Do heated gibbsite, kaolinite and goethite rehydroxylate?

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The effects of burning on soil characteristics vary with the duration and intensity of fire, fuel and soil type, including the amount of soil organic matter present at the time of fire. The effects of fire on plant nutrient cycles have been widely studied for forests as well as for slash and burn agriculture in tropical forests (Ketterings et al, 1999). In contrast, there is relatively little known of the effects of fire on hydrous soil minerals although during fires soil temperatures in excess of 500^{o}C can be reached which will dehydroxylate most minerals (Ketterings et al, 2000). In particular there is no information on the possible rehydroxylation of heated minerals subsequent to fire. A study has been done on the impact of heating on three pure minerals (kaolinite, goethite and gibbsite) and their recovery during wet incubation.

Changes in mineral properties due to dehydroxylation and rehydroxylation were studied by several techniques. Conventional XRD analysis was conducted with a Philips PW3020 diffractometer and synchrotron XRD (SXRD) analysis was performed at the Australian Synchrotron. Fourier transform infrared spectrometry (FTIR) was carried out using a Perkin Elmer Spectrum One spectrometer. The samples were prepared in KBr disks with sample to KBr ratio of 1: 300. Thermogravimetric analysis (TGA) was performed on a STA 6000 instrument (Perkin-Elmer, Norwalk, CT, USA). Transmission electron microscopy analysis used a JEOL 3000 FEG electron microscope equipped with an Oxford Instruments INCA 200 Energy Dispersive Spectrometer (EDS). Specific surface area (SSA) was measured using a Micrometrics Gemini 2375 instrument with a VacPrep 061 using the 5point BET method with N_2 as the absorbate. Major and minor elements were determined by inductively coupled plasma with an optical emission spectroscopy (ICP-OES) instrument (Perkin-Elmer, Norwalk, CT, USA) after perchloric acid digestion.

The infrared spectra for kaolinite, goethite, gibbsite and their dehydroxylated and rehydroxylated derivatives are shown in Figure 1. The intensity of infrared bands due to OH and H_2O is reduced by heating and the position of IR bands is also affected by heating. Increasing heating temperatures generally caused the bands due to lattice vibration modes to shift to lower wave numbers (Freund, 1974). Rehydroxylated heated gibbsite wet incubated at 55 and 95^{o}C for 400 days show OH stretching modes of bayerite at 3658, 3546, 3419 and 3496cm^{-1}. Lee and Condrate Sr (1995) report OH stretching modes for bayerite at 3656, 3546-3550 and 3465-3477cm^{-1} respectively.

Table 1. Infrared absorption spectra for dehydroxylated gibbsite wet incubated at 55/95°C, 0-400days.

Infrared absorption spectra of dehydroxylated gibbsite wet incubated at 55/95°C, 0-400days, wavenumber region 400-4000cm^{-1}						Reference			Assignment
Gibbsite	Gi250	Gi300	Gi350	Gi350-55-400	Gi350-95-400	Gibbsite[1]	Boehmite[1]	Bayerite[2]	
483-517-582-666-731	517-582-666-731	519-583-666-735	611-735	459-514-556-623	514-627	743	755		γ(OH)
800	800	798		758	747	802			
914	914					914			ð(OH)
968	968	967	1078	975	974	958	1080		
1022	1022	1022	1380-2090	1019-1071	1019-1073-2083	1020	1160		
3371-3392	3371-3392	3371-3392	3098	3098	3093-3292	3380	3090	3440	ν(OH)
3435	3435	3447	3435	3419-3479	3419-3496	3428	3297	3465-3477	
3526	3526	3526		3548	3546	3520		3546-3550	
3621	3621	3620		3617-3658	3616-3658	3617		3656	

[1]:Kloprogge et al. 2002, [2]: Lee and Condrate Sr (1995).

Dehydroxylation of kaolinite, goethite and gibbsite caused slight to moderate increases in their specific surface area (SSA). The TGA and DSC results show that all three minerals had lost all or most structural water during heating but had clearly acquired structural water (we define this as water lost at temperatures above 110°C) during the rehydroxylation treatment. XRD indicated that the metakaolinite formed from kaolinite heated at 600°C experienced no change in structure for wet incubation times up to 400 days (Fig. 2). Hematite formed from goethite at 350°C also experienced no change in structure. XRD showed that rehydroxylation of heated gibbsite (initially boehmite and amorphous material) was extensive after 14 days at 95°C additional boehmite (Bo), bayerite (Ba) and gibbsite (Gi) had formed. This trend continued for incubation up to 400 days for heated gibbsite. The process was much slower at 55°C.

