Pyroxene Stoichiometry and the Breakdown of Omphacite[1]

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Abstract

The breakdown of eclogitic omphacite to pyroxene + plagioclase symplectite cannot proceed in a strictly isochemical manner if all phases are stoichiometric. Analyses of omphacites and their breakdown products show that symplectitization usually involves oxidation of iron in the pyroxene.

Various mechanisms for the breakdown reaction are considered. The assemblage omphacite + breakdown products may in this case act as an oxygen buffer and f_{o_2}, as well as P and T, should be considered as controlling factors for the reaction to proceed.

Introduction

The omphacite of eclogites occurring in gneiss terranes is commonly replaced by a symplectitic intergrowth of diopsidic pyroxene and sodic plagioclase. Eskola (1921) demonstrated that this symplectite was the result of exsolution of the plagioclase components from a jadeitic pyroxene, and suggested that the breakdown resulted from a decrease in pressure and/or increase in temperature. This suggestion has been supported by recent experimental work in the jadeite-diopside system (Kushiro, 1969; Wikstrøm, 1970a).

It follows that the degree of breakdown and the composition of the breakdown products will be a function not only of the original omphacite composition, but also of the *P-T* history of the eclogite. The work of Kushiro (1969) suggests that an omphacite which is uplifted and cooled along a *P-T* gradient less than about 20 bars/degree could retain its jadeite in solution, while heating or an uplift rapid in relation to cooling would result in instability and consequent exsolution of jadeite. The kinetics of the exsolution process relative to cooling and the pressure and temperature at which exsolution begins will also affect the nature of the breakdown products.

The *mechanism* of the exsolution process remains a problem. Exsolution of plagioclase from pyroxene components (jadeite, $NaAlSi_2O_6$; tschermakite $CaAl_2SiO_6$) requires addition of SiO_2. The process can only be isochemical through more complex reactions like:

$$2NaAlSi_2O_6 \rightarrow NaAlSi_3O_8 + NaAlSiO_4 \qquad (1a)$$

$$CaAl_2SiO_6 + NaAlSi_2O_6 \rightarrow CaAl_2Si_2O_8 + NaAlSiO_4 \quad (1b)$$

$$MgAl_2SiO_6 \cdot NaAlSi_2O_6 \rightarrow NaAlSi_3O_8 + MgAl_2O_4 \quad (2a)$$

$$CaAl_2SiO_6 \cdot Mg_2Si_2O_6 \rightarrow CaAl_2Si_2O_8 + Mg_2SiO_4 \quad (2b)$$

where the residual diopside is left out of the equations for simplicity.

It is possible to write more equations than these, but they all involve the appearance of a third subsilicic phase unless the parent omphacite incorporates non-pyroxene components. No such third phase is observed in the symplectite assemblage (A photomicrograph of omphacite breaking down to symplectite has been published by Mysen, 1972, Fig. 6). Microprobe data of the plagioclase suggest that it is stoichiometric (Wikstrøm, 1970b). This situation suggests that either the primary omphacites or the symplectite pyroxenes are non-stoichiometric, or that the exsolution process has involved metasomatic exchange of material between the omphacite and its surroundings.

Symplectitization

Forster (1947) was the first to realize the process of symplectitization was more involved than that proposed by Eskola (1921). He tried to define the exsolution process by determination of the composition and proportion of plagioclase in the symplectite.

He proposed that the exsolution requires oxidation of Fe^{2+} (in omphacite) to Fe^{3+} (in diopside) to maintain charge balance during the loss of Al from the pyroxene.

Vogel (1966) separated and analyzed symplectite from a Spanish eclogite. Recasting this analysis to a pyroxene formula, he found a deficiency of cations relative to six oxygens, and assigned this vacancy to the W (Ca) position of the original omphacite. His proposed breakdown reaction thus became:

$$\square Ca_{1/2}AlSi_2O_6 \cdot NaAlSi_2O_6 \rightarrow NaCa_{1/2}Al_2Si_4O_{12}(An_{33.3}) \quad (3)$$
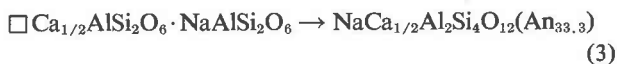
The mechanism proposed requires 33.3 percent An in the plagioclase (Vogel, 1966) whereas microprobe analyses of the plagioclase (Wikstrøm, 1970b; Mysen, 1971) consistently give 10–22 percent An. Thus the proposed mechanism does not seem to solve the problem.

