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Planet Alsioff: Solutions to problems posed in the previous issue

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INTRODUCTION

In the previous issue (*American Mineralogist*, v. 73, p. 936–938) I described a hypothetical planet Alsioff whose crusts and atmosphere contain only Al, Si, O, and F. A series of ten problems were then posed about possible metamorphic and metasomatic phase equilibria on such a planet. An internally consistent set of qualitatively derived answers is given below. Note that a strict thermodynamic analysis would yield different answers (which would be inconsistent with the problems). Some of these inconsistencies are indicated in the answers.

SOLUTIONS TO PROBLEMS

1. Water exposed to the SiF_4 atmosphere might react as follows:

$$2H_2O + SiF_4 = 4HF + SiO_2 \text{ (quartz)}$$

or (if we consider fluosilicic acid, inasmuch as $2HF + SiF_4 = H_2SiF_6$)

$$2H_2O + 3SiF_4 = 2H_2SiF_6 + SiO_2.$$

You were not asked to calculate this, but either reaction involves about a 37% volume decrease (from 2 mol of liquid water to quartz) at room *T* and *P*. (Actually, SiF_4 is extremely stable, and thermodynamic calculations reveal that the top reaction proceeds to the left at room *T* and *P*, allowing HF to attack quartz.)

Wollastonite exposed to SiF_4 should react as follows:

$$2CaSiO_3 + SiF_4 = 2CaF_2 + 3SiO_2.$$

2. The principal control on relative F_2 and O_2 abundance is $SiO_2 + 2F_2 = SiF_4 + O_2$, which implies that $K_{eq} = f_{O_2} f_{SiF_4}/f^2_{F_2}$ or that P_{O_2} is proportional to $P^2_{F_2}$. (There must be at least some O_2 to give rise to the quartz snow; F_2 is exponentially less abundant.

3. Planar polyhedra (showing compositions for Problem 3, stable tie lines for Problem 4, and three-phase assemblage labels for Problem 5) are shown in Figures 1 and 2.

Figure 1 shows two possible triangular representations of the ternary system $AlO_{1.5}$-SiO_2-F_2O_{-1} (Fig. 1A) or Al_2O_3-SiO_2-F_2O_{-1} (Fig. 1B). For these figures, note that F_2O_{-1} is the proper oxide of fluorine, although it does not exist physically. It is a component known as an "exchange operator" (a term coined by me in 1974; the concept originated with J. B. Thompson, Jr.) that expresses the exchange of 2 fluorines for 1 oxygen. It could also be expressed as $FO_{-0.5}$. Phase abbreviations are given in Table 1 for Problem 3 in the previous issue (Burt, 1988).

The molar compositional relations needed to plot the positions of the phases other than quartz and corundum on the triangles (barycentric coordinates) are given below:

$$\begin{aligned} SiF_4 &= SiO_2 + 2F_2O_{-1} \\ 2AlF_3 &= 2AlO_{1.5} + 3F_2O_{-1} = Al_2O_3 + 3F_2O_{-1} \\ Al_2SiO_5 &= 2AlO_{1.5} + SiO_2 = Al_2O_3 + SiO_2 \\ Al_2SiO_4F_2 &= 2AlO_{1.5} + SiO_2 + F_2O_{-1} = Al_2O_3 + SiO_2 \\ &\quad + F_2O_{-1}. \end{aligned}$$

The physically realizable parts of Figures 1A and 1B are quadrilaterals, not triangles. It should therefore come as no surprise that the phase compositions can also be represented on a rectangle or square (Fig. 2A). We are then talking about the reciprocal ternary system /Al,Si//O,F/. This notation expresses the simultaneous substitution of Si for Al and of F for O.

The charge-balanced substitutions (vectors, in this case) are Si_3Al_{-4} (vertical) and $6F_2O_{-1}$ (horizontal). Figure 2A is a planar cross-section through the tetrahedron Al-Si-O-F (Fig. 2B).

The compositional relations needed to plot the two noncorner phases on Figure 2A are given below:

$$\begin{aligned} 6Al_2SiO_5 &= 3Al_4O_6 + 2Si_3O_6 = 5Al_4O_6 + 2Si_3Al_{-4} \\ 6Al_2SiO_4F_2 &= 2Al_4O_6 + 2Si_3O_6 + Al_4F_{12} \\ &= 5Al_4O_6 + 2Si_3Al_{-4} + F_{12}O_{-6}. \end{aligned}$$

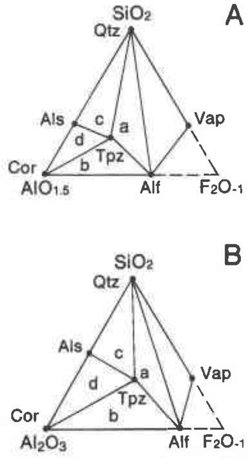

Fig. 1. Composition triangles $AlO_{1.5}$-SiO_2-F_2O_{-1} (**A**) and Al_2O_3-SiO_2-F_2O_{-1} (**B**) in answer to Problem 3. Shows stable tie lines in answer to Problem 4 and three-phase mineral assemblages related to Problem 5.

