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THE ORIGIN OF FLUORINE IN SURFACE WATERS

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INTRODUCTION

The fluoride content in surface waters is important for two very different reasons, i.e. pollution and mineral prospecting. The usual fluoride level is normally much lower than the assumed harmful value of 1.5 ppm F (WHO, 1984 in Yirgu et al., 1999), and essentially depends on leaching from rocks and soils involved in the water flow. Moreover, it is affected by the occurrence and distribution of fluorite-bearing mineral deposits (Pirisi and Valera, 1974) and/or by the direct or indirect influence of some types of volcanic activity and volcanic products, thermal springs included (Caboi et al., 1986; Calderoni et al., 1993; Yirgu et al., 1999).

Van Alstine (1976) pointed out the close association all over the world of major fluorspar districts and continental rifts and lineaments. According to the data in several studies, it is interesting to note that this structural control seems to extend well beyond the mineralisation processes.

RIFTS AND FLUORITE MINERALISATION - THE SARDINIAN AND EAST AFRICAN CASES.

Rifts are here considered expressions of regionally important fracture systems, developing until noticeable depths, and thus reaching the apical boundaries of possibly existing magmatic chambers or their neighbourhood. They, therefore, mark the easiest way for the upward migration of magmatic fluids, which commonly belong to the residual melt often particularly enriched in fluorine. Hydrothermal solutions start being very active, and fluorspar deposits may form in suitable equilibrium conditions. The genetic temperature interval of fluorite is very wide: it may participate in paragenetic sequences of pneumatolytic to epithermal conditions. Fluorspar deposits are therefore the best source of fluorine leaching by surface waters, and it is clear that measured values in mineralised districts are expected to be frequently highly anomalous, by comparison with the regional average.

The scientific literature bears many good examples of fluorspar mineral deposits, whose occurrence can be recognized immediately as genetically and structurally related to rift fracture systems, or to fracture lineaments of regional importance. A very good example of fluorine behaviour is given by the geological history of

Sardinia. In the centre of the Mediterranean sea, Sardinia can be considered a faithful record of the events that characterized the geological history of the European lithosphere since the late Precambrian. The structural fabric reflects Caledonian, Hercynian and Alpine orogeneses, accompanied by important magmatic events.

The Hercynian magmatism was responsible for the emplacement of a major high-K calc-alkaline association, followed by post-granitic Permo-Triassic acid to basic dike injections. After the post-Hercynian exhumation, Sardinia was periodically and partially affected by marine invasions, and also during the Cainozoic it was repeatedly subjected to marine sedimentation and long-lasting emersion periods with several intense volcanic cycles of a variable composition ranging from early andesite lavas and tuffs to late basaltic flows. Tertiary repercussions of Alpine tectonic activity were especially characterized by the Sardinian Rift (Cherchi & Montadert, 1982), which is sensibly affected by the contemporaneous formation of a complex European rift system. The N-S trending Sardinian rift is considered an aborted arm of this system, and cuts throughout the island, displacing both the crystalline basement and the volcano-sedimentary cover. During its evolution, the Sardinian rift was infilled with thick sedimentary sequences, and with the products of important calc-alkaline volcanic phases. The last tectonic movements, accompanied by minor volcanic activity, reactivated the Alpine systems, and were also responsible for the Pliocene-Quaternary "Campidano Graben", a NW-SE trough superimposed on the southern part of the Oligocene-Miocene rift structure.

During such a long history, Sardinia developed an important metallogenic province, where several types of ore deposits occur. Pb-Zn-(Ag) ores associated with minor or major quartz, fluorite, barite, and calcite in discordant veins, hosted in various Paleozoic country rocks, are very frequent; and Pb-Zn-(Ag) in massive or disseminated orebodies, and barite in stratabound or massive karst-filling orebodies, are typical in the "Metalliferous" Cambrian limestones. Many other types of Paleozoic mineralisations are reported: copper and mixed sulfides in concordant stratabound lenses, W-Mo-Sn ores in pneumatolytic setting, stibnite and scheelite in shear zones. Last but not least, epithermal gold deposits of economic importance are hosted in volcanics of the Sardinian Tertiary rift.

