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LOW TEMPERATURE HYDROTHERMAL SYNTHESIS FROM DOLOMITE OR CALCITE, QUARTZ AND KAOLINITE

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Abstract– Dolomite or calcite, quartz and kaolinite in various proportions were reacted at 250–300°C temperatures and pressures up to 90 bars in a hydrous environment. Reactions which approached completion produced talc, calcite, montmorillonite, anorthite (both metastable hexagonal and stable triclinic polymorphs) and the rare Ca–zeolite, garronite. These reactions are applicable to diagenesis, low-grade metamorphism and hydrothermal alteration.

INTRODUCTION

MONTMORILLONITES have been synthesized from mixtures of glasses, gels and pure crystalline chemicals as summarized by Deer *et al.* (1962). Kinetic experiments on the crystallization of amorphous silica by Carr and Fyfe (1958), and Campbell and Fyfe (1960) indicate that amorphous reactants in laboratory experiments may not duplicate natural processes. Some experimentors, for example Hawkins (1969), alter natural glasses and rocks hydrothermally, but they introduce a fixed starting material of composition known only approximately. Naturally occurring minerals (various carbonates, quartz, and kaolinite or illite or feldspar) have been used to synthesize montmorillonites by Coombs (1960), Levinson and Vian (1966) and Levinson and Day (1968).

The work reported in this paper is an extension of the previously published hydrothermal synthesis work, but under more controlled conditions. In this study, 140 bomb runs were made with various quantities of hand picked (purity confirmed by X-ray diffraction) naturally occurring dolomite or calcite, quartz and kaolinite (1 Md). Reactions of these minerals from stoichiometric quantities approached completion in contrast to earlier experiments in the literature, which show partial reaction from nonstoichiometric amounts. Reactions in these dolomite or calcite, quartz and kaolinite systems in nature help explain the results of diagenesis, low-grade metamorphism and hydrothermal activity on limestone and dolomite assemblages, as well as other sedimentary rocks with traces of calcite or dolomite. Temperatures of about 250°C are commonly found at depths of 20,000 to 30,000 ft in sedimentary areas with normal thermal gradients.

EXPERIMENTAL

Approximately 0·4g of a <200 mesh mixture together with 50 ml of distilled water was placed in a stainless steel bomb with 100–150 ml capacity. The quantity of water vaporized under these experimental conditions is calculated to be less than 2 ml at all temperatures. The water generates a vapour pressure of 40 bars at 250°C or 90 bars at 300°C. Smaller quantities of starting material resulted in difficulties owing to a low yield and the excessive differential loss of the elements into the aqueous phase. Larger quantities of material or less water increased the reaction time because the surface area to water ratio has decreased. Too much water (more than 50 ml) does not allow space for the 30 per cent increase in volume at 300°C and also makes shaking the solids into suspension more difficult.

With the 0·4g of material used, experience indicated that at least 6 weeks reaction time is needed at 250°C and three weeks at 300°C for the mass transfer to approach equilibrium. Each bomb was shaken every week to increase the reaction rate, and air quenched when removed from the oven. The products, both solids and water, were measured to check for leakages in the bombs. Occasionally the pH and magnesium and calcium content were measured in the product waters. The solids (powder) were identified after glycol treatment with the X-ray diffractometer. Accurate measurement of the calcite d_{1014} was used to calculate the percentage of magnesium in the newly-formed calcite with the aid of the data by Graf (1961, p. 1297). The composition of the montmorillonite was calculated from chemical analysis for Si, Al, Mg and Ca determined by atomic absorption, after the calcite had been completely removed

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with two cold 1% acetic acid (pH $5\frac{1}{2}$) treatments and confirmed by X-ray diffraction. This treatment has minimal effect on other minerals as found by Chester and Hughes (1967).

DISCUSSION

The reactions described in Table 1 are controlled by the fugacities of CO_2 and H_2O with the Ca^{2+}, Mg^{2+}, Al^{3+} and Si^{4+} conserved among the solid phases. These reactions are hypothetical in the sense that some of the starting elements remain in solution rather than entering one of the products.

