Compositions of Aqueous Fluids in Equilibrium with Pyroxenes and Olivines at Mantle Pressures and Temperatures

I.D. Ryabchikov¹, W. Schreyer², and K. Abraham²

¹ IGEM, 35 Staromonetny, Moscow 109017, USSR

² Institut für Mincralogie, Ruhr-Universität, Postfach 102148, D-4630 Bochum 1, Federal Republic of Germany

Abstract. Solubility experiments were performed at 30 kbars in the system $Mg_2SiO_4 - SiO_2 - H_2O$, and at 20 and 30 kbars on omphacitic pyroxene-water mixtures. They confirm that the solubility of the forsterite component in aqueous fluids remains rather low (up to 5 wt.%), whereas the solubility of the SiO₂ component from solids of appropriate SiO₂-rich compositions in the system $Mg_2SiO_4 - SiO_2 - H_2O$ increases with temperature up to some 75% at 1,100° C. At this temperature a simplified harzburgite consisting of forsterite and enstatite coexists with a fluid containing about 35% (MgO+SiO₂). Hydrous fluids coexisting with omphacitic clinopyroxenes leach sodium silicate component from the solid leaving less jadeitic pyroxenes behind. Most interestingly, the amount of sodium leached at constant temperature increases with decreasing pressure.

Comparison of the results with previous solubility studies in the system $K_2O-MgO-Al_2O_3-SiO_2-H_2O$ indicates that hydrous fluids in the mantle must be alkaline rather than silicanormative. Alkali metasomatism caused by such fluids would lead to potassium enrichment in deeper portions of the upper mantle and to sodium enrichment at shallower levels, where amphiboles become stable. This K/Na fractionation in the upper mantle may explain the generation of K-rich or of Na-rich magmas through partial melting at different depths.

Introduction

Geochemical studies of basaltic rocks and mantle-derived nodules reveal that, for the differentiation of mantle material, fluid phases play a role that cannot be neglected. It is, therefore, desirable to expand the knowledge of phase equilibria between fluids and typical minerals of mantle periodite.

Previous experimental data obtained at high temperatures and at pressures above 10 kbar provide information on the composition of aqucous fluids in equilibrium with quartz (Nakamura 1974), forsterite and enstatite (Nakamura and Kushiro 1974), diopside (Eggler and Rosenhauer 1978), and with phlogopitecontaining phase assemblages (Ryabchikov and Boettcher 1980). In order to provide information on the solubilities of mafic minerals at various depths in the mantle the present work was aimed at determining the composition of aqueous fluids in equilibrium with simplified harzburgite consisting of enstatite and forsterite over a more extended P-T range than covered by the work of Nakamura and Kushiro (1974). We also performed a series of runs bearing on the sodium contents of water-rich fluids in equilibrium with omphacitic clinopyroxenes. Together with the results of previous work by Ryabchikov and Boettcher (1980) these results permit comparison of the behaviour of sodium and potassium in aqueous fluids interacting with mantle minerals.

Experimental Procedures

Starting Materials

A variety of mixtures of a fired gel of forsterite composition with fired reagent grade SiO_2 was used for the experiments in the system MgO-SiO₂-H₂O. For the system diopside-jadeitewater the starting material was a mixture of oxides and sodium carbonate corresponding to the formula (Na_{0.3}Ca_{0.7}) (Mg_{0.7}Al_{0.3}) Si₂O₆, which was sintered at 1,000° C.

Experiments were performed in sealed gold capsules on mixtures of known proportions of silicate components and water ranging from 96 to 15 weight per cent H_2O .

Apparatus

All the experiments were performed in piston-cylinder apparatus similar to that described by Boyd and England (1960). The pressure cells were made from sodium chloride with graphite heaters as described by Mirwald et al. (1975). The temperature was measured with a chromel-alumel thermocouple with no correction of the pressure effect on the emf.

Identification of Phases

The products of all the runs included aqueous solution, amorphous material and crystalline phases precipitated from the fluid during the quenching, and, in the majority of cases, also crystalline phases which were in equilibrium with fluid under the conditions of the run.

