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Metamorphic geology - II

P–T Pseudosection

1. Definition and Fundamental Concept

- ✓ A P–T pseudosection is an equilibrium phase diagram calculated for a specified bulk-rock composition over a selected range of pressure and temperature.
- ✓ It predicts the stable mineral assemblage expected at every pressure-temperature condition within the calculated range.
- ✓ Each field of a pseudosection represents a particular equilibrium mineral assemblage appropriate to the chosen bulk composition.
- ✓ Unlike a conventional petrogenetic grid, a pseudosection is composition-specific and therefore provides a direct framework for interpreting the metamorphic evolution of an individual rock.
- ✓ P–T pseudosections are also termed equilibrium assemblage diagrams because their fields represent calculated equilibrium phase assemblages.

2. Principle of Construction

- ✓ Construction of a pseudosection is based on calculation of the mineral assemblage having the lowest total Gibbs free energy at each pressure-temperature condition.
- ✓ The calculation requires the bulk chemical composition of the rock, an internally consistent thermodynamic dataset and suitable activity-composition models for solid-solution minerals.
- ✓ Pressure and temperature are varied systematically while the effective bulk composition is held constant.
- ✓ The stable phase assemblage is calculated repeatedly throughout the selected P–T range.
- ✓ Boundaries between adjacent fields mark conditions at which one or more phases appear, disappear or undergo a change in equilibrium relations.

3. Thermodynamic Basis

- ✓ The thermodynamic foundation of pseudosection calculation is the principle of Gibbs free-energy minimization.
- ✓ At equilibrium, the stable mineral assemblage is the combination of phases that minimizes the total Gibbs free energy of the system at the specified pressure, temperature and composition.
- ✓ Competing assemblages may possess different Gibbs free energies, but only the minimum-energy assemblage represents stable equilibrium.
- ✓ Changes in pressure and temperature modify the relative Gibbs free energies of the possible phases and consequently alter the stable assemblage.
- ✓ A pseudosection is therefore a graphical representation of calculated equilibrium states of a particular bulk composition.

4. Importance of Bulk-Rock Composition

- ✓ Bulk-rock composition is a fundamental control on pseudosection topology because mineral stability depends on the chemical components available within the system.
- ✓ Two rocks subjected to identical pressure and temperature may develop different mineral assemblages if their bulk compositions differ.

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- ✓ The analysed whole-rock composition is commonly used as the starting composition for pseudosection calculation.
 - ✓ Major components such as SiO_2 , Al_2O_3 , FeO , MgO , CaO , Na_2O and K_2O strongly influence the calculated mineral assemblages.
 - ✓ Consequently, a pseudosection calculated for one rock should not be applied quantitatively to a chemically different sample.

5. Effective Bulk Composition

- ✓ The effective bulk composition is the composition of the chemical domain that actually participates in equilibrium at a particular stage of metamorphism.
- ✓ It may differ from the measured whole-rock composition if some minerals become chemically isolated from the reacting system.
- ✓ Growth of compositionally zoned porphyroblasts can progressively remove chemical components from the reactive matrix.
- ✓ Melt loss, fluid infiltration and metasomatism may also modify the effective composition during metamorphism.
- ✓ Correct estimation of effective bulk composition is therefore one of the most important requirements for reliable pseudosection modelling.

6. Choice of Chemical System

- ✓ Natural metamorphic rocks contain many chemical components, but pseudosection calculations are performed within a defined model chemical system.
- ✓ Pelitic rocks are commonly modelled using systems containing potassium, iron, magnesium, aluminium, silicon and hydrogen, with additional sodium, calcium, titanium, manganese and oxygen where required.
- ✓ The selected chemical system must contain the components necessary to represent the important minerals observed in the rock.
- ✓ Exclusion of a significant component may suppress a mineral phase or alter calculated mineral stability.
- ✓ Increasing the number of components generally improves geological realism but also increases thermodynamic complexity.

7. Model Phases

- ✓ A pseudosection calculation requires specification of the mineral, fluid and melt phases that are permitted to occur.
- ✓ The selected phases should be appropriate to the rock type and the pressure-temperature range under investigation.
- ✓ Pelitic calculations may include garnet, biotite, chlorite, muscovite, staurolite, cordierite, feldspar, the Al_2SiO_5 polymorphs, quartz, fluid and melt.
- ✓ Mafic pseudosections require a different set of phases, commonly including amphibole, pyroxene, garnet, plagioclase and related minerals.
- ✓ Omission of a geologically important phase may produce an incorrect calculated topology.

8. Activity–Composition Models

- ✓ Most metamorphic minerals are multicomponent solid solutions rather than chemically pure end members.
- ✓ Activity-composition models describe the relationship between mineral composition and thermodynamic activity within these solid solutions.
- ✓ Such models are essential for minerals including garnet, biotite, amphibole, pyroxene, feldspar and chlorite.

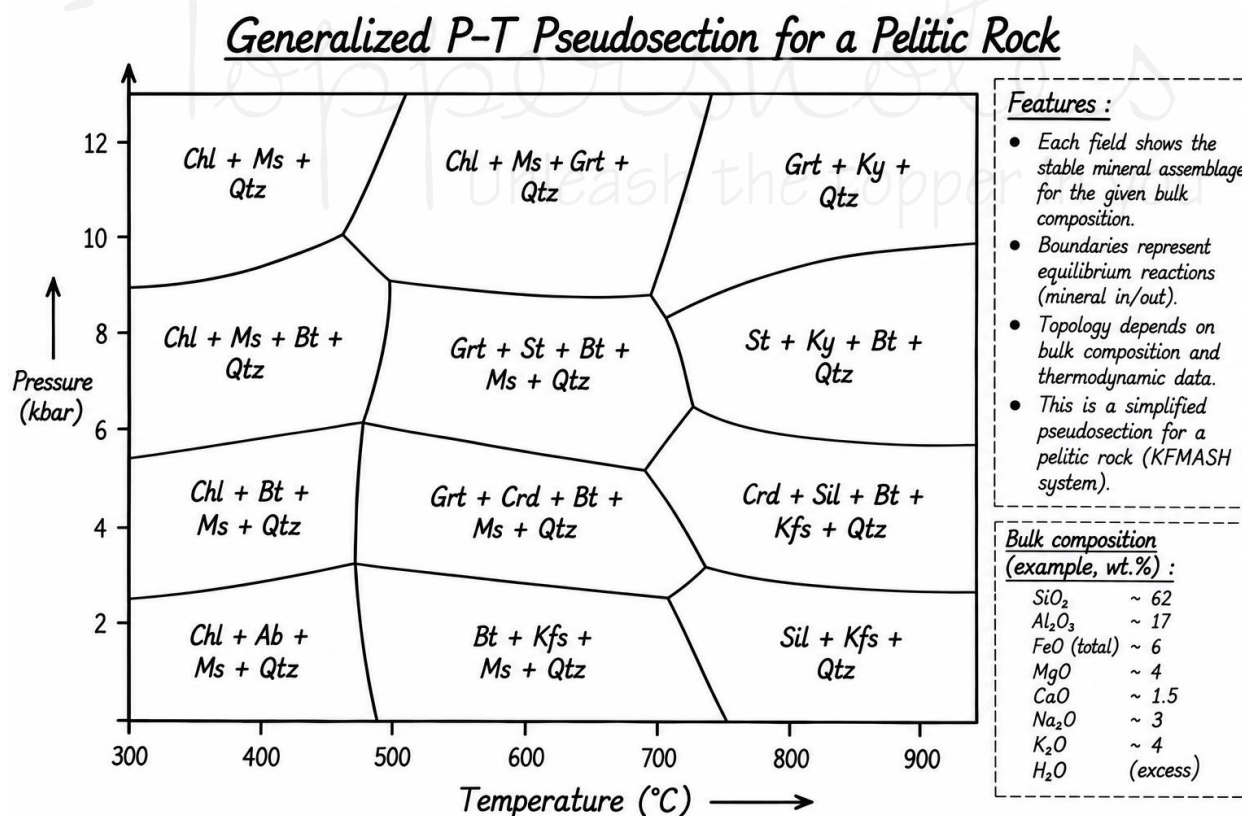
- ✓ The calculated positions of phase boundaries and mineral compositions depend partly upon the quality of the adopted activity-composition models.
- ✓ Improvement of these models has been a major factor in the development of quantitative pseudosection analysis.