The formation of talc (equation 1) is limited, since Mg-trioctahedral montmorillonite forms rather than talc when either the solids to water ratio is low (4 g/l.) or the gas pressure is low ($P_{CO_2} = 1$ bar). Calculations show the approximate activities in these experiments are $\log(a_{Mg^{2+}}/a_{H^{2+}}) = 7$ and $\log(a_{Ca^{2+}}/a_{H^{2+}}) = 8$. These experimental results agree with the theoretical activity diagram (p. 135) of Helgeson *et al.* (1969), which show talc and calcite are stable at these temperatures providing that the P_{CO_2} is sufficiently high. Their theoretical equilibrium diagrams which are based on mass transfer calculations assume that the reaction products maintain equilibrium with the aqueous phase. This assumption appears realistic for both experimental and natural processes as demonstrated by the kinetic work of Helgeson (1971). Equation (1) has been studied extensively by Gordon and Greenwood (1970) and Metz and Puhan (1970) at higher temperatures and pressures. Only a small quantity of aluminum prevents the formation of talc (equation 2). The rare occurrence of talc in sediments is partially explained by this reaction, since aluminum-bearing minerals such as kaolinite or illite are ubiquitous.

The Ca/(Ca + Mg) ratio in the water recovered from the bomb with dolomite, quartz and kaolinite (equations (1) and 2) is approximately constant at 0·9 with calcite formation acting as a buffer. Therefore since the Mg is precipitated preferentially, the Mg-rich minerals such as talc and Mg-trioctahedral montmorillonite are formed in these experiments. The $MgCO_3$ content of calcite formed in these reactions was 1 per cent at 250°C and 2 per cent at 300°C. These values of the solid substitution range of $MgCO_3$ for $CaCO_3$ in calcite at low temperatures reasonably extend the high temperature data of Graf (1961).

The Mg trioctahedral montmorillonite has a composition range because of the substitution of $2Al^{3+}$ for $Mg^{2+} + Si^{4+}$ and also a small cation deficiency in the octahedral positions. Its approximate compositional range is shown diagramatically in Fig. 1, and Fig. 2 illustrates that the aluminum substitution is limited at lower temperatures. The compositional range of the Mg trioctahedral montmorillonite (equation 2) in Fig. 1 is significantly different from the dioctahedral montmorillonite (equation 4) in Fig. 3. Failure to synthesize a solid solution series between these minerals accords with a corresponding hiatus in the naturally occurring minerals.

Both the metastable hexagonal and stable triclinic anorthite polymorphs are formed (equation 5) at 250°C and above, but if dolomite is substi-

Table 1. Theoretical chemical equations based on hydrothermal synthesis

1 $3\underset{\text{dolomite}}{MgCa(CO_3)_2} + 4\underset{\text{quartz}}{SiO_2} + H_2O \xrightarrow[250°C,300°C]{H_2O} \underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + 3\underset{\text{calcite}}{CaCO_3} + 3CO_2\uparrow$

2 $24\underset{\text{dolomite}}{MgCa(CO_3)_2} + 28\underset{\text{quartz}}{SiO_2} + \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 6H_2O \xrightarrow[250°C,300°C]{H_2O} 8\underset{\text{montmorillonite}}{Ca_{1/8}Mg_3(Si_{3(3/4)}Al_{1/4})O_{10}(OH)_2} + 23\underset{\text{calcite}}{CaCO_3} + 25CO_2\uparrow$

3 $\underset{\text{dolomite}}{MgCa(CO_3)_2} + \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} \xrightarrow[300°C]{H_2O} \underset{\text{anorthite}}{CaAl_2Si_2O_8} + 2CO_2\uparrow + Mg^{2+}_{aq} + 2(OH)^-$

4 $\underset{\text{calcite}}{CaCO_3} + \underset{\text{quartz}}{8SiO_2} + 7\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} \xrightarrow[250°C,300°C]{H_2O} 6\underset{\text{montmorillonite}}{Ca_{1/6}Al_2(Si_{3(2/3)}Al_{1/3})O_{10}(OH)_2} + CO_2\uparrow + 8H_2O$