Differences between equilibrium and quench crystals were sufficiently distinct. For the join $Mg_2SiO_4 - H_2O$ the equilibrium forsterite formed was represented by large cuhedral crystals measuring up to 0.5 mm (at 1,000° C and 30 kbar), while the quench crystals are of variable size and show skeletal and dendritic morphology.

For compositions more siliceous than those of the $Mg_2SiO_4-H_2O$ join, olivine was never observed among the quenched crystals. Quench products here were represented by finegrained amorphous material and quench-orthopyroxenes, which sometimes formed thin and very long needles (up to $5 \times 600 \ \mu\text{m}$), but, more typically, were minute (several μm) den-

dritic grains. Equilibrium orthopyroxenes were much thicker grains (typically up to $40 \times 100 \ \mu$ m) with euhedral terminations, and thus are again markedly different from quench orthopyroxene.

The composition of the fluid phase could not be determined by direct analysis, but had to be deduced from the locations of phase boundaries, just as it is usual to derive melt compositions from isothermal isobaric sections of liquidus diagrams.

The products of the runs along the join diopside-jadeite-water were represented by euhedral equilibrium clinopyroxene crystals (up to $200 \times 20 \ \mu$ m), small skeletal quench clinopyroxene grains (typically $1 \times 10 \ \mu$ m), and a glass-like amorphous material which formed small spheres (1–3 μ m), rods, and other irregularly shaped aggregates. The compositions of equilibrium clinopyroxene crystals were determined by electron microprobe analyses, and these results, compared with starting composition, were used to calculate the amount of sodium in the aqueous phase. For microprobe analysis the synthetic products were imbedded in epoxy resin, polished, and coated with carbon. MgO, Al₂O₃, SiO₂, NaAlSi₂O₆, and CaSiO₃ were used as standards. Single crystals were analyzed with the automated electron microprobe CAMEBAX, CAMECA, France, operated at 15 KV and 14 nA. The totals ranged between 99.5 and 100.5%.

Experimental Results

System $Mg_2SiO_4 - SiO_2 - H_2O$

The results of our experiments at 30 kbar and at four different temperatures are summarized in Table 1 and led to the construction of the isobaric-isothermal phase diagrams given in Fig. 1. In the following two examples are given to show how the solubility data were derived: In the products of run 8 at 1,000° C large (0.2-0.3 mm) equilibrium crystals of olivine were found to weigh 0.57 mg which, by comparison with the amounts of silicate (0.67 mg) and water (10.35 mg) sealed into the capsule, permits to estimate forsterite solubility as approximately 1 wt%. For run 41 at 1,100° C the volumes of equilibrium and quench crystals of olivine were estimated visually to be about equal, which indicates an increase of forsterite solubility to about 2 wt.%.

From Fig. 1 a strong increase of the solubility of silicate components in the aqueous fluid with temperature is evident. A comparison with the data presented by Nakamura and Kushiro (1974) shows that the concentrations of the silicate components in fluids coexisting with forsterite and enstatite at $1,000^{\circ}$ C and 30 kb are approximately the same as for $1,300^{\circ}$ C and 15 kb. This means that the requisite isopleths in the crystal+fluid-region have a negative slope, i.e. the solubility of solid phases rises with both pressure and temperature.

The solubility of enstatite retains its incongruent character previously noticed by Nakamura and Kushiro (1974), but – with decreasing temperature – it seems to approach conditions of congruent solubility.

Forsterite is dissolved in the fluid in a congruent manner, but its solubility is much smaller than that of enstatite. However, the techniques employed in this work do not permit a very precise determination of forsterite solubility. Adding excess SiO_2 to the join forsterite-H₂O leads to drastic increases of the SiO_2 contents in the fluid, as already recognized by Nakamura and Kushiro (1974). At 1,100° C and 30 kbars (Fig. 1d) SiO_2 may comprise up to 75% of all the solids dissolved, while the forsterite component in the fluid is less than 5%.

