行政院國家科學委員會補助專題研究計畫期中報告

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※　有機物 礦物及水在深埋或隱沒沉積物中交互作　※
※　用之實驗研究　※
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計畫編號：NSC　92－2116－M－002－018
執行期間：　92 年　8 月　1　日至　93 年　9 月　30 日

計畫主持人：黃武良(wlhuang@ntu.edu.tw)
計畫參與人員：蘇冠華 莫慧偵

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□赴國外出差或研習心得報告一份
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□國際合作研究計畫國外研究報告書一份

執行單位：國立台灣大學地質科學系

中　華　民　國　92　年　9　月　23　日

行政院國家科學委員會專題研究計畫期中報告

有機物、礦物及水在深埋或隱沒沉積物中交互作用之實驗研究

計畫編號：NSC 92-2116-M-002-018
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The geochemical evolution of carbonaceous matter as a function of temperature, pressure, and other geological factors is essential to our understanding of the fate of organic matter, through a series of geological processes, in burial or subducted sediments. Previous studies focused mostly on the effect of temperatures and pressures on organic reactions with little concern on the influence of other geological factors. This three-year research project covers a series of experimental programs, which will be conducted successively to elucidate several important issues. Our research in the first year focuses on the influence of oxidation-reduction condition on the generation of methane and carbon dioxide from organic matter in diagenetic environments. The preliminary results have been reported in the 2004 Gordon Research Conference (Organic Geochemistry). Attached is an abstract submitted to the conference. The feedbacks through the discussions with worldwide scientists in the conference will be incorporated into our future research program. In addition, we have conducted preliminary experiments on the visual and FTIR studies of organic matter at high temperature and pressures. The results show that the DAC-pyrolysis technique is useful for identifying the oil vs. gas prone organic matter. Three papers derived from researches supported by NSC were published in internationally known SCI journals during his research period including:

Huang, W.L., The nucleation and growth of polycrystalline quartz: Pressure effect from 0.05 to 3 GPa. European Journal Mineralogy 15, 843-853 (SCI). Impact factor: 1.335.

Lin, S.J., Huang, W.L., 2004. Polycrystalline calcite to aragonite transformation kinetics: experiments in synthetic systems. *Contributions to Mineralogy and Petrology* **147**, 604-614. (SCI), impact factor: 2.433

Cheng, A.L., W.L., Huang, 2004. Selective adsorption of hydrocarbon gases on clay and organic matter. *Organic Geochemistry* **35**, 413-423. (SCI). impact factor: 1.756.

附件一

Abstract presented in Gordon Research Conference

The generation of hydrocarbon gases and CO_2 from a humic coal: Experimental study on the effect of mineral-water reactions

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ABSTRACT:

The yields and composition of hydrocarbon gases and CO_2 generated from a coal have been experimentally determined under different lithological conditions simulated by adding a variety of minerals, including hematite, siderite, pyrrhotite, gypsum, Fe, Ni and V in the coal sample using confined hydrous pyrolysis technique. The experiments were conducted at 340 and 360 °C for durations ranging from 24 to 240 hours. The results reveal that the studied mineral-water environments have a small, but measurable influence on both the yields and composition of the generated gases. The difference in hydrocarbon gas yields in different mineral environments at same maturity can be as high as 15 mol. %. The hydrocarbon gas yields, in general, increase slightly with decreasing oxygen fugacity of the experiments; this trend becomes more pronounced at higher maturity. Sulfide (pyrrhotite) tends to inhibit the production of hydrocarbon gases while sulfate (gypsum) does not. Carbonate (siderite) or the generated CO_2 exerts an adverse influence on the production of hydrocarbon gases. The effect of mineral environments on the variations of CO_2 yields is more pronounced than those of hydrocarbon gases at the studied conditions. CO_2 production is highest in carbonate and least in metallic iron or nickel environments.

附件二

2003, **15**, 843-853 meeting in Zurich, Switzerland (March 2002)

The nucleation and growth of polycrystalline quartz: Pressure effect from 0.05 to 3 GPa

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Abstract: Polycrystalline quartz was formed from amorphous silica in seawater and distilled water at temperatures and pressures ranging from 50 to 450°C and 50 MPa to 3 GPa, respectively. The data at 100 and 200 MPa pressures can be reasonably modeled using Avrami's nucleation and growth equation. Experimental results reveal a dramatic pressure effect on transformation rate, which increases approximately by five orders of magnitude as pressure increases from 50 MPa to 3 GPa at 400°C. The effect is more prominent in a low-pressure regime than in a high-pressure regime; the transition pressure between the high- and low-pressure regimes is temperature-dependent. The pressure can significantly enhance both nucleation and growth rates although the effect is stronger on nucleation than on growth. This finding leads to the successful synthesis of polycrystalline quartz at a temperature as low as 50°C at 3 GPa in a few days, and helps predict its formation at ambient temperature and higher pressures. SEM measurements show that grain sizes decrease significantly with increasing pressure, giving rise to a new method for synthesizing nano-size (< 100 nm) polycrystalline quartz in neutral solutions.

