Carbonaceous material in S-type Xihuashan granite

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(Received May 2, 2000; Accepted February 14, 2001)

In order to verify the presence of residual organic matter in some S-type granites, a method used conventionally in petroleum geochemistry for isolation of kerogen was employed to separate carbonaceous material (CM) from the Xihuashan granite, Jiangxi Prov., China. Optical, XRD and SEM/EDAX analyses identified the acid-insoluble residue as mainly composed of various mineral debris, with a minor carbonaceous fraction found in the residue. LMR and micro-FTIR studies showed that the residue contained a small amount of CM, which is heterogeneous in composition and structural state. The occurrence of CM in the granite implies that this granitic magma originated from sediments and crystallized at relatively lower temperatures and high pressures. This deduction is consistent with geological and geochemical studies of the Xihuashan granite. A tentative model was suggested which connects CM in S-type granite with organic matter in sedimentary rocks. The conditions under which CM can be preserved in S-type granite are discussed. The occurrence of some heavy hydrocarbons is expected in the Xihuashan granite.

INTRODUCTION

The physico-chemical transformation of organic matter during the geological history of sedimentary basins is controlled by the same major factors as determine the chemical composition of the inorganic solid phases and of the interstitial water of the sediments, such as temperature and pressure (Tissot and Welte, 1984). The following evolutionary stages of sediments classified by burial depth have been proposed: diagenesis, catagenesis, metagenesis and metamorphism. Petroleum geochemistry commonly deals with the evolution of organic matter in sediments during diagenesis, catagenesis and metagenesis (the beginning of metamorphism), and is mostly concerned with the transformation of biopolymers to geopolymers called kerogen and with the generation of hydrocarbons (HCS), that is, oil and gas through thermal degradation and cracking of kerogen. With further time and burial, accompanying the loss of H, N and O, organic debris is gradually converted to increasingly crystalline and pure carbonaceous material (CM), with graphite as the end product.

CM is a common constituent of metamorphosed sedimentary rocks. The isolation and identification of CM in metamorphic rocks are of great petrologic importance in view of the ability of graphite to control the partial pressure of oxygen in the coexisting gaseous phase (French, 1964). As the graphitization of CM in rocks is believed to be irreversible, the extent of graphitization may be a useful indicator of the maximum metamorphic grade attained (Wada et al., 1994), so that many petrologists working at metamorphism have paid attention to the chemical composition and structural state of CM in metamorphic rocks and its geological applications. On the basis of previous works (e.g., Swain et al., 1958; French, 1964; Izawa, 1968; Landis, 1971; Grew, 1974; Itaya, 1981; Okuyama-Kusunose and Itaya, 1987; Wang, 1989; Kribek et al., 1994), the characteristics of so-called CM can be summarized as follows:

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CM is dispersed in metamorphosed rocks and is the residual of thermal evolution of organic debris originating in protolith-sediments; (2) The chemical compositions, crystallinity and structural states of CM range between rather mature kerogens and graphite, but CM has not yet developed into crystalline graphite.

When sediments are deeply buried in the earth’s crust where temperature and pressure are high, they may be changed to metamorphosed rocks. From the estimation of Suk (1983), for example, metamorphic temperature and pressure for amphibole facies approximate to 480–700°C and 4.5–8 kb. Under certain tectonic conditions, partial melting of sediments would generate granitic magma at such temperature and pressure in the deep crust, which would eventually emerge on the surface as granite; such are the S-type granites proposed by Chapell and White (1974). Although the formation of the S-type granite differs from regional and contact metamorphism in both geologic conditions and physico-chemical condition, the occurrence of CM in some S-type granites should be possible, by analogy to metamorphosed rocks.

The fate of organic matter during the transformation process from sediments to S-type granite at depth is one of the leading problems in the terrestrial carbon cycle. Previous studies have shown that organic carbon occurs in small amounts in granites. For example, Mogarovsky et al. (1980) reported the occurrence of dispersed bitumens in granites in the granite-gneiss bed at Pamir. Ishihara and Terashima (1989) examined the carbon contents of the magnetite-series and ilmenite-series granitoids in Japan, and presented non-carbonate carbon contents ranging from tens to hundreds of ppm for these granite. According to Hoefs (1973), the non-carbonate carbon found in igneous rocks may occur as elemental carbon (graphite), as carbide, and as organic compounds or as all three combined. Sugisaki and Mimura (1994) detected HCS in rock samples from the Ohsumi granite, a typical S-type granite in Japan, and considered them as recycled biogenic mantle HCS. However, to date few reports about CM in granite have been published in the geological literature.

