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PÓS-GRADUAÇÃO EM GEOCIÊNCIAS

ÁREA DE CONCENTRAÇÃO: METALOGÊNESE

Jorge Enrique Coniglio

NATUREZA E EVOLUÇÃO DOS FLUIDOS HIDROTERMAIS NOS DEPÓSITOS DE FLUORITA FILONAR DO BATÓLITO CERRO ASPERO, PROVINCIA DE CÓRDOBA, ARGENTINA

DISSERTAÇÃO DE MESTRADO

CAMPINAS - SÃO PAULO

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ORIENTADOR: Prof. Dr. Roberto Perez Xavier

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Campinas, 15 de 09 de 1999.

A Vivi, Nico, Santi e Joaquin

por estes maravilhosos e inesquecíveis

momentos vividos no Brasil.

A mis padres

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RESUMO

DISSERTAÇÃO DE MESTRADO

Jorge Enrique Coniglio

Os depósitos de fluorita filonar, no setor sul das Sierras Pampeanas de Córdoba, Argentina, ocorrem em rochas cálcio alcalinas, de idade Devoniana, constituídas principalmente por biotita monzogranito porfiríticos que compõem o batólito Cerro Aspero. Os veios de fluorita são de idade Cretácea e encontram-se controlados por sistemas de falhas transcorrentes, subverticais. Além da fluorita, estes veios também estão compostos por calcedônia, localmente pirita e, eventualmente, coffinita e pitchblenda. Os veios mostram texturas típicas de preenchimento de espaços abertos (bandamento, crustificação, brechamento, geodos, etc) e estão intimamente relacionados com intensa silicificação e argilitização das rochas graníticas hospedeiras.

Três sucessivos estágios de mineralização foram distinguidos por evidências de campo, através da cronologia relativa de deposição de fluorita, dados de ETR e inclusões fluidas em fluorita. Estes estágios mostram geralmente padrões de ETR pouco fracionados (La/Yb=1.4 – 14), notando-se que a distribuição dos ETR na fluorita é principalmente governada pelo fracionamento dos ETR leves. Sugere-se que a composição em ETR do fluido hidrotermal e, consequentemente, da fluorita, foram amplamente controlados pela diferente mobilidade dos ETR leves a depender do tipo de alteração hidrotermal. Enquanto uma lixiviação preferencial de ETR pesadas sobre ETR leves ocorreu durante a alteração silícica e argílica, nesta última, os ETR leves praticamente não foram removidos.

As temperaturas de homogeneização total de inclusões fluidas aquosas, primárias, occorreram invariavelmente na fase liquida entre 187°C e 104 °C, com concentrações de valores em torno de 160°C, 136°C e 116°C (estágios I, II e III, respectivamente), definindo uma marcante tendência de resfriamento da solução. Este resfriamento está associado com importantes variações na fO_2 do fluido, de oxidante a redutor, inferido a partir da relação Eu/Eu* e da assembléia mineral (pirita, pitchblenda e coffinita). As inclusões aquosas nestes três estágios de deposição de fluorita mostram temperaturas de fusão do gelo no intervalo entre -0,3°C - +0,4°C, indicando que o fluido mineralizante sempre manteve uma salinidade muito baixa, próxima a água pura. Não foram encontradas evidencias de ebulição nem mistura de fluidos. Os dados de inclusões fluidas sugerem que os três estágios de mineralização propostos foram o resultado de um único e progressivo evento hidrotermal e suportam um reservatório único e uniforme para as soluções mineralizantes, provavelmente de águas meteóricas aquecidas e não de fluidos gerados em zonas mais profundas da crosta.

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THE ORE-FORMING FLUIDS OF VEIN-TYPE FLUORITE DEPOSITS OF CERRO ASPERO BATHOLITH, SOUTHERN CORDOBA PROVINCE, ARGENTINA.

ABSTRACT

MASTER DISSERTATION

Jorge Enrique Coniglio

Vein-type fluorite deposits in the southern part of the Sierras Pampeanas, Córdoba, Argentina, occur mainly hosted by calc-alkaline porphyritic biotite granites, which belong to the Paleozoic, post-tectonic Cerro Aspero batholith. The fluorite veins, of Cretaceous age, occupy steeply dipping, strike-slip fault zones and are composed of fluorite and chalcedony, locally pyrite and, eventually, coffinite and pitchblende. These veins show typical open-space-filling textures and are closely related with pervasive silicic and argillic alteration of the hosted granite.

Three successive stages of mineralization were distinguished on the basis of vein chronology, REE data and fluid inclusions study in fluorite ores. These stages generally display slightly fractionated REE patterns (La/Yb=1.4-14), with REE behavior given by a relatively stronger LREE fractionation with respect to HREE. Thus, it is suggested that the REE composition of the fluids responsible for fluorite deposition was largely controlled by a different mobility of the REE during the silicic or argillic alteration of the host granite. Preferential leaching of HREE over LREE occurred during both alteration types, but in the argillic alteration the LREE were practically not removed.

