PREPARATION OF CLAY SPECIMENS FOR X-RAY DIFFRACTION BY SPRAY DRYING: A PRELIMINARY QUANTITATIVE EVALUATION.

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INTRODUCTION

Using mixtures of commercially available clays, we have evaluated some quantitative aspects of spray drying as a method of preparing specimens for X-ray diffraction (XRD). Clays used were kaolinite (CMS Source Clay KGa-1b), illite (CMS Source Clay IMt-1), and montmorillonite (Ward's Natural Science, Catalog No. 46V0435). Clay fractions were separated and deflocculated by standard methods (Moore and Reynolds 1997) and then processed with a commercial spray dryer (Fig. 1) manufactured at The Macaulay Institute, Aberdeen, Scotland. Spray dried specimens were prepared for the three pure clays and for the three 50:50 binary mixtures. Previous work (Hillier 1999) has shown that spray drying yields reproducible XRD patterns, even when samples are prepared by different workers—notoriously challenging for oriented clay mounts.

Figure 1. Insulation-wrapped spray dryer and senior author using air brush to inject clay slurry. Droplets dry into spherules and are collected on glossy paper under furnace.

METHODS

The spray dryer furnace was operated at 125°C, with 12psi air pressure to the air brush. Appropriate solid-water ratios were judged by experience and depended on smectite content. Figure 2 shows typical spray dried spherules, which range from subspherical to strongly oblate and distorted. Diameters of aggregates range from ~10μm to ~150μm, with some larger irregular aggregates.

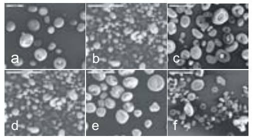

Figure 2. a,b,c. Kaolinite, montmorillonite, and illite, respectively. Note collapse to "red blood cell" shapes, which does not adversely affect random orientation for XRD. d,e,f. Kaolinite-illite, kaolinite-montmorillonite, and montmorillonite-illite 50:50 spray dried mixtures. (Scale bars 200μm, except for e, which is 100μm.)

X-ray diffraction was performed with a Scintag XDS-2000 θ-θ diffractometer with an intrinsic Ge detector, using CuKα radiation and fixed slits. All runs were step scans with 3 sec per 0.02°2θ step. Mounts were 2.5cm in length.

XRF analyses were done with a Bruker/Siemens SRS 303 X-ray fluorescence spectrometer. Samples were prepared as pressed pellets, with 2g of clay per sample.

RESULTS AND DISCUSSION

Some methods of preparation of clay mixtures for X-ray diffraction are susceptible to differential loss of components of the clay fraction. For example, the "Millipore filter transfer method," described by Moore and Reynolds (1997) produces good oriented mounts, but some clay passes through the filter into the filtrate. It cannot be assumed that the same proportions of clays in a mixture remain on the filter as pass through in the filtrate. Figure 3 shows XRD patterns for a 50:50 mixture of kaolinite and illite, and similarly for montmorillonite and kaolinite. For both the k-i and k-m mixtures, it appears that kaolinite is slightly but preferentially enhanced in the filtrate. In addition, the location of the 001 smectite peak is clearly different in the two fractions.

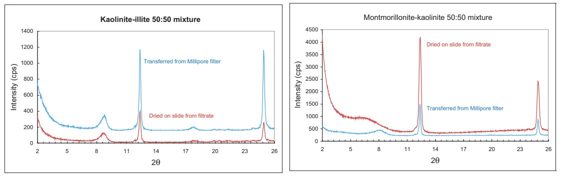

Figure 3. Comparison of oriented diffraction patterns for mixtures using the "Millipore filter transfer method" of preparation. Blue diffractograms from clays collected on filter, red from clays in filtrate.

To test whether spray drying causes differential loss of clay in a mixture, trace and major element XRF analyses were compared in two ways: (1) trace element concentrations in mixtures made by combining spray dried pure clays ("post-mixed" clay mixtures) were plotted against analyses of samples mixed from pure clays before spray-drying ("pre-mixed" clay mixtures) (Fig.4); (2) expected concentrations for 50:50 mixtures, based on analyses of pure clays, were plotted against those obtained experimentally from spray-dried mixtures (Fig. 5).

The slopes of all plots in Figures 4 and 5 are close to unity, suggesting that clay components preserved in the process of spray drying single clay minerals are also preserved in spray drying mixtures. Moreover, tests of the null hypotheses that the slope is 1 and the intercept is 0 show in every case of Figures 4 and 5 that the null hypotheses cannot be rejected at the 0.05 level, with three exceptions (both i-m major element slopes and one k-i trace element slope). Figure 6 shows XRD traces for the three pre- and post-mixed 50:50 mixtures, providing further evidence that the pre- and post-mixed specimens are essentially identical.

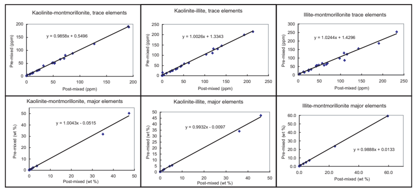

Figure 4. XRF analyses for "pre-mixed" and "post-mixed" clay mixtures (see text for definitions).

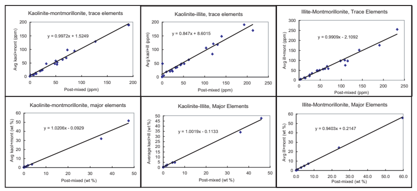

Figure 5. XRF analyses for "post-mixed" 50:50 clay mixtures plotted against the means of corresponding "pure" clay analyses.

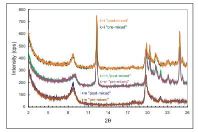

Figure 6. Comparison of XRD patterns for 50:50 mixtures for both pre-mixed and post-mixed samples.

Figure 7 demonstrates that the spray-dried specimens can be successfully treated with ethylene glycol for characterization of the smectite component without seriously damaging the clay aggregates. At 60°C, the time required for complete glycolation of the montmorillonite we used is about 36 hours.

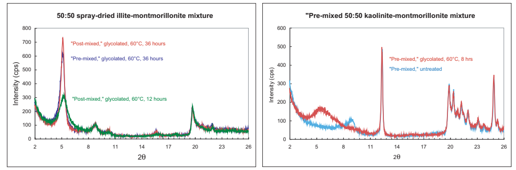

Figure 7. The effect of ethylene glycol treatment on spray dried aggregates.

CONCLUSION

These preliminary results suggest the likelihood that spray drying will produce XRD samples containing the same proportions of clay minerals as does the clay separate from which it is prepared. This constitutes an obvious advantage for quantitative work over some other methods of sample preparation. XRD analyses of our spray-dried specimens demonstrate the following: (1) The production of randomly oriented XRD samples of clay mixtures by spray drying seems largely insensitive to variation in the morphology of spray dried aggregates and to operator variance. (2) Glycolation of spray-dried smectite is easily accomplished, even in pre-mixed samples, by extended exposure to an ethylene glycol atmosphere. For the montmorillonite used in this study, exposure for 36 hours at 60°C yields full glycolation without deterioration of the clay aggregates. (3) XRD patterns of pre-mixed and post-mixed clay mixtures are essentially indistinguishable, adding confidence to the XRF evidence that spray drying would yield quantitatively reliable diffraction data for natural clay mixtures. This has not been found to be true of oriented mounts.

REFERENCES

Hillier, S. (1999) Use of an air brush to spray dry samples for X-ray powder diffraction. Clay Minerals, 34, 127-135.

Moore, D.M., and Reynolds, R.C., Jr. (1997) X-ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford University Press.