

Problems with argon: K–Ar ages in Gulf Coast shales

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Abstract

K–Ar ages of Gulf Coast shales do not correspond to diagenetic ‘events’, but are a combination of inherited detrital ages and authigenic overprints. The key to understanding K–Ar ages of shales is the fate of the ⁴⁰Ar when the host minerals dissolve or react during the illitisation reaction: is ⁴⁰Ar incorporated within the illite, or is it lost to the porewaters? Ages are modelled as due to a single illitisation reaction, assuming a uniform precursor sediment and open-system import of K. Both whole-rock and clay mineral fraction data can be reproduced by modelling. The ⁴⁰Ar incorporated into illite is a surprisingly high proportion (75–100%) of that produced within detrital phases (smectite, K-feldspar, mica), perhaps implying that the illitisation reaction is a solid-state transformation, or that ⁴⁰Ar is imported into the shales along with incoming K. The model does not provide a good fit to the data below 4000 m, when the illitisation reaction is apparently complete, but shales lose ⁴⁰Ar by solid-state diffusion or recrystallisation.

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1. Introduction

The K–Ar age-dating system is an important tool in the study of shales, though the ages are potentially a combination of detrital age and authigenic overprint (Hurley et al., 1963), making interpretation difficult. Does a date of, for example, 100 Ma, indicate that there was a diagenetic ‘event’ at 100 Ma BP? Or is the date a composite which must be modelled if it is to be interpreted? Although these questions are diffi-

cult to answer, the systematics of K–Ar dating is well understood (see Faure, 1986). K-bearing minerals contain a small proportion of ⁴⁰K which decays to ⁴⁰Ar, enabling ages to be measured (Faure, 1986). A shale inherits the age of the K-bearing detrital components at the time of deposition, and this detrital age will be more-or-less overprinted by subsequent diagenesis. Within the Gulf Coast, diagenesis commonly involves the dissolution of K-feldspar and detrital mica, and the transformation of smectite to illite (Milliken, 1992; Lynch et al., 1997). Both these processes will release trapped ⁴⁰Ar into the porewater, although some ⁴⁰Ar may be retained within illitising smectite. It is the fate of the K and ⁴⁰Ar from the dissolving phase, and their uptake (or otherwise) into

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authigenic illite, with which this paper is concerned. It is only by understanding the impact of diagenetic processes on the chemistry of shales that K–Ar dates can be correctly interpreted.

Several authors have made the reasonable assumption that the K required for the illitisation of smectite is at least partly derived by the local dissolution of K-feldspar (e.g. Berger et al., 1999). However, dissolving a K-bearing mineral will inevitably release ^{40}Ar , and the fate of this is more controversial. Velde and Renac (1996) assumed that the ^{40}Ar would not be incorporated into the growing illite, while Clauer and Chaudhuri (1996) suggested that the ^{40}Ar was being retained within the solid portion of the rock.

It is the purpose of this paper to determine the fate of the ^{40}Ar liberated from dissolving K-rich detrital phases during shale diagenesis. This is only possible in a very well constrained system, where extensive data is available on the petrology, chemistry and isotope geochemistry of the shales. The only area known to the authors where such information is available is the Texas Gulf Coast of the USA (Fig. 1), and the only study to present a sufficient range of information is that of Hower et al. (1976) and Aronson and Hower (1976). The study rocks here are the shale-dominated Oligo-Miocene Frio Formation. These are sampled over the depth interval of ca. 1250–5500 m, which covers the range of the smectite to illite transformation. We have attempted to model the evolution of these rocks during burial, in terms of

K and ^{40}Ar abundance, and hence model the K–Ar ages. We use the model to constrain the fate of the ^{40}Ar liberated from the dissolving detrital phases, and to determine what proportion of this is retained within the solid rock.

2. Methods

Modelling of the illite to smectite transformation with depth has been undertaken by numerous authors, and here the model of Wilkinson et al. (1992) is adopted, which uses an Arrhenius relationship between reaction rate and temperature. The geochemical model uses the following assumptions, which are evaluated in Discussion.

(1) The initial mineralogical composition of the shales was uniform through out the stratigraphic column.

(2) The shale is an open system with respect to K, such that K is imported into the shale during burial. No explicit assumption about Ar export or import into the shales is required, as the Ar budget is one of the model outputs.

(3) The initial age of detrital K feldspar and mica are constant, i.e. the source of the detrital minerals did not change during deposition. This is only relevant to the whole-rock model as the $<0.1\ \mu\text{m}$ size fraction separates were deemed to be free of detrital contamination.

