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Chloritisation of hornblende and biotite: a HRTEM study

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ABSTRACT:

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The coarse textures produced by hydration of hornblende and biotite during retrograde metamorphism of the rocks of the Kłodzko-Złoty Stok area were identified easily by both optical microscopy and scanning electron microscopy (SEM). However, the micro-textures that are a few unit cell in dimensions were identified through high resolution transmission electron microscopy (HRTEM) only. For the alteration of biotite to chlorite the replacement of potassium in the interlayer by a brucite-like layer and the subsequent increase in volume was observed. There were, however, some missing brucite-like layers within the chlorite units. Moreover, both topotactic and low angle replacement of biotite to chlorite were identified. For the direct hydration of hornblende to chlorite, HRTEM and selected area electron diffraction pattern (SAED) showed that the c^* and a^* of chlorite were parallel to the b^* and a^* of hornblende, respectively. Nevertheless, other orientation relationships were also observed by optical microscopy.

INTRODUCTION

In biopyriboles (biotite + pyroxene + amphibole) structural perturbations such as chain-width defects, stacking faults, mixed layering and other intergrowths are common. Together with grain boundaries, these defects are important in understanding metamorphic textures in rocks. Moreover, these micro-defects serve as important channels for the transport of fluids during metamorphism, determine the mechanisms of deformation of the rocks, and control the kinetics of crystal growth during metamorphic reactions. These structural peculiarities are discussed in some detail by Veblen (1985).

Powder X-ray diffraction, compositional imaging by scanning electron microscopy (SEM), and microprobe analysis are useful for characterising the metamorphic textures in minerals. For minerals with micro-defects, however, they provide an averaged information. For textures that are not accessible by standard petrologic techniques, transmission electron microscopy (TEM) provides an attractive choice. The two techniques commonly used are conventional TEM (CTEM) and high resolution (HRTEM). The former is used, for example, to study linear defects and the latter to study planar defects. Nevertheless, since CTEM does not provide details on atomic arrangements in linear defects, even such defects as stacking faults, Wadley defects, twinnings, and anti-phase boundaries have also been studied by HRTEM.

The selected area electron diffraction pattern (SAED) obtained in TEM provides complementary information to electron imaging. For example, SAED can be used to identify phases and to determine their orientations. It is, therefore, possible to determine the exsolution mechanism of lamellae by combining HRTEM and SAED. Moreover, additional information such as polytypism and ordering can be identified using SAED.

Just as in conventional microprobe analysis, TEM can be provided with both energy dispersive spectrometer (EDS) and electron energy-loss spectrometer (EELS) for chemical analysis. EELS can also be used to determine the dominant oxidation state for multivalent elements like Fe and Ti.

It is thus possible to combine imaging, diffraction, and chemical analysis in TEM over a region 0.5 nm in diameter and less than 0.1 nm in thickness. These three properties make TEM a powerfull technique in mineralogy and petrology. A usefull collection on the application of the different techniques available in TEM to petrologic problems is provided by WHITE (1985).

The purpose of this study is to show how HRTEM and SAED data can be used in studying metamorphic textures and processes. We have therefore chosen the alteration of hornblende to chlorite and the alteration of biotite to chlorite as examples. The rocks come from the Kłodzko-Złoty Stok area in SW Poland. The geology and petrology of these rocks are well characterised (BAGIŃSKI 1989; BAGIŃSKI & FERROW 1993; WIERZCHOŁOWSKI 1976; WOJCIECHOWSKA 1975). Furthermore, a detailed study of the textures, compositions, and reaction mechanisms using conventional techniques and experimental HRTEM is in progress.

EXPERIMENTAL TECHNIQUES AND IMAGE INTERPRETATION

Transmission electron microscopy (TEM) was performed using a Philips 420T microscope operated at 120 keV. A Super Twin (ST) objective lens with spherical aberration coefficient $C_s = 1.2$ mm, chromatic aberration $C_c = 1.2$ mm, giving a point resolution of 0.3 nm was used. The specimens used for TEM were milled to perforation from petrographic thin sections using a Gatan dual ion mill. The milled specimens were lightly carbon coated to remove specimen charging.