9. Thermodynamic Dataset

- ✓ Pseudosection calculations require internally consistent thermodynamic data for all end-member phases included in the model.
- ✓ These data include properties such as enthalpy, entropy, molar volume and heat capacity.
- ✓ Internal consistency allows different mineral equilibria to be compared within the same thermodynamic framework.
- ✓ Uncertainties in the thermodynamic properties of individual phases can influence calculated stability boundaries.
- ✓ Quantitative interpretation should therefore recognize that pseudosection boundaries possess finite thermodynamic uncertainty.

10. P–T Space

- ✓ In a P–T pseudosection, temperature is conventionally plotted on the horizontal axis and pressure on the vertical axis.
- ✓ The selected pressure-temperature range should encompass the metamorphic conditions expected for the sample.
- ✓ Low-grade, high-grade or high-pressure rocks may require substantially different ranges of calculation.
- ✓ The calculated P–T space is subdivided into numerous mineral-assemblage fields.
- ✓ The arrangement of these fields constitutes the topology of the pseudosection.



11. Assemblage Fields

- ✓ Each field within a pseudosection represents a stable equilibrium mineral assemblage for the specified bulk composition.

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- ✓ Adjacent fields generally differ by the appearance or disappearance of one phase.
 - ✓ Large fields indicate assemblages stable over relatively broad ranges of pressure and temperature.
 - ✓ Narrow fields may represent assemblages stable only over restricted conditions and can be particularly important for precise P–T constraints.
 - ✓ Identification of the observed natural assemblage allows the possible metamorphic conditions to be restricted to the corresponding calculated field.

12. Field Boundaries

- ✓ Boundaries between assemblage fields mark equilibrium changes in phase stability.
- ✓ Crossing a boundary commonly causes one phase to appear or disappear from the stable assemblage.
- ✓ In multicomponent systems containing solid solutions, phase compositions may change continuously as the boundary is approached.
- ✓ Field boundaries are therefore calculated equilibrium relationships rather than direct representations of the spatial isograds observed in metamorphic terrains.
- ✓ Natural reaction overstepping may cause mineral appearance to occur beyond the theoretical equilibrium boundary.

13. Variance and Pseudosection Fields

- ✓ The variance of an assemblage describes the number of intensive variables that can change independently while the equilibrium assemblage remains stable.
- ✓ High-variance assemblages generally occupy relatively large fields within a pseudosection.
- ✓ Lower-variance assemblages tend to occupy narrower fields, lines or special intersections.
- ✓ In natural multicomponent systems, solid solutions substantially increase the range over which particular assemblages can remain stable.
- ✓ Variance therefore contributes directly to the geometry and dimensionality of pseudosection fields.

14. Mineral-In Boundaries

- ✓ A mineral-in boundary marks the calculated pressure-temperature conditions at which a mineral first becomes stable for the specified bulk composition.
- ✓ Crossing such a boundary during prograde metamorphism may produce the first stable occurrence of the new mineral.
- ✓ Garnet-in, staurolite-in and biotite-in boundaries are important examples in pelitic metamorphic modelling.
- ✓ The actual appearance of a mineral in a natural rock may occur later than the equilibrium prediction because nucleation requires a finite thermodynamic driving force.
- ✓ Mineral-in boundaries should therefore be interpreted as equilibrium limits rather than exact field isograds.

15. Mineral-Out Boundaries

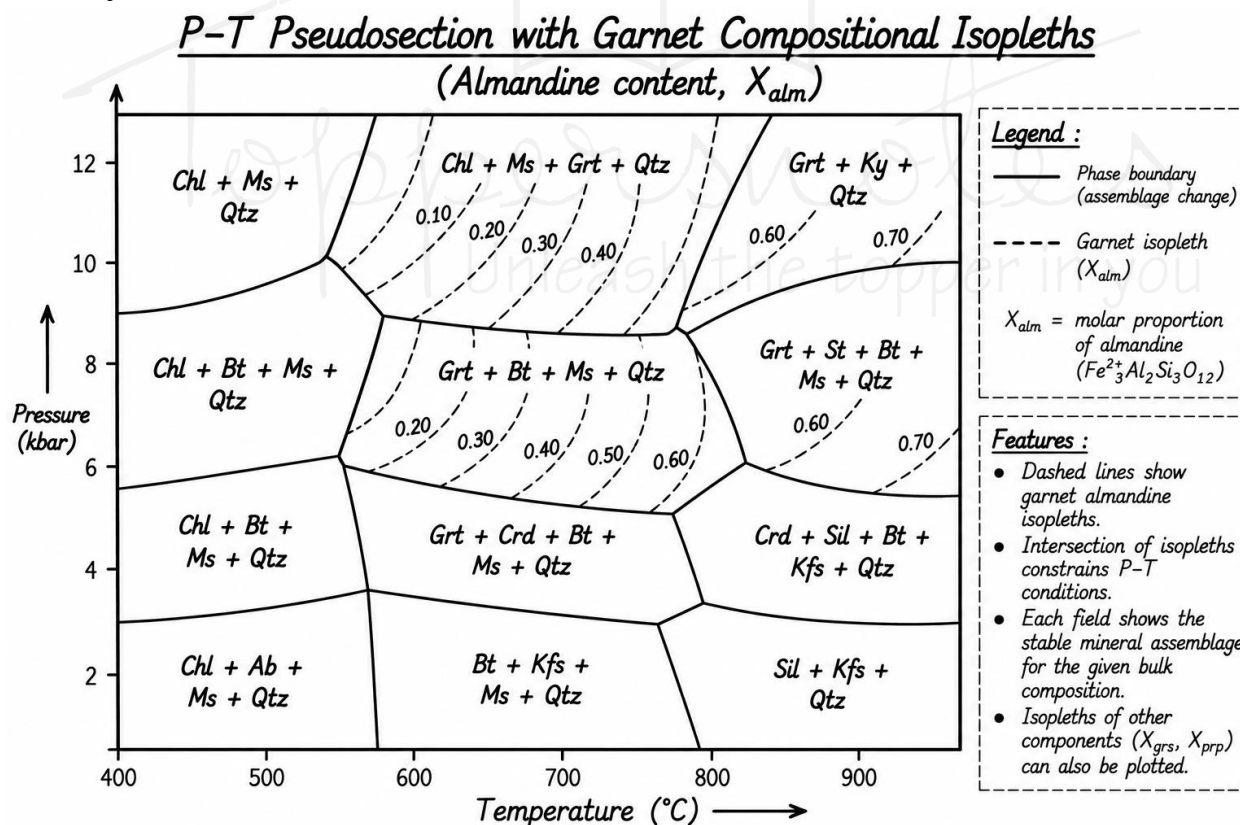
- ✓ A mineral-out boundary marks conditions at which a previously stable mineral disappears from the equilibrium assemblage.
 - ✓ Such boundaries commonly correspond to mineral-consuming net-transfer reactions.
 - ✓ Chlorite-out, staurolite-out and muscovite-out relations are important in progressive pelitic metamorphism.
 - ✓ A mineral may survive metastably beyond its calculated out-boundary if reaction kinetics are sluggish.
 - ✓ Textural evidence is therefore necessary to establish whether a preserved mineral belongs to the equilibrium assemblage or represents a relict phase.
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16. Mineral Assemblage Matching

- ✓ The first stage of applying a pseudosection to a natural rock is comparison of the observed mineral assemblage with the calculated assemblage fields.
- ✓ The field containing the complete observed equilibrium assemblage provides an initial estimate of metamorphic pressure-temperature conditions.
- ✓ Relict, retrograde and accessory phases must be distinguished from minerals that genuinely belonged to the equilibrium assemblage.
- ✓ Petrographic relationships are therefore essential before quantitative pseudosection interpretation.
- ✓ Phase presence alone may provide a broad P–T field, while mineral compositions can subsequently refine the estimate.

17. Compositional Isopleths

- ✓ An isopleth is a contour joining pressure-temperature conditions at which a specified compositional parameter of a mineral has the same calculated value.
- ✓ Garnet isopleths commonly represent parameters such as grossular, pyrope, almandine or spessartine content.
- ✓ Biotite, chlorite, amphibole and other solid-solution minerals may also provide useful compositional isopleths.
- ✓ Intersections between independently constrained isopleths can restrict metamorphic conditions to a much smaller region than assemblage matching alone.
- ✓ Isopleth thermobarometry is one of the most powerful applications of modern pseudosection analysis.



18. Garnet Isopleth Thermobarometry

- ✓ Garnet is particularly useful in pseudosection analysis because its composition responds systematically to changing pressure, temperature and matrix composition.
- ✓ Core compositions may preserve conditions associated with early garnet growth if subsequent intracrystalline diffusion has been limited.