Table 1. Experimental data for the system $Mg_2SiO_4-SiO_2-H_2O$ at 30 kbar

Run No.	Temp. (°C)	Dura- tion (h)	Composition of silicate material	Water content (wt.%)	Phase assemblage, interpreted from run products
39	900	20	F0 _{0.6} Qz _{0.4}	92.0	Ol + Opx + Fl
36	900	16	$Fo_{0.6}Qz_{0.4}$	82.5	Opx + Fl
34	900	17	Fo _{0.6} Qz _{0.4}	80.6	Opx + Fl
25	900	22.5	Fo _{0,3} Qz _{0,7}	91.5	Opx + Fl
42	900	23	Fo _{0.1} Qz _{0.9}	82.0	FÍ
35	900	17	F00.05Qz0.95	81.4	Fl
40	900	22	Qz	48.9	Co+Fl
29	960	22	Fo _{0.6} Qz _{0.4}	80.1	Ol+F1
23	960	19	Fo _{0.3} Qz _{0.7}	84.4	Opx + Fl
32	960	8.5	F00.05Qz0.95	81.1	FÍ
30	960	17	Qz	50.6	F1
31	960	5	Qz	46.4	Fl
7	1,000	14	Fo	95.5	Ol+Fl
8	1,000	20.5	Fo	93.9	Ol + Fl
4/2	1,000	15	Fo	81.7	Ol + Fl
4/1	1,000	15	Fo	70.3	Ol + Fl
3	1,000	14	Fo	51.05	Ol+Fl
11/2	1,000	17	Fo _{0.33} Qz _{0.67}	65.0	Ol + Opx + Fl
33	1,000	21	$Fo_{0.3}Qz_{0.7}$	69.9	Ol + Opx + Fl
22	1,000	12	Fo _{0.3} Qz _{0.7}	66.3	Opx + Fl
21	1,000	8	Fo _{0.3} Qz _{0.7}	61.1	Opx + Fl
18/1	1,000	21	F00,15QZ0.85	80.4	Ol(s.a.) + Fl
15	1,000	17	$Fo_{0,1}Qz_{0,9}$	85.7	FI
13	1,000	14.5	Fo _{0.1} Qz _{0.9}	79.9	Fl
10	1,000	21	Fo _{0.1} Qz _{0.9}	77.0	Fl
14	1,000	16	Fo _{0,1} Qz _{0,9}	39.5	Opx + Fl
17/1	1,000	16	Fo _{0.1} Qz _{0.9}	34.9	Opx + Qz(s.a.) + Fl
12	1,000	18.5	Fo _{0.05} Qz _{0.95}	80.2	Fl
19/2	1,000	20.5	Fo _{0.05} Qz _{0.95}	40.4	Opx(s.a.) + Fl
41	1,100	20	Fo	96.1	OI+FI
5/1	1,100	6.5	Fo	83.0	01+F1
5/2	1,100	6.5	Fo	65.3	Ol + Fl
24	1,100	19	$Fo_{0.3}Qz_{0.7}$	61.4	Ol + Opc + Fl
27	1,100	5	Fo _{0.3} Qz _{0.7}	55.05	Opx + Fl
20/1	1,100	16	Fo _{0.3} Qz _{0.7}	50.0	Opx + Fl
$\frac{20}{2}$	1,100	16	$Fo_{0.3}Qz_{0.7}$	37.5	Opx + Fl
26	1,100	12	$Fo_{0.15}Qz_{0.85}$	65.8	Ol + Fl
28	1,100	15	Fo _{0.1} Qz _{0.9}	65.6	FI

Abbreviations: Fo=forsterite component; Qz=quartz (as component and phase); Ol=olivine; Opx=orthoenstatite; Co=coesite; Fl=fluid; s.a. = small amount

Join Diopside-Jadeite-Water

The results of the 5 runs for this join at 900° C are given in Table 2. The silicate starting material had the composition 70 mol% diopside – 30 mol% jadeite. Wet chemical analysis yielded the values given in the table. At 900° , 20-30 kb, a single-phase omphacitic pyroxene of this composition is stable according to the data of Bell and Kalb (1969). The microprobe data of the pyroxene single crystals analyzed were recalculated to 100%. No phases other than pyroxene were observed.