However, it is very important to point out that HRTEM, due to dynamic scattering effects and due to the limitation of the optical system, the electron distribution at the image plane may not correspond to the structure of the specimen. Thus image interpretation in HRTEM is not straightforward. In fact, the dark regions in HRTEM images correspond to the regions of high electron density only for very thin specimens and for images taken under the Scherzer focus. It is, therefore, essential to compare the experimental HRTEM images with the images that have been simulated for the known structures using the computer.

Image simulation was done by use of MacTempas, a commercially available program for simulating HRTEM images and diffraction patterns, adopted for Macintosh (FERROW 1993). The program is based on the multi-slice method of evaluating scattered amplitudes as worked out by COWLEY & MOODIE (1957). The multi-slice approach has been described in details on many occasions before (*e.g.* SELF 1992) and will not be discussed here.

Text-fig. 1 is an example of a simulated HRTEM image of a monoclinic chlorite projected down the [100] axis, calculated on the basis of the

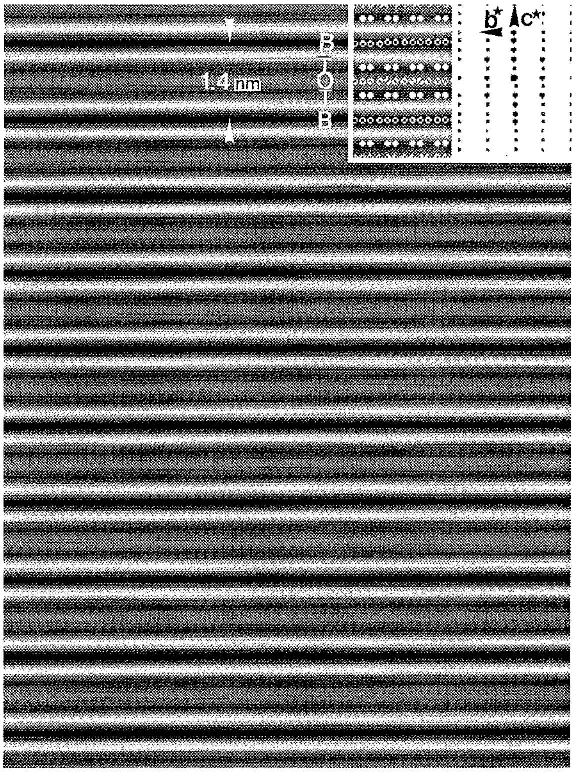

Fig. 1. Calculated HRTEM image and the corresponding SAED of chlorite projected down [100]; octahedral cations (open circles) and tetrahedral cations (closed circles) are overlaid; light elements, oxygen and hydrogen, are not included; brucite-like (B) and the talc-like (TOT) layers are marked

neutron diffraction data of Joswig & *al.* (1989). The microscope parameters of the Philips 420T were used for the defocus and thickness values of -50 nm and 5 nm, respectively. For the parameters chosen, two dark regions can be recognised. The dark but narrow regions correspond to the brucite-like layers (B); and the wide but less intense regions correspond to the talc-like layers (TOT). The position of the octahedral (open circles) and tetrahedral cations (full circles) are overlaid on the image. The calculated SAED, and the dimension of the c-parameter 1.4 nm of which corresponds to the width of the brucite-like plus the width of the talc-like layers, are also indicated.

DISCUSSION OF THE EXPERIMENTAL RESULTS

The retrograde hydration of hornblende to chlorite usually takes place in steps, resulting first in the alteration of hornblende to biotite, followed by the alteration of biotite to chlorite (Text-fig. 2). The example, obtained by backscattered scanning electron microscopy, comes from the Kłodzko-Złoty Stok rocks. In this study, the hydration of hornblende to biotite will not be discussed. Neverthless, the characteristic texture resulting from the hydration of biotite to chlorite is the pervasive intergrowth of chlorite in biotite. The degree of chloritisation is not uniform. Some biotite grains are more chloritised than others. Another common textural feature of the breakdown of biotite to chlorite is the presence of ilmenite along the basal planes of chlorite and along the grain boundaries as shown by white arrows in Text-fig. 2. This indicates that Ti and Fe released by the breakdown of biotite are not transported far from the reaction sites.

