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Utilizing smear mounts for X-ray diffraction as a fully quantitative approach in rapidly characterizing the mineralogy of shale gas reservoirs

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ABSTRACT

X-ray diffraction (XRD) sample preparation methods were compared for fine grained reservoir rocks. The viability of using a hand ground, smear mount method was investigated compared to the widely used micronized, cavity mount method of sample preparation for quantitative phase analysis. Micronizing a sample before analyzing by XRD has been used successfully to reduce the average crystallite size to 10 μm. However, because of the fine grained nature of shale gas reservoirs, the average crystallite size is already below 10 μm. Therefore, the sample only requires disaggregation of larger particles which is easily accomplished by hand grinding. Samples were prepared using smear and cavity mount methods to compare the differences in quantitative phase abundances determined by Rietveld refinement. In addition, samples of known composition were prepared to assess the accuracy and precision of the methods. Quantitative analysis on whole rock samples shows excellent precision between the methods of sample preparation with an absolute error of ±2.25 wt.% at the 95% confidence level per individual phase. Quantitative analysis on artificially prepared samples using the smear mount method shows both excellent precision and accuracy with an absolute error of ±0.9 wt.% at the 95% confidence level per individual phase. A hand ground, smear mount method is therefore a quantitative and viable method for quickly assessing the mineralogy of shale gas reservoirs and fine grained rocks.

Introduction

The emergence of fine grained lithologies, such as mudrocks, as economical reservoirs for hydrocarbons (i.e. shale gas and shale oil) has prompted a revision of methodologies for measuring the geological properties of rocks with structures and particle sizes in the sub-micrometer range. An important part of reservoir characterization is identifying and quantifying mineral phases present. Reservoir properties such as matrix permeability, rock moduli, porosity and texture are dependent on mineralogy. Important reservoir properties have been correlated with mineralogy (i.e. Clarkson et al., 2013; Kuila and Prasad, 2013) to identify the associations of more favorable reservoir, such as higher permeability and greater porosity, with various minerals or mineral groups. In fine grained reservoirs where stimulation by hydraulic fracturing is necessary, small changes in mineralogy can have large impacts on overall well performance, as mineralogy along with texture will define the reservoir zone, less prospective reservoir and potential fracture barriers. Therefore, a method to quickly and accurately characterize the mineralogy of a reservoir rock is an extremely valuable exploration tool.

XRD methodology background

There are numerous methodologies for preparing, analyzing and quantifying the mineralogy of rocks by XRD (Bish and Post, 1989). Each methodology can be broken into four parts: (1) sample grinding; (2) sample drying; (3) sample mounting; and (4) diffraction pattern analysis. Artificial mixtures serve as a means to test the accuracy and precision of a methodology (i.e. Hillier, 2000; Środoń et al., 2001; McCarty, 2002; Kleeberg, 2005; Omotoso et al., 2006; Ufer et al., 2008). Certain methodologies have been shown to produce accurate and precise quantitative results (i.e. within ±3 wt.% of known mixtures, see discussion in Hillier, 2000), while others may be more suited for semi-quantitative or qualitative assessment (Moore and Reynolds, 1997).

Sample grinding involves an initial crushing of the whole rock sample, sieving of the sample, and further grinding in order to produce a sufficiently small crystallite-particle size. The recommended average crystallite size for accurate diffraction intensities

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is 5–15 μm or smaller (see discussion in Bish and Reynolds, 1989; Klug and Alexander, 1974), which reflects a compromise between grinding time, crystallite size and repeatability. Diffraction errors increase significantly for particles larger than 5–15 μm (Bish and Reynolds, 1989). Phases with good cleavage planes and a platy habit (i.e. clays) have a stronger tendency for preferred orientation when the crystallite size is larger than 30 μm compared to a crystallite size that is <5 μm (Bish and Reynolds, 1989). There is an assortment of equipment available to reduce the average crystallite size, ranging from simple hand grinding in a mortar with pestle to automatic grinding machines such as the McCrone™ micronizing mill. The McCrone™ mill has been used as the primary grinding method in experiments investigating the accuracy of quantitative analysis on artificial mixtures (Hillier, 2000; Środoń et al., 2001; Omotoso et al., 2006; Ufer et al., 2008), within general earth science literature (Ugolini et al., 2008; Day-Stirrat et al., 2010; Jeong et al., 2011) and the industry. However, a McCrone™ mill is an expensive and time consuming method that does not always add accuracy to diffraction pattern analysis of certain rock types. Published grinding times for clay rich rocks are anywhere from five minutes (Środoń et al., 2001; Omotoso et al., 2006) to 12 min (Hillier, 2000; Omotoso et al., 2006) compared to two minutes for a hand ground method. To "micronize" and recover the sample from the slurry requires significant processing time, commonly on the order of 24 h depending on the milling fluid used.

