compositions of the phases first must be projected into seven-component space (CaO–MgO–MnO–FeO–Fe_2O_3–TiO_2–SiO_2) before they are used in program QUILF; routines to accomplish this are included in the program, and also are available as separate BASIC programs.

Key Words: Equilibrium, Geothermometry, Geobarometry, Oxybarometry, Fe–Ti oxides, Pyroxene, Olivine, Quartz, Pressure, Temperature, Oxygen fugacity, Silica activity, QUIlF, Ti-magnetite, Ilmenite, Augite, Pigeonite, Orthopyroxene, Solution model.

BACKGROUND

The QUIlF equilibrium

Reaction between Fe–Ti oxides (Ti-magnetite and ilmenite solid solution) and ferromagnesian silicates can be expressed by the equilibrium:

$$\begin{array}{ccccccc} SiO_2 & + & 2Fe_2TiO_4 & = & 2FeTiO_3 & + & Fe_2SiO_4 \quad (1) \\ \text{\underline{Q}uartz} & & \text{\underline{U}lvöspinel} & & \text{\underline{I}lmenite} & & \text{\underline{F}ayalite} \end{array}$$

which we abbreviate to QUIlF (Frost, Lindsley, and Andersen, 1988). Equilibrium (1) strictly involves only end-member (ferric- and Mg-free) phases, but as magnetite (Fe_3O_4) and hematite (Fe_2O_3) components are added to the oxides, the equilibrium is displaced to higher values of oxygen fugacity (fO_2). The displaced equilibrium can be expressed by four equilibria in addition to equilibrium (1):

$$6Fe_2O_3 = 4Fe_3O_4 + O_2 \qquad (2)$$

$$2Fe_3O_4 + 3\ SiO_2 = 3\ Fe_2SiO_4 + O_2 \qquad (3)$$

$$2Fe_2O_3 + 2\ SiO_2 = 2Fe_2SiO_4 + O_2 \qquad (4)$$

and

$$Fe_2TiO_4 + Fe_2O_3 = Fe_3O_4 + FeTiO_3. \qquad (5)$$

Equilbria (2) and (3) are, respectively, the magnetite–hematite [MH] and fayalite–magnetite–quartz [FMQ] oxygen buffers; (4) is the (metastable) fayalite–hematitie–quartz equilibrium; and (5) governs the exchange of Fe^{2+} plus Ti with 2 Fe^{3+} [$Fe^{2+}Ti\,Fe^{3+}_{-2}$ exchange vector] between Ti-magnetite and ilmenite. These equilibria are not all independent [(4) can be obtained by adding 2 to twice (3), and twice (5) results from adding (4) to (1) and then subtracting (3)], but each can be calibrated and used to extract useful information from assemblages of two oxides + fayalite + quartz. As Frost, Lindsley, and Andersen (1988) pointed out, one use of the QUIlF equilibrium is to place mugh tighter constraints on temperature and oxygen fugacity than could be determined from the oxides alone (e.g. Andersen and Lindsley, 1988). Because the QUIlF assemblage is overdetermined, equilibria (1)–(5) can be used to "see through" the effects of the later alteration (such as oxidation of Ti-magnetite), or to calculate the activity of a phase that is missing from the assemblage.

Effects of MgO and CaO on the QUIlF equilibrium. Relatively few rocks contain pure fayalite, however; usually the fayalite contains some Mg (forsterite component). As Mg content increases, the oxides

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become Mg-bearing, and eventually olivine can no longer coexist with quartz: orthopyroxene (Opx) becomes stable and can coexist with the oxides and with either olivine or quartz. Opx-QUIlF equilibria greatly extend the range of rocks to which the system can be applied (Lindsley and others, 1990), but an even greater set of rocks contains calcic pyroxene. This paper describes the derivation and use of the program QUILF to assess these equilibria (Lindsley and Frost, 1992; Frost and Lindsley, 1992). The program is flexible, and can be used to determine temperature and fO_2 from coexisting oxides; to determine pressure and temperature for pyroxene + olivine + quartz assemblages; to perform calculations on Mg-free QUIlF assemblages; to extract information for Opx-QUIlF, and to assess Ca–pyroxene QUIlF. Thus it should have a broad range of applications. (Once quartz and olivine are no longer stable together, the QUIlF equilibrium is no longer applicable in the strict sense. We have retained the term QUIlF both to emphasize its importance in deriving the pyroxene-bearing equilibira and to help limit the proliferation of acronyms.)

Solution models

We have calibrated Ca-pyroxene QUIlF by combining a solution model for coexisting Fe–Mg–Mn–Ti oxides and olivine (Andersen, 1988; Andersen, Bishop, and Lindsley, 1991) with a solution model for coexisting Ca–Mg–Fe pyroxenes and olivines plus quartz (Davidson and Lindsley, 1989). The solution models that we use are not unique; however, it absolutely is essential that any models used be mutually consistent. Thus Sack and Ghiorso (1989, 1990; Ghiorso and Sack, 1989, 1991; Ghiorso, 1990) have derived solution models for coexisting oxides, olivine, orthopyroxene, and quartz. Similar to our own, their models are consistent internally, but the two approaches are incompatible mutually, the major reason being that the oxide and silicate equilibria are linked by different solution models for olivine. Sack and Ghiorso use their olivine model (1989), which is nearly three times as nonideal as the olivine model of Davidson and Mukhopadhyay (1984) that we use. It is not our purpose here to argue that one olivine model is "right" and the other "wrong", but rather to emphasize that they—and thus any other solution models derived using them—are mutually incompatible. For example, it would be a serious mistake to try to combine, say, our pyroxene model with the Sack–Ghiorso oxide models. When the Sack–Ghiorso models become available, we urge petrologists to apply them in addition to our own.

Program QUILF combines thermodynamic solution models for ilmenites ($FeTiO_3-Fe_2O_3-MgTiO_3-MnTiO_3$), spinels ($Fe_3O_4-Fe_2TiO_4-MgFe_2O_4-Mg_2TiO_4-MnFe_2O_3-MnTiO_4$), clino- and orthopyroxenes ($Mg_2Si_2O_6-Fe_2Si_2O_6-CaMgSi_2O_6-CaFeSi_2O_6$) and olivine ($Mg_2SiO_4-Fe_2SiO_4-CaMgSiO_4-CaFeSiO_4$), as related through equilibria (1)–(5) and the reaction

$$Fe_2SiO_4 + SiO_2 = Fe_2Si_2O_6. \qquad (6)$$

Thus QUIlF involves a portion of the seven-component system Fe–O–MgO–MnO–CaO–TiO_2–SiO_2 (alternatively, FeO–Fe_2O_3–MgO–MnO–CaO–TiO_2–SiO_2). We can handle up to three pyroxenes (augite, pigeonite, Opx), two oxides, quartz, and olivine (two-olivine assemblages have been reported but are extremely rare, and cannot be treated directly by the program). It is possible to have a seven-phase assemblage, although that would be extremely rare in nature. This assemblage would be univariant in a phase-rule sense, but as we shall see, it would be overdetermined by all the equilibria possible among these phases. At fixed pressure the assemblage would be (isobarically) invariant, and there would be seven (isobarically) univariant subassemblages possible. (In theory these subassemblages would be six-phase but many are compositionally degenerate and thus involve fewer than six phases.) Thus there would be seven *independent* reactions among the seven phases. However, because six of the phases are solid solutions, the total number of equilibria is greater, owing to constraints on the chemical potentials of the end-member components of the solid solutions. The Appendix lists 82 equilibria that we have quantified among these phases [as well as eight additional equilibria involving rutile (TiO_2) or metallic iron or both]. Of the 82 equilibria, 11 (which are preceded by ";") are redundant completely and are ignored by the program. Even though not all the remaining 71 equilibria are independent, it is useful to apply all or most of them to our assemblage: some are more sensitive to temperature, some more to pressure; some yield oxygen fugacity or other useful intensive parameters. The overdetermined system permits us to ask whether the phases can have been in equilibrium; whether one or more may have changed in composition after equilibrium had been established; or even whether the solution models may be in error. The QUILF program is structured so as to help provide the answers.

Oxides. The solution models incorporated in the QUILF program are described in the original papers and will only be summarized here. Ilmenite is treated as a four-component, asymmetric Margules solution with the components being $FeTiO_3$ (Il), Fe_2O_3 (Hem), $MgTiO_3$ (Gk), and $MnTiO_3$ (Py) (Andersen and Lindsley, 1988; Andersen, Bishop, and Lindsley, 1991). The spinels are somewhat more complicated, because site occupancies are potentially important. Andersen, Bishop, and Lindsley (1991) presented two formulations for Fe–Mg–Ti spinels—a site-mixing form and a simpler one (which also includes Mn) based on the Akimoto site distribution—and both worked equally well. Accordingly, we selected the simpler modified-Akimoto model for program QUILF. The modified-Akimoto cation distribution makes the approximation that (1) the spinels are perfectly inverse, (2) Ti always replaces Fe^{3+} in the octahedral site, and (3) Fe^{2+}, Mg, and Mn^{2+} are distributed randomly between the octohedral and tetrahedral sites of the spinel. Although there are six spinel end members (Fe_3O_4, $MgFe_2O_4$, Fe_2TiO_4, Mg_2TiO_4, $MnFe_2O_4$, and Mn_2TiO_4), these assumptions result in only three independent compositional parameters: N_{Ti} (the number of Ti in one four-oxygen formula unit), N_{Mg} (the number of Mg per formula unit), and N_{Mn} (the number of Mn per formula unit). Note that N_{Mg} and N_{Mn} range from zero to one for Ti-free spinels but can range up to two for the ferric-free join.

Pyroxenes and olivine. Ca–Mg–Fe olivines and pyroxenes each have four nominal end members—$Mg_2Si_2O_6$, $Fe_2Si_2O_6$, $CaMgSi_2O_6$, and $CaFeSi_2O_6$ for pyroxenes, and analogously for olivines. Variations in bulk composition can be expressed by only two compositional parameters, x ($=X_{En}$) and y ($=X_{Wo}$). Based on crystal-chemical constraints, Ca is restricted to the M2 sites. Mg and Fe then fill the M1 and M2 sites. Unlike the situation for the spinels, however, we do not treat the distribution of Mg and Fe as random for these sites (Davidson and Mukhopadhyay, 1984; Davidson, 1985). Instead we employ a long-range order parameter t ($=X_{Fe}^{M2}$-X_{Fe}^{M1}) and calculate site occupancies by minimizing free energy with respect to the order parameter ($dG/dt = O$; see eq. 3, Davidson and Lindsley, 1989, p. 19). Because the site occupancies are functions of temperature, it is not possible to solve equilibria involving pyroxenes and olivines directly for temperature; instead we use a trial temperature, calculate site occupancies, solve for temperature, and then iterate until temperatures converge. This feature places important constraints on the QUILF program: because a trial value is required for temperature, the program requires trial values for *all* intensive parameters that are to be calculated. Usually a wild guess suffices, but the interations are more efficient (and, in a few situations, successful only) if the guess is reasonable.

Application of QUILF

Under optimum conditions—which include attainment of equilibrium among the phases in a rock and subsequent preservation of the equilibrium compositions, perfect chemical analyses of those phases, and perfect thermodynamic models—all desired information could be extracted using the minimum number of independent equilibria among the phases. Reality is different: the phases may never have been in equilibrium, or one or more may have continued to react at different conditions from the initial equilibrium; the analyses of one or more phases may be inaccurate; and the solution models may be in error. Furthermore, in all natural examples, the phases are chemically more complex than can be described by our models. For example, both the oxides and the ferromagnesian silicates usually contain Al_2O_3 (at least in spinels and pyroxenes) and MnO. When complete thermodynamic models become available, these (usually but not always "minor") components can be treated rigorously. At present, however, we must use projections into the seven-component space of our models. Wherever possible, our recommended projections are based on experimental data, but at best they are approximations, and they must introduce some uncertainty into the calculations. Errors resulting from the projections must affect some equilibria more than others. For all these reasons, therefore, we have written our QUILF program so as to allow the petrologist maximum flexibility in applying it to a given rock or suite. The user of the program may decide to apply only an independent set of equilibria, to use only a subset of all the equilibria or the phases, or to use the entire set to determine a least-squares "best" fit to the data. This flexibility, however, puts a heavy burden on the user, for he or she must use both intuition and any available qualitative constraints to guard against implausible results. Or occasionally an "implausible" result may force the petrologist to reexamine the basic data (or even a thin section!). Two examples illustrate these ideas.