These results suggest that dehydroxylated minerals and possibly their rehydroxylated forms are likely to be present in naturally heated soils and may have significant effects on the chemical behavior of the soil.

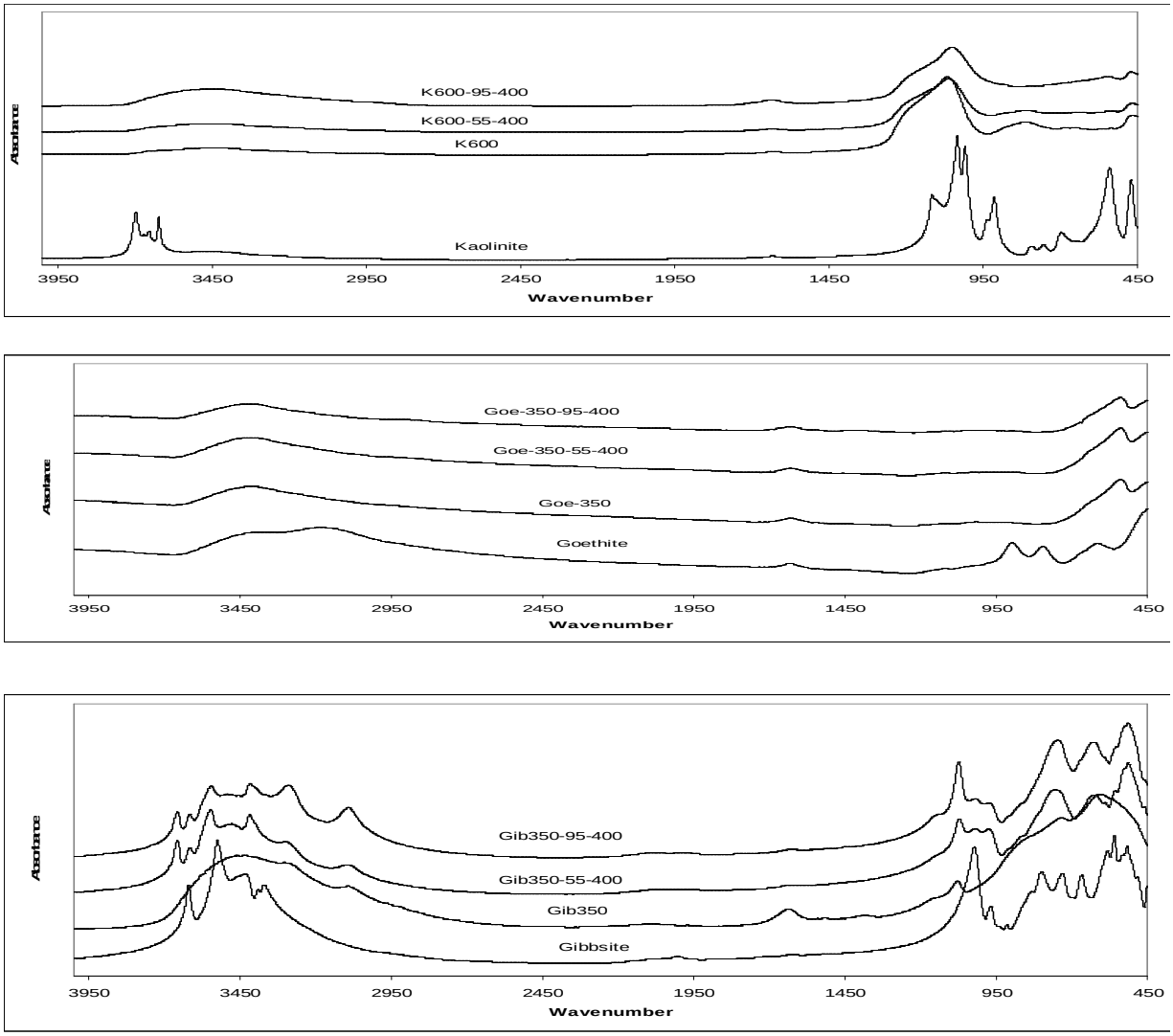

Fig. 1. Infrared spectra of original and dehydroxylated kaolinite (600°C), goethite (350°C) and gibbsite (350°C) and rehydroxylated samples incubated for 400 days at 55 and 95°C.

