It has been shown that clay minerals transform into (Mg, Al) or (Ni, Al) serpentine-like phases if treated hydrothermally in the presence of MgCO$_3$ or NiCO$_3$ (Shitov et al., 1974, Frank-Kamenetskii et al., 1978, 1983a,b; Kotel'nikova et al., 1976; Varela et al., 1983; Kotov et al., 1985; Ryumin et al., 1978) and that the polytypism of the initial kaolins is inherited by the products. It has also been shown that (Mg, Al) serpentine-like phases react with KCl to form dioctahedral micas and Mg-rich serpentine phases, but the latter do not react to trioctahedral micas (Kotel'nikova et al., 1976). Consequently, it was desirable to look for mechanisms for obtaining trioctahedral micas from serpentine-like phases.

**Experimental**

Experiments were performed in unsealed (capped) Pt capsules in cold-seal bombs (Kotov & Kopeikin, 1972) at $P_{H_2O} = 100$ (2.5) MPa, and $T$ between 500(5) and 550(5)$^\circ$C (Fig. 1). Kaolins were mixed with NiCO$_3$ and allowed to form (Ni, Al) serpentine-like phases which, in turn, reacted with KCl to form micas. Reaction products were examined by X-ray powder diffraction using a DRON-2.0 diffractometer with Ni-filtered or graphite monochromatized Cu-$K$ radiation, and no Soller slits on the detector arm.

![Fig. 1. Schematic drawing of the reaction vessel (a cold-seal bomb) near its hot spot. Capsules (1,2) are placed in a well in the filler rod (3), close to the Pt-Pt10%Rh thermocouple (4).](image-url)
Fig. 2. X-ray powder patterns of (Ni, Al) serpentine phase grown from kaolinite (a) and nacrite (c), and patterns of micas grown from them (b, d). Patterns (a) and (c), and (b) and (d) were produced by phases grown in parallel runs at 500°C. The micas were grown in an excess of 3 M solution of KCl.
The starting materials used were natural water-leached fine-grained fractions of kaolinite (Prosynovsk, USSR), dickite (Turomcha, Siberia, USSR), and nacrite (Muruntau, UzSSR), all displaying a high degree of structural order.

**Synthetic (Ni,Al) serpentine-like phases**

As can be seen in Fig. 2a and c, the (Ni,Al) serpentine phases formed from kaolinite or nacrite are dominant among the run products and display basal peaks with lower d spacings than those of the starting materials. The presence of 020 reflections at 4.50–4.52 Å and those near or at 1.52 Å indicate the predominance of trioctahedral phases. The presence of a low-intensity peak at 1.49 Å possibly indicates the presence (among the products) of some (Ni,Al) di,trioctahedral chlorite analogous to that grown by Kotov et al. (1985). As a whole, the diffraction data of the products can be assigned to structural types B and D (Zvyagin et al., 1965, 1966), or groups A and D (Bailey, 1969), or sub-families A and D (Weiss & Đurović, 1984). Although no chemical analysis was performed, some deductions can be made regarding the composition of the product serpentine. There was no additional Ni phase present in products of experiments with 10 mg kaolinite (nacrite) plus 15 mg NiCO₃, but experiments with 17 mg NiCO₃ (and 10 mg kaolinite or nacrite) yielded some NiO₂, indicating that a trioctahedral phase close to the limiting composition Ni₁₂₃₅Al₉₆₇Al₁₆₆₇Si₁₃₃₃O₄(OH)₄ must have resulted. However, in experiments where the addition of NiCO₃ constituted 2-5 mg NiCO₃ per 10 mg kaolin, (Ni,Al) serpentine phases formed in quantities proportional to the amount of Ni available; according to the position of the 060 reflection, the serpentine was trioctahedral rather than intermediate between di- and trioctahedral in character.

**Nickel micas**

Several concentrations of KCl solutions added to the (Ni,Al) serpentine phases were tested, all containing at least the quantity of K needed to convert all serpentine into mica. At 0.5–2.0 M KCl concentrations, only some mica formed. The introduction of quartz and K-feldspar (placed under capsules in the well in filler rod in Fig. 1) did not significantly increase the yield of mica. The best mica percentages were obtained in 3.0 M KCl solutions. This was done so that some of the reactant KCl was placed directly (as a solid) inside the capsules, together with the serpentine phase. It can be seen in Fig. 2b that 100% yields of mica could be obtained. According to the d spacings and intensities, the Ni phlogopite-like mica appears to be trioctahedral, and displays not only 00l peaks, but also hkl reflections that identify the polytype as 1M (or 37). A possible small admixture of a dioctahedral mica cannot be ruled out. An analogous mica was obtained from a (Ni,Al) serpentine grown from nacrite (Fig. 2d), but some unreacted serpentine phase persisted (hatched peaks) apparently because of a coarser grained starting material.

**Discussion**

The transformation of kaolins into (Ni,Al) serpentines is easy to accomplish, and the fact that the pattern of (Ni,Al) serpentine grown from kaolinite differs from that of (Ni,Al) serpentine grown from nacrite indicates that it proceeds without substantial alteration of the three-dimensional structure. Specifically, the orientation of octahedra remains intact,
resulting in different structural types of the resultant (Ni,Al) serpentines. To transform (Ni,Al) serpentine layers, which consist of one octahedral and one tetrahedral sheet, into the structure of a mica, not only must the plane of interlayer cations be added, but also the relative numbers of tetrahedral and octahedral sheets must be altered. There has to be either addition of one tetrahedral sheet per unit-layer of serpentine, or destruction of every second octahedral sheet, let alone the necessary change in orientation of the tetrahedra. The first alternative need not affect the orientation of octahedra and might lead to the formation of micas with different polytypic structures, depending on whether the starting material was a kaolinite (1M) or a nacrite (2M2). While this mechanism has been successful in dioctahedral micas (Frank-Kamenetskii et al., 1978; Kotov et al., 1980), it apparently did not prevail in the present experiments, even if the additional Si,Al-containing phases were available as a source of elements needed to form the tetrahedral sheet.

The synthesis of micas from (Ni,Al) serpentines was not straightforward, and only at high concentrations of KCl did it proceed well. The fixation of K frees hydrochloric acid that is apparently instrumental in dissolving the octahedral sheets. These changes in the structure are so far-reaching that inheritance of polytypic stacking is prevented, and a uniform orientation of layers results.

Department of Crystallography, Leningrad State University, University Embankment 7/9, Leningrad V-034 USSR 199034, and *Institute of Geological Sciences, Charles University, Albertov 6, 12843 Praha 2, Czechoslovakia.

Received 14 March 1989; revised 18 September 1989

REFERENCES


KOTOV N.V. & KOPEIKIN N.N. (1972) Apparatus for, and some aspects of, experiments at high temperatures and pressures. II. Device for hydrothermal studies at $P_{H_2O} = 2000 \text{ kg/cm}^2$ and $T$ up to $850^\circ C$. Vestn. Leningr. Univ. Ser. Geol. Geogr. 2, 139–143 (in Russian).


