

SHORT PAPER

**Mineralogical and chemical variation of francolites with geological time**

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**Francolites, carbonate fluorapatites, occur in temporally and spatially related sedimentary phosphorite deposits that range in age from the Proterozoic to the Neogene. Previous mineralogical studies of francolites have established that systematic relationships exist between chemical composition and crystallographic data. The unit-cell dimensions and indices of refraction of francolites decrease with increasing substitution of  $\text{CO}_3^{-2}$  for  $\text{PO}_4^{-3}$  in the francolite structure. Accompanying cation substitutions of  $\text{Na}^{+1}$  and  $\text{Mg}^{+2}$  for  $\text{Ca}^{+2}$  also are significant. Fluorine contents of more than 2 moles/unit-cell also are typical of francolites, and the 'excess' fluorine is related to the basic  $\text{CO}_3^{-2}$  for  $\text{PO}_4^{-3}$  substitution.**

Francolites are thermodynamically metastable with respect to fluorapatite. Studies of francolites from deposits of various geological ages demonstrate systematic trends in chemical composition and crystallographic properties with time. Francolites in rocks of Palaeozoic or older ages usually have compositions close to fluorapatite. Mesozoic and younger francolites have wide range of compositions that vary with the type and intensity of post-depositional alteration. These alteration processes can result in mobilization of cations and anions, decarbonation of the francolite, and changes in crystallographic properties. The extent and intensity of alteration processes often are restricted by variations in francolite composition and associated accessory minerals.

Recent publications (e.g. in Notholt & Jarvis 1990), summarizing the state of research on phosphorites, have shown that considerable progress has resulted from more than a decade of intense work on this topic. But as Cook *et al.* (1990) have noted in their historical review of phosphorite research, more work is needed in such areas as the palaeoenvironmental implications of phosphorite formation. Before such work can be properly interpreted, a better understanding of the mineralogical variation of francolites, carbonate fluorapatites, in phosphorite deposits is required.

**Distribution of phosphorites in time and space.** Prior to 1979, there was little systematic information on the distribution of phosphorites through geological time. Then, applying the principles of plate tectonics, Cook & McElhinny (1979) compiled several types of data on the distribution of sedimentary phosphorites in the geological record which showed there were times in earth history when phosphorites were preferentially deposited. From these data, Cook & McElhinny (1979) formulated models to explain the spatial and temporal distribution of phosphorites through earth history. These models indicated that phosphorites were most commonly associated with low latitudes, warm climates, and conditions favouring oceanic upwelling on continental shelf areas. Such

favourable conditions occasionally have occurred during geological time resulting in phosphorite deposition. More recent work (see Cook *et al.* 1990, for the literature review) has confirmed and elaborated on this model of the non-uniform deposition of phosphorites.

**Mineralogy and chemistry of francolites.** Because of the economic significance of phosphorite deposits, considerable work has been done on the mineralogy of francolites (McClellan & Van Kauwenbergh 1990 and references therein). Summaries of the various substitutions proposed for francolites and other apatites have been presented by McClellan (1980) and McConnell (1973). These studies have established that the mineralogy of sedimentary francolites is characterized by a systematic series of anion and cation substitutions. The fundamental  $\text{CO}_3^{-2}$  for  $\text{PO}_4^{-3}$  substitution takes place in a 1:1 ratio and about 30% of the  $\text{PO}_4^{-3}$  can be replaced by  $\text{CO}_3^{-2}$ . Electro-neutrality of the francolite structure is preserved by accompanying cation substitutions ( $\text{Na}^{+1}$  and  $\text{Mg}^{+2}$  for  $\text{Ca}^{+2}$ ) and  $\text{F}^{-1}$  for  $\text{O}^{-2}$  at some  $\text{CO}_3^{-2}$  for  $\text{PO}_4^{-3}$  sites. The latter substitution results in the 'excess' fluorine (i.e., the fluorine in excess of that present in fluorapatite) commonly observed in francolites. The unit-cell dimensions (particularly the *a*-value) and index of refraction vary systematically with these various substitutions. In general, the unit-cell *a*-value and the indices of refraction decrease with increasing  $\text{CO}_3^{-2}$  for  $\text{PO}_4^{-3}$  substitution. Thus, variations in these parameters can be used to detect changes in francolite composition.

