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Chemical, isotopic and mineralogical characteristics of volcanogenic epithermal fluorite deposits on the Permo-Mesozoic foreland of the Andean volcanic arc in Patagonia (Argentina)

Harald G. Dill[a,*], Liliana I. Luna[b], Nicole Nolte[c], Bent T. Hansen[d]

[a] Gottfried Wilhelm Leibniz University, Welfengarten 1, D-30167 Hannover, Germany
[b] Departamento de Geología, Universidad Nacional del Sur San Juan, 670 8000 Bahía Blanca, Argentina
[c] MAS-Analytics UG—Institute for Material Analysis and Science, Goldschmidtstraße 3, D-37077 Göttingen, Germany
[d] Geoscience Centre of the Georg-August University, Goldschmidtstrasse 3, D-37077 Göttingen, Germany

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ABSTRACT

Epithermal deposits mined for fluorite in Patagonia, Argentina, are closely related to late Triassic through Jurassic magmatic activity which brought about felsic to intermediate magmatic rocks. The fluorite mineralization in the Patagonian epithermal system resulted from gaseous F-and CO_2-enriched magmas which lead to an explosive phreatomagmatic volcanism, when getting in contact with groundwater near the surface. As a result of these hydrothermal processes, rapid cooling took place in the epithermal mineralization. Changes in the viscosity along with the cooling down of mineralizing fluids caused mottled mineral colors blurring the boundaries between the stages and ore textures.

The fluids accountable for the main constituents fluorite, quartz, barite and silica were operative over a vertical extension of roughly 600 m. Their temperature of formation dropped from 379 °C through 64 °C, while the pH decreased from the heat center towards the paleosurface under oxidizing conditions. This steep temperature gradient conducive to the telescoping of mineral associations into each other was accompanied by a rapid loss in CO_2, and a mixing of meteoric and magmatic fluids. Even the boundary between the hypogene and supergene alteration cannot be drawn precisely within the assemblage of Mn oxides, which bridge the gap between hypogene and supergen mineralization. The physical-chemical parameters of the fluids, particularly, the redox conditions did not allow sulfides to be preserved. A classification of the epithermal system as to its degree of sulfidation is based on K-feldspar and kaolinite which are present in significant amounts, whereas APS (aluminum-phosphate-sulfate) minerals are absent. Therefore a categorization as an epithermal fluorite deposit of low- to intermediate sulfidation is justified, because the only mineral of economic interest in the system is fluorite.

The data obtained during this joint study render the Patagonian fluorite district a reference type of fluorite in an epithermal system of low- to intermediate sulfidation which are widespread in Argentina, e.g., Sierras Pampeanas, and evolved on part of the stable craton, called Gondwana and which grade into epithermal Au, Ag, In, Pb and Zn deposits.

1. Introduction

Fluorite (fluorspar), the only commercially used F mineral which in its pure minerals contains 48.9 wt.% F, is ranked by the European Union (2010) among 14 raw materials considered as critical in terms of supply. Great efforts have been taken to find new mineral deposits as well as enhance the exploitation of fluorite from existing deposits which occur in magmatic and sedimentary environments of deposition as well as bound to faults in a wide range of host rocks (Table 1). Dill (2010) provided a list of fluorine deposits with the pertinent literature for each type of deposit. In Patagonia, southern Argentina, structure-related fluorite deposits and mineral occurrences occur in different magmatic and sedimentary rocks of Paleozoic through Mesozoic age (Hayase and Manera, 1973; Menoyo and Brodtkorb, 1975; Aliotta, 1986; Márquez et al., 1994; Aliotta and Luna, 1996; Ducart, 2007). Similar deposits and mineral occurrences were described from across the globe, partic-

* Corresponding author.
E-mail address: haralddill@web.de (H.G. Dill).
URL: http://www.hgeodill.de (H.G. Dill).

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Table 1
Classification scheme of fluorine deposits with codes used in the "Chessboard classification scheme of mineral deposits" See also text "Introduction".

(1) Magmatic deposits
(1) Fluorite deposits related to granitic intrusions with F-Sn-W-(Be) and fluorite skarn W-Sn and Pb-Zn deposits (32e D)
(2) Fluorite deposits related to U-REE carbonatites and alkaline intrusive rocks (32a E)
(3) Granite-related Be-Nb-Ta-fluorite deposits (32d D)
(4) Pegmatite-hosted F-(Sc) deposits (32a D)
(5) Volcanic-hosted F-U-Mo deposits (32 g CD)
(6) Volcanic-hosted topaz (32f D)
(7) Granite-related topaz deposits (gemstone) (32b D)
(8) Intragranitic fluorite deposits (32c D)
(9) Cryolite deposit related to metasomatic A-type granites (32b E)
(2) Structure-related deposits
(1) F-bearing mega breccia (32c F)
(2) Epithermal ("hot brine") fluorite breccia veins (32a G)
(3) Epithermal F-(Ba) deposits (maars) (32a F)
(4) Unconformity-related (shallow veins) Pb-Zn-Ba fluorite deposits (32b G)
(5) Thrustbound and replacement topaz deposits (gemstone) (32c G)
(3) Sedimentary deposits
(1) Stratabound Pb-Zn-Ba fluorite deposits in carbonate rocks (MVT) including replacement deposits (mantos") (32a K)
(2) Stratabound fluorite-celestite deposits in carbonate rocks (32b K)
(3) Residual and karst-related fluorite deposits
(4) Fluorite cavity-fillings and calcretes (32a H)
(5) Fluorite replacement/calamine deposits (32b H)
(6) Phosphorites with F apatite(32c IJK)
(7) Topaz placers (32a l)