Mao (1971) has demonstrated that pyroxenes on the Jd–Ts join can dissolve SiO_2 at high pressures, so that the pyroxenes approach the Jd–An join. These pyroxenes could, with decreasing *P,* exsolve albite, leaving Ts behind:

$$CaAl_2Si_2O_8 \cdot NaAlSi_2O_6 \rightarrow NaAlSi_3O_8 + CaAl_2SiO_6 \quad (4)$$

However, the primary omphacites contain little Ts and therefore will accept little excess SiO_2 in solution, so this mechanism is probably not important in the breakdown of omphacites.

Similarly, some Al_2SiO_5 in solid solution in the primary omphacite (O'Hara and Yoder, 1967) may give:

$$CaMgSi_2O_6 \cdot NaAlSi_2O_6 \cdot Al_2SiO_5$$
$$\rightarrow NaAlSi_3O_8 + CaAl_2SiO_6 \cdot 1/2 \ Mg_2Si_2O_6 \quad (5)$$

However, the alumina in the omphacite analyses can be accounted for with the tschermakite and the jadeite molecules, and such a solid solution is probably insignificant.

The electron microprobe has made it possible to examine the chemistry of the breakdown process in more detail, through analysis of the omphacite and its breakdown products. Wikstrøm (1970b) obtained such analyses from several Norwegian eclogites, and calculated the Fe^{3+}/Fe^{2+} ratio assuming stoichiometry. He found that many of the symplectite pyroxenes had a calculated Fe^{3+}/Fe^{2+} ratio greater than their parent omphacites. He therefore postulated a metasomatic introduction of oxygen, even in a completely anhydrous example.

Experimental Methods

During the last two years, we have made microprobe analyses of a large number of omphacites and sodic augites and of their anhydrous breakdown products (Griffin, 1971, 1972; Mysen, 1971, 1972). We have calculated the Fe^{3+}/Fe^{2+} ratio of these pyroxenes as suggested by Essene and Fyfe (1967), but with minor modifications. This method *assumes stoichiometry,* and uses the following procedure:

(1) Al^{IV} is added to Si to bring Z = 2.0

(2) All Ti is taken as $CaTiAl_2O_6$(Ti-Di)

(3) The remaining Al^{IV} is taken as Tschermak's molecule, $CaAl_2SiO_6$(Ts)

(4) If $Al^{VI} > Al^{IV}$ after (2), the equation $Na-Fe^{3+} = Al^{VI}-Al^{IV}$ is solved for Fe^{3+}.

(5) The calculation is reiterated until no further change in Fe_2O_3 is possible at the 0.1 percent level.

The calculation is sensitive to errors in SiO_2, but within the limits of the probe analyses and of the chemical determination Fe^{3+}/Fe^{2+} it appears to give good results for normal eclogite pyroxenes. Some examples are given in Table 1. This is in accordance with the results of Mysen (1971) who compiled about fifty published analyses of eclogite clinopyroxene from all over the world, recalculated Fe_2O_3 to FeO and added this amount to the analytical FeO. The new FeO value was used to calculate Fe_2O_3 and FeO. The calculated $Fe^{3+}/Fe^{3+} + Fe^{2+}$ was within 20 percent of the analytical values.

Results

Using this calculation method we obtain results similar to Wikstrøm's (1970b). Sodic augites and omphacites which show no exsolution features generally have low Fe^{3+}/Fe^{2+}. Pyroxenes which have exsolved plagioclase, on the other hand, may show large and variable Fe^{3+}/Fe^{2+}, and this is always higher in a symplectite pyroxene than in the parent omphacite. This is true even in completely anhydrous rocks, in which there is no apparent evidence of metasomatism.

We found it difficult, in the absence of other evidence, to accept that all of the rocks we have examined, as well as most of those studied by Wikstrøm, had been metasomatically oxidized. We were interested especially in several exsolved pyroxenes (diopsides) analyzed by us which appeared to have all iron present as Fe^{3+}. We therefore considered the possibility that this apparent oxidation results from non-stoichiometry plus our calculation procedure.