Example 1. Bohlen and Essene (1977) used two-oxide and two-feldspar thermometry to estimate maximum temperatures of (granulite-facies) metamorphism in the Adirondacks. The two thermometers gave broadly comformable results, indicating peak temperatures near 800°C. Many rocks in the area also contain relatively Fe-rich augite and Opx. These pairs were *not* used in determining metamorphic temperatures, but they provide useful constraints, for had the granulite-facies temperatures exceeded 808°C, these pyroxenes would have reacted to form metamorphic pigeonites. The absence of such pigeonites thus indirectly supports the maximum temperatures inferred from the oxides and feldspars. Had the oxides and feldspars suggested temperatures above 808°C, on the other hand, those values would have had to be treated with great suspicion.

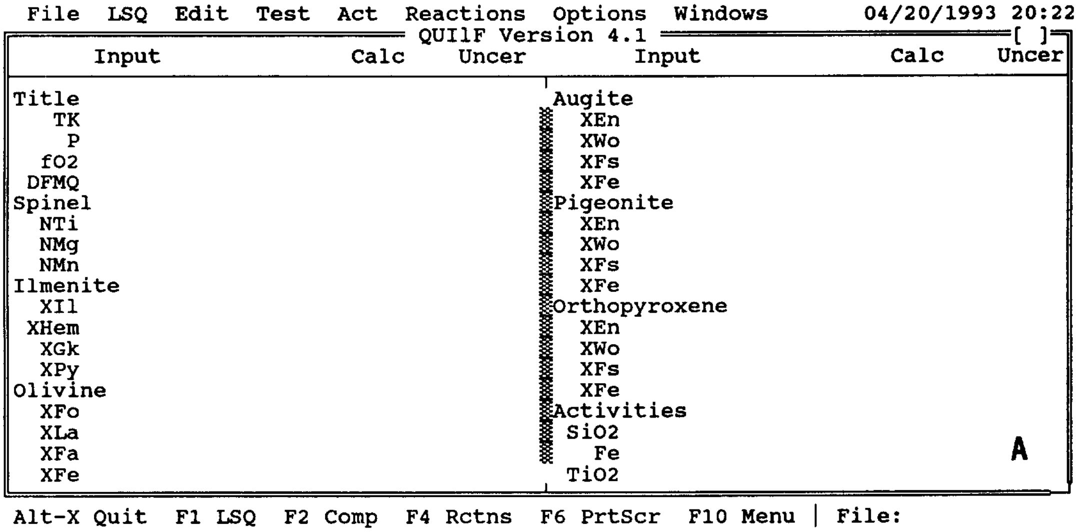
Example 2. Occasionally however, we may be forced to reexamine cherished ideas. For example, the famous "Skaergaard trend" (Brown, 1957) had long been considered definitive for the compositions of augite coexisting with low-Ca pyroxene or olivine or both during the differentiation of basaltic magma. However, in a graphical version of the two-pyroxene thermometer now included in the QUILF program, Lindsley and Andersen (1983; Lindsley, 1983) determined that the Skaergaard trend seemed to reflect *increasing* temperature as differentiation progressed, clearly an implausible result. Either the experiments and the graphical thermometer were wrong, or the Skaergaard trend did not reflect equilibrium. Upon examination of Skaergaard thin sections, Lindsley and Andersen determined unambiguous evidence for granule exsolution of low-Ca pyroxene from the Mg-rich augites. The textures (and later experiments) showed that the augites originally had contained less

$CaSiO_3$ component, but that during cooling, these relatively low-Ca augites had exsolved low-Ca Opx *as separate grains.* The remaining augite thus was enriched in Ca. Because Brown (1957) made wet-chemical analyses of mineral separates, the exsolved granules were analyzed along with the primary Opx, not with the parental augite. The point is that evidence of granule exsolution might never have been searched for if the (graphical) model had not indicated a discrepancy. It is no accident that in both these examples it is the rocks themselves that helped the petrologists reach their conclusions!

THE MAIN PROGRAM

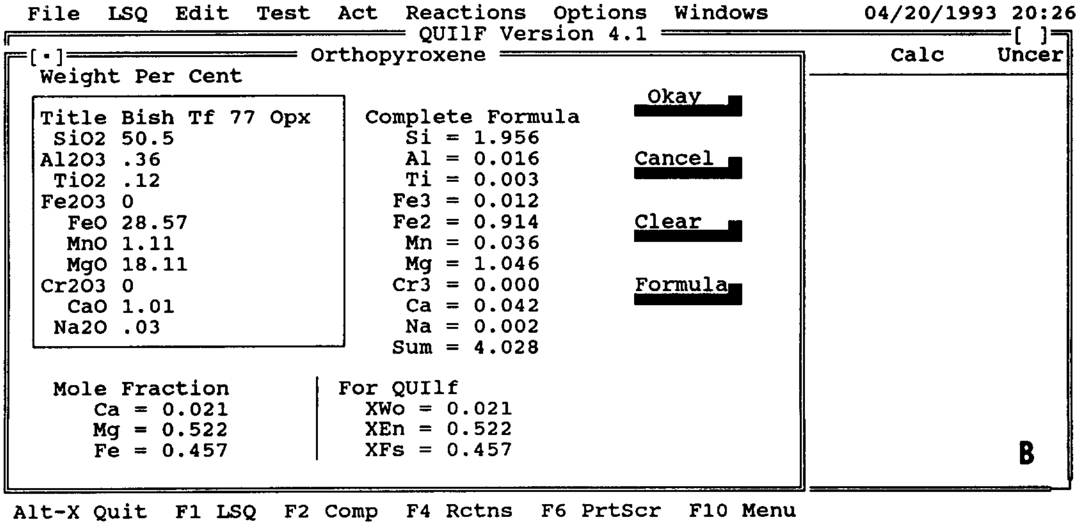
Program QUILF is written in Turbo Pascal for the IBM PC using DOS 2.1 or higher. The compiled program QUILF.EXE is approximately 210 kbytes; it requires two data files (QUILF.RCT, see Appendix; and QUILF.SLN) that total an additional 10 kbytes. It requires 512 K of memory, and runs more efficiently when a math coprocessor is present. Use of a mouse is convenient but not essential. The program is designed to provide the petrologist maximum flexibility in applying the QUIlF equilibria in a wide variety of ways. One can determine temperature and fO_2 from two oxides alone; or temperature and pressure from the silicates alone; or combine all or parts of these. One can calculate phase diagrams by using the program to cycle through portions of T-fO_2 space, or P-T space, or composition space.

Program QUILF uses the solution models and mutually consistent standard-state date to search for equilibrium by free-energy minimization. After each iteration, the free energies indicated by the standard states are compared with those derived from $RT \ln a$



```
Input                  Calc    Uncer        Input                Calc    Uncer

Title                                      Augite
   TK                                        XEn
    P                                        XWo
  fO2                                        XFs
 DFMQ                                        XFe
Spinel                                     Pigeonite
  NTi                                        XEn
  NMg                                        XWo
  NMn                                        XFs
Ilmenite                                     XFe
  XIl                                      Orthopyroxene
 XHem                                        XEn
  XGk                                        XWo
  XPy                                        XFs
Olivine                                      XFe
  XFo                                      Activities
  XLa                                       SiO2
  XFa                                         Fe
  XFe                                       TiO2
```



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Weight Per Cent

Title Bish Tf 77 Opx      Complete Formula
 SiO2 50.5                   Si = 1.956
Al2O3 .36                    Al = 0.016
 TiO2 .12                    Ti = 0.003
Fe2O3 0                     Fe3 = 0.012
  FeO 28.57                 Fe2 = 0.914
  MnO 1.11                   Mn = 0.036
  MgO 18.11                  Mg = 1.046
Cr2O3 0                     Cr3 = 0.000
  CaO 1.01                   Ca = 0.042
 Na2O .03                    Na = 0.002
                            Sum = 4.028