Methods for recovering the powder from the ground slurry are numerous. Assuming the sample has been ground in a McCrone™ mill, the powder must be recovered by settling, decanting, filtering, or evaporating the milling fluid. The recovered dried powder must then be disaggregated, either by hand grinding in a mortar, sieving, shaker-milling with balls, or using a vibrating mill (Kleeberg et al., 2008). Each of these requirements to recover the powder increases processing time, possibility of contamination, and requires specialized equipment and laboratory experience. A method of spray drying the slurry to produce spherical, randomly oriented agglomerates has been experimented with for a number of years (Jonas and Kuykendall, 1965; Hughes and Bohor, 1970; Smith et al., 1979a, 1979b) but did not gain wide spread usage until the innovations by Hillier (1999, 2002). The spray drying technique is faster than evaporation; however, the drying chamber must be heated to 150 °C, with lower temperatures resulting in insufficient drying of the slurry before reaching the chamber floor (Hillier, 1999). At these temperatures alteration of minerals may occur. For example, some common sulfates such as gypsum can dehydrate to bassanite (Hillier, 2002). Lower chamber temperatures of 60 °C along with fast drying ethanol as the slurry liquid has been successfully used to spray-dry specimens with minerals susceptible to alteration at low temperatures (Jeong et al., 2008). However, as with most specialized methodologies, the spray drying technique adds additional cost, time and experience required to operate the laboratory setup. Commercial laboratories commonly employ one of the simpler sample preparation techniques (Kleeberg et al., 2008).

The most utilized mounting techniques for generating randomly oriented specimens are dry powder cavity mounts. For powder cavity mounts, the specimen powder is packed into the mount from the back, side or front. These methods provide good results (Bish and Reynolds, 1989), with the side- and top-mount methods used to accurately and precisely quantify artificial mixtures (Hillier, 2000; Środoń et al., 2001; Omotoso et al., 2006; Ufer et al., 2008). However, if not loaded properly, the powder in the cavity mount can be deformed during long analyses times and movement in the sample chamber. If samples are packed too loosely, the sample can slump before or during analysis, especially when automatic sample changers are used and the time between packing and analyzing is long. On the other hand, if samples are packed too densely, preferred orientation of crystallites will increase as they align perpendicular to the direction of packing. This requires experience with the mounting technique and may not be reproducible for different users.

Quantitative X-ray diffraction phase analysis (QPA) is well established within the literature (Klug and Alexander, 1974; Zevin and Kimmel, 1995; Jenkins and Snyder, 1996; Cullity and Stock, 2001; Madsen and Scarlett, 2008). Phase analysis is most commonly done by one of two methods, the reference intensity ratio (RIR) method (Snyder and Bish, 1989) or the Rietveld method (Rietveld, 1967). The RIR method is based on the comparison of selected observed diffraction intensities versus reference intensities from added internal or external reference phases (Snyder and Bish, 1989). The RIR method requires a large collection of reference mineral patterns and calibration may be different from instrument to instrument and therefore may only be applicable to the laboratory in which the standards were developed (Hillier, 2000; Ufer et al., 2008). The Rietveld method uses a whole pattern multiphase calculation of the observed data versus ideal structure models for individual phases. The difference between the calculated pattern and the observed data is minimized by structure refinement. Preferred orientation correction by the March–Dollase method (March, 1932; Dollase, 1986) can be further applied to refine mineral weighting. Modern Rietveld quantitative analysis is easily accessible (i.e. commercial software) and can be successfully operated by researchers having a practical knowledge of the theory. The Rietveld method has proven to be accurate and precise in tests on artificial mixtures (Hillier, 2000; Omotoso et al., 2006), while still being accessible to infrequent users.

Modified smear mount method

The purpose of these tests are to investigate the ability of a modified hand ground, smear mount method to quantify mineralogy of fine grained rocks compared to other laborious methods. The published smear mount method (Theisen and Harward, 1962; Gibbs, 1965; Poppe et al., 2000) has been generally reserved as a method to produce oriented clay mounts to increase the detection limit of clays (Cody and Thompson, 1976) and for illite crystallinity tests (Robinson et al., 1990; Kisch, 1991).

By definition, fine grained lithologies such as siltstones and mudrocks contain at least 50% of particles less than 62.5 μm (Folk, 1974). Potter et al. (1980) further subdivide this definition into siltstones (0–32% clay-sized particles), mudstones (33–65% clay-sized particles), and claystones (66–100% clay-sized particles). The recommended XRD crystallite size of 10 μm is within the lower range of fine silt (15.6–7.8 μm). Since the boundary between clay and silt is 3.9 μm (Wentworth, 1922), mudstones, by definition, inherently have at least 40–69% of constituent grains below the 10 μm recommendation (Fig. 1).

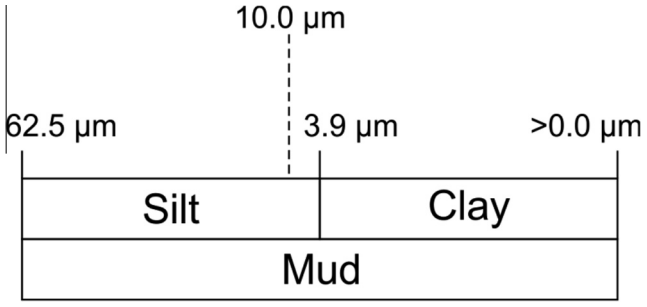

Fig. 1. Relation of the 10 μm recommended crystallite size to the particle size of fine grained rocks (Wentworth, 1922).