

INDIRECT DATING OF SEDIMENT-HOSTED ORE DEPOSITS:  
PROMISES AND PROBLEMS

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Chronological information on sediment-hosted ore deposits is essential for the detailed construction of their genesis. Unfortunately, direct dating of ore minerals, such as sulfides or oxides, is often difficult if not impossible by common isotopic methods, because of both the difficulty of measuring very small amounts of radiogenic isotopes due to the very low parent element to daughter element ratios of these minerals and the lack of precise knowledge of the isotopic compositions of the minerals at their formation. Uranium minerals are among the very few ore minerals known to contain significantly large amounts of radiogenic Pb isotopes, making them amenable to dating by the U-Pb method. However, the time of U deposition measured directly from U minerals is often questioned, because these minerals frequently lose intermediate isotopes of the U decay chain when exposed to near surface condi-

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surface conditions (Miller and Kulp, 1963). Maas et al. (1986) and Turpin et al. (1991) suggested recently that U minerals could contain measurable amounts of radiogenic Nd because of favorable Sm/Nd ratios. As the rare-earth elements (REE) are hardly fractionated by geologic processes in surface or near-surface conditions, the Sm-Nd isotope method might prove useful for direct dating of different types of ore deposits, as shown recently by Chesley et al. (1991) on fluorite. Although this direct evidence for the time of ore mineralization is generally difficult to obtain, isotopic studies, especially with the Pb-Pb method, have been found useful to trace the sources of metal concentrates (e.g. Faure, 1986).

In the recent years, the limited available means for direct dating of ores have prompted studies of minerals from barren zones close to ore concentrations. The minerals which have been sought for such purposes include clay minerals, alkali-feldspars, and other silicate phases, because they are potentially capable of recording chemical disturbance events related to ore concentrations. Some isotopic studies of fluid inclusions in ore minerals or gangue minerals for determining their periods of mineralization have also been considered. As fluid inclusions do not occupy any specific atomic sites in minerals, we have considered the isotopic analyses of their fluids as an indirect means of dating ores, much the same way isotopic dating of minerals outside the ore zones provides information about the period of ore concentration. The present chapter reviews the results of attempts to determine the isotopic ages on ore deposits hosted in sedimentary rocks, and analyzes the merits or potentials of methods which may determine indirectly the time of mineralization of these ores.

#### DATING OF FLUID INCLUSIONS

Studies of fluid inclusions in ore minerals for dating purposes are few, and they have been carried out exclusively with the Rb-Sr method. Before discussion, some cautionary remarks on the existing analytical approach might be useful. Indeed, during sample

preparation, special care should be taken to avoid any contamination, as the Rb and Sr concentrations in fluid inclusions are very low, often only a few tenths of  $\mu\text{g/g}$  (Shepherd et al., 1982; Lange et al., 1983; Darbyshire and Shepherd, 1985). Sample crushing should be done thoroughly, and the leaching of powder with dilute acid (1N HCl) seems appropriate. Mass balance calculations and petrographic data are desirable to assess the sources of Rb and Sr in the minerals.

### Some Case Studies

Shepherd et al. (1982) reported a study on the Pb-Zn-fluorite-barite deposits of the North Pennine orefield in Scotland, providing a Rb-Sr isochron on quartz fluid inclusions from "Great Sulphur" vein. Previous fluid inclusion microthermometry studies established that fluorite was deposited from moderately hot (90 to  $160^\circ\text{C}$ ) and highly saline brines (Sawkins, 1966; Smith, 1974). The Rb-Sr isochron fitted through 8 data points with  $^{87}\text{Rb}/^{86}\text{Sr}$  ratios from 0.5 to 1.83, and gave an age of  $206 \pm 9$  Ma with an initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.7106 \pm 0.0002$  (Fig. 1). Unfortunately the ana-

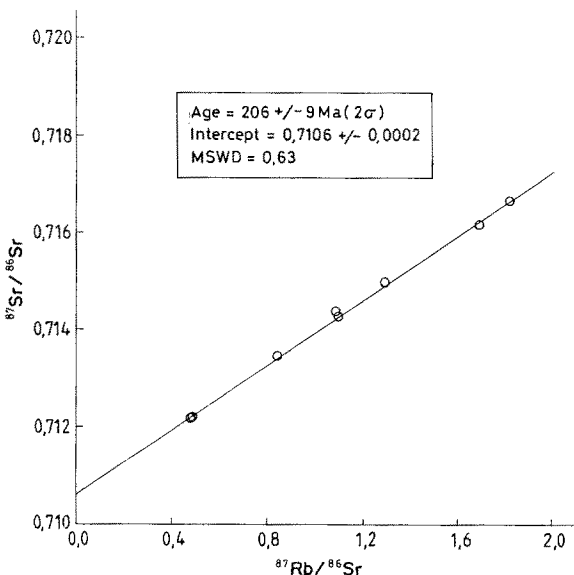


Figure 1: Fluid inclusion Rb-Sr isochron of Great Sulphur vein, North Pennine orefield (Shepherd et al., 1982)

analytical data were not provided in the publication. As this Triassic age agrees with results reported for other fluorite deposits in Western Europe (Baubron et al., 1980), Shepherd et al. claimed that the isochron dates the fluorite deposition, although previous investigation by Bunham et al. (1968) argued for a Permo-Carboniferous depositional age. Shepherd et al. also suggested, on the basis of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the isochron intercept, that the most likely source rocks for the Sr, and hence possibly for the metals of the deposit, are the Carboniferous shales of the sedimentary sequence subjected to the ore-bearing veins. Based on Sm-Nd data, Halliday et al. (1986) ruled out a plutonic source for the Nd and Sr of the mineralizing fluids, and suggested that most of Nd and Sr derived from Carboniferous sediments.

Lange et al. (1983) studied the Sr isotope chemistry of barites and the Rb-Sr systematics of fluid inclusions contained in cubic galena samples of Mississippi Valley-type ore deposits in southeast Missouri. The temperature of the ore fluids, based again on fluid inclusion microthermometry, could have been as high as 110°C (Leach, 1979). Four samples with  $^{87}\text{Rb}/^{86}\text{Sr}$  spread between 0.13 and 2.16 defined an Rb-Sr isochron, but a fifth sample was significantly off the line. The calculated age was  $392 \pm 21$  Ma with an initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.7104 \pm 0.0004$ . Kish and Stein (1979), Posey et al. (1983), Grant et al. (1984), and Stein and Kish (1985) reported Rb-Sr isochron and conventional ages on glauconites separated from ore-bearing strata of the district, generally between 350 and 400 Ma. Hearn and Sutter (1985) published a  $^{40}\text{Ar}/^{39}\text{Ar}$  age of  $290 \pm 20$  Ma for authigenic feldspars, suggesting ore deposition was possibly connected with the brine migration at that time. In addition, K-Ar data on Upper Cambrian glauconies from the Ozark region suggest two recrystallization ages, one at 385-390 Ma and the other less than 355 Ma (Clauer and Chaudhuri, unpublished). On the basis of all data, it seems that the southeast Missouri region underwent at least two hydrothermal events which could have been related to ore deposition: one at about 390 Ma, and the other possibly as late as at 290 Ma. The existence of an early thermal episode in the region is also suggested by an age of  $380 \pm 25$  Ma obtained for the Avon diatremes (Zartman et al., 1966). In contrast to all these Devonian or younger ages, York et al. (1981) reported a  $^{40}\text{Ar}/^{39}\text{Ar}$

isochron age of  $549 \pm 20$  Ma for pyrite samples from same deposits, the meaning of which remains questionable; one reason being possible recoil effects.