  Mole Fraction         For QUIlf
     Ca = 0.021           XWo = 0.021
     Mg = 0.522           XEn = 0.522
     Fe = 0.457           XFs = 0.457
```

Figure 1. A—Display (Main Screen) for entering data into QUILF; B—projected composition of orthopyroxene, calculated within QUILF. See text for details.

(activity) terms. When the difference between these becomes less than 0.1% for a reaction (or equilibrium), the constraints for that reaction are considered to have been satisfied.

Because the solution models and standard-state terms *must* remain mutually consistent, *no* data in QUILF.SLN should be modified or "updated". Changing *any* values would require remodeling the entire system, a daunting task.

Entering data

To begin executing the program, one types QUILF [cr]. The display illustrated in Figure 1 (the Main Screen) will appear after a status message. The upper left entry (Title) will be highlighted, and the cursor will be just to the right of Title. A short, descriptive title should be entered here; 40 spaces are displayed, but longer titles can be used, as the title scrolls. The full title—up to one line—will be printed in the Print option (see next). The operator then types in the appropriate variables as defined in Table 1. For maximum flexibility, each variable can be input in any of four forms: #; #?; #1, #2, #3; or #1(#2), where # indicates a numeric value. The first form indicates that the variable is to be fixed during the calculations—for example, 1173 (temperature in kelvin), -11.0 ($\log_{10} fO_2$), 0.598 (mole fraction). The second form—a numeric value followed by ?—indicates that it is a trial value only, with a final value to be calculated by the program. For example, a trial temperature of 1173? might yield a calculated value of 902.6 (or 1469.3) K, depending on the compositional variables. The third form sets up a For ... Next loop in the value of the variable. For example, an entry for TK of 923,1474,50 would run the program at 923 K and at 50 K increments up to and including 1473 K. (Because of the vagaries of real numbers, it is best if the upper bound is slightly larger than the target value to assure that the upper limit will be included in the calculations.) In the fourth form, #1 is a preferred value which is followed by an estimated uncertainty (#2) in parentheses. Usually this would be used for compositions [for example, an entry of 0.043(0.004) for XGk refers to a mole fraction of 0.043 ± 0.004 for $MgTiO_3$ in ilmenite] but also can be applied to any other variable. This form computes identically to the second [#?] *unless* it is combined with the third form in at least one of the other variables. When coupled with one or more loops in other variables, the fourth form directs the program to determine an optimum value of the variable that is as close as possible to the input value within its range of uncertainty. For example, if the temperature is being cycled via a For ... Next loop, the program will flag and display that temperature which provides the best fit to, say, a composition that is entered as 0.547(0.01). The four types of data entries are illustrated in the worked examples near the end of this paper.

Editing the Main Screen. Right and left arrow keys are used to position the cursor within an entry. Mistakes can be erased or trial values altered by use of the backspace and Del keys. The Tab key is used to switch between the two sides of the screen. Once a value has been entered (in one of the four forms as described), the operator simply moves the cursor to the next desired entry by using the up and down arrows. It is not necessary to type [CR] to complete an entry; doing so is permitted, but acts simply as the equivalent of down arrow. Temperature in kelvin [TK] and pressure in bar [P] *must* be entered for all calculations, but any other entry can be left blank if

Table 1. Names, definitions, and limits for input variables used in QUILF

Variable	Definition	Input Limits	
TK	Temperature in kelvins	400	1800
P	Pressure in bars	0	100000
fO2	Log_{10} oxygen fugacity	-30	-5
NTi	Number of Ti in spinel (3 cations/4 oxygens)	0	1
NMg	Number of Mg in spinel (3 cations/4 oxygens)	0	2
NMn	Number of Mn in spinel (3 cations/4 oxygens)	0	2
XGk	$MgTiO_3/(Fe_2O_3 + FeTiO_3 + MgTiO_3)$ in ilmenite	0	1
XHem	$Fe_2O_3/(Fe_2O_3 + FeTiO_3 + MgTiO_3)$ in ilmenite	0	1
XFo	Fo/(Fo + Fa + La) in olivine	0	1 - XLa
XLa	La/(Fo + Fa + La) in olivine	0	0.1
XEn	En/(En + Fs + Wo) in augite or pigeonite	0	1 - XWo
XWo	Wo/(En + Fs + Wo) in augite or pigeonite	0	0.5
XEn	En/(En + Fs + Wo) in orthopyroxene	0	1 - XWo
XWo	Wo/(En + Fs + Wo) in orthopyroxene	0	0.2
SiO2	Activity of SiO_2, relative to quartz at P,T	0	1
Fe	Activity of Fe°, relative to pure Fe° at P,T	0	1
TiO2	Activity of TiO_2, relative to rutile at P,T	0	1
Other terms that cannot be input but that appear on the screen:			
DFMQ	log fO_2 relative to FMQ buffer at P,T		
Xil	$FeTiO_3/(Fe_2O_3 + FeTiO_3 + MgTiO_3 + MnTiO_3)$ in ilmenite		
XFe	$Fe^{2+}/(Mg + Fe^{2+})$ in olivine or pyroxene		
XFa	1 - XFo - XLa in olivine		
XFs	1 - XEn - XWo in pyroxene		

desired. Reasons for leaving an entry blank can differ; the most obvious one is that a phase is absent from the assemblage being assessed. However, also it is possible to see how the calculations will run ignoring a phase even if it *is* present. Likewise, if the petrologist does not wish to calculate values for any of the intensive parameters [fO_2; and the activities of SiO_2, Fe, or TiO_2], the appropriate entry or entries should simply be left blank. Of course, if the phases present do not permit calculation of one of those parameters, the entry *must* be left blank or the program will go into an endless loop or print an error message. It also is possible to leave blank a part of a composition. For example, in a two-oxide + olivine + quartz assemblage, the calcium content of the olivine [XLa] may well be small or unknown and can be omitted. Such omissions can be dangerous, however, because one component of each phase [xl (or X_{Mt}) for spinel XIl for ilmenite; the iron end members for the pyroxenes and olivine] is calculated by difference. Thus the omission of, say, XGk from ilmenite or XWo from Opx when these values are nontrivial can introduce substantial errors into the calculations. The user cannot enter values (either trial or fixed) for DFMQ [$\Delta \log fO_2$, or the difference between the calculated $\log fO_2$ and that for the FMQ buffer at the indicated temperature and pressure] or XIl (the mole fraction of $FeTiO_3$ in ilmenite), so the cursor skips these entries. Those headings are present so that the calculated values can be displayed after the program is executed.

To avoid confusion in the ensuing discussion, only values entered in the second [#?] and fourth [#1(#2)] forms will be referred to as *variables*. Other values, which are not allowed to change during a given calculation, will be termed *fixed values*. For simplicity, the discussion also uses the term "reaction" to include both mass-transfer reactions and equilibria such as Fe–Mg exchange or displaced equilibria.

Projection of mineral compositions

Compositional parameters to be entered into the QUILF program *must* have been projected into the appropriate compositional subsystems: $FeO–MgO–MnO–Fe_2O_3–TiO_2$ for the oxides, $CaO–MgO–FeO–SiO_2$ for the ferromagnesian silicates. In addition, the compositions must be expressed in the appropriate form. We recommend strongly that users of the QUILF program use the projection programs that we have developed explicitly for this purpose. The projection from the weight percent of the oxides can be accomplished by using the separate BASIC programs PXPROJ and OXPROJWT, or from within QUILF by selecting Edit from the main menu, selecting the appropriate phase, and entering the composition. The latter approach is particularly convenient for working with only a few assemblages; for large numbers of samples, separate projection may be more efficient.

Projection from within QUILF. To project a composition from within QUILF, from the main screen (Fig. 1A), activate Edit by (1) clicking with the mouse, or from the keyboard (2) by pressing F10, using right arrow to move the highlight to Edit and pressing Enter, or (3) by pressing Alt E. In the window that appears, select a phase to project (for example, Opx) using the mouse or by typing the highlighed hot key. A composition window will open. Type a brief description (if desired), then enter the weight percents of oxides in the phase. Enter zero for Fe_2O_3 if you want the program to calculate ferric iron by charge balance. When sure the entries are correct, activate Formula by clicking or by pressing Alt F. The mineral formula will be calculated and displayed at the right of the window, and the projected components will be shown at the bottom of the screen (Fig. 1A). If the results are satisfactory, activate Okay (click or press Alt k), and the components will be transferred automatically to the Main Screen. There they may be edited as needed, for example converted from the first (fixed value) form to one of the other forms.

PXPROJ program. This projection routine yields suitable values of XEn and XWo for pyroxene thermometry by our methods (Lindsley and Andersen, 1983; Lindsley, 1983; Davidson and Lindsley, 1989). We emphasize that other projections, including those built into many electron microprobe data-reduction programs, will *not* yield suitable results. Particularly egregious are those programs that combine Mn with Fe^{2+}; this is an ancient procedure stemming from the geochemical similarity of Mn and Fe^{2+}. However, an abundance of experimental data shows that Fe^{2+} and Mn have different—and probably opposite—effects on the stability of pyroxenes and olivine. If readers insist on using programs other than those included to provide input into QUILF, we urge them to state so clearly in any publication of the results.

Olivine. We have not developed a separate projection program (except for the projection within QUILF) for olivine; usually the Ca and "others" components are so low that the selection of projection should make little difference. One can use PXPROJ; simply identify the analysis as "opx". As is the situation for pyroxenes, it is important that Mn *not* be lumped with Fe^{2+}.

Oxides. We recommend the use of our projection program OXPROJWT because its output is tailored specifically to the needs of the QUILF program, so that mistakes are less likely to be made in converting the typical X_{Usp} and X_{Ilm} of the earlier programs to the NTi, NMg, NMn, XGk, XPy, and XHem needed in QUILF. As in the situation for the pyroxene projections, we urge petrologists who use QUILF to state clearly, in any publication, the oxide projection scheme used.

Executing the program

Once the input data have been entered to the user's satisfaction, they can be processed in several ways by the short-cut keys, as listed at the base of the screen or the menu items at the top of the screen. Alt-X quits the program. The function key F2 returns to the Main Screen when in another window. Once a set of compositions has been entered, the function key F4 (or Reactions from the menu) allows a subset of possible reactions to be selected. The function key F6 is similar to the Print Scrn key but performs a screen dump more faithfully than does the combination Shift-Print Scrn. The function key F10 allows the Menu items shown on the top of the screen to be selected from the keyboard rather than by using a mouse. The bottom right-hand corner of the screen shows the name of the current file if a set of compositions has been saved from the File menu. Calculations (see next) can be halted by pressing Esc.

Least-squares calculations. In most situations, the user probably will want to perform a least-squares fit to the data. Clicking on LSQ or pressing F1-LSQ uses least-squares to get the "best" values of the variables. When this mode is invoked, the program searches the file QUILF.RCT (see Appendix) to locate all the reactions that are possible among the phases listed *and* that can affect the value of one or more of the variables being refined. In almost all situations the number of possible reactions used exceeds the number of *independent* reactions. Once these have been identified (they may be displayed from the Reactions menu), the program then performs the least-squares calculations and displays the results in the column labeled "Calc". It is easy to compare the initial and model results. Next is a column labeled "Uncer"; this is *not* a statistical uncertainty, but rather an expression of the amount by which the input variables would have to change to permit an exact solution—one that would precisely satisfy all the equilibria. Unless the program determines an exact solution (defined as the residuals for all reactions being less than 0.1%), the reactions that "failed" and their residuals may be displayed in the Test Reactions window (and in the text-file or printer if Print has been activated). The tolerance of 0.1% is necessary in only a few situations, and it is possible to obtain a good solution even if all the reactions are listed as "failed". For example, a residual of 500 J corresponds to an error of approximately 10 degrees—well within the uncertainties of the models—for the FeTi ($Fe^{2+}Ti^{4+}Fe^{3+}_{-2}$) reaction.