(4) K feldspar and detrital mica minerals show similar depth-abundance patterns and are treated together. Dissolution was modelled using an Arrhenius relationship with activation energy of 120 kJ/mol and a rate constant of $10,000\ \text{year}^{-1}$.

(5) The initial age of detrital illite/smectite (I/S) was a constant at the time of deposition, e.g. the I/S was always 35 Ma old at the time of deposition. This corresponds to the I/S being of weathering origin, and being renewed within the source area while undergoing erosion. Since deposition ended ca. 15 Ma ago, the most shallowly buried sediments are now 50 Ma old. The ages of the K-feldspar, detrital mica and the I/S are only loosely constrained by available data, and are adjusted to give a suitable age for the shallow sediments.

(6) During the dissolution of the detrital minerals, and the illitisation of smectite, a constant proportion

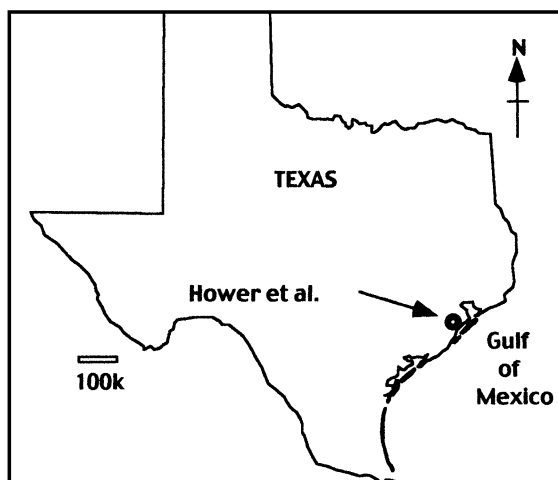


Fig. 1. Map showing location of Hower et al. (1976) study borehole.

of the released ^{40}Ar was incorporated into authigenic illite. The model was run for various values of this constant, to investigate its importance. The smectite component of the I/S only loses its Ar upon illitisation, any unreacted smectite retains its original Ar, plus any formed by K-decay since burial.

K–Ar age was calculated using methods and constants from Faure (1986). Modelling was undertaken for both whole-rock and $<0.1\ \mu\text{m}$ size fractions.

3. Results

For both whole-rock (Fig. 2) and $<0.1\ \mu\text{m}$ size fractions (Fig. 3), a reasonable fit can be produced between model and data for the depth range 1500–4000 m, for the following parameters: % illite in illite/smectite, % K_2O , total ^{40}Ar and K–Ar age. In both cases, the proportion of ^{40}Ar retained during growth of authigenic illite is high, between 75% and 100%,