The total homogenization temperatures of primary-like aqueous inclusions took place invariably in the liquid phase at temperatures ranging from 187°C to 104 °C, with concentration of values around 160°C, 136°C and 116°C (stage I, II and III, respectively), defining a clear trend of fluid cooling. This cooling is accompanied by large changes in the fO_2 of the fluid, from oxidizing to reducing, as inferred from the Eu/Eu* ratios and the mineral assemblage (pyrite, pitchblende and coffinite). The three stages of fluorite depositions exhibit temperature of ice melting within the interval -0,3°C - +0,4°C, indicating that the mineralizing fluids were exclusively aqueous and highly diluted. No evidence of fluid mixture or boiling were found. The fluid inclusion data suggest that the proposed three stages of mineralization was probably the result of a single hydrothermal event and strongly support a single and uniform fluid reservoir for the ore-forming solutions, probably heated meteoric waters rather than fluids generated in deep-seated environments within the crust.

I. INTRODUÇÃO

I. INTRODUÇÃO

No setor sul das Sierras de Córdoba, Sierras Pampeanas da Argentina, uma série de filões de fluorita encontram-se encaixados em rochas graníticas Paleozóicas pertencentes ao batólito Cerro Aspero, em uma área de aproximadamente 440 Km^2 (Fig. 1). Estas mineralizações estão hospedadas em monzogranitos epizonais que se colocam em um complexo metamórfico de médio grau, de idade Précambriana – Paleozóica inferior.

Nas últimas três décadas, estes depósitos tiveram longos períodos de inatividade na mineração devido a instabilidade do mercado interno associado aos baixos teores em CaF_2 do minério e dificuldades de acesso às minas. Em 1992, a empresa Fluorita Córdoba S.A. retomou a mineração da mina Cerros Negros (Fig. 1) a um ritmo de 1500 ton/mês, com um conteúdo médio de 56% de CaF_2. A mina Cerros Negros, destaca-se por ser o único depósito de fluorita atualmente em produção na Argentina. O acondicionamento das antigas instalações de flotação têm permitido a produção de um material de alta qualidade (superior a 98% de CaF_2), onde parte é utilizado na indústria química e na de eletrodos, o restante, é exportado.

O Departamento de Geologia da Universidad Nacional de Río Cuarto (UNRC), Provincia de Córdoba, Argentina, vêm realizando estudos nesta área há mais de dez anos e os resultados têm permitido o mapeamento e caracterização petrológica do batólito Cerro Aspero, na escala 1:60.000, assim como a abordagem da metalogênese associada, particularmente no que se refere aos depósitos de fluorita.

A controvérsia sobre a idade e a fonte dos elementos destas jazidas constata-se desde os primeiros estudos de Geología Econômica realizados na década do 70. Assim, a opinião sobre a gênese estava dividida entre a teoria tradicional de filiação hidrotermal magmática (magma granítico do Cerro Aspero) e a teoria que associava a formação da fluorita à atividade hidrotermal do vulcânismo Terciário, o qual tem escassa manifestação na área. Galindo *et al.* (1997) utilizando isótopos de Sr e Sm-Nd em fluorita e rochas hospedeiras sugerem que a fluorita foi formada durante o Cretáceous inferior (117 ± 26 Ma) e que sua composição isotópica deriva das rochas hospedeiras.

Embora estes estudos tenham contribuído a um melhor conhecimento da gênese destas jazidas, a ausência de dados sobre a origem e composição dos fluidos hidrotermais, assim como sua evolução no tempo foi o que motivou a proposta da presente Dissertação de Mestrado.

Neste estudo, a origem, composição e evolução física e química dos fluidos responsáveis pela deposição da fluorita no batólito Cerro Aspero é abordada a partir da determinação da seqüência relativa da deposição da fluorita, de dados de inclusões fluidas em fluorita e de elementos terras raras (ETR) em fluorita, granitos e na alteração hidrotermal.

Primeiramente foi efetuado o mapeamento e amostragem nas frentes de lavra dos principais depósitos de fluorita do batólito (Fig. 1). Posteriormente, foram efetuados estudos mineralógicos, mediante petrografia convencional, microscopia eletrônica de varredura, e inclusões fluidas em fluorita, incluindo microespectroscopia Raman a laser. Todos estes estudos foram desenvolvidos no Instituto de Geociências –UNICAMP- Campinas. As determinações dos ETR em fluorita foram realizadas por ativação com nêutrons (INAA) no Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN), São Paulo. As determinações dos ETR nas rochas graníticas hospedeiras e as alterações hidrotermais associadas foram obtidas segundo o método de plasma indutivamente acoplado - espectrometria de massa (ICP-MS) no Activation Laboratories LTD, Canadá.

Parte da metodologia seguida nesta dissertação está detalhada nos trabalhos de Marchand *et al.* (1976); Grappin *et al.* (1979); Bastos Neto e Savi (1985) e Coelho (1987). Aplicações podem ser encontradas nos trabalhos de Dardenne e Savi (1984); Constantopoulus (1988); Coelho *et al.* (1990); Bastos Neto *et al.* (1991); Ronchi *et al.* (1993); Subías e Fernández Nieto (1985); Fanlo *et al.* (1998), dentre outros.

É importante ainda salientar que a aplicação combinada de dados de inclusões fluidas e ETR está, pela primeira vez, sendo utilizada em depósitos de fluorita da República Argentina.

