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EVALUATION OF IDENTIFICATION METHODS FOR CHRYSOCOLLA — A Cu-SMECTITE-LIKE HYDROUS SILICATE: IMPLICATIONS FOR HEAP-LEACHING EXTRACTION OF COPPER

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Abstract: Chrysocolla has been characterized by XRD, FTIR, DTA-TG, TEM and EPMA in order to clarify properties of this phase and to identify a suitable routine identification method. Chrysocolla is X-ray amorphous, although in some cases slightly sensitive to EG-treatment. IR spectra indicate a trioctahedral layer-silicate structure, resembling in many features that of trioctahedral smectites. HRTEM images do not show a phyllosilicate-like repetitive layering in accordance with XRD results. The SiO_2/CuO ratio is considered responsible for the degree of crystal ordering achieved. SiO_2/CuO ratio near 1 results in an amorphous phase, while SiO_2/CuO near 1.3 generates more smectite-like characteristics. For routine analyses in mining operations, DTA-TG is considered feasible, once basic mineralization types are known at a site.

Key words: Cu-leaching, mineral analysis, Cu-smectite, chrysocolla.

Introduction

Chrysocolla occurs in oxidation zones of porphyry copper deposits and has often been used as exploration guide (Meach 1981). With colour shades from turquoise-blue and emerald-green to blackish green and most frequently developed as colloidal crusts and aggregates, it is a stable member of many mineral collections. Hardness of only 2 to 4 on the Mohs scale makes chrysocolla unsuitable for a widespread application in jewelry or ornamental items (Ďuďa & Rejl 1997). The mineral is translucent to opaque, biaxial (-), with α = 1.575–1.858, β = 1.597, γ = 1.598–1.635 (Anthony et al. 1995). Fine intergrowths with the host rock make optical identification difficult, in particular for frequent associations of chrysocolla with azurite, malachite and atacamite and intergrowths with phyllosilicates or zeolites of the ore host rock. This has been manifested by the need to use alternative methods of characterization, in particular for metallurgical applications (US Patent 1980). Mineralogical reference databases (e.g. JCPDS — International Centre for Diffraction Data) cite chrysocolla as $Cu_{2-x}\ Si_2O_5\ (OH)_3\ .\ H_2O$ (Van Oosterwyck-Gastuche 1970). The original formula, $CuSiO_3\ .\ H_2O$ (Foote & Bradley 1913), is still used in mineral atlases (Ďuďa & Rejl 1997). Newberg (1967) proposed the decomposition of feldspar in the presence of copper-rich solutions as a mechanism for the formation of exotic (i.e. sulphide ore body-distant) chrysocolla ores. According to this author, conditions favouring this reaction are: low copper concentrations, silica concentration below the equilibrium level for amorphous silica, low concentration of interfering anions and a moderate to high pH (superior to 9). The latter point has been experimentally reassessed by Yates et al. (1998), indicating a pH window between 5–9, with optimum conditions at neutrality.

Chrysocolla is a widespread exotic copper ore, with Mina Sur (Chuquicamata) and Dona Ines de Collahuasi as the prime examples in Chile. Research concerning the conditions of chrysocolla formation and its characterization has been generated as collateral information in the synthesis of trioctahedral smectites (Kloprogge et al. 1999 and papers cited therein) as well as by metallurgical studies aiming to predict the behaviour of chrysocolla in flotation or acid leaching processing (Meach 1981 and Lindsay 1994). These process-oriented studies focus in particular on the physico-chemical characteristics of the ore minerals. EXAFS studies (McKeown 1994) have been used to clarify the Cu-O and Cu-Cu environments using copper oxide, dioptase and metal reference materials.

Chrysocolla often impregnates altered host rocks containing smectite, chlorite, and laumonite. The Chile-based authors are frequently faced with the need to unequivocally identify chrysocolla finely dispersed with the above phases and to predict possible causes for elevated acid consumption in leaching processes. The smectite-group minerals have been identified as the main acid consumer from copper solutions in heap leaching extraction processes (Gomer et al. 1991). However, routine methods such as microscopy and XRD do not always allow a satisfactory identification of minor admixtures of either phase. It is therefore considered important to understand single mineral characteristics before attempting to predict the leaching behaviour, for example, of chrysocolla and smectite or zeolite mixtures in a future stage of study.

Therefore, six apparently pure chrysocolla samples have been selected, with the aim of elucidating the texture and composition of the mineral at TEM level and thus to contribute indirectly to the understanding of its behaviour in leaching processes. The parallel use of high resolution observation and analyses as well as more rapid and cheaper methods is aimed at recommending an analytical procedure that will ease characterization on a more routine and larger scale basis.

Methods

X-ray diffraction analyses have been performed using a Rigaku D max X-ray diffractometer with Ni-filtered Cu radiation at the following slit settings: 1° divergence and antiscatter slits, 1.5 mm receiving slit. Also a Philips PW 1710 (Ni-filtered Cu-Kα radiation) diffractometer has been used. Oriented specimens have been recorded in an air-dry state and saturated with ethylene glycol overnight at 70 °C.

The dehydration pattern of chrysocolla has been observed using a differential thermal/gravimetric analyser (Rigaku TAS 100) at heating speeds of 10 °C/min in an air atmosphere with approximately 30 mg of sample compacted in a Pt microcrucible.

Infrared spectra have been obtained on a Nicolet Magna 750 Fourier transform infrared spectrometer equipped with a DTGS detector. For each sample, 128 scans were recorded in the 4000–400 cm^{-1} range. The samples had been prepared as pressed KBr disks (1 mg of sample and 200 mg of KBr). The disks were heated overnight at 150 °C to minimize the amount of residual water in the KBr.

The HRTEM measurements were performed using a JEOL 1200 EXII and a Philips 420 STEM microscope operated at 120 kV. Rock chips and small portions of water-saturated <2 μm fractions in Na-form were coated with agar, embedded in Spurr resin and sectioned by ultramicrotome. Under such conditions, any potential smectite layers intercalated by organic compounds produce interlayer distances of about 1.35 nm (Tessier 1984).

Electron microprobe analyses (EPMA) were carried out on a wavelength dispersive Jeol 8600 probe with a defocused beam (40 μm), 15 kV acceleration voltage and 10^{-8} A probe current.

