Multi-stage illite evolution in Upper Proterozoic shales: Rb–Sr, XRD and TEM studies

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Introduction

Clastic sedimentary rocks contain mineral phases which are distinct in age and origin. As a consequence, the dating of shales by the Rb–Sr whole-rock method usually gives meaningless values. By contrast, a study of fine clay fractions is very promising for dating particular stages of sedimentary evolution. Of special interest is the technique that uses fractions with the sizes of clay particles varying within narrow limits (Clauer *et al.*, 1984; Morton, 1985; Gorokhov *et al.*, 1994). This paper provides some examples of its application for ancient shales. Upper Proterozoic shales of the Olenek Uplift, Northern Siberia, and of the Sredni Pen-insula, NW Kola Region, have been studied.

Analytical techniques

The < 5-μm clay fraction was extracted using the conventional sedimentation technique. The < 0.1-, 0.1–0.2-, 0.2–0.3-, 0.3–0.6-, 0.6–2- and 2–5 μm subfractions (SFs) were separated from this fraction by centrifugation and ultra-filtration. X-ray diffractometry (XRD) of oriented slides was used to determine mineral composition of the SFs and the illite crystallinity index (I_k) as defined by Kubler (1967). The SFs were also examined by transmission electron micro-scopy (TEM).

Rb and Sr contents in the SFs were measured by isotope dilution mass spectrometry, together with the $^{87}Sr/^{86}Sr$ ra-tios. Previous studies (Chaudhuri, Brookins, 1979; Clauer *et al.*, 1984; Gorokhov *et al.*, 1994) have shown that the Sr ad-sorbed onto clay particles may be of different origin than that contained in mineral structures. Because this adsorbed Sr might give valuable information about the evolutionary path of clay minerals, the SFs were leached with 1N ammo-nium acetate. The Rb–Sr 'leachochrons' for triplets including an untreated size fraction, its leachate and residue, gave the apparent age and intercept for each of the SFs.

Results

The Olenek Uplift. Middle Riphean shale of the Debengda Formation exposed within a stable cratonic area, remains ne-arly flat lying, and it is essentially unmetamorphosed. Al-Mg illite-smec-tite is the dominant mineral phase in all SFs and chlorite content in all but the 2–5-μm SF is under 5%. I_k values vary in the range of 1.28–1.58° Δ2θ tending to a decrease in finer SFs. 1M-1Md illite dominates the SFs smaller than 0.2-μm and 1Md illite prevails in the rest of the SFs. With the size of particles decreasing from 0.6–2-μm to < 0.1-μm, $^{87}Rb/^{86}Sr$ ratio in the residues after leaching rises in two samples from 9.0 to 16.1–18.1. The apparent Rb–Sr age values unidirectionally decrease from 1212–1234 Ma for the 0.6–2-μm SF to 1040 Ma for the < 0.1-μm SF, while the apparent $^{87}Sr/^{86}Sr$ initial ratios are lowered from 0.7143 to 0.7134 in one sample and from 0.7132 to 0.7126 in another.

The NW Kola Region. The sedimentary succession on the Sredni Peninsula is a part of Upper Proterozoic strata in coastal area of the Kola Peninsula. This shallow-marine cla-stic and carbonate succession comprises the Pumanka and the Poropelon Formations. The SFs of the Pumanka and the Porope-lon shales are composed of illite and chlorite. The propor-tion of illite undergoes a rise from 65% in the 0.6–2-μm SFs to 85–90% in the < 0.1-μm SFs. Illite changes between ferriferous in coarser and aluminous in finer SFs. I_k increases from 0.35–0.39° Δ2θ for the 2–5-μm SFs to 0.92–1.00° Δ2θ for the < 0.1-μm SFs. $^{87}Rb/^{86}Sr$ ratio in the residues also increases from 6.0–10.6 for the 2–5-μm SFs to 29.5–55.7 for the < 0.1-μm SFs. As the clay particles decrease in size, the apparent Rb–Sr age values for the SFs tend to diminish (807–834 Ma for the 0.6–2-μm SFs *vs* 571–611 Ma for the < 0.1-μm SFs). The apparent $^{87}Sr/^{86}Sr$ initial ratio for the Pumanka shale increases from 0.7254 for the 0.6–2-μm SF to 0.7294 for the < 0.1-μm SF. As to the Poropelon shale, this ratio rises initially from 0.7216 for the 0.6–2-μm SF to 0.7230 for the 0.2–0.3-μm SF and then goes down to 0.7212 for the < 0.1-μm SF.

