

LETTER

Alpha-decay-induced condensation of phosphate anions in a mineral

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ABSTRACT

Griphite is a U-Th-bearing phosphate mineral with the unusual property that structural alterations due to the radioactive decay of U and Th are preserved over geologic time periods. Results of differential scanning calorimetry show that the recrystallization temperature required for the annealing of displacive damage in griphite is relatively high, and, therefore such damage can accumulate unchecked with time. Accordingly, griphite that contains U or Th occurs in the amorphous or metamict state unlike other U-Th-bearing phosphate minerals (e.g., monazite) that are found in the crystalline state even after large displacive radiation doses. In its crystalline form, griphite has a structure in which isolated phosphate anions are bonded to adjacent metal cations. In this work, however, linked phosphate groups (i.e., chains of PO₄ tetrahedra) have been detected in metamict, amorphous U-Th-bearing griphite by means of a chromatographic technique. The occurrence of such linked phosphate units in mineralogical systems is unusual, since the P-O-P bond is relatively easy to hydrolyze.

INTRODUCTION

Naturally occurring phosphate crystals are, in general, monophosphates, i.e., the phosphate anions are isolated structural units and are not directly joined to other phosphate tetrahedra. One somewhat questionable exception is the mineral canaphite, α -CaNa₂P₂O₇·4H₂O (Rouse et al., 1988). Although the occurrence of linked PO₄ units in a phosphate mineral is unusual [probably due to hydrolyzing of the P-O-P bonding (Byrappa, 1983; Liebau, 1970)], synthetic phosphates can be prepared with a wide range of condensation where the PO₄ tetrahedra are linked to form short chains, ring structures, etc. For both crystalline and amorphous phosphate materials, it is possible to determine the type and distribution of phosphate anions present in the structure by means of the technique of high-performance liquid chromatography (Brazell et al., 1984; Sales et al., 1986, 1989, 1990; Sales and Boatner, 1987). In particular, this technique has recently been used to show that for lead pyrophosphate crystals that were rendered amorphous by energetic ion bombardment, the displacive radiation damage produces both a splitting of the basic pyrophosphate unit (i.e., two corner-linked PO₄ tetrahedra) and a condensation of these units to form longer chains of PO₄ tetrahedra (Sales et al., 1989, 1990).

Griphite is a relatively rare mineral occurring in only six known localities and, thus far, only in granite pegmatites. Griphite occurs in large masses up to 1 m³, but the timing of its crystallization during the cooling of a

pegmatite magma is problematic. It could be a product of subsolidus solid-state replacement of a primary phosphate mineral or the result of primary crystallization from the pegmatite melt (Moore and Molin-Case, 1974). In the latter case, the large masses once were probably large single crystals.

The exceptional ability of the phosphate mineral griphite to preserve α -decay damage over long time periods is exemplified by samples from granitic pegmatites in the 1700 Ma Harney Peak intrusive complex, Black Hills, South Dakota (Peacor and Simmons, 1972). Those griphite samples are amorphous, as determined by both X-ray diffraction (XRD) and electron diffraction. As previously noted, such long-term retention of displacive radiation damage in the form of an amorphous phase (i.e., metamictization) has not been observed for other well-known U- and Th-bearing phosphate minerals, such as monazite or xenotime, that have received integrated doses in excess of 10¹⁷ α -decay events per mg (Ewing et al., 1987; Boatner and Sales, 1988).

METHODS

Uncovered petrographic thin sections of metamict griphite from the Sitting Bull pegmatite, near Keystone, Pennington County, South Dakota, were used to record autoradiographs using Kodak direct exposure X-ray film and exposure times of about 3 weeks. A powdered aliquot of the metamict sample was dissolved in nitric acid and the U and Th contents were determined by inductively

coupled plasma atomic-emission spectroscopy. Assuming a formation age of 1700 Ma, the accumulated α -decay dose in units of α -decay events per milligram was computed using the procedure of Holland and Gottfried (1955).

Several pieces of the metamict graphite were recrystallized by heating them in Ar to 600 °C at 10 °C/min in a Perkin-Elmer DSC-4 differential scanning calorimeter. A thermogravimetric analysis scan was also recorded using a Perkin-Elmer instrument to determine the extent of weight loss accompanying the recrystallization. The hydrous component in the metamict sample, prepared as a doubly polished section, was determined by infrared absorption spectroscopy using a Nicolet spectrometer.