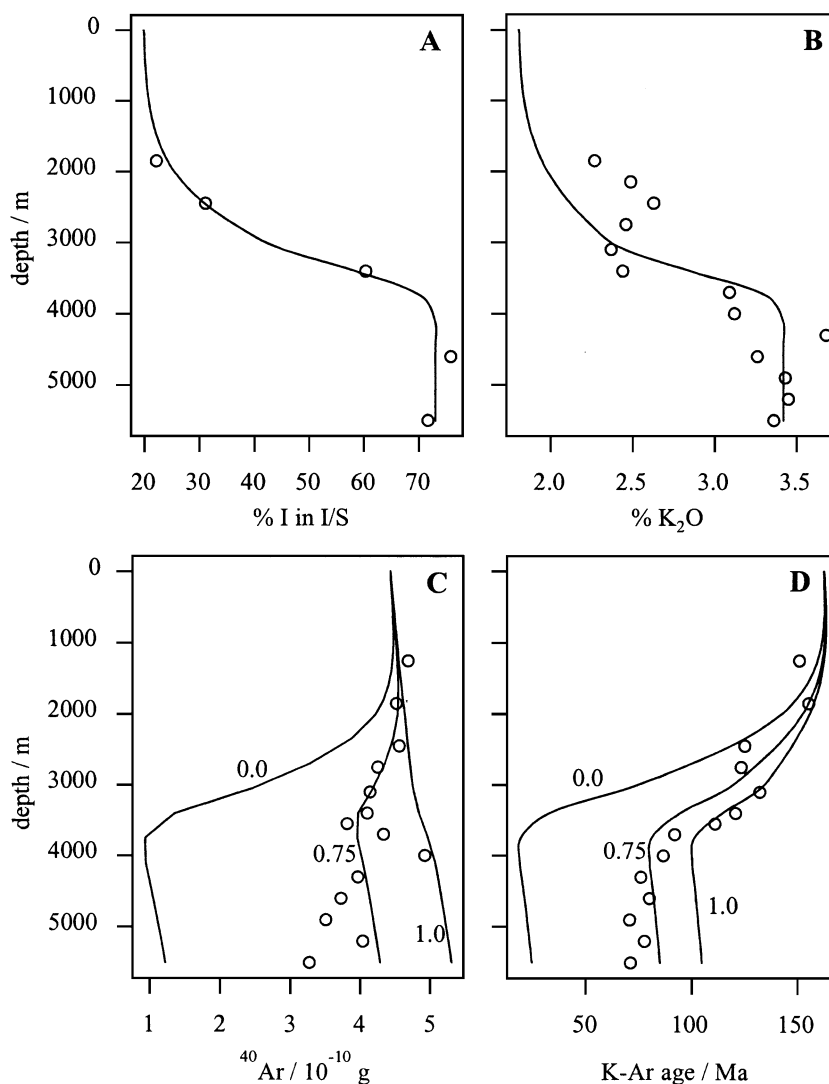


Fig. 2. Model of K–Ar ages for whole-rock data. (A) Proportion of I in I/S, (B) wt.% K_2O , (C) ^{40}Ar in moles per gram of solid rock, (D) calculated K–Ar age. For C and D include modelled curves for different % retention of ^{40}Ar within the solid rock during the dissolution of K-feldspar and the illitisation of smectite. “0.0” corresponds to total loss of ^{40}Ar to the porewater, “1.0” to total retention within authigenic illite.

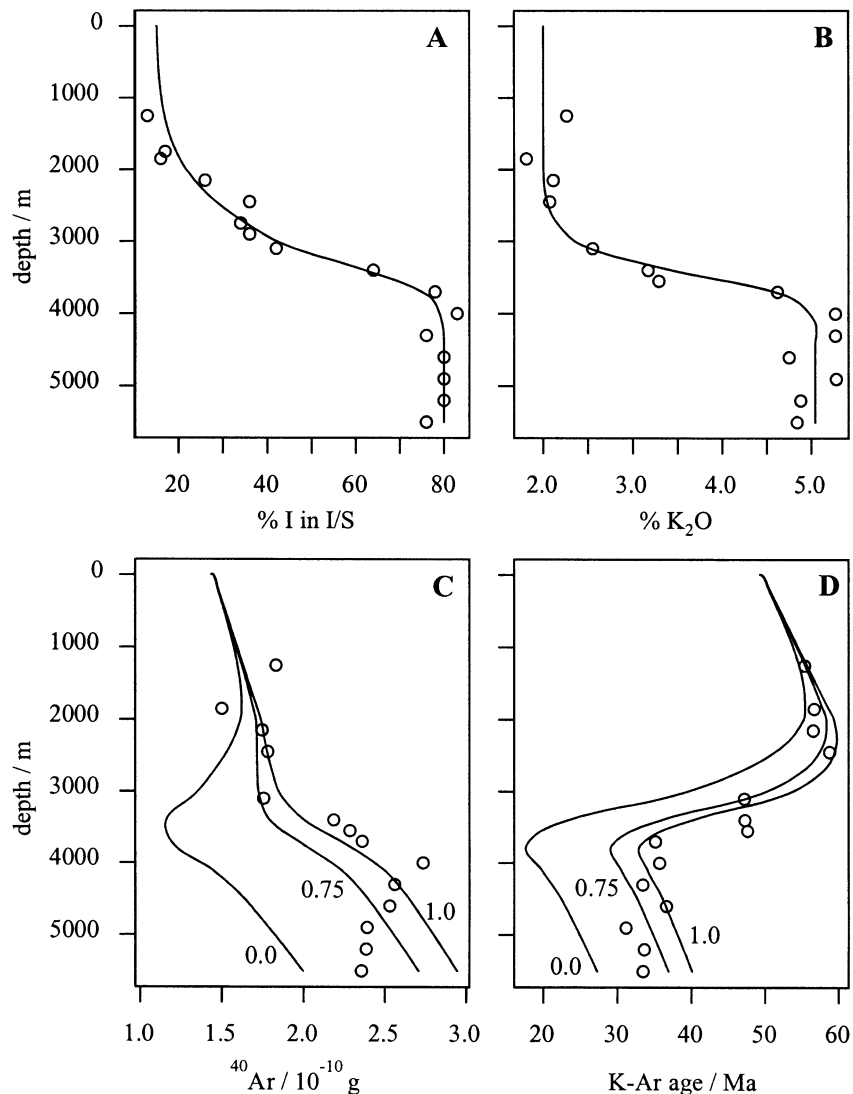


Fig. 3. Model of K–Ar ages for $<0.1 \mu\text{m}$ size fraction. See Fig. 2 for description.

though import of ^{40}Ar into the shale is not required. The fit of the model is poor below 4000 m, as discussed below.