Selecting a subset of reactions. Occasionally one may wish to perform the calculations on a subset of the possible equilibria rather than using the whole set. F4 or Reactions-Select provides a window listing all possible equilibria that can affect the values of the variables to be calculated. The petrologist then may select the equilibria desired to solve for the variables. The cursor movement keys are used to move to the desired reactions. Pressing the space-bar selects the highlighted reactions, which then is marked by an [X]. Pressing the space-bar when the cursor is on a reaction already selected will deselect that reaction. The selection process is terminated by pressing Enter. One may SELECT more reactions than there are variables and press F1-LSQ; the program will perform a least-squares fit using only the selected reactions.

Displaying activities. Selecting activities (Act, using the mouse; otherwise Alt A) displays the values of the activities as *calculated for the initial trial values.* Note that the displayed activities are *not* updated to the new, calculated values following the calculations. To see a display of the final activities, one must first run the program to obtain a solution and then *rerun* it using the *calculated equilibrium values* as new input. Selecting Act (Alt A) will display the activities for the equilibrium values. The standard state values that are displayed are those values used in the program and are internally consistent. The standard-state values have been adjusted so that the differences calculated from the equilibria in QUILF.RCT are consistent with one another and should *NOT* be used outside of the program. They are provided only to provide a check on the calculated equilibria and are *NOT* to be compared to other thermodynamic databases.

Options: Watch and Print. Two choices may be set from the Options menu. The first (Watch) is to set a flag so that the intermediate compositions and other values will be displayed on the screen as the program iterates towards a solution. This can be useful especially if the program has failed to converge on a solution, for one may see the intermediate answers approaching an impossible value such as negative pressure or silica activity greater than unity. The second option (Print) allows one to accumulate the calculated values, activities, and tests of equilibria. An output file must be named; selecting the name "PRN" will send the output to the printer; selecting any other name will cause the results to accumulate in an ASCII file of that name.

Files menu. The Files menu allows values to be entered onto the Main Screen from a file, the current input values to be saved to a file, clearing of the Main Screen, or exiting the program.

Windows menu. The Windows menu—which is based on Borland's Turbo Pascal TurboVision environment—provides flexibility in the size and placement of display windows. From this menu, the Main Screen, Activity, Test Reactions, and Selected Reactions windows may be resized, closed, rearranged, or (with the exception of the Main Screen) moved. The windows may be moved by dragging the top of the window frame with a mouse, closed by clicking on the "close" icon at the top left-hand corner of the frame, or resized by dragging the lower right-hand corner. More details on the use of this menu are given in the README file that accompanies the program.

SOME CAVEATS; POTENTIAL PROBLEMS IN USING QUILF

Because the QUIlF equilibria are complex, there are a number of possible pitfalls in using the program. We have identified a number of these; the user is warned by one of the error messages in Table 2. If it seems that the program is hung up, one can abort the calculations by pressing Esc. However, users should be aware that generally, the more phases that are included, and the more variables to be calculated, the longer the program will take to converge to a solution. One must avoid inputting impossible compositions (for example, those for which XEn + XWo > 1 for a pyroxene), or requesting calculation of a variable that is not governed by

Table 2. Error messages and prompts

Message	Meaning
An output file must be specified	A valid DOS filename must be entered.
Calculations halted	The Escape key was pressed, terminating the calculations.
Cannot find file FILENAME	The file FILENAME does not exist in the current drive.
Error # in opening file FILENAME	A Dos Error has occurred (error number #).
Error in Activities of NAME	The program is unable to calculate the activites of NAME. Either the temperature or pressure is outside of the valid range, or the calculation of the site occupancies failed to converge.
Error in calculating the derivatives	The temperature or pressure has reached a value outside of the valid range.
Error in Standard State Routines	The temperature or pressure has reached a value outside of the valid range.
Error reading file: FILENAME Status: # ErrorInfo: # Error writing file: FILENAME Status: # ErrorInfo: #	A DOS error has occurred in reading or writing a file. Either the file doesn't exist, a hardware fault has occurred or the disk is full.
LSQ Error	The matrix inversion routine has failed. The matrix is singular and can't be inverted.
Missing) in LINE	A right paren is needed in LINE.
Missing * in LINE	An asterisk is needed in LINE.
Missing ; in:LINE	A semicolon is needed after the reaction name.
Missing reaction in:LINE	There is no name for the reaction.
No Reactions have been selected	Select reactions before finding a LSQ model or there are no reactions corresponding the variables that have been chosen.
No selected reactions	No reactions are possible with the chosen set of variables.
No variables	At least one parameter must be variable for a LSQ solution.
Not enough independent reactions	There are more variables than there are reactions. A LSQ solution is not possible.
Not enough memory to complete operation	There is insufficient memory to do what was selected.
Syntax error: missing components LINE	A syntax error in the file QUILF.RCT. The reaction must specify the name of appropriate components.

Message	Meaning
Temperature/pressure outside of allowable range	The temperature or pressure has exceeded the allowable limits of the standard state values.
The current solution is no longer valid	In order to test the reactions, the solution must be current. The compositions have been changed since the model was calculated.
The file FILENAME will be overwritten	The file FILENAME already exists in the current directory.
The NAME must be alpha-numeric characters	The reaction name can only be composed of letters and digits.
The reaction name NAME is too long	The name of the reaction is too long. Shorten it.
The temperature and pressure must be specified	Initial values for temperature and pressure must be specified.
The value of NAME can't be changed	Should not happen. The identifier of a cell has been edited.
Too many components in the reaction: LINE	The reaction has too many components. The maximum is four.
Too Many For/Next Variables The maximum is #	There are too many for/next variables.
Too many iterations (#)	Failed to converge within a reasonable number of iterations. Start with values closer to the calculated values or set more compositions constant.
Too many reactions	There are too many reactions possible among the current variables.
Too many reactions (#) in the file MaxAvail # MemAvail #	The file QUILF.RCT has too many reactions for the available amount of memory.
Too many variables maximum is #	You are trying too solve for too many compositions at once.
Too many variables (#) not enough reactions (#)	A model can't be calculated if the number of independent reactions is less than the number of variables.
Unknown component: NAME	The file QUILF.RCT has been edited. NAME is not a valid component.
Unknown error reading file: FILENAME	An unknown DOS error has occurred.

any possible reaction among the phases. Examples include the calculation of fO_2 if no redox equilibria are possible (neither an oxide nor Fe° is present; Fe° is indicated by setting Fe = 1); the calculation of the activity of SiO_2 if no reaction involving SiO_2 is possible; or the calculation of pressure if the phases do not permit assessment of an equilibrium like reaction (6) or a redox derivative of (6). A usual (but subtle) error is to request calculation of the activity of SiO_2 for Fe-rich Opx coexisting with olivine and oxides; if the resulting value of the activity of SiO_2 would exceed 1.0, the program interates for a long time and eventually gives error message "Too many independent variables, not enough independent reactions:". Use of the Options—WATCH On option should enable the user to detect this problem; the value of SiO_2 will advance to and remain pinned at 1.0 for all iterations. Values of XEn or XFo close to 0 or 1 may lead to error messages, as the program may be unable to calculate the corresponding derivatives.

Special problems with pyroxenes. Calculation of pyroxene equilibria can pose problems: for example, the program will calculate (metastable) augite + opx equilibrium even though pigeonite or olivine + quartz + augite may be more stable. One may wish to calculate such metastable equilibria, but in any situation, it is the user's responsibility to test whether another assemblage may be more stable.

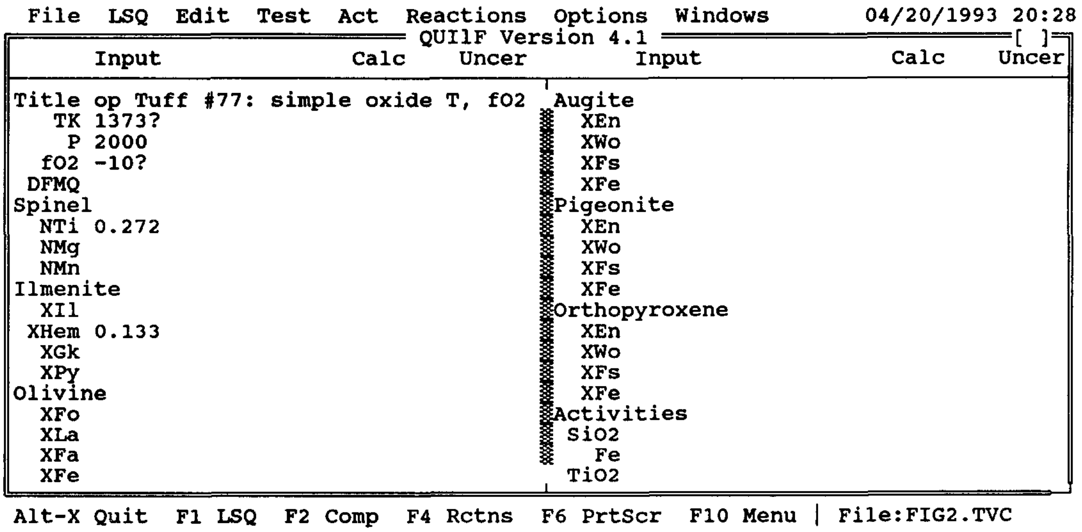
Pigeonite. Calculations involving pigeonite can be particularly difficult. Because the pyroxene solution model treats (high temperature) pigeonite and augite as the same clinopyroxene solution, attempts to calculate coexisting augite + pigeonite may yield identical compositions for both phases even for bulk compositions for which two clinopyroxenes are stable. This problem usually can be avoided by selecting trial compositions close to the equilibrium compositions. Another problem is the calculation of pigeonite + opx equilibria. These phases can coexist for Fe-rich compositions at temperatures above approximately 808°C; up to approximately 1200°C, however, as compositions become more magnesian, the stable assemblage becomes pigeonite + augite + opx and eventually augite + opx. The QUILF program may continue to calculate pigeonite in (apparent) equilibrium with orthopyroxene even for Mg-rich compositions and even when the initial composition of the clinopyroxene is calcic. This problem apparently results from the gentle curvature of the clinopyroxene free-energy curve near the crest of the miscibility gap; evidently the program can calculate a "minimum" free energy (within the 0.1% tolerance) for pigeonite + opx within this region. If the user suspects this problem is occurring, we recommend comparison of the results with published pyroxene quadrilateral diagrams such as those given by Lindsley and Frost (1992). This problem generally can be avoided by starting the calculations at magnesian compositions (near the Di–En join) and using each calculated XWo as the trial value for the next, slightly more Fe-rich bulk composition to be calculated.

Pressure from two pyroxenes. The user must be careful not to let the program calculate pressure from the compositions of coexisting pyroxenes. Small differences in pyroxene compositions—well within analytical error—can affect apparent pressures *as calculated from two pyroxenes* by many kilobars. This is because the pyroxene models have nonzero differences in their volume terms, and the program happily will "refine" the pressure so as to "improve" the fit to the compositions. The cure of this problem is simple, but must not be overlooked: *never* allow pressure to vary when the compositions of two pyroxenes are completely fixed! Either fix the pressure also, or allow at least one component of the pyroxene to differ.

SOME WORKED EXAMPLES

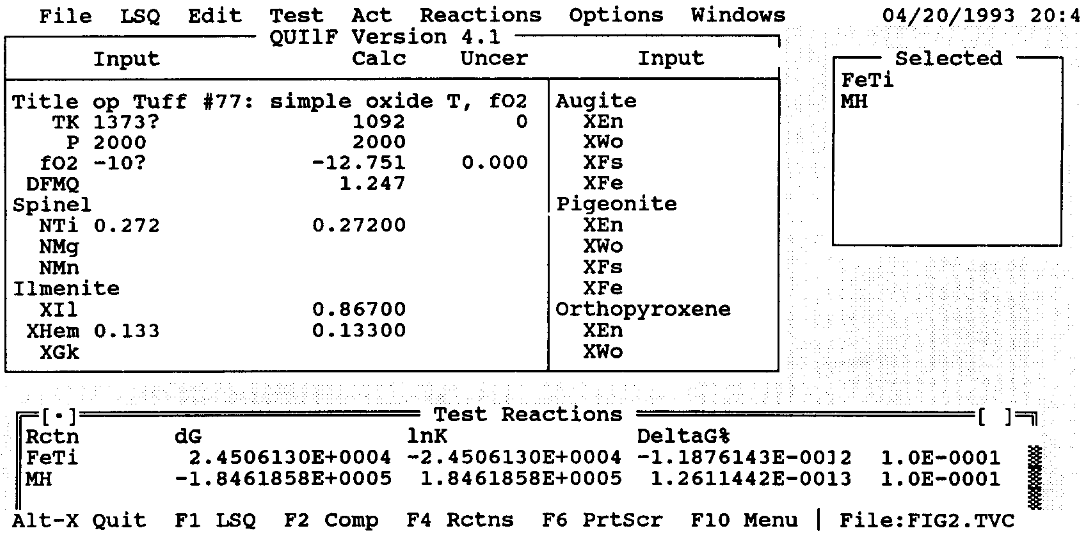
Because running Program QUILF can be tricky, we give a number of worked examples to illustrate its application. The examples have been selected for a sample from the Bishop Tuff (Hildreth, 1977). The sample (#77) contains Ti–magnetite (NTi = 0.272; NMg = 0.043), ilmenite (XGk = 0.062; XHem = 0.133), Opx (XEn = 0.522; XWo = 0.021), augite (XEn = 0.383; XWo = 0.383), and quartz. We strongly recommend that a new user work through these examples before attempting calculations on his or her samples.

Two-oxide temperature. First we obtain a conventional two-oxide temperature and fO_2. A trial value of 1373? is entered for TK, and a fixed pressure of 2000 bar is used. (The selection of pressure is unimportant here because the two-oxide thermometer is essentially independent of pressure.) Then comes a trial value of − 10? for fO2, and the values of NTi and XHem are entered, as shown in Figure 2. Next, the petrologist presses F1-LSQ to start the calculation. The results are shown in Figure 3. The temperature is calculated as 1092 K (819°C); values also are given for fO2 (log fO_2) and DFMQ (Δ log fO_2, the difference between the calculated log fO_2 and that for the FMQ buffer at the same P and T). The value for XIl (which here is simply 1 − XHem) also is shown. The uncertainties are shown as zero because this is an



