Brines and Metasomatism

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ABSTRACT. — The frequent observation of saline fluids in deep seated groundwaters of metamorphic terrains as well as in fluid inclusions of metamorphic minerals indicates that brines are common participants in metamorphism and metasomatism. The most abundant components in these brines are H_2O, CO_2 and NaCl. Available experimental data permit a quantitative P-T projection to 900°C and 2Kbar for the system, CO_2-H_2O-NaCl. Extrapolation of this diagram to higher pressures shows that at even moderate salt contents, two fluids, i.e. an aqueous brine and a CO_2-rich vapour, coexist over a wide range of metamorphic conditions. Prograde or retrograde metamorphic reactions can cause an originally homogenous supercritical brine to evolve into a two-phase fluid that may eventually reach saturation in salt. As an example, metasomatic interaction of a carbonate rock mass with an aqueous brine is discussed. The process of evolution towards a two-phase fluid and finally to a salt saturated fluid may be facilitated by boiling.

Salt saturation can be demonstrated if primary solid inclusions of salt are found. Criteria that prove the primary nature of solid salt inclusions are discussed by means of an example from the Central Alps.

Metasomatic brine-rock interaction may result in considerable variation of reaction rates, which may explain some of the characteristic textures observed in metasomatic rocks. Metasomatic brine-rock interaction may also result in the precipitation of dissolved components, thus leading to the formation of mineral deposits.

Introduction

Saline solutions are commonly present in metamorphic and metasomatic rocks. A direct indication of the abundance of brines is given by recent studies of deep seated groundwaters in metamorphic rocks of the Canadian Shield (FRAPE et al., 1984) and of the Fennoscandian Shield (NORDSTROM, 1983) and also by the analysis of deep-seated fluids from the Kola borehole (KOZLOWSKY, 1985). Evidence of the saline character of many fluids during metamorphism has been found in fluid inclusions from metamorphic rocks (POTY, STALDER and WEISBROD, 1974; TOURET, 1977; SCHUILING and KREULEN, 1979; KREULEN, 1980; HENDEL and HOLLISTER, 1981; SISSON et al., 1981; MERCOLLI, 1982; WALTHER, 1983; YARDLEY et al., 1983).

The origin of these saline solutions may in part be due to the release from magmatic rocks. A considerable part of ROEDDER'S (1984) recent book is on fluid inclusions of magmatic origin. The saline nature of many formation waters of sediments is also a well known fact and in many cases the metamorphism of evaporitic rocks must have contributed to the presence of saline solutions during metamorphism (RICH, 1979; MERCOLLI et al., 1986; TROMMSDORFF et al., 1985).

Processes leading to the concentration of saline solutions in metamorphic rocks are only partly understood. Metamorphic reactions that consume H_2O, fluid unmixing, and the segregation of two fluids (boiling), are processes that concentrate salt components in the liquid phase (TROMMSDORFF and SKIPPEN, 1986).

Under metamorphic conditions at even moderate salt contents, brines are capable of dissolving and transporting chemical species. Recent investigations (BALLHAUS and

STUMPFL, 1986; CHRYSSOULIS and WILKINSON, 1983; DIAMOND, 1987) show the capability of brine to transport even so-called immobile elements. This has also been shown through the analysis of fluid inclusions by the decrepitation ICP method (CRYSSOULIS, 1983). A direct experimental indication of the corrosive nature of CO_2-H_2O-NaCl solutions was given by GEHRIG (1980). Not only the saphire window of the apparatus but also the noble metals of the reaction vessels were attacked by these solutions at 3000 bars and 550 C. It is therefore not astonishing that saline solutions are considered responsible for

the formation of many types of mineral deposits (EUGSTER, 1986).