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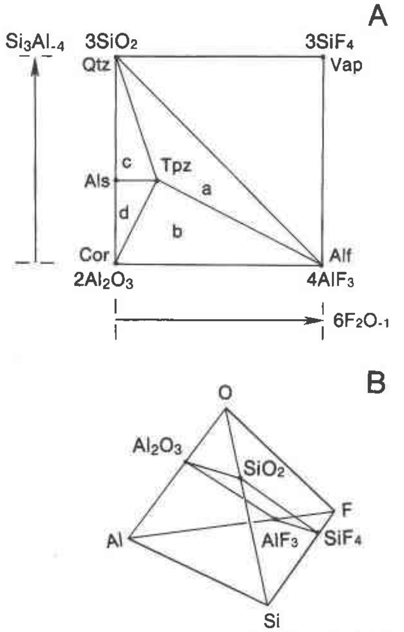

Fig. 2. Alternative answer to Problem 3. (**A**) Square $2Al_2O_3$-$4AlF_3$-$3SiF_4$-$3SiO_2$ for the reciprocal ternary system /Al,Si//O,F/. Shows stable tie lines in answer to Problem 4 and three-phase mineral assemblages related to Problem 5. (**B**) Tetrahedron Al-Si-O-F showing position of the reciprocal ternary plane /Al,Si//O,F/.

These relations indicate that aluminosilicate (Al_2SiO_5) is ⅖ of the way up and that topaz ($Al_2SiO_4P_2$) is ⅖ of the way up and ⅕ of the way across.

4. For stable tie lines, refer to Figures 1 or 2A.

5. Progressive devolatilization involves the breaking of tie lines that prevent SiF_4 vapor from being stable with the less F-rich phases. The sequential breaking of tie lines is indicated by the five numbered divariant triangles in Figure 3, which are separated from each other by the four univariant devolatilization reactions listed below:

$$2AlF_3 + 2SiO_2 = Al_2SiO_4F_2 + SiF_4 \qquad (a)$$
Alf + Qtz = Tpz + Vap

$$2AlF_3 + 3Al_2SiO_4F_2 = 4Al_2O_3 + 3SiF_4 \qquad (b)$$
Alf + Tpz = Cor + Vap

$$2Al_2SiO_4F_2 + SiO_2 = 2Al_2SiO_5 + SiF_4 \qquad (c)$$
Tpz + Qtz = Als + Vap

$$2Al_2SiO_4F_2 = Al_2O_3 + Al_2SiO_5 + SiF_4. \qquad (d)$$
Tpz = Cor + Als + Vap

Note that each of the lettered reactions above corresponds to a lettered 3-phase assemblage or SiF_4 buffer in Figures 1 and 2A. Note also that Reaction (a) could be called "topaz in," Reaction (b) "corundum in," Reaction (c) "aluminosilicate in," and Reaction (d) "topaz out," in keeping with the common labeling of isograd reactions in metamorphic petrology.

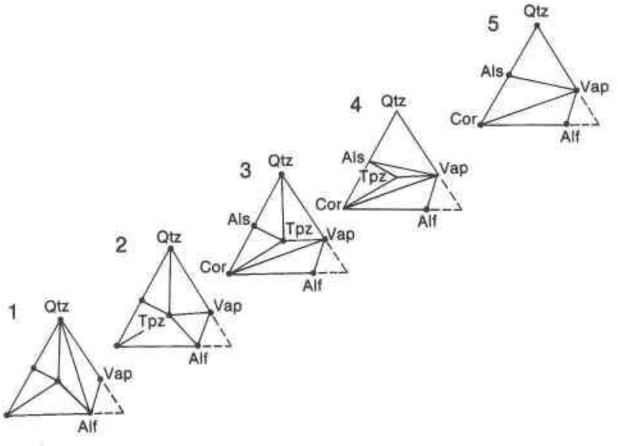

Fig. 3. Five divariant configurations of the composition triangle Al_2O_3-SiO_2-F_2O_{-1} that show the progressive increase in tie lines to SiF_4 vapor (Problem 5). See text for discussion.