O regulamento do Curso de Pós-Graduação em Geologia da UNICAMP permite que a Dissertação de Mestrado possa ser estruturada na forma de artigo para ser submetido para publicação em periódico com corpo editorial. Neste contexto, esta Dissertação de Mestrado centraliza-se no artigo denominado *"The ore-forming fluids of vein-type deposits of Cerro Aspero batholith, southern Córdoba Province, Argentina"*, a ser submetido ao *International Geology Review*, e que se encontra fiel no formato previsto neste periódico.

II. THE ORE-FORMING FLUIDS OF VEIN – TYPE FLUORITE DEPOSITS OF CERRO ASPERO BATHOLITH, SOUTHERN CORDOBA PROVINCE, ARGENTINA

THE ORE-FORMING FLUIDS OF VEIN–TYPE FLUORITE DEPOSITS OF CERRO ASPERO BATHOLITH, SOUTHERN CORDOBA PROVINCE, ARGENTINA

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Abstract

Vein-type fluorite deposits in the southern part of the Sierras Pampeanas, Córdoba Province, Argentina, occur mainly hosted by calc-alkaline porphyritic biotite granites, which belong to the Paleozoic, post-tectonic Cerro Aspero batholith.

The fluorite veins, of Cretaceous age, occupy steeply dipping, strike-slip regional fault zones and are composed of fluorite and chalcedony, locally with subordinate amounts of pyrite and, eventually, coffinite and pitchblende.

These veins show typical open-space-filling textures and are closely related with pervasive silicic and argillic alteration of the hosted granite.

Three successive stages of mineralization were distinguished on the basis of vein chronology, REE data and fluid inclusions study in fluorite ores.

These stages generally display slightly fractionated REE patterns (La/Yb=1.4-14), with REE behavior given by a relatively stronger LREE fractionation with respect to HREE. Thus, it is suggested that the REE composition of the fluids responsible for fluorite deposition was largely

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The three stages of fluorite depositions exhibit temperature of ice melting within the interval -0,3°C - +0,4°C, indicating that the mineralizing fluids were exclusively aqueous and highly diluted. No evidence of fluid mixture or boiling were found. The fluid inclusion data suggest that the proposed three stages of mineralization was probably the result of a single hydrothermal event and strongly support a single and uniform fluid reservoir for the ore-forming solutions, probably heated meteoric waters rather than fluids generated in deep-seated environments within the crust.

Introduction

THE CORDOBA Province has been part of an important metallogenic district in Argentina, particularly with respect to the occurrence of significant vein-type fluorite deposits. In the southern part of this province almost all the fluorite veins are restricted to an area of 440 km^2 within the Cerro Aspero batholith (Fig. 1), from which 666.000 t of CaF_2 ore has been estimated as reserves (Menoyo and Brodkorb, 1975). Most of the fluorite production has been derived from the Cerros Negros and Bubú deposits and, in minor proportions, from the La Saida and Francisco deposits (Fig. 1). At present, Cerros Negros is the only vein-type fluorite deposit being exploited in Argentina, with calculated reserves of 270.000 t and average grade of 56% of CaF_2.

These deposits are hosted by Paleozoic, post-tectonic porphyritic biotite monzogranites that intruded, at shallow depths, upper Precambrian-lower Paleozoic medium to high grade metamorphic rocks.

The veins occupy steeply dipping, NE, E-W and NW-striking fault zones and the mineralogy is predominantly fluorite and chalcedony, which display typical open-space-filling texture. Occasionally pyrite and uranium minerals also occur.

Previous studies focused mainly on the geology and mineralogy of these veins were made by Gonzalez Díaz (1972) and Coniglio (1992, 1993). They emphasized that the veins were generated by multiple stages of opening and sealing, however, no detailed description of the mineral deposition sequence was made. Galindo et al.(1997), based on Sr and Sm-Nd isotopic geochemistry of fluorite veins and host rocks, postulated that the mineralization took place in the lower Cretaceous, during late Gondwanian extensional tectonic regime, and that the host rocks were an important as REE source of the hydrothermal fluids.

Although these studies contributed to a better understanding of the genesis of these fluorite deposits, no strong evidence was provided indicating the physic-chemical characteristics, evolution, and possible sources for the ore-forming fluids.

In this study, the determination of the relative sequence of fluorite deposition, together with fluid inclusion study in fluorite and REE data in the ore and host rocks, permitted to further constrain the thermal and chemical history of the fluids responsible for the ore deposition.

Geological Setting

The Cerro Aspero batholith is located in the southern part of the Sierras de Córdoba in the eastern Sierras Pampeanas of Argentina (Fig 1).

The Sierras de Córdoba are constituted by Upper Precambrian to Paleozoic plutonic-metamorphic basement which is locally covered by continental deposits and mafic volcanic rocks, assigned as Cretaceous in age (Gordillo and Lencinas, 1979). The basement was uplifted as north-south trending blocks as a result of the Andean orogeny (Jordan and Allmendinger, 1986).

