Application of Electron Microscopy to the study of smectites and zeolites.

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INTRODUCTION.

Electron beam techniques namely Scanning Electron Microscopy (SEM), the closely related Electron Probe Microanalysis (EPMA) and Transmission Electron Microscopy (TEM) find ample applications on the characterization of various types of geological materials including clays. They provide morphological, structural and chemical information down to the atomic scale. The principal advantage of the electron microscope over the light microscope is the much improved resolution, due to the very low wavelength of the energetic electron (<1 Å) compared to the visible light, which is employed in the optical microscope. An additional advantage of the microbeam instruments is the generation of X-rays from excitation of the samples when bombarded by electrons (Pownceby & Macrae, 2009). For these reasons the microbeam techniques have been employed successfully in the study of clay materials during the past 45 years.

The SEM can be performed using three different instrument types, the traditional SEM, the variable-pressure scanning electron microscope (VP-SEM) and the electron probe microanalyser (EPMA). In this presentation we will discuss applications of the traditional SEM and the EPMA to the study of smectites and zeolites.

APPLICATIONS OF SEM.

The traditional SEM, including its improvements for better spatial resolution like the warm or cold field emission gun (FEG) SEM, is used either in the secondary electron (SE) mode for study of crystal size and morphology or the back-scattered electron (BSE) mode for study of the texture of smectite and zeolite-bearing rocks. Under the SEM smectite crystallites are usually wavy and flaky often yielding characteristic honeycomb textures. Platy crystallites are less common. Elongated-acicular crystallites are more typical for Fe-rich smectites like nontronites. In the case of zeolites different species have different particle shapes. Fore instance mordenite forms acicular-fibrous crystals, HEU-type zeolites (heulandite-clinoptilolite) form coffin-type crystals and fauasite forms well formed octahedral crystals.

A significant contribution of SE images to the study of smectite and alkali-zeolites is the determination of the mode of their origin, either through alteration of volcanic glass or less often from other precursor minerals, such as feldspars or micas. Alteration of volcanic glass by smectites often leads to pseudomorphic textures. Both minerals can form either directly via dissolution-precipitation of volcanic glass or via crystallization from precursor amorphous gels or from poorly crystalline phases, often called protocrystalline precursors. The role of intermediate precursors, either amorphous or crystalline can be important because more soluble (thus metastable) phases are favored over less soluble (thus more stable) phases according to the Ostwald-step rule. The latter states that the most likely phase to form is not necessarily the most stable thermodynamically, and that equilibrium is reached gradually through a sequence of intermediate steps. In the case of smectites the role of intermediate precursors is not always necessary.

Secondary electrons reveal also the textural relationships of other authigenic minerals often associated with smectites or zeolites. For instance fibrous clay minerals such as palygorskite may form from alteration of smectite, although the opposite process has also been reported in the Georgian palygorskite deposits (USA). The same is true for kaolin minerals, kaolinite and halloysite, which form at the expense of smectite. Also opal-CT is a common mineral associated with smectites and zeolites. It forms either spherulitic crystals or more rarely acicular (axiolitic) crystals. The presence of opal-CT is indicative of high Si-activity in the pore fluid and is common in bentonites which form at the expense of acidic rocks. Authigenic K-feldspar may also be present in bentonites or zeolite-bearing rocks. It usually forms medium to fine silt-size or even clay-size euhedral crystals.

The use of BSE images provides important information for the textural relationships among minerals in clays. They are useful for microanalyses because they assist to avoid contamination by Ti and Fe oxides and sulfides and to distinguish coarse-grained minerals (quartz, feldspars) from smectite or zeolites. With the exception of Si-polymorphs which appear darker than smectites, the remaining minerals are brighter. BSE images assist to identify accessory or trace phases, which are not detected with other conventional mineralogical techniques, such as powder X-ray diffraction. This is especially the case for Fe- and Ti-oxides and phosphates such as apatite and monazite. The latter minerals may be the main host for REE in smectite-bearing clays. BSE images are also helpful to identify textural relationships between smectite and fine-grained accessory minerals, which may affect physical properties especially the rheological and foundry properties of bentonites.

APPLICATIONS OF EPMA.