Comparison of the clinopyroxene compositions obtained in these runs with the composition of the starting material reveal a noticeable decrease in sodium content as a function of increasing water to silicate ratios. It is also interesting to note that at 30 kbars the relic pyroxenes contain increasing amounts of $CaAl_2SiO_6$ - and $MgAl_2SiO_6$ -components in addition to diopside and jadeite, when the water to silicate ratio of the run rises (Table 2). These results imply that the content of sodium-bearing



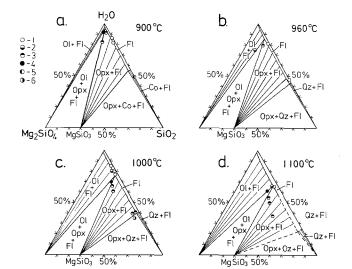


Fig. 1a-b. Isobaric-isothermal phase diagrams (in weight per cent) for the system $Mg_2SiO_4 - SiO_2 - H_2O$ at 30 kbar pressure. Compositions corresponding to the runs listed in Table 1 are shown by *circles* and the phase assemblages obtained are shown by the symbols depicted and numbered in the *upper left* to indicate the following: I =fluid; 2 =olivine + fluid; 3 =orthopyroxene + fluid; 4 =olivine + orthopyroxene + fluid; 5 =crystalline silica + fluid; 6 =crystalline silica + orthopyroxene + fluid

components in the aqueous phase is substantial under these PTconditions and is indeed the decisive factor for the chemistry of the pyroxenes grown.

It may be noticed that the losses of sodium from the solid phase starting material for the runs with similar water/silicate ratios are not markedly different for 20 and for 30 kbars. This seems to indicate that the distribution of sodium between clinopyroxene and fluid is not pressure-dependent, which is in marked

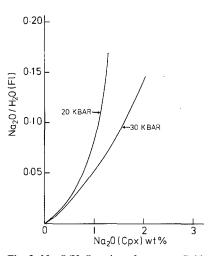


Fig. 2. Na_2O/H_2O ratios of aqueous fluids plotted against the Na_2O contents of co-existing elinopyroxenes as calculated from the data summarized in Table 2 by Eq. (3) at Z=0.05 for 900° C

contrast with the behaviour of potassium in phlogopite-bearing phase assemblages (Ryabchikov and Boettcher 1980).

Furthermore it may be seen from Table 2 that the Na/Al ratios in the clinopyroxenes synthesized are less than 1 for all our runs, while it was 1.0 for the starting material. This shows that sodium is present in the fluid at least partly in the form of sodium silicate components.

For a more quantitative evaluation of Na_2O contents in aqueous fluids co-existing with clinopyroxenes the following procedure has been used. The balance of mass equations for Na_2O and diopsidic component in the system under consideration may be written in the following way:

Table 2. Conditions for runs at 900° C in the system jadeite-diopside-water and compositions of the clinopyroxenes synthesized