The purpose of this study is to verify the presence of CM in the Xihuashan S-type granites, and to provide clues about the origin and the conditions of formation of the granite.

**GEOLOGY AND GEOCHEMISTRY OF THE XIHUASHAN GRANITE**

Two main magmatic types of granite have been recognized during the Yanshanian (Mesozoic era) orogeny in south China (e.g., Xu et al., 1982, 1992; Wang et al., 1984) and are usually compared to the I- and S-type granites of Chapell and White (1974). The Nanaling region consists mainly of S-type granites related to W, Sn, Nb-Ta and REE mineralization. The Xihuashan granite can be considered as a representative of the S-type granite in this region.

The Xihuashan pluton, famous for its large tungsten mine, is located about 8 km to northwest of the Dayu County, Jiangxi Province, China. This granite complex intruded into Cambrian shales and greywackes, which have suffered strong contact metamorphism, giving rise to a ring-shaped hornfels zone around the granite. There is a sharp boundary between the granite and country rocks, and xenolith is scattered along the periphery of the granite. The pluton is well exposed because of the rugged terrain, and the extensive mine workings allow an extremely good three-dimensional view into the granite body. A relict of metamorphic country rocks was found on top of the pluton. The granite complex is divided into two phases: the first phase, porphyritic medium-grained biotite granite, is genetically related to W-mineralization, and makes up the major part of the granite body; the second phase is medium- to fine-grained biotite granite (Liu, 1992).

Rb-Sr isotope data of whole rock samples of the granite form isochrons indicating ages of 155 ± 2 Ma (initial value of $^{87}\text{Sr}/^{86}\text{Sr} = 0.7169 \pm 0.0014$) (Li et al., 1986), and 156 ± 4 Ma (initial value of $^{87}\text{Sr}/^{86}\text{Sr} = 0.7186 \pm 0.0008$) (Li et al., 1993), respectively. For whole rock samples, the δ^{18}O values of 11.4–12.5 per mil (Zhang et al.,
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1982; Zhang et al., 1984) and an average of 11.94 ± 0.30 of 8 samples (Mu et al., 1982) were reported. The Sm-Nd isotope compositions of this granite show a high \(^{147}\text{Sm} / {^{144}\text{Nd}}\) ratio of 0.1638–0.3382, and rather consistent values of \(\varepsilon_{\text{Nd}}\) of –10.74~–11.40 (Shen et al., 1994). The peraluminous Xihuashan granite is characterized by strong depletion of Eu and enrichment of HREE, high contents of incompatible elements, rare metals and volatile components (Maruejol et al., 1990; Shen et al., 1994). The available Sr and Nd isotope data corroborate geological studies, which demonstrate that the granite originated from upper crustal materials. Some scientists think that the Xihuashan biotite granite was formed at a relatively lower temperature and high pressures. For example, the crystallization temperature of the Xihuashan granite calculated from the \(\delta^{18}\text{O}\) data of quartz-biotite pair are 425–550°C (Zhang et al., 1982) and 460–550°C (Zhang et al., 1984). These temperature values seem to be somewhat lower than expected, probably due to the hydrothermal alteration of the biotite. Melting experiments showed that the initial melting temperatures of biotite granite samples from the Xihuashan granite are: 710, 680 and 655°C at pressures of 1, 2 and 3 kb, respectively (Liu et al., 1984), and that the solidus of the granite is very close to that of the artificial standard granite in the Ab-Or-Qz-H\(_2\)O system. It is known that saturation temperatures of zircon and monazite can be estimated from whole rock Zr content (e.g., Watson, 1987), LREE (e.g., Montel, 1987) and major element chemistry of the granite. Maruejol et al. (1990) indicated that the saturation temperatures (675–765°C) calculated from LREE (Montel, 1987) agreed closely with those calculated from Zr abundance (Watson, 1987) in the Xihuashan granite.

The porphyritic biotite granite sample we studied was collected from unaltered granite in an underground gallery of the Xihuashan tungsten mine, which is located at the southwestern margin of the pluton. The distances from the sampling point to country rocks and to relict cap on the top of the pluton were more than 500 m and 300 m, respectively. The granite sampled was composed of 34% quartz, 29% K-feldspar (microcline and orthoclase), 31% plagioclase, 2% biotite and abundant accessory minerals, including xenotime, gadolinite, monazite, apatite, zircon, garnet, scheelite, wolframite, cassiterite, fluorite, tourmaline, ilmenite, magnetite, etc.