### Discussion

A very basic question shrouds the meaning of Rb-Sr isochrons from fluid inclusions: why are the lines stratigraphically meaningful isochrons and not meaningless mixing lines? The ore fluids in the Viburnum district, for instance, are known to have had varied Sr isotope compositions during the entire period of the mineralization, as suggested by the data obtained on different gangue minerals (e.g. Kessen et al. 1981; Chaudhuri et al., 1983; Baumann and Hofmann, 1988). For example, early dolomite associated with octahedral galena had low initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between 0.7093 and 0.7097, while that of the intermediate dolomite and calcite, and of some quartz associated with cubic galena ranged from 0.7102 to 0.7106; the late calcite displaying  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.7119 to 0.7123 (Fig. 2). These values are systematically higher than those of the host carbonate rocks, which range from 0.7083 to 0.7089. Thus, considering this variation of the Sr isotope composition of the Viburnum ore fluids, the isochron obtained on fluid inclusions of the cubic galena samples could have been biased by samples characterized by high  $^{87}\text{Sr}/^{86}\text{Sr}$  and high Rb/Sr ratios: in this case the line would be a mixing line. The magnitude of that bias would, of course, depend on the differences in both the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  and the Rb/Sr ratios of the end-members. Hence, the isotopic age for the Viburnum galena would then only set a maximum value for the mineralization event. Lines of evidence in favor of the existence of an isochron, instead of a mixing line, are that the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of both the fluid inclusions in the galena samples and the glauconitic minerals from the nearby ore-bearing strata are the same within analytical uncertainty, and that their ages are identical at  $392 \pm 21$  Ma and  $393 \pm 6$  Ma, respectively. These similarities favor also the idea of migrating chemically homogeneous ore fluids at that time.

The constancy of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio during ore formation is,

indeed, an essential requirement for dating of fluid inclusions in ore-minerals or associated gangue minerals by the Rb-Sr method. As the conclusions of the study on the Viburnum deposits suggest, this requirement should be critically tested in any study by analyzing the Sr isotope compositions of associated Rb-free gangue minerals. Sample selection should be critically guided by the study of the paragenetic mineral sequences of the ores to be dated.

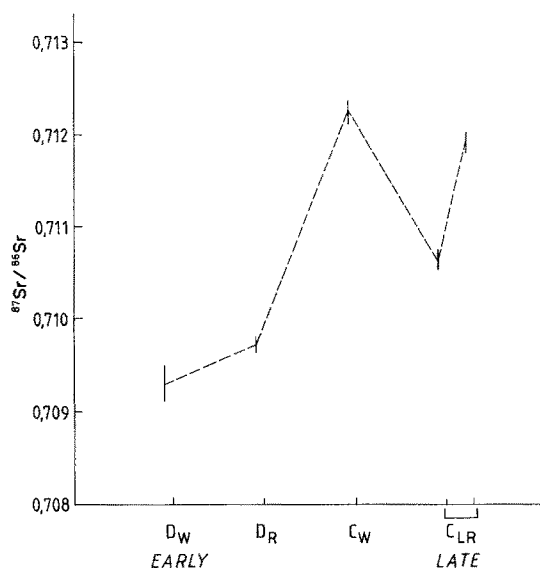


Figure 2: Temporal variation in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of carbonate minerals at Bushy Creek, Viburnum Trend, Southeast Missouri (Chaudhuri et al., 1983).  $D_W$  = white rhombic dolomite;  $D_R$  = reddish white dolomite;  $C_W$  = white calcite;  $C_{LR}$  = large yellowish rhombohedral calcite

Aside from the difficulty of ascertaining whether or not the samples had the same  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio during deposition, the Rb-Sr isochron technique suffers basically from the disadvantage of not having sufficient spread in the Rb/Sr ratio among the samples. The ratios range, for example, from 0.05 to 0.75 in the Viburnum galeana, which induces a large factor of uncertainty on the calculated ages.

Some potentially new lines of research on isotopic dating of fluid inclusions could be developed. For instance, crushing of ore samples under vacuum in an apparatus equipped with a mobile pestle

and connected to a high vacuum gas extraction line should theoretically allow application of the K-Ar method. The amount of K could be measured on the same split after Ar extraction and analysis or on a separate split, by isotope dilution. Although technically feasible, this sort of investigation should be approached with cautions because a study of Rama et al. (1965) indicated that "excess"  $^{40}\text{Ar}$  could be present in the fluid inclusions. Kelley et al. (1986) outlined in great detail a study of Ar isotope chemistry in fluid inclusions generated during mineralization processes. They could relate the "excess"  $^{40}\text{Ar}$  observed in their study to the chlorine-Ar component of the brines present in the inclusions. This behavior, if general, would limit the routine application of this method, as liquid phases in fluid inclusions are often found to be Cl-rich.

Another potentially useful alternative to the Rb-Sr and K-Ar methods related to fluid inclusions could be the  $^{40}\text{Ar}/^{39}\text{Ar}$  laser-fusion technique. Application of this technique, which is discussed more extensively in a later section of this chapter, would avoid the tedium of separation of the minerals and of the chemical preparation prior to mass spectrometric analyses. However, indiscriminate application of this method can lead to questionable data, as Kelley et al. (1986) observed  $^{39}\text{Ar}$  recoil losses from samples studied in sealed vials. Recoil-related losses were strongly hinted by a study of pyrite by York et al. (1981) who found ages to be higher by about 170 Ma than all other ages obtained with independent means. This recoil effect is not surprising considering that fluids of inclusions do not occupy specific atomic sites but are trapped in vugs generated during mineral growth. Among the causes for these recoil effects are the occurrence of cracks near the surface of the host grains and the decrepitation of some inclusions induced by temperature increase during the necessary irradiation of the samples in a reactor (Kelley et al., 1986). However, the  $^{40}\text{Ar}/^{39}\text{Ar}$  laser-fusion technique has still application possibilities, as fluid inclusions sometimes contain solid phases beside the usual liquid and vapor phases. When the solids are authigenic sericite-type minerals, they can be dated by  $^{40}\text{Ar}/^{39}\text{Ar}$  laser-fusion. A successful application of this technique seems to depend on careful sample selection to avoid the effects of induced artifacts.

## DATING OF COMMON GANGUE MINERALS

Gangue minerals of ore deposits are very much devoid of radio-genic isotopes because of the very low parent to daughter isotope ratio. Consequently these minerals are not generally amenable to dating by conventional methods. However, studies may be made of the parts of host rocks which are most intimately associated with ore or gangue minerals to determine the time of mineralization.

A Case Study

Ruiz et al. (1984) suggested a new Rb-Sr approach to determine the period of mineralization of ore bodies by analyzing the Sr isotopic compositions and the Rb/Sr ratios of common gangue minerals and their associated wall rocks. This technique has the potential of overcoming the small spread in the Rb/Sr ratios among the minerals of an ore body, as the spread in the Rb/Sr ratio might be favorably influenced by the wall rocks, which commonly have much higher Rb/Sr ratios than the gangue minerals. Nevertheless, the technique requires, as demanded by the principle of isotopic dating, that the gangue minerals and their wall rocks have the same isotopic composition at the time of mineralization. Failure to comply with this requirement produces a model age derived from average data of the wall rocks and based on an assumed initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, which can be very different from the real age of mineralization. The precision of the calculated mineralization ages of samples from zones where isotopic homogeneity occurred, are less dependent on the exact value of the initial Sr ratios which may be deduced from the values of the gangue minerals. Ruiz et al. elaborated on the conditions which govern the precision of the ages. To demonstrate the feasibility of using the Rb-Sr isotopic method, they reported isotopic results of gangue minerals and associated wall rocks from three separate ore districts. The ages of the mineralizations were previously established by other means. Ruiz et al. found that the age based on assumed isotopic homogeneity between gangue minerals and wall rocks was reasonably in agreement



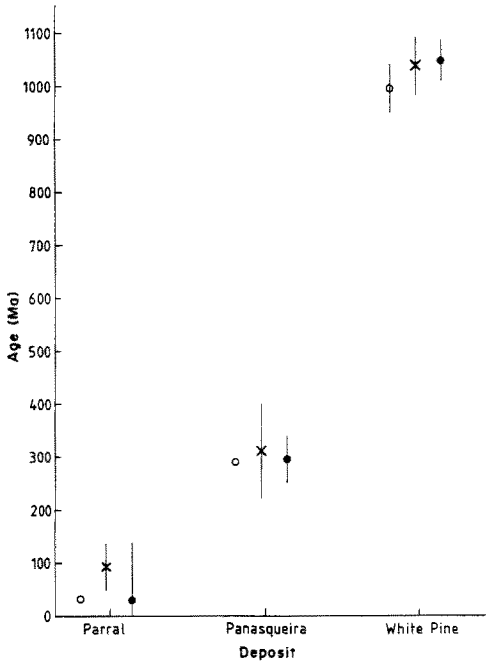


Figure 3: Comparison of mineralization dates for Parral, Panasqueira and White Pine (Ruiz et al., 1984). Squares are ages with errors obtained by other workers, bars with stars and triangles indicate ages and errors obtained by Ruiz et al.'s technique

with previously published data, for the White Pine Cu deposit in the Late Precambrian Nonesuch Shale in Michigan. For the two other examples, the Parral Pb-Zn ores in Mexico and the Panasqueira Sn-W deposit in Portugal, the generated data were greatly lacking in the precision necessary to equate the isotopic ages with the presumed mineralization ages (Fig. 3).