Metasomatic veins resulting from the interaction of brines with rocks have commonly been observed in metamorphic terranes. Classical examples of such veins have been described from the Alps, for example Adamello (DRESCHER-KADEN, 1969), Bergell (BUCHER-NURMINEN, 1981), Campolungo, Central Alps (MERCOLLI, 1982; WALTHER, 1983; MERCOLLI et al., 1987). The study of such metasomatic veins and accompanying solutions deserves more attention than so far attained.
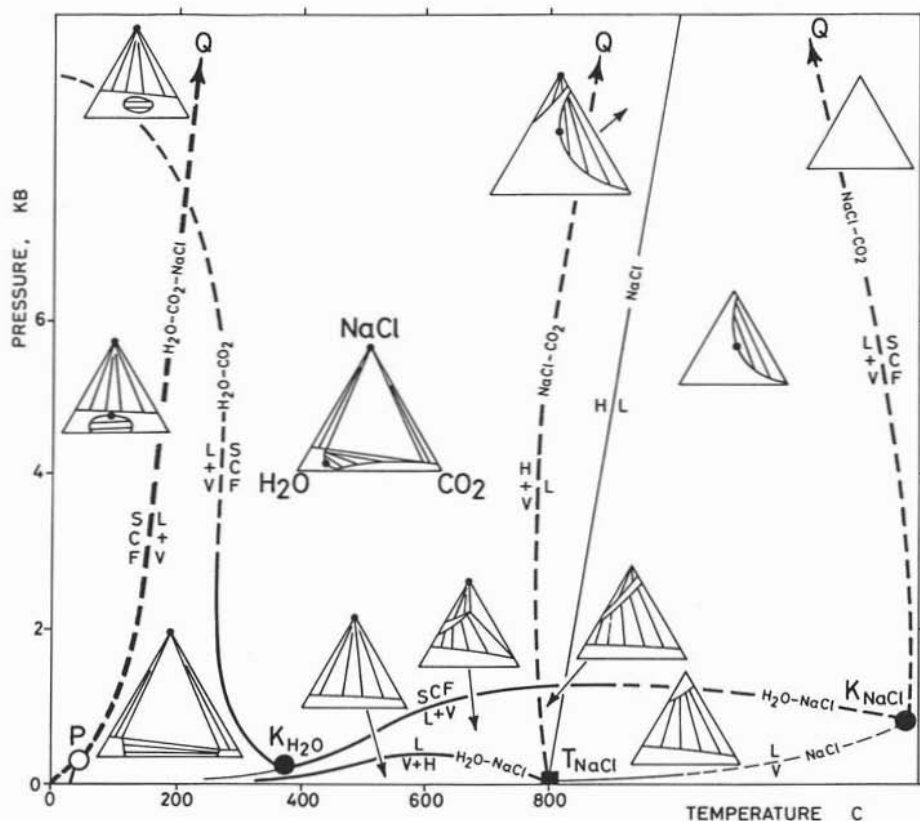

Fig. 1. — Pressure-temperature projection for the ternary system CO_2-H_2O-NaCl. Unary curves with a thin signature binary curves with an intermediate thickness, a portion of the ternary supercritical curve with a heavy signature. The experimentally measured parts of the curves are solid and estimated curves are dashed. No scale is indicated above 900°C and 6 kilobars as the position of curves at these conditions is uncertain. All three curves extrapolated above 900°C meet at the experimentally undetermined critical point for NaCl. Those curves labeled Q are coincident at a single point at a high pressure beyond the diagram. This single point and point P are critical endpoints in the binary CO_2-NaCl that limit the ternary critical curve. Chemographic relationships in CO_2-H_2O-NaCl are shown schematically with three chemographies enlarged that were used to construct Fig. 3. L = liquid, V = vapour, SCF = supercritical fluid, H = halite, K = critical point, T = triple point.

CO₂-H₂O-NaCl brines

SKIPPEN and TROMMSDORFF (1986) used available experimental data (ADAMS, 1931; KEEVIL, 1942; SOURIRAJAN and KENNEDY, 1962; GRYOTHEIM et al., 1962; TOEDHEIDE and FRANK, 1963; TAKENOUCHI and KENNEDY, 1964; AKELLA et al., 1969; HILBERT, 1979; GEHRIG, 1980; CHOU, 1982; GUNTER et al., 1983; BODNAR, 1985) to construct a schematic, geologically relevant P-T projection of the system, CO_2-H_2O-NaCl (Fig. 1). Many of the phase elements of the system (GEHRIG, 1980) which plot outside the P-T range of most metamorphic rocks have been omitted. Schematic chemographic projections corresponding to the various P-T regimes of Fig. 1 have been added. Thin lines represent unary equilibria between phases of constant composition. The composition of fluid phases varies continuously along the phase-boundaries of binary subsystems (lines of medium thickness). A part of the ternary

critical curve (PQ) has been added to the diagramm using a heavy signature. The phase relations in the ternary composition space can be read from the chemographies. Two-phase fields have been shown by schematic tie-lines connecting coexisting liquid and vapour; three-phase triangles and single-phase fields are left blank. Three geologically important chemographies (a, b, c) are enlarged.

