FRY-N 69-1098

ɴssᴅöʀғғᴇʀ with collaboration of C. W.
rage zur Mineralogie und Petrographie".
ɴɴsᴅöʀғғᴇʀ with collaboration of C. W.
ᴇᴛᴢ.

ᴇɴs with collaboration of F. K. Dʀᴇsᴄʜᴇʀ-
-4 on: C. W. Cᴏʀʀᴇɴs with collaboration
d H. Sᴛᴇɪɴᴍᴇᴛᴢ.

nd Petrographie".

logy and Petrology" / "Beiträge zur Mi-

(including isotope geology), the petrology
ntary rocks, experimental petrology and
ments and their isotopes in the rocks.

utions to Mineralogy and Petrology" are
bers constitute one volume. The price is
ocieties belonging to the "International
ential price of DM 76.80.

arge; additional copies may be purchased

pyright for all languages and countries is
script is accepted for publication. It is a
ted shall have been or will be published

e publishers, no photographic reproduc-
ns of a similar nature may be made of the
ein or of extracts therefrom.

, etc. in this journal, even if not specially
ch names, as defined by the laws affecting
uncontrolled and therefore for the free use

hes Institut der Universität, Lotzestraße 13,

Institut der Universität, Wilhelmstraße 56,

Manchester University, Manchester 13, Great

and Geophysics, University of California,

gen

O. 1780; Telephone (06221) 49101,

3
22001

Springer-Verlag
New York Inc.
175 Fifth Avenue
New York, N.Y. 10010

Contr. Mineral. and Petrol. 24, 1—6 (1969)

Eclogites and Water Pressure

N. Fʀʏ and W. S. Fʏғᴇ
Manchester University, England

Received June 30, 1969

Abstract. Available data on the stability of amphibolites and the basalt-eclogite transition allow an estimate of the stability field of eclogites in wet systems. It appears that if water and load pressures are comparable, eclogites cannot be stable in the crust; the formation of eclogites in the crust requires moderate total pressures and low water pressures. If the reactions forming eclogites occur in essentially dry rocks, their formation may reflect kinetic as well as equilibrium factors.

Introduction

In recent years there has been intense interest in the physical conditions necessary to produce eclogites in the crust of the earth. There is no longer any doubt that omphacite-garnet rocks of approximately basaltic composition can be the product of metamorphism of rocks originally formed at or near the earth's surface.

We shall not attempt here to refer to the various views on the conditions of formation of eclogites but suffice to mention two extremes. Yᴏᴅᴇʀ and Tɪʟʟᴇʏ (1962) studied the melting behaviour and stability of amphibolites in the basalt system under conditions where excess water was present and $P_{\mathrm{H_2O}}$ must be nearly equal to total pressure. As they produced no eclogites and only a wide field of amphibolites up to 10 kb, they concluded that if excess water is present in the basalt system, eclogites are excluded by amphibolites. These experiments at that time could hardly be totally satisfying because pressures were thought to be, in general, too low to form eclogites, even if water had been absent.

Essᴇɴᴇ and Fʏғᴇ (1967) challenged their conclusions on the basis of observations in the eclogite-amphibolite-glaucophane schist terrances of California. There were two reasons for their doubt of the Yᴏᴅᴇʀ and Tɪʟʟᴇʏ conclusions. First, minerals with affinities to eclogites (omphacites-garnets) are frequently found as vein and vug-filling minerals suggesting an ample fluid phase. Second, if we consider the reaction:

$$\text{amphibolite} \rightarrow \text{eclogite} + \text{water}$$
$$A \quad \rightarrow \quad E \quad + \quad W$$

it is clear that at all moderate pressures:

$$V_A \quad > \quad V_E \; + \; V_W$$

and hence the transition $A \rightarrow E$ may occur with increased water pressure.

Essᴇɴᴇ and Fʏғᴇ went further to suggest that as ΔV of the reaction is quite large and negative and that as the amount of water involved is small, ΔS might

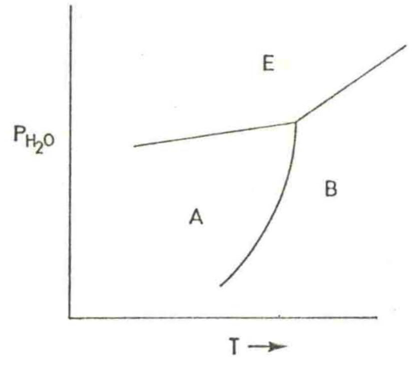

Fig. 1. Form of phase relations between amphibolites (*A*), basalts (*B*) and eclogites (*E*) proposed by ESSENE and FYFE (1967). Melting phenomena have been ignored

also be negative. Hence the phase boundary of the above reaction could have positive slope, even if only at low temperatures, and eclogites could be stable with excess water at low temperatures and moderate pressures. This would lead to a phase diagram as in Fig. 1. Such an $A \rightarrow E$ boundary would be in accord with MIYASHIRO's (1961) well known facies diagram.