### Discussion

The Rb-Sr dating of ore deposits by the method suggested by Ruiz et al. (1984) should be approached with carefully considered supporting information. The failure to do so would add more confusion to the already existing problem of finding the age of ore concentrations. The foremost question of this dating technique is whether or not the wall rocks and the gangue minerals had the same or nearly identical Sr isotopic compositions at the time of mineralization. From above discussions, any claim of isotopic homogeneity

between wall rocks and gangue minerals is of extremely dubious nature. It must be demonstrated by complementing chemical or petrographic data, and not simply assumed. In one instance, we have failed to observe an isotopic homogeneity between host rock and vein even on a scale of few millimeters (Clauer et al., 1989). Defining the zone of isotopic homogeneity within wall rocks is critical to the selection of the most appropriate samples, and in this respect analyzing whole rocks is the least desirable option, as they are multi-component systems. A particular group of minerals, but not all minerals, in a wall rock could have isotopically equilibrated with the mineralizing fluids, and analysis of its separates would be far more desirable and accurate than that of the probably more heterogeneous whole rock.

Two potential sources of error in the age of ore deposits from wall-rock analyses are analytical scatter of the Rb/Sr ratios of the wall rocks and of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the fluids at the time of mineralization. Ore fluids often appear to have varied Sr isotopic compositions, as has been reported in studies on gangue minerals and ore deposits (Chaudhuri et al., 1983; Kesler et al., 1983; Fontbote and Gorzawski, 1988). Ruiz et al. remarked that precise knowledge of the Sr isotopic composition of the mineralizing fluid is less critical when the mean Rb/Sr ratio of the wall rocks is high. Accuracy and precision of the ages obtained by this method are, in fact, not only dependent on the knowledge of the Rb/Sr and initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the wall rocks, but also on the degree of scatter in the Rb/Sr ratios. The most preferred rocks are those with high but no scatter in the Rb/Sr ratios. In general, shales, sandstones and siltstones among sedimentary rocks are high, but spatially much varied in their Rb/Sr ratios. Selection of samples from the same bed, or from different beds with similar Rb/Sr ratios, could, therefore, improve the precision of the model ages.

#### DATING OF ASSOCIATED CLAY MINERALS

Clay minerals are common products which precipitate or recryst-

tallize during low-temperature hydrothermal processes. Their isotopic ages may therefore be used to document the time of hydrothermal processes which might have induced ore concentrations. A number of studies with somewhat varied analytical approaches among them have addressed the issue of dating ore deposits through isotopic analyses of the clay components. Most of these studies are reviewed here to point out to what extent this approach provides reliable results, and to suggest some precautionary measures that might avoid failure of getting the intended ages.

### Results of Case Studies

In the early 1970's, Ineson and co-workers reported a number of K-Ar data obtained from clay minerals of wall rocks or vein gouges of metallogenic igneous provinces from United Kingdom and Norway (Ineson and Mitchell, 1972; Ineson, 1974, 1975; Ineson et al., 1975). The basis of these datings was that cogenetic minerals, as long as non unambiguous evidence for the age of the ores is available, could be dated to constrain the age of vein emplacements. The clay fraction analyzed consisted mainly of illite-chlorite assemblages, very often mixed with kaolinite and occasionally with zeolites. Unfortunately, in most of the studies mentioned, both the lack of knowledge about the time of mineralization constrained by other means, and the lack of information about the meaning of some minerals like kaolinite and about the morphology of the clay particles, which both will be discussed later, prevent any assessment of the real significance of the ages from these clay fractions. However, the authors claimed that: "clay minerals from host rocks do constitute reliable geochronometers, at least for vein deposits which are post-Carboniferous."

Lee and Brookins (1978), and Brookins (1980) reported on an extensive Rb-Sr study of  $<2\mu\text{m}$  bulk clay separates related to U mineralization in the Upper Jurassic Morrison Formation of New Mexico. They defined the earliest mineralization period at  $139 \pm 9.5$  Ma, based on an isochron of smectite-rich clay fractions from barren rocks and chlorite-rich clay fractions from ore zones. The U-Pb data on the same ore deposit yielded consistently lower and

discordant ages from 87 to 113 Ma. These low values and their relatively large scatter might have resulted from loss of intermediate daughter products of the U decay chain by the U minerals near surface. This discrepancy strongly suggests that the U-Pb method applied to altered U minerals systematically underestimates the time of U deposition. Lee and Brookins also obtained low Rb-Sr isochron ages from 110 to 115 Ma for clay minerals from Laguna district, which they interpreted as later periods of mineralization. The latest ore concentration in the district might have occurred about 9 to 10 Ma ago, based on the U-Pb data of an uranophane. In contrast to the Rb-Sr data, the K-Ar values of all the clay minerals were widely scattered between 138 and 49 Ma. This scatter could be due to more or less extensive resets affecting the K-Ar systems during the different mineralization events.

Halliday (1977, 1980a, 1980b), Bonhomme et al. (1980), Pop et al. (1980), Bonhomme (1982), Bonhomme et al. (1983), and Halliday and Mitchell (1983, 1984) reported many K-Ar results obtained on clay fractions associated with ore mineralizations mainly in igneous rocks, but also in sedimentary sequences. They considered these K-Ar ages as being minimum ages for the mineralization, and that the dates probably reflect late hydrothermal activities in the host rocks. The results are widely scattered in most of these investigations, and the values which are believed to be "true ages" are chosen on a basis of "regional consistency" with other previously published results. In fact, most of these data did not provide unambiguous interpretation, because of the lack of information about separation and characterization of the clay fractions.

Clauer et al. (1985) reported K-Ar results of carefully separated and characterized  $<2\mu\text{m}$  bulk clay fractions associated with U-ore deposits from Cluff Lake in Saskatchewan, Canada. Eleven clay fractions were selected from mylonitized parts of the sedimentary sequence which were affected by the same tectono-thermal event as the basement. They consisted largely of illite ( $> 50\%$ ) with smaller amounts of chlorite, and their K-Ar apparent ages averaged  $1293 \pm 36$  Ma. These clay samples are never located farther than 40 m from the massive U ore-deposits and were, therefore, considered to have experienced the tectono-thermal event responsible for the

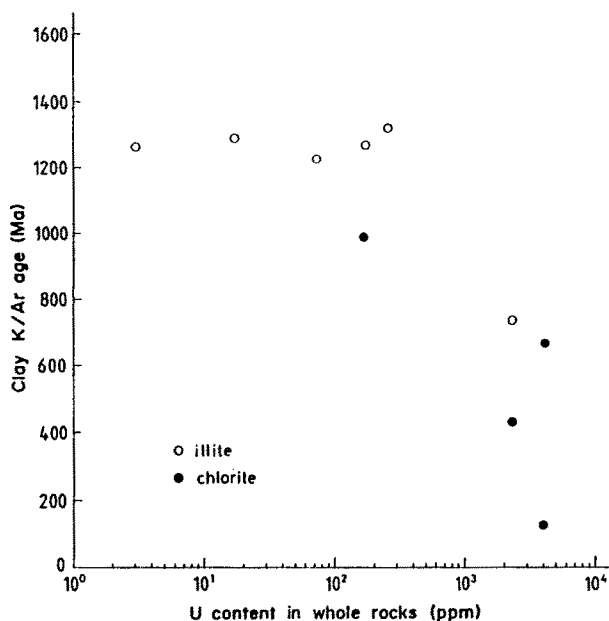


Figure 4: Relationship between K-Ar ages of clay minerals and U content of the corresponding host whole rocks (Halter et al., 1987)

major U concentration in the area. Previously published U-Pb dates on the ore minerals were systematically lower at 1050 to 1150 Ma (Bellon et al., 1976; Gancarz, 1979). Only recently, Philippe (1988) obtained U-Pb ages of  $1278 \pm 31$  Ma on unaltered pitchblende from the same area. To elucidate further on the extent of the thermal event in this region, eight additional  $<2\mu\text{m}$  clay fractions were analyzed by Clauer et al. (1985). Five were taken from tectonically undisturbed barren sandstones close to the ore pit, and the three others were collected outside the Carswell structure, several km away from any U show. This second set of clay fractions gave a K-Ar isochron age of  $1222 \pm 52$  Ma, which is similar to the age of the clay fractions associated with the ore-bearing zone. The similarity in ages suggests that the hydrothermal event was widespread at this time, and that the U concentrated only locally at the contact between basement and the sedimentary cover. The temperature of this event was estimated at  $200 \pm 50^\circ\text{C}$ , based on microthermometry determinations in the fluid inclusions of the quartz overgrowths (Pagel et al., 1980). Wilson et al. (1987), combining

