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AN INVESTIGATION OF EXPERIMENTAL AND NATURAL HIGH-PRESSURE ASSEMBLAGES FROM THE SESIA ZONE, WESTERN ALPS, ITALY.

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This thesis is an examination of the equilibration of natural and synthetic assemblages under the conditions associated with blueschist and eclogite facies metamorphism. The natural assemblages are from the Sesia Zone of the Italian Western Alps and the synthetic assemblages are experimental, quartz-bearing biopyroxene assemblages found in the system Na₂O-MgO-Al₂O₃-SiO₂-H₂O (NMASH) at high pressures. Natural high-pressure amphiboles from the Sesia Zone are either glaucophanitic (from quartz-bearing mafic and non-mafic assemblages) or barroisitic (found in some quartz-absent mafic assemblages). Glaucophanitic amphiboles appear to be ordered along the NaAlCa₁Mg₁ exchange vector to near end-member glaucophane composition (xA/H₂O = 0.89 to 0.96) with further displacement occurring along the Fe³⁺Al⁻¹ and Fe²⁺Mg⁻¹ exchange vectors. A marked preference of M2 sites in the amphiboles for Mg relative to Fe²⁺ is demonstrated with the use of data from occurrences of coexisting amphiboles. This preference gives rise to a coupling effect of the NaAlCa₁Mg₁ and Fe²⁺Mg₁ exchange vectors. In addition, restriction of Al⁴⁺ to M2 sites prohibits the existence of a significant tschermak component (AlOAlMg₁Si₁⁻¹) in glaucophanitic amphiboles, but not in calcic amphiboles. This gives rise to further coupling of the Fe³⁺Al⁻¹ and NaAlCa₁Mg₁ solid solutions.

Garnets from all assemblages in the Sesia Zone exhibit a depletion of grossular component from garnet core to rim with respect to the
almandine and pyrope components. A model is developed for the formation of atoll structures in the garnets in which rapid nucleation and unidirectional growth result in the distinctive textures found in some samples from the Sesia Zone.

The high-pressure pyroxenes vary in composition from Jd$_{15}$, found in marbles, to Jd$_{95}$ found in some quartzofeldspathic rocks and in metamorphosed acid pegmatites. The majority of the pyroxenes are omphacites and in some samples two pyroxenes apparently coexist.

The tschermak content of high-pressure phengites is highly dependent upon the host assemblage. The most phengitic micas occur in the quartz-absent metabasites and the least phengitic micas are found in the metapelites. Paragonites exhibit little compositional variation.

Element partitioning among the high-pressure phases is strongly influenced by the ordering behavior of the phases. Octahedral ordering in both the amphiboles and the pyroxenes results in $X_{\text{Amp}}^{\text{Amp}}$ being greater than $X_{\text{Pyx}}^{\text{Fe}}$ in glaucophane-omphacite pairs and less than $X_{\text{Pyx}}^{\text{Fe}}$ in glaucophane-jadeite pairs. In addition, $X_{\text{Amp}}^{\text{Fe}}$ is less than $X_{\text{Pyx}}^{\text{Fe}}$ in glaucophane-omphacite pairs and greater than $X_{\text{Pyx}}^{\text{Fe}}$ in barroisite-omphacite pairs.

Garnet-clinopyroxene geothermometry has been applied to numerous rock types from the blueschist and eclogite terrain of the Sesia zone in the Western Alps and discrepancies in apparent temperatures of up to 800°C have been found. The variations in temperature determinations
suggest that there is substantial deviation from ideal behavior of the garnet-clinopyroxene equilibria in certain assemblages. Assemblages containing jadellite pyroxenes rather than omphacitic or diopsidic pyroxenes yield very low \( K_D = \frac{X_{\text{Fe}}^{\text{Gar}}}{X_{\text{Mg}}^{\text{Gar}}} \cdot \frac{X_{\text{Fe}}^{\text{Pyx}}}{X_{\text{Mg}}^{\text{Pyx}}} \) values and correspondingly high temperatures. The garnets coexisting with the high-Na pyroxenes have similar compositions to those coexisting with omphacitic pyroxenes. Departure from ideal behavior of these garnets is likely to be minor and is accommodated in the formulation of the geothermometer. Examples of numerous coexisting garnet-clinopyroxene pairs indicate that there is no obvious relationship of \( K_D \) with the jadellite content in pyroxenes with jadellite content less than \( \approx 70\% \), but at higher jadellite values, \( K_D \) varies inversely with the jadellite content. The dependence of \( K_D \) upon the jadellite content in the high-Na pyroxenes is believed to be due to preference of M2 sites for Fe\(^{2+}\) in the enstatite-jadellite substitution \((\text{Fe}^{2+}\text{MgNa}_1\text{Al}_1)\) in the pyroxenes. This substitution is usually very limited and has no demonstrable effect upon \( X_{\text{Fe}}^{\text{Pyx}} \) when the M1(Fe\(^{2+}\)Mg) content of the pyroxenes is high as in omphacitic and diopsidic pyroxenes. However, when the M1(Fe\(^{2+}\)Mg) is low as in jadellite pyroxenes, the non-ideality of the enstatite type exchange \((\text{MgMgNa}_1\text{Al}_1)\) has a marked effect on \( X_{\text{Fe}}^{\text{Pyx}} \) and consequently on any garnet-clinopyroxene calculations.