TABLE 1. ANALYSES OF PYROXENES

SAMPLE Fe³⁺ DET. BY:	7011/4 CORE C.	SYMPL. C.	109 W.C.	C.	2A M.	C.	2E M.	C.
SiO_2	54.9	54.9	53.0	53.0	52.0	52.0	52.3	52.3
TiO_2	0.2	0.4	0.3	0.3	0.1	0.1	0.2	0.2
Al_2O_3	10.4	7.4	8.0	8.0	7.7	7.7	7.7	7.7
Fe_2O_3	0.0	0.5	3.8	2.8	1.3	0.6	0.9	1.1
FeO	3.9	3.5	4.6	5.5	3.8	4.4	4.2	4.0
MnO	0.1	0.1	–	–	0.1	0.1	–	–
MgO	9.2	11.1	10.2	10.2	13.6	13.6	13.2	13.2
CaO	15.9	18.3	15.2	15.2	19.7	19.7	19.4	19.4
Na_2O	5.0	4.0	4.4	4.4	1.8	1.8	2.2	2.2
K_2	–	–	–	–	–	.	–	–
Sum	99.7	99.6	99.5	99.4	100.1	100.0	100.2	100.1
Si	1.967	1.965	1.933	1.938	1.884	1.890	1.900	1.897
Al^{IV}	0.033	0.035	0.067	0.062	0.116	0.110	0.100	0.103
Al^{VI}	0.406	0.280	0.277	0.283	0.213	0.220	0.230	0.226
Ti	0.005	0.011	0.008	0.008	0.003	0.003	0.005	0.005
Fe^{3+}	0.000	0.014	0.104	0.077	0.035	0.017	0.023	0.031
Fe^{2+}	0.117	0.106	0.140	0.168	0.115	0.132	0.130	0.121
Mn	0.003	0.003	–	–	0.003	0.003	–	–
Mg	0.491	0.597	0.555	0.556	0.734	0.737	0.713	0.713
Ca	0.611	0.708	0.594	0.595	0.765	0.767	0.753	0.754
Na	0.347	0.280	0.311	0.312	0.126	0.127	0.155	0.155
K	–	–	–	–	–	–	–	–
X	1.980	1.999	1.989	1.999	1.994	2.000	2.005	2.001
$Fe^{3+}/Fe^{2+}+Fe^{3+}$	–	0.12	0.43	0.31	0.23	0.11	0.15	0.20
Ti-Di	0.5	1.1	0.8	0.8	0.3	0.3	0.5	0.5
Ts	2.3	1.2	5.1	4.7	11.0	10.4	9.0	9.3
Ac	–	1.4	10.4	7.7	3.5	1.7	2.3	3.1
Jd	34.7	26.6	20.7	23.5	9.1	11.0	13.7	12.4
Di + Hd	59.5	69.1	56.1	56.4	70.7	71.2	70.3	70.2
En + Fs	0.9	0.6	6.7	8.0	7.1	7.8	7.0	6.6
Residual Cat.	+2.2	+0.0	+0.2	–1.1	–1.7	–2.4	–1.8	–1.1

SAMPLES:

M.: Mössbauer spectroscopy
W.C.: Wet chemistry
C.: Calculated (see text) from probe analyses
7011/4: Omphacite grain (core) with coarse symplectite (symplect) at rim; Ulsteinvik (Norway) eclogite, probe analyses from Mysen (1972)
109: Sodic augite from garnet-pyroxene layer in anorthosite, Bergen Arcs, Norway (Griffin, 1972)
2A: Clinopyroxene shell in opx-cpx-gnt corona, Bergen Arcs anorthosite. Probe analysis from Griffin (1972) except for CaO, which was redetermined; Mössbauer determination by S. Hafner (per. comm.)
2E: As for 2A.

A deficiency in Si will, in this calculation, be compensated by increased Al^{IV} and decreased Al^{VI}. This in turn will lead to an increase in Tschermak's molecule. Thus in step (4) above, excess Fe^{3+} will be generated to form acmite from the remaining Na. A deficiency in Si relative to 6 oxygens therefore will result in an apparent increase in Fe^{3+}/Fe^{2+}.

The problem can be resolved by wet-chemical analyses of the symplectite pyroxenes, but the very nature of the intergrowths makes necessary purity of material very difficult to obtain. We have tried to get around this difficulty by using some coarse-grained pyroxenes which appear to have exsolved jadeite component without breaking down to symplectite.