**Stability of francolite.** Chien & Black (1976) determined the solubility products ( $K_{sp}$ ) for a series of mineral francolites and showed that their calculated free energies of formation increased linearly with increases in the number of moles of carbonate/mole of francolite. This study clearly established the metastability of members of the francolite series with respect to fluorapatite, the stable end member. Geochemical metastability is a particularly important concept in understanding the alteration of francolites in ancient sediments.

Once francolite has formed under a given set of conditions, any change in the conditions will cause the francolites to alter to form with a lower free energy of formation (i.e., a less  $\text{CO}_3^{-2}$  substituted francolite and ultimately, fluorapatite. In the experience of the authors, there are no known examples of a reversal of this process (i.e., francolites gaining  $\text{CO}_3^{-2}$  substitution after deposition). The details of this francolite decarbonation process are unknown, but may involve some dissolution and re-precipitation steps. Also, the process's activation energy is unknown, but must be low because the effect has taken place at or near the surface in several deposits.

Low temperature and pressure diagenesis, and weathering also can affect francolite mineralogy. Most of the literature on phosphorite alteration has been based on the deposits of the southeastern United States (North Carolina and Florida) and West Africa (Van Kauwenbergh & McClellan 1990; Flicoteaux *et al.* 1977). In these deposits, low temperature alteration has led to the systematic decarbonation of francolites, resulting in a wide range of

apatite compositions as well as the formation of some Fe–Al phosphates. The clay minerals associated with these phosphates also show systematic alterations (McClellan & Van Kauwenbergh 1990).

In 1967, Lehr *et al.* showed that the thermal stability of francolites decreased as the  $\text{CO}_3^{2-}$  for  $\text{PO}_4^{3-}$  substitution increased. Calcination at temperatures as high as 1000 °C resulted in progressive alteration of francolites to fluorapatite with attendant losses in structural  $\text{CO}_2$  and a systematic change in unit-cell  $a$ -values. Thermal effects of metamorphism may have contributed to the variation in francolite  $\text{CO}_2$  values that have been interpreted as resulting from palaeoenvironmental controls on the deposition of the Permian Phosphoria Formation by Gulbrandsen (1970). McArthur (1985) showed the Na and  $\text{CO}_2$  contents of francolites from the Phosphoria Formation could be correlated to the depth of burial across the region. Mathews & Nathan (1977) used francolite decarbonation as a palaeotemperature indicator for thermally metamorphosed rocks of the 'Mottled Zone' in Israeli phosphorites. The thermal alteration of francolites can be an important factor in changing their composition through geological time although these effects may not always be apparent in the deposit or sample.

Five of the six samples that Chien & Black (1976) used in their study were ground to –200 mesh and extracted with ammonium citrate to remove free carbonates, washed with water, and dried for 16 hours at 105 °C. One-gram portions of each sample then were heated for 1 hour in open platinum crucibles at 500°, 600°, 700°, 800°, and 950 °C. Each calcined product was chemically analysed and its unit-cell  $a$ -value was determined. The results (Figs 1 and 2) show a decrease in thermal stability of the francolite with increasing  $\text{CO}_3^{2-}$  for  $\text{PO}_4^{3-}$  substitution. The most highly substituted francolites begin losing their  $\text{CO}_2$  between 500° and 600 °C (Fig. 1); those with intermediate substitution begin losing  $\text{CO}_2$  between 600° and 700 °C; and those with the lowest substitution begin losing  $\text{CO}_2$  between 700° and 800 °C. After calcination at 950 °C, all samples contain less than 0.5%  $\text{CO}_2$ .

The unit-cell  $a$ -values of the francolites also changed regularly during calcination (Fig. 2) and approached the  $a$ -value of fluorapatite (9.370 Å). The data show that the thermal decarbonation of francolite is a gradual structural alteration rather than an abrupt decomposition to form fluorapatite. This result suggests that during calcination the decarbonation of francolite can occur by solid state transformation and does not necessarily require dissolution and reprecipitation.