**Separation of CM from Granite Matrix**

The granite sample was thoroughly washed with water and dried, and then crushed and pulverized finer than 0.15 mm using carefully cleaned crusher and mill. This powdered granite is the starting material for the separation of CM. Rock-Eval pyrolysis detected trace amounts of organic carbon in the granite sample studied; extractable hydrocarbon contents (S\(_1\) peak) of 40 ppm and “kerogen” (S\(_2\) peak) of 30 ppm were found. Since Rock-Eval techniques are designed for source-rocks instead of granites, these data should be considered only as a reference.

The CM was separated from the rock matrix using a method for kerogen isolation from petroleum geochemistry (Durand and Nicaise, 1980). This conventional method is based upon the dissolution of carbonates, oxides, hydroxides and some sulfides by HCl and the dissolution of silicates by HF. The powdered granite of total 2 kg was repeatedly treated with 6 mol/l HCl, and a mixed acid (6 mol/l HCl + 40 vol% HF, HCl:HF = 2:3). Between acid-dissolution, the residues were washed with heated deionized water and with 1 mol/l HCl solution, respectively. All chemical operations were performed between 60 and 70°C. At the end of the procedure, a dark brown insoluble residue of about 0.8 g was obtained. Then, an ultrasonic cleaning was carried out with chloroform twice (2 hours each time) to dissolve free HCS from the insoluble residue, if they existed.

**Identification of CM in the Acid-Insoluble Residue**

*Optical, XRD and SEM/EDAX studies*

Polished thin sections were made of the residue after cleaning with chloroform and these were...
studied using a polarized microscope. Small amounts of black fragments, a few grains of zircon, tourmaline, quartz, feldspar and a lot of fine fragments of unidentified minerals were observed under transparent-light. The microscopic study showed that the residue is a mixture of remnant minerals in large amounts and trace amounts of fine black fragments which probably are of CM. Further physical separation of the black material was not attempted, due to the low quantity of the residue.

To identify the mineral composition of the residue, X-ray diffraction study was done. From the assignment of the peaks on the X-ray diffractogram, the residue consisted mainly of xenotime, as well as minor zircon and tourmaline. Comparing to the previous XRD studies of CM in metamorphic rocks (e.g., Landis, 1971; Grew, 1974; Wopenka and Pasteris, 1993), neither characteristic peaks for well-crystallized graphite nor ill-defined peaks centered about 26°2θ for poorly-crystallized CM were found on the diffractogram possibly because of the very low content of black material in the residue.

In order to distinguish the black material from other remnant minerals, the residue plated with carbon was examined using a field emission scanning electron microscope (AMRAY 1910 FE) to perform energy dispersive X-ray analysis (EDAX). Besides large amount of mineral debris, also a little fragment of <30 µm and with irregular shapes (e.g., Fig. 1, bottom) was observed by the SEM. No peaks of Al, Si, P or other inorganic elements were found on the EDAX spectrum of these fragments. This means that the fragments are carbonaceous. It is of note that a porous carbonaceous fragment (see Fig. 1, top) was observed, and this fragment is morphologically very similar to the fusinite referred to in the SEM observation (see figure 7a of Norby et al., 1998).

**LMR and micro-FTIR spectroscopic studies**

In order to obtain complementary information on the composition and structural state of the carbonaceous fragments in the residue, LMR and micro-FTIR spectroscopic studies were performed. Before these studies, the carbonaceous fragments in the residue was relatively concentrated by simple sink-flotation in chloroform.

Raman microsampling spectrometry of two samples was done using RENISHAW-1000 LMR with a Leica microsampling accessory. Each sample (a pinch of the residue) was scanned from 1000 to 3500 cm⁻¹, and the important spectral windows were scanned for first- and second-order Raman bands of CM at 1200–1700 and 2350–3350 cm⁻¹, respectively. On the Raman spectra of samples A and B (Fig. 2), no peaks were found in the range of 2350–3350 cm⁻¹, while a relatively wide peak at 1600 cm⁻¹, and a weak peak at 1355 cm⁻¹ were observed. From the Raman spectroscopic study of kerogens, Wopenka and Pasteris (1993) indicated that the peak at 1600 cm⁻¹ was due to
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The first-order Raman band, the peak at \( \approx 1355 \text{ cm}^{-1} \) was due to disordered-induced first-order Raman band, and peak at \( \approx 2715 \text{ cm}^{-1} \) was caused by main second-order Raman band. It is known that single crystals of graphite yield only one sharp Raman peak around 1575 cm\(^{-1}\) (Tuinstra and Koenig, 1970). According to Wopenka and Pasteris (1993), Precambrian kerogens have Raman properties grossly different from well-ordered graphite: (1) the kerogens have no (or a very weak) second-order Raman band at 2715 cm\(^{-1}\); (2) the position of the ordered peak has higher wavenumbers and a relatively high intensity ratio of the disordered peak to the ordered peak compared to well-crystallized graphite; (3) a very wide first-order peak is present. In comparison with studies of Tuinstra and Koenig (1970), Wopenka and Pasteris (1993) and Tsuchiya (1993), it can be concluded that some material is included in the residue similar to kerogen or CM rather than crystalline graphite.