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- ✓ Rim compositions may represent later stages of growth closer to peak metamorphic conditions.
 - ✓ Calculated compositional isopleths can be compared with measured garnet compositions to estimate the conditions at which different portions of the crystal developed.
 - ✓ This approach can reconstruct portions of a prograde P–T path when zoning has been preserved.

19. Mineral-Mode Isopleths

- ✓ Pseudosections can also show contours representing the calculated modal proportion of a mineral.
- ✓ These contours are commonly termed mode isopleths.
- ✓ Comparison of calculated and observed mineral proportions may provide additional constraints on pressure-temperature conditions.
- ✓ Changes in predicted garnet mode can be particularly useful for interpreting progressive garnet growth.
- ✓ Modal information must nevertheless be applied carefully because deformation, segregation, melt loss and incomplete reaction can modify the observed proportions of minerals.

20. Mineral Composition and P–T Evolution

- ✓ Mineral compositions commonly vary systematically across a pseudosection even where the mineral assemblage remains unchanged.
- ✓ Such compositional variation records the continuous redistribution of chemical components among coexisting phases.
- ✓ Zoned minerals may therefore preserve information about movement through a single assemblage field as well as crossings of field boundaries.
- ✓ Comparison between observed zoning and calculated compositional changes can constrain the direction of metamorphic evolution.

21. Prograde P–T Path Reconstruction

- ✓ A prograde P–T path can be reconstructed by combining mineral assemblages, compositional zoning and calculated pseudosection relationships.
- ✓ Successive portions of a zoned porphyroblast may preserve compositions corresponding to different stages of metamorphic growth.
- ✓ Garnet cores commonly retain information from earlier stages, whereas mantle and rim compositions may record progressively higher-grade conditions.
- ✓ Matching these compositions with calculated isopleths permits successive segments of the prograde metamorphic trajectory to be constrained.
- ✓ Reliable reconstruction requires preservation of primary growth zoning and petrographic evidence that the analysed compositions belong to the interpreted metamorphic stages.

22. Peak Metamorphic Conditions

- ✓ Peak metamorphic conditions can be constrained by identifying the assemblage and mineral compositions that represent the highest-grade equilibrium stage preserved in the rock.
- ✓ The observed peak assemblage is first matched with the appropriate stability field on the pseudosection.
- ✓ Mineral compositional isopleths can then provide more precise constraints within that field.
- ✓ Peak temperature and maximum pressure need not have occurred simultaneously, and pseudosection results must therefore be interpreted in conjunction with the reconstructed P–T path.
- ✓ Textural evidence is essential for distinguishing peak minerals from earlier inclusions and later retrograde phases.

23. Retrograde P–T Evolution

- ✓ Pseudosections can also be used to interpret mineralogical changes produced during decompression and cooling.

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- ✓ Reaction rims, symplectites and replacement textures may indicate that the rock entered new assemblage fields during retrogression.
 - ✓ Retrograde equilibrium is commonly incomplete because decreasing temperature reduces diffusion and reaction rates.
 - ✓ Fluid availability strongly influences the extent to which retrograde assemblages develop.
 - ✓ Consequently, the preserved retrograde mineralogy may represent only partial equilibration along the retrograde P–T path.

24. Garnet Fractionation

- ✓ Growth of garnet can progressively modify the composition of the reactive matrix because elements incorporated into the garnet interior may no longer participate effectively in subsequent equilibrium.
- ✓ Manganese, iron, magnesium and calcium can be selectively incorporated into garnet during different stages of growth.
- ✓ If the garnet core becomes chemically isolated, the effective bulk composition available to later reactions differs from the original whole-rock composition.
- ✓ This process is commonly termed garnet fractionation.
- ✓ Fractionation must be considered when modelling strongly zoned garnet-bearing rocks because a single fixed whole-rock composition may not accurately reproduce the entire prograde history.

25. Fractionation-Corrected Pseudosections

- ✓ A fractionation-corrected pseudosection attempts to account for progressive chemical isolation of material incorporated into growing porphyroblasts.
- ✓ The composition removed into earlier garnet growth is subtracted from the reactive bulk composition before later stages are modelled.
- ✓ Successive calculations may therefore use progressively modified effective bulk compositions.
- ✓ This approach can improve agreement between calculated and observed garnet zoning.
- ✓ Its reliability depends upon accurate estimation of mineral modes, compositions and the degree to which earlier crystal domains remained isolated from later equilibration.

26. Role of Mn in Garnet Stability

- ✓ Manganese can exert a strong influence on the calculated stability of garnet in pelitic rocks.
- ✓ Spessartine component commonly stabilizes garnet at lower metamorphic grades than would be predicted in a manganese-free chemical system.
- ✓ Exclusion of Mn from the model may therefore shift the calculated garnet-in boundary toward higher-grade conditions.
- ✓ Mn is particularly important when modelling the earliest stages of garnet nucleation and growth.
- ✓ Appropriate chemical systems for garnet-bearing pelites should therefore include manganese where its concentration is petrologically significant.

27. Role of Fe³⁺ and Oxidation State

- ✓ The oxidation state of iron can influence calculated phase equilibria because ferric and ferrous iron enter different minerals in different proportions.
- ✓ Treating all iron as Fe²⁺ may be inappropriate for rocks containing significant Fe³⁺.
- ✓ Ferric iron can affect the stability of minerals such as epidote, magnetite, hematite, amphibole and some silicate solid solutions.
- ✓ The assumed oxidation state may consequently alter pseudosection topology and calculated mineral compositions.
- ✓ Redox state should therefore be considered when it materially affects the mineral assemblage of the rock.

28. Role of H₂O

- ✓ Water is a major control on metamorphic phase equilibria because it participates directly in hydration, dehydration and melting reactions.
- ✓ A water-saturated calculation assumes that sufficient water is available to maintain a free aqueous fluid under the relevant conditions.
- ✓ Natural rocks may instead become water-undersaturated after progressive dehydration reactions consume or expel fluid.
- ✓ The amount of available water strongly influences the stability of hydrous minerals and the temperature at which partial melting begins.
- ✓ The assumed water content must therefore be appropriate to the metamorphic history being modelled.

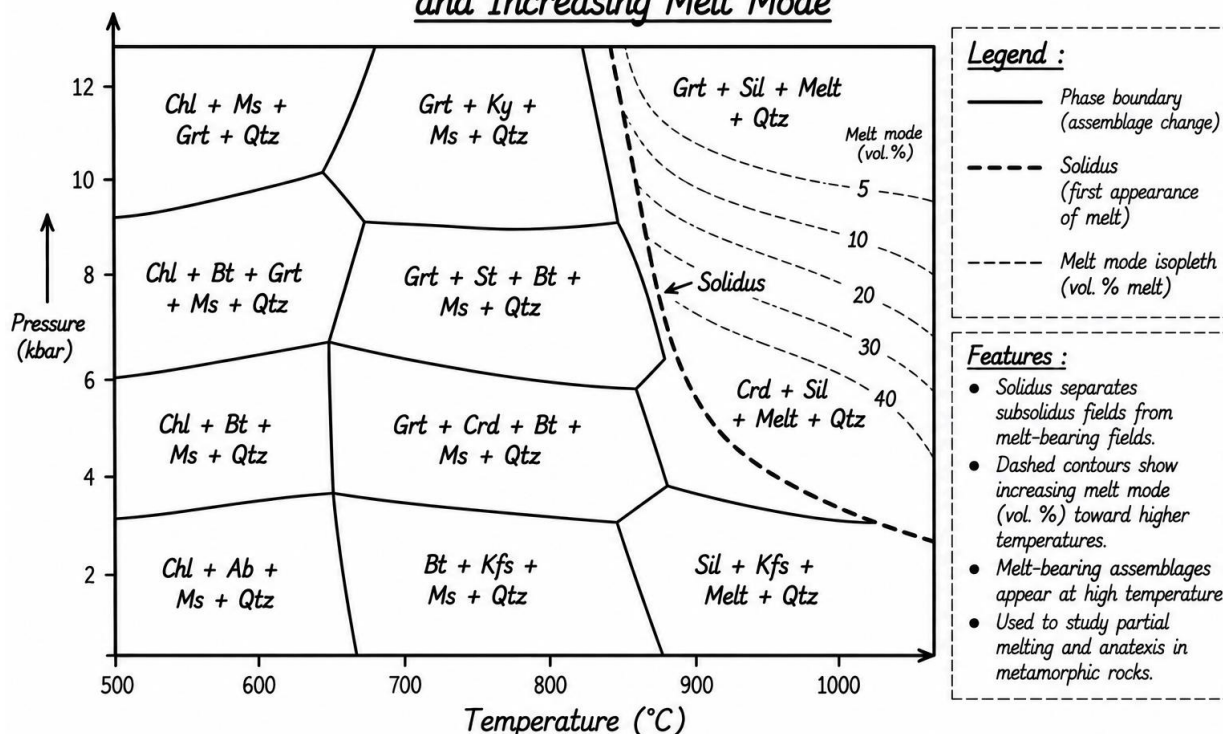
29. Fluid-Saturated and Fluid-Undersaturated Conditions

- ✓ Under fluid-saturated conditions, a free fluid phase is stable and its chemical potential is constrained by the imposed fluid composition.
- ✓ Under fluid-undersaturated conditions, the system contains insufficient volatile material to maintain a free fluid phase throughout the entire P–T range.
- ✓ Hydrous minerals may consequently remain stable to different conditions in fluid-limited rocks.
- ✓ Fluid saturation also strongly influences melting reactions because water lowers the temperature at which silicate melting can occur.
- ✓ Interpretation of pseudosections must therefore distinguish clearly between fluid-present and fluid-absent conditions.