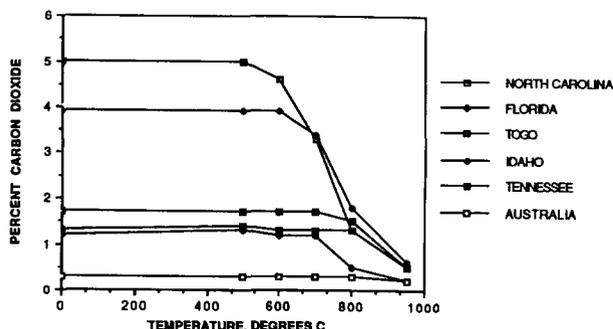


Fig. 1. Changes in carbonate content of francolites (arranged by increasing geological age) with calcination.

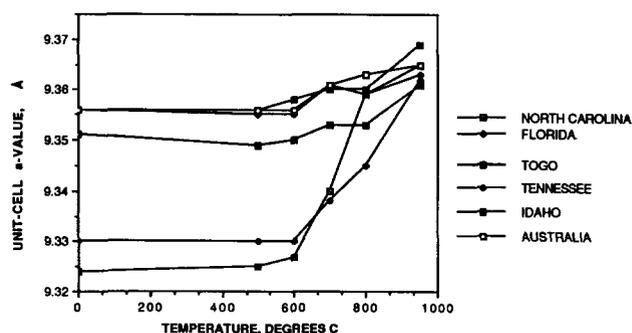


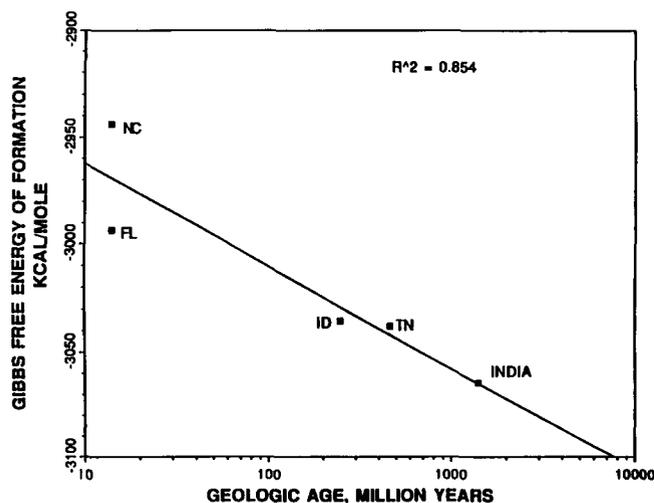
Fig. 2. Changes in unit-cell  $a$ -values of francolites (arranged by increasing geological age) with calcination.

Interestingly, the results in Figs 1 and 2 also show a trend in the thermal stability of francolites with geological time. The geologically youngest samples (North Carolina and Florida from middle Miocene sediments) also are the francolites with the highest degree of  $\text{CO}_3^{2-}$  for  $\text{PO}_4^{3-}$  substitution and show the greatest changes during calcination. The Idaho (Permian) and Tennessee (Ordovician) samples are geologically older, have lower amounts of  $\text{CO}_3^{2-}$  for  $\text{PO}_4^{3-}$  substitution and show smaller changes during calcination. The Australian (Cambrian) and igneous fluorapatite show only small changes during calcination because they contain little or no  $\text{CO}_3^{2-}$  for  $\text{PO}_4^{3-}$  substitution.

**Composition of francolite.** Over the past 25 years, a considerable database has been developed and interpreted on francolite. Yet, the question of the 'original' or 'primary' composition of francolite has received little attention. In 1978, McArthur proposed the hypothesis of an 'original constant composition' for francolites suggesting that most francolites formed with nearly the same crystal chemical composition. These 'original' francolites could then be altered by a variety of processes to form the variable mineral species that is seen today. McClellan (1980) presented data to support this hypothesis and proposed that weathering, metamorphism, and time could combine to alter highly  $\text{CO}_3^{2-}$  substituted francolites to fluorapatite compositions. McArthur (1985) modified his position on the 'original constant composition' hypothesis, feeling that it oversimplified the problem and underestimated the effects of post-depositional alteration processes.