```
Title op Tuff #77: simple oxide T, fO2  Augite
   TK 1373?                                XEn
    P 2000                                 XWo
  fO2 -10?                                 XFs
 DFMQ                                      XFe
Spinel                                  Pigeonite
  NTi 0.272                                XEn
  NMg                                      XWo
  NMn                                      XFs
Ilmenite                                   XFe
  XIl                                   Orthopyroxene
 XHem 0.133                                XEn
  XGk                                      XWo
  XPy                                      XFs
Olivine                                    XFe
  XFo                                   Activities
  XLa                                    SiO2
  XFa                                      Fe
  XFe                                    TiO2
```

Figure 2. Display after title, trial temperature, pressure, and oxide compositions have been entered, but before calculations have been initiated by pressing F1. Pressure and compositions are fixed; TK and fO2 are allowed to differ in calculations as shown by "?" following trial values.



```
File  LSQ  Edit  Test  Act  Reactions  Options  Windows       04/20/1993 20:4
                   QUIlF Version 4.1
      Input              Calc     Uncer          Input                  Selected
                                                                     FeTi
Title op Tuff #77: simple oxide T, fO2   Augite                     MH
   TK 1373?              1092         0    XEn
    P 2000               2000              XWo
  fO2 -10?            -12.751     0.000    XFs
 DFMQ                   1.247              XFe
Spinel                                   Pigeonite
  NTi 0.272           0.27200              XEn
  NMg                                      XWo
  NMn                                      XFs
Ilmenite                                   XFe
  XIl                 0.86700            Orthopyroxene
 XHem 0.133           0.13300              XEn
  XGk                                      XWo

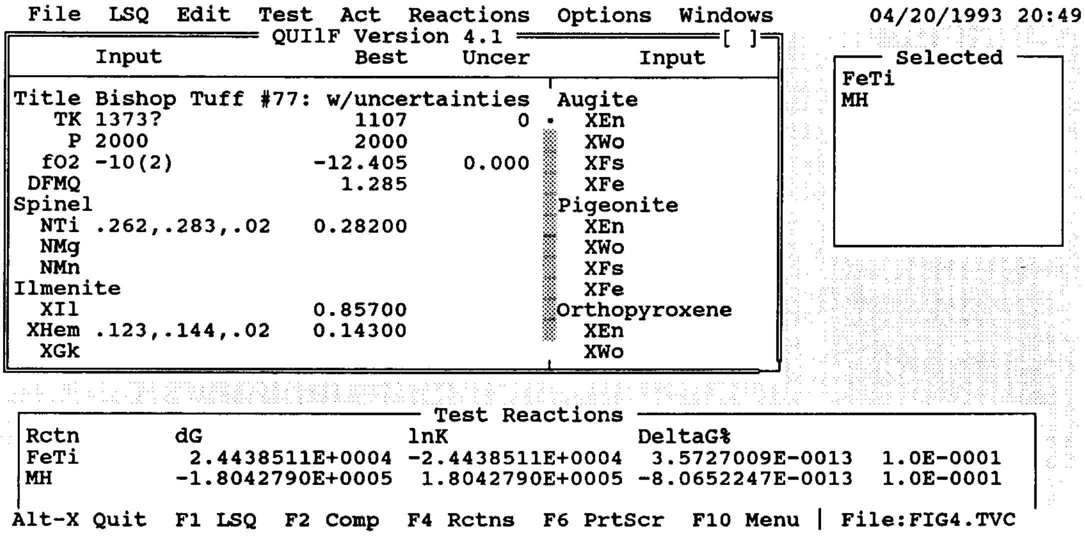
[•]                        Test Reactions                          [ ]
Rctn          dG                lnK               DeltaG%
FeTi           2.4506130E+0004 -2.4506130E+0004 -1.1876143E-0012  1.0E-0001
MH            -1.8461858E+0005  1.8461858E+0005  1.2611442E-0013  1.0E-0001

Alt-X Quit  F1 LSQ  F2 Comp  F4 Rctns  F6 PrtScr  F10 Menu | File:FIG2.TVC
```

Figure 3. Display after calculations have been completed. Calculated temperature in kelvin, Δlog fO_2 relative to FMQ buffer, and log fO_2 are shown in column headed "Calc", together with fixed values. *Note*: two windows have been tiled onto main screen: Selected Reactions at right and Test (Reactions) at bottom. These do not appear automatically; for illustration, they have been invoked by selecting Reactions and Test from upper menu of Main Screen. Two "Selected Reactions"—FeTi and MH—used in calculations are displayed at right.

exact solution: there are two unknowns (TK and fO2) and two reactions (FeTi and MH), as shown on the right. In Figure 3 (also Figs. 4–6), we have tiled two windows onto the Main Screen: the Reactions on the right, and Test (Reactions) at the bottom. These will not appear automatically, but would have to be invoked by selecting Reactions and Test from the upper menu. After calling either of these, the user can return to the Main Screen by pressing F2.

Uncertainties. Of course, the real uncertainties in temperature and fO_2 are not zero. Uncertainties resulting solely from the solution models for the oxides are approximately ±10°C and ±0.1 log units in fO_2 (Andersen and Lindsley, 1988). If we assume reasonable uncertainties of ±0.01 mol fraction in the compositions for the oxides of #77, we can calculate their effect by cycling the calculations through the extreme compositions. One enters the extreme compositional values in the third form (Fig. 4). Purely for illustrative purposes, we show fO2 entered in the fourth form [−10(2)]. Figure 4 shows the input data with the compositions in For ... Next form.

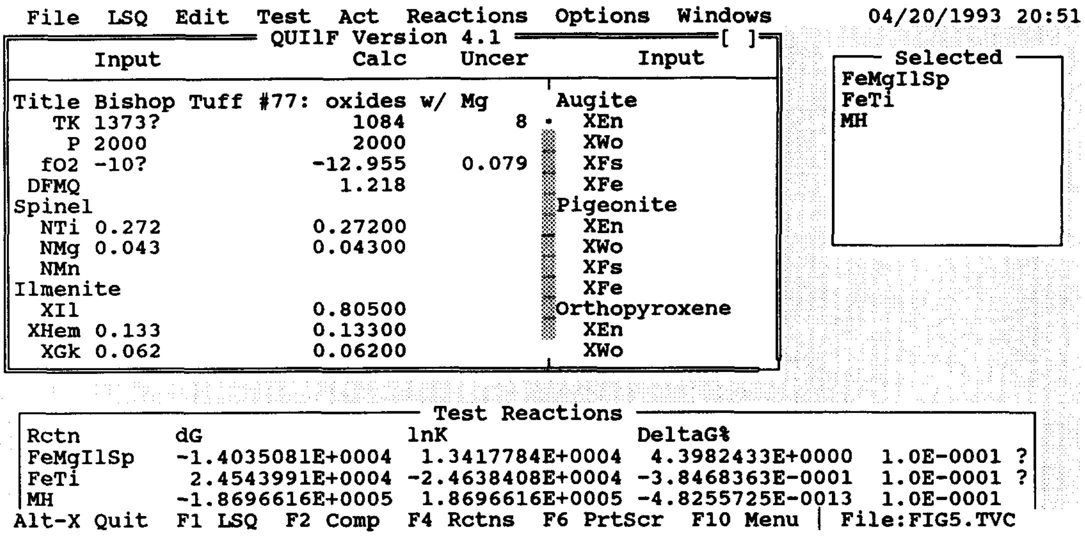


```
File  LSQ  Edit  Test  Act  Reactions  Options  Windows       04/20/1993 20:49
                   QUIlF Version 4.1                 [ ]
      Input              Best     Uncer          Input                  Selected
                                                                     FeTi
Title Bishop Tuff #77: w/uncertainties   Augite                     MH
   TK 1373?              1107         0 •  XEn
    P 2000               2000              XWo
  fO2 -10(2)          -12.405     0.000    XFs
 DFMQ                   1.285              XFe
Spinel                                   Pigeonite
  NTi .262,.283,.02   0.28200              XEn
  NMg                                      XWo
  NMn                                      XFs
Ilmenite                                   XFe
  XIl                 0.85700            Orthopyroxene
 XHem .123,.144,.02   0.14300              XEn
  XGk                                      XWo

                           Test Reactions
Rctn          dG                lnK               DeltaG%
FeTi           2.4438511E+0004 -2.4438511E+0004  3.5727009E-0013  1.0E-0001
MH            -1.8042790E+0005  1.8042790E+0005 -8.0652247E-0013  1.0E-0001

Alt-X Quit  F1 LSQ  F2 Comp  F4 Rctns  F6 PrtScr  F10 Menu | File:FIG4.TVC
```

Figure 4. Calculations of T and log fO_2 for assumed analytical uncertainties of 0.01 mol fraction in both Ti-magnetite and ilmenite. Compositions are entered in third form (see text) to set up For ... Next loops. Entry for fO2 is in fourth form [#1(#2)] so that program will select set of compositions that yields log fO_2 closest to this value. "Best Fit" values are displayed at end of calculations. This is shown for illustration only, and has no petrological significance here.



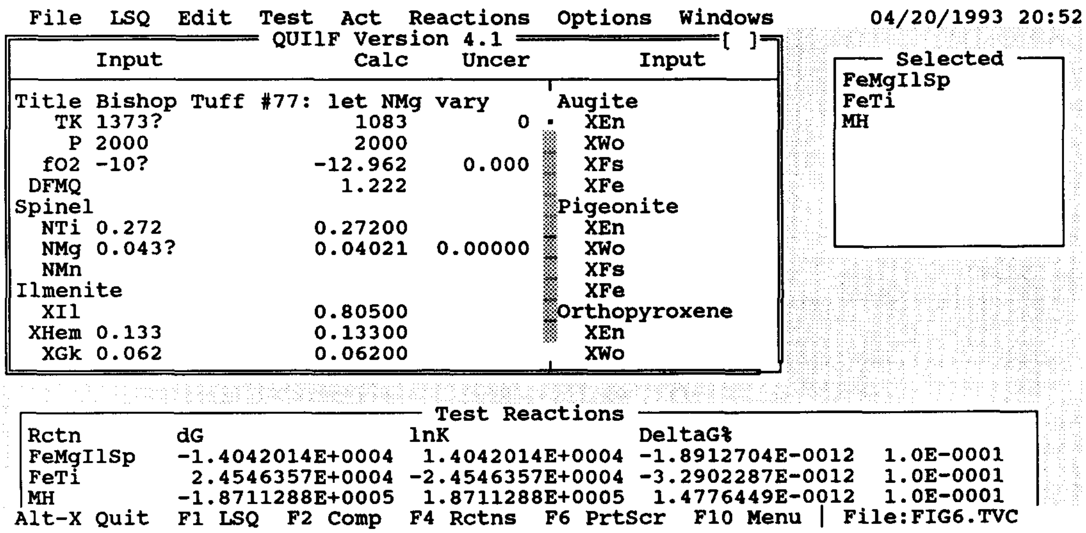
```
                                                              04/20/1993 20:51
                  QUIlF Version 4.1
     Input              Calc      Uncer          Input
Title Bishop Tuff #77: oxides w/ Mg           Augite                Selected
   TK 1373?            1084            8       XEn                FeMgIlSp
    P 2000             2000                    XWo                FeTi
  fO2 -10?          -12.955        0.079       XFs                MH
 DFMQ                 1.218                    XFe
Spinel                                        Pigeonite
  NTi 0.272         0.27200                    XEn
  NMg 0.043         0.04300                    XWo
  NMn                                          XFs
Ilmenite                                       XFe
  XIl               0.80500                   Orthopyroxene
 XHem 0.133         0.13300                    XEn
  XGk 0.062         0.06200                    XWo

                          Test Reactions
Rctn        dG                lnK               DeltaG%
FeMgIlSp    -1.4035081E+0004  1.3417784E+0004  4.3982433E+0000  1.0E-0001 ?
FeTi         2.4543991E+0004 -2.4638408E+0004 -3.8468363E-0001  1.0E-0001 ?
MH          -1.8696616E+0005  1.8696616E+0005 -4.8255725E-0013  1.0E-0001
```

Figure 5. Repetition of calculations of oxide temperatures, except now Mg contents have been included. Of three possible reactions shown at right, two "failed" because their residuals were greater than 0.1%. "Uncertainties" shown for TK and fO2 are formal mathematical errors and are smaller than real uncertainties.

Pressing F1 now will lead to the calculation of four T-fO_2 pairs based on the four possible combinations of extreme ilmenite and magnetite compositions. These values will appear quickly on the screen; they may be saved by first using Options (upper menu) to turn on the printer (file PRN) or to make an ASCII file (e.g. FIG4.OUT) of the results. Examination of the model values show a range in temperature of 30°; DFMQ differs through a range of 0.256 log units (note that the range in log fO_2 is greater because it includes the temperature effect on fO_2). Thus the combined errors in temperature and DFMQ for this sample are approximately ±25°C and 0.133, respectively. At the end of these calculations, the screen displays the "best" value—defined as the set of compositions that yielded the calculated value of log fO2 closest to the trial value of −10(2). The closest match to that value was obtained for NTi = 0.282, XHem = 0.143. We emphasize that this "best" fO_2 has no petrologic significance in our example; it was included only to illustrate the effect of combining an entry in the fourth form [#1(#2)] with one or more For ... Next loops in other values.

Effects of MgO. Next we can include the effects of MgO in the oxides; we restore *N*Ti and *X*Hem to their nominal values, and add NMg and XGk. Figure 5 shows the input values at the left, the results after LSQ calculation in the "Calc" column, formal errors in TK and fO2 under "Uncer", and three reactions—FeMgIlSp in addition to FeTi and MH—in the