Key-words: polycrystalline quartz, nucleation and growth, silica transformation, cristobalite, coesite.

Introduction

Polycrystalline quartz may occur in a variety of geological settings. It has long been recognized in the form of semiprecious gems as onyx, jasper, chalcedony, and agate precipitated from silica-rich solutions (White & Gorwin, 1961), and as cryptocrystalline quartz or its polymorphic precursors in petrified wood (Stein, 1982). Bedded chert and siliceous shales have been frequently found in sedimentary basins, in particular, those rimming the Pacific Ocean. These basins consist of thick biogenic silica-bearing sediments such as those in the Monterey formation, southern California, (*e.g.* Mizutani, 1970 and 1977; Murata & Nakata, 1974; Murata & Randall, 1975; Murata *et al.*, 1977; Mitsui & Taguchi, 1977; Pisciotto, 1981; Isaacs, 1982; Bohrmann *et al.*, 1994). The Deep Sea Drilling Project (DSDP) and the Ocean Drilling Project (ODP) have revealed silica–rich sediments presently accumulating in certain deep seas (Scholl & Creager, 1973; Hein *et al.*, 1978; Riech & von Rad, 1979; Kastner, 1982; Tada & Iuima, 1983; Thein & von Rad, 1987; Behl & Smith, 1990; Compton & Locker, 1992). In these siliceous sediments, polycrystalline quartz was formed via a series of transformations from opal-A to opal-CT to polycrystalline quartz (Mizutani, 1970). Polycrystalline quartz also occurs as quartz veins in metamorphic and igneous rocks, which result from the secondary fillings of fissures by hydrothermal fluids. Polycrystalline quartz has been found as inclusions in ultra-high pressure minerals such as garnet and zircon. Some of these quartz inclusions are believed to be derived from the high-pressure SiO_2 polymorph, coesite, during exhumation (Wang & Liou, 1991; Mosenfelder & Bohlen, 1997; Zhang & Liou, 1996).

Fine-grained polycrystalline quartz is commonly believed to form at a high nucleation rate with relatively slow growth rate (Crerar *et al.*, 1981; Williams *et al.*, 1985). A high nucleation rate may be due to significant silica over-saturation of a solution with respect to quartz. Solutions saturated with amorphous silica or cristobalite in the siliceous sediments favor the high nucleation rate for the formation of polycrystalline cristobalite or quartz because their solubilities are higher than that of quartz (Marshall, 1980; Williams *et al.*, 1985; Azaroual *et al.*, 1997). Since the degree of oversaturation of such solutions with respect to quartz varies with temperature and pressure (Fournier & Potter, 1982; Millero, 1982; Manning, 1994), the nucleation and growth rates of polycrystalline quartz in such solutions are anticipated to vary as a function of temperature and pressure.

Most previous studies on the formation of polycrystalline quartz focused on the bulk transformation rate between silica polymorphs (Carr & Fyfe, 1958; Cambell &

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附件三

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ORIGINAL PAPER

Shueh-Jung Lin · Wuu-Liang Huang

Polycrystalline calcite to aragonite transformation kinetics: experiments in synthetic systems

Received: 2 July 2003 / Accepted: 5 March 2004 / Published online: 1 April 2004

Abstract The kinetics of the calcite to aragonite transformation have been investigated using synthetic polycrystalline calcite aggregates, with and without additional minerals present. The reaction progresses as a function of time were measured at four temperature/pressure conditions: (1) 550 °C/1.86 GPa; (2) 600 °C/2.11 GPa; (3) 650 °C/2.11 GPa, and (4) 700 °C/2.29 GPa. Experiments reveal that Mg-calcite and Fe-calcite transforms to aragonite at considerably slower rates than pure calcite, and that Sr-bearing calcite and calcite + quartz aggregates transform at significantly higher rates than pure calcite. The reaction progresses vs. time data for pure calcite were fitted to Cahn's grain-boundary nucleation and interface-controlled growth model. Evidence for interface-controlled growth is provided by petrographic observations of grain boundaries. The activation energy for aragonite growth from the synthetic polycrystalline calcite determined in this study is significantly lower than that previously determined from a natural marble. The discrepancy in rates and activation energy may be attributed to the nature of grain boundaries, to deformational strain or the presence of impurities in the studied samples, and likely to uncertainties in experimental conditions. The results of this study imply that the variation of local petrologic conditions, in addition to temperature, pressure and grain size, may play an important role in determining the rates for the calcite to aragonite transformation in nature.