McClellan & Lehr (1969) used their statistical models to predict that the maximum  $\text{CO}_2$  of francolite would be about 6.3 wt%. This would represent the 'original' francolite composition based on their data. McArthur (1985) later reached a similar conclusion using a smaller database of Eocene to Recent samples. Glenn *et al.* (1988) determined that 6.0 wt%  $\text{CO}_2$  was the maximum found in Recent francolite nodules from the Peru–Chile margin. McClellan & Van Kauwenbergh (1990) report the maximum  $\text{CO}_2$  of francolites is between 6 and 7 wt% for a series of Eocene and younger francolites that show little or no evidence of post-depositional alteration.

Thus the various studies seem to show that no single composition may represent the 'original' or 'primary' francolite. The 'original' composition may vary over a narrow range in response to variations in environments of

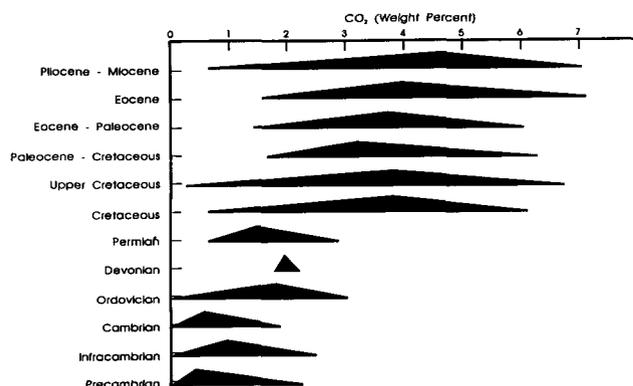


**Fig. 3.** Variation of free energy of formation with geological age for some francolites. Sample designations are Florida (FL), North Carolina (NC), Tennessee (TN), and Idaho (ID).

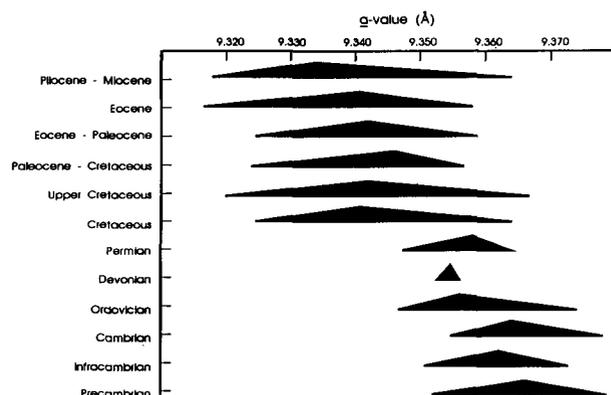
deposition of phosphorites. Bendor (1980) has pointed out that important differences exist between present and past phosphorite deposition. He proposed that most Recent phosphorite deposits formed by diagenetic processes below the sediment-water interface, while many older phosphorites formed on the sea floor above this interface. He concluded that phosphorite deposition in the past took place in several ways, only one of which is operating today.

**Variation in composition with geological time.** When Chien & Black's data (1976) are presented on a semi-logarithmic plot (Fig. 3) of geological time versus free energy of formation, clearly a systematic relationship exists. The statistical correlation is good even with the wide variation in data reported for the North Carolina and Florida samples of approximately the same geological age. The variation in thermodynamic data observed in these two samples represents differences in their  $\text{CO}_3^{2-}$  contents and the intensity of post-depositional alteration that must be considered when using Neogene phosphorites as indicators of palaeoenvironments or palaeoclimates.

When a large database of francolite samples is used, the changes in  $\text{CO}_2$  contents (Fig. 4) and francolite unit-



**Fig. 4.** Range in  $\text{CO}_2$  content of francolites of varying geological ages (472 samples from 165 deposits).



**Fig. 5.** Variation of unit-cell  $a$ -values of francolites of varying geological ages (472 samples from 165 deposits).

cell  $a$ -axis values (Fig. 5) with geological time show some regular trends in the data. There is a systematic decrease in the  $\text{CO}_2$ -contents and an increase in unit-cell  $a$ -values (i.e., decarbonation of francolite) with increasing geological time. The lengths of the horizontal lines in these figures represent the range of values, and the triangular peak shows the average value for each line of data. McClellan (1980) first reported this trend of the transformation of metastable francolites toward fluorapatite compositions with geological time using a much smaller database.