30. Pseudosections and Partial Melting

- ✓ At sufficiently high temperature, pseudosections can include silicate melt as an equilibrium phase.
- ✓ The calculated appearance of melt defines the solidus appropriate to the chosen bulk composition and volatile content.
- ✓ With increasing temperature, the predicted proportion and composition of melt may change progressively.
- ✓ Melt-producing reactions commonly involve the breakdown of hydrous minerals such as muscovite or biotite.
- ✓ High-temperature pseudosections are therefore particularly valuable for investigating the transition from metamorphism to anatexis.

P–T Pseudosection Showing Solidus, Melt-bearing Fields and Increasing Melt Mode



31. Melt Loss and Effective Bulk Composition

- ✓ Once melt forms, it may migrate away from its source region and thereby remove chemical components from the residual rock.
- ✓ Melt loss changes the effective bulk composition of the residue and can alter subsequent mineral equilibria.
- ✓ A pseudosection calculated using the original pre-melting composition may therefore become inappropriate after substantial melt extraction.
- ✓ Modelling high-grade migmatites may require sequential calculations that account for changing residual composition.
- ✓ Melt loss is consequently one of the major complications in pseudosection modelling of high-temperature metamorphic rocks.

32. Pseudosections for Pelitic Rocks

- ✓ Pelitic rocks are widely used for pseudosection analysis because they contain numerous pressure- and temperature-sensitive minerals.
- ✓ Their assemblages may include chlorite, biotite, garnet, staurolite, cordierite, muscovite, feldspar and the Al_2SiO_5 polymorphs.
- ✓ Changes in these phases provide strong constraints on progressive metamorphism.
- ✓ Garnet zoning and Al_2SiO_5 stability are particularly useful when combined with calculated assemblage fields and compositional isopleths.
- ✓ Pelitic pseudosections therefore provide detailed information about regional metamorphic P–T evolution.

33. Pseudosections for Mafic Rocks

- ✓ Mafic rocks can also be modelled using pseudosections constructed in chemical systems appropriate to basaltic compositions.
- ✓ Important phases may include plagioclase, amphibole, clinopyroxene, orthopyroxene, garnet, epidote and quartz.
- ✓ Their relative stability provides constraints from greenschist- and amphibolite-facies conditions to granulite- and eclogite-facies metamorphism.
- ✓ High-pressure mafic pseudosections are particularly useful for examining the progressive stabilization of garnet and omphacitic clinopyroxene.
- ✓ Appropriate treatment of ferric iron and water may be especially important in mafic systems.

34. Pseudosections for High-Pressure Rocks

- ✓ Pseudosection modelling provides a powerful method for reconstructing the evolution of blueschist- and eclogite-facies rocks.
- ✓ High-pressure assemblages may contain garnet, omphacite, glaucophane, lawsonite, epidote, phengite and related phases depending upon composition and conditions.
- ✓ Mineral compositional isopleths can help constrain the pressure-temperature conditions of growth of high-pressure minerals.
- ✓ Inclusion assemblages preserved within garnet may record earlier stages of subduction-related metamorphism.
- ✓ Integration of these observations can provide detailed constraints on burial and exhumation paths.

35. Pseudosections and Reaction Textures

- ✓ Reaction textures provide essential evidence for determining which calculated pseudosection fields correspond to actual stages of rock evolution.

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- ✓ Mineral inclusions may identify earlier assemblages, whereas reaction rims and symplectites may record later transformations.
 - ✓ Textures establish the relative chronological order of mineral growth and breakdown.
 - ✓ This sequence can be compared with the succession of fields predicted along a proposed P–T path.
 - ✓ Pseudosection interpretation without petrographic control may incorrectly combine minerals that were never in equilibrium simultaneously.

36. Pseudosection versus Petrogenetic Grid

- ✓ A petrogenetic grid presents reaction boundaries that are generally applicable to a defined chemical system, whereas a pseudosection is calculated for one specified bulk composition.
- ✓ Petrogenetic grids emphasize reaction topology and the relationships among important metamorphic equilibria.
- ✓ Pseudosections predict the complete stable assemblage for the chosen composition within each calculated P–T field.
- ✓ Mineral compositions and modal proportions can also be contoured on pseudosections.
- ✓ Pseudosections therefore provide more composition-specific information, while petrogenetic grids remain valuable for understanding general reaction relationships.

37. Pseudosection versus Conventional Phase Diagram

- ✓ Conventional phase diagrams may describe phase relations in relatively simple systems or represent generalized mineral stability relationships.
- ✓ A pseudosection is a particular section through a multicomponent compositional system at a fixed bulk composition.
- ✓ Only assemblages accessible to that specified composition are represented.
- ✓ This restriction greatly simplifies the complex phase relationships of a multicomponent natural rock into a two-dimensional pressure-temperature diagram.
- ✓ The term pseudosection therefore reflects the fact that the diagram represents a restricted compositional section through a much larger phase-equilibrium space.

38. Sources of Uncertainty

- ✓ Uncertainty in pseudosection modelling arises from bulk-composition measurements, thermodynamic datasets, activity-composition models and assumptions concerning volatile content and oxidation state.
- ✓ Uncertainty may also result from the selection or omission of model phases.
- ✓ Effective bulk composition can change during porphyroblast growth, fluid-rock interaction or melt extraction.
- ✓ Natural rocks may fail to attain complete equilibrium because of kinetic limitations.
- ✓ Calculated boundaries should therefore be treated as thermodynamic estimates rather than infinitely precise natural reaction conditions.

39. Limitations of Pseudosection Modelling

- ✓ Pseudosections represent equilibrium predictions and cannot independently determine whether equilibrium was actually attained in a natural rock.
- ✓ Metastable minerals, reaction overstepping and sluggish diffusion may produce assemblages that differ from the calculated stable state.
- ✓ A single whole-rock composition may be inappropriate where the rock contains chemically isolated reaction domains.
- ✓ Fluid infiltration, metasomatism and melt loss may invalidate the assumption of constant bulk composition.
- ✓ Reliable interpretation therefore requires integration of pseudosection calculations with petrography, mineral chemistry, reaction textures and geological context.

40. Petrological Significance

- ✓ P–T pseudosections provide one of the most powerful quantitative methods for interpreting metamorphic mineral equilibria in natural multicomponent rocks.
- ✓ Their principal strength lies in calculating phase relations specifically for the bulk composition of the investigated sample.
- ✓ Assemblage fields constrain the broad stability range, whereas mineral compositional and modal isopleths can provide substantially finer pressure-temperature resolution.
- ✓ Zoned porphyroblasts can be combined with pseudosections to reconstruct progressive stages of metamorphic growth.
- ✓ Consideration of effective bulk composition, fluid availability, oxidation state, mineral fractionation and melt loss is essential for advanced applications.

Geothermobarometry

1. Definition and Fundamental Concept

- ✓ Geothermobarometry is the quantitative estimation of the pressure and temperature at which a metamorphic mineral assemblage approached or attained chemical equilibrium.
- ✓ A geothermometer is primarily sensitive to temperature, whereas a geobarometer is primarily sensitive to pressure.
- ✓ The method is based on experimentally or thermodynamically calibrated relationships between mineral compositions, mineral reactions and metamorphic P–T conditions.

2. Basis of Geothermometry

- ✓ Geothermometry commonly utilizes temperature-sensitive exchange of chemical components between coexisting minerals.
- ✓ The equilibrium distribution of an element between two minerals is expressed by a distribution coefficient (K_D).
- ✓ Because element partitioning is temperature dependent, the measured compositions of equilibrium mineral pairs can be converted into an estimate of equilibration temperature.
- ✓ Reliable temperatures require minerals that were chemically equilibrated during the same metamorphic stage.