Discussion

The recent studies (Burley, Flisch, 1989; Mossmann, 1991; Gorokhov *et al.*, 1994) indicate that size clay fractions are usually constituted by mixtures of minerals which were generated at different points in time and in dissimilar geochemical environments. Because of this, calculated values of the apparent age and $^{87}Sr/^{86}Sr$ initial ratio are meaningful only for the SFs which contain essentially pure or at least highly enriched end-members of such mixtures. For intermediate SFs, contrastingly, these values are meaningless. This is also true for the studied Upper Proterozoic shales. A number of features testify that clay SFs of the Debengda and the Pumanka shales consist of two illite generations not too different in morphology and contain them in variable proportions. Among these features which vary smoothly and unidirectionally with a variation of the size of particles are the following: (1) an illite crystallinity index, (2) Rb and Sr contents in the residues after leaching, (3) an apparent Rb–Sr age and (4) an apparent $^{87}Sr/^{86}Sr$ initial ratio. In addition, a linear arrangement of data points for all re-sidues of each shale on the $^{87}Rb/^{86}Sr$–$^{87}Sr/^{86}Sr$ diagram is a sufficient demonstration of the two-component mixing. The first illite generation with a lower Rb/Sr ratio dominates the 2–5-μm and 0.6–2-μm SFs for both of these shales. The second generation with higher Rb/Sr ratio is most abundant in the < 0.1-μm SFs. I_k values, Rb and Sr contents in the residues and the apparent Rb–Sr age for the Poropelon SFs vary monotonically with the change of their size. Yet the tendency for an increase in the apparent $^{87}Sr/^{86}Sr$ initial ratio with a dearease of the size of particles is reversed in the vicinity of the 0.2–0.3-μm SF. What is more, data points of the finest fractions are deviated from the mixing line on the $^{87}Rb/^{86}Sr$–$^{87}Sr/^{86}Sr$ diagram for residues. This disruption of a mixing systematics is precisely the same as founded for Cambrian claystones of Estonia (Gorokhov *et al.*, 1994) and is undoubtedly associated with forming the third illite generation in the 0.1–0.2-μm and < 0.1-μm SFs. The lath-like particles indicative of a high water/rock ratio during mineral transformations are typical for this illite.

Conclusions

The studied Upper Proterozoic shales incorporate the mi-xtures of illites of different age and origin. The data are illustrative of three distinct situations.

(1) The mixture of two low-temperature generations of illite. The Debengda shale contains two generations of authigenic illite. The first of them formed during early diagenesis. Its age, 1212–1234 Ma, is consistent with a stratigraphic position of the rock and with the Rb–Sr and K–Ar ages of associated glauconite. The second-generation illite developed 1040 Ma ago in the coarse of late diagenesis or, perhaps, retrograde catagenesis.

(2) The mixture of high-temperature and low-temperature generations of illite. The first-generation illite in the Pumanka shale was produced under anchizonal conditions c. 800–840 Ma ago and is most likely detrital. The second, authigenic generation of illite presumably originated during a burial and early diagenesis of sediments about 610–620 Ma ago.

(3) The mixture of one high-temperature and two low-temperature generations of illite. The first and second generations of illite in the Poropelon shale are similar to those in the Pumanka shale both in age and in origin. The process involved in the formation of the authigenic third-generation illite can be defined as a retrograde catagenesis. It was probably induced by influx of non-marine subsurface water due to faulting and/or regional emergence. Its maximum age is of 570 Ma.

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