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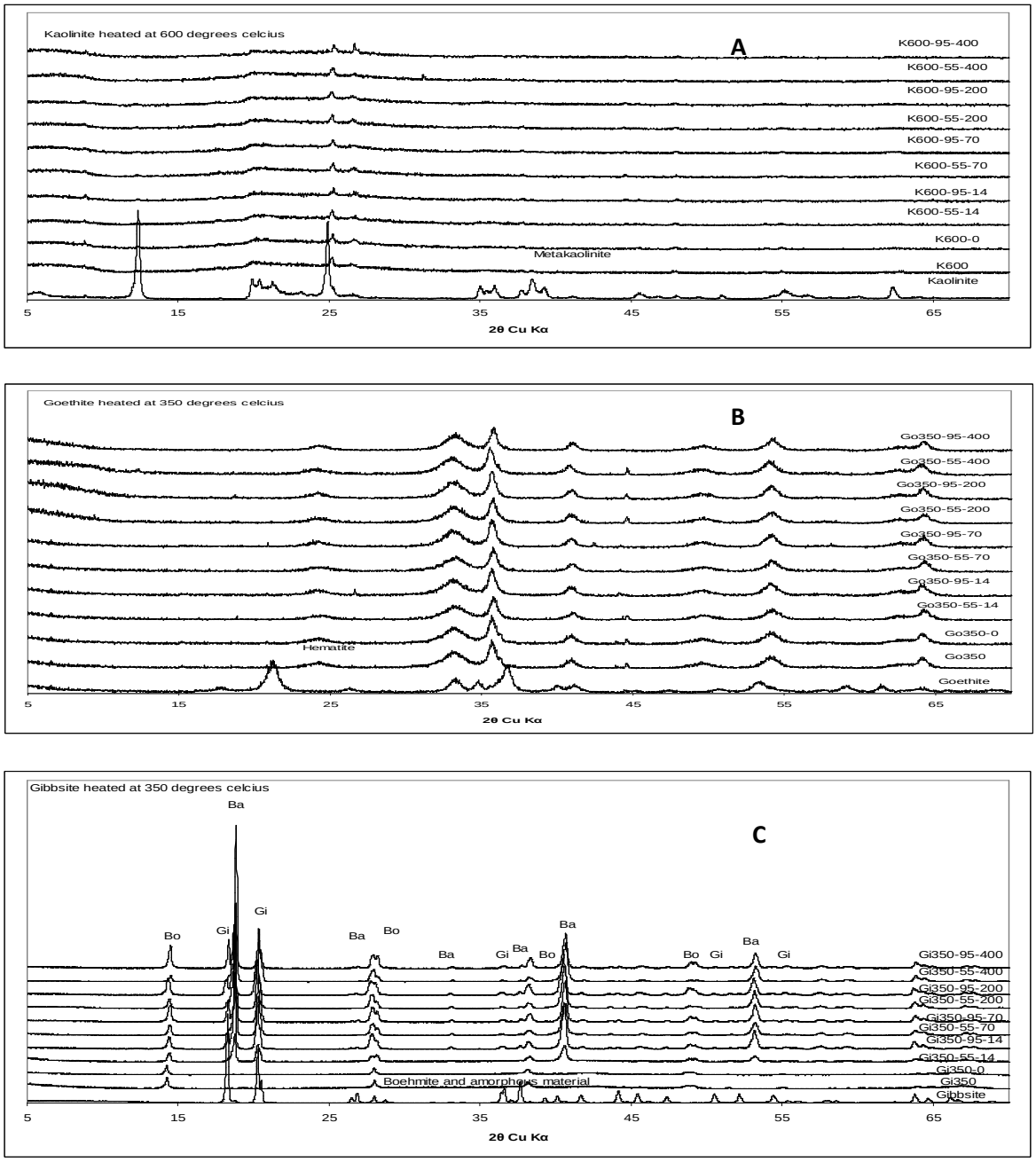

Fig. 2. XRD patterns for heated kaolinite (A), goethite (B) and gibbsite (C), wet incubated at 55/95°C, 0-400days. Kaolinite (d = 4.46 Å), goethite (d = 4.18 Å), hematite (d = 2.69 Å), Gi = gibbsite (d = 4.82 Å), Ba = bayerite (d = 4.71 Å), and Bo = boehmite (d = 6.11 Å), Cu Kα radiation.