3. Distribution Coefficient

- ✓ The distribution coefficient expresses the relative partitioning of selected elements between two coexisting mineral phases.
- ✓ Fe–Mg exchange is especially important because Fe^{2+} and Mg^{2+} substitute readily in many ferromagnesian minerals.
- ✓ For a mineral pair A and B, an Fe–Mg distribution coefficient may be represented as:
$$K_D = (\text{Fe/Mg})_A / (\text{Fe/Mg})_B$$
- ✓ The temperature dependence of this equilibrium forms the basis of several widely used exchange geothermometers.

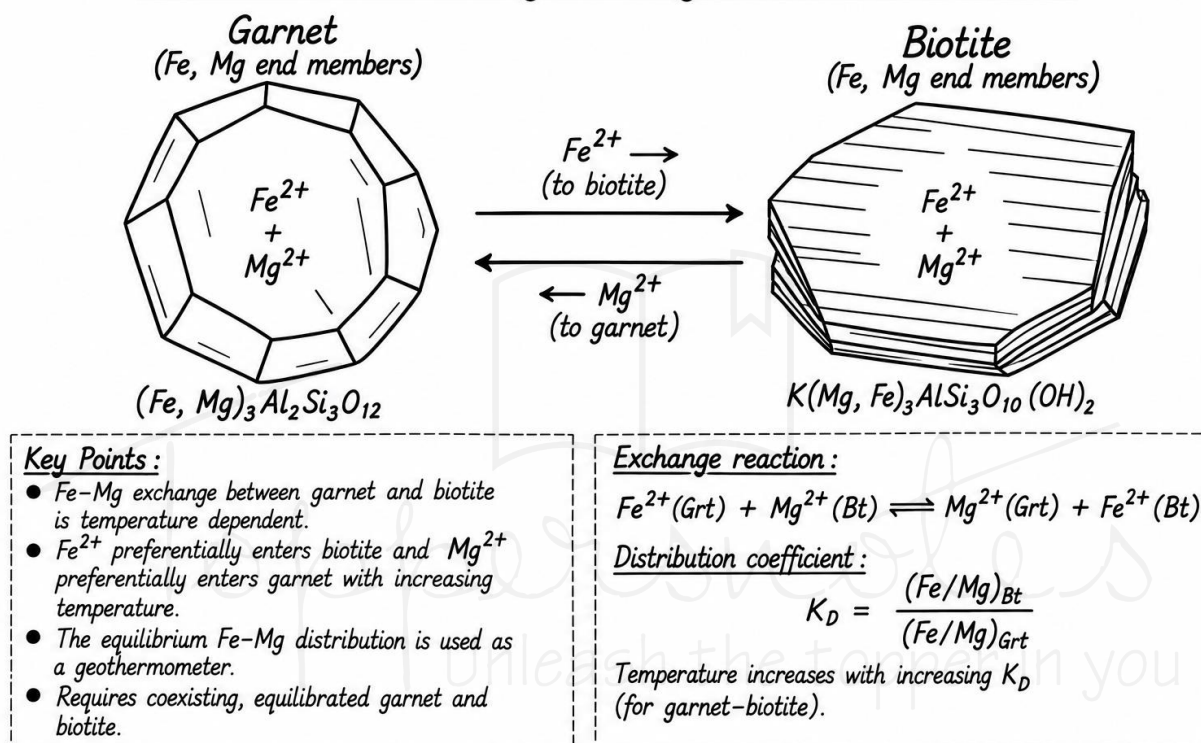
4. Exchange Reactions

- ✓ Exchange reactions redistribute elements between coexisting minerals without necessarily producing or consuming the minerals themselves.
- ✓ Fe–Mg exchange between garnet and biotite is a classic example of a temperature-sensitive metamorphic equilibrium.
- ✓ The equilibrium constant of an exchange reaction changes systematically with temperature and can therefore be calibrated as a geothermometer.
- ✓ Exchange thermometers are most reliable when the analysed mineral domains preserve equilibrium compositions.

5. Garnet–Biotite Geothermometer

- ✓ The garnet–biotite thermometer is one of the most widely used geothermometers for pelitic metamorphic rocks.
- ✓ It is based principally on the temperature-dependent distribution of Fe^{2+} and Mg between coexisting garnet and biotite.
- ✓ With increasing temperature, the equilibrium Fe–Mg partitioning between these minerals changes predictably.
- ✓ The thermometer is commonly applied to schists and gneisses containing texturally equilibrated garnet and biotite.
- ✓ Retrograde Fe–Mg exchange or inappropriate selection of garnet core and rim compositions may significantly modify the calculated temperature.

Garnet–Biotite Fe–Mg Exchange (Geothermometer)



6. Other Exchange Geothermometers

- ✓ Fe–Mg exchange between garnet and clinopyroxene is particularly useful in high-grade and high-pressure metamorphic rocks.
- ✓ Garnet–orthopyroxene exchange can be applied to granulite-facies assemblages.
- ✓ Mineral pairs used for geothermometry must coexist in equilibrium and possess compositions appropriate to the calibration being applied.
- ✓ The choice of thermometer therefore depends strongly on rock type and mineral assemblage.

7. Solvus Geothermometry

- ✓ Solvus geothermometry is based on the temperature-dependent mutual solubility of components between coexisting mineral phases.
- ✓ At high temperature, solid solutions commonly accommodate greater amounts of substituting components than at lower temperature.
- ✓ The compositions of coexisting phases can therefore provide an estimate of their equilibration temperature.
- ✓ Two-feldspar thermometry is an important example in which the compositions of coexisting alkali feldspar and plagioclase are used to estimate temperature.

8. Reaction-Based Geothermometry

- ✓ Some metamorphic reactions possess equilibrium boundaries that are strongly temperature dependent.
- ✓ If the relevant equilibrium assemblage and mineral compositions are known, the calibrated reaction can constrain metamorphic temperature.
- ✓ Reaction-based thermometry complements exchange and solvus thermometers and is particularly useful where suitable mineral pairs are absent.

9. Basis of Geobarometry

- ✓ Geobarometry estimates metamorphic pressure from mineral equilibria that are strongly sensitive to pressure.
- ✓ Pressure-sensitive reactions commonly involve a significant change in the molar volume of the participating mineral assemblage.
- ✓ The pressure dependence of Gibbs free energy is related to volume, so reactions with substantial volume changes provide useful pressure constraints.
- ✓ Mineral compositions participating in these equilibria are used in calibrated expressions to calculate pressure.

10. Net-Transfer Reactions

- ✓ Many geobarometers are based on net-transfer reactions in which minerals are produced and consumed as equilibrium conditions change.
- ✓ Such reactions differ from simple exchange reactions because they alter the proportions or identities of the participating phases.
- ✓ Net-transfer equilibria are particularly useful as geobarometers when the reaction has a strong pressure dependence.
- ✓ Correct identification of the equilibrium mineral assemblage is essential before applying a net-transfer barometer.

11. Garnet–Al₂SiO₅–Plagioclase–Quartz Barometer

- ✓ The garnet–Al₂SiO₅–plagioclase–quartz equilibrium is an important pressure-sensitive relationship in suitable pelitic metamorphic rocks.
- ✓ It is commonly abbreviated as the GASP barometer.
- ✓ The equilibrium involves garnet, an Al₂SiO₅ polymorph, plagioclase and quartz.
- ✓ Its pressure sensitivity makes it useful for estimating metamorphic pressure where the required assemblage occurs in equilibrium.
- ✓ Accurate application requires appropriate mineral compositions and correct identification of the stable Al₂SiO₅ polymorph.

12. Garnet–Clinopyroxene–Plagioclase–Quartz Barometry

- ✓ Equilibria involving garnet, clinopyroxene, plagioclase and quartz can provide pressure estimates in appropriate mafic and high-grade metamorphic rocks.
- ✓ Their pressure sensitivity results from compositional and volumetric changes associated with the relevant net-transfer reactions.
- ✓ These barometers are useful only within the compositional and P–T ranges for which their calibrations are valid.

13. Al-in-Hornblende Barometry

- ✓ Aluminium content in hornblende can show a systematic relationship with pressure in suitable calc-alkaline mineral assemblages.
- ✓ Empirical calibrations have therefore been developed in which total aluminium in hornblende is used as a pressure indicator.
- ✓ Its application requires the appropriate equilibrium assemblage and should not be extended indiscriminately to rocks outside the calibration conditions.