The age of I/S ($<0.1 \mu\text{m}$) was set to 35 Ma at the time of deposition. For the whole-rock model, the ages of I/S, K-feldspar and detrital mica, and the initial amount of K-feldspar and detrital mica are inter-dependant. For example, 3% of K-feldspar and mica of 250 Ma BP age, with I/S set to 115 Ma at the time of deposition gives an almost identical result to 3% of K-feldspar of 400 Ma BP age, with I/S of 70

Ma at the time of deposition. This is the illustrated example (Fig. 2). These input data are constrained by having to match the age of shallow buried sediment, which has only a minimal diagenetic overprint.

4. Discussion

K–Ar data of Gulf Coast shales must be interpreted with reference to the mechanics of the smectite to illite reaction. Aronson and Hower (1976) assumed

that there was only a single, continuous reaction mechanism, which was supported using mineralogical evidence by [Ohr et al. \(1991\)](#). In contrast, [Eberl \(1993\)](#) reinterpreted the mineralogical and chemical data as showing three successive zones of reaction. Using data from a number of world-wide locations, [Velde and Vasseur \(1992\)](#) recognised only two reaction stages, which [Berger et al. \(1999\)](#) related to the source of K. The kinetic parameters of [Velde and Vasseur \(1992\)](#) predict a rate of reaction which is slightly too great for the Gulf Coast data. Hence, our model uses only a single reaction mechanism down to ca. 4000 m (when both the illitisation and K-feldspar reactions are complete), to produce an acceptable fit over this depth range ([Wilkinson et al., 1992](#)). Below this, there is continued ^{40}Ar -loss, which is not explained by the model. By implication, either a reaction is taking place at these depths, or Ar is leaking from the I/S by solid-state diffusion, as follows.

Based upon the study of Gulf Coast cored shale samples, [Lynch et al. \(1997\)](#) concluded that there is no evidence that the illitisation reaction actually stops at ca. 80% illite content, but continues perhaps to completion. Continued illitisation below 4000 m would allow for the loss of ^{40}Ar . Alternatively, ^{40}Ar could be lost during Ostwald ripening of the illite ([Eberl, 1993](#); [Inoue et al., 1988](#)). However, most of the supposed evidence for Ostwald ripening has been reinterpreted following detailed work by [Clauer et al. \(1997\)](#) and [Eberl et al. \(1998\)](#). Lastly, loss of ^{40}Ar by solid-state diffusion could be important at temperatures of 100–150 °C ([Aronson and Hower, 1976](#); [Hamilton et al., 1989](#)). It is unclear which of the above mechanisms is causing ^{40}Ar loss below 4000 m.

5. Uniform composition shale and K-metasomatism

That there are changes with depth in the composition of the shales within the Gulf Coast Tertiary has been undeniable since they were described by [Burst \(1959\)](#). The cause of these changes has been more controversial. Both, [Burst \(1959\)](#) and [Hower et al. \(1976\)](#) believed that these changes were of diagenetic origin, operating on precursor sediment of approximately uniform bulk composition. Recently, [Bloch et al. \(1998\)](#) disputed this assumption, claiming particu-

larly that the increase in K_2O with depth ([Figs. 2B and 3B](#)) is a primary effect of changing source area. This was strongly countered by [Lynch et al. \(1999\)](#).

The increase in K_2O with depth is observed at both the NE ([Hower et al., 1976](#)) and SW ([Lynch et al., 1997](#)) ends of the Texas Gulf coast, which were supplied by different paleo-river systems (the Mississippi and the Rio Grande, respectively), from different source areas. It seems unlikely that both source areas should undergo almost identical evolution over the time of deposition of the Frio Formation. Hence, the observed changes in shale mineralogy and chemistry with depth are here considered to be of diagenetic origin. Scatter in the real data is probably related to small variations in the proportion of K-bearing minerals in the original sediment, we assume that the *average* composition remains constant.