The Cerro Aspero batholith is an elliptical body comprising three main sub-circular plutons that intrude migmatites, gneisses, amphibolites, marbles, ultramafic and mafic rocks in upper amphibolite facies. Lower Cambrian age was suggest for the metamorphic peak (Rapela et al., 1995; Stuart Smith et al., 1996). The emplacement of the batholith is interpreted to have taken place during the mid to upper Devonian. The Rb/Sr age of 369 ± 9 Ma and a K/Ar age of 389 ± 19 Ma probably reflect the magma crystallization and the cooling age of the granitics rocks, respectively (Pinotti, 1998).

The Cerro Aspero batholith is characterized by a high lithological homogeneity dominated by monzogranitic compositions, although, exceptionally, granodioritic rocks also occur.

Three main granitic types were recognized as dominant in the Cerro Aspero batholith (Coniglio and Esparza, 1988; Porta, 1992; Pinotti, 1998), but only the first two are considered as the most representative:

(1) Porphyritic to coarse-grained equigranular biotite monzogranite (PBM) which comprises nearly 80% of the batholith. The PBM granite is characterized by microcline phenocrysts, up to 14 cm long, which constitute 15% to 30% of the volume of the rocks. Microcline also occurs in the groundmass together with oligoclase, quartz and biotite. Apatite, zircon, sphene, rutile, monazite, xenotime, fluorite, allanite, pyrite, and Ti and Fe oxides are the main accessory minerals. Fluorite is present as inclusions from 5 to 120 μm in size inside biotite or, less frequently, as interstitial crystals. Fine-grained enclaves rich in biotite and apatite are frequently present within the PBM granite.

(2) A two-mica leuco-monzogranite (LM) which frequently occupies the upper portions of the batholith as roughly tabular sub-horizontal bodies. In the southern part of the batholith this granite forms a prominent annular shape and appears emplaced between the metamorphic host rocks and the PBM granite, with which it shows sharp contact relationships. The LM granite is composed of microcline, oligoclase, quartz and muscovite ± biotite and displays a medium to coarse-grained equigranular texture. The accessory minerals are less abundant than in PBM granite and are mainly apatite, rutile and pyrite. Greisenization, commonly bearing fluorite, is frequent in this rock.

(3) Fine-grained monzogranite and aplo-pegmatitic dikes (MD) intruding both the PBM and LM granites and, locally, the metamorphics rocks. They were emplaced either as subhorizontal dikes or as cone-sheet dikes. Muscovite dominates over biotite and scarce garnet occur in the more leucocratic dikes.

The granites of the Cerro Aspero suite belong to a high-K calc-alkaline series and display a progressive peraluminous trend from PBM to MD granite in relation to the magmatic differentiation (Porta, 1992; Pinotti, 1998). These granites have high contents of large-ion lithophile elements, as well as P and Ti.

The magmatic-hydrothermal stage of this granites is characterized by extensive tungsten-bearing quartz veins and disseminated Mo-W mineralization, which were largely mined during the Second World War (Fernandez Lima et al., 1963; Hillar, 1968; Gonzalez Diaz, 1972). In both cases, fluorite is a conspicuous gangue mineral. In contrast, the economic fluorite deposits belong to a low temperature vein-type category and were formed without temporal relation with the crystallization of magma. On a regional scale, these deposits have similar characteristics to those hosted in the Achala batholith (Fig. 1) (Paredes, 1987; Galindo et al., 1997), and constitute the easternmost fluorite veins of a wide belt of approximately 400 km (Magliola Mundet, 1990).

Geology of the Vein-Type Fluorite Deposits

Modes of occurrence

The fluorite deposits occur as veins uniformly distributed throughout the margin of the Cerro Aspero batholith and frequently close to the contact with the enclosing metamorphic rocks.

The veins occupy steeply dipping, NE, E-W and NW strike-slip regional fault zones, along which they extend up to 400 meters, with thickness varying from a few centimeters up to 12 meters. At the Cerros Negros deposit the present mining operations exposed the veins at a depth of 70 m, but drilling revealed that the veins may continue to as far as 200 m deep.

The economic fluorite deposits are hosted only by the PBM granite, and no major veins are known to occur within other granitic rock types or in the enclosing metamorphic rocks.

The mineralogy of the veins is simple and is mainly of fluorite associated with chalcedony, pyrite and minor uranium minerals. The veins commonly display banded, cockade, crustiform, and colloform textures, typical of an environment of open-space-filling. Chalcedony veinlets of millimeter to meter width are commonly found either intercalated with the fluorite banding or intimately intergrown with fluorite and, in these cases, the grade of CaF_2 can be as low as 30%.

Dark fluorite spatially associated with economic uranium concentrations (pitchblende and secondary uranium minerals) is particularly present at the Estela Mine (Fig. 1). Stipanicic et al. (1982) pointed out that this association could be only fortuitous and that the genetic relation between fluorite and uranium minerals has never been proved. These authors relate the formation of vein-uranium deposits in Sierras de Córdoba to the Tertiary. The mining operations at Estela mine closed down in the end of the 80's, and the uranium mineralization is now buried by environmental preservation works.

The upper parts of the fluorite veins at Cerro Aspero present a supergene alteration evidenced by conspicuous leaching of fluorite, late oxidation of pyrite and locally formation of secondary uranium minerals.