14. Thermodynamic Calibration

- ✓ A thermodynamic calibration derives the relationship between mineral equilibrium and P–T conditions using thermodynamic properties of the participating phases.

- ✓ Equilibrium constants, activities and standard-state thermodynamic data are incorporated into the calibration.
- ✓ Such calibrations provide a theoretical basis for relating measured mineral compositions to pressure and temperature.

15. Experimental Calibration

- ✓ Experimental calibration is based on laboratory determination of mineral equilibrium under controlled pressure and temperature.
- ✓ Mineral compositions obtained from experiments are used to establish the relationship between chemical partitioning and P–T conditions.
- ✓ Experimental calibrations are most reliable within the pressure, temperature and compositional ranges investigated experimentally.

16. Empirical Calibration

- ✓ Empirical calibrations are derived by relating mineral compositions to independently constrained metamorphic conditions from natural or experimental systems.
- ✓ Their accuracy depends upon the quality and range of the dataset used for calibration.
- ✓ Extrapolation far beyond the original calibration range may produce unreliable P–T estimates.

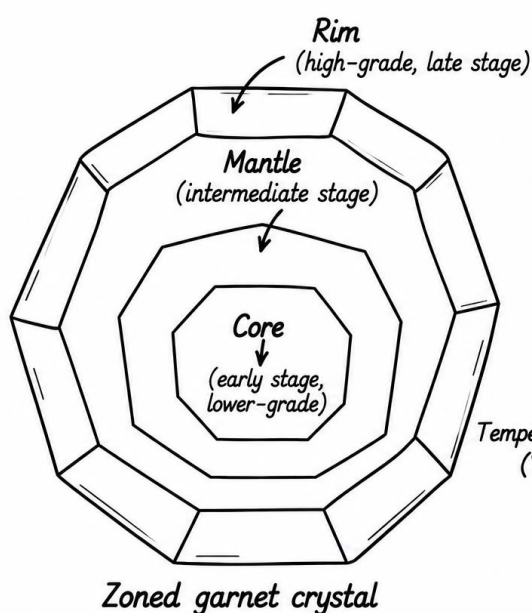
17. Mineral Equilibrium and Textural Control

- ✓ Geothermobarometry assumes that the analysed minerals or mineral domains represent an equilibrium assemblage.
- ✓ Petrographic textures must therefore be examined before selecting mineral analyses for calculation.
- ✓ Mineral inclusions, cores, rims and retrograde reaction products may represent different stages of metamorphic evolution.
- ✓ Analyses from minerals that did not coexist in equilibrium should not be combined in a single thermobarometric calculation.

18. Mineral Zoning and Choice of Analysis

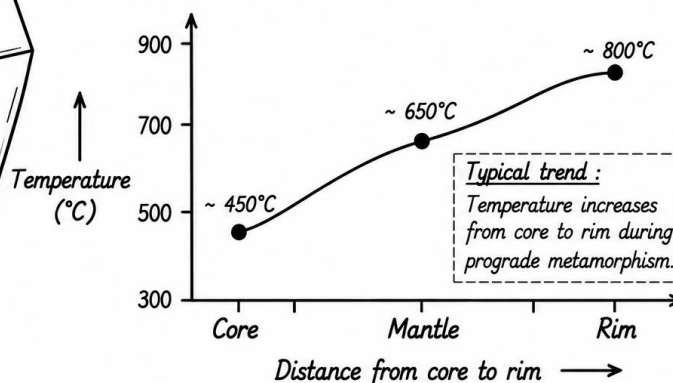
- ✓ Compositionally zoned minerals can preserve different stages of metamorphic growth.
- ✓ Garnet cores may preserve earlier prograde compositions, whereas rims may record later equilibration closer to peak conditions.
- ✓ Diffusion and retrograde exchange may modify original compositions, particularly near grain boundaries and mineral rims.
- ✓ Selection of appropriate mineral domains is therefore essential for meaningful geothermobarometric results.

Zoned Garnet and Its Use in Geothermobarometry



Significance :

- Garnet commonly shows compositional zoning.
- Core preserves early prograde conditions.
- Mantle records intermediate conditions.
- Rim represents later, higher-grade (peak) conditions.
- Different zones can be analysed for geothermobarometry to reconstruct the P–T path.

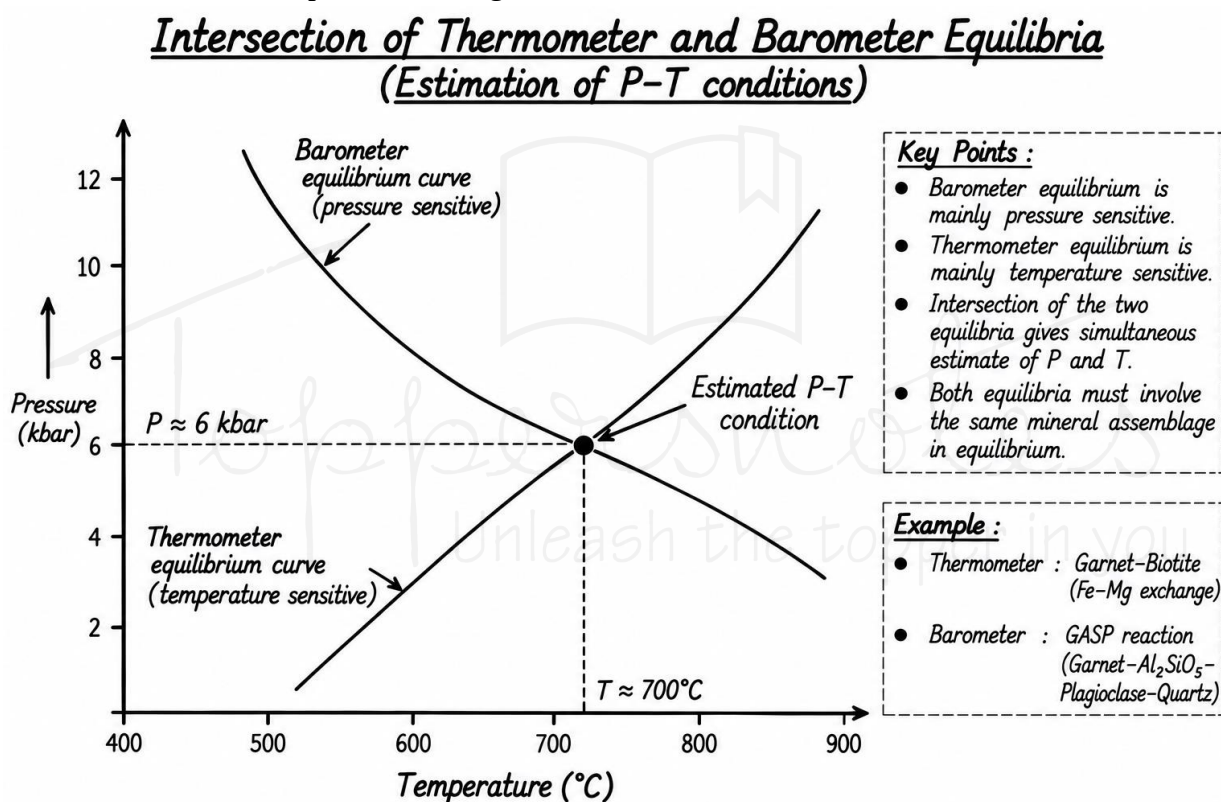


19. Combined Thermobarometry

- ✓ Temperature and pressure estimates are commonly obtained by applying a suitable geothermometer together with an independent geobarometer to the same equilibrium mineral assemblage.
- ✓ Because many thermometers possess some pressure dependence and many barometers possess some temperature dependence, the two variables may need to be solved iteratively.
- ✓ The resulting P–T estimate represents the conditions recorded by the particular mineral domains selected for analysis.

20. Intersection of Thermometer and Barometer Equilibria

- ✓ A thermometer and a barometer can be represented as equilibrium curves in pressure-temperature space.
- ✓ The intersection of the two independently calibrated equilibria provides an estimate of the pressure and temperature at which both relationships were simultaneously satisfied.
- ✓ A well-defined intersection is most meaningful when both equilibria involve minerals belonging to the same metamorphic assemblage.



21. Conventional Thermobarometry

- ✓ Conventional thermobarometry uses individual calibrated mineral equilibria or mineral pairs to determine pressure and temperature.
- ✓ Exchange thermometers, solvus thermometers and net-transfer barometers constitute the principal basis of this approach.
- ✓ Several independent thermometers and barometers may be applied to the same assemblage to evaluate the consistency of the calculated conditions.