The micro-FTIR spectra of the sample (a pinch of the residue) were recorded in the range of 700–4000 cm\(^{-1}\) on a Nicolet MAGNA-IR 750 spectrometer. In order conveniently to interpret the four FTIR spectra obtained in this work, the most likely functional groups of kerogen along with the frequency of the main bands associated these functional groups are compiled in Table 1. The spectra for samples A, B, C and D, on the whole, have somewhat similar features (Fig. 3). The band around 1010–1020 cm\(^{-1}\) with a shoulder or shoulders is the strongest, and may contain contributions of C-O stretching, of P-O stretching of phosphates, and of Si-O stretching of silicates. Considering the optical and XRD study results of the residue, it can be argued that the C-O band has been overwhelmed by very strong P-O band (around 1090 cm\(^{-1}\)) and Si-O band (around 1000 cm\(^{-1}\)). Bands around 2850–2950 cm\(^{-1}\) are mainly due to the asymmetric and symmetric stretching of alkyl CH\(_3\) and CH\(_2\). The absorption band at \( \approx 750 \text{ cm}^{-1} \) is due to out-of-plane deformation vibrations of aromatic CH groups (Rouxhet \textit{et al.} 1980). The relatively strong \( \approx 1260 \text{ and } \approx 1320 \text{ cm}^{-1} \) bands in spectrum C can be assigned to C-O stretching and C-OH stretching. The band near 1710–1720 cm\(^{-1}\) in spectra D and B is attributed to C=O stretching of carbonyl and carboxyl. The
weak absorption band at \(\approx 1455 \text{ cm}^{-1}\) in spectra A, B and D is due to asymmetric bending of \(\text{CH}_2\) and \(\text{CH}_3\) groups. A wide and very weak band around 1600 cm\(^{-1}\) in spectra A and B may contain contributions from a different type of vibrations. Absorption in this region may be assigned to C=O stretching of aromatic rings, olefins and polyaromatic layers (Rouxhet et al., 1980). There is a wide asymmetric band centered near 3300–3400 cm\(^{-1}\) on the spectra related to OH stretching vibration. These FTIR spectra demonstrate that the residue include some material containing aromatic and oxygenated functional groups as well as aliphatic chains.

To sum up the examination of the residue described above, it can be concluded that the insoluble residue contains trace amounts of CM, which are heterogeneous in composition and structural state.

**DISCUSSION**

It is suggested by the above results that a small amount of CM is contained in the Xihuashan granite. In this study all possible precautions were taken in the field to avoid sampling weathered rock and in the laboratory to prevent contamination during the acid-dissolution procedure. As indicated before, the sampling point is far way from the xenolith zone and relict on top of the Xihuashan pluton. Therefore, we believe that the CM isolated from the Xihuashan granite matrix is an inherent constituent of the rock.

Up to now, only Robb et al. (1992) have reported the occurrence of nodular kerogen in some Archaean peraluminous granitoids adjacent to the Au- and U-bearing Witwatersrand Basin, South Africa, and presented a model that links granitoids- and sediment-hosted kerogen to a single event of oil production in the Basin about 2300 Ma ago. According to their model, light HCS migrated through the sediments and into underlying and adjacent granitic rocks, undergoing polymerization and fixation in response to radiation accompanying the presence of high-U phases. Evidently, this is a quite special case.