The results presented in Figs 4 and 5 clearly show that Mesozoic and Cenozoic phosphorites contain a wide range of francolite compositions varying from the highest degrees of  $\text{CO}_3^{2-}$  for  $\text{PO}_4^{3-}$  substitution to nearly zero substitution (essentially fluorapatite). Permian and older phosphorites have a narrow range of francolite compositions. Geochemical metastability is an important factor resulting in decreasing  $\text{CO}_2$ -contents and a narrowing of francolite compositions with increasing geological time (vertical axes in these figures).

Weathering, diagenesis, and metamorphism also can alter the  $\text{CO}_2$ -contents and range of francolite compositions (the horizontal axes in these figures). The extent and intensity of these alteration processes are quite variable. The wide variation in francolite compositions in Cretaceous and younger phosphorites is mainly attributed to these processes.

The result of these two types of processes (time and alteration) over geological time is the same; conversion of francolite to fluorapatite. Unless the geological history of a phosphorite is well known, it may not be possible to separate the effects of time and alteration processes. However, these effects must be considered when interpreting the geological history of francolites and possible palaeoenvironmental conditions during deposition.

Assuming that the francolites with the minimum  $a$ -values for each time period are the least affected by diagenetic, weathering, and metamorphic processes, the minimum  $a$ -values from Fig. 5 were plotted on a semi-logarithmic scale versus the geological age (Fig. 6). The result shows systematic changes in crystallographic properties (and implied crystal chemical compositions) for much of Phanerozoic and Proterozoic time. The data are non-uniformly distributed because of the spatial and temporal controls on phosphorite formation discussed in

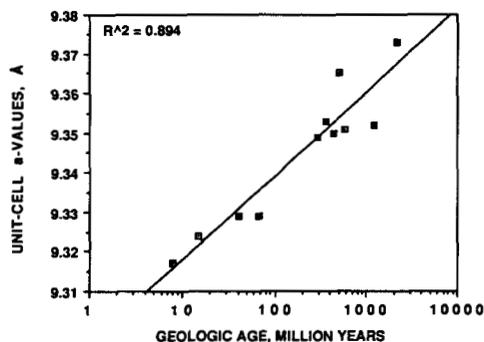


Fig. 6. Variation in minimum measured unit-cell  $a$ -values of francolites of varying geological ages. Note that the age scale is logarithmic.

Cook & McElhinny (1979) and others in more recent publications.

The good semi-logarithmic correlation of the minimum  $a$ -values through Phanerozoic time could be interpreted as support for the 'original constant composition' hypothesis for francolites (McArthur 1978). While the data may be inadequate to suggest a single 'original' francolite composition, the strong correlation shows some unifying compositional trend. Part of this trend is explained by the processes of decarbonation and recrystallization. From this large francolite database, it seems a simple, progressive relationship exists between the 'original', high degree of  $\text{CO}_3^{2-}$  for  $\text{PO}_4^{3-}$  substituted, metastable francolite and the final francolite compositions found in sediments today.

**Geological implications.** As Cook *et al.* (1990) have suggested, phosphorites have been inadequately studied as indicators of palaeoenvironmental conditions. The results of this study show that detailed studies of the geochemistry of phosphorites need to be tempered with the knowledge that these are dynamic materials that often are being changed by a variety of geological processes. The significance, intensity, and extent of these changes must be considered when interpreting the results of petrographic, mineralogical, trace element, and isotope geochemical studies.

This improved model of the systematic relationship of variations in francolite compositions with geological time can be used as a guide in assessing the extent of change that may have occurred in phosphorite deposits. In addition, data collected on diverse samples can now be compared, quantitatively, with the results of this francolite database. As the database on francolites continues to expand and is

analysed with improved methods, relationships will be refined and redefined that will further our understanding of phosphorites. While much progress has been made, much remains to be done.

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