K-Ar data with stable isotope chemistry on clay fractions from fracture zones or highly altered zones, reported K-Ar apparent ages much lower than 1200 Ma. These data seem to have no geological meaning, but they record external effects on the K-Ar system of clay particles. These results are complemented by a study of Halter et al. (1987) on clay fractions directly in contact with the U-concentrates. Relationships between the U content in the whole rocks, the K-Ar data, the D values, and the water content of the clay fractions could be observed (Fig. 4). They emphasized radiation-catalyzed retrograde exchanges of the clay particles, which have been damaged by the irradiations, with recent meteoric waters at low temperatures. These studies emphasize how important it is to characterize thoroughly the clay fractions extracted from well documented samples.

An U chemical age of about 160 Ma was obtained for pitchblende of the sediment-hosted U deposit of Muellenbach, near Baden-Baden in Western Germany (Zuther, 1983), but U-Pb determinations of pitchblende from the same region gave higher values of  $240 \pm 6$  Ma (Holliger et al., 1989). This age was derived from a model based on continuous Pb and Ra diffusion. Also determined were K-Ar apparent ages of  $<2\mu\text{m}$  bulk clay fractions from different types of sedimentary rocks which have been altered to different degrees during the thermal event responsible for the U deposition (Brockamp et al., 1987). Seven illite-rich clay fractions of arkoses near the U-ore body gave K-Ar values between  $150 \pm 3$  Ma and  $159 \pm 4$  Ma, whereas two clay fractions immediately adjacent to the ore were found to be  $143 \pm 3$  Ma old. As discussed in the preceeding section, this difference between the two ages could have resulted from irradiation damages, but it could also reflect a span of time during which the U-ores were deposited. A noteworthy aspect of this study is that the clay fractions from all arkosic rocks, whether collected from the highly altered ore zone, the moderately altered sericitized zone, or the weakly altered albitized zone, always gave similar K-Ar values averaging  $155 \pm 4$  Ma. The clay fractions extracted from other lithologic units, such as shales or silts, gave systematically higher K-Ar values, suggesting that only the arkoses, with high porosities and permeabilities tended to have clay mineral assemblages that were in chemical equilibrium with the

hydrothermal fluids. Based on coalification measurements, the temperatures of the hydrothermal solutions responsible for the U ores near Baden-Baden, were probably somewhere between 190 and 240°C. This is high enough, according to Hunziker et al. (1986), to erase the Ar memory of any detrital illite-type components of sedimentary occurring rocks. Clearly, in this instance, the clay fractions of the arkoses were able to record a thermal event about 155 Ma ago. The major U concentration could, however, have occurred about 50 Ma earlier, as suggested by the U-Pb data, during another event, the memory of which could have been erased entirely from clay fractions of the highly permeable arkoses and, to a lesser extent, from clay fractions of the other lithologies.

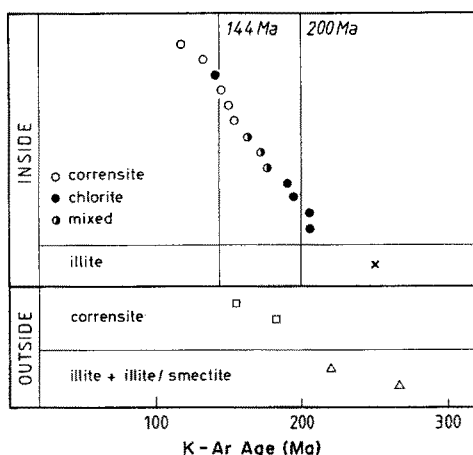
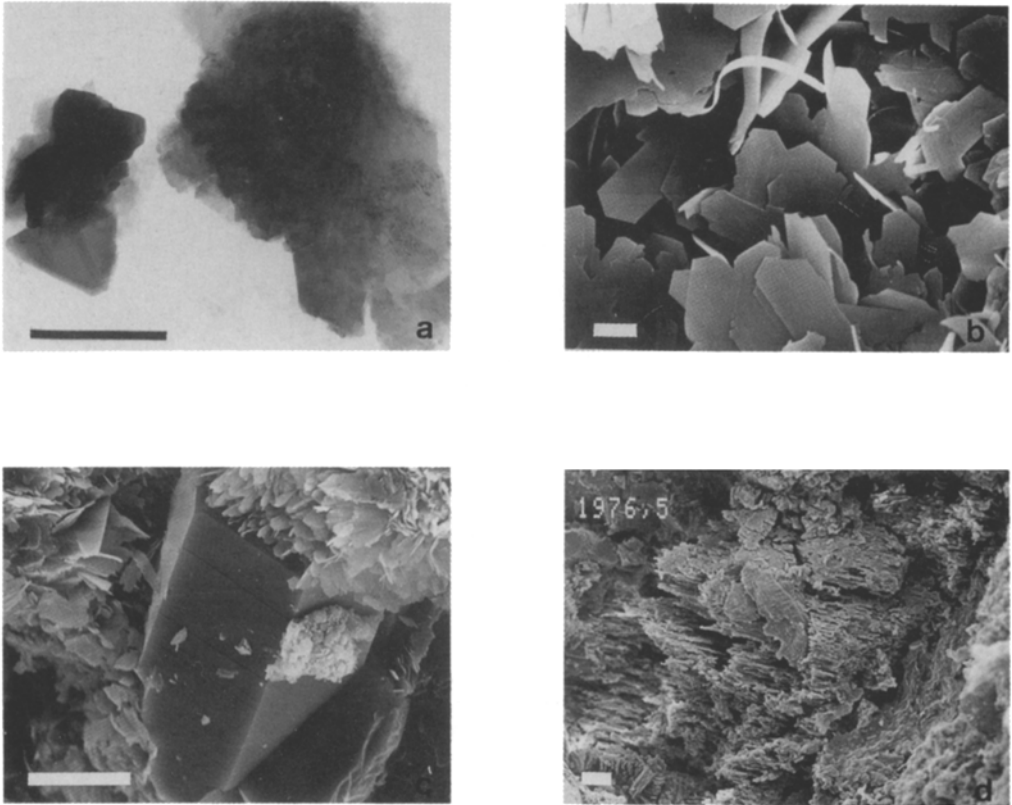


Figure 5: K-Ar ages of the clay fractions associated with the Akouta U deposits (Turpin et al., 1991). The numbers at the top represent the U-Pb ages of the pitchblende

The temperature of the mineralizing fluids from which the U deposits of Akouta in Central Niger precipitated in sandstones, and the temperature of the mineralizing fluids could have been as high as 160°C (Forbes et al., 1987). Turpin et al. (1991) contended that the deposition occurred between 260 and 150 Ma, based on U-Pb determinations on well characterized pitchblende. The clay fractions in close proximity to the ore gave K-Ar ages of  $148 \pm 6$  Ma for the corrensite-rich ones, while the chlorite-rich assemblages suggested the existence of an earlier hydrothermal event at  $199 \pm 8$  Ma (Fig. 5). Again, slightly lower K-Ar data at  $134 \pm 4$  Ma and

117  $\pm$  6 Ma were obtained on clay fractions from the ore body itself. Additional age determinations are needed to constrain better the U-Pb age, to define the extent of this early hydrothermal event in the region, and to determine the relationship of this activity to the U deposition.