Nitrogen adsorption at 77K measurements has been obtained on a Gemini 2370 instrument after pre-treating samples (0.153 g) in a nitrogen atmosphere for two hours at 350 °C, as well as on a NAPLO 58301 equipment at 60 °C after degassing under vacuum. Two samples (Chuqui 1 and 3) have been selected for this analysis due to mineral purity and abundance of sample material. Determinations have been carried out on the < 200 Tyler mesh fraction.

Samples

For the present study, a total of six samples have been used. Samples Chuquicamata 1 to 5 (Chuqui 1–5) are from the Mina Sur exotic ore sector of the Chuquicamata porphyry copper deposit. Chrysocolla impregnates gravel and basement rock along a 6 km long and 200 m to 1200 m wide paleochannel (Ruiz & Peebles 1988). Sample Chuqui 1 corresponds to a colloidal dark green chrysocolla-gypsum vein of about 10 cm diameter in the basement rock. Chuqui 2 is a conglomerate cemented with green chrysocolla. Chuqui 3 is a pale blue colloidal chrysocolla sample from a 10 cm thick vein from a core in the basement rock. Chuqui 4 represents a colloidal blue chrysocolla sample from an approximately 1 m thick vein. Chuqui 5 is a mixture of black and light blue chrysocolla, forming veins of 3–5 cm thickness. A green-blue sample (collection specimen) of unspecified origin has been incorporated. All samples represent collection specimens, where chrysocolla has been separated by handpicking for all stages of analyses (see below). The chrysocolla of samples Chuqui 1, 3 and 5 are obvious fillings of void spaces, thus minimizing the admixture of host rock minerals during separation.

Results

XRD analyses

Greenish transparent and bluish parts of the sample, which were visually identified with chrysocolla, were handpicked and X-rayed in both random and oriented specimens (Figs. 1, 2). Samples of random orientation show broad peaks as indicated by the ICCD reference card No. 27-188 of chrysocolla accompanied by minor minerals (except for Chuqui 2) of the host rock and vein phase gypsum (Table 1).

All patterns obtained, except for sample Chuqui 3, were without distinct peaks, displaying only elevated background between 0.59 nm and 0.225 nm. Oriented specimens show poorly resolved peaks in a low 2°θ region. The shape of the poor peaks seems to be slightly sensitive to ethylene glycol saturation (insert of Fig. 2). XRD patterns of Chuqui 3 sample slightly differ from other patterns. Both air-dried and glycolated patterns show much better resolved peaks in the low two theta region and at about 0.44–0.38 nm, 0.30 nm, and 0.256–0.225 nm. This pattern is much more sensitive to glycolation than other samples. The most intensive change after EG saturation has been observed at about 1.7 nm, which may also indicate traces of 1.7 nm smectite peak, and in the 0.44–0.38 nm region. No EG sensitivity for chrysocolla has been reported so far. Prosser et al. (1965) indicate a possible water uptake of 25 % without noticeable lattice expansion.

FTIR analyses

The IR spectra of all chrysocolla samples are similar in the whole spectral range (Fig. 3). Spectral features resemble those of trioctahedral 2:1 layer silicates (Farmer 1974). Xiao & Villemure (1998) and Decarreau et al. (1992) reported similar spectra for synthetic Cu smectites. A sharp band near 3620 cm^{-1} is supposed to correspond to OH stretching vibrations of structural OH group coordinated to three octahedral cations, although a band at 3680 cm^{-1} for trioctahedral smectites is missing (Decarreau et al. 1992). Due to the high content of Cu in the chrysocolla samples, Cu_3OH is the most probable octahedral arrangement. A broad absorption in the 3500–3000 cm^{-1} range is attributed to the OH stretching vibrations of water

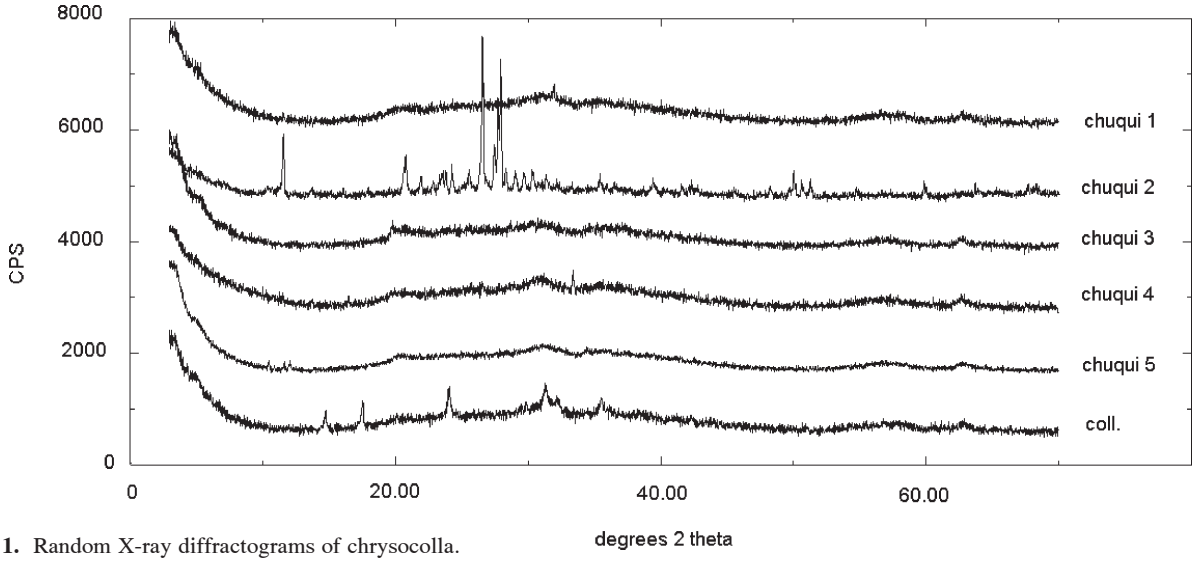

Fig. 1. Random X-ray diffractograms of chrysocolla.