Most of the fluorite structure were reactivated several times during the Andean orogeny. However, the deformation remained concentrated along narrow shear zones in the veins, or in the selvage zone parallel to the general strike of the veins, without modifying the original mineral deposition sequence.

Hydrothermal Alteration

The hydrothermal alteration associated with the fluorite deposits is concentrated particularly in the PBM granite and, subordinately, in the LM granite. In contrast, the metamorphic rocks show negligible effects of alteration. This evidence and the lack of mineralization in these rocks suggest that they acted as a strong lithological control for the hydrothermal fluids.

The altered zones around the fluorite veins may be up 10 m width and extend generally up to 2 km in length. In some cases, as in the Francisco mine area, they may reach up to 5 km along strike. In all the investigated deposits one side of the wall rock consists of silicified granite and the other side of mylonitic granite altered to an argillic assemblage. In addition, evidences of recurrent formation of these alteration types were found. Sericitic alteration is uncommon and only locally observed, as for instance at the Bubú, Ubaldina and Estela deposits, generally associated with incipient silicification. Exceptionally, the uranium mineralization at Estela mine also exhibits scarce propylitic alteration.

Silicic alteration. This alteration is remarkably widespread throughout the fluorite deposits and evidently occurred during all the mineralizing process, although with varying intensity. Within the fault domains, silicification forms pervasive zones with fine-grained, jasperoid-like quartz in the monzogranite rocks, and comprises the best field evidence for the fluorite exploration. The most prominent feature indicating silicification is a red to brown color acquired by the granitic rocks, due to the decomposition of biotite into hydrous iron oxides. The replacement of biotite by muscovite (or rarely chlorite) and the "rubefaction" of microcline are typical of the initial changes in the altered zones. Microcline is incipiently replaced by secondary quartz associated with coeval formation of sericite and argillic minerals (Fig. 2A). At this stage the original texture of the rocks remains relatively preserved. In an advanced stage of silicification, the original texture of the rock is totally obliterated and the granitic minerals are replaced by quartz in a fine-grained to aphanitic texture, which in turn undergoes strong brecciation, with clasts cemented by cryptocrystalline quartz or chalcedony (Fig. 2B). This results in development of multidirectional quartz veinlets and almost mono- mineralic alteration of the granitic rocks.

Argillic alteration. This is characterized by the predominance of kaolinite in the pre-mineral stage, generally associated with silicic alteration, whereas montmorrillonite and illite are better developed during fluorite deposition (Coniglio, 1993). In this case, fragments of argillitized granite are common in mineralized breccias, and frequently the fluorite vugs are filled with clay minerals. In zones of intense faulting, as at Bubú, or locally at the La Saida and Cerros Negros deposits, a strong bleaching of the altered rocks is typical. The granite is heavily fragmented and its feldspar totally replaced by clay minerals.

Stages of Fluorite Mineralization

In order to determine the relative chronology of mineral deposition in the vein-type fluorite deposits, the Cerros Negros deposit was selected as a case study, due to its excellent outcrops with well defined multiphase sequence of fluorite deposition.

The field work was complemented with data and sample profiles that were taken in all the other fluorite veins in the investigated area (Fig. 1). In important mines, such as Bubú, La Estela, Francisco and La Saida, field observations were in general too fragmentary to enable an overview of the complete sequence of mineral deposition, due to poor quality of outcrops. Particularly at the Cerros Negros deposit, the fluorite occurs as open-space filling in a tabular E-W trending tension fracture.

Eleven successive generations of fluorite deposition were identified on the basis of vein chronology, textural relationships and mineralogical data. These fluorite generations can be regrouped into three main mineralizing stages whose spatial arrangements are illustrated in Figure 3. Such arrangements cannot be generalized for all the deposits since deviations of these vein filling patterns frequently occur, including locally at the Cerros Negros, and because in most of the veins some of the fluorite generations, or stages, can be absent.

Stage I. This stage is characterized by deposition of yellow fluorite, followed by white and subordinately pink fluorite. Their texture is mostly massive and coarsely crystalline, and gradually changes to banded, in association with the crystallization of a light blue fluorite.

Stage II. The transition to this stage is marked by fracturing accompanied by deposition of green fluorite (sample 6) and white chalcedony, and formation of tectonic breccias with concentric banded texture around the clasts (cockade texture). Subordinately, the fluorites of stage II are separated by sharp contacts and, by unconformity surfaces from the banded fluorites of stage I. The onset of stage II is characterized by purple, white, violet and green fluorite arranged in a millimeter- to centimeter width crustiform banded texture, with rhythmic variations in color.

The end of stage II is marked by a gradual change in the texture from crustiform to colloform and by the local formation of tectonic breccias together with the deposition of dark violet and black fluorite, brown to black chalcedony and pyrite. SEM studies confirmed the presence of coffinite and pitchblende occurring either as inclusions of 2 μm to 10 μm in diameter, or in sharp contact with pyrite (i.e. La Saida Mine).

Stage III. This stage comprises purple and yellow fluorite associated with meter-wide white chalcedony veins, deposited in contact with the granite wall rock or as discordant veinlets within the vein structure. Symmetric crustification, well-developed colloform textures and vugs are typical features of this stage. In the vugs the yellow fluorite is later than the purple one.