5 $\underset{\text{calcite}}{CaCO_3} + \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} \xrightarrow[250°C,300°C]{H_2O} \underset{\text{anorthite}}{CaAl_2Si_2O_8} + CO_2\uparrow + 2H_2O$

6 $\underset{\text{calcite}}{CaCO_3} + \underset{\text{quartz}}{4SiO_2} + \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 4H_2O \xrightarrow[250°C]{H_2O} \underset{\text{garronite}}{CaAl_2Si_6O_{16}\cdot 6H_2O} + CO_2\uparrow$

7 $\text{dolomite} + \text{quartz} + \text{kaolinite} + \text{water} \xrightarrow[250°C]{H_2O} \text{garronite} + \text{montmorillonite} + \text{calcite} + CO_2\uparrow$

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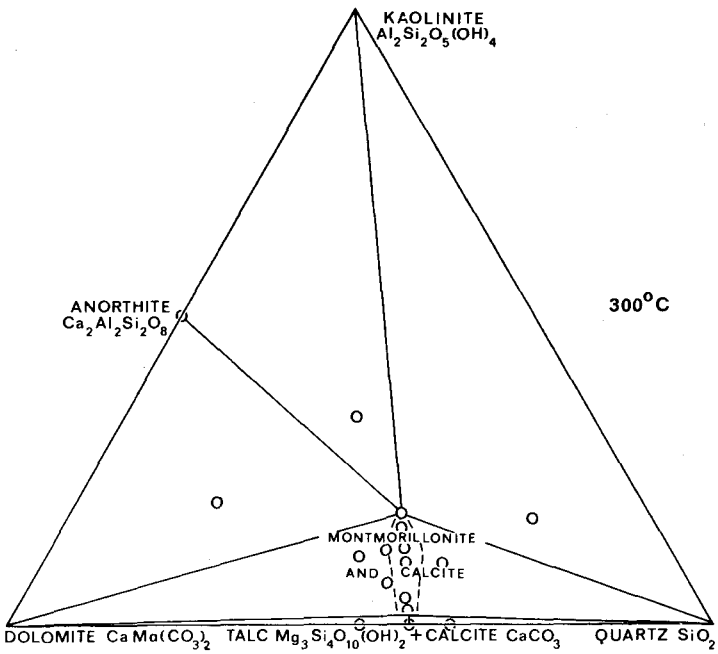


Fig. 1. Dolomite, quartz and kaolinite (equations 1, 2 and 3) react in a hydrous environment at 300°C to form products illustrated in the ternary diagrams. The area within the dotted line represents montmorillonite and calcite. Each circle represents a single bomb reaction.

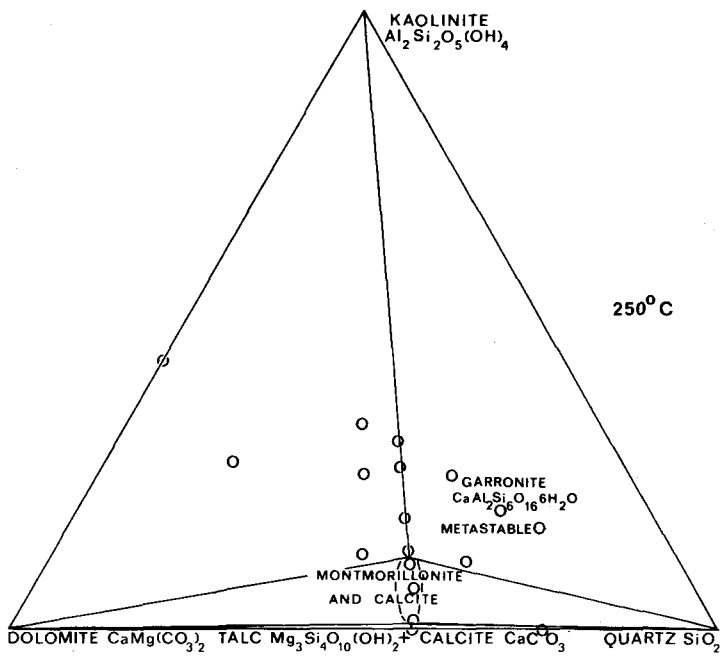


Fig. 2. Dolomite, quartz and kaolinite (equations 1, 2 and 7) react in a hydrous environment at 250°C to form products illustrated in the ternary diagram. The area within the dotted line represents montmorillonite and calcite. Each circle represents a single bomb reaction.