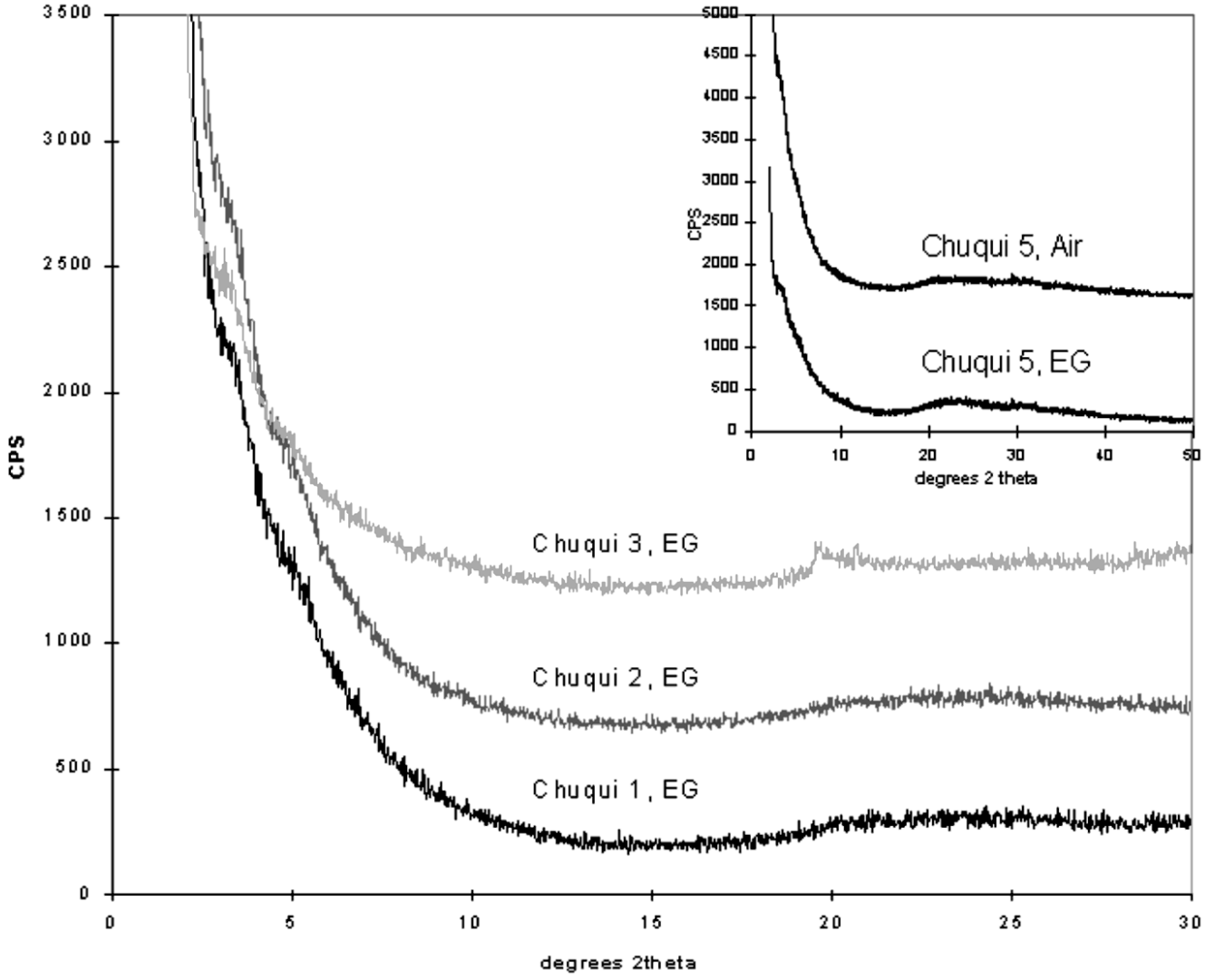

Fig. 2. Oriented diffractograms of EG-saturated samples Chuqui 1–3. EG sensitivity is demonstrated on the inset Chuqui 5 sample.

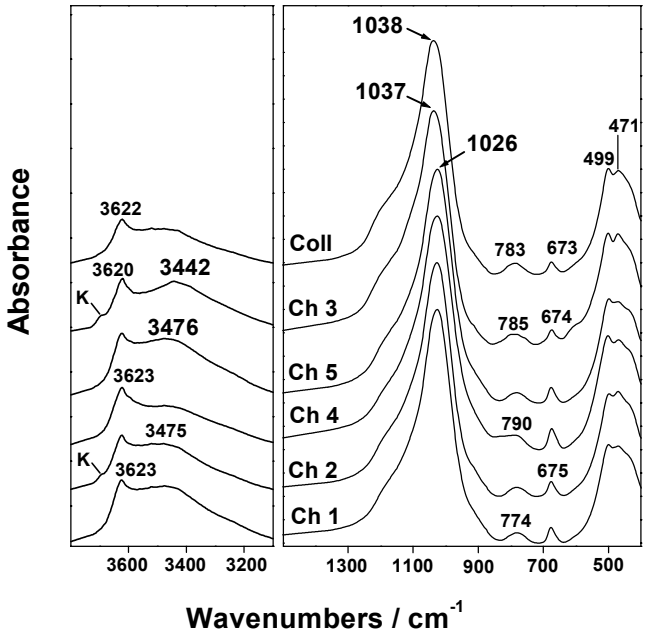

Fig. 3. The FTIR spectra of chrysocolla samples from Chuquicamata (Ch1 to Ch 5) and collection specimen (Coll).

molecules. A maximum of this band occurs near 3475 cm^{-1} for all chrysocollas except Chuqui 3, where a 3442 cm^{-1} position is observed (Fig. 3). Differences in the water band position may indicate a change in the environment of the bound water molecules. A shoulder near 3698 cm^{-1} may indicate traces of kaolinite present as admixture in Chuqui 2 and 3; this trace has not been detected by XRD. The Si-O stretching band observed near 1026 cm^{-1} in the IR spectra of Chuqui 1, 2, 4 and 5 is shifted by about 10 cm^{-1} towards higher frequencies for Chuqui 3 and collection sample. In accordance with Decarreau et al. (1992) a band near 780 cm^{-1} is due to Si-O vibration, while Cu_3OH bending vibration absorbs nearly 677 cm^{-1}. In the region below 600 cm^{-1}, two clearly resolved bands are present. The absorption bands near 500 and 470 cm^{-1} are related to Cu-O-Si and Si-O-Si bending, respectively.

TEM observations

Although all samples have been apparently pure handpicked chrysocolla, differences in hardness have been observed during impregnation with Spurr resin and subsequent cutting of the samples. This may be due to different states of hydration of the samples (see also DTA analyses); colloidal light blue samples (sample 3 and collection specimen) tended to disintegrate easily but required longer periods of impregnation, whereas dark green-black samples did not pose any problem with cutting (samples 1, 5).