In the Sesia Zone of the Western Alps, Italy, early Alpine blueschist to eclogite metamorphism of rocks of quartzofeldspathic composition has produced the same high-pressure assemblage of; quartz, Na-pyroxene, Na-amphibole, paragonite, phengite, zoisite, garnet, magnetite, sphene and Fe-sulphide (= the "QFS assemblage") over an area
> 150 Km². Relative gradients in pressure and temperature over this region are reflected in the variations in mineral chemistries of the individual phases of the quartzofeldspathic assemblage through continuous reactions and mineralogical discontinuities do not occur in the "QFS assemblage" of this region. Increases in the jadeite content (NaAlCa₁Mg₁) of the pyroxenes (Xjadi₄₈ to Xjadi₉₃) and in the glaucophane content of the amphiboles (Xgla₈₉ to Xgla₉₆) occur from the southwest to the northeast of the region studied and analysis of coexisting garnets and pyroxenes indicate that the compositional variation of amphiboles and pyroxenes is associated with a decrease in the grossular component of the coexisting garnet. Zoned pyroxenes and garnets, together with the regional trends in mineral chemistries suggest the following pressure-sensitive, continuous reactions among pyroxene, garnet, amphibole, paragonite, and zolsite in the presence of excess quartz:

\[
\text{zolsite + glaucophane + NaAlCa₁Mg₁ + MgCa₁ + H₂O} \rightleftharpoons \text{omphacite + paragonite}
\]

and

\[
\text{zolsite + glaucophane + NaAlCa₁Mg₁ + MgCa₁ + H₂O} \rightleftharpoons \text{garnet + paragonite}
\]

Amphibole, zolsite and the more jadelitic pyroxene constitute the high-pressure assemblage. Chemographic constraints allow the positioning in pressure/temperature space of the compositional isopleths of the continuous reactions involving these phases. The low dP/dT slope (~20 bars/°C)of these isopleths causes the continuous reactions to be useful
for geobarometric calculations at pressures above the absolute breakdown of albite to jadeite plus quartz. In addition the pseudobinary loops for the other continuous reactions which are potentially useful geobarometers and involve either the NaAlCa\textsubscript{1-Mg\textsubscript{1}} exchange or the MgCa\textsubscript{1} exchange are calculated. Comparison of mineral chemistry with the isopleths yields a relative barometric scheme for the locations studied. With these barometric observations, it is possible to show that the PT path which the Sesia body travelled towards the final recorded state was one of increasing pressure. Other blueschist and eclogite occurrences which contain rocks of quartzofeldspathic composition are also examined.

Mineral relations in pelitic rocks having undergone regional metamorphism in greenschist and amphibolite facies are reasonably well understood in terms of reactions in the felsic model system, KNASH, and the mafic system + muscovite, KFMASH, where biotite is the only mixed "felsic-mafic" phase. However, in blueschist and eclogite metamorphism albite and chlorite become unstable relative to the mixed felsic-mafic phase, glaucophane, and a sodic pyroxene (plus quartz) may coexist with AFM phases. The appearance of sodic amphibole or pyroxene in high-pressure, low-temperature metamorphism indicates greater mineralogical similarities of pelitic rocks to mafic (and carbonate) rocks than are found in lower pressure facies series.

Existing petrogenetic grids of pelitic rocks in the greenschist and amphibolite facies can be extended into high-pressure conditions through an examination of the discontinuous reactions relating chloritoid-chlorite-talc-kyanite-garnet together with amphibole,
pyroxene and mica.

Mafic rocks from the Sesla Zone are represented by quartz-present glaucophanites and quartz-absent metabasites. No mineralogical characteristics indicative of reaction history have been found in the glaucophanite assemblage which consists of glaucophane, omphacite, garnet, paragonite, phengite, zoisite, quartz, dolomite, calcite, rutile and Fe-sulfides. In the quartz-absent metabasites in which carbonate does not exist, the presence or absence of amphibole may be shown to be a function of the Ca content of the bulk rock. Those compositions richer in Ca have zoisite and no amphibole coexisting with a more calcic garnet, omphacite, paragonite and phengite. In some quartz-absent samples the reaction of omphacite with $\text{H}_2\text{O}$ and $\text{CO}_2$ yields dolomite, calcite and glaucophanitic rims on the barroisitic amphiboles.