Hematite, lepidocrocite and submicroscopic barite were formed by partial oxidation of the pyrite deposited in the previous stage.

The fluorite from stages I and II are the principal targets of the present mining activity at the Cerros Negros deposit. The stage III normally appears very poorly developed or with a low grade of CaF_2.

REE in Fluorite Ores

REE analyses were performed in fluorite ores by means of neutron activation analysis (INNA) at Instituto de Pesquisas Energéticas e Nucleares (IPEN), São Paulo, Brazil. Two standard reference materials, named GS-N and BE-N, were used. Additionally, the REE contents of granite and hydrothermally altered equivalents (host rocks) were determined by INAA and fusion – inductively coupled plasma-mass spectrometry method (ICP/MS) respectively, at the Activation Laboratories, Ltd. (Ontario, Canada). Precision was estimated to be within 2 to 3,5 percent for La and Eu, and 5 to 12 percent for Ce, Yb, Nd, Sm, Tb and Lu. REE contents less than 0.1 ppm probably are below the analytical accuracy. All the REE data are given in Table 1. They were normalized to REE contents in chondrites according to the data of Evensen et al. (1978).

The three fluorite stages previously described can also be distinguished on the basis of chondrite-normalized REE patterns (Fig. 4), La/Yb ratios (Fig. 5) and Eu anomalies (Fig. 6).

The stage I fluorite ores exhibits low to intermediate REE contents, ranging from 6.8 ppm to 36.9 ppm, large positive Eu anomaly with lower and constant La/Yb ratios (1.4 – 1.7). Their normalized REE patterns are slightly LREE depleted.

The fluorite breccia (sample CN6), which marks the change from stage I to stage II in the mineralized zone, displays the highest REE contents (213.2 ppm), with a marked flat REE patterns, but La/Yb ratio and positive Eu anomaly similar to those of the stage I fluorite ore.

The stage II fluorite ores reveal higher REE contents, (17 to 110 ppm) than the previous stage, and patterns of moderate LREE enrichment. Additional features include negative Eu anomaly and higher and variable La/Yb ratios (3.6 – 14.0). The dark fluorite breccia (sample CNL), which marks the transition from the stage II to III, displays LREE distributions similar to stage II, but the fractionation between the HREE is like that of the stage III fluorite ores. The anomalous contents in some REE elements of sample 9 cannot be accounted for.

The stage III fluorite ore is marked by low REE concentrations, ranging from 9.9 ppm to 10.5 ppm, a small positive Eu anomaly and intermediate La/Yb ratios (2.1 – 2.8), resulting in flat REE patterns, slightly enriched in LREE.

Figures 4 and 5 show that the variations of the REE distribution in fluorite ores of the three stages was governed by a relatively more fractionated LREE than HREE, the fractionation between the stage I and II being the most marked.

Fluid Inclusion Studies

Fluid inclusion petrography

Fluid inclusions in fluorite from the Cerros Negros deposit are generally abundant and may be separated into primary, pseudosecondary and secondary groups, according to their modes of occurrence in the host crystals using the criteria of Roedder (1984).

Most of the primary-like inclusions in fluorite occur isolated or as isolated groups in size varying from 10 to 100 μm. The more frequent morphological types include negative crystals, tubular, and irregular to sub-spherical shapes with serrated borders (Figs. 7A and B).

As pseudo-secondary type was considered a particular group of inclusion that present sub-spherical shape (< 15 μm in diameter) and commonly exhibit oriented arrays along short healed microfractures or fluorite growth planes (Fig. 7C).

The secondary inclusions range in size from 10 to 80 μm and generally exhibit very flat and irregular morphologies, i.e. branched shapes, and are concentrated along fractures or (111) cleavage planes (Fig. 7C).

Primary, pseudosecondary and secondary inclusions are present in fluorites of the three stages with no great differences in terms of inclusion populations. They consistently contain two phases at room temperature: an aqueous liquid and a vapor phase (bubble). The vapor phase commonly fills approximately 10 to 20% of the bulk volume of the inclusions, implying an originally homogeneous fluid at the time of trapping.

Microthermometry

Microthermometric measurements in inclusion fluids hosted by fluorite were performed on a heating-freezing stage at the Fluid Inclusion Laboratory of the Instituto de Geociências, Universidade Estadual de Campinas (IG/UNICAMP), Campinas, Brazil. The stage was calibrated using synthetic inclusions containing pure water, manufactured by Syn Flinc. The uncertainly is ± 0,1°C for freezing runs, and better than 5°C for heating runs up to 200 °C .

Reproducibility in all cases is within the estimated accuracy of the recorded temperature. Control of stretching was made using the criteria of Lawler and Crawford (1983) and Bodnar and Bethke (1984).

Primary, pseudosecondary and secondary inclusions were measured by microthermometry but, in order to determine the physical and chemical characteristics of the hydrothermal fluids during the mineralizing stages, only primary and pseudosecondary inclusions were taken into account.