Direct alteration of hornblende to chlorite is also common in the rocks studied (Text-fig. 3). The optical micrograph, taken with one nicol, shows a hornblende crystal (hbl) that is partly replaced by small chlorite flakes (chl). Calcium released by the breakdown of hornblende entered epidote (epi) developed along the basal planes of chlorite. For example, in the Text-fig. 3, the c axis of hornblende, indicated by the slightly disoriented cleavage planes, is nearly parallel to the c axis of chlorite. However, we have also observed examples where the b axis of hornblende was apparently parallel to the c axis of chlorite.

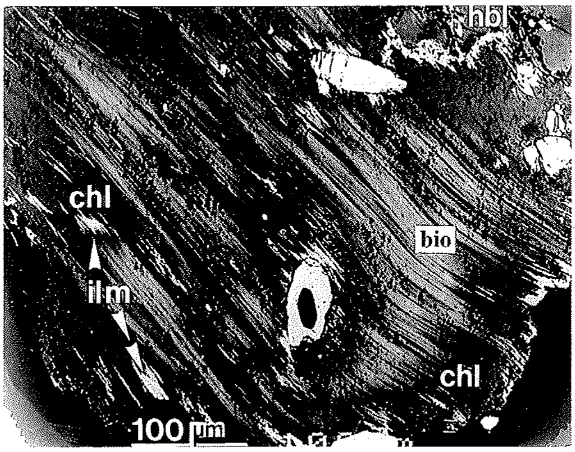

Fig. 2. Backscattered SEM image of partially chloritised biotite; Ti and Fe released by the breakdown of biotite were fixed as ilmenite along the layering and along the grain boundaries; biotite grain comes from the hydration of hornblende

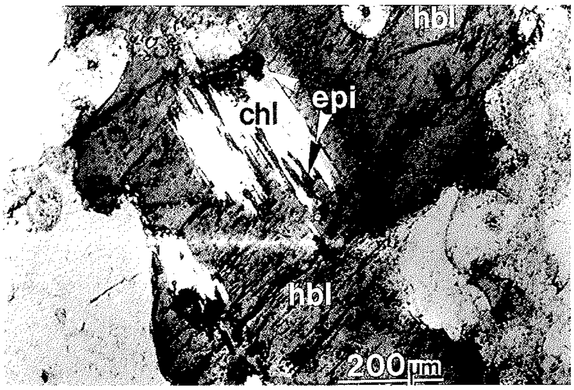

Fig. 3. Optical micrograph taken with one nicol; an example of the direct alteration of hornblende to chlorite; Ca released by the reaction is accommodated in epidote; texture produced is similar to that shown by ilmenite and chlorite in Text-fig. 2

The alteration of biotite to chlorite has been studied by TEM extensively (Bagiński & Ferrow 1992; Eggleton & Banfield 1985; Ferrow & *al.* 1990; Ferrow & Ripa 1991; Maresch & *al.* 1985; Olives Banos & Amouric, 1984; Olives Banos & *al.* 1983; Veblen & Ferry, 1983). According to Veblen & Ferry (1983), there are two different mechanisms for the hydration of biotite to chlorite. In the first reaction mechanism, one biotite molecule is altered to one chlorite molecule by the brucitisation of the interlayer. In the second reaction mechanism, however, two biotite are altered to one chlorite by the brucitisation of the talc-like layer. Both the fugacities and compositions of the fluids involved in the two reaction mechanisms are different. For example, starting with flogopite, $KMg_3[AlSi_3O_{10}](OH)_2$, hydration by the first reaction mechanism can be written as:

$$KMg_3[AlSi_3O_{10}](OH)_2 + 3H_2O + 1.5O_2 + 2Mg^{2+}$$
$$+ Al^{3+}\ [Mg_2Al]\ (OH)_6Mg_3[AlSi_3O_{10}](OH)_2 + K^+$$

while hydration by the second reaction mechanism can be expressed by the following mode:

$$2KMg_3[AlSi_3O_{10}](OH)_2 + 5H_2O + 0.5O_2$$
$$[Mg_2Al]\ (OH)_6Mg_3[AlSi_3O_{10}](OH)_2 + 2K^+ + Mg^{2+}$$
$$+ 3H_2SiO_4$$