```
                                                              04/20/1993 20:52
                  QUIlF Version 4.1
     Input              Calc      Uncer          Input
Title Bishop Tuff #77: let NMg vary           Augite                Selected
   TK 1373?            1083            0       XEn                FeMgIlSp
    P 2000             2000                    XWo                FeTi
  fO2 -10?          -12.962        0.000       XFs                MH
 DFMQ                 1.222                    XFe
Spinel                                        Pigeonite
  NTi 0.272         0.27200                    XEn
  NMg 0.043?        0.04021      0.00000       XWo
  NMn                                          XFs
Ilmenite                                       XFe
  XIl               0.80500                   Orthopyroxene
 XHem 0.133         0.13300                    XEn
  XGk 0.062         0.06200                    XWo

                          Test Reactions
Rctn        dG                lnK               DeltaG%
FeMgIlSp    -1.4042014E+0004  1.4042014E+0004 -1.8912704E-0012  1.0E-0001
FeTi         2.4546357E+0004 -2.4546357E+0004 -3.2902287E-0012  1.0E-0001
MH          -1.8711288E+0005  1.8711288E+0005  1.4776449E-0012  1.0E-0001
```

Figure 6. Calculation including Mg contents, but this time NMg is allowed to differ so as to be in equilibrium with XGk. Calculated value of NMg is within analytical accuracy of trial value.

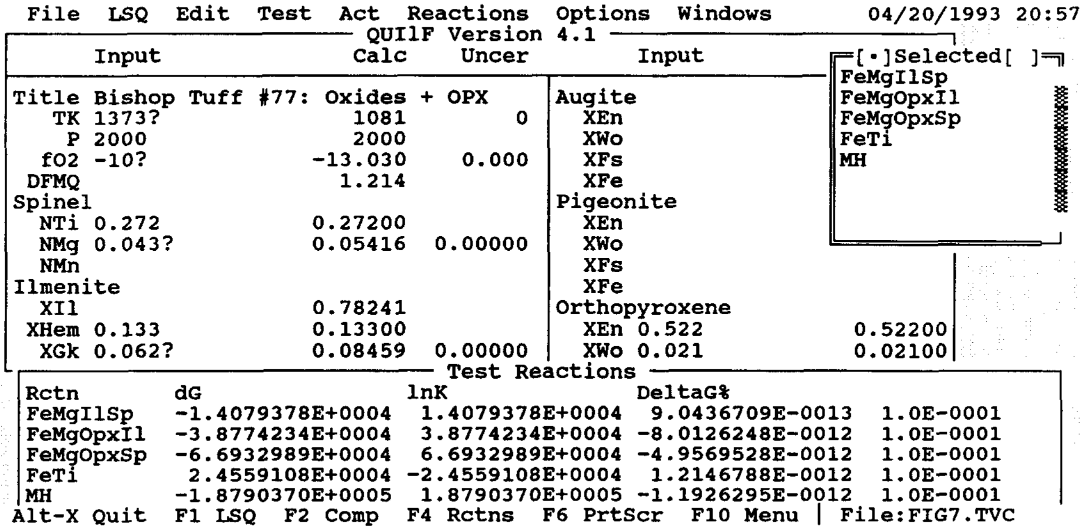
Selected Reactions and Test Reactions windows. Note that two reactions "failed" (that is, their residuals are greater than 0.1%) as indicated by the ? following FeMgIlSp and FeTi in the Test Reactions window. This is because the Mg contents of the Ti-spinel and the ilmenite are not in perfect equilibrium (at least according to the solution models). The indicated temperature is slightly (but not significantly) lower than that obtained by ignoring MgO. We can determine just how far the oxides are from mutual Fe–Mg exchange equilibrium by letting one Mg component differ; in Figure 6, XGk has been fixed and NMg allowed to differ. The calculated value for NMg (0.0402) is within 10% (and probably within analytical uncertainty) of the original value; the effect of the change on temperature is trivial. Note that once again we have three variables and three reactions, so the solution is mathematically exact, and there are no formal errors. The reader is invited to practice by repeating this step fixing NMg and allowing XGk to be calculated.

Now we can ask whether the reported MgO contents of the oxide minerals are in Fe–Mg exchange equilibrium with one of the pyroxenes—say, Opx. The values of *X*En and *X*Wo for orthopyroxene are entered, and both NMg and XGk are allowed to differ (Fig. 7). The calculated values of NMg and XGk show marginally significant increases of approximately 25%. It is possible that these increases are artifacts of the solution models; however, Frost and Lindsley (1992) have argued strongly that even quickly cooled oxides such as those in the Bishop Tuff tend to expel Mg upon cooling. For purposes of this illustration, we shall assume that the calculated values are more nearly correct. Note that there are now five possible reactions—FeTi, MH, FeMgIlSp, FeMgOpxIl, and FeMgOpxSp—but note also that the fifth one can be derived from the third and fourth. Thus we have four unknowns and four independent reactions, and hence an exact solution. The "Selected" window that had been tiled over previous figures has been removed from Figure 7 so that the Opx compositions are visible.

Pyroxene equilibria for Bishop Tuff # 77

At this stage it is useful to determine the temperature using the two pyroxenes. Use backspace to delete the entries for fO2, NTi, NMg, XGk, and XHem, and then add the values for XEn and XWo in augite. The effect of pressure is no longer completely negligible, but for the moment we shall retain the fixed value of 2000 bar and allow temperature to vary. Figure 8 shows the results of the calculation; there is one unknown (temperature) but four equations (only three of which are independent)—the equality of each pair of end-member chemical potentials for Opx and augite. The residuals (DeltaG%) range in relative magnitude from 0.6 to 259%; the formal uncertainty in temperature is 16.1 K. The relatively low value of that uncertainty indicates that the Opx and augite as input are close to being in equilibrium according to the models. The high *percentage* of the residuals results from the relatively low numeric values for both d*G* and ln*K*.

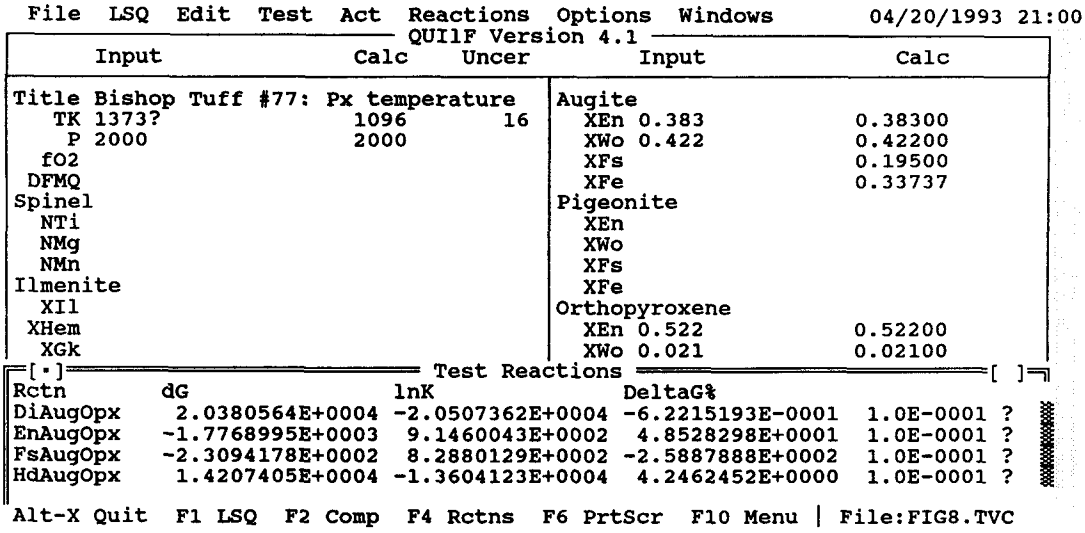
Note that the augite and Opx compositions are each separate geothermometers, so long as it is specified that the other phase is present. As was the situation for the oxides, therefore, we can test for departure from equilibrium by allowing the composition of one pyroxene to differ so as to be in equilibrium with the other. Either composition could be allowed to differ; in this example we let augite differ, because there is some ambiguity in the amount of Fe^{3+} in the projected analysis, an ambiguity that carries over into the projected values of XEn and XWo. Thus in Figure 9, the augite composition was



```
 File  LSQ  Edit  Test  Act  Reactions  Options  Windows      04/20/1993 20:57
      Input                    Calc     Uncer          Input
Title Bishop Tuff #77: Oxides + OPX           Augite
   TK 1373?                    1081         0    XEn
    P 2000                     2000              XWo
  fO2 -10?                  -13.030     0.000    XFs
 DFMQ                         1.214              XFe
Spinel                                        Pigeonite
  NTi 0.272                 0.27200              XEn
  NMg 0.043?                0.05416   0.00000    XWo
  NMn                                            XFs
Ilmenite                                         XFe
  XIl                       0.78241           Orthopyroxene
 XHem 0.133                 0.13300              XEn 0.522            0.52200
  XGk 0.062?                0.08459   0.00000    XWo 0.021            0.02100
                              Test Reactions
 Rctn       dG                lnK               DeltaG%
 FeMgIlSp   -1.4079378E+0004  1.4079378E+0004  9.0436709E-0013  1.0E-0001
 FeMgOpxIl  -3.8774234E+0004  3.8774234E+0004 -8.0126248E-0012  1.0E-0001
 FeMgOpxSp  -6.6932989E+0004  6.6932989E+0004 -4.9569528E-0012  1.0E-0001
 FeTi        2.4559108E+0004 -2.4559108E+0004  1.2146788E-0012  1.0E-0001
 MH         -1.8790370E+0005  1.8790370E+0005 -1.1926295E-0012  1.0E-0001
```

```
[•]Selected[ ]
FeMgIlSp
FeMgOpxIl
FeMgOpxSp
FeTi
MH
```

Figure 7. Calculations allowing Mg contents of oxides to be in Fe–Mg exchange equilibrium with Opx. Both NMg and XGk calculate to be about 25% greater than original values.



```
 File  LSQ  Edit  Test  Act  Reactions  Options  Windows       04/20/1993 21:00
                                QUIlF Version 4.1
       Input                  Calc    Uncer         Input                  Calc

Title Bishop Tuff #77: Px temperature   Augite
   TK 1373?               1096        16  XEn 0.383                 0.38300
    P 2000                2000            XWo 0.422                 0.42200
   fO2                                    XFs                       0.19500
  DFMQ                                    XFe                       0.33737
Spinel                                  Pigeonite
   NTi                                    XEn
   NMg                                    XWo
   NMn                                    XFs
Ilmenite                                  XFe
   XIl                                  Orthopyroxene
  XHem                                    XEn 0.522                 0.52200
   XGk                                    XWo 0.021                 0.02100
[•]                           Test Reactions                                [ ]
Rctn          dG                 lnK                DeltaG%
DiAugOpx      2.0380564E+0004 -2.0507362E+0004 -6.2215193E-0001  1.0E-0001 ?
EnAugOpx     -1.7768995E+0003  9.1460043E+0002  4.8528298E+0001  1.0E-0001 ?
FsAugOpx     -2.3094178E+0002  8.2880129E+0002 -2.5887888E+0002  1.0E-0001 ?
HdAugOpx      1.4207405E+0004 -1.3604123E+0004  4.2462452E+0000  1.0E-0001 ?