Run numbers	38	2	37	6/1	16	Silicate Starting material
Pressure, kbar	20	20	30	30	30	_
Duration, hours	41.5	14.5	77	12	73	-
H ₂ O content, wt.%	16.71	44.8	15.72	43.3	77.32	<u> </u>
Composition of crysta	als (in weight %) ^a					
SiO ₂	55.1 (1.06)	54.5 (1.4)	55.1 (0.8)	54.0 (1.0)	51.0 (2.4)	56.62
Al_2O_3	2.7 (0.32)	1.8 (1.2)	4.3 (1.8)	3.8 (0.7)	9.7 (4.7)	7.21
MgO	17.1 (0.25)	18.4 (0.8)	16.5 (1.5)	17.3 (0.4)	14.7 (3.1)	13.29
CaO	23.8 (0.31)	24.6 (0.8)	22.2 (1.6)	23.9 (0.3)	24.2 (0.9)	18.50
Na ₂ O	1.3 (0.16)	0.7 (0.3)	2.0 (0.9)	0.9 (0.15)	0.3 (0.2)	4.38
Number of points analyzed	5	12	10	24	15	
Structural formula of	pyroxene based o	n 6 oxygens:				
Na	0.09)	0.05	0.14)	0.06	0.02)	0.3
Са	0.92	0.95	0.85	0.92	0.93 1.97	0.7
Mg	$0.91 \left(\begin{array}{c} 2.01 \\ \end{array} \right)$	$0.99 \left(\begin{array}{c} 2.03 \\ \end{array} \right)$	0.86 2.00	0.93 (2.01	0.78	0.7
Al ⁶	0.09	0.04	0.15	0.10	0.24	0.3
Al ⁴	$\left\{ \begin{array}{c} 0.02 \\ 1.02 \end{array} \right\}$ 2.00	$\left\{ \begin{array}{c} 0.04 \\ 1.06 \end{array} \right\} 2.00$	$\left\{\begin{array}{c} 0.03\\ 1.07\end{array}\right\}$ 2.00	$\left\{ \begin{array}{c} 0.06 \\ 1.04 \end{array} \right\} 2.00$	$\left\{\begin{array}{c} 0.17\\ 1.02\end{array}\right\}$ 2.00	-
Si	1.98 ∫ 2.00	1.96 ∫ 2.00	1.97 ∫ 2.00	1.94 ∫ 2.00	1.83 ∫ 2.00	2.0
Total	4.01	4.03	4.00	4.01	3.97	4.00

^a Values in brackets are standard deviations

$$c_{\mathrm{Di}}^{\mathrm{Cpx}} \cdot m_{\mathrm{Cpx}} + Z \cdot m_{\mathrm{H_2O}} = c_{\mathrm{Di}}^0 m_{\mathrm{S}}^0 \tag{2}$$

where $c_{\text{Na}_{2O}}^{\text{Qpx}}$ and $c_{\text{Di}}^{\text{Qpx}}$ are concentrations of Na₂O and the sum (CaSiO₃ + MgSiO₃), respectively, in clinopyroxene co-existing with fluid expressed in mass fractions; X is the Na₂O/H₂O mass ratio in the fluid under the experimental conditions; Z is (CaSiO₃ + MgSiO₃)/H₂O for the same fluid; $c_{\text{Na}_{2O}}^{0}$ and c_{Di}^{0} are concentrations of Na₂O and CaMgSi₂O₆ in the starting silicate mixture; m_{Cpx} is the mass of clinopyroxene crystals in equilibrium with the fluid under the conditions of a given run; m_{S}^{0} is the total mass of the silicate component for a given run; $m_{\text{H}_{2O}}$ is the mass of water present in the capsule.

Solving Eq. (1) and (2) with respect to X we obtain the following formula

$$X = \frac{m_{\rm S}^{\rm 0}(c_{\rm Na_{2}O}^{\rm 0} \cdot c_{\rm Di}^{\rm Cpx} - c_{\rm Na_{2}O}^{\rm Cpx} \cdot c_{\rm Oi}^{\rm 0}) + Z \cdot c_{\rm Na_{2}O}^{\rm Cpx} \cdot m_{\rm H_{2}O}}{c_{\rm Di}^{\rm Cpx} \cdot m_{\rm H_{2}O}}$$
(3)

The right hand side of the Eq. (3) includes only values, which are known from the results of our experiments except for Z which is approximately equal to the diopside solubility in an aqueous fluid. These values were determined experimentally by Eggler and Rosenhauer (1978) at 20 and 30 kbar and at temperatures of 1,100–1,200° C, and were found to lie close to 10 wt.% for these conditions. Because the temperature of our experiments (900° C) is significantly lower, we expect that Z-values should be lower than 0.1, and we performed the calculation of Na₂O/ H₂O (fluid)=X ratios setting arbitrarily Z to 0.05. The results of these calculations are shown at Fig. 2.