To illustrate the phase relations, the chemography b is shown separately for a temperature of 500 C and a pressure of 2KB. A three-phase triangle for coexisting H_2O-rich liquid (L), CO_2-rich vapour (V), and halite (H), is surrounded by three two-phase fields, H + L, H + V, and L + V. The composition of coexisting liquid and vapour phases is given by the schematic tie-lines on the L + V field. At point C, the consolute point, the tie-line is reduced to a point and the liquid and vapour become indistinguishable. The field along the
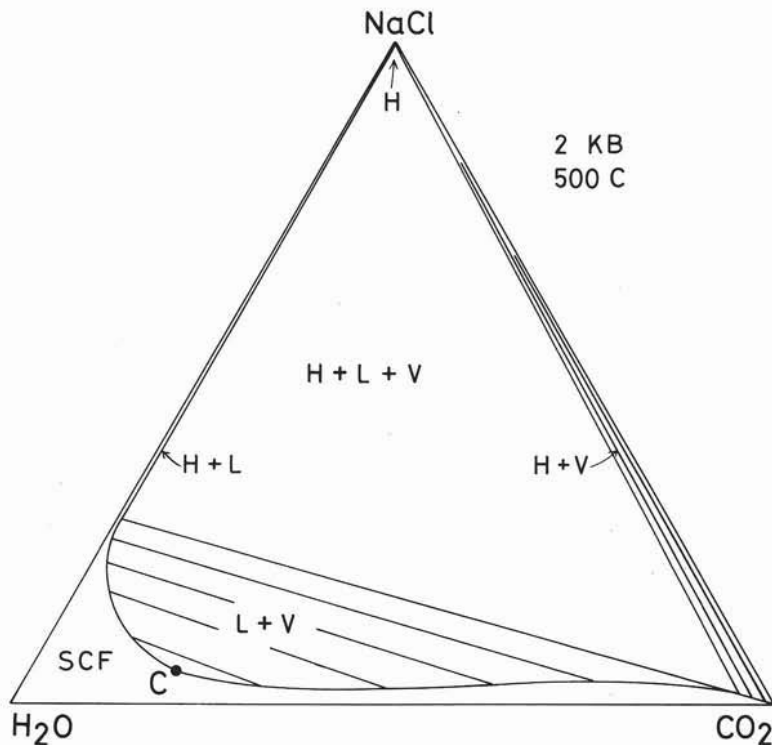