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<tr>
<th>Table 1. Frequency (cm(^{-1})) and assignments of bands for the infrared spectra of kerogens</th>
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<tr>
<td><strong>Functional group</strong></td>
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<tr>
<td>OH stretching</td>
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<tr>
<td>CH(_2) and CH(_3) stretching</td>
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<tr>
<td>C=O stretching</td>
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<td>C=C deformation and C=O deformation</td>
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<td>C-H deformation</td>
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<td>C=O stretching and C-OH bending</td>
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To sum up the examination of the residue described above, it can be concluded that the insoluble residue contains trace amounts of CM, which are heterogeneous in composition and structural state.
From studies on the graphitization of CM in metamorphic rocks, the temperature of the complete graphitization of CM differs from one metamorphic terrain to another (Itaya, 1981). For example, Landis (1971) studied CM in metamorphic rocks from New England and Japan, and inferred that true graphite probably formed above 400°C under metamorphic conditions. Grew (1974) pointed out that well-ordered graphite in the Narragansett basin probably formed at 660–690°C and 4.5–5.0 kbar. Luque et al. (1993) suggested that the temperature of appearance for fully-ordered graphite is about 500°C based on their XRD studies of CM in slate from the Spanish Central Range. Although the estimates of the formation temperature of well-ordered graphite vary widely, it is reasonable to argue that CM in S-type granite, if it were present, should be fully converted to well-crystallized graphite. This is because the formation temperature for the granite is generally close to or higher than the temperature values listed above. On the basis of the investigation into the mechanism for the graphitization of CM in regionally metamorphosed rocks (Grew, 1974; Wintsch et al., 1981; Wada et al., 1994), it is known that the graphitization of CM is affected by temperature and pressure, the fugacity of O-, H-, S- and N-bearing gases, permeability of the host rock, the duration of metamorphism and metamorphic fluid, and even the lithology and texture of the original organic tissues. Obviously, lower temperatures, higher pressures, high fugacity of volatile components, and low rock permeability might prolong the graphitization of CM. Therefore, the occurrence of CM in the Xihuashan granite suggests the granite was formed at relatively lower temperatures and higher pressures and high fugacity of volatile. This condition is consistent with the geological and geochemical studies of the Xihuashan granite (Mu et al., 1982; Zhang et al., 1982; Zhang et al., 1984; Liu et al., 1984; Maruejol et al., 1990; Shen et al., 1994).

On the basis of graphitization mechanism of CM above described and the idea of Sugisaki and Mimura (1994) which explained the origin of HCS detected in the Ohsumi granite of S-type as recycled biogenic mantle HCS, a tentative model is proposed which links the CM in S-type granite with the organic matter in the primitive sedimentary rocks. That is, when the sedimentary rocks are rapidly buried deeply in the earth’s crust during orogeny and partially melted to generate granitic magma at high pressures and relatively lower temperatures, organic materials in these rocks would be gradually degraded and converted to CM. If the viscous granitic magma were crystallized in a relatively closed magma chamber, the H, O, N, S in the organic matter would not easily escape, so the degradation of organic matter and the graphitization of CM would be either prevented or prolonged or both. For this reason, trace amount of CM might be preserved in the granite.

In addition, Sugisaki and Mimura (1994) detected recycled biogenic mantle HCS in S-type granite as mentioned before, and Price et al. (1998) provided new analytical data which demonstrated a surprising thermal stability of biogenically-derived C_{15} HCS in some high temperature metamorphic rocks. Considering their study results, the occurrence of some heavy HCS in the Xihuashan granite can be expected.

**Summary**

A small amount of CM was separated from the Xihuashan granite matrix using a method conventional to petroleum geochemistry, and optical, XRD, SEM/EDAX LMR, and micro-FTIR techniques were employed to identify the CM. The occurrence of CM in the granite not only provided new evidence indicating that the protolith of the granite was sediments, but also implied that the granite was crystallized at relatively lower temperatures and higher pressures. Information extracted from the occurrence of CM in the granite is consistent with geochemical data about the Xihuashan granite, such as stable isotope and trace element data. The structural state and the composition of CM in the granite may be an indicator of intensive factor for the formation of S-type granite.
Acknowledgments—We are grateful to Dr. L.C. Price for his careful and highly instructive review of the first draft of the manuscript, and to two anonymous reviewers for their very valuable comments improving the manuscript. Our sincere thanks are also due to Ms. L. Martin of Department of Geology, University of the Witwatersrand Johannesburg for her sending of a copy of Information circular, EGRU. The LMR, micro-FTIR and SEM/EDAX studies were carried out in the Department of Physics, Department of Chemistry and Electron Microscopy Laboratory of Peking University, respectively. Our colleague, Dr. Peiying Wang, completed the XRD analysis. The authors are also very grateful to Dr. J. Richards of Oregon State University for improving our English. Rock-Eval pyrolysis was performed in Laboratory Center, Research Institute of Petroleum Exploration and Development, CNPC, Beijing. This research was supported by the National Natural Science Foundation of China (Grants No. 49673193 and No. 40073025).

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