Fluorite occurrences are widespread in Sardinia, but fluorine activity did not affect any Cambrian environment. In other words, nowhere do Cambrian outcrops show traces of fluorine activity, i.e., fluorite mineralisation is totally absent, even in presence of the frequent and often large Pb-Zn- and Ba-bearing orebodies. F-bearing mineral associations are typical of discordant veins or concordant or stratabound orebodies, or skarn lenses, which are particularly clustered in the neighbourhood of the Cambrian region of SW Sardinia and mainly hosted by Ordovician-Silurian metasediments and metavolcanics or by Hercynian magmatic products. The first appearance of fluorine in the stratigraphic Paleozoic sequence of Sardinia is confined to the Caledonian with widespread fluorite-barite infillings in paleokarst systems, that developed close to the erosion paleosurface in Cambrian limestones just below the Ordovician unconformity.

The sudden appearance of fluorite in the Ordovician series was formerly explained (Valera, 1975) according to a possible leaching and mobilization of F-bearing protores from post-Cambrian sequences, followed by deposition in available open spaces (karst systems related to the pre-Ordovician paleosurface and/or fracture infillings in post-Cambrian competent rocks). We now propose to consider the assumption of Vai (1991) concerning a major oblique rifting cycle developing from the late Cambrian to the early Ordovician in the circum-Mediterranean area. In the Sardinian Paleozoic, therefore, it is reasonable to interpret a deep-seated source, connected with a rifting process, as the fluorine supplier of existing hydrothermal circuits. Such "early fluorine" can be considered responsible for the syngenetic protores in Silurian-Devonian volcano-sedimentary sequences that were remobilized and concentrated in both concordant and discordant orebodies during Hercynian magmatic activity. "Early fluorine" could therefore have been active long enough to join the onset of the Hercynian magmatic cycle.

Fluorine plays a substantial role during Hercynian magmatic activity and becomes even more important in the late orogenetic phase, while fluorite occurrences especially characterize the last pluton emplacement (leucogranites) in the Sardinian-Corsican batholith. Fluorite is a common accessory in the mineral association of leucogranites and may at times reach high concentrations. Very frequently, fluorite mineralisation occurs in composite association with basic dikes, in fractures where fluorite is clearly deposited last. The dikes appear to belong to a late- to post-Hercynian magmatic phase, mostly showing calc-alkaline basaltic to lamprophyric composition. Both the common occurrence and field relations suggest the existence of a chronologic, and perhaps even genetic, link between emplacement of basic dikes and invasion of F-bearing hydrothermal solutions strictly confined to the same fractures. Sometimes basic