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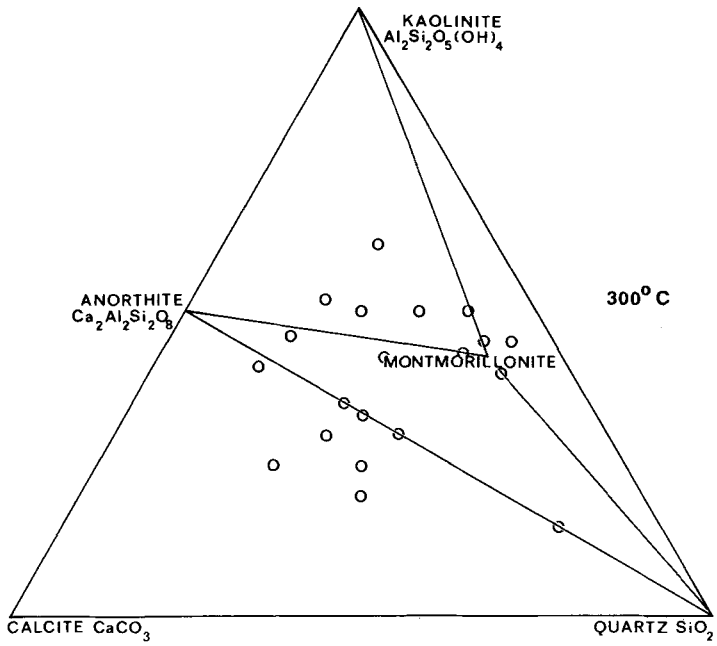


Fig. 3. Calcite, quartz and kaolinite (equations 4 and 5) react in a hydrous environment at 300°C to form products illustrated in the ternary diagram. Each circle represents a single bomb reaction.

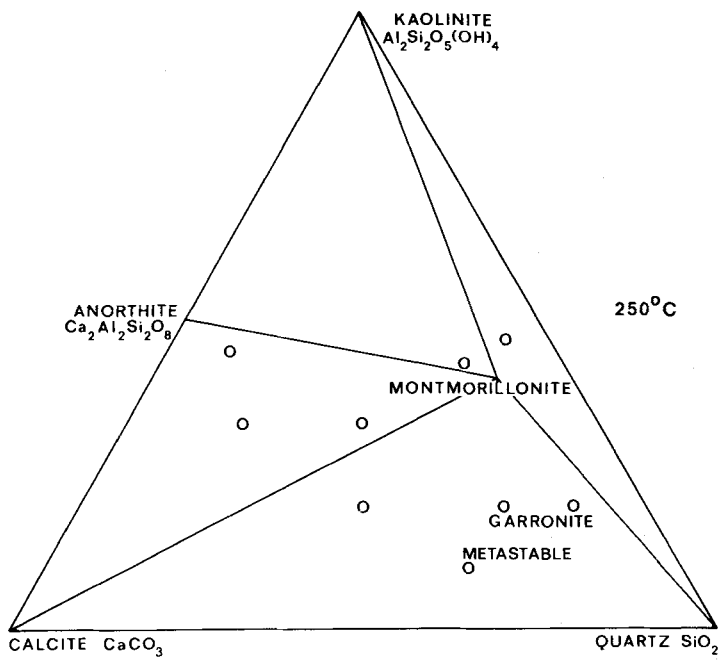


Fig. 4. Calcite, quartz and kaolinite (equations 4–6) react in a hydrous environment at 250°C to form products illustrated in the ternary diagram. Each circle represents a single bomb reaction.