The first reaction results in 40% increase in volume, while the second one results in 30% decrease in volume. Moreover, while the first reaction is initiated by fluids enriched in Mg^{2+} and Al^{3+} , the second reaction releases Mg^{2+} and Si^{4+} to the fluid. However, FERROW & RIPA (1991) and YAU & *al.* (1984) reported alteration of biotite to chlorite by combination of the two reaction mechanisms in such a ratio whereby the volume change small.

Some of the textures produced by hydration of biotite to chlorite are shown in Text-fig. 4. This HRTEM micrograph shows a topotactic alteration of biotite to chlorite. The talc-like and brucite-like layers in chlorite, denoted T and B in the Text-fig. 4, are distinctly imaged. Furthermore, the missing brucite-like layers, indicated by white arrows, are also shown. These regions would give a relatively higher Si content compared to chlorite that are free from such defects. A good example of the first reaction mechanism as in VEBLEN & FERRY (1983), the brucitisation of the interlayer, is shown in the Text-fig. 4. A schematic diagram of the reaction mechanism is also included. The increase in volume accompanying the insertion of the brucite-like layer into the interlayer is quite evident. The diffraction pattern shows that the image is projected down the [010] axis. Moreover, the streaking indicates the presence of defects and the slight misalignment of the chlorite crystals.

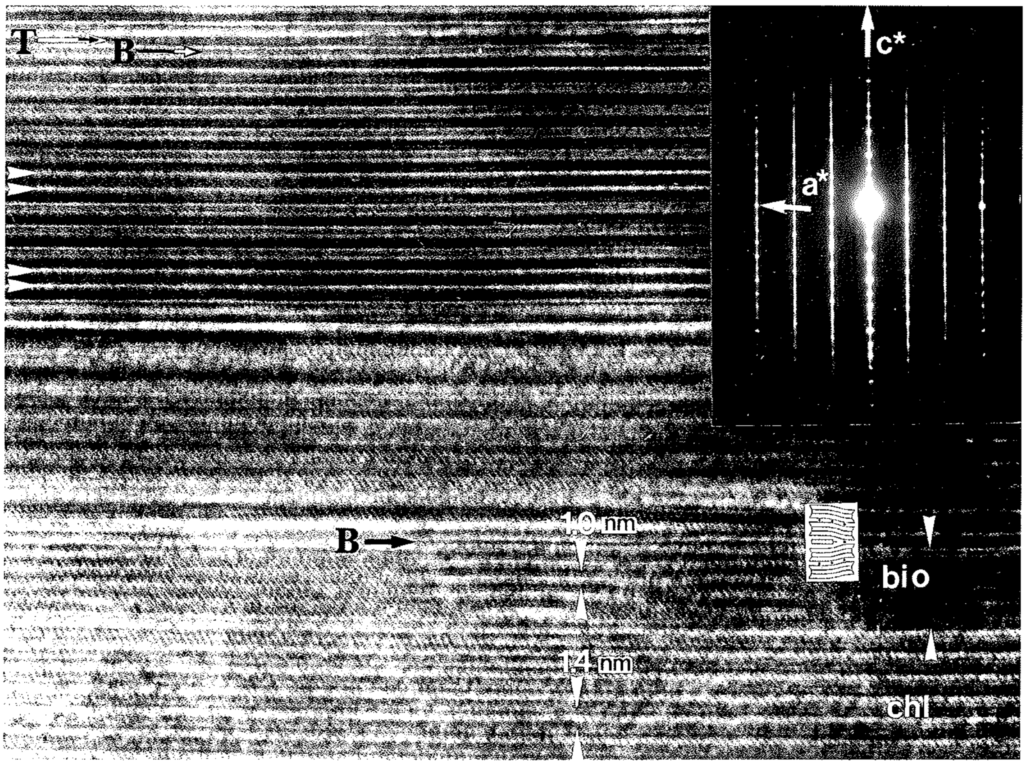

Fig. 4. An experimental HRTEM image and the SAED of chlorite with some remnant biotite units; talc-like and brucite-like layers are marked T and B, respectively; missing brucite-like layers, corresponding to biotite layers are shown by white arrows; an example of the brucitisation of the interlayer in biotite is indicated and the cartoon of the reaction is also included; streaking in the SAED shows phases which are not fully topotactic