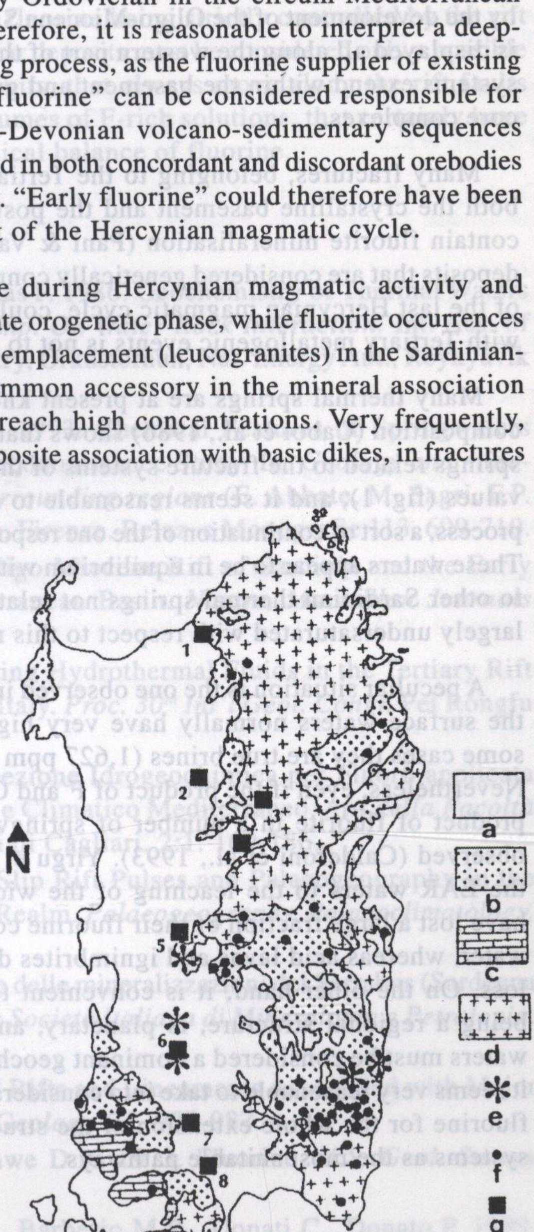

Fig. 1. Fluorine in Sardinia. Symbols: a. undifferentiated post-Paleozoic series (mostly corresponding to the Tertiary rift); b. undifferentiated Paleozoic series; c. SW Cambrian series ("Metalliferous Complex" p.p.); d. late Hercynian granitoids; e. "Alpine" fluorite deposits; f. "Hercynian" fluorite deposits; g. present thermal springs, F content in ppm (Caboi et al., 1986): 1. 2.96; 2. 1.35; 3. 8.90; 4. 4.95; 5. 9.10; 6. 11.50; 7. 8.36; 3.99. Modified from Pani and Valera (1997).

dikes are cut and displaced by fluorite mineralised fractures, suggesting a prolonged hydrothermal activity long after the last emplacement of post-Hercynian magmatic products.

The dramatic Cainozoic evolution of Sardinian geological history, characterized by various marine invasions, regressions and repeated phases of volcanic activity, is basically controlled by the rotation of the Corsican-Sardinian microplate and by the development of the Oligo-Miocene Sardinian rift. This important structure is displayed all along the western part of the island, and its N-S to NW-SE fault systems extend within the basement and give rise to the uplift of metamorphic core complexes.

Many fractures, belonging to the Tertiary rift fault systems and displacing both the crystalline basement and the post-Paleozoic (mostly Tertiary) cover, contain fluorite mineralisation (Pani & Valera, 1997). Moreover, some of the deposits that are considered genetically connected with the hydrothermal activity of the last Hercynian magmatic cycle, could now be postdated, since their link with Tertiary metallogenic events is not to be ruled out.

Many thermal springs are at present known in Sardinia. The study of their composition (Caboi et al., 1986) shows that the fluoride content of waters from springs related to the fracture systems of the Tertiary rift have remarkably high values (fig. 1), and it seems reasonable to accept a still ongoing hydrothermal process, a sort of continuation of the one responsible for Tertiary fluorite deposition. These waters appear to be in equilibrium with fluorite, whereas waters belonging to other Sardinian thermal springs not related to the Tertiary rift structures are largely undersaturated with respect to this mineral (Caboi et al., 1986).

A peculiar situation is the one observed in the East African Rift (EAR), where the surface waters normally have very high fluorine concentrations, since in some cases they are true brines (1,627 ppm F in lake waters: Worl et al., 1973). Nevertheless, even if the product of F^- and Ca^{2+} activities exceeds the solubility product of fluorite in a number of springwaters, precipitation of CaF_2 is not observed (Calderoni et al., 1993). Yirgu et al. (1999) attribute the F supply in the EAR waters to the leaching of the widespread pumices, which appear to have lost a large fraction of their fluorine contents during their interaction with water, whereas acid lavas and ignimbrites do not show any significant fluorine loss. On the other hand, it is convenient to notice that the EAR, rather than being a regional structure, is planetary, and that the F content in its surface waters must be considered a dominant geochemical feature. In these conditions, it seems very reasonable to take into consideration a deep-seated source supplying fluorine for the whole extension of the structure, and utilising the rift fracture systems as the most suitable pathways.

CONCLUSIONS

The already proposed link between fluorite districts and continental rifts and lineaments is continuously supported by the results of other studies. The emplacement of fluorspar deposits appears to be a major consequence of the very intense activity of F-bearing hydrothermal fluids along the important fault systems typical of the rift structures. The given examples of Sardinia and EAR witness to the origin and consequent behaviour of fluorine being strictly controlled by the rift fracture systems. Actually, the fluorspar deposits must be considered only a possible end effect of the hydrothermal circuits, that always move along the rift faults and fractures, and involve huge volumes of F-rich solutions, that certainly have a substantial effect on the geochemical balance of fluorine.

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