A spotty appearance of irregular by contoured aggregates are common features observed in TEM images (Fig. 4). Spots are present from the initial incidence of beam, becoming more focussed and darker during the first minute of observation and remaining stable even under long-term observation (>30 min). Spot diameters for dark green (possibly more hydrated, see DTA data) samples are larger than those for light blue ones. Photographs represent the "definite" state of the spots (Figs. 4 and 5). HRTEM permits the observation of elongated diffuse filaments, similar to fringe images, but with no regular spacing observed between them. The width of the filaments is approximately 1.3 nm (white) and 1.6 nm (dark). They may also occur as individual laths in an otherwise undifferentiated groundmass (Fig. 6). Because of the size of the aggregates and their dispersed nature, it has not been possible to obtain a usable electron diffraction image. When trying to focus diffraction images, diffuse spots are observed frequently to disappear during adjustment of the image, leaving only "amorphous" rings. Similar changes have been observed by Van Oosterwyck-Gastuche (1970) and McKeown (1994).

Ultrathin sections of sample Chuqui 4 show at very low magnification dominant lath-shaped particles (Fig. 7), which display at higher magnification a homogeneous amorphous-like image. The image is very similar to that observed by Šucha et al. (1998) for very early stages of illite syntheses from gel and glass.

DTA-TG analyses

Analyses were carried out at ambiental humidity of 45–50 % (Fig. 8A and B). The pure samples of chrysocolla (Chuqui 1 and 3) show a broad endothermic peak below 200 °C, followed by a continuous endothermic drift between 250 and 650 °C (Fig. 8B). Weight losses up to 200 °C have been 17 % for dark green Chuqui 1 and only 13 % for pale blue Chuqui 3 (Fig. 8A). A marked exothermic peak occurs at 695–705 °C. At 1027 °C an endothermic peak is observed. Fusion starts above 1100 °C.

Compared to DTA spectra of many smectite group minerals, chrysocolla lacks the bifurcated low temperature peak of most smectite samples (Patterson & Swaffield 1987) attributed to the loss of externally adsorbed and interlayer-bound water. No endothermic peaks have been observed at 700 °C, nor the shallow endothermic/exothermic signal between 800 and 900 °C (Paterson & Swaffield 1987), except for a slight endothermic indentation at 550 °C for Chuqui 3.

To observe the formation of potential new phases, samples have been heated for one hour to 350 and subsequently to 850 °C with each step checked by XRD analyses. No phase change has been found at 350 °C. Sample Chuqui 1 exhibits a faint 1nm peak on the diffractogram, which may possibly be attributed to a smectite collapse, although no such phase has been detected by XRD. Tenorite formed at 700 °C, followed by oxidation to cuprite at 1027 °C.

DTA/TG characteristics of chrysocolla reported by Meach (1981) are similar to the samples analysed in this study. However, for the present samples, the initial endothermic peak is observed at about 100 °C, that is 50° lower than the description by Meach. It is possible that this difference is due to using a high temperature DTA/TG equipment, which does not yield best results below 100 °C. The water uptake of up to 25 % reported by Prosser et al. (1965) could also contribute to this shift.

Chuqui 2 is a polymineralic sample with two dehydration peaks at 80 and 130 °C, respectively (Fig. 8). It is doubted that this endotherm doublet is attributable only to smectite.

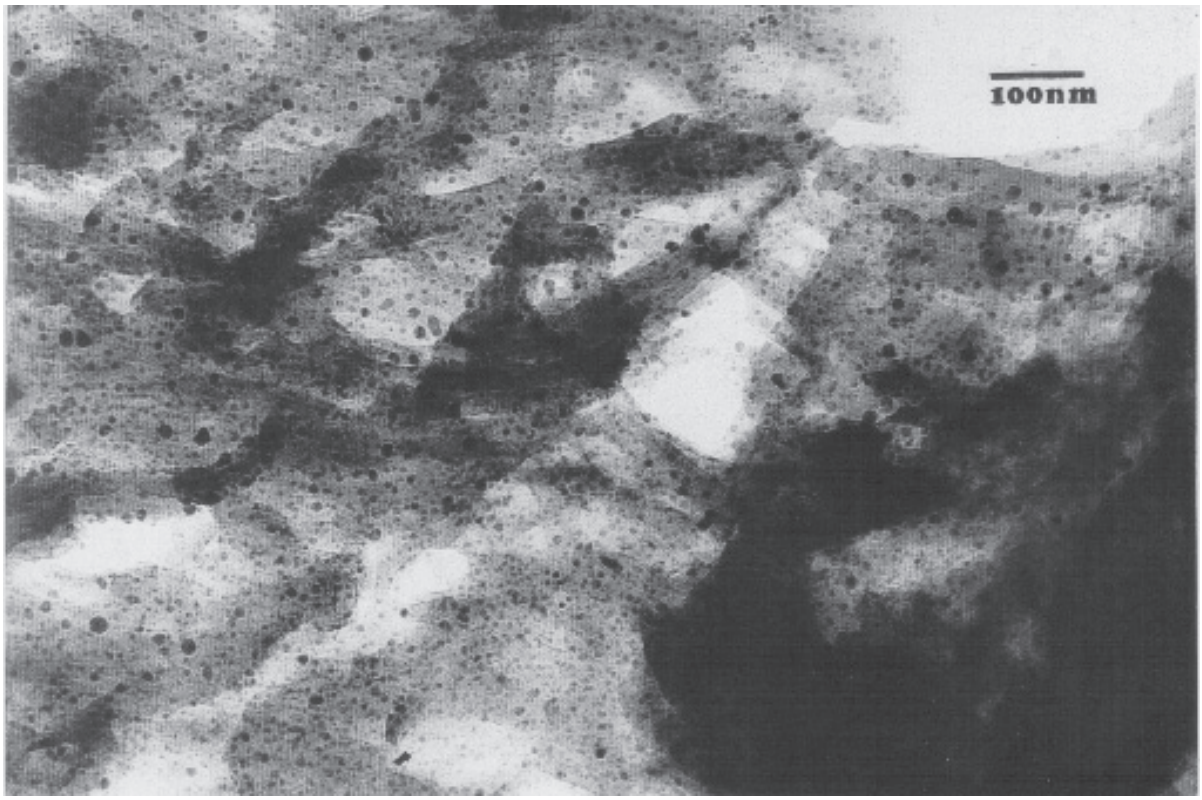

Fig. 4. Spotty appearance of chrysocolla surfaces under electron beam (TEM).