Editorial responsibility: W. Schreyer

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Introduction

The polymorphic transformation of calcite to aragonite and its reverse reaction, aragonite to calcite, are key reactions during the high pressure-low temperature metamorphism of carbonate rocks. Understanding the equilibrium and kinetics of the transformation is essential to studies of thermobarometry, geochronology, and tectonics for carbonate terrains (Hacker et al. 1992). The kinetic information of the reaction enables us to estimate the timing and temperature (or depth) when and where the transformation occurs. The calcite to aragonite transformation can cause up to a 7% volume change of a carbonate unit, a change that can induce the tectonic movement of the subducted terrain. Its transformation kinetics, therefore, enable us to estimate the timing of tectonic events during regional metamorphism. However, the complexity of nucleation and growth processes involved in the transformation impedes the development of kinetic models based on experimental data for predicting natural processes accurately (e.g. Rubie and Thompson 1985). Previously determined rates of the transformations are inconsistent, probably due to differences in experimental conditions and nature of the starting materials (Rubie and Thompson 1985). While most previous studies have focused on aragonite to calcite transformation kinetics, experimental studies on the calcite to aragonite reaction, which requires high-pressure experiments, are relatively rare (e.g. Brar and Schloessin 1979, 1980; Hacker et al. 1992; Rubie and Thompson 1985). Hacker et al. (1992) experimentally measured the progress of transformation as a function of time (t) over a wide range of temperatures (T) and pressures (P) for a natural polycrystalline marble; they predicted the amounts of the transformation along a given P-T-t path by extrapolating their experimentally determined growth rates of aragonite using Turnbull's equation (Turnbull 1956; Rubie et al. 1990). Similar kinetic studies for polycrystalline samples were conducted for

附件四

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Selective adsorption of hydrocarbon gases on clays and organic matter

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Abstract

The adsorption selectivity for C_1–C_6 hydrocarbons in a gas mixture on a variety of adsorbents was measured at 26 and 80 °C at total pressures of 1, 2 and 3 atm. The adsorption isotherm reveals that the adsorption levels are higher for organic matter than for clays, although the selectivity is similar. Coal adsorbs gases more than oil shale, kaolinite adsorbs less total gases but more methane than montmorillonite whereas activated carbon shows much stronger adsorption capacity than the other studied samples. The proportion of the adsorptive amount relative to the initial amount for each gas component at steady state condition increases with decreasing their vapor pressures (p_o) (from C_1 to C_6). The normalized adsorptive amount for each adsorbed gas increases with increasing partial pressures (p_i) of the gas in the system. The trends, in the case of oil shale, follow nearly a single trend curve as the adsorption level was plotted against relative pressure (p_i/p_o). This confirms that the adsorption selectivity is mainly caused by variations in the vapor pressure of the gases. In addition, the measured adsorption rates of gases on the studied adsorbents can be reasonably described using the Elovich kinetic model.

1. Introduction

The composition of reservoir hydrocarbon gas is generally significantly different from that predicted by experimental simulation of the gas generation from its inferred source rocks (Mango, 1992; Snowdon, 2001; Behar and Vandenbroucke, 1996). In particular, the methane fraction in the gases generated during artificial maturation is usually lower than that observed in actual petroleum reservoirs (e.g. 85±15% of methane; Mango, 1996). Based on the study of gas from cuttings, Snowdon (2001) suggests that the composition of gas generated in geological environments is much wetter (20±10% of methane). The compositional difference between generated and accumulated gases is attributed mainly to various geological processes. The difference of organic matter types and maturity (Behar and Vandenbroucke, 1996; Hunt, 1995), and compositional fractionations during primary and secondary migration are believed to be major causes for the observed differences (Price and Schoell, 1995). These include well known geological processes, such as the mixing with biogenic gas in nature (e.g. Hunt, 1995), formation and decomposition of gas hydrate (Snowdon, 2001), evaporative fractionation through vertical migration (Thompson, 1987, 1988; Snowdon, 2001), and bio-degradation and secondary cracking of oils (Behar et al., 1991, 1995; Behar and Vandenbroucke, 1996). Other less-understood processes include the preferential retention of wet hydrocarbon gases in coal, organic matter, clays and other geological materials during primary and secondary migration.

The adsorption of hydrocarbon gases on coals has been reported by many previous studies (Crosdale, 1998; Siahaan, 1990; Crosdale et al., 1998; Smith and Williams, 1987; Ting, 1987; Ettinger, 1984). Most of these studies, however, focus mainly on methane

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