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tuted for calcite in the starting material, then anorthite only formed above 288°C (equation 3). The metastable hexagonal anorthite is formed in the presence of more water (40 ml average), whereas the stable triclinic anorthite formed in the presence of less water (20 ml average). These data do not agree with those of Goldsmith and Ehlers (1952), who considered the role of water as principally that of a flux with no systematic effect on either compound. Anorthite has a stability region above 330°C at 500 bars according to the reversible reaction of wairakite $\rightleftharpoons$ anorthite + quartz + water (Liou, 1970).

The Ca-zeolite garronite (equation 6) which formed at 250°C but not at 300°C, was identified by comparison with X-ray data of Taylor and Roy (1964) who also indicate that garronite converts to wairakite at 295°C. If dolomite is substituted for calcite in the starting material then garronite formed together with montmorillonite (equation 7). Compositions are not given because of the variability of both montmorillonite and garronite. The rarity of garronite in nature suggests that it is metastable; however if garronite has a stability field relative to wairakite, then the data of Liou (1970) indicate it will be at a much lower temperature than 330°C. Its metastability is also implied by its unexpected absence in most bomb runs (Figs. 2 and 4).

Some other minerals which could theoretically form from these compositions are chlorite $Mg_5Al(Si_3Al)O_{10}(OH)_2$ and tremolite $Mg_5Ca_2Si_8O_{22}(OH)_2$. Stoichiometric amounts of dolomite or calcite, quartz and kaolinite were heated to attempt to synthesize the above minerals, but they were not observed to form under these experimental conditions. Calculations, based on solubility and ionization constants of calcite or dolomite in aqueous solutions under these experimental conditions in Clark (1966), show P_{CO_2} to be 0·001 bars with almost no dissociation of CO_2. However CO_2 is a reaction product in all the equations to produce P_{CO_2} up to 3 bars calculated from the decomposition of the starting carbonate of either dolomite or calcite. The diagrams (pp. 125, 155, 158 and 165) of Helgeson *et al.* (1969) indicate P_{CO_2} prevents the synthesis of chlorite and tremolite.

The pH of the water recovered from the bombs was approximately neutral (6·0–7·2) so the pH in the bomb at 300°C would be 5 to 6 (Clark, 1966). Therefore these experiments at low temperature and pressure with slightly acid pH which approximate natural conditions are applicable to diagenesis, low grade metamorphism and hydrothermal alteration. The reactions approach completion, which indicates that the products are more stable than the reactants in this environment, however, no exact conditions of temperature and pressure were established by reversible reactions.

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Résumé– De la dolomite ou de la calcite, du quartz et de la kaolinite en différentes proportions, ont été amenés à réagir en milieu aqueux, à des températures comprises entre 250 et 300°C et à des pressions atteignant 90 bars. Les réactions qui ont été presque complètes ont produit du talc, de la calcite, de la montmorillonite, de l'anorthite (à la fois les polymorphes hexagonal métastable et triclinique stable) et une zéolite – Ca rare, la garronite. Ces réactions sont applicables à la diagenèse, au métamorphisme peu poussé et à l'altération hydrothermale.

Kurzreferat– Dolomit oder Calcit, Quarz und Kaolinit in verschiedenen Proportionen wurden bei Temperaturen von 250 bis 300°C und Drucken von bis zu 90 bars in wässrigem Medium zur Reaktion gebracht. Annähernd vollständige unter den Reaktionen ergaben Talk, Calcit, Montmorillonit, Anorthit (sowohl metastabil hexagonale und stabil triklinische Polymorphe) und den seltenen Ca–Zeolith Garronit. Diese Reaktionen gelten für Diagenese, niedrige Metamorphose und Hydrothermische Veränderung.

Резюме — Доломит или кальцит, кварц, каолинит в различных соотношениях подвергались обработке нагреванием от 250 до 300°C и действию давления до 90 бар в водной среде. Продуктами завершенных реакций оказывались тальк, кальцит, монтмориллонит, анортит (как в виде метастабильной гексагональной, так и в виде стабильной триклинной модификации) и реже Ca–цеолит (гарронит). Подобные реакции применимы к интерпретации процессов диагенеза, метаморфизма низкой ступени и гидротермального изменения.

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