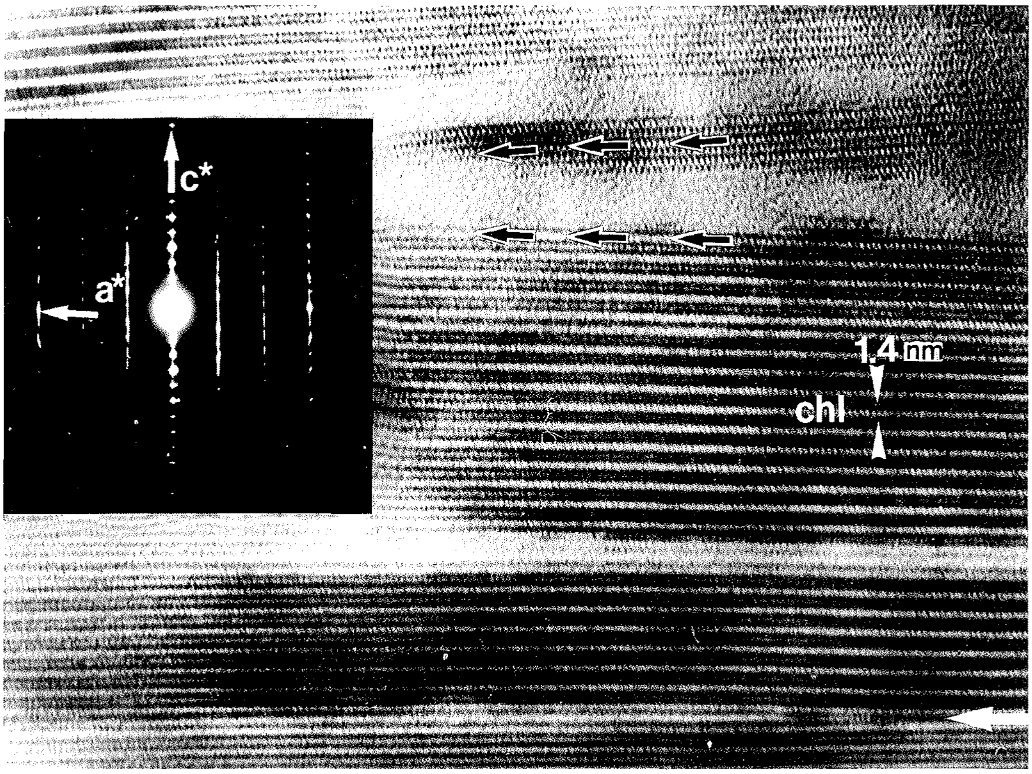

Fig. 5. An experimental HRTEM image and the SAED of a fully chloritised biotite; only two remnant biotite units could be observed (white arrow); the image shows a good example of low-angle less than 10 degrees grain boundary of chlorite grains indicated by dark arrows

Another textural feature observed in these rocks is the low angle grain boundary shown in Text-fig. 5. The low angle, of 8 to 10 degrees, between the two chlorite grains,, is shown by black arrows. The low angle grain boundary could be either a primary function of two biotite grains or a result of non-topotactic alteration of biotite to chlorite. In this example, the hydration of biotite to chlorite developed almost completely. There are only few remnant biotite units (white arrow) within chlorite. Again as in Text-fig. 4, the diffraction pattern is streaked due to the slight misalignment of the chlorite grains.