**Figure 6:** Scanning and transmission electron microscope photographs. 6a: poorly crystallized illite with ill-defined edges (bar = 2.5  $\mu\text{m}$ ); 6b: well crystallized illite with well defined edges (bar = 1  $\mu\text{m}$ ); 6c: authigenic feldspar in a sandstone (bar = 10  $\mu\text{m}$ ); 6d: detrital altered feldspar in a sandstone (bar = 10  $\mu\text{m}$ )

A promising isotopic technique for dating clay minerals associated with ore deposits appears to be the  $^{40}\text{Ar}/^{39}\text{Ar}$  method. Halliday (1978) reported results of  $^{40}\text{Ar}/^{39}\text{Ar}$  stepheating determinations on



six clay concentrates from ore bodies in Ireland. The age distribution patterns from stepheating were complex, suggesting that irradiation of the clay particles in the reactor induced  $^{39}\text{Ar}$  and radiogenic  $^{40}\text{Ar}$  losses. These effects seem, as hinted by Halliday (1978), to be related to the mineralogy of the clay fractions, the size of the grains, and the morphology of the particle edges. Reuter and Dallmeyer (1989), who carefully documented the  $^{39}\text{Ar}$  recoil effect on clay fractions and the related redistribution of  $^{39}\text{Ar}$  from high-K to low-K bearing phases, could show that both, recoil and redistribution seem to occur preferentially in particles with large surface areas and poorly defined grain edges, which relate to poorly crystallized minerals, relative to well crystallized counterparts with straight edges (Fig. 6a and b). Bell (1985) reported some  $^{40}\text{Ar}/^{39}\text{Ar}$  data obtained by laser-fusion technique on "alteration products" of basement crystalline rocks near U shows from southern Carswell structure in Saskatchewan, Canada. As mentioned by the author, the size of the individual clay particles being of 1 to  $10\mu\text{m}$ , laser-fusion required analysis of grain clusters, because the diameter of the laser beam was of 200 to  $300\mu\text{m}$ . The ages of the nine samples ranged from  $500 \pm 50$  Ma to  $1615 \pm 5$  Ma; most of them being between  $1175 \pm 15$  Ma and  $1615 \pm 5$  Ma. Bray et al. (1987) presented a study in which they compared laser-

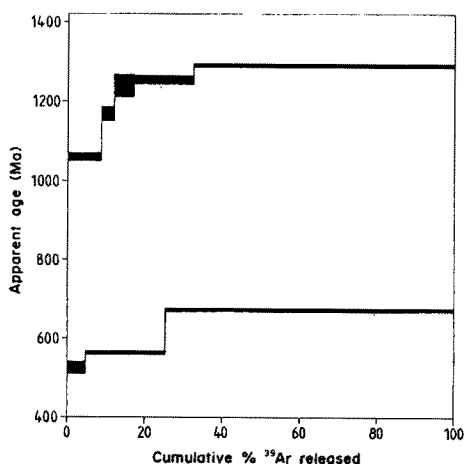


Figure 7:  $^{40}\text{Ar}/^{39}\text{Ar}$  stepheating age spectra for potassic silicates, Mc Clean deposits, Northern Saskatchewan (Bray et al., 1987). Top diagram for sample 1208-458 and bottom diagram for sample 2045-517

probe  $^{40}\text{Ar}/^{39}\text{Ar}$  and conventional K-Ar datings of illite associated with U deposits from northern Saskatchewan, Canada. The illite fractions collected in the alteration halo next to the mineralization, had a larger scatter for the conventional K-Ar ages, from  $1321 \pm 44$  Ma to  $1002 \pm 33$  Ma, than for the laser-probe  $^{40}\text{Ar}/^{39}\text{Ar}$  ages, from  $1319 \pm 3$  Ma to  $1178 \pm 4$  Ma. The larger scatter in the conventional K-Ar values could be due to sample preparation and clay fraction purification. As in the previous example, the scatter in the  $^{40}\text{Ar}/^{39}\text{Ar}$  ages could be partly due to the energy of the beam and its size. Fusion of nearby minerals has to be expected as long as the size of the laser beam is larger by one to two orders of magnitude than the size of the particles. But this effect will have no consequences when the adjacent grains are depleted in Ar, like quartz. The results of Bray et al. (1987) look promising: they obtained some flat  $^{40}\text{Ar}/^{39}\text{Ar}$  step-heating spectra (Fig. 7), compared to the complicated ones presented by Reuter and Dallmeyer (1989; Fig. 8, a and b). The plateau ages, however, remained scattered.

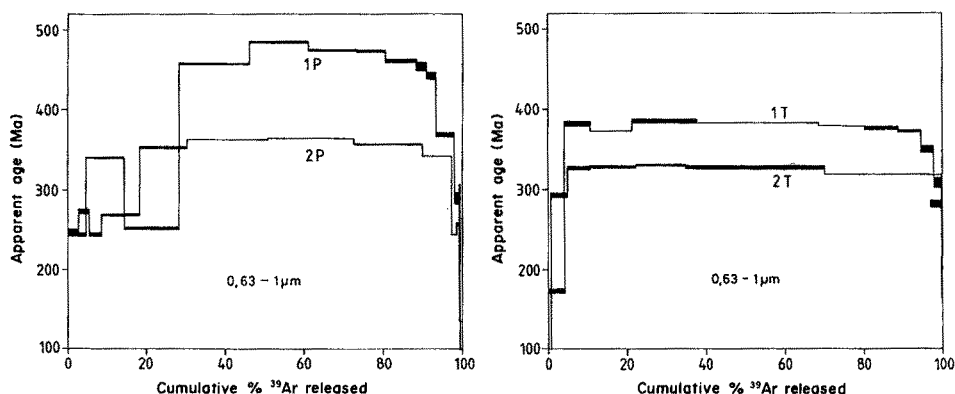


Figure 8:  $^{40}\text{Ar}/^{39}\text{Ar}$  step-heating age spectra for  $0.63\text{--}1\mu\text{m}$  clay size fractions (Reuter and Dallmeyer, 1989). 1P: clay fraction extracted from a phyllite of middle anchizone metamorphic intensity. 2P: clay fraction from a phyllite of upper anchizone intensity. 1T: clay fraction extracted from an associated metatuff of middle anchizone intensity; 2T: clay fraction extracted from an associated metatuff of upper anchizone intensity. Note that the clays from metatuff give systematically less complicated patterns than the counterparts from phyllites. The upper anchizone clays have also less complicated patterns than the counterparts from middle anchizone

## Discussion

To our experience, many problems of clay isotope dating arise because investigators do not take necessary care in sample preparation and clay separation prior to mass spectrometric determinations. Liewig et al. (1987) and Clauer et al. (1992 and in this volume) have addressed some of these problems in recent studies on K-Ar dating of authigenic clay minerals in oil-bearing sandstone reservoirs. Routine crushing of the whole-rock samples systematically produces overcrushing of detrital components to clay-sized particles, the presence of which automatically invalidates the isotopic data of the intended clay minerals, as discussed earlier. Appropriate gentle disaggregation techniques must be adopted to avoid incorporation of artificially created clay-sized grains in the separated clay fractions.

The analytical procedures are suspect, for instance, when the K-Ar ages of clay fractions which are supposedly related to the same thermal event are widely scattered. Arbitrary selections of numbers from clouds of data can no longer be considered as "true ages" just because they seem consistent on a regional basis. Interpretation of isotope data must counter all possible factors, which fall into both isotopic and non-isotopic categories, contributing to the dispersion of the data. The presence of contaminating minerals in clay samples and the mixtures of clay particles of different generations are very common reasons for data clouds. Depending on their origin, contaminating components, such as feldspars, might influence the isotopic values of the  $<2\mu\text{m}$  bulk clay fractions. If feldspar peaks can be recognized in X-ray diagrams, their relationship with the clay minerals should be examined under electron microscopy. If these feldspars are authigenic, they display characteristic forms by SEM (Fig. 6c), and they could have formed during the same hydrothermal event as the clay minerals, which in turn implies that these feldspar grains should not influence the isotopic results of the clay fractions. If, on the other hand, the feldspars are detrital in origin, as those on figure 6d, they will definitely "increase" the K-Ar or the Rb-Sr ages of the associated clay assemblages, because they contain an excess of radiogenic  $^{40}\text{Ar}$  or  $^{87}\text{Sr}$  relative to the clays formed

during the hydrothermal event.