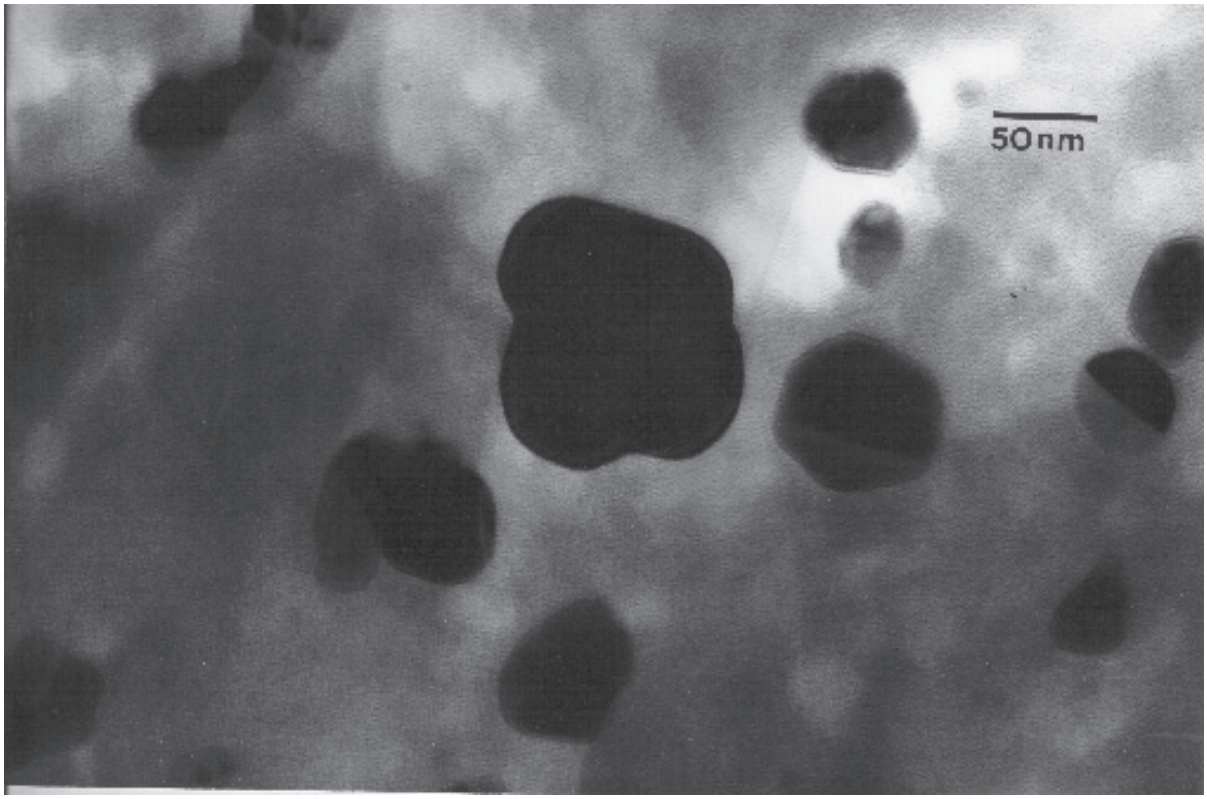

Fig. 5. Large spots, which initially change their morphology under the electron beam.

Fig. 6. Short-range, non-repetitive fibres, most noticeable grey sector along the lower image margin.

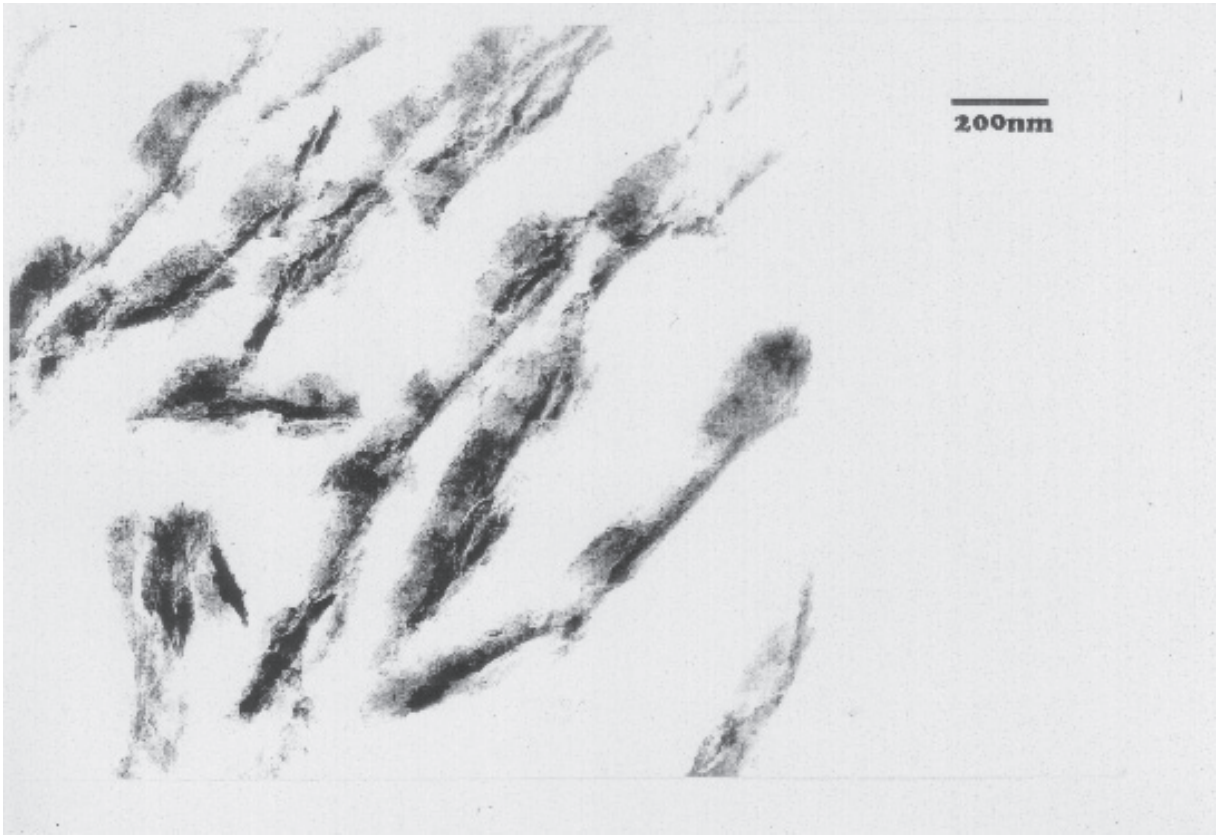

Fig. 7. General lath-shaped aggregates at low TEM magnification.