Finally, an example of the direct alteration of hornblende to chlorite is shown in Text-fig. 6. Both the HRTEM image and the SAED pattern show that the alteration takes place with the c^* and a^* of chlorite parallel to the b^* and a^* of hornblende, respectively. The orientation relation between the host hornblende and the product chlorite can be used to calculate the number of chlorite moles produced during the hydration of one mole of hornblende. It is then possible to estimate the minimum fugacities and composition of the fluids present during hydration (FERROW & RIPA 1991). The white dots between two phases, marked by a white arrow, show the misfit between the structures of the two phases. These vacancies serve as important channels for the transport of fluids during metamorphism.

CONCLUSIONS

As the two examples of chloritisation of hornblende and biotite have shown, TEM is a useful technique in studying the textures and reaction mechanisms produced during metamorphism. The elegance of TEM is that it provides these information at the unit cell level. Thus, while the coarse textures such as grain boundaries and exolution lamellae can be identified easily by either optical microscopy or backscattered scanning electron microscopy, the fine textures missing brucite-like or talc-like layers in chlorite can be identified only by TEM. Moreover, it is possible

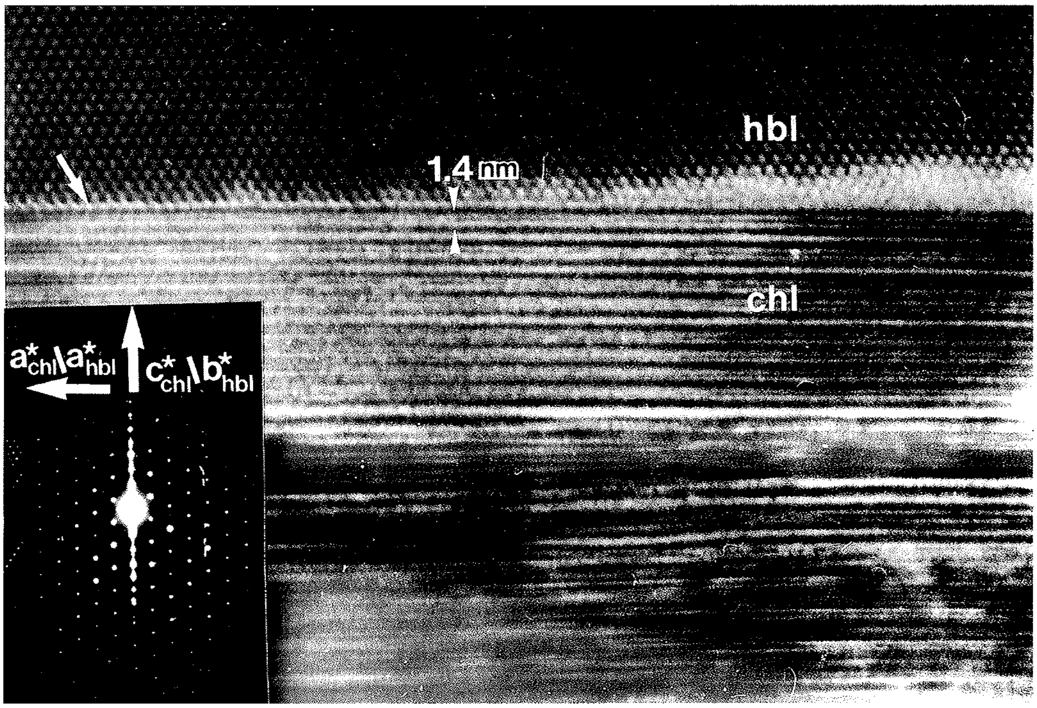

Fig. 6. An experimental HRTEM image of hornblende altered directly to chlorite; the diffraction patter shows that c* and a* of chlorite are parallel to the b* and a* of hornblende, respectively; the grain boundary shows white spots (arrow) created by the structural misfit between the two phases

to determine the orientation relationship between the host and the product and thereby, identify the reaction mechanism. As already shown by BAGIŃSKI & FERROW (1993) and FERROW & RIPA (1991), the data obtained as described above, could then be used to calculate the fugacities and compositions of the fluids present during metamorphic processes.

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