As the study of Wilson et al. (1987) demonstrated, clay fractions containing kaolinite should also be avoided for dating purposes, because the conditions favorable to their genesis are often conducive to leaching of interlayer cations from the K-(and Rb) bearing clay minerals, which should adversely affect their isotopic ages. Clay fractions collected within U-ore deposits should also be considered with special care, as Halter et al. (1987) noted that radiation damage tends to promote loss of radiogenic isotopes from the altered lattices of the clay minerals.

However, the overall conclusion of the previous studies is that any lowering in the age of clay fractions can be caused by crystallization of younger generations of clay minerals. Diffusion of radiogenic  $^{40}\text{Ar}$  from clays is not a commonly observed behavior, as it occurred only in cases related to irradiation damages of the mineral lattices, or to chemical exchange with environmental fluids at low temperature in deeply weathered zones. This lack of exchange at low temperatures is a basic requirement for dating clay fractions, and it has been recently substantiated by O'Neil (1987), on the basis of the stable isotope chemistry.

To determine isotopic ages by the  $^{40}\text{Ar}/^{39}\text{Ar}$  method, the samples have to be irradiated with fast neutrons in a reactor to produce  $^{39}\text{Ar}$  from  $^{39}\text{K}$ . The temperature in the reactor can be as high as  $200^\circ\text{C}$ , which, of course, is expected to induce radiogenic  $^{40}\text{Ar}$  loss from minerals that have crystallized at lower temperatures. This loss of  $^{40}\text{Ar}$  might occur in addition to a  $^{39}\text{Ar}$  loss from recoil effect induced by the neutron activation, and detected preferentially in small and poorly crystallized particles. We suspect that in many published accounts of  $^{40}\text{Ar}/^{39}\text{Ar}$  data obtained on clay minerals, a combined loss of  $^{39}\text{Ar}$  and radiogenic  $^{40}\text{Ar}$  produced isotopic dates that appear reasonably close to the expected ages, although the final results are technically faulty. Before the  $^{40}\text{Ar}/^{39}\text{Ar}$  technology can be applied routinely to the dating of clay particles, with or without a laser-probe, much more basic work is needed to determine the effects of irradiation and laser fusion. Studies of clay samples loaded in breakseal quartz vials before

irradiation would certainly be helpful to understand more about the effects of combined losses of recoiled  $^{39}\text{Ar}$  due to neutron activation and radiogenic  $^{40}\text{Ar}$  due to temperature in the reactor.

While paying close attention to the technical aspects and selection of samples for clay age determinations, geological considerations are equally important in the interpretation of the ages. It must be kept in mind that hydrothermal activities affect the evolution of clay minerals in rocks by either inducing partial or complete alteration of preexisting clay fractions, or promoting crystallization of new minerals. These activities, however, do not always relate to ore concentrations. If dates of associated clay minerals do not match the ages of the ore deposition, as might be the case for the U ore-deposit of Muellenbach in Germany, a geologic explanation should be favored, before considering obscure Ar diffusion effects. On the other hand, when the K-Ar ages of very carefully characterized clay fractions are higher than those of the U-minerals, like in the Akouta deposit of Niger, a mineralogic reason might be searched such as the presence of illite in the clay fractions (Fig. 5), which is considered here of detrital origin.

Lithology is also an important consideration in the isotopic dating of ore mineralizations by the means of clay minerals from host-rocks, as suggested by the study on the U-ore deposit of Muellenbach in Germany (Brockamp et al., 1987). Clay minerals from arkoses, and by extension from sandstones, are apparently more suited for dating than those from siltstones and shales. Sandstones with high porosity and permeability facilitate pervasive fluid migration, offering more opportunities than siltstones and shales for the growth of neoformed or recrystallized clay minerals and the alteration of unstable detrital components. Hence, if the occurrence of sandstones and arkoses increase the possibilities of dating properly the time of hydrothermal activity related to ore deposition because their clay minerals are most likely completely recrystallized, they also require special care in sample preparation because the detrital components such as the feldspars are often deeply altered so that routine crushing might reduce these altered detrital components to clay-sized grains and introduce artifacts, as suggested by Clauer et al. (1992).

## DATING OF OTHER SILICATE MINERALS

Beside clay minerals, some other alkali-bearing silicates can be occasionally found associated with ore deposits, and therefore represent potential materials for dating ores by isotopic means. Among these minerals are K-feldspars (adularia and orthoclase). While Hearn and Sutter (1985) reported promising results on orthoclases related to the Mississippi-Valley type (MVT) deposits, Halliday and Mitchell (1976) published scattered K-Ar analytical data between  $156 \pm 3$  and  $220 \pm 3$  Ma for adularia feldspars from Lizard Complex in England. Halliday and Mitchell could relate the age variations to changes in the triclinicity of the minerals. They also measured  $^{40}\text{Ar}/^{39}\text{Ar}$  on the same adularia splits, which matched with the K-Ar data suggesting that probably no recoil effect occurred. The results were explained in terms of post-crystallization reorganization of the lattices of the minerals, which seem to have induced Ar loss by interaction with low-temperature alkali solutions. These results on adularia feldspars suggest limitations to the use of these minerals for dating ore deposits.

## CONCLUSIONS

Presently, the dating of sediment-hosted ore deposits is proceeding along two major lines of approach. One is the isotopic dating of fluid inclusions in ore minerals or gangue minerals, and the other is the isotopic dating of clay minerals associated with ores. Careful selection of samples based on factual information is needed to help avoid ambiguity in the translation of the isotopic data to a meaningful geologic age, which has relevancy to the ore deposition.

Critical to isotopic dating of fluid inclusions in ore or gangue minerals by the Rb-Sr isotopic method is total knowledge of any variation of the isotopic composition of Sr in the fluids during the entire mineralization episode. A Rb-Sr isochron from

fluid inclusions will indicate a mineralization age, provided the ore fluids had the same or nearly the same Sr isotopic composition during mineral growths. When the ore fluids varied in their initial Sr isotopic compositions, sample selection should be guided by information on the paragenetic mineral associations, as only minerals of the same generation as the ore fluids can be expected to have the same or nearly the same Sr isotopic composition. Hence, all gangue minerals should be analyzed in an ore district for their  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios to determine both the magnitude and the direction of the Sr isotopic change in the fluids during mineralization.

Clay minerals in host rocks or ore deposits have been viewed as suitable materials for K-Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  isotopic dating to define the period of ore mineralizations. Ore-related hydrothermal events can be intense enough to either erase previous Ar (or Sr) isotopic memories from detrital clay components or cause authigenesis of new clay particles in the host rocks. Some confusion exists in the literature about the meaning of the ages obtained from clay minerals. Selection of samples, separation and characterization of the clay size-fractions, and, in some situations, analytical problems have greatly contributed to the confusion. Lithology of the rocks is certainly another important consideration. Clay minerals of sandstones, arkoses, and even siltstones, seem to meet the test for age determinations as the porosity in these rocks often facilitates pervasive fluid migration.

Careful mineral separation and detailed characterization of clay minerals are essential preliminary steps toward isotopic dating of ore mineralization. Any clay fraction containing a recognizable contaminant should be discarded for mass spectrometer determinations. Routine characterization of the separated clay fractions by X-ray diffraction should be complemented by transmission electron microscope (TEM) observations.

The use of a laser-probe combined  $^{40}\text{Ar}/^{39}\text{Ar}$  technique, providing in situ isotopic determinations, would solve the delicate aspect of clay separation. Some above mentioned data are promising, but more systematic studies are needed before the technique can be applied on a routine basis on clay particles. It now seems from the

available data that the small size of clay particles ( $<2\mu\text{m}$ ) is not the major reason for the  $^{39}\text{Ar}$  loss due to the recoil effect. The recoil loss is insignificant when the particles are well crystallized, which can be verified under TEM by the presence of their sharp and straight edges. It should also be noted that all  $^{40}\text{Ar}/^{39}\text{Ar}$  dating on clay particles should be complemented by conventional K-Ar determinations on the same size fractions, so that the  $^{39}\text{Ar}$  recoil effects, the redistribution of  $^{39}\text{Ar}$  from K-rich illite into K-poor components, such as chlorite, kaolinite or plagioclases, and the eventual loss of radiogenic  $^{40}\text{Ar}$  could be clearly evaluated. Clay fractions containing these K-poor phases should be avoided for  $^{40}\text{Ar}/^{39}\text{Ar}$  determinations, as they tend to obscure the patterns. In addition, irradiation of clay minerals should be performed in sealed quartz vials, which would allow to determine more precisely the combined effects of losses of  $^{39}\text{Ar}$  and  $^{40}\text{Ar}$  from the minerals. One should also be concerned about the temperature attained during irradiation of clay in a reactor. Radiogenic  $^{40}\text{Ar}$  diffusion might be expected out of mineral structures that crystallized at temperatures lower than that reached in the reactor.