Fig. 2. — Composition section at 500°C, 2 kilobars for the ternary system, CO_2-H_2O-NaCl. H = halite, L = liquid, V = vapour, SCF = supercritical fluid. C represents the consolute point at which the tie-line between liquid and vapour is reduced to a point.
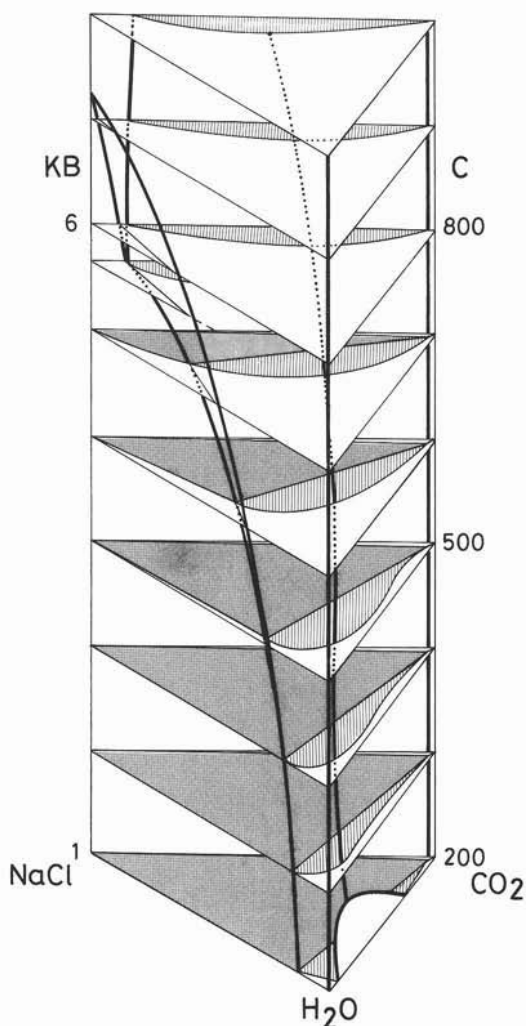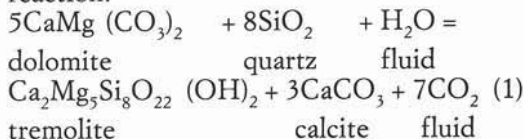
Fig. 3. — Ternary composition section in the system CO_2-H_2O-NaCl plotted along a temperature-pressure gradient. The binary phase element, H + L, in the system, H_2O-NaCl, is shown from the base of the prism to the melting temperature of pure NaCl. Two binary elements in the system CO_2-NaCl are shown on the left back of the prism at high pressure; these are liquid in equilibrium with vapour and liquid in equilibrium with halite. The latter curve terminates at the melting point of pure NaCl. These binary elements converge to a point with decreasing pressure and temperature where they encounter a ternary phase element representing liquids in equilibrium with vapour. The corresponding ternary curve for vapour in equilibrium with liquid is shown on the opposite side of the prism. The ternary consolute point curve begins at low temperature in the CO_2-H_2O- binary and ends on the CO_2-NaCl binary at temperatures and pressures above those illustrated. In the chemographic sections the liquid plus vapour fields are indicated by a hatching and the liquid plus vapour plus halite triangles by shalding.

CO_2-H_2O side of the projection is characterized by the occurrence of a single supercritical fluid phase. Fig. 2 shows that by far the largest area of the CO_2-H_2O-NaCl composition space is characterized by the coexistence of two fluid phases (fields L + V and H + L + V). This has important consequences for equilibria and reactions of metamorphic mineral assemblages involving fluid components.

The behaviour of the CO_2-H_2O-NaCl system between 200°C and 800°C and from 1 to 6KB can be read from the ternary prism, Fig 3. The five dimensions needed to fully represent the relationships between P, T, X_{CO2}, X_{H2O} and X_{NaCl} have been reduced by projecting along a P-T gradient. This P-T gradient includes the chemographies of the enlarged triangles (a, b, c) from Fig. 1. In the nine sections shown on Fig. 3, compositions that comprise the coexistence of two fluid phases, L + V, are hatched. Shading corresponds to the three-phase field, H + L + V. In contrast to the subsystem CO_2-H_2O that has a solvus at only relatively low temperatures, the ternary P-T-X_{NaCl}-X_{CO2}-X_{H2O} space is characterized by the coexistence of two fluid phases, L + V, over a wide range of conditions.

Metasomatic reactions in CO_2-H_2O-NaCl solutions

In order to construct isobaric, isothermal equilibriurm lines for dehydration, decarbonation and mixed volatile reactions on the X_{CO2}-X_{H2O}-X_{NaCl} surface, it is necessary to consider phase relations in μ_{H2O}-μ_{CO2}-μ_{NaCl} space (SKIPPEN and TROMMSDORFF, 1986). Fig. 4 schematically illustrates the equilibrium boundary of a typical hydration-decarbonatio reaction:

$5CaMg(CO_3)_2$ + $8SiO_2$ + H_2O =
dolomite   quartz   fluid
$Ca_2Mg_5Si_8O_{22}(OH)_2$ + $3CaCO_3$ + $7CO_2$ (1)
tremolite   calcite   fluid

at three different temperatures. Fig. 4a, 4b and 4c show isothermal isobaric triangular sections of the P-T-X_{CO2}-X_{H2O}-X_{NaCl} space corresponding to the topology of Fig. 2. Several of the stability fields on the triangles
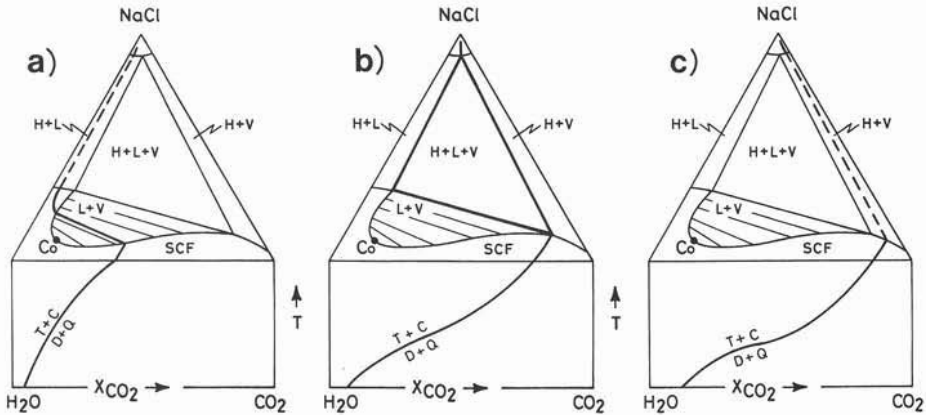
Fig. 4. — Isothermal-isobaric composition section as shown in Fig. 2 with a part of the binary T-X_{CO2} section added below. Sections a, b, and c refer to increasing temperatures, each with a schematic isotherm for reaction (1) added (heavy line). H = halite, L = liquid, V = vapour, SCF = supercritical fluid, Co = consolute point, C = calcite, D = dolomite, Q = quartz, T = tremolite.

have been enlarged for clarity. Below the triangles, a part of the adjacent T-X_{CO2}-X_{H2O} space is shown. Fig. 4a corresponds to relatively lower, Fig. 4b to medium and Fig. 4c to relatively higher temperature. In the T-X_{CO2} sections the typical shape of the hydration-decarbonisation equilibrium (1) namely a curve of the inflection type (GREENWOOD, 1962) is shown by a heavy line. In the adjacent isothermal ternary composition space of Fig. 4a the equilibrium boundary continues through the fields SCF, L + V, SCF and L + H towards the NaCl-apex. Because of the equality of the chemical potentials in coexisting phases the equilibrium line for reaction (1) must run parallel to the tielines within the two-phase fields. In Fig. 4b the equilibrium (1) coexists wich L + V + H, the three-phase region, and in Fig. 4c with V + H.

For the temperature range considered on Fig. 4 the following phase assemblages are represented (D = dolomite, Q = quartz, T = tremolite, C = calcite): DQTCSCF, DQTCLV, DQTCLH, DQTCHV, DQTCH, DQTCLVH. In the three-dimensional isobaric T-X_{CO2}-X_{H2O}-X_{NaCl} space, these equilibria correspond to surfaces which share edges with each other. Fig. 5 schematically shows equilibrium (1) in T-X_{CO2}-X_{H2O}-X_{NaCl} space. The three sections labeled, a, b, c, correspond to those of Fig. 4a, 4b, 4c

respectively. In Fig. 5 the equilibrium surface of reaction (1) rises from the NaCl-H_2O side of the projection towards the NaCl-CO_2 side. At the temperature corresponding to section b, the X_{CO2} values in the ternary
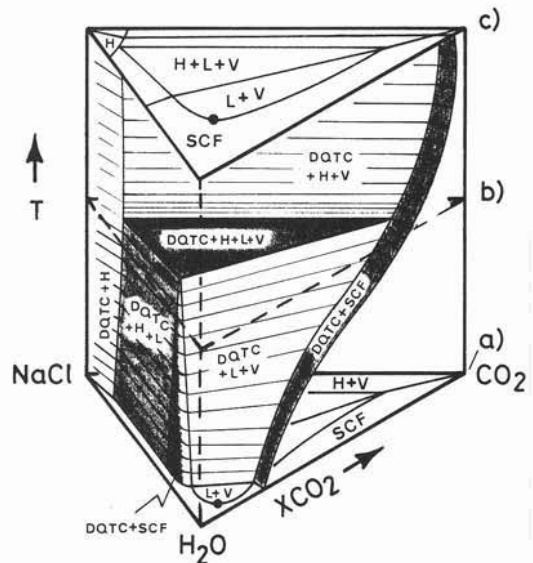