ularly from Spain (Canals and Cardellach, 1993; Pique et al., 2008), France (Jebrak et al., 1985), Great Britain (Cann and Banks, 2001), Italy (Barbieri et al., 1987; Hein et al., 1990) and Germany (Dill, 1985; Schwinn and Markl, 2005; Dill and Weber, 2010; Dill et al., 2011). The fluorite deposits and mineral occurrences under study La Alegria, Doña Feliza, Mina Delta, Puerto San Antonio, Don Antonio and Bienvenida are located in the Provincia de Rio Negro, Argentina (Fig. 1). Considering their structure, their mineral assemblages and host rocks, these fluorite deposits reflect a composite of fluorite concentration coded as 32 g CD, 32a G, 32a F, and 32b G sensu Dill (2010) in the "Chessboard classification scheme of mineral deposits änd suggest a rather complex mode of formation in an otherwise lithologically rather monotonous region as being compared with the modern fold belt of the Andes, which extents along the western edge of the study area in South American (Table 1) (Cucchi et al., 2001).

The number of publications on epithermal deposits is big and thus only a few papers can be cited for reference. An overview of epithermal metal deposits has been presented by White and Hedenquist (1994), Leach and Corbett (1995), Albinson et al. (2001) and Corbett (2002). All the studies mentioned above focus their investigation on precious and base metals. Industrial minerals such as barite or fluorite in epithermal systems have not been studied in detail and therefore fluorite deposits deserve a more detailed treatment (Bulnayev, 2001; Alvin et al., 2004; Pi et al., 2005).

The key questions addressed in the current study are:

- How do fluorite and its associated minerals evolve in an epithermal system?
- What is the impact of the geodynamic setting on these mineral deposits in northern Patagonia, which lie today between an active margin along the Pacific Ocean and a passive margin along the South Atlantic Ocean?
- Which are the features diagnostic for this concentration of fluorite and what is the physical-chemical regime like?

The data are meticulously elaborated and discussed in context with other structure-related fluorite mineralization, mainly from the northern hemisphere, so as to be useful for exploration geologists. In order to tackle this issue, the classical geological, mineralogical and chemical investigations are combined with isotope analyses of Sm, Nd, Rb, Sr, O, C, S and fluid inclusion studies. The data presented can be used to render the Patagonian fluorite district a reference type of fluorite in an epithermal system.

2. Geological setting

The fluorite deposits as part of the S Argentine epithermal province are situated in a region known as the North Patagonian Massif (Ministeria de Agricultura, 1943; Servicio Geologico, 1994; Shatwell et al., 2011). The oldest rocks in the basement comprise a metasedimentary sequence of Cambrian age, called the Nahuel Niyeu Formation (Servicio Geologico, 1994). Ordovician and Silurian rocks are present in the study area but only at subordinate amounts. Fluorite deposits reside within Late Paleozoic and Mesozoic magmatic rocks, whose host rock stratigraphy is depicted in the succeeding paragraphs (Fig. 1a, b).

Fluorite mineralization at La Alegria and Doña Feliza has been discovered over some hundred meters along faults running through ignimbrites, rhyolites and tuffs of Triassic through lower to middle Jurassic age, pertaining to the Complejo Los Menucos (Fig. 1a) (Cucchi et al., 2001), whereas at Mina Delta and Puerto San Antonio, fluorite was accumulated in host rocks similar as to the lithology but slightly younger as to the age of formation (Busteros et al., 1998). Potassium-argon age dating by Nuñez et al. (1975) and Pankhurst et al. (2000) yielded an age of formation of the volcanic rocks in the Complejo Marifil spanning the interval 160–192 Ma (Early and Middle Jurassic). The geological setting is different for the fluorite mines at Bienvenida and Don Antonio (Fig. 1b). Both vein systems reside in Permian granites (Facies Gimenez) and granodiorites (Facies Prieto), respectively, at different distances from the Jurassic magmatic rocks. The veins of Don Antonio are less than 2 km away from the next outcrop of Jurassic volcanic rocks, whereas at La Bienvenida the distance between the fluorite veins and the younger volcanic rocks measures more than 10 km (Fig. 1b).

Fluorite is used as acid spar for the production of hydrofluoric acid, as metallurgical grade fluorspar during steelmaking and as a fluxing agent in the aluminum production and in subordinate amounts as ceramic spar for enamels and glass (Miller, 2013). The major production of fluorite in Argentina derived from Cordoba Province (98.4%), followed by the Rio Negro and San Juan