American Mineralogist, Volume 74, pages 936–937, 1989

Silver fluoride (AgF) as a source of fluorine in experimental petrology

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ABSTRACT

Silver fluoride (AgF) is an effective method of introducing F as a component in experimental petrology when it is essential to introduce F in a form that does not add other silicate-compatible cations to the system and when the introduction of OH must be avoided. AgF decomposes during the experimental run, releasing F to the system; Ag is dispersed through the charge at lower temperatures and plates onto or alloys with the enclosing Au capsule at higher temperatures. AgF is inexpensive and readily available and, although somewhat deliquescent, presents no problems when stored carefully and when capsules are loaded in a sealed dry-box.

INTRODUCTION

F is an important element in many rock-forming minerals and usually has a significant effect on their stability field, yet it has been a difficult element to work with and to control in experimental petrology. One of the earliest studies is that of Wyllie and Tuttle (1961) in which the effect of F on granite liquids was established. There followed the pioneering work on F-buffered systems by Munoz and Eugster (1969), and then a detailed analysis of the fluoride-hydroxyl exchange involved in the established F buffer technique (Munoz and Ludington, 1974).

All of this work involved F and H_2O since it was concerned with water-bearing magmas or with the (OH-F) substitution in silicate minerals. There are times, however, when it is necessary to study the effect of F on liquids in isolation from water. Foley et al. (1986) have used MgF_2 for this purpose on the principle that it substitutes directly for MgO by the exchange vector F_2O_{-1}. CaF_2 can also be used; it melts to an ionic liquid with F present as loosely bound ions. Other fluorides such as NaF or KF can be used in the same way if compatible with the system being studied. The main drawbacks to this approach, however, are that F is introduced in the stoichiometric proportions of a compound and there is some uncertainty about what is changing the properties of the liquid: dissolved CaF_2, Ca, or F. It is not clear whether the fluoride ions are able to react freely with all other cations in the liquid or whether they form complexes, such as with Ca (Forland, 1957; Levy and Danford, 1964; Lumsden, 1966). There is, therefore, no certainty that F is present in excess of the stoichiometric requirements of a mineral such as fluorite (CaF_2) or villiaumite (NaF). A further problem with fluoride compounds is that they introduce other cations that may change the composition of the system in an undesirable way. The ideal is some way of adding F alone.

Clemens (1984) suggested palladium fluoride (PdF) as a F source in hydrothermal silicate systems and noted that the compound decomposes during the experimental run and releases F to the system; Pd does not react with the charge but remains dispersed through it as tiny beads. However, nobody has yet reported on the use of metallic fluorides as a F source in dry systems.

Our work on carbonatite magma genesis and evolution has led us to an extensive study of the role of F in developing an alkali-rich carbonatite magma of the type erupted as lavas by the Tanzanian volcano Oldoinyo Lengai, as well as in controlling the solubility of P and Nb and the consequent crystallization of apatite and pyrochlore. A necessary starting point in this study has been to establish whether F has an effect similar to that of H_2O on liquidus temperatures, and this in turn necessitates the study of F-bearing, H_2O-absent carbonate systems.

EXPERIMENTAL METHOD

PdF is expensive and does not now seem to be readily available. We have, therefore, experimented with silver fluoride (AgF) and found it to be very suitable for our purpose. It is available as a brown to amber, finely crystalline compound that melts at 435 °C. Although it is deliquescent in humid weather, no problems are encountered if it is stored over phosphorus pentoxide in a small-volume desiccator and loaded into the Au capsules in a sealed dry-box.

Silver fluoride decomposes during the experimental run. Although silver carbonate exists, it is a compound that decomposes at 218 °C (at atmospheric pressure), which is well below the solidus of any carbonate system that we have studied. F is released to the system while Ag either plates onto the surface of the Au capsule (in runs below 600 °C) or alloys with it (above 600 °C). At temperatures from the subsolidus to slightly above the solidus, the Ag is dispersed as tiny globules or forms a small slug. Carbonate melting experiments are usually only a few hours at most in duration, and so we have not investigated in

0003–004X/89/0708–0936$02.00

detail the effect of longer runs on Ag mobility. However, in runs of a few days, the Ag tends to plate or alloy rather than remain dispersed, and it is likely that with even longer runs all the Ag would eventually alloy with the Au of the enclosing capsule.

We have found silver fluoride to be a very useful means of studying systems containing Na_2CO_3, K_2CO_3, $CaCO_3$, apatite, and pyrochlore with up to 20 wt% of F and recommend its wider use in experimental petrology.

ACKNOWLEDGMENTS

Our carbonatite research has been supported by the Natural Sciences and Engineering Research Council of Canada and by the Ministry of Energy, Mines and Resources (Geological Survey of Canada), both of which are gratefully acknowledged.

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MANUSCRIPT RECEIVED DECEMBER 5, 1988
MANUSCRIPT ACCEPTED MARCH 17, 1989