If the Frio Formation shales were initially of uniform bulk composition, then the increase in K_2O with depth must imply the open-system import of K (e.g. [Awwiller, 1993](#); [Land et al., 1997](#)). A corresponding export of K from interbedded sandstones has been observed ([Milliken et al., 1994](#)), though insufficient K is released from the sands to mass-balance the apparent import into the shales ([Wilkinson et al., 2002](#)). The source of the imported K is unknown, though K-metasomatism is an accepted phenomenon in other geological settings (e.g. [Beratan, 1999](#)). It might be expected that, if K were mobile during diagenesis, Ar would be also. The model does not constrain whether Ar is imported into the shales, but it does produce a reasonable fit to the real data without the need to import Ar.

6. Implications

The illitisation reaction within Gulf Coast shales has been described both as a progressive, continuous reaction, and as a series of events of limited duration. Event diagenesis is apparently supported by Rb–Sr ([Morton, 1985](#)) and Nd data ([Ohr et al., 1991](#)), and by the presence of ‘constant’ K–Ar age sediments over substantial depth intervals (e.g. ca. 33–35 Ma below 3500 m for the <0.1 micron size fraction of [Aronson and Hower, 1976](#); [Fig. 3D](#)). However, this ‘constant’ sediment age has also been attributed to diffusive Ar loss ([Aronson and Hower, 1976](#)) and to Ostwald

ripening (Eberl, 1993), as discussed above. As it is possible to model the K–Ar ages as the result of a continuous, temperature controlled, reaction, we follow Burst (1969) and Perry and Hower (1970) in assuming the illitisation is progressive and not episodic. Hence, the K–Ar ages of shales do not record diagenetic ‘events’, but are partly the result of the inherited detrital ages, and partly the result of resetting by diagenesis. As such, K–Ar ages from shales are meaningless unless carefully interpreted. This is in contrast to K–Ar ages of authigenic illites in sandstones, which do seem to record ‘events’, e.g. oil filling of a reservoir (Hamilton et al., 1992).

Our modelling implies that a high proportion (75–100%) of ^{40}Ar released by the dissolution of ‘old’ detrital phases is reincorporated into authigenic illite, as noted qualitatively by Clauer and Chaudhuri (1996). It is not possible to model the K–Ar ages with the ^{40}Ar from the dissolution of detrital phase being lost to the porewaters (Figs. 2 and 3). ^{40}Ar retention within the $<0.1\ \mu\text{m}$ size fraction (which is almost entirely I/S) is in excess of 75%. Hence, either the ^{40}Ar is retained during the illitisation reaction, implying a solid-state reaction mechanism, or the ^{40}Ar is released into the porewaters during detrital phase dissolution and subsequently incorporated into the growing illite in a manner analogous to the incorporation of the excess Ar. A solid-state mechanism for all or part of the smectite/illite reaction has been proposed (Hower et al., 1976; Eberl, 1993; Altaner and Ylagan, 1997), but has been opposed using petrographic evidence (e.g. Velde and Renac, 1996). As an alternative, it is possible that the Ar released into the porefluids by the dissolution of detrital minerals is swamped by imported Ar from the same source as the imported K, when conclusions about the illite/smectite reaction mechanism could not be drawn. The model cannot be used to constrain Ar import, only to state that an import of Ar is not required by mass-balance considerations.

7. Conclusions

The K–Ar ages of shales do not record diagenetic ‘events’, but are the result of progressive diagenesis acting upon detrital ages. This is true for both the whole-rock and clay mineral size fractions of the sediment. Without modelling, K–Ar of shales are

meaningless. This is in contrast to K–Ar ages of authigenic illites in sandstones, which do seem to record geological ‘events’.

The ^{40}Ar incorporated into authigenic illite corresponds to between 75% and 100% of ^{40}Ar released by the dissolution of detrital phases. The proportion retained is highest for the clay-mineral fraction of the sediment. Presuming that Ar import into the formation is minor, then this is consistent with a solid-state illitisation reaction, when the ^{40}Ar remains trapped within the clay lattice. If Ar import into the formation (along with K) is important, then no constraints can be put upon the mechanism of the illitisation reaction, as the Ar may be incorporated into the authigenic illite in a manner analogous to ‘excess Ar’. The model does not constrain import of Ar into the shales, though import is not required for mass-balance.

The assumption that the Frio Formation had a uniform initial (detrital) composition, both in terms of mineralogy and K–Ar age, results in a reasonable model for K–Ar ages. This does not prove that the Frio had a uniform initial composition, but is at least consistent with it.

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