X-ray powder diffraction patterns were recorded for both metamict and recrystallized graphite using $\text{CuK}\alpha$ radiation and a Scintag diffractometer equipped with a high-purity Ge detector. Powdered aliquots of both metamict and recrystallized graphite were also deposited onto holey C films supported by a Ni grid for examination in a transmission electron microscope. Thin edges of grains were examined with a Philips EM 400 microscope operated at 100 kV. Selected area electron diffraction patterns were recorded to determine the crystallinity, and qualitative elemental analyses were made using an ORTEC system for energy-dispersive analysis of X-rays to determine the phase homogeneity.

Liquid chromatograms of metamict graphite and the same sample recrystallized in the differential scanning calorimeter were made to determine the size distribution of phosphate anions. Each sample was first ground into a fine powder and then dissolved in an aqueous solution of 0.22 M NaCl and 5 mM Na_4EDTA . The EDTA is a chelating agent that effectively surrounds the metal cations as they are released from the dissolving sample. This acts to prevent metal ions in solution from reacting with phosphate anions that are also released from the dissolving sample. Once the phosphate chains are in solution, the solution is injected into a high-pressure liquid chromatography (HPLC) system that separates the phosphate chains on an anion-exchange column. By increasing the NaCl concentration, the phosphate anions are sequentially released from the exchange column. Back in the reagent stream, the phosphate anions are hydrolized to monophosphate and form complexes with Mo so that the relative concentration of phosphorous present in each chain type can then be determined by an optical absorption method. The HPLC system was calibrated using a standard mixture of known crystalline phosphates.

RESULTS

The HPLC technique has been used to detect condensed phosphate anions in the α -decay-damaged mineral graphite, a complex monophosphate ($\text{Li}_{0.36}\text{Na}_{7.05}\text{-Ca}_{0.99}\text{Mn}_{15.60}\text{Fe}_{1.14}\text{Ca}_4(\text{Fe}_{1.14}^{2+}\text{Fe}_{0.37}^{3+}\text{Mn}_{1.49}\text{□}_{1.00})_{24}(\text{Al}_{7.14}\text{Fe}_{0.86}^{3+})_{28}(\text{PO}_4)_{23.3}(\text{OH})_{0.7}(\text{F}_{7.1}\text{Cl}_{0.3}\text{OH}_{0.6})_{28}$ (Rinaldi, 1978; Fontan et al., 1978). The results of an HPLC analysis of metamict

graphite from the Black Hills, South Dakota, are illustrated in Figure 1, which shows peaks corresponding to 89% PO_4 monomers (P_1), 10% P_2O_7 dimers (P_2), 1% P_3O_{10} trimers (P_3), and $\ll 1\%$ P_4O_{13} tetramers (P_4). These results show that the metamictization process in graphite has produced structural alterations leading to the condensation of the monophosphate units initially present in the crystalline phase to form phosphate chains consisting of both two- and three-linked phosphate tetrahedra.

Metamict graphite samples were annealed by heating at 10 °C/min in Ar to 600 °C in a differential scanning calorimeter (DSC) to recrystallize the radiation-damaged amorphous phase of the material. The HPLC results for such a recrystallized specimen are shown in Figure 1b. These results show that, following the thermal treatment, the recrystallized material consists of 99% P_1 or monophosphate units with $< 1\%$ P_2 remaining and no detectable (i.e., $\ll 1\%$) P_3 trimers. An XRD powder analysis of this recrystallized graphite sample showed only the presence of crystalline graphite, and no other phases were detected—results that confirm the HPLC analysis.