22. Average P–T Approach

- ✓ Average P–T methods use several independent mineral equilibria simultaneously rather than relying upon a single reaction.
- ✓ The method seeks the pressure and temperature that provide the best overall agreement among the selected equilibria.

-
- ✓ Use of multiple equilibria can reduce dependence on the uncertainty associated with any single reaction.
 - ✓ The reliability of the result still depends on equilibrium among the minerals and the quality of the thermodynamic data.

23. Mineral Activities

- ✓ Thermobarometric calculations require mineral activities rather than simply the concentrations of chemical components.
- ✓ In solid-solution minerals, activity depends on composition and on the thermodynamic behaviour of the solid solution.
- ✓ Appropriate activity-composition models are therefore required for minerals such as garnet, biotite, pyroxene, amphibole and feldspar.
- ✓ Errors in calculated activities can directly affect estimated pressure and temperature.

24. Effect of Retrograde Re-equilibration

- ✓ Mineral compositions established near peak metamorphic conditions may be modified during subsequent cooling and decompression.
- ✓ Fe–Mg exchange can continue between adjacent minerals during cooling, producing temperatures lower than the original peak temperature.
- ✓ Mineral rims are particularly susceptible to retrograde modification where diffusion or fluid-assisted reactions remain effective.
- ✓ Thermobarometric interpretation must therefore distinguish preserved peak compositions from later re-equilibrated compositions.

25. Closure Temperature

- ✓ Closure temperature is the temperature below which diffusion becomes sufficiently slow for a mineral or mineral pair to preserve its chemical composition effectively.
- ✓ Closure temperature depends on diffusion rate, cooling rate, grain size and the element being considered.
- ✓ A thermometric composition preserved below closure may therefore record the temperature of chemical closure rather than the maximum temperature attained by the rock.
- ✓ This distinction is important when interpreting thermobarometric results from slowly cooled metamorphic rocks.

26. Disequilibrium and Reaction Overstepping

- ✓ Natural metamorphic rocks do not always attain equilibrium exactly at the thermodynamically predicted reaction conditions.
- ✓ Nucleation barriers and slow reaction kinetics may allow a mineral assemblage to persist metastably beyond its equilibrium stability limit.
- ✓ Such reaction overstepping can cause calculated P–T conditions to differ from the conditions at which visible mineral growth actually began.
- ✓ Textural and compositional evidence should therefore be used to evaluate equilibrium before accepting thermobarometric estimates.

27. Uncertainty in Geothermobarometry

- ✓ Every thermobarometric estimate possesses uncertainty arising from analytical error, calibration uncertainty, thermodynamic data and assumptions concerning mineral activities.
- ✓ Additional uncertainty may result from zoning, retrograde re-equilibration and incorrect pairing of mineral compositions.
- ✓ Pressure and temperature values should therefore be interpreted as estimates within an uncertainty range rather than as exact physical values.

28. Internal Consistency of P–T Estimates

- ✓ Reliability increases when several independent equilibria yield mutually compatible pressure-temperature conditions.
- ✓ Strong disagreement between different thermometers or barometers may indicate disequilibrium, inappropriate calibration or analysis of minerals formed during different metamorphic stages.
- ✓ Comparison of independent estimates is therefore an important test of thermobarometric consistency.

29. Relation with P–T Pseudosections

- ✓ Conventional geothermobarometry calculates P–T conditions from selected mineral equilibria, whereas pseudosection modelling evaluates the stability of complete mineral assemblages for a specified bulk-rock composition.
- ✓ Thermobarometric estimates can be compared with the assemblage fields predicted by a P–T pseudosection.
- ✓ Agreement between mineral-equilibrium calculations, observed assemblages and pseudosection results strengthens the interpretation of metamorphic conditions.
- ✓ Mineral compositional isopleths in pseudosections provide an additional method of quantitative P–T estimation.

30. Reconstruction of Metamorphic P–T History

- ✓ Different generations or compositional zones of minerals can preserve different stages of metamorphic evolution.
- ✓ Appropriate thermobarometric calculations on these domains may constrain prograde, peak and retrograde conditions.
- ✓ The resulting estimates can be integrated with mineral textures and zoning to reconstruct portions of the metamorphic P–T path.
- ✓ A meaningful P–T history therefore requires both quantitative calculations and petrographic evidence.

31. Limitations of Geothermobarometry

- ✓ Geothermobarometry assumes that the selected minerals attained equilibrium and that their equilibrium compositions have been sufficiently preserved.
- ✓ Chemical zoning, diffusion, retrograde exchange and reaction textures may violate these assumptions.
- ✓ Different calibrations of the same thermometer or barometer may produce somewhat different results because of differences in experimental or thermodynamic datasets.
- ✓ No thermobarometric result should therefore be interpreted independently of mineral assemblage, texture and geological setting.

32. Petrological Significance

- ✓ Geothermobarometry provides quantitative estimates of the pressure and temperature recorded by metamorphic mineral assemblages.
- ✓ Geothermometers principally exploit temperature-sensitive mineral equilibria, whereas geobarometers exploit pressure-sensitive equilibria.
- ✓ When applied to texturally constrained equilibrium assemblages, these methods allow metamorphic conditions to be related to mineral growth and reaction history.

Time Scales of Metamorphism

1. Fundamental Concept

- ✓ The time scale of metamorphism refers to the duration and timing of metamorphic processes such as burial, heating, mineral growth, peak metamorphism, cooling and exhumation.
- ✓ Metamorphic rocks record not only pressure and temperature but also the time over which these conditions were attained and maintained.
- ✓ Determination of metamorphic time scales is therefore essential for converting a P–T path into a quantitative P–T–t history.

2. Duration of Metamorphism

- ✓ Metamorphic processes may operate over widely different durations depending upon the tectonic and thermal setting.
- ✓ Regional metamorphism associated with crustal thickening and mountain building commonly develops over geological time scales of millions to tens of millions of years.
- ✓ Contact metamorphism around igneous intrusions may develop over substantially shorter periods because heat is supplied locally by magma.
- ✓ The duration recorded by a mineral may represent only a particular stage of the total metamorphic event rather than the complete tectonothermal history.

3. Timing of Mineral Growth

- ✓ Different metamorphic minerals may grow at different stages of the P–T–t evolution of a rock.
- ✓ Minerals formed during prograde metamorphism may record the timing of burial and heating, whereas minerals formed near peak conditions may date the high-grade stage.
- ✓ Retrograde minerals may record cooling, decompression or fluid-assisted reactions during exhumation.
- ✓ Correct interpretation of metamorphic ages therefore requires identification of the textural and metamorphic significance of the dated mineral.

4. Geochronology of Metamorphic Minerals

- ✓ Metamorphic geochronology uses radioactive decay systems preserved in minerals to determine the timing of metamorphic processes.
- ✓ Minerals such as zircon, monazite, garnet, titanite and mica can preserve chronological information related to different stages of metamorphism.
- ✓ The age obtained from a mineral must be interpreted together with its texture, composition and relationship to the metamorphic assemblage.
- ✓ A numerical age alone does not necessarily identify whether it represents mineral growth, peak metamorphism or subsequent cooling.

5. Growth Age

- ✓ A growth age represents the time at which a mineral crystallized during a metamorphic reaction.
- ✓ If the dated mineral can be linked texturally to a specific metamorphic assemblage, its age can be related to a particular stage of the P–T path.
- ✓ Growth ages are especially valuable for determining the timing of prograde or peak metamorphic mineral formation.