The Amphibolite-Eclogite Transition

At the present time, no direct experimental study of the $A \rightarrow E$ boundary is available. However, data is available which indicates that ESSENE and FYFE's conclusion is most improbable.

Firstly, the entropies of amphiboles seem rather low on the additivity model (see FYFE, TURNER and VERHOOGEN, 1958) compared to pyroxenes Thus, if we use the normal approach we might estimate the entropy of tremolite by adding diopside, enstatite, quartz and ice:

$$S(\mathrm{Ca_2Mg_5S_8iO_{22}(OH)_2}) = 2\,S(\mathrm{CaMgSi_2O_6}) + 3\,S(\mathrm{MgSiO_3}) + S(\mathrm{SiO_2}) + S(\mathrm{ice}).$$

This would give:

$$S_{\mathrm{trem}} = 136.54 = 68.4 + 48.66 + 98.8 + 9.6 \text{ e.u.}$$

The observed entropy of tremolite is 131 e.u., considerably lower than the additivity estimate. If this is also true for hornblendes, then ESSENE and FYFE's guessed negative ΔS of $A \rightarrow E + W$, looks unlikely. The boundary between amphibolite and eclogite will therefore be negative in slope and continue to go to increasingly high $P_{\mathrm{H_2O}}$ with lowering of temperature.

More significantly, we now know approximately the positions of the boundaries

$$\begin{array}{lcl} \text{amphibolite (with plagioclase)} & \rightarrow & \text{basalt + water} \\ A & \rightarrow & B + W \end{array} \qquad (1)$$

and:

$$\begin{array}{lcl} \text{basalt} & \rightarrow & \text{eclogite} \\ B & \rightarrow & E \end{array} \qquad (2)$$

Form of phase relations between amphi- (A), basalts (B) and eclogites (E) proposed ENE and Fyfe (1967). Melting phenomena een ignored

ry of the above reaction could have atures, and eclogites could be stable l moderate pressures. This would lead →E boundary would be in accord with ram.

ntal study of the $A \to E$ boundary is ch indicates that Essene and Fyfe's

m rather low on the additivity model) compared to pyroxenes Thus, if we te the entropy of tremolite by adding

$$) + 3\,S(\mathrm{MgSiO_3}) + S(\mathrm{SiO_2}) + S(\mathrm{ice}).$$

$$8.66 + 98.8 + 9.6 \text{ e.u.}$$

e.u., considerably lower than the addi- ornblendes, then Essene and Fyfe's oks unlikely. The boundary between negative in slope and continue to go to mperature.

ximately the positions of the boundaries

clase) → basalt + water

$$\to \quad B \quad + \quad W \qquad (1)$$

→ eclogite

$$\to \quad E \qquad (2)$$

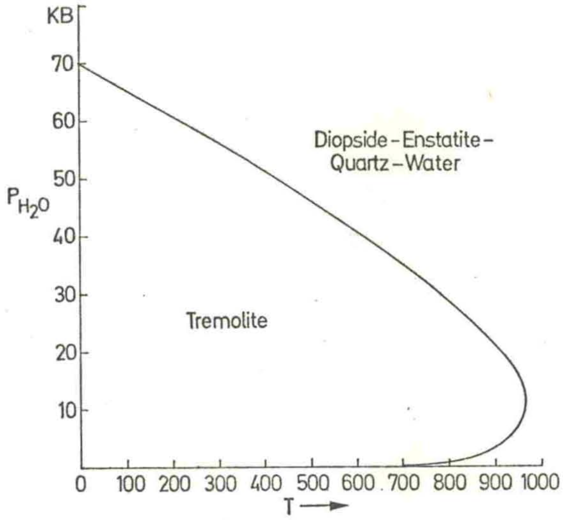

Fig. 2. Form of the vapor pressure curve of tremolite. The numbers must be considered very approximate because of the distance of some extrapolations involved

These boundaries give a fix on the free energies of these separate reactions and hence, by addition, $\Delta G_1 + \Delta G_2$ gives the ΔG_3 of the reaction:

$$A \to E + W.$$

Using data from Green and Ringwood (1966) and Yoder and Tilley (1962); at 900° C, reaction (1) is in equilibrium at about 1 kb (water pressure) and reaction (2) at 15 kb (total pressure). Assuming that the water content of an amphibolite is about 2% and densities of 3.42 (E), 2.96 (B) and 2.99 (A), then based on 100 g of amphibolite, $\Delta G_{(3)}$ is about 1350 cal at 900° C and 1 kb. From this figure and thermodynamic data for water of Sharp (1962), reaction (3) will be in equilibrium at about 35 kb (water pressure) at 900° C. The estimate is very approximate but can hardly be in error by as much as 15 kb which would be necessary to accomodate Essene and Fyfe's positive boundary.