Total homogenization temperatures (Th_t) on nearly 370 aqueous inclusions were measured in 9 fluorite samples, being 4 of stage I, 3 of the stage II and 2 of the stage III. In these inclusions, the Th_t which took place within the range 187°C - 104°C, invariably to the liquid phase, may be grouped according to the depositional sequence observed in the field (Fig. 8). A trend of temperature decrease from stage I to III is quite remarkable:

Stage I: median value = 160°C;

Stage II: median value = 136°C;

Stage III: median value = 116°C

In these cases, the median values were used since the Th_t data present no gaussian distribution.

Because of the optical limitations, no microthermometric data were obtained in the dark violet to black uranium bearing fluorite of stage II. However, its does not preclude an estimate of the possible range of its formation temperature because their occurrence is confined to finely banded fluorite and vuggy purple fluorite in stage III, which display Th_t of ~136°C and ~122°C, respectively. The secondary inclusions have consistently recorded lower Th_t than the associated primary ones, generally with values as low as 90 °C.

Since the shallow environment of deposition inferred for this type of mineralization, less than 2 km of the paleosurface, (Coniglio, 1993), no pressure correction was applied to the Th_t data, and the median values are considered as close estimates of the original trapping temperatures of the inclusion fluids.

On the other hand, temperatures of ice melting (150 measurements) display values systematically within the interval of -0,3°C to +0,4°C indicating salinity very close to 0 (zero) equivalent weight percent NaCl. This low salinity was observed for all the fluorite ore stages and fluid inclusion types. Inclusions showing positive values for the ice melting (about 20% of the investigated inclusions) were not used for salinity determination, since these values indicate metastability (Roedder, 1984). Further evidence for the metastable behavior of such inclusions is indicated by the occurrence of vapor-free fluid inclusions at room temperature (Fig. 7D) (Shepherd et al., 1985). Carbon dioxide as liquid or other volatiles dissolved in the vapor phase was neither detected by microthermometry (formation of clathatre) nor by Raman microspectroscopy.

Discussion

Constraints on the ore forming fluids

The low temperature (187°C - 104°C) and the consistently very low salinity of the inclusion fluids in fluorite support a single, uniform fluid reservoir for the ore-forming solutions, probably heated meteoric waters, rather than fluids generated in deep-seated environments within the crust.

Same characteristics and nature determined for the mineralizing fluids in the fluorite deposits of the Cerro Aspero batholith, have also been reported in several other fluorite districts (Ruiz et al., 1980; Constantopoulos, 1988; Coelho et al, 1990; Bastos Neto et al., 1991).

As a contrast, important differences can be noted for the mineralizing fluids in fluorite deposits genetically related to magmatism which show salinities ranging from 9 to 50 equivalent weight percent NaCl and a higher range in the homogenization temperatures (50 - 500 °C) (Kesler, 1977, Strong et al., 1984, Gunnesch and Jaksch, 1984, Satish Kumar and Santosh, 1994). In addition, the fluorite deposit of Mato Preto, Brazil, whose genesis is partially linked to alkaline magmatism, show a strong variability in the homogenization temperatures (75 - 275°C) (Ronchi, 1993 *in* Bastos Neto, et al., 1996).

From this data, the hypothesis that the origin of the fluorite deposits in the Cerro Aspero batholith is related to hydrothermal fluids genetically derived from magmatic activity, ie. Cretaceous alkaline magmatism, is not tenable.

On the other hand, the constant degree of fill of the primary and pseudosecondary fluid inclusions populations in the Cerros Negros fluorites indicate that these fluids were homogeneous and no boiling or fluid mixture took place during the mineralizing stages. Furthermore, the absence of boiling suggests that the hydrostatic pressure was always higher than the vapor pressure of the solution (Hass, 1971). Moreover, the well defined trend of progressive cooling of the hydrothermal fluids appears to be one of the most distinctive characteristics of the mineralizing process at Cerros Negros deposit. These evidences allow to infer that the proposed three stage fluorite deposition was probably the result of a single hydrothermal event.

Constraints on the REE signature of the fluids

In an open system condition as inferred for the Cerros Negros deposits, the following factors could be taken into account for the relatively stronger LREE fractionation observed in the fluorite ores:

(1) Different sources of the REE. From the comparison of the La/Yb vs Yb distributions between granite host rocks and fluorite ores (Fig. 5), two different REE sources appears to be a possibility. Thus, an REE inherited from LM granite for the fluorite ores of the stage I and a REE inherited from PBM granite for the fluorite ores of the stages II and III can be suggested. Although this hypothesis cannot be totally ruled out, it appears unlikely, since the lack of interaction of the solutions responsible for the deposition of fluorite ores of stage I with the PBM granite, the main host rock of the fluorite deposits, is hard to explain.

(2) Fluid-rock interaction. Galindo et al. (1997) pointed out this mechanism as a probable cause for the Nd-Sm and Sr isotopic composition in fluorites from the Achala and Cerro Aspero batholiths, but no further constraints on the mechanisms of REE release to the fluids and

mineralization stages were made. In the present study, field and mineralogical evidences demonstrate that only silicic and argillic alterations were relevant processes during the formation of the fluorite deposits.

Whereas petrography of the silicic alteration attests that the vein-forming fluids acquired their REE composition from pervasive leaching of the bulk granite mineralogy, but not from any preferential mineral phase, the argillic alteration appears to have been different and more selective, destroying partially the feldspars and biotite of the granite.