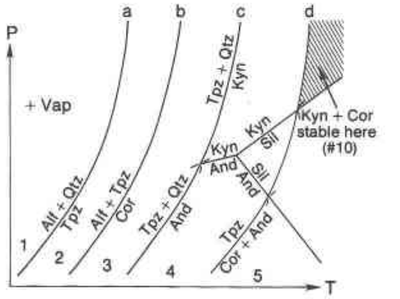

Fig. 4. Schematic *P-T* diagram showing phases in equilibrium with vapor in the system Al_2O_3-SiO_2-F_2O_{-1}, in answer to Problem 6. Shaded area is in answer to Problem 10.

6. Figure 4 shows a schematic *P-T* diagram of phases in equilibrium with SiF_4 vapor; the diagram is consistent with the data given in Problem 6 and earlier problems. The lettered univariant devolatilization reactions (a to d) are those listed above; the numbered divariant fields (1

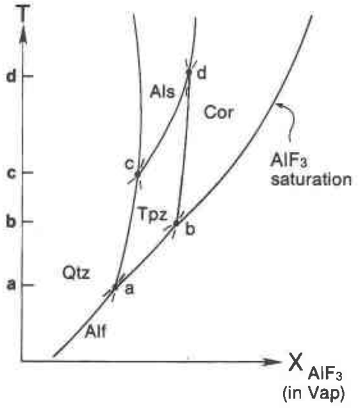

Fig. 5. Isobaric T-X_{AlF_3} diagram in answer to Problem 7.

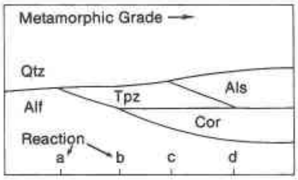

Fig. 6. Diagram in answer to Problem 8 showing monomineralic reaction bands developed between beds of quartz and of "alfite" at different grades of metamorphism. Letters correspond to the four univariant reactions of Problem 5.

to 5) are those of Figure 3. Note that topaz is thermodynamically much more stable than this exercise would indicate; I made up the problems to make the system Al_2O_3-SiO_2-F_2O_{-1} somewhat analogous to Al_2O_3-SiO_2-H_2O. In reality, it is not.

7. A schematic isobaric T-X_{AlF_3} diagram showing crystalline phases in equilibrium with various vapor compositions is shown in Figure 5. The letters next to the invariant points correspond to the univariant reactions listed in the answer to Problem 5.

The "alfite"[1] and quartz solid inclusions in topaz are caused by univariant Reaction (a) in question 5 going in the reverse direction with falling T: $Al_2SiO_4F_2$ (wall of fluid inclusion) + SiF_4 (fluid inclusion) = $2AlF_3$ + $2SiO_2$ (solid inclusions). Note that unless the original trapped SiF_4 fluid was quite dense (concentrated), seeing the solid inclusions under the microscope might be rather difficult owing to the small amount of solid products formed.

8. Progressive metamorphism of alternating "alfite" and quartz beds would lead to the development of monomineralic bands between the beds because of reaction between the phases. The resulting topology, and the change with increasing temperature (metamorphic grade) are shown diagramatically in Figure 6. Note that this has the same general topology as Figure 5.

The data and map given with the exercise would indicate that a migmatic melt layer would form between corundum and "alfite" at grades of metamorphism somewhat above those of Reaction (d). (In actuality, crystalline AlF_3 is thermally stable, and at 1 bar, it sublimates, rather than melts, at temperatures well above 1000 °C. Cryolite, Na_3AlF_6, has many of the properties herein ascribed to AlF_3, including a low melting temperature and an ability to dissolve Al_2O_3.)

9. Metamorphic isograds on the sample locality map are given in Figure 7. This has the same general topology as the P-T diagram of Figure 4, except for the contact aureole at low grades. Isograds, as mentioned in the answer to Problem 5, are +Tpz, +Cor, +Als, and −Tpz (or Cor + Als), in addition to the aluminosilicate isograds themselves (+And, +Kyn, +Sil).

10. Highest metamorphic pressure indicator is the assemblage kyanite-corundum, which occurs toward the northwest corner of the map (see also the shaded area in Fig. 4).

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[1] The word "alfite" is not a valid mineral name. See Disclaimer in Burt (1988, p. 938).