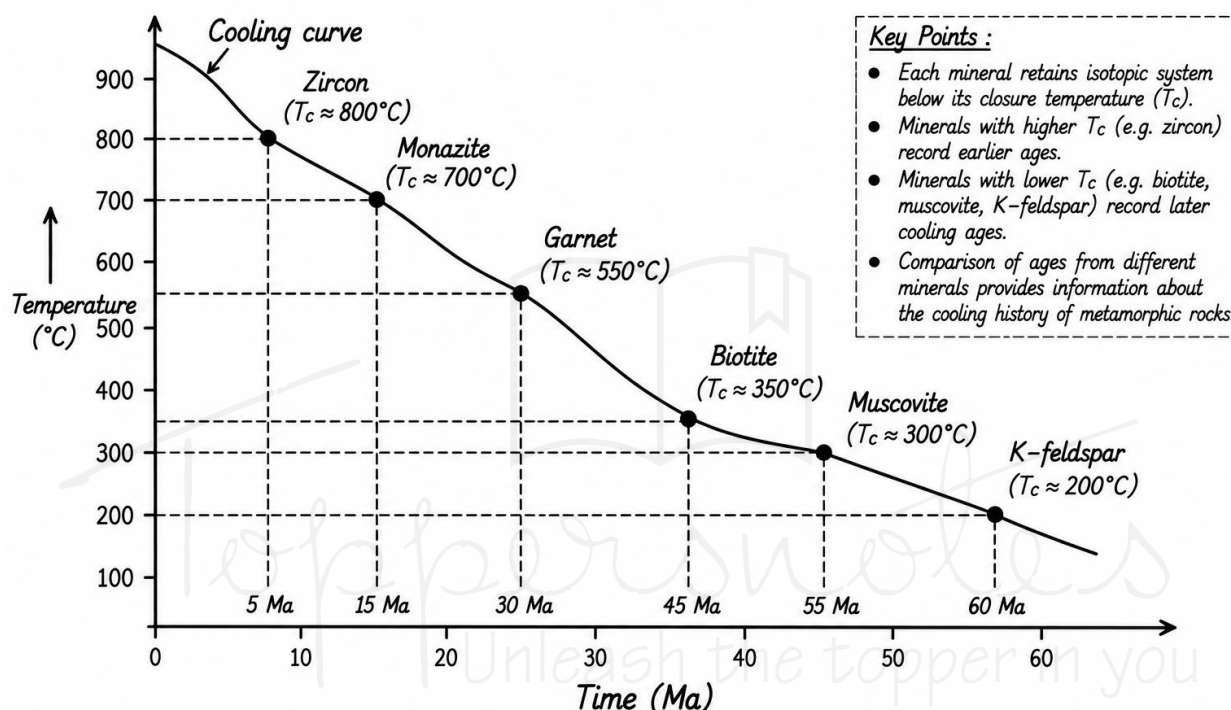
6. Closure Age

- ✓ A closure age records the time at which a mineral cooled sufficiently for diffusion of a particular radiogenic system to become effectively negligible.
- ✓ Closure age therefore need not correspond to the time at which the mineral originally crystallized.
- ✓ The difference between growth age and closure age is fundamental when reconstructing the thermal history of metamorphic rocks.
- ✓ Closure behaviour depends on the mineral, isotopic system, grain size and cooling rate.

7. Closure Temperature

- ✓ Closure temperature is the approximate temperature below which an isotopic or chemical system becomes effectively closed to diffusion during cooling.
- ✓ Minerals and isotopic systems possess different closure temperatures and can therefore record different stages of the cooling history.
- ✓ Higher-closure-temperature systems generally retain information from earlier, hotter stages than lower-closure-temperature systems.
- ✓ Comparison of ages from systems having different closure temperatures can provide constraints on post-metamorphic cooling.

Cooling Curve Showing Closure Temperatures and Closure Ages of Common Metamorphic Minerals



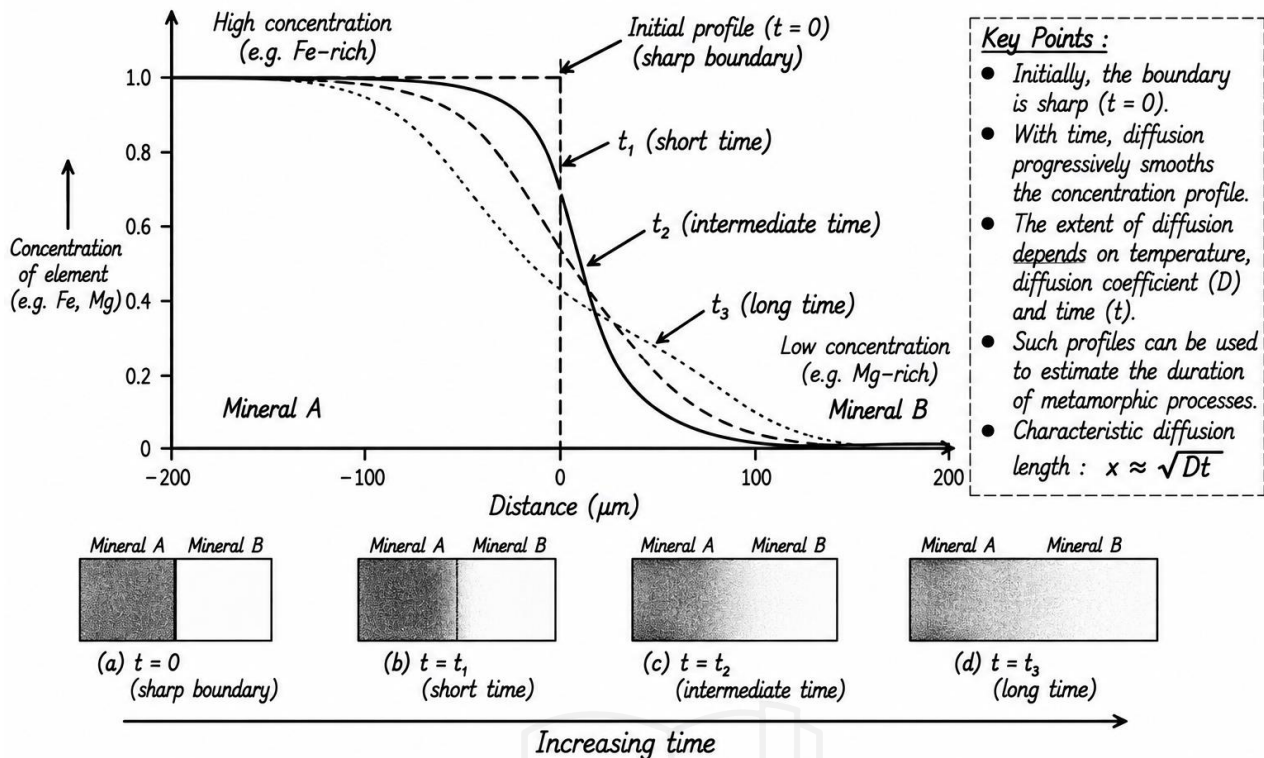
8. Diffusion and Metamorphic Time Scales

- ✓ Diffusion is strongly dependent on temperature and provides an important link between mineral chemistry and metamorphic duration.
- ✓ At high temperature, diffusion can modify or erase pre-existing compositional zoning in minerals.
- ✓ Rapid metamorphism or rapid cooling may preserve sharp compositional zoning because insufficient time is available for extensive diffusion.
- ✓ Slowly cooled rocks are more likely to undergo substantial diffusive re-equilibration.

9. Diffusion Profiles

- ✓ Concentration gradients preserved across mineral grains or mineral boundaries may be used to estimate the duration of high-temperature processes.
- ✓ Diffusion progressively smooths an initially sharp compositional boundary.
- ✓ The extent of profile modification depends primarily on diffusion coefficient, temperature and elapsed time.
- ✓ Numerical modelling of measured diffusion profiles can therefore provide estimates of metamorphic durations or cooling rates.

Diffusion Profiles in a Mineral with Increasing Time



10. Diffusion Coefficient

- ✓ The diffusion coefficient expresses the rate at which a chemical species diffuses through a mineral.
- ✓ Diffusion coefficients generally increase strongly with increasing temperature.
- ✓ Different elements diffuse at different rates even within the same mineral.
- ✓ Reliable diffusion chronometry therefore requires experimentally or theoretically constrained diffusion parameters for the mineral and element being investigated.

11. Diffusion Length and Time

- ✓ The characteristic distance over which diffusion modifies a mineral increases with both diffusion coefficient and duration.
- ✓ The basic relationship may be expressed approximately as:
 $x \approx \sqrt{Dt}$
 where x is diffusion length, D is the diffusion coefficient and t is time.
- ✓ For a known diffusion coefficient and measured diffusion length, the duration of diffusion can be estimated.
- ✓ Because the diffusion coefficient is strongly temperature dependent, an independently constrained thermal history is important for reliable time estimates.

12. Geospeedometry

- ✓ Geospeedometry is the estimation of rates or durations of geological processes from kinetic information preserved in minerals.
- ✓ In metamorphic petrology, it commonly uses diffusion profiles, mineral zoning or reaction kinetics to constrain the rates of heating, cooling or mineral re-equilibration.
- ✓ Geospeedometry complements geochronology because it provides information about the duration and rate of processes rather than only their absolute ages.

13. Heating Rate

- ✓ The heating rate describes the increase in temperature per unit time during prograde metamorphism.
- ✓ It is obtained when temperature information from the P-T evolution can be related to independently determined ages.
- ✓ Rapid heating may preserve disequilibrium textures and chemical zoning, whereas prolonged heating provides greater opportunity for reaction and diffusion.