Back scattered electron images are used for EPMA of smectites and zeolites either in SEM or in electron microprobes. In general Energy Dispersive Systems (EDS) instead of Wavelength Dispersive Systems (WDS) are used for EPMA of smectites and zeolites, because they cause less beam damage. Usually a focused or slightly unfocused beam (1 μm wide), a low sample current (1-2 nA), a low acceleration current potential and long counting times (90-120 s) provide reliable analyses. For a 1 μm wide focused beam and 2 nA sample current the excited sample area has <3 μm diameter. In the case of smectites these analytical conditions excite ~2000 crystals. Usually an adequate number of

microanalyses is obtained from each sample (≥ 20), which will allow statistically significant calculations. In the case of zeolites the reliability of microanalyses is controlled by means of the error factor (Gottardi & Galli, 1985), whereas in the case of smectites there is no acceptable way of considering a microanalysis as reliable. A rational procedure to consider smectite microanalyses as reliable is to obtain balanced structural formulae and a rational layer charge. Sources of error in microanalyses of smectites and zeolites are the loss of alkalis, the contamination by fine-grained impurities, the allocation of Mg exclusively in octahedral sites (in smectites) and the oxidation state of iron. Most of these limitations can be avoided by careful selection of analytical points and by applying suitable analytical conditions. Also analyses of smectites and zeolites always yield low totals, due to the presence of adsorbed water (interlayer, inter- and intra-aggregate and zeolitic water) and to the porosity. In the case of smectites accepted totals may be as low as 73% (Christidis 2006 and references therein).

The use of SEM and/or microprobe analysis has provided a very powerful means of understanding the geological conditions which control the formation of clays and zeolites, notwithstanding the uncertainties and limitations of microanalyses of these minerals and the lower detection limit of EDS compared to the WDS. For instance it is now well established that smectites forming in bentonites display considerable compositional heterogeneity, which reflects the microenvironmental heterogeneity during their formation (e.g. Christidis, 2006 and references therein). This compositional heterogeneity is present in the form of certain trends between the various structural cations, especially between ^{VI}Al and Fe^{3+}. These trends are considered statistically important and do not reflect the influence of analytical errors during microanalyses. The influence of the analytical errors is visible in the form of clusters around an average composition. Similar important information may be obtained for the composition of exchangeable cations of

smectites and zeolites, which may reflect the influence of the pore water on the chemistry of these minerals or *vice versa* (Christidis 2001). Finally, the use of microanalyses obtained from SEM and electron microprobe has allowed the distinction of smectites which form from different types of precursor rocks. Hence, alteration of basic rocks usually yields Fe-rich smectites, whereas alteration of acidic rocks often yields Al-rich smectites.

APPLICATIONS OF TEM.

Transmission Electron Microscopy has been used for many decades for the characterization of clay minerals including smectites. Based on TEM observations Grim & Güven (1978) classified smectites according to their crystal shape. High resolution lattice fringe images of smectites show the presence of many structural defects, in accordance with the characteristic XRD traces of smectites which show turbostratic disorder. However, low resolution conventional TEM may provide important information about the possible mechanism of formation of smectite crystals in bentonites. For this purpose particle size distribution of the clay fraction is required. The particle size distribution of smectites yield lognormal profiles. Similar particle size distribution profiles have been observed during illitization of smectite. Such profiles may indicate crystal growth in supply-controlled open systems or supply-controlled random ripening in closed systems (Eberl et al., 1998). Unlike Ostwald ripening, random ripening is not controlled by the surface area of the reactive particles but might be controlled by other factors such as strain or environmental heterogeneity. Bentonites form in open systems characterized by high water:rock ratios and remarkable microenvironmental heterogeneity, in full accordance with the TEM particle size distribution data (Christidis 2001).

IMPLICATIONS AND CONCLUSIONS.

The data obtained from the different electron microscopy techniques may be used to predict the performance of the

smectites in various industrial applications. Hence the presence of large platy crystals may be indicative of certain rheological or bonding properties. The same is the case for smectites which are in close association with fine-grained minerals. Also, the presence of abundant octahedral Fe^{3+} in smectite structure (ferruginous smectites) suggests that the smectites are *trans* vacant and hence are not suitable for applications which require stability at high temperatures, because of their low dehydroxylation temperatures. These smectites are not suitable for foundry applications. Similar observations may be done in the case of HEU-type zeolites, because the thermal stability of these zeolites depend on the Si:Al ratio and on the type of exchangeable cation present. In conclusion electron microbeam techniques are powerful and may assist not only in understanding of the geological parameters controlling the formation of smectites and zeolites, but they may allow prediction of key physical properties of these minerals as well.

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