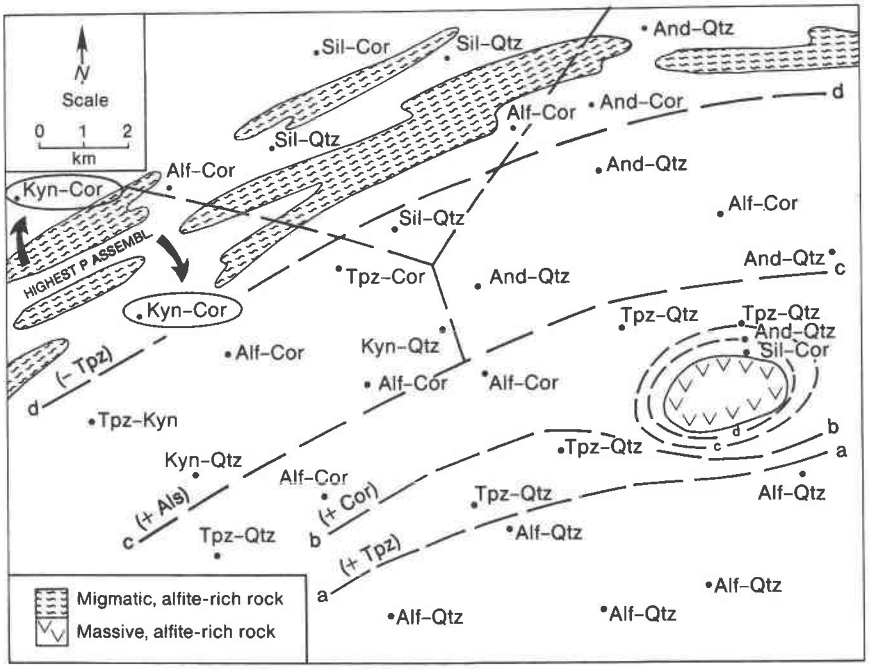

Fig. 7. Isograd map of sample localities, in answer to Problem 9. Also indicates the area of kyanite-corundum assemblages in answer to Problem 10.

ACKNOWLEDGMENTS

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BOOK REVIEW

CHEMICAL TRANSPORT IN METASOMATIC PROCESSES (NATO ASI Series C: Mathematical and Physical Sciences, vol. 218). Edited by Harold C. Helgeson. D. Reidel, Dordrecht, Holland, 1987, 782 pages, $149.00.

This book is an outgrowth of a NATO Advanced Studies Institute in Corinthia and the Cycladic Islands, Greece. It contains 28 papers, 6 abstracts, and a Seriphos, Syros, and Naxos excursion guide. Although the book does not cover metasomatism at earth surface conditions, there is an incredible array of contributions by both established leaders and younger scientists in metasomatic processes. No Greek gods made contributions perhaps because Mount Olympus was not visited. However, as did the conference, the 50-page excursion guide will undoubtedly increase the geological interest in the Greek islands.

The book is not a textbook in format, but rather is a collection of provocative research contributions of particular interest to those who are interested in chemical changes in crustal and mantle rocks. For a large conference volume, the overall quality of the contributions is particularly high. I detected only one production error, a poorly printed page 351. The book contains a nice blend of theoretical, field, and experimental work. Even a casual perusal of the book demonstrates the importance of fluid during metasomatism. Fluid-rock interactions are clearly basic to our understanding of metamorphism, ore deposition, and weathering.

Although the price is high, particularly for camera-ready copy, I am considering using the book for a graduate seminar class in geochemistry. This would be after a good foundation in thermodynamics and introductory geochemistry. The contributions clearly show how research at the forefront is handled. It is instructive to the student to determine or read about what is correct, what is wrong, and what is a matter of personal conjecture.

Rather than an extensive list of titles of the articles, perhaps it is more appropriate to list first authors and thereby to give an idea of the international character and the scope of the book. These are G. M. Anderson, D. K. Bailey, T. Bowers, D. M. Carmichael, H. J. Greenwood, H. C. Helgeson, D. R. Janecky, P. Lichtner, G. van Marcke de Lummen, G. Michard, A.M.R. Neiva, D. L. Norton, D. Papanikolaou, Tj. Peters, H. R. Pfeiffer, R. Sack. J. Salemink, M. Schliestedt, J. Schott, W. Schreyer, R. Schuiling, S. Steinthórsson, H. P. Taylor, Jr., J. B. Thompson, Jr., J. Touret, V. Trommsdorff, and R. Vollmer.

Included in the book are contributions concerned with controls on the composition of metamorphic, geothermal, and mantle fluids, alteration of oceanic crust, metamorphism of peraluminous and ultramafic rocks, skarn deposits, hydrothermal alteration, isotopic behavior, fluid inclusions, rocks buffering fluid composition, CO_2–H_2O-NaCl fluids, fluid advection and reaction, constant volume, equilibrium and disequilibrium mineral textures, tennahedrite, moderation theorems, and four articles on metamorphism in the Greek islands.

This NATO volume clearly shows that the conference was a worthy successor to the last A. S. I. on a similar subject, Volatiles in Metamorphism, held in 1974. As a thought-provoking book, it should stimulate exciting future research. The book ought to take its place on one's bookshelf next to *Researches in Geochemistry,* volume 2, 1967, edited by P. H. Abelson. In many ways it is an expanded and updated version of this book.

May Zeus and Pallas be with us.

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