Fig. 5. — Ternary composition section in the system, CO_2-H_2O-NaCl plotted along a temperature gradient. a), b) and c) refer to the sections a), b), and c) from Fig. 2. The equilibrium plane for reaction (1) is shown within the prism with the individual phase elements labeled. The typical inflection type curve of reaction (1) is visible on the binary, H_2O-CO_2. H = halite, L = liquid, V = vapour, SCF = supercritical fluid, C = calcite, D = dolomite, Q = quartz, T = tremolite.

composition space representing equilibrium (1) vary from 0.1 to 0.9. It is evident therefore, that the addition of NaCl to H_2O-CO_2 fluids can significantly change the stability of mineral assemblages in fluid composition space (SKIPPEN and TROMMSDORFF, 1986).

Fluid evolution in CO_2-H_2O-NaCl space

The evolution of fluids as a consequence of metamorphic reactions was discussed by TROMMSDORFF and SKIPPEN (1986). Fluid evolution is a function of initial composition, reaction stoichiometry and reaction progress. The theoretical endpoint of fluid evolution is defined by reaction stoichiometry. In the ternary system, CO_2-H_2O-NaCl, an originally homogeneous supercritical fluid can evolve as a result of mineral reaction to a two-phase fluid and finally to salt-saturation of the fluids.

As an example, fluid evolution in CO_2-H_2O-NaCl is shown for reaction (1) in Fig. 6a and Fig. 6b. All lines of fluid evolution converge at a theoretical endpoint, point P in Fig. 6a with the coordinates $X_{CO2} = 1.167$, $X_{H2O} = -0.167$ and $X_{NaCl} = O$ as defined by the stoichiometry of reaction

(1). Fig. 6b corresponds to Fig. 4c and contains a schematic topology for the system CO_2-H_2O-NaCl together with a dashed equilibrium line for reaction (1). The area in which reaction (1) proceeds to the right is shaded; the area in which reaction (1) proceds to the left is blank. At the boundary of the two areas, products and reactants are in mutual equilibrium and reaction progress is zero. Fluid evolution as a consequence of positive progress in reaction (1) is indicated by the thick arrows. An initial fluid composition I, corresponding to a supercritical aqueous chloride solution, evolves towards point P. At point A, which is at the intersection of the fluid evolution curve IP and the boundary of the two-phase region, L + V, an infinetesimal amount of a vapour phase of composition A' in equilibrium with the liquid A is formed. Further reaction progress creates liquids along curve AB and coexisting vapours along curve A'B'. At point B and B' the system reaches salt-saturation.

Further progress in reaction (1) leads to consumption of the liquid and simultaneous precipitation of salt. The endpoint of the evolution of the system lies at poit E, the intersection of the fluid evolution curve IP
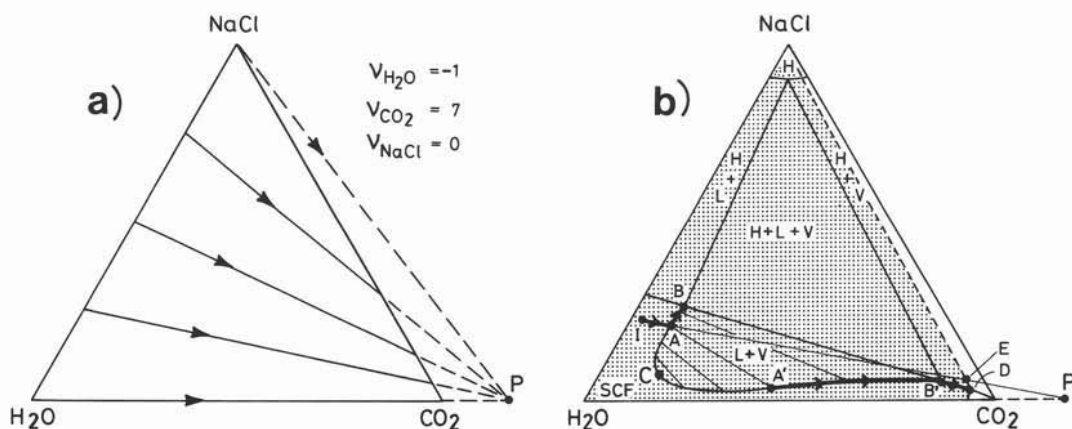