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#### REFERENCES

- Baubron J.C., Jebrak M., Joannes C., Lhegu J., Touray J.C. and Ziserman A. (1980) Nouvelles datations K/Ar sur des filons à quartz et fluorine du Massif Central français. C. R. Acad. Sci., Paris, 290D, 951-953.
- Baumann A. and Hofmann R. (1988) Strontium isotope systematics of hydrothermal vein minerals in deposits of West Germany. Geol. Rundsch., 77, 747-762.
- Bell K. (1985) Geochronology of the Carswell area, Northern Saskatchewan. In: The Carswell Structure Uranium deposits, Saskatchewan. Laine R., Alonso D. and Svab M. (eds.), Geol. Ass.



- Can. Sp. Paper, 29, 33-46.
- Bellon H., Devillers C., Hagemann R. and Touray J.C. (1976) Dater les minéralisations. Mém. Hors Série de la Soc. géol. Fr., 7, 265-268.
- Bonhomme M. (1982) Age triassique et jurassique des argiles associées aux minéralisations filoniennes et aux phénomènes diagénétiques tardifs en Europe de l'Ouest. Contexte géodynamique et implications génétiques. C. R. Acad. Sci., Paris, 294D, 521-524.
- Bonhomme M. G., Yerle J.J. and Thiry M. (1980) Datation K-Ar de fractions fines associées aux minéralisations. Le cas du bassin uranifère permio-houiller de Brousse-Broquies (Aveyron). C. R. Acad. Sci., Paris, 291D, 121-124.
- Bonhomme M., Buhmann D. and Besnus Y. (1983) Reliability of K-Ar dating of clays and silicifications associated with vein mineralizations in Western Europe. Geol. Rundsch., 72, 105-117.
- Bray C.J., Spooner E.T.C., Hall C.M., York D., Bills T.M. and Krueger H.W. (1987) Laser probe  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  and conventional K/Ar dating of illites associated with the McClean unconformity-related uranium deposits, North Saskatchewan. Canada. Can. Jour. Earth Sci., 24, 10-23.
- Brockamp O., Zuther M. and Clauer N. (1987) Epigenetic-hydrothermal origin of the sediment-hosted Muellenbach uranium deposit, Baden-Baden, W-Germany. Mon. Series on Min. Dep., 27, 87-98.
- Brookins D.G. (1980) Geochronologic studies in the Grants mineral belt. New Mex. Bur. Mines & Min. Res. Mem., 38, 52-58.
- Chaudhuri S., Clauer N. and Ramakrishna S. (1983) Strontium isotopic composition of gangue carbonate minerals in the lead-zinc sulfide deposits at the Bushy Creek Mine, Viburnum trend, Southeast Missouri. In: Intern. Conf. on Mississippi Valley-Type lead-zinc deposits. Kisvarsanyi G., Grant S.k., Pratt W.P. and Koenig J.W. (eds.), Univ. Missouri-Rolla, Rolla MI, 140-144.
- Chesley J.T., Halliday A.N. and Scrivener (1991) Samarium-Neodymium direct dating of fluorite mineralization. Science, 252, 949-951.
- Clauer N., Chaudhuri S. and Subramaniam R. (1989) Strontium isotopes as indicators of diagenetic recrystallization scales within carbonate rocks. Chem. Geol. (Isot. Geosc. Sect.), 80, 27-34.
- Clauer N., Ey F. and Gauthier-Lafaye F. (1985) K-Ar dating of different rock types from the Cluff Lake uranium ore deposits (Saskatchewan, Canada). In: The Carswell Structure Uranium Deposits, Saskatchewan. Laine R., Alonso D. and Svab M. (eds.), Geol. Ass. Can. Sp. Pap., 29, 47-53.
- Clauer N., Cocker J.D. and Chaudhuri S. (1992) Isotopic dating of diagenetic illites in reservoir sandstones: Influence of the investigator effect. In: Origin, Diagenesis, and Petrophysics of Clay Minerals in Sandstones, Houseknecht D.W. (eds.), Soc. Econ. Paleont. Miner., Spec. Pub., 47,
- Darbyshire D.P.F. and Shepherd T.J. (1985) Chronology of granite magmatism and associated mineralization, SW England. Jour. Geol. Soc. London, 142, 1159-1177.
- Dunham K.C., Fitch F.J., Ineson P.R., Miller J.A. and Mitchell J.G. (1968) The geochronological significance of argon $^{40}$ /argon $^{39}$  age determinations on White Whin from the northern Pennine ore-field. Proc. Roy. Soc. London, A, 307, 251-266.
- Faure G. (1986) Principles of Isotope Geology. Second Edition. J.

- Wiley, New York, N.Y., 589p.
- Fonbote L. and Gorzawski H. (1988) Isotopic trends (Sr, C, O, S) during diagenetic formation of stratabound Pb-Zn-(F-Ba) deposits in carbonate basins. *Terra cognita*, 8, 31.
- Forbes P., Landaïs P., Pagel M. and Meyer A. (1987) Thermal evolution of the Guezouman Formation in the Akouta uranium deposit (Niger). *Terra cognita*, 7, 343.
- Gancarz A.J. (1979) Chronology of the Cluff Lake uranium deposit, Canada. In: Intern. Uranium Symp. on the Pine Creek Geosyncline, N.T., Australia. Ext. Abstr., 91-94.
- Grant N.K., Laskowski T.E. and Foland K.A. (1984) Rb-Sr and K-Ar ages of Paleozoic glauconites from Ohio and Missouri, U.S.A. *Isot. Geosc.*, 2, 217-239.
- Halliday A.N. (1977) K-Ar dating of mineralization episodes- A discussion. *Econ. Geol.*, 72, 870-871.
- Halliday A.N. (1978)  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  stepheating studies of clay concentrates from Irish orebodies. *Geochim. Cosmochim. Acta*, 42, 1851-1858.
- Halliday A.N. (1980) The timing of early and main stage ore mineralisation in S.W. Cornwall. *Econ. Geol.*, 75, 752-759.
- Halliday A.N. (1980) K-Ar dating of mineral deposits. *Jour. Geol. Soc. London*, 137, 101-102.
- Halliday A.N. and Mitchell J.G. (1976) Structural, K-Ar and  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  age studies of adularia K-feldspars from the Lizard Complex, England. *Earth Plan. Sci. Lett.*, 29, 227-237.
- Halliday A.N. and Mitchell J.G. (1983) K-Ar ages of clay concentrates from Irish orebodies and their bearing on the timing of mineralisation. *Trans. Royal Soc. Edinburgh, Earth Sci.*, 74, 1-14.
- Halliday A.N. and Mitchell J.G. (1984) K-Ar ages of clay-size concentrates from the mineralisation of the Pedroches batholith, Spain, and evidence for Mesozoic hydrothermal activity associated with the break up of Pangaea. *Earth Plan. Sci. Lett.*, 68, 229-239.
- Halliday A.N., Shepherd T.J., Dickin A.P., MacLaren F. and Darbyshire F. (1986) Sm-Nd dating and fingerprinting of the North Pennine fluorite deposits. *Terra cognita*, 6, 227.
- Halter G., Sheppard S.M.F., Weber F., Clauer N. and Pagel M. (1987) Radiation-related retrograde hydrogen isotope and K-Ar exchange in clay minerals. *Nature*, 330, 638-640.
- Hearn P.P. and Sutter J.F. (1985) Authigenic potassium feldspar in Cambrian carbonates: Evidence of Alleghanian brine migration. *Science*, 228, 1529-1531.
- Holliger P., Pagel M. and Pironon J. (1989) Losses in lead and radon as a mean of estimating the age of sedimentary pitchblende deposits: The Mullenbach uranium ore. *Chem. Geol. (Isot. Geosc. Sect.)*, 80, 45-53.
- Hunziker J.C., Frey M., Clauer N., Dallmeyer R.D., Friedrichsen H., Flehmig W., Hochstrasser K., Roggwiler P. and Schwander H. (1986) The evolution of illite to muscovite: mineralogical and isotopic data from the Glarus Alps, Switzerland. *Contr. Mineral. Petrol.*, 92, 157-180.
- Ineson P.R. (1974) K-Ar isotopic age determinations from some Lake district mineral localities. *Geol. Mag.*, 111, 521-537.
- Ineson P.R. (1975) K-Ar isotopic age determinations from some Welsh mineral localities. *Inst. Min. Metall. Trans.*, B, 84, 7-16.
- Ineson P.R. and Mitchell J.C. (1972) Isotopic age determinations on clay minerals from lavas and tuffs of the Derbyshire ore-