For the second peak, the loss of adsorbed water from feldspar surfaces is suspected. For the collection sample with malachite, the second endotherm corresponds to the loss of CO_2 from the copper carbonate. The shift of tenorite formation to a temperature of about 730 °C could be due to the presence of the CO_2 generated in a static atmosphere (Bish & Duffy 1990). Sample Chuqui 5 shows a faint indentation of the principal peak of water desorption at about 130 °C. This could be due to the presence of a 1.4 nm, 0.7 nm or smectite-type phyllosilicate not identifiable by XRD due to superposition with chrysocolla, although oriented XRD mounts do not show clear smectite peaks. Chrysocolla is characterized by a broad dehydration endotherm, lack of dehydroxylation endotherms typical of smectite and a conversion to tenorite. The latter two aspects mark a clear difference to discrete smectite. Higher temperatures of tenorite formation in Chuqui 5 could correspond to the presence of Mn in the sample (Table 2, black chrysocolla).

Specific surface area

Nitrogen adsorption indicated similar specific surface areas for samples 1 and 3 (purest and abundant samples available, Table 1), 465 and 457 m^2/g respectively for <200 mesh Tyler samples. However, it should be taken into consideration that the samples have been heated to 350 °C, implying a measurement post-dehydration. BET values drop to 276 and 229 m^2/g respectively, if this analysis is carried out post degasification in vacuum at only 60 °C. These values agree with specific surface areas of 200 m^2/g calculated by Wright & Prosser (1965). Prosser et al. (1965) further described chrysocolla to have high porosity, permitting a water uptake up to 25 % without noticable expansion of the lattice. However, leaching or sintering drastically reduces specific surface areas to < 50 m^2/g (Pohlman & Olsen 1976; Raghaven & Fuerstenau 1977).

Chemical analyses

Results are presented in Table 2. Due to the reduced amount of sample available, electron microprobe analyses have been chosen as the most adequate method to overcome this restriction. Despite careful handpicking, traces of quartz, feldspar, gypsum and possibly kaolinite have been detected in three samples (Table 1). These are reflected as minor contents of Al_2O_3, Na_2O, SO_3 and CaO (Table 1, samples 1, 4, 5, collection sample). However, only sample Chuqui 2 proved to be a very fine impregnation of feldspar by chrysocolla, making EPMA single phase analysis impossible.

With respect to total and soluble copper analyses, it is interesting to note that two very pure chrysocolla samples (Chuqui 1 — dark green, Chuqui 3 — light blue) correspond to the highest and lowest Cu solubilities respectively (Table 2).

Discussion and conclusions

Research on chrysocolla has developed along three lines: (1) metallurgy with a focus on methods to characterize bulk ore for flotation and leaching for process design and quality control, (2) synthesis of transition metal smectites and (3) crystallographic work at TEM scale. Unfortunately, cooperation between these closely related subjects has been restricted. The present discussion will first focus on the texture and structure of the mineral and then routine methods best suited for mineral identification will be examined.

Texture and structure

With respect to crystallographic characterization Van Oosterwyck-Gastuche (1970) has pointed out the presence of fibrous phases on low magnification TEM images. That author proposed a palygorskite-like structure and rejected smectite-type structures as well as a completely amorphous character. She proposes for the c-dimension a distorted kaolinite lattice; the distortion being due to the incorporation of Cu^{2+} in Al^{3+} sites thus resulting in a chain structure perpendicular to the c-axis. The present TEM observations confirm the presence of fibrous aggregates without regular stacking (Fig. 6), appearing as individual strings in an apparently amorphous groundmass. XRD traces show the lack of long range ordering, whereas FTIR suggests the presence of trioctahedral layer-silicate phases. Fibres have thicknesses of approximately 1.3–1.5 nm, but no HRTEM stacks or packages could be observed. EXAFS studies (McKeown 1994) have explored the Cu-Cu and Cu-O environment of chrysocolla, suggesting possibly linked CuO_4 units similar to tenorite and dioptase; however Cu-Si correlations remain unknown.

The presence of poorly crystallized material is corroborated by (1) the difficulty of focus for diffraction images and (2)

Table 1: Mineralogy of chrysocolla samples.

Chuqui 1	Chrysocolla***	Quartz*		
Chuqui 2	Chrysocolla**	Plagioclase***	Quartz**	Gypsum**, Smectite or 1.4 o 7 nm Phyllosilicate?
Chuqui 3	Chrysocolla***			
Chuqui 4	Chrysocolla***	Gypsum*		
Chuqui 5	Chrysocolla***	Gypsum*	Quartz*	1.4 or 0.7 nm Phyllosilicate?
Collection Sample	Chrysocolla**	Malachite**	Quartz*	

*** major phase, **phase present, *phase at trace level, ? phase difficult to identify due to very low peak intensities and/or superposition of peaks