The meta-quartz diorite (MQD) found in the Central Sesla Zone occurs with non-foliated lenses enclosed within foliated material of the same composition. The differing degree of deformation has yielded distinctly different metamorphic assemblages, with the non-foliated MQD exhibiting relict igneous textures, the preservation of biotite and jadeite-quartz pseudomorphs after plagioclase. In contrast the foliated MOD contains no relict igneous textures and has the assemblage omphacite-quartz-paragonite-phengite-garnet-zoisite. The omphacitic pyroxene composition is believed to represent the near-equilibrium pyroxene composition for the whole rock composition at high-pressures. The jadeite in the non-foliated MQD is preserved due to the lack of chemical communication throughout the rock in the absence of penetrative
deformation.

The behavior of an amphibole in the NMASH system and its relationships with sodium micas have been examined experimentally at high pressures. A sodium mica of composition intermediate between wonesite and preiswerkite is produced from low pressures to at least 28 kbar at 750°C from differing bulk compositions in water excess experiments. Minor amphibole has been found in water excess runs, but a C2/m amphibole approaching glaucophane composition exists only in water undersaturated systems. This amphibole coexists with quartz in runs on glaucophane composition from ≈18 kbar to ≈24 kbar at 700°C. In this pressure range the amphibole is displaced from ideal glaucophane composition by substitution of Na⁴⁺Al⁴⁺ for Si and Mg⁴⁺Mg²⁺ for Na⁴⁺Mg²⁺. Above ≈24 kbar the A-site of this amphibole empties, and the coexistence of amphibole-jadeite-quartz between ≈24 kbar and ≈28 kbar is observed. Above ≈28 kbar talc forms while the modal amount of amphibole decreases. Tight buffering of the amphibole to ideal glaucophane composition does not occur and small amounts of NaAlSi₄ substitution are found in the talc. This is reflected modally in the persistence of quartz with talc, jadeite and amphibole. Amphibole and quartz continue to decrease in modal proportions with rising pressures, but remain in the run products of synthesis experiments to at least 35 kbar at 750°C.

On the basis of the experimental data, a 298.15°C molar volume of 262.2 cm³ and an entropy value of 529.6 Joules/°K/gfw have been calculated for the synthetic amphibole. A comparison of the synthetic amphibole with natural glaucophanes suggests similarities in cation
substitutions on all sites. Examination of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} fractionation trends among natural, glaucophane-like amphiboles and coexisting phases permits qualitative description of equilibria shifts due to compositional variation.
Zusammenfassung

Die Untersuchungen an natürlichen und synthetischen Mineralparagenesen können wie folgt zusammengefasst werden:

1) Bei den experimentellen Bedingungen von $P = 10-35$ Kb und $T = 500-800^\circ C$ ist glaukophanartiger Amphibol im System $Na_2O-MgO-Al_2O_3-SiO_2-H_2O$ (NMASH) in Gegenwart einer von Wasser Phase nicht stabil. An seine Stelle tritt Na-reicher Glimmer. Glaukophanartiger Amphibol, mit untergeordneter $NaAlSi_4$ und $MgMgNa_{1.5}Al_{1.5}$ Substitution, tritt nur im $H_2O$-untersättigten Teil des Systems NMASH auf.

2) Die Verteilung der Hauptelemente auf die koexistierenden Phasen natürlicher eklogitischer Paragenesen wird signifikant beeinflusst durch Ordnungsphänomene in Amphibolen und Pyroxenen. Ordnung von Fe$^{2+}$ und Mg auf den Oktahederräumen von Klinopyroxen erklärt die beobachtete Abnahme von $K_D$ (Gar/Cpx) und die scheinbare Zunahme der Aquilibrierungstemperatur mit steigendem Jadeltiegel im Pyroxen.

3) Die Art des chemischen Zonierungsdruck der Pyroxene und Granate weist auf eine Zunahme des Drucks während der Metamorphose hin. Die Aquilibrierungsdrucke waren im NE der Sesia Zone höher als im
4) Phasenbeziehungen in hochdruckmetamorphen pelitischen Gesteinen lassen sich durch Änderungen langs des \(\text{AlAlMg_1Si_1-}\) Vektors und durch \(\text{Fe}^{3+}\text{Al}_1\) sowie \(\text{Fe}^{2+}\text{Mg}_1\)-Austausche charakterisieren.

5) Der chemische Zonarbau der Pyroxene in den Metaquarzditloriten der zentralen Sesia Zone weist darauf hin, dass in diesem Gestein vor seiner Deformation und teilreisen Rekristallisation Phasenungleichgewichte und Ungleichgewichtsstrukturen auftraten.