The results of the DSC analysis show that recrystallization of graphite occurs at ~ 500 °C in an Ar atmosphere with a heating rate of 10 °C/min (Fig. 2a¹). A comparison of the DSC results with those obtained by thermogravimetric analysis (Fig. 2b¹) shows that, at this temperature, a weight loss begins, abruptly at first (0.1 wt%), then gradually rises to 800 °C (0.4 wt% in total), and finally proceeds more rapidly to the measurement limit of 950 °C (2.8 wt% in total). A loss of 0.44 wt% corresponds to one H_2O per formula unit. As the metamict graphite recrystallizes, nonessential H_2O that is incorporated in the metamict state is expelled. In graphite, one might expect H_2O to be incorporated as OH groups or possibly as an H_2O substitution for PO_4 —a suggestion made by Rinaldi (1978) and Fontan et al. (1978). The infrared absorption (IR) spectrum from a polished section of metamict graphite shows a broad absorption band peaking between 3520 and 3400 cm^{-1} , which is indicative of OH stretching modes in a variety of structural environments. Such water of hydration is a common feature of metamict minerals from the terrestrial environment. The absence of an IR absorption band at 1650 cm^{-1} , corresponding to the bending mode of molecular H_2O , suggests that the hydrous component of metamict graphite is not molecular H_2O . The heat released during recrystallization of the metamict graphite is 150 J/g (36 cal/g), which is comparable to the range of 125–210 J/g determined for α -recoil-damaged minerals of the pyrochlore type (Lumpkin et al., 1986).

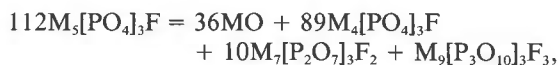
The U and Th contents of the graphite specimens used in this investigation were determined by inductively coupled plasma atomic-emission spectroscopy to be 2100 \pm

¹ A copy of Figure 2 may be ordered as Document AM-90-445 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

100 ppm and 230 ± 20 ppm, respectively. Autoradiographs of thin sections of griphite show that the U and Th are evenly dispersed. Assuming a formation age of ~ 1700 Ma, the accumulated radiation dose is 8.8×10^{14} α -decay events/mg. In contrast to the well-defined saturation dose for zircon and thorite of $\sim 1 \times 10^{16}$ α -decay events/mg, the saturation dose for griphite must be at least one order of magnitude lower.

DISCUSSION

In the condensation of phosphate anions in metamict griphite, the conversion of monophosphate units into polyphosphate chains of length n does not conserve mass and charge in the material by means of the phosphate anions alone, and free metal oxide must be produced. For metamict griphite, the condensation reaction is $P_1 \rightarrow 89\% P_1 + 10\% P_2 + 1\% P_3 + \ll 1\% P_4$, to which free metal oxide must be added for mass and charge balance, assuming that the number of ions is fixed and the system is closed. If a substantial loss or gain of ions had occurred for metamict griphite, then the recrystallization by annealing would not restore the single-phase parent structure. Using a simplified formula for griphite and ignoring the small amount of P_4 , a balanced condensation reaction can be written.



where M represents the different collections of metal cations that neutralize the anion charge. This particular balanced reaction maintains, for each of the phosphate anions, the same P:F ratio and the same average metal charge, but not the same M:P ratio. The average metal charge associated with each phosphate anion and the free metal oxide could be somewhat higher or lower than two, depending on the actual F contents and M:P ratios of these components. In griphite, the various metal cations (Li, Na, Al, Ca, Mn, Fe) with a wide range in relative ionic radii (0.53 to 1.02 Å) and formal valences (+1, +2, +3) create numerous possible combinations for M . Balanced reactions involving combinations of free metal oxide and free oxide are also possible.

The role of the nonessential H_2O in metamict griphite is not clear, but presumably it has reacted to form OH groups [i.e., $MO + H_2O = M(OH)_2$] that effectively dilute the anion charge and may provide additional stability to the structure of the metamict state (Aines and Rossman, 1986).

The structures of phosphate glasses formed by quenching melts have recently been shown to be different from those of amorphous phosphates produced by energetic ion bombardment (Sales et al., 1989, 1990). This result is not totally unexpected because, for the two cases, the processes that destroy the lattice periodicity are essentially quite different. In melting a crystal and quenching the melt to form a glass, the long-range lattice periodicity is lost, but the short-range order (such as the PO_4 unit)