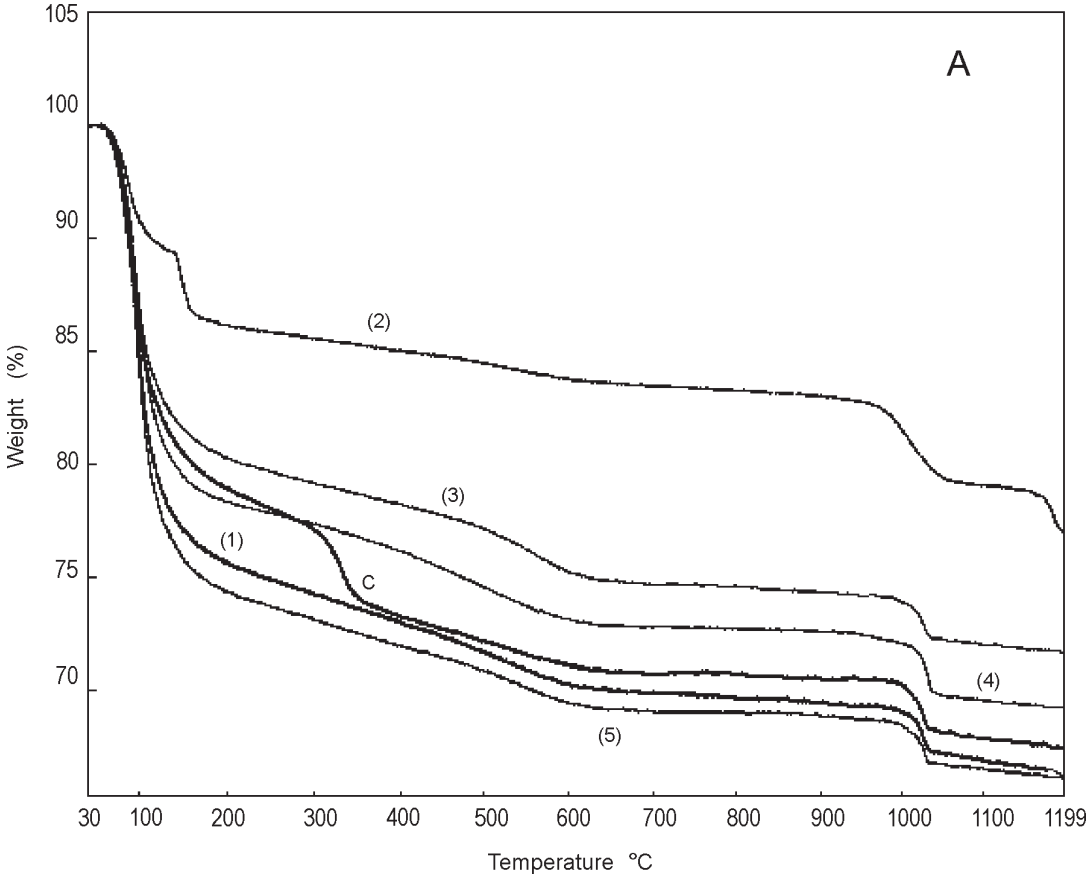

Fig. 8A. TG curves of chrysocolla separates.

blister like TEM images (Figs. 4, 5) adjusting under the electron beam.

Electron microprobe defocussed spot analyses indicate the presence of 1–1.5 % $MgO+CaO+K_2O+Na_2O$ (Table 2). These oxides are attributed to "contaminating" matrix minerals such a feldspar and traces of chlorite, although the latter has not been clearly identified in the present samples; its presence is known from the study of the host rocks impregnated by chrysocolla. The respective Al_2O_3 contents for monomineralic samples Chuqui 1 and 3 are 3.7 % and 3.1 %. Ratios of SiO_2/CuO are 1.19 and 1.39. Results are in good agreement with wet chemical analyses compiled by Van Oosterwyck-Gastuche (1970), although differences in the analytical method (AAS) and the date of the cited analyses have to be taken into consideration. Given the obvious partially amorphous character of chrysocolla, it is felt that at present no compositional formula based on crystalline smectite can be given. The uncertainty of proposing a definite mineral formula has also been observed for natural Cu incorporating smectites from Peru (Plötze & Wolf 1999). The specification of Cu content in the crystalline phase has only been possible for synthetic smectites of transition elements. Conditions of synthesis permitting the incorporation of Cu in the octahedral sheet require Cu/(Cu + Mg) ratios <0.5 (Kloprogge et al. 1999), otherwise formation of chrysocolla occurs (Güven 1988). The element contents determined for the present study (Table 2) do not indicate conditions favourable for the formation of smectite phases. Xiao & Villemure (1998) report synthesis experiments in which a non-expanding chrysocolla phase results in the SiO_2/CuO ratio close to 1. At ratios around 1.3, an expandable phase forms. Chuqui 1, 4, 5 and the collection sample have ratios close to 1, Chuqui 3 approaches a ratio of 1.3 (Table 2). The presence of minor quartz in the samples may affect the ratio. For most samples no clear shift upon EG treatment has been observed, although they seem to be sensitive to this treatment. The only sample clearly sensitive to EG treatment is Chuqui 3, although devoid of a discrete peak, which would support the above mentioned observation by Xiao & Villemure (1998). The collection sample should be considered with caution due to the presence of malachite, although this mineral can be texturally distinguished from chrysocolla under EPMA.

The large difference in the total and soluble copper analyses between Chuqui 1 and 3 may point to the bonding of Cu in a possibly better developed phyllosilicate structure, which is more resistant against an acid attack. However, the increased hydration of Chuqui 1 could have promoted leaching, although further samples are needed to afirm or reject this suspicion. Furthermore, chrysocolla is a high surface area mineral. Values of >400 m^2/g (heated 350 °C) or 250 m^2/g (60 °C) are comparable with smectites, thus making acid attack easy. FTIR (Si-O stretching band and OH-stretching vibration) and XRD data show clear differences between Chuqui 3 and other samples. FTIR seems to be more sensitive to the structuring of the starting medium for crystallization (natural or synthetic),