It is interesting to note that for the comparable reaction

$$\text{tremolite} \to 2 \text{ diopside} + 3 \text{ enstatite} + \text{quartz} + \text{water}$$

the phase diagram must be about as shown in Fig. 2. This type of diagram is probably general for all known mineral hydrates if we consider lower crust and upper mantle presures, and obviously has bearing on water in the deeper portions of th earth.

In Fig. 3 we give a schematic diagram for some phase relations in the basalt water system.

Line X-Y is the basalt-eclogite transition line of Green and Ringwood.

Curve C-D is the amphibolite-basalt transition of Tilley and Yoder.

Line D-Z is the calculated amphibolite-eclogite transition.

Curve F-G-H is the beginning of melting curve of basalt with excess water.

Portion F-G is based on Yoder and Tilley; portion G-H is based on data of Lambert and Wyllie (1968).

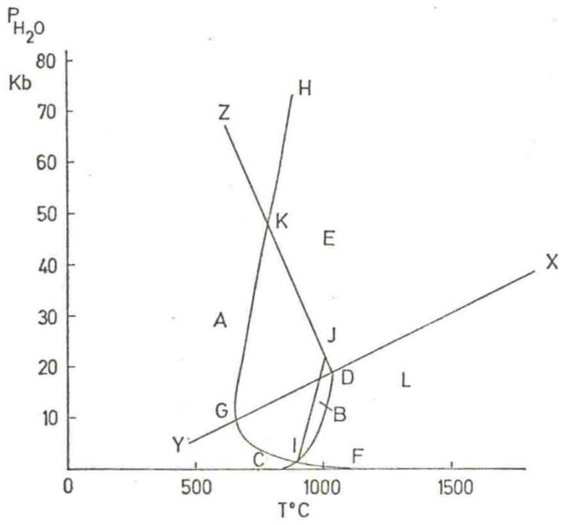

Fig. 3. An approximate diagram showing the region of stability of eclogites (region bounded by *Z-K-H*) in a system with excess water. For further details see text

Line *I-J* is a curve for the reaction: amphibolite-melt without excess water, a reaction which must have positive slope.

The field of amphibolite lies below the curves *C-I-J-K-Z*. Partial melting will occur in the field bounded by *F-G-K-H* is excess water is present. If excess water is not present, then liquids will form from amphibolites to the right of the *F-I-J-K-H*. Eclogite and water, without melt, will exist in the area bounded by *Z-K-H*. It is clear that this region is not within any normal crust.

All the simple boundaries shown must be highly smeared by solid or liquid solution phenomena. It should be noted that the amphibolite-eclogite boundary (*D-K-Z*) represents a metastable equilibrium between eclogite and plagioclase amphibolite. As the latter will transform to more stable plagioclase-free amphibolite somewhere above *X-Y*, amphibolite will restrict the eclogite field even further than shown.

Our conclusion is, that crustal eclogites form in dry environments where $P_{\mathrm{Load}} \gg P_{\mathrm{H_2O}} \cdot P_{\mathrm{Load}}$ need not be very high according to the line *X-Y*. $P_{\mathrm{H_2O}}$ is likely to be determined and buffered by incomplete hydration reactions.

It perhaps seems feasible that the necessary conditions for eclogite formation could be generated by suitable water buffers in the environment. Thus, one might ask the question: is the not uncommon association of eclogites with partially serpentinized ultrabasic rocks due to a low partial pressure of water generated by the buffer system

$$\text{pyroxene} + \text{olivine} + \text{water} = \text{serpentine ?}$$

For such a buffer system to lower water pressure to an extent that amphiboles are dehydrated requires that their vapour pressure should be lower than that of hornblendes at the same temperature. As amphiboles tend to have very low vapor pressures and hence high thermal stability relative to almost all common hydrates, it appears unlikely that this is a common way by which eclogites could be formed. In fact, if water could diffuse freely, eclogites would be expected to