It may be demonstrated, however, that even large uncertainties in Z would not introduce significant errors into the calculated X-values. Thus, for the results of run 6/1 (cf. Table 2) calculations using formula (3) with variable Z yield the following values: for Z=0 X=0.0488; for Z=0.1 X=0.0497 and for Z=0.2X=0.0506, indicating that the error does not exceed 5 per cent.

From Fig. 2 it may be seen, that in the range of higher sodium contents of clinopyroxenes the Na₂O concentrations of the fluid even decrease with a pressure rise from 20 to 30 kbar, whereas at lower $C_{\text{Na}_2\text{O}}^{\text{Cpx}}$ these two isobars approach one another. Nevertheless, the low pressure-dependence of the Na₂O distribution between clinopyroxene and aqueous fluid remains quite obvious. The geological significance of this fact will be discussed in the subsequent section.

Discussion

Experimental studies of decarbonation reactions in the presence of mixed (H_2O+CO_2) -fluids and thermodynamic calculations revealed that the predominant volatile component of interstitial fluids which may exist in the deeper levels of the upper mantle is H_2O (Wyllie 1979; Ryabchikov et al. 1981; M. Rosenhauer, personal communication). It implies that the solubilities of phase assemblages including pyroxenes and forsterite as determined in the present work are directly applicable to potential metasomatic processes in the mantle.

Similarly to the results obtained by Nakamura and Kushiro (1974) at 15 kbar we observe substantial concentrations of the SiO₂ component in aqueous fluid co-existing with both enstatite and forsterite, while the amount of forsterite component in the fluid along the join $Mg_2SiO_4-H_2O$ appears to be rather low even at 30 kbar. In addition, our results demonstrate very pronounced temperature dependence of magnesium silicate solubility in the aqueous phase: the total amount of $MgO+SiO_2$ in-

crease in fluids in equilibrium with the simplified harzburgite (enstatite+forsterite) from 4 wt.% at 900° C to about 35 wt.% at $1,100^{\circ}$ C (all at 30 kbar).

The SiO₂/MgO ratios of aqueous fluids coexisting at 30 kbar with both forsterite and enstatite are extremely high, which is in accord with the earlier results of Nakamura and Kushiro (1974) for 15 kbar. These authors argued, based on this fact. that a silicification of shallower levels of the mantle must occur. if aqueous fluids are ascending from deeper parts. We may note however, that the content of silicate components in the aqueous phase in equilibrium with forsterite + enstatite (predominantly silica) at 30 kbar and 1,100° C is lower (about 1.5 times) than the concentration of dissolved substances (predominantly potassium aluminosilicates) in equilibrium with forsterite + phlogopite under the same conditions (Ryabchikov and Boettcher 1980). This implies that traces of interstitial fluids co-existing in the mantle with olivine, orthopyroxene, and phlogopite would be characterized by alkaline rather than silica-normative composition and are thus likely to cause alkaline wall-rock alteration. The presence of sodium compounds, that were leached from clinopyroxenes (this work), would also contribute to the alkaline character of interstitial mantle fluids. This conclusion is consistent with the analysis of similar equilibria at 15 kbar (Ryabchikov 1980), for which experimental data for both phlogopite+ forsterite + fluid and phlogopite + forsterite + enstatite + spinel + fluid phase assemblages were available (Ryabchikov and Boettcher 1980).

