An apparatus for measuring the potassium and argon released from clay samples by treatment with quaternary ammonium ions

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Chaudhuri et al. (1994) and Sears et al. (1995) have demonstrated that treatment of clay samples with aqueous octadecylammonium chloride causes changes in the K-Ar apparent ages of the clays. Specifically, the organic ions selectively replace K ions from some illite particles while having little effect on other illite particles. Expansion of the interlayers as the large organic ions replace the K ions presumably allows concomitant escape of the associated radiogenic argon. Sears et al. (1995) summarized earlier research that has identified 'expandable illite' as clay whose interlayers will not expand upon treatment by smaller organic ions but will expand upon treatment with octadecylammonium ions. The 'expandable illite' in a clay mixture may be either detrital or diagenetic in origin, depending on the composition and history of the detritus and on the diagenetic history of the sedimentary material.

Selective removal of potassium and argon from the 'expandable illite' in a clay mixture allows determination of the K-Ar relationship in the remaining ('non-expandable') illite, but the K-Ar relationship in the 'expandable illite' can be determined only by difference if K-Ar determinations are done in the conventional way. Such determinations are problematic, because exchange of K ions by the large octadecylammonium ions causes a substantial increase in mass of the exchanged clay. Direct measurement of the K and Ar released by treatment of clay with organic ions would provide a much better way to determine the K-Ar relationship in the 'expandable illite.' Even more useful information should be obtainable by measuring K and Ar released during successive time intervals as an exchange process proceeds.

An apparatus for determination of the argon isotopes and potassium released stepwise by treatment of clay samples with aqueous organo-ammonium salts has been developed at Georgia Institute of Technology. Glass boats within the apparatus are pre-loaded with organo-salts and water. The amount of organo-salt in each boat is appropriate for one exchange step, and the total amount of water in all the boats is appropriate to make the solution used in one step. During evacuation of the apparatus, water is retained in a trap cooled by ethanol slush. The organo-salt solutions are degassed as the water evaporates and moves to the cold trap. After the apparatus has been thoroughly degassed in respect to materials more volatile than water, the water is transferred to the first boat by condensation of water vapour so that the product liquid drains into the boat. Then the clay sample, held between filters, is lowered into the liquid to begin the ion exchange reaction. Thermal control of water-vapour pressure creates small differences in head to move the liquid through clay; such movement allows the continual mixing that would be caused by agitation in a conventional batch process. To end the first step, the sample is raised out of the solution and rinsed by condensed water that drains downward through the clay into the boat. After the rinsing, the argon within the apparatus is transferred to a mass spectrometer for isotopic measurement. Then the second boat is moved into place below the clay sample and the water is transferred to that boat to make the solution for the second step. The potassium released during the first step remains in the first boat for later determination.

The apparatus is most convenient to use for reactions at room temperature, and the selectivity of the exchange process may be greater at room temperature than at elevated temperature. For these reasons and also because movement of water through clay is slow, the schedule for stepwise ion exchange reactions in this apparatus is one in which a step extends for one or more days. Because the entire apparatus remains at or below room temperature, contamination of the sample's argon by atmospheric argon from the apparatus is negligible, even for steps that extend over a number of days. The organic salts are stable enough in aqueous solution that the argon released from a sample is exceptionally clean – argon may be transferred from the reactor through cold traps directly to the mass spectrometer.
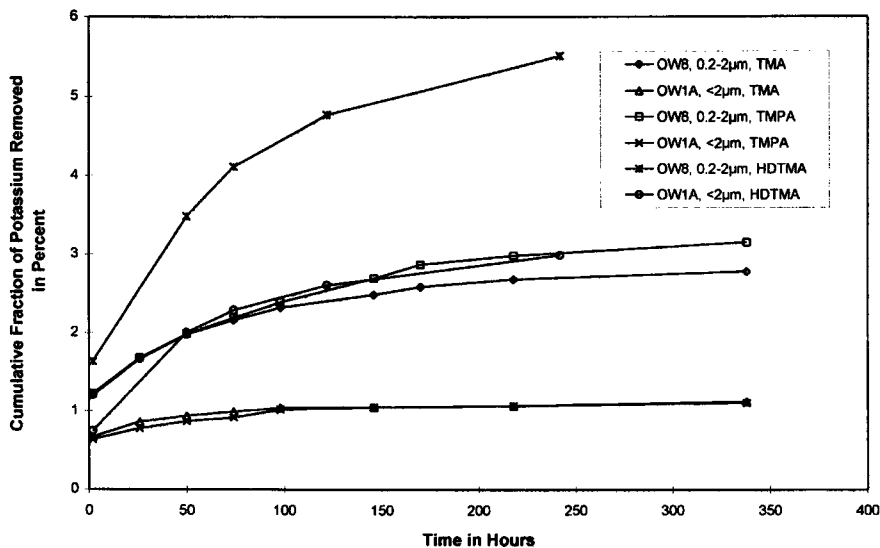
FIG. 1. Results of preliminary potassium-exchange experiments at room temperature.

It is important to know that the rates of the exchange processes at room temperature are appropriate for a schedule that involves daily (or longer) steps. For this purpose, preliminary batch experiments have been used to examine the room-temperature exchange of potassium by three different quaternary ammonium ions in 0.1M solution. Two clay samples from the Conasauga Formation of northwestern Georgia, U.S.A., were used in these experiments. Figure 1 is a plot of the cumulative fraction of potassium released in each experiment against time. OW1A, <0.2 μm, is fine illite from a portion of the Conasauga Formation that experienced epizone metamorphism; OW8, 0.2−2 μm, is from the diagenetic zone and is about two-thirds mixed-layered illite-smectite (Broekstra, 1978; Weaver and Associates, 1984).

The relatively small quaternary ammonium ions tetramethylammonium (TMA) and trimethylphenyl-ammonium (TMPA) replaced about 1% of the K of the fine epizonal illite and then became ineffective for further exchange. Hexadecyltrimethylammonium (HDTMA), which has a 16-carbon chain, replaced 3% of the K from this clay in about 250 hours and may have continued to replace potassium had the experiment continued. The smaller ions were more effective at extracting K from the diagenetic clay (OW8) than from the epizonal illite, as expected. The large HDTMA ion removed K from OW8 at about twice the rate that the smaller ions had; after 5 days,

5% of the K had been removed.

These preliminary potassium-exchange experiments show that quaternary ammonium ions exchange for K at rates appropriate for stepwise determination of K and Ar released by the exchange process. They show that larger quaternary ammonium ions are more effective at removing K than are smaller ions, which parallels what earlier workers had determined for exchange by primary n-alkylammonium ions. The apparatus for stepwise K-Ar determinations permits exchange reactions with smaller ions to be followed by exchange reactions with larger ions. A maximum of information could be obtained by stepwise determination of K and Ar released by reactions with successively more powerful exchange ions.

References

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