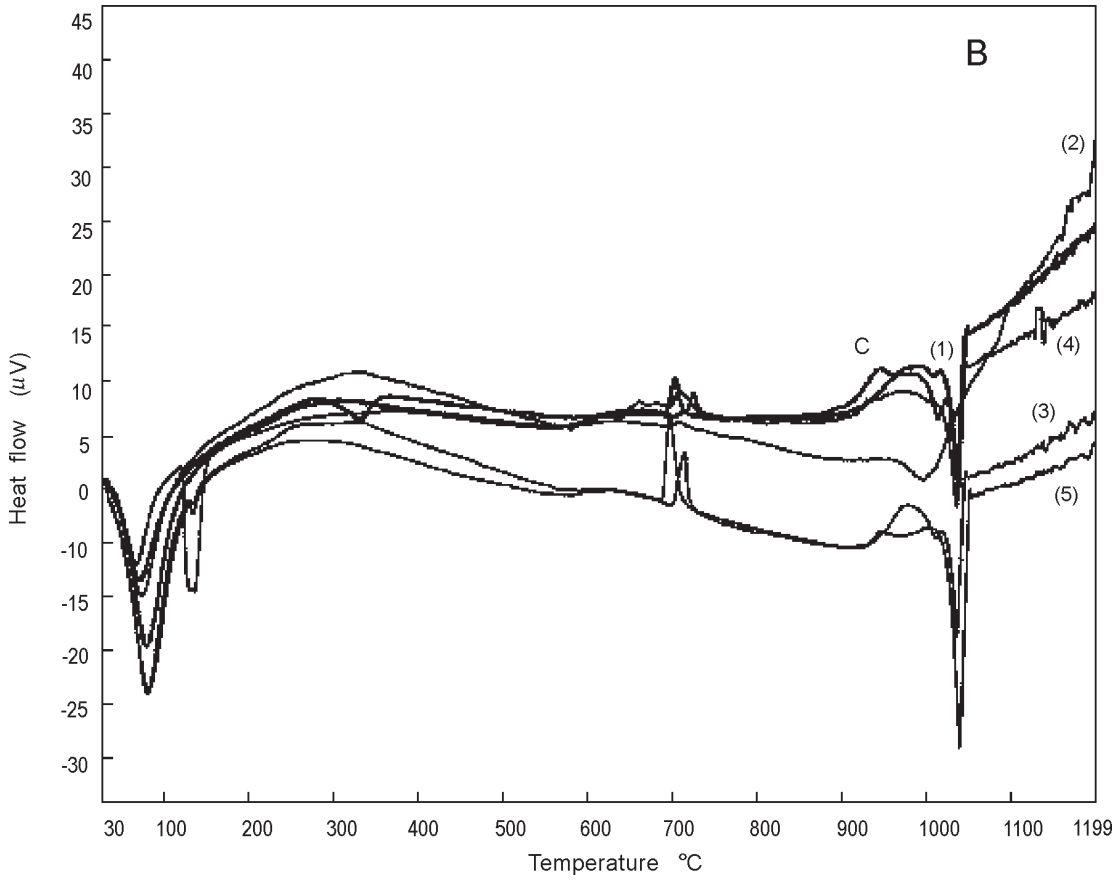

Fig. 8B. DTA curves of chrysocolla separates.

Table 2: Chemical analyses of chrysocolla samples by electron microprobe (EPMA) and atomic absorption spectroscopy (AAS). Electron microprobe analyses represent averages of 4-5 determinations. A complete set of analyses is available from the authors. Sample Chuqui 2 represents a mixture of chrysocolla and feldspar (Table 1), no single phase analyses could be obtained.

Sample	Method	Chuqui 1	Chuqui 2	Chuqui 3	Chuqui 4	Chuqui 5 blue-green	Chuqui 5 black	Collection Sample
Total Cu % (CuO %)	AAS	27.4 (34.3)	10.6 (13.25)	26.1 (38.75)	31.0 (32.25)	25.8 (32.25)		31.95 (39.9)
Soluble Cu % (CuO %)*	AAS	27.0	9.5	18.1	28.9	24.8		29.38
SiO_2 %	EPMA	51.28		55.45	49.84	52.47	45.86	50.00
TiO_2 %	EPMA	0.02		0.02	0.01	0.00	0.00	0.02
Al_2O_3 %	EPMA	3.68		3.06	0.84	4.00	3.99	4.21
FeO %	EPMA	0.02		0.01	0.00	0.16	0.03	0.00
MnO %	EPMA	0.02		0.02	0.07	0.01	6.94	0.01
MgO %	EPMA	0.44		0.28	0.11	0.39	0.39	0.49
CaO %	EPMA	1.05		0.59	0.24	0.94	0.86	1.44
Na_2O %	EPMA	0.24		0.26	0.01	0.39	0.57	0.03
K_2O %	EPMA	0.05		0.11	0.00	0.12	0.10	0.02
CuO %	EPMA	43.07		39.87	48.72	41.07	41.24	43.71
SO_3 %	EPMA	0.07		0.32	0.17	0.22	0.06	0.01
SiO_2/CuO		1.39		1.02	1.28	1.11	0.95**	1.14

* Leaching by 1 molar citric acid for 1.5 hours. ** SiO_2/ (CuO + MnO)

as it was observed also for synthetic ammonium illite (Šucha et al. 1998) where XRD has shown no reflection, but FTIR clearly indicated evolution of the structure towards dioctahedral ammonium mica. As each layer of a layer silicate absorbs infrared radiation almost independently of its neighbours, the recognition of their structures by their absorption pattern does not depend on the presence of the packets of layers required to give a distinct X-ray diffraction (Farmer 1974). Chrysocolla samples, except Chuqui 3, show no clear XRD peaks, but FTIR indicate several trioctahedral layer silicate features, most

probably without any periodicity. Chuqui 3 seems to be a more evolved stage towards a phyllosilicate with a periodical structure. The differences in perfection of the sample structure could ultimately be an explanation of the differences in the Cu-leaching experiments, but further verification with more samples is required. Conclusions explaining the <0.5 substitution of Mg by Cu in synthesis experiments of smectites may also support the above ideas. Güven (1988) considers important the similarity of the Si/metal ratio of the initial precipitate to that of the resulting smectite (a feature also observed in zeolite synthesis, Sanhueza et al. 1999). Under natural conditions, environments favourable for formation of chrysocolla or smectite-like phases are likely to fluctuate on a small scale under natural conditions. The dominance of Cu over other metals (see qualitative EDAX and EPMA analyses) also may prevent the formation of smectite as observed by Mosser et al. (1990), who found chrysocolla at Cu/Mg ratios >0.5. These authors explain this phenomenon (using EXAFS) by a string distortion of Cu octahedra due to the Jahn-Teller effect.

Methods of routine analysis

In determining differences among the chrysocolla-phyllosilicate materials, both DTA-TG and FTIR appear as powerful tools, which could be applied also for technological purposes. The only concern is that samples have to be picked very carefully in order to avoid any admixture which can affect the final result of detailed XRD and FTIR measurement. XRD is potentially useful, provided samples are of high purity and careful EG treatment is carried out.

For routine analyses of chrysocolla ores, availability of the method(s), easy use and time requirements have to be considered. For purposes of production, time available for analyses may be only several hours. Unequivocal identification of chrysocolla by X-ray diffraction is only possible when samples have high contents of the mineral and EG treatment is carried out. The simultaneous presence of chrysocolla and discrete smectite is problematic with respect to identification of the expanding phase and its potentially elevated acid consumption during leaching. IR spectra show chrysocolla with several features of a trioctahedral smectite-like phase. Differentiation of the mineral from a separate smectite phase will require considerable interpretation skills, not easily found in quality control laboratories on site or in mining contract services. For the samples analysed, a difference has been observed in the DTA-TG curves for chrysocolla and chrysocolla-smectite samples. The routine analyses of total and soluble copper in bulk samples do not help the identification of chrysocolla and especially chrysocolla-smectite mixtures, unless performed first on carefully picked monomineralic specimens. On the basis of the present study, despite the reduced data set, the authors propose identification of chrysocolla-containing mineralization types by combining X-ray diffraction and infrared spectroscopy at the stage of mineralization type study. For a later fast identification of chrysocolla and chrysocolla–smectite mixtures in a production process, where mineralization types and general rock mineralogy are already known, thermal analysis represents a potential alternative, due to its ease of sample preparation and interpretation (once calibrated) and the comparative low cost of a thermobalance.

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