Alt-X Quit  F1 LSQ  F2 Comp  F4 Rctns  F6 PrtScr  F10 Menu | File:FIG8.TVC
```

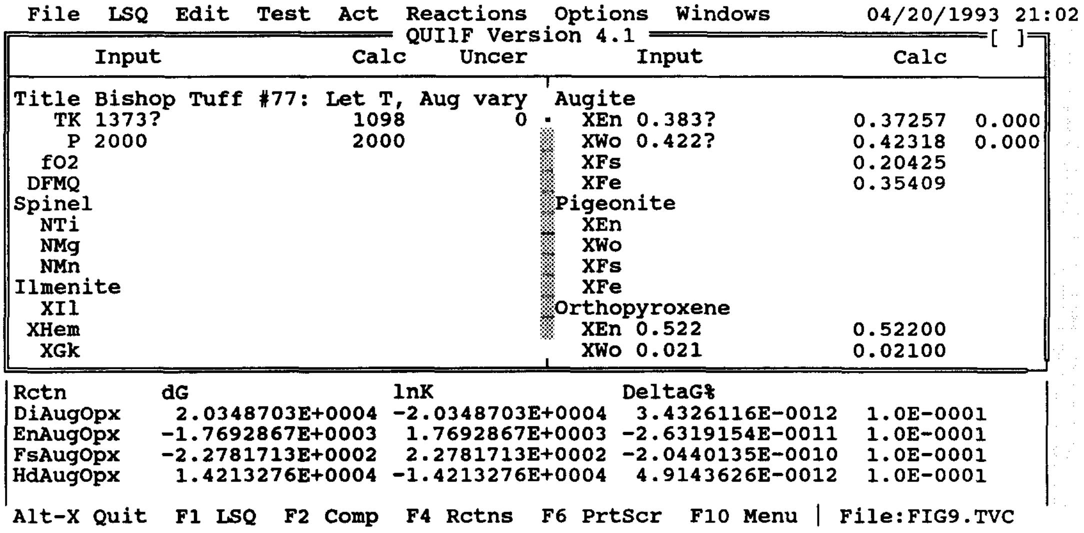
Figure 8. Least-squares calculation of pyroxene temperature for 2000 bar. Nonzero values for Uncertainties show that compositions as entered are not in perfect equilibrium according to models.

allowed to differ. The model values are within analytical uncertainty of the input composition, and the calculated temperature changes insignificantly. We conclude that the augite and Opx of sample #77 were in equilibrium at approximately 1098 K. That temperature is slightly greater than, but within the overall uncertainty of, the temperature inferred from the oxides. For simplicity in the next example, we shall continue to allow the augite compositions to differ so as to remain in exact equilibrium with Opx.

Putting it all together

Figure 10 illustrates the results of using all five phases to calculate QUIlF equilibria. For the first time in these examples, we allow pressure to vary. To permit the oxide temperature to equal that indicated by the Opx, we allow XHem to differ. (We could have allowed NTi in the Ti-magnetite to differ, but modal data for the Bishop Tuff indicate that magnetite is about 10 times as abundant as ilmenite, so that if either phase has reset slightly it is likely to be the ilmenite.) Now there are 17 possible reactions used in the least squares. The result is an "exact" solution that yields 1100 K and 2553 bar. Calculations on numerous other samples from the Bishop Tuff led Frost and Lindsley (1992) to conclude that the overal uncertainties in temperature and pressure are approximately ±20 K and ±500 bar. The reader is invited to repeat the calculations by allowing different compositions to differ. One obvious choice is to fix augite and to allow the Opx to differ. The results should include 1111 K, 2452 bar, with XEn = 0.54357 and XWo = 0.02099 calculated for Opx.

It is important to note that the calculations illustrated in Figure 10 will not yield meaningful pressures



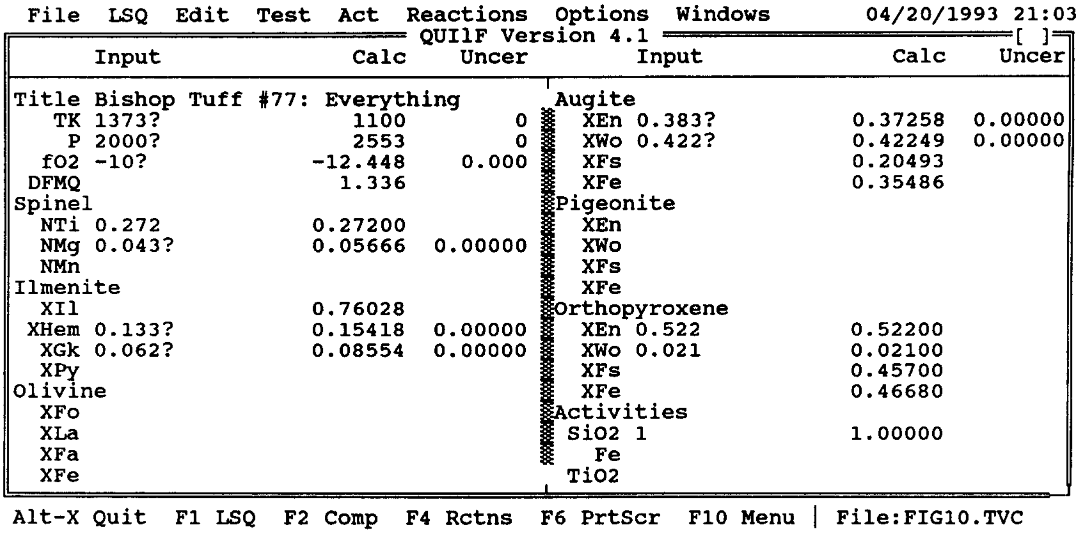
```
 File  LSQ  Edit  Test  Act  Reactions  Options  Windows       04/20/1993 21:02
                                QUIlF Version 4.1                           [ ]
       Input                  Calc    Uncer         Input                  Calc

Title Bishop Tuff #77: Let T, Aug vary  Augite
   TK 1373?               1098         0 • XEn 0.383?               0.37257  0.000
    P 2000                2000             XWo 0.422?               0.42318  0.000
   fO2                                     XFs                      0.20425
  DFMQ                                     XFe                      0.35409
Spinel                                   Pigeonite
   NTi                                     XEn
   NMg                                     XWo
   NMn                                     XFs
Ilmenite                                   XFe
   XIl                                   Orthopyroxene
  XHem                                     XEn 0.522                0.52200
   XGk                                     XWo 0.021                0.02100

Rctn          dG                 lnK                DeltaG%
DiAugOpx      2.0348703E+0004 -2.0348703E+0004  3.4326116E-0012  1.0E-0001
EnAugOpx     -1.7692867E+0003  1.7692867E+0003 -2.6319154E-0011  1.0E-0001
FsAugOpx     -2.2781713E+0002  2.2781713E+0002 -2.0440135E-0010  1.0E-0001
HdAugOpx      1.4213276E+0004 -1.4213276E+0004  4.9143626E-0012  1.0E-0001

Alt-X Quit  F1 LSQ  F2 Comp  F4 Rctns  F6 PrtScr  F10 Menu | File:FIG9.TVC
```

Figure 9. Least-squares calculation of orthopyroxene temperature for 2000 bar; augite composition is allowed to differ. Initial and calculated compositions for augite agree within analytical uncertainty, showing that augite were essentially in equilibrium with Opx.



```
 File  LSQ  Edit  Test  Act  Reactions  Options  Windows      04/20/1993 21:03
════════════════════════════ QUIlF Version 4.1 ═══════════════════════════[ ]═
      Input                 Calc    Uncer         Input              Calc    Uncer
Title Bishop Tuff #77: Everything       Augite
   TK 1373?                 1100        0    XEn 0.383?          0.37258  0.00000
    P 2000?                 2553        0    XWo 0.422?          0.42249  0.00000
  fO2 -10?               -12.448    0.000    XFs                 0.20493
 DFMQ                      1.336             XFe                 0.35486
Spinel                                      Pigeonite
  NTi 0.272              0.27200             XEn
  NMg 0.043?             0.05666  0.00000    XWo
  NMn                                        XFs
Ilmenite                                     XFe
  XIl                    0.76028            Orthopyroxene
 XHem 0.133?             0.15418  0.00000    XEn 0.522           0.52200
  XGk 0.062?             0.08554  0.00000    XWo 0.021           0.02100
  XPy                                        XFs                 0.45700
Olivine                                      XFe                 0.46680
  XFo                                       Activities
  XLa                                        SiO2 1              1.00000
  XFa                                          Fe
  XFe                                        TiO2
Alt-X Quit   F1 LSQ   F2 Comp   F4 Rctns   F6 PrtScr   F10 Menu | File:FIG10.TVC
```

Figure 10. Calculations for all five phases, including quartz. Only NTi, SiO2, and composition of Opx are fixed; other values are allowed to differ so as to permit exact solution. There is greater number of possible reactions (not shown). Coexistence of oxides, Opx, and quartz permits pressure to be calculated, along with T and fO_2.

if the compositions of both pyroxenes are fixed. This is because small variations in XEn in both augite and orthopyroxene—well within analytical error—can result in apparent pressure differences of thousands of bars as calculated from pyroxene–pyroxene equilibria (see the section "Special Problems with Pyroxenes"), and these apparent pressures overwhelm the appropriate values calculated from reaction (6) and its derivatives. As emphasized earlier, only pressures that are calculated from reaction (6) and its redox derivatives should be believed. For Bishop Tuff sample #77, the appropriate equilibria are (see Appendix): OmQ ($3Fe_2Si_2O_6$ (in Opx) + $O_2 = 2Fe_3O_4 + 6SiO_2$), OHQ ($2Fe_2Si_2O_6$ (in Opx) + $O_2 = 2Fe_2O_3 + 4SiO_2$), AMQ ($3Fe_2Si_2O_6$ (in augite) + $O_2 = 2Fe_3O_4 + 6SiO_2$) and AHQ ($2Fe_2Si_2O_6$ (in augite) + $O_2 = 2Fe_2O_3 + 4SiO_2$). In all these situations, fayalite in the primary equilibrium (6) has been replaced by its oxidized equivalents magnetite + quartz or hematite + quartz.

SUMMARY AND RECOMMENDATIONS

QUILF is a powerful program, but its use should never be a replacement for thought. Rarely does one obtain interpretable results by plunging ahead and including all phases of an assemblage in the initial calculation. We recommend that users follow the gradual build-up to the full assemblage that we illustrate for the Bishop Tuff. The more gradual approach may enable the petrologist to identify a phase whose analysis is suspect. "Routine" microprobe analyses that may seem satisfactory when one applies a single geothermometer or barometer may not be adequate when multiple equilibria are considered simultaneously as in QUILF. Indeed, one of our "Beta" testers reports that the first result of his use of QUILF was to force him to re-do many of his microprobe analyses! Rarely does one encounter a set of phases as well analyzed and well behaved as those of the Bishop Tuff, and even there we were forced to the conclusion that the ilmenite could not have been in equilibrium with the other phases. We like to think that our solution models are realistic and that the QUILF program is sophisticated—but nothing substitutes for petrologic intuition and common sense. Please use the program wisely! Experiment by letting various components of various phases differ; this will help the user to get a feel as to whether the assemblage is close to equilibrium and where any problems may lie.

Acknowledgments—We thank Ron Frost for encouraging us to think about QUIlF equilibria at many stages through the years and for serving as a guinea pig in using the program. Support by NSF grant EAR-9104024 and its predecessors to DHL is gratefully acknowledged.

Obtaining working copies of the programs—Readers who wish to obtain copies of QUILF should send an unformatted diskette (either 3.5 or 5.25", regular or high density) to DHL. A self-addressed adhesive mailing label, *unattached*, would be helpful. It has been our experience that approximately one in ten 5.25" diskettes becomes physically (not magnetically) damaged in the mail; accordingly, readers should be sure that their diskettes are well protected, preferably in sturdy mailers. We will provide QUILF.EXE, QUILF.RCT, QUILF.SLN, and README; the projection programs OXPROJWT.BAS and PXPROJ.BAS; and some input files (*.TVC) that will generate several of the screens shown in the figures of this report. Because we have had bad experiences in the past of users modifying our programs and then announcing publicly that "our" programs were flawed, we prefer to supply compiled programs. Readers who feel they need the source programs should send two medium-density diskettes or one high-density diskette (the source code and additional files total about 670 K) and a convincing statement as to why they require the source codes.

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APPENDIX

QUILF.RCT Listing (Reactions and Equilibria used by QUILF.EXE)