Fig. 6. — a) Fluid evolution for reaction (1) in the system, H_2O-CO_2-NaCl. All fluid evolution curves for positive progress in reaction (1) tend towards the endpoint, P, as, indicated by arrows.
b) Schematic phase relations in CO_2-H_2P-NaCl with an equilibrium line for reaction (1), dashed. In the shaded area progress of reaction (1) is positive in the white area it is negative. A fluid of starting composition I evolves through positive progress in reaction (1) towards the two phase region and reaches it at point A. Liquids evolving within the two-phase region are defined by curve AB and coexisting vapours by A'B'. At point A and B' halite saturation is reached. Further fluid evolution ends at point E, the intersection of the fluid evolution line IP and the equilibrium line for reaction (1). At point E halite coexists with a vapour of composition D. H = halite, L = liquid, V = vapour, SCF = supercritical fluid, C = consolute point.

and the equilibrium line for reaction (1). At point E, a vapour with composition D coexists with halite and the product and reactant minerals of reaction (1).

Fluid evolution is more efficient if boiling occurs during the reaction and the vapour can leave the system. In this case the residual liquid evolves as in the foregoing case from point A to saturation at point B. Further reaction progress accompanied by boiling leads to the consumption of the liquid and simultaneous precipitation of salt. The residual bulk compositions within CO_2-H_2O-NaCl then evolve along the boundary between the areas $H + L$ and $H + L + V$ until they reach the field H (halite) near the NaCl-apex.

Primary salt inclusions in metasomatic rocks

The recognition of primary solid inclusions of salt is of special interest for the interpretation of brine-rock interaction. Such inclusions are taken to indicate the presence of a salt-saturated fluid phase during metasomatism. In addition, primary inclusions of (Na, K) Cl are a useful geothermometer because of the temperature dependency of the mixing of KCl and NaCl. The bulk composition of these inclusions is preserved during cooling if no fluid surrounds the solid inclusion.

An axample of primary solid inclusions of salt has been described form the classic mineral locality of Campolungo, Central Alps, Switzerland (TROMMSDORFF et al., 1985). Boudins and nodules of preexisting quartz veins reacted with sorrounding dolomite rock to from tremolite plus calcite according to reaction (1) (WALTHER, 1983). There is agreement among the various authors who worked on these veins (MERCOLLI, 1982; WALTHER, 1983; MERCOLLI et al., 1987) that the fluid necessary to produce the tremolite of the veins was an aqueous brine introduced from outside into the dolomite layer containing the quartz nodules.

At least three kinds of salt have been recognized withn quartz crystals from Campolungo (Lepontine Alps, Switzerland):
1. Salt particles crystallized from residues of decrepitated fluid inclusions. They are easily recognizable on basis of their dendritic growth and will not be further considered here.
2. Dauhter crystals within fluid inclusions.
3. Primary inclusions of salt which existed before the growth of the enclosing host mineral, mostly quartz.

The distinction between daughter crystals and primary inclusions is not possibile on basis of their shape and, if pure NaCl, also impossibile on the basis of their chemistry.
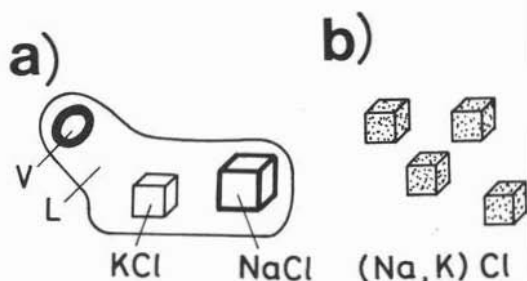

Fig. 7. — Schematic sketches of a fluid inclusion with daughter crystals (left) of the system CO_2-H_2O-KCl at room temperature and of solid inclusions (K, Na) Cl (right). The four crystals to the right all show the same features i.e. unmixing from an original solid solution of halite + sylvite. The daughter crystals within the inclusion are halite and sylvite

Solid inclusions, however, tend to occur in groups of several crystals with the same characteristics whereas daughter minerals of NaCl almost invariably occur as one single crystal per inclusion (see also ROEDDER, 1984, p. 53). This distinction, however, is not unambiguos.