Finally, the comparison of the contrasting behaviour of sodium versus potassium in dense aqueous mantle fluids is also of potential petrological importance. Earlier data by Ryabchikov and Boettcher (1980) demonstrated that the K₂O/H₂O ratios of aqueous fluids co-existing with phlogopite increase at least by a factor of 3 when pressure rises isothermally from 20 to 30 kbar, while the Na concentrations of water-rich fluids interacting with clinopyroxenes are either not affected by pressure or they show an opposite pressure dependence. This contrasting behaviour of the two main alkali elements may be explained by the very high partial density of the jadeitic component in clinopyroxene solid solution. As a result of this behaviour one may assume that during the upward transport of alkaline fluids in the mantle, the major part of potassium may be fixed as phlogopite at deeper levels while sodium would be mainly retained in the fluid phase, and its precipitation would be postponed until the fluid pressure is low enough to reach the upper stability limit of amphibole.

The subsequent loss of water from the fluid due to amphibolization of surrounding mantle rocks must result in the fast fixation of sodium and other non-volatile oxides still remaining in the fluid up to this point. This mechanism would favour a hypothesis that the regions of the mantle anomalously enriched in sodium or potassium, respectively, are spatially separated, with potassium-rich zones being mainly confined to greater depths. The subsequent involvement of such regions in the processes of partial melting may explain the generation of K-rich or of Na-rich magmas. The presence of garnet lherzolite nodules in K-rich basalts and the occurrence of only spinel lherzolite nodules in Na-rich basalts in the regions of young alkali basaltic volcanism in Mongolia (Kepezhinskas 1979) seem to be consistent with the above hypothesis.

Acknowledgements. This work was performed at Institut für Mineralogie, Ruhr-Universität Bochum, while the first author (I.D.R.) was a Visiting Scientist under the auspices of the exchange program between the USSR Academy of Sciences and Deutsche Forschungsgemeinschaft. I.D.R. thanks for the hospitality and for making available research facilities. The help of Dr. P.W. Mirwald in experimental techniques is greatly appreciated. The manuscript was reviewed by T. Sekine, Chicago.

References

- Bell PM, Kalb J (1969) Stability of omphacite in the absence of excess silica. Carnegie Inst Washington Yearb 67:97-98
- Boettcher AL, O'Neil JR (1980) Stable isotope, chemical, and petrographic studies of high-pressure amphiboles and micas: evidence for the metasomatism in the mantle source regions of alkali basalts and kimberlites. Am J Sci 280a: 594–621
- Boyd FR, England JL (1960) Apparatus for phase equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750° C. J Geophys Res 65:741–748
- Eggler DH, Rosenhauer M (1978) Carbon dioxide in silicate melts: II. Solubilities of CO_2 and H_2O in $CaMgSi_2O_6$ (diopside) liquids and vapors at pressures to 40 kb. Am J Sci 278:64–94
- Kepezinskas VV (1979) Cenozoic alkaline basaltoids of Mongolia and deep-seated inclusions (in Russian). Nauka Publishers, Moscow, 312 p

- Mirwald PW, Getting IC, Kennedy GC (1975) Low-friction cell for piston-cylinder high-pressure apparatus. J Geophys Res 80:1519–1525
- Nakamura Y (1974) The system $SiO_2-H_2O-H_2$ at 15 kbar. Carnegie Inst Washington Yearb 73:259-263
- Nakamura Y, Kushiro I (1974) Composition of gas phase in $Mg_2SiO_4-SiO_2-H_2O$ at 15 kbar. Carnegie Inst Washington Yearb 73:255-258
- Ryabchikov ID (1980) On the nature of kimberlitic "magmas" (in Russian). Geol Rudn Mest: 18-26
- Ryabchikov ID, Boettcher AL (1980) Experimental evidence at high pressure for potassic metasomatism in the mantle of the Earth. Am Mineral 65:915–919
- Ryabchikov ID, Green DH, Wall VJ, Brey G (1981) The oxidation state of carbon in the environment of the low velocity zone. Geokhimia: pp 221–232
- Stosch H-G, Seck HA (1980) Geochemistry and mineralogy of two spinel peridodite suites from Dreiser Weiher, West Germany. Geochim Cosmochim Acta 44:457–470
- Wyllie PJ (1979) Magmas and volatile components. Am Mineral 64:469-500

Received September 10, 1981; Accepted January 25, 1982