Fig. 3. An approximate diagram showing the region of stability of eclogites (region bounded by Z-K-H) in a system with excess water. For further details see text

hibolite-melt without excess water, a

urves C-I-J-K-Z. Partial melting will
xcess water is present. If excess water
mphibolites to the right of the F-I-J-
l exist in the area bounded by Z-K-H.
y normal crust.
be highly smeared by solid or liquid
at the amphibolite-eclogite boundary
um between eclogite and plagioclase
to more stable plagioclase-free amphi-
e will restrict the eclogite field even

rm in dry environments where $P_{\mathrm{Load}} \gg$
ng to the line X-Y. $P_{\mathrm{H_2O}}$ is likely to
hydration reactions.
sary conditions for eclogite formation
s in the environment. Thus, one might
association of eclogites with partially
w partial pressure of water generated

water = serpentine ?

essure to an extent that amphiboles are
ressure should be lower than that of
s amphiboles tend to have very low
tability relative to almost all common
common way by which eclogites could
freely, eclogites would be expected to

dehydrate serpentinites to give the stable combination amphibolite plus peridotite. It is worth noting that partial melting can lead to diminished water pressure but this aspect of the problem will be discussed elsewhere.

Two factors alter the position of the dehydration curves mentioned. The first is the effect of increasing P_{Load} for constant $P_{\mathrm{H_2O}}$. This cuts back the field of high volume hydrates, such as serpentine, but hardly effects the breakdown of amphiboles. Thus serpentinite buffer reactions are moved even further into the field of amphibole stability. The second factor is the substitution of eclogite for the normal basaltic dehydration products of amphibolite. This increases the vapour pressure of amphibolite breakdown, but not to the extent required to cut the dehydration curves of minerals like serpentine.

It thus appears that the following points can be noted regarding crustal eclogites:

(1) Although the basalt-eclogite equilibrium curve is not well known at low temperatures, for dry rocks eclogite can be assumed to be a stable low pressure and temperature assemblage. Whether such assemblages occur then becomes a problem of all the factors involved in solid state reaction kinetics.

(2) If partially wet assemblages are depressed in the crust, we would anticipate a primary reaction producing appropriate hydrate mineralogy, followed by eclogitisation. Such a mixture of hydrous and anhydrous minerals could be in equilibrium, or may react to an equilibrium assemblage of minerals of intermediate water content.

Many problems remain unsolved. Why, for instance, are some eclogitic rocks so curious in composition that they appear to be metasomatic rocks ? Metasomatism generally implies activity of an ample fluid phase. We suggest that some of these metasomatic processes may occur prior to the total destruction of the basalt mineralogy, and are followed by the draining of free water by hydration reactions. Sealing of the rocks by increased load pressure could then be followed by eclogite formation. The metasomatism may thus be part of early diagenetic or zeolite facies reactions.

ESSENE and FYFE (1967) suggested that some eclogites in the low temperature regime of California might be formed in the thermal aureoles of deep basic intrusives. This must still be considered a possibility for such heating of dry basaltic material might well be sufficient to overcome the kinetic barrier of eclogite formation in this generally cold environment.

And what of the eclogite facies ? Does it exist in the crust ? We prefer to leave these questions to those concerned with nomenclature. It would be premature to eliminate the facies or to restrict it to mantle inclusions in volcanic rocks until we understand these processes better. The important thing now is that we recognise wet and dry equivalents of metamorphism at the same P_{Load} and T or metamorphism where total pressure and water pressure are significantly different.

References

ESSENE, E. J.. and W. S. FYFE: Omphacite in Californian metamorphic rocks. Contrib. Mineral. Petrol. **15**, 1—23 (1967).

FYFE, W. S., F. J. TURNER, and J. VERHOOGEN: Metamorphic reactions and metamorphic facies. Geol. Soc. Am. Mem. **73** (1958).

Green, D. H., and A. E. Ringwood: An experimental investigation of the gabbro to eclogite transformation and its petrological applications. Dept. Geophysics and Geochemistry, Australian National University, Pub. 444, 1—59 (1966).

Lambert, I. B., and P. J. Wyllie: Stability of hornblende and a model for the low velocity zone. Nature **219**, 1240—1241 (1968).

Miyashiro, A.: Evolution of metamorphic belts. J. Petrol. **2**, 277—311 (1961).

Sharp, W. E.: The thermodynamic functions for water in the range — 10 to 1000° C and 1 to 250,000 bars. Univ. of California Lawrence Radiation Lab. Pub. 7118 (1962).

Yoder, H. S., and C. E. Tilley: Origin of basalt magmas: An experimental study of natural and synthetic rock systems. J. Petrol. **3**, 342—532 (1962).

Prof. Dr. W. S. Fyfe
Department of Geology, Manchester University
Manchester, England