For crystals of NaCl and KCl, as in the case of the Campolungo occurrence (TROMMSDORFF et al., 1985) the distinction between daughter minerals and solid inclusions becomes easier (Fig. 7). Fluid inclusions that are saturated with respect to KCl and NaCl at room temperature contain two daughter crystals of different composition i.e. a halite and a sylvite cube. In contrast to such daughter minerals, the solid inclusions in the Campolungo quartz crystallized as KCl-NaCl solid solutions. During cooling they unmixed in a manner similar to that discussed by HEIDE and BRUECKNER (1967) for the experimental work of NACKEN (1918).

Unmixing phenomena in the Campolungo example were visible in a group of four adjacent salt crystals each of about 10 μm diameter and were analyzed by means of the electron microprobe (TROMMSDORFF et al., 1985, Fig. 2d-f). A temperature of about 500°C was determined from the bulk analyses of these crystals using the solvus calculated by THOMPSON and WALDBAUM (1969) for the halite-sylvite system. This temperature agrees well whith those determined by MERCOLLI (1982) and WALTHER (1983) for the Campolungo veins using calcite-dolomite geothermometry.

Phenomena as described for the primary solid inclusions of salt from Campolungo are also possibile for daughter crystals that become separated from the enclosing fluid by «necking down» processes. But in this case the temperatures resulting from the halite-sylvite geothermometer should fall below those independently determined for the rock system.

Independent evidence for the existence of saturated brines at Campolungo results from salt to liquid homogenization temperatures in fluid inclusions from the same sample that contains solid inclusions of salt. In this sample homogenization temperatures were determined by MERCOLLI as 495-498°C for several inclusions, which is well in agreement with the 500°C determined on calcite-dolomite pairs for the formation of the metasomatic veins. The inclusions of H_2O-rich saline liquid at Campolungo invariably coexist with very CO_2-rich inclusions (MERCOLLI, 1982, p. 281on). It is therefore possible that the reacting salt saturated brines at Campolungo were two-phase fluids that evolved as discussed in the foregoing chapter.

Solid inclusions of salt were also observed in monticellite from Cornone di Blumone, and in diopside from Val Caffaro, Adamello, Italy (TROMMSDORFF et al., 1985) as well as in cordierite from the Central Alps (IROUSCHEK, 1984). Proof for the primary nature of the inclusions in these occurrences has not been obtained so far; the inclusions do confirm the saline nature of fluids attending metasomatism in these rocks.

Conclusion

It has been shown in the foregoing chapters that metasomatic reaction during brine-rock interaction may lead to the formation of two-phase, salt-saturated fluids. Reaction progress during such brine-rock interaction may vary considerably, depending upon the availability of heat to drive the reaction and of fluid to permit the reaction to go on. MERCOLLI et al. (1987) have shown that the heat stored in the surrounding rock mass is sufficient to drive reaction (1) during the formation of metasomatic veins caused by introduced brines at Campolungo. During reaction, fluid evolution across ascending isotherms of the SCF field and of the L + V field (Fig. 4) requires considerable superheating of the rock mass surrounding the veins. On the other hand, the only heat that is necessary to drive the reaction at salt-saturation is the heat of reaction.

If the vapour phase produced during ongoing reaction can leave the system, the rates of reaction may be relatively fast compared to rocks that from in a «closed» system. Different textures could result from the two cases: whereas in the Campolungo rock mass tremolite shows well-developed granoblastic textures, it radiates from a point source in the veins (see also photos in TROMMSDORFF and SKIPPEN, 1986). We anticipate much higher rates for reaction (1) in the veins as compared with the rock. A systematic study of textures in metasomatic rocks that formed by brine-rock interaction may help to solve this problem.

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