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On the discrimination of semi-graphite and graphite by Raman spectroscopy

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ABSTRACT

Graphite samples from several mines (Austria, Brazil, China, Madagascar, Mozambique, Norway, Russia, Sri Lanka and Ukraine) were investigated by reflectance measurements, X-ray-diffraction, high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and Raman spectroscopy. X-ray-diffraction indicates that the structural order of the carbonaceous matter (CM) varies in dependence on the metamorphic rank of the host rock. Semi-graphite is found in lower greenschist facies samples from the Kaisersberg mine (Austria). At the nanoscale, micropores characterize semi-graphite. They are polygonized in the transition zone between semi-graphite and graphite. During progressive graphitization within the greenschist facies, semi-graphite is transformed continuously to graphite. HRTEM images and SAED data show a transformation of the microporous nano-texture to a predominantly lamellar texture. Perfect graphite is observed in samples from the granulite facies. Raman spectroscopy mirrors this evolution. The observed spectral characteristics, the width of the Raman G band and the D1 / (G + D1 + D2) area ratio of the CM Raman spectrum discriminate semi-graphite and graphite.

1. Introduction

Organic metamorphism transforms natural carbonaceous materials (CM) to anthracite, meta-anthracite, semi-graphite and graphite (Kwiecińska and Petersen, 2004). Whereas advanced coalification during deep sedimentary burial may result in (meta-) anthracitic coal ranks (e.g. Sachsenhofer et al., 2002; Bruns and Littke, 2015), intense contact metamorphism (Zheng et al., 1996; Sachsenhofer et al., 2002), precipitation of CM from hot fluids (Luque et al., 2014; Rumble, 2014), or tectonic burial of organic matter rich sediments below overthrusting nappes (e.g. Schrauder et al., 1993; Wilde et al., 1999; Rantitsch et al., 2004; Feng et al., 2015; Martín-Méndez et al., 2015) is necessary to form semi-graphite and graphite. Graphitization transforms the structurally disordered CM of anthracite to a higher structural state. As a result, semi-graphite represents a transitional phase between (meta-) anthracite and graphite (Kwiecińska and Petersen, 2004).

A clear classification of graphitic materials is of particular importance, because their unique material properties influence directly the technological use of this important raw material (e.g. Beyssac and Rumble, 2014). The International Committee for Coal and Organic Petrology (ICCP) proposed reflectance measurements, X-ray and chemical analysis to discriminate semi-graphite from graphite (Kwiecińska and Petersen, 2004: Table 1). However, reflectance measurements on highly evolved CM are of restricted significance (Kwiecinska et al., 2010), and both, X-ray and chemical analysis give a bulk estimate, not representing the significant structural heterogeneity of graphitic CM (Diessel and Offler, 1975; Kribek et al., 1994; Rantitsch et al., 2004; Suárez-Ruiz and García, 2007). According to Kwiecinska et al. (2010), the exact identification of semi-graphite requires TEM investigations. Raman spectroscopy may provide a powerful alternative.

Following the pioneer work of Tuinstra and Koenig (1970), several studies (Lespade et al., 1984; Pasteris and Wopenka, 1991; Wopenka and Pasteris, 1993; Yui et al., 1996; Beyssac et al., 2002a, 2002b; Aoya et al., 2010; Lahfid et al., 2010) demonstrated Raman spectroscopy as an effective tool to trace the evolution of CM during regional metamorphism. Consequently, Raman spectroscopy of CM (RSCM) was widely applied to investigate past tectono-thermal processes. In a multi-methodological approach, Beyssac et al. (2002a) investigated high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and Raman spectroscopy on CM enclosed in high pressure — low temperature metamorphic rocks. They confirmed previous work of Wopenka and Pasteris (1993) and Bustin

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Table 1
Investigated samples.

Sample	Graphite type	Sample processing	Tectonic unit	Locality	Age	T	P	Reference
					Very-low grade metamorphism			
T1		hp	Austroalpine	Turrach, Austria	Palaeozoic			Rantitsch and Russegger (2000)
					Greenshist-facies			
1A	mc	gr	Austroalpine	Kaisersberg, Austria	Palaeozoic	360°–410°	>2 kbar	Raith and Vali (1998)
2A	mc	gr						
6A	mc	hp						
					Contact metamorphism			
4A	mc			Hunan, China	Palaeozoic			Zheng et al. (1996)
5A	mc			Uncertain				
					Amphibolite-facies			
2B	fl	gr + fl	West Troms Complex	Skaland, Norway	Archaean–Proterozoic			Bergh et al. (2010, 2012); Henderson and Kendrick (2003)
3A	mc	hp	Moldanubic unit	Runds, Austria	Proterozoic	700°–800°	7–9 kbar	Petrakakis (1986), Petrakakis (1997)
8B	fl	gr + fl	Yangtze Craton	Hubei, China	Archaean	700°	4 kbar	Geng (2015)
12B	fl	hp	Moldanubic unit	Weinberg, Austria	Proterozoic	700°–800°	7–9 kbar	Petrakakis (1986, 1997)
					Amphibolite-granulit-facies			
1B	fl	gr + fl	Mozambique Belt	Balama, Mozambique	Proterozoic	600–850°	6–10 kbar	Feneyrol et al. (2013)
3B	fl	gr + fl	São Francisco Craton	Minas Gerais, Brasil	Proterozoic	>750 °C		Chaves et al. (2015)
5B	fl	gr + fl	East Uralian Zone	Tayginka, Russia	Palaeozoic	650–750 °C	6–8 kbar	Echtler et al. (1997)
					Granulite-facies			
4B	fl	gr + fl	Ukrainian shield	Zavalje, Ukraine	Archaean			Dagelaysky (1997), Zagnitko et al. (2013)
6B	fl	fl + at	N-China Craton	Inner Mongolia, China	Proterozoic	860°–930°		Yang et al. (2014), Zhang et al. (2014), Santosh et al. (2013)
7B	fl	gr + fl	Jiamusi Massif	Heilongjian, China	Proterozoic	800–850°	5.3–6.2 kbar	Wilde et al. (1999)
9B	fl	gr + fl		Uncertain				
11B	fl	gr + fl	Madagaskar Basement	S-Madagaskar	Archaean-Proterozoic	700°–880°	8–11 kbar	Jöns and Schenk, (2011), Parthasarathy et al. (2006)
					Fluid deposited			
10B	Vein-type	hp		Sakura Kandy, Sri Lanka				Touzain et al. (2011); Luque et al. (2014)
	mc = microcrystalline		hp = handpicked	fl = floatated				
	fl = flake		gr = grinded	at = acid treated				