Griffin (1972) has described corona structures 3–5 cm in diameter in meta-anorthosite, consisting of orthopyroxene cores surrounded by successive shells of sodic augite and garnet. These structures have evolved from a primary olivine-plagioclase assemblage, during cooling at 8–12 kbar. Microprobe analyses show a considerable drop in the calcium content of the garnet toward the interior of the corona, and the degree of zoning is inversely proportional to the jadeite content of the clinopyroxene in the intermediate corona shell. In some cases a thin zone of andesine appears between this garnet and the clinopyroxene. The concurrent loss of Ca from the garnet and Na from the pyroxene, leading to the formation of the plagioclase, has been interpreted as an effect of slow uplift following deep-seated metamorphism.

We have drilled or chipped out the clinopyroxene from polished slabs of these corona structures. Microchemical determinations of Fe^{2+} were carried out by B. Bruun; precision was estimated to ± 10 percent. Mössbauer determinations of Fe^{3+}/Fe^{2+} were kindly obtained by Dr. S. Hafner. Wet chemical data were also obtained for a sodic augite (from a garnet-clinopyroxene rock) which has not exsolved visible plagioclase (109). All of these pyroxenes contain thin scattered ($<2\%$ modal) orthopyroxene lamellae which are included in the bulk analyses but not in the probe analyses, but the effect of these on the Fe^{3+}/Fe^{2+} will be negligible.

Of the two corona pyroxenes, the one which on other grounds appears to have lost more jadeite (2A) also has the higher oxidation state. Wet chemical analyses of Fe^{3+}/Fe^{2+} in two other corona pyroxenes from the same area (Griffin, 1972) confirm this trend.

Conclusions

Our data, therefore, support the suggestion of Forster (1947) and Wikstrøm (1970b) that the pyroxene stoichiometry may be maintained during jadeite exsolution by oxidation of Fe^{2+} to Fe^{3+}. Of course this mechanism is not the only one. If SiO_2 can be supplied rapidly enough, then the reaction

$$NaAlSi_2O_6 + SiO_2 \rightarrow NaAlSi_3O_8 \qquad (6)$$
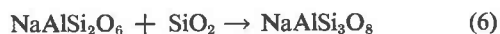
can proceed and leave a stoichiometric unoxidized pyroxene. For instance, Wikstrøm (1970b) gives an analysis of symplectite pyroxene bordering a quartz grain; this pyroxene contains no (calculated) Fe^{3+}.

On the other hand, the symplectititic breakdown of the pyroxenes appears in general to be a rapid process (Mysen, 1972), and diffusive exchange of SiO_2 may not be possible even over short distances within this time span. This may explain why 3/5 of the symplectite pyroxenes from quartz-bearing eclogites analyzed by Wikstrøm (1970b) contain calculated Fe^{3+}. All of those analyzed by Mysen (1971, 1972) have calculated Fe^{3+}/Fe^{2+} higher than the host pyroxene, even though quartz is ubiquitous in the rocks.

The cause of this apparent oxidation is not clear. The symplectites examined by Wikstrøm (1970b) are all from small eclogite lenses, and most contain amphibole in addition to pyroxene + plagioclase. In this case it might seem reasonable to conclude, as Wikstrøm did, that the introduction of an aqueous phase has facilitated oxidation. On the other hand, Mysen and Heier (1972) have described a very large (6 km³) eclogite body which is nearly everywhere free of hydrous minerals. Here the pyroxenes are almost completely symplectitized, with accompanying oxidation of iron in the secondary pyroxene.

We propose that a generalized reaction of the type

Ferrous omphacite + O_2 → ferric augite + plagioclase
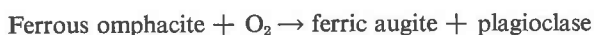
acts as an oxygen buffer, and would be represented by a line (or a band) with positive slope on a f_{o_2}-T diagram. As the eclogite cooled following the peak of metamorphism, the f_{o_2} would remain on this curve, resulting in progressive oxidation of the omphacite and expulsion of jadeite as plagioclase, until all of the omphacite was converted to symplectite. Thus a certain mobility of O_2 is implied. However, the prevailing P, T and f_{o_2} conditions during symplectitization were, in some cases (*e.g.*, Mysen and Heier, 1972), unfavorable for the formation of amphibole and/or mica.

This casts some doubt on the role of P and T driving the reaction. A rise in T will destabilize the omphacite, but will not necessarily produce the observed symplectite mineralogy because of the buffering effect noted above. Decompression of eclogite bodies now on the surface has clearly occurred, and certainly favors breakdown of the omphacite, but provides in itself no means of balancing the breakdown equations.

It seems probable that a combination of uplift and cooling, with associated oxidation, is responsible for most cases of omphacite symplectitization.

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