- field. *Geol. Mag.*, 109, 501-512.
- Ineson P.R., Mitchell J.C. and Vokes F.M. (1975) K-Ar dating of epigenetic mineral deposits: An investigation of the Permian metallogenic province of the Oslo region, Southern Norway. *Econ. Geol.*, 70, 1426-1436.
- Kelley S., Turner G., Butterfield A.W. and Shepherd T.J. (1986) The source and significance of argon isotopes in fluid inclusions from areas of mineralization. *Earth Plan. Sci. Lett.*, 79, 303-318.
- Kesler S.E., Ruiz J. and Jones L.M. (1983) Strontium-isotopic geochemistry of fluorite mineralization (Coahuila, Mexico). *Isot. Geosc.*, 1, 65-75.
- Kessen K.M., Woodruff M.S. and Grant N.K. (1981) Gangue mineral  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and the origin of Mississippi Valley-type mineralization. *Econ. Geol.*, 76, 913-920.
- Kish S.A. and Stein H.J. (1979) The timing of ore mineralization, Viburnum Trend, southeast Missouri lead-zinc district: Rb-Sr glauconite dating. *Geol. Soc. Amer. Annual Meeting, Abstr. with Progr.*, 11, 458.
- Lange S., Chaudhuri S. and Clauer N. (1983) Strontium isotopic evidence for the origin of barites and sulfides from the Mississippi Valley-Type ore deposits in southeast Missouri. *Econ. Geol.*, 78, 1255-1261.
- Leach D.L. (1979) Temperature and salinity of the fluids responsible for minor occurrences of sphalerite in the Ozark region of Missouri. *Econ. Geol.*, 74, 931-937.
- Lee M.J. and Brookins D.G. (1978) Rubidium-strontium minimum ages of sedimentation, uranium mineralization, and provenance, Morrison Formation (Upper Jurassic), Grants mineral belt, New Mexico. *Am. Ass. Petrol. Geol. Bull.*, 62, 1673-1683.
- Liewig N., Clauer N. and Sommer F. (1987) Rb-Sr and K-Ar dating of clay diagenesis in Jurassic sandstone oil reservoirs, North Sea. *Am. Ass. Petrol. Geol. Bull.*, 71, 1467-1474.
- Maas R., McCulloch M.T., Page R.W. and Campbell I.H. (1986) Sm-Nd isotopic systematics of uranium deposits. *Terra cognita*, 6, 225-226.
- Miller D.S. and Kulp J.L. (1963) Isotopic evidence on the origin of the Colorado plateau uranium ores. *Geol. Soc. Am. Bull.*, 74, 609-630.
- O'Neil J.R. (1987) Preservation of H, C, and O isotopic ratios in the low temperature environment. In: *Stable isotope geochemistry of low temperature*. Kyser T.K. (ed.), Short Course Handbook 13, Min. Ass. Canada, 85-128.
- Pagel M., Poty B. and Sheppard S.M.F. (1980) Contribution to some Saskatchewan uranium deposits mainly from fluid inclusion and isotopic data. In: *Uranium in the Pine Creek Geosyncline*, IAEA, Vienna, 639-654.
- Philippe S. (1988) *Systématique U-Pb et évolution comparée de minéralisations uranifères du bassin d'Athabasca (Saskatchewan, Canada). Cas de gisements de la structure Carswell et de Cigar Lake. Thèse Univ. Montpellier, France, 350p.*
- Pop G., Baciuc F., Gata G., Popescu G. and Soroiu M. (1980) K-Ar dating of clay minerals produced by hydrothermal alteration, a method for determining the age of ore deposits emplacement. *Rev. Roum. Géol. Géophys. Géogr.*, 24, 277-291.
- Posey H.H., Stein H.J., Fullagar P.D. and Kish S.A. (1983) Rb-Sr isotopic analyses of Upper Cambrian glauconites, southern Missouri: Implications for movement of Mississippi Valley-

- type ore fluids in the Ozark region. In: Intern. Conf. on Mississippi Valley-Type lead-zinc deposits. Kisvarsanyi G., Grant S.K., Pratt W.P. and Koenig J.W. (eds.), Univ. Missouri-Rolla, Rolla MI, 166-172.
- Rama S.N.I., Hart S.R. and Roedder E. (1965) Excess radiogenic argon in fluid inclusions. *Jour. Geophys. Res.*, 70, 509-511.
- Reuter A. and Dallmeyer R.D. (1987) Significance of  $^{40}\text{Ar}/^{39}\text{Ar}$  age spectra of whole-rock and constituent grain-size fractions from anchizonal slates. *Chem. Geol. (Isot. Geosc. Sect.)*, 66, 73-88.
- Reuter A. and Dallmeyer R.D. (1989) K-Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  dating of cleavage formed during very low-grade metamorphism: A review. In: *Evolution of metamorphic belts*. Daly J.S., Cliff R.A. and Yardley B.W.D. (eds.), *Geol. Soc. Spec. Publ.*, Blackwell Oxford, 43, 161-172.
- Ruiz J., Jones L.M. and Kelly W.C. (1984) Rubidium-strontium dating of ore deposits hosted by Rb-rich rocks, using calcite and other common Sr-bearing minerals. *Geology*, 12, 259-262.
- Sawkins F.J. (1966) Ore genesis in the North Pennine orefield in the light of fluid inclusion studies. *Econ. Geol.*, 61, 385-401.
- Shepherd T.J., Darbyshire D.P.F., Moore G.R. and Greenwood D.A. (1982) Rare earth element and isotope geochemistry of the North Pennine ore deposits. *Bull. B.R.G.M.*, (2), sect. II, 4, 371-377.
- Smith F.W. (1974) Factors governing the development of fluospar ore bodies in the North Pennine orefield. Ph.D. Thesis, Univ. Durham.
- Stein H.J. and Kish S.A. (1985) The timing of ore formation in southeast Missouri: Rb-Sr glauconite dating at the Magmont mine, Viburnum Trend. *Econ. Geol.*, 80, 739-753.
- Turpin L., Clauer N., Forbes P. and Pagel M. (1991) U-Pb, Sm-Nd and K-Ar systematics of the Akouta uranium deposit, Niger. *Chem. Geol. (Isot. Geosc. Sect.)*, 87, 217-230.
- Wilson M.R., Kyser T.K., Mehnert H.H. and Hoeve J. (1987) Changes in the H-O-Ar isotope composition of clays during retrograde alteration. *Geochim. Cosmochim. Acta*, 51, 869-878.
- York D., Masliwec A., Hall C.M., Kuybida P., Kenyon W.J., Spooner E.T.C., Scott S.D. and Pye E.G. (1981) The direct dating of ore minerals. *Ont. Geol. Surv. Misc. Pap.*, 98, 334-340.
- Zartman R.E., Brock M., Heyl A.V. and Thomas H.H. (1966) K-Ar and Rb-Sr ages of some alkalic intrusive rocks from central and eastern United States. *Am. Jour. Sci.*, 265, 848-870.
- Zuther M. (1983) Das Uranvorkommen Muellenbach/Baden Baden, eine epigenetisch-hydrothermale Impraegnationslagerstaette in Sedimente des Oberkarbons. Teil 1: Erzmineralbestand. *N. Jb. Miner. Abh.*, 147, 191-216.