```
; Qtz+Usp+IL+Fa+Px+Iron+Qtz+Rutile
;
;
; Format of a reaction, assumes a balanced reaction
;
;
; 'ReactionName'; reactantl + reactant2 = productl + product2
;
;
; The ReactionName is in quotes, followed by a semicolon
; if the coefficent of the reactant or product is not one, preceed the
; name of the component with the coefficent.
;
;
; Lines beginning with a semicolon are comments.
;
;
; 2 oxides
;
;
'FeTi';                 Fe3O4 + FeTiO3 = Fe2TiO4 + Fe2O3
'MH';                   4Fe3O4 + O2 = 6Fe2O3
'FeMgIlSp';             MgFe2O4 + FeTiO3 = Fe3O4 + MgTiO3
'FeMnIlSp';             MnFe2O4 + FeTiO3 = Fe3O4 + MnTiO3
;
;
; silicate + oxide
;
;
'FeMgOlIl';             oFe2SiO4 + 2MgTiO3 = oMg2SiO4 + 2FeTiO3
'FeMgAugIl';            aFe2Si2O6 + 2MgTiO3 = aMg2Si2O6 + 2FeTiO3
;'FeMgCaAugIl';         aCaFeSi2O6 + MgTiO3 = aCaMgSi2O6 + FeTiO3
'FeMgPigIl';            pFe2Si2O6 + 2MgTiO3 = pMg2Si2O6 + 2FeTiO3
'FeMgOpxIl';            oFe2Si2O6 + 2MgTiO3 = oMg2Si2O6 + 2FeTiO3
;'FeMgCaOpxIl';         oCaFeSi2O6 + MgTiO3 = oCaMgSi2O6 + FeTiO3
'FeMgOlSp';             oFe2SiO4 + 2MgFe2O4 = oMg2SiO4 + 2Fe3O4
```

```
'FeMgOpxSp';          oFe2Si2O6 + 2MgFe2O4 - oMg2Si2O6 + 2Fe3O4
'FeMgAugSp';          aFe2Si2O6 + 2MgFe2O4 - aMg2Si2O6 + 2Fe3O4
'FeMgPigSp';          pFe2Si2O6 + 2MgFe2O4 - pMg2Si2O6 + 2Fe3O4
;
; olivine + pyroxene
;
'FeMgOlAug';          oMg2SiO4 + aFe2Si2O6  - oFe2SiO4 + aMg2Si2O6
'FeCaOlAug';          oFe2SiO4 + aCaFeSi2O6 - oCaFeSiO4 + aFe2Si2O6
;'FeMgCaOlAug';       oCaMgSiO4 + aCaFeSi2O6 - oCaFeSiO4 + aCaMgSi2O6
'MgCaOlAug';          oMg2SiO4 + aCaMgSi2O6 - oCaMgSiO4 + aMg2Si2O6
'FeMgOlPig';          oMg2SiO4 + pFe2Si2O6 - oFe2SiO4 + pMg2Si2O6
'FeCaOlPig';          oFe2SiO4 + pCaFeSi2O6 - oCaFeSiO4 + pFe2Si2O6
;'FeMgCaOlPig';       oCaMgSiO4 + pCaFeSi2O6 - oCaFeSiO4 + pCaMgSi2O6
'MgCaOlPig';          oMg2SiO4 + pCaMgSi2O6 - oCaMgSiO4 + pMg2Si2O6
'FeMgOlOpx';          oMg2SiO4 + oFe2Si2O6 - oFe2SiO4 + oMg2Si2O6
'FeCaOlOpx';          oFe2SiO4 + oCaFeSi2O6 - oCaFeSiO4 + oFe2Si2O6
;'FeMgCaOlOpx';       oCaMgSiO4 + oCaFeSi2O6 - oCaFeSiO4 + oCaMgSi2O6
'MgCaOlOpx';          oMg2SiO4 + oCaMgSi2O6 - oCaMgSiO4 + oMg2Si2O6
;
; 2 pyroxenes
;
'EnAugPig';           aMg2Si2O6 - pMg2Si2O6
'FsAugPig';           aFe2Si2O6 - pFe2Si2O6
'DiAugPig';           aCaMgSi2O6 - pCaMgSi2O6
'HdAugPig';           aCaFeSi2O6 - pCaFeSi2O6
'EnAugOpx';           aMg2Si2O6 - oMg2Si2O6
'FsAugOpx';           aFe2Si2O6 - oFe2Si2O6
'DiAugOpx';           aCaMgSi2O6 - oCaMgSi2O6
'HdAugOpx';           aCaFeSi2O6 - oCaFeSi2O6
'EnPigOpx';           pMg2Si2O6 - oMg2Si2O6
'FsPigOpx';           pFe2Si2O6 - oFe2Si2O6
'DiPigOpx';           pCaMgSi2O6 - oCaMgSi2O6
'HdPigOpx';           pCaFeSi2O6 - oCaFeSi2O6
;
; olivine + pyroxene + quartz
;
'MgOlQAug';           aMg2Si2O6 - oMg2SiO4 + SiO2
'FeOlQAug';           aFe2Si2O6 - oFe2SiO4 + SiO2
;'CaMgOlQAug';        aCaMgSi2O6 - oCaMgSiO4 + SiO2
;'CaFeOlQAug';        aCaFeSi2O6 - oCaFeSiO4 + SiO2
'MgOlQPig';           pMg2Si2O6 - oMg2SiO4 + SiO2
'FeOlQPig';           pFe2Si2O6 - oFe2SiO4 + SiO2
;'CaMgOlQPig';        pCaMgSi2O6 - oCaMgSiO4 + SiO2
;'CaFeOlQPig';        pCaFeSi2O6 - oCaFeSiO4 + SiO2
'MgOlQOpx';           oMg2Si2O6 - oMg2SiO4 + SiO2
'FeOlQOpx';           oFe2Si2O6 - oFe2SiO4 + SiO2
;'CaMgOlQOpx';        oCaMgSi2O6 - oCaMgSiO4 + SiO2
;'CaFeOlQOpx';        oCaFeSi2O6 - oCaFeSiO4 + SiO2
;
; oxide + silicate + quartz
;
'FMQ';                3oFe2SiO4 + O2 - 2Fe3O4 + 3SiO2
'AMQ';                3aFe2Si2O6 + O2 - 2Fe3O4 + 6SiO2
'PMQ';                3pFe2Si2O6 + O2 - 2Fe3O4 + 6SiO2
'OMQ';                3oFe2Si2O6 + O2 - 2Fe3O4 + 6SiO2
'FHQ';                2oFe2SiO4 + O2 - 2Fe2O3 + 2SiO2
'AHQ';                2aFe2Si2O6 + O2 - 2Fe2O3 + 4SiO2
'PHQ';                2pFe2Si2O6 + O2 - 2Fe2O3 + 4SiO2
'OHQ';                2oFe2Si2O6 + O2 - 2Fe2O3 + 4SiO2
;
; oxide + olivine + pyroxene
;
'FAM';                6oFe2SiO4 + O2 - 2Fe3O4 + 3aFe2Si2O6
'FPM';                6oFe2SiO4 + O2 - 2Fe3O4 + 3pFe2Si2O6
'FOM';                6oFe2SiO4 + O2 - 2Fe3O4 + 3oFe2Si2O6
'FAH';                4oFe2SiO4 + O2 - 2Fe2O3 + 2aFe2Si2O6
'FPH';                4oFe2SiO4 + O2 - 2Fe2O3 + 2pFe2Si2O6
'FOH';                4oFe2SiO4 + O2 - 2Fe2O3 + 2oFe2Si2O6
;
; 2 oxides + silicate + quartz
;
'DFMQ';               oFe2SiO4 + 2Fe2O3 - 2Fe3O4 + SiO2
'DAMQ';               aFe2Si2O6 + 2Fe2O3 - 2Fe3O4 + 2SiO2
'DPMQ';               pFe2Si2O6 + 2Fe2O3 - 2Fe3O4 + 2SiO2
'DOMQ';               oFe2Si2O6 + 2Fe2O3 - 2Fe3O4 + 2SiO2
;
; 2 oxides + olivine + pyroxene
;
'DFAM';               2oFe2SiO4 + 2Fe2O3 - 2Fe3O4 + aFe2Si2O6
'DFPM';               2oFe2SiO4 + 2Fe2O3 - 2Fe3O4 + pFe2Si2O6
'DFOM';               2oFe2SiO4 + 2Fe2O3 - 2Fe3O4 + oFe2Si2O6
```

```
; 2 oxides + rutile
;
'SpIlRut';            TiO2 + Fe2TiO4 = 2FeTiO3
;
; 2 oxides + iron
;
'SpIlFe';             2FeTiO3 + 2Fe + O2 = 2Fe2TiO4
;
; oxide + iron + rutile
;
'IlFeRut';            2Fe + 2TiO2 + O2 = 2FeTiO3
'SpFeRut';            2Fe + TiO2 + O2 = Fe2TiO4
;
; silicate + iron + quartz
;
'OlFeQtz';            2Fe + SiO2 + O2 = oFe2SiO4
'AugFeQtz';           2Fe + 2SiO2 + O2 = aFe2Si2O6
'PigFeQtz';           2Fe + 2SiO2 + O2 = pFe2Si2O6
'OpxFeQtz';           2Fe + 2SiO2 + O2 = oFe2Si2O6
```

Notes: in the abbreviations of the left column, Fe, Mg, Ca, Ti are cations; Ol, Opx, Aug, Pig are Ca–Mg–Fe olivine, orthopyroxene, augite, and pigeonite; Sp and Il are Fe–Mg–Mn–Ti spinel (Ti-magnetite) and ilmenite. In redox and displaced (D) equilibria, F is fayalite end-member; O, P, and A refer to $Fe_2Si_2O_6$ component in orthopyroxene, pigeonite, and augite, respectively. Q and Rut are quartz and rutile or the equivalent components; M and H refer to Fe_3O_4 and Fe_2O_3 components in spinel and ilmenite, respectively. En, Fs, Di, and Hd are the pyroxene end-members $Mg_2Si_2O_6$, $Fe_2Si_2O_6$, $CaMgSi_2O_6$, and $CaFeSi_2O_6$. Fe is metallic iron or its component.

In the formulae, prefix o for an olivine formula [Mg_2SiO_4] indicates an olivine component; prefixes o, a, p before pyroxene end-member formulae indicate that component in Opx, augite, or pigeonite, respectively. Fe_2O_3, $FeTiO_3$, $MgTiO_3$, and $MnTiO_3$ are components of ilmenite; Fe_3O_4, Fe_2TiO_4, $MgFe_2O_4$, and $MnFe_2O_4$ are components of spinel (Ti-magnetite).

The eleven reactions or equilibria preceded by ; are redundant and thus ignored by the program; they are listed here for completeness.