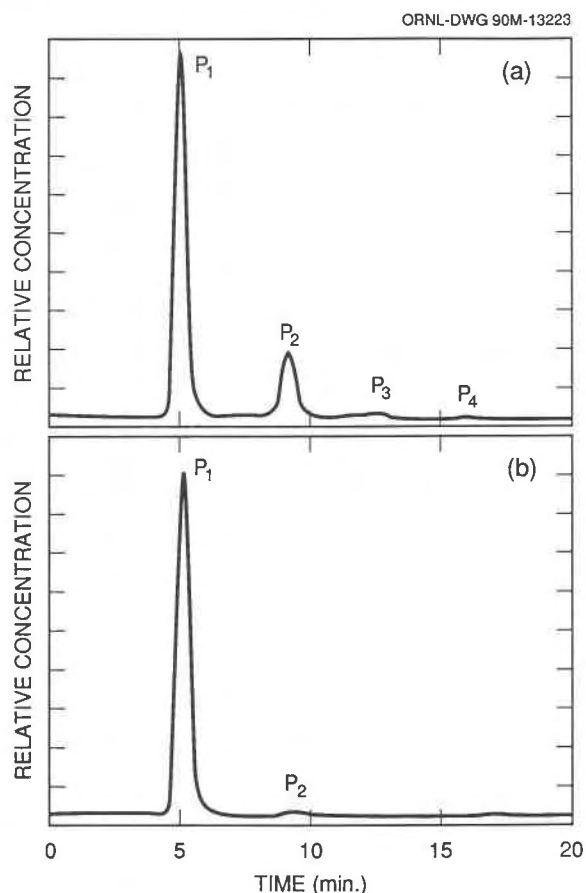


Fig. 1. Liquid chromatograms of (a) natural, unaltered metamict griphite from the Sitting Bull pegmatite, Keystone, South Dakota, and (b) the same sample heated to 600 °C at 10 °C/min under flowing Ar in a differential scanning calorimeter. The amount of phosphate present in linear tetrahedral chains of length i is proportional to the area under the peak labeled P_i .

persists. Structural reorganization is thermally activated and occurs by atomic diffusion, and the equilibrium distribution of the phosphate chains that form on cooling depends on the chemical composition and intensive conditions, such as the pressure, temperature, f_{O_2} , etc. of the melt.

In the case of energetic ion bombardment, however, the lattice damage occurs catastrophically, under highly nonequilibrium conditions with each bombarding ion producing a cascade of a few thousand displaced atoms that extends for many unit cells in the crystal. During the cascade, even short-range order is disrupted, but subsequently short-range order is reestablished. The process of metamictization is simply an energetic ion bombardment occurring within the initially crystalline mineral, where the bombarding ions are recoiling nuclei (and α particles) from the α decay of constituent U and Th. In the case of amorphization by ion bombardment, Sales et al. (1989, 1990) have suggested that local variations created in the chemical composition, plus the requirement of electro-

static neutrality, may be the driving force for the creation of the longer phosphate chains. In the case of a mineral such as graphite, this process may also be aided or stabilized by the conversion of absorbed H_2O molecules into OH ions, which then bind to the available metal cations (Aines and Rossman, 1986).

The ability of a mineral to maintain structural order for a given dose of energetic ions generated by α decay of constituent U and Th depends, in part, on how readily crystallinity can be restored during and after the ongoing damage process. The activation energy for recrystallization apparently depends in a complex way on the nature of the chemical bonding in the crystal and its structural complexity (Naguib and Kelly, 1975). In the case of monazite, a mixed U-Th-bearing rare-earth monophosphate, the existing evidence indicates that although it is relatively easy to produce displacive radiation damage, it is also relatively easy to anneal this damage at a low temperature and, hence, monazite occurs in nature in the crystalline rather than metamict state even after large radiation doses (Boatner and Sales, 1988; Karioris et al., 1981).

Graphite remains metamict over geologic periods of time in contrast to other well-known U-Th-bearing phosphate minerals (e.g., monazite, xenotime) that are found in the crystalline state even after large integrated radiation doses. For graphite, the results of an analysis by DSC reveal a relatively high temperature of recrystallization [~ 500 °C, as compared to 227 °C for monazite (Karioris et al., 1981)] and, thus, radiation damage can more readily accumulate with time. For graphite the present structural analysis by HPLC techniques shows that displacive radiation damage is manifested in the formation of linked phosphate groups.

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