The comparison of the REE patterns between altered and fresh granite reveals that argillic or silicic alterations had important consequences on the REE mobility (Fig. 9). In the argillic alteration the total REE composition of the granite was relatively unchanged, with the LREE being practically not removed. As a contrast, the silicic alteration resulted in progressive leaching of all the REE, as a function of the increasing intensity of alteration, with strong removal of Eu and preferential leaching of HREE over LREE. These observations can partly be explained by dilution effects caused by the modal increase of quartz, the inability of the secondary minerals to fix all the released REE during alteration, and the extensive leaching effect of the recurring circulation of hydrothermal solutions, which could have been broadly favored by low pH conditions and the presence of fluorine (Rubin et al., 1993).

In this context, the more intense leaching of the HREE observed during all the alteration process can be explained because they form stronger complexes with F^- than LREE (Taylor and Fryer, 1982). The LREE retention observed in the argillic alteration as against silicic ones can be attributed to the potential of phyllosilicates for LREE adsorption (Alderton et al., 1980).

In summary, this different mobility of the LREE dependent on argillic or silicic alteration strongly suggests that their alternate development (due, for instance, to changes in fluid/rock ratios or pH), could have exerted a significant control on the REE compositions of the hydrothermal solutions.

(3) Chemical REE complexation in the fluid. As was previously discussed, the more important HREE mobility that occur during the hydrothermal alteration of the granite attest that the associated fluids are not purely aqueous and the REE could have been transported in solutions mainly as fluoro complexes.

At Cerros Negros deposits, the formation of fluorite ores always richer in HREE than LREE, if they are normalized to the host granites, could provide further indirect evidence of the presence of F^- complexing in the fluids. This observation is in good agreement with the complexes stability constants, which increase from La to Lu (Wood 1990; Möller 1991; Bau and Möller, 1991).

Despite the fact that REE are very sensitive to transport with Cl^-, CO_3^{2-} or OH^- (Bau and Möller, 1991), the low salinity and lack of CO_2 in the fluid inclusions, together with the absence of carbonates in the ore, and the acidic conditions inferred for the alteration of the host rocks (Coniglio, 1992), indicate that the formation of these complexes was not favored.

Considering that several mechanisms could produce fractionation in a fluoro-complexing medium (Bilal et al., 1979; Strong et al., 1984; Möller, 1991; Bau and Möller, 1991), the fractionation of LREE due to chemical complexation during migration process appears to be more likely.

The presence of pyrite-coffinite-pitchblende assemblage in the ore suggests that the formation of H_2S and probably uranous fluoride complexes in the hydrothermal fluids were other factors that indirectly controlled the REE composition in fluorites from the end of stage II and stage III. The association of pyrite with pitchblende or coffinite, in the case of a medium saturated with silica, is likely to have formed by the following reaction (Cunningham et al.,1998):

$$UO_2F_3^- + FeO \text{ (in silicates)} + 2\ H_2S = UO_2 + FeS_2 + 3F^- + 2\ H^+ + H_2O$$

In this case, the LREE could have been partially extracted to the fluid and concentrated by substituting U^{4+} in the pitchblende lattice (Leroy and Turpin, 1988).

On the basis of these constraints, it is probably realistic to suggest that the REE distribution observed in the Cerros Negros deposits was mainly dependent upon the fluid-rock interaction through which the REE mobility was driven by fluoro complexes.

Eu Anomaly

As it was show in figure 9, strong leaching of Eu was produced during the alteration of the host granite, testifying that this element was not depleted in the solution. Hence, variations of the Eu anomalies in fluorite could be readily interpreted in terms of changes in fO_2 which controlled the Eu^{2+}/Eu_{total} ratio ($Eu_{total} = Eu^{2+} + Eu^{3+}$) (Meary et al., 1984; Jebrak et al., 1985), assuming fixed values of pH (Sverjensky, 1984). In this context, oxidizing conditions and effective incorporation of Eu^{3+} in fluorite ores of the stages I and III are inferred from the positive Eu anomalies.

The progressive decrease in the Eu anomaly in fluorite ores from highly positive, in stage I, to strongly negative in stage II (Fig 6; Table I), suggests an evolution of mineralizing fluids driven by progressive drops in the fO_2. Such a condition could be attained by simple cooling of the hydrothermal fluids (Meary et al., 1984). The resurgence of positive Eu anomalies in fluorites from the stage III was probably produced by increase in fO_2, due to the increase in the mSO_4^{2-}/ mS^{2-} ratio in the fluid, as result of massive precipitation of pyrite.

Considering the coexistence of coffinite-pitchblende and pyrite with fluorite ores of the stage II and using thermochemical data (Cunningham et al., 1998), it is possible to infer that the fluids responsible for the deposition of the fluorite had fO_2 about 10^{-47} to 10^{-50} bar. Moreover, the formation of hematite, lepidocrocite and barite by oxidation of pyrite suggests that the fO_2 probably remained higher than 10^{-35} bar during the deposition of stage III fluorite.

Further considerations on the genetic model

In the Cerros Negros deposit evidence for recurrent changes in the alteration style, together with temperature decrease during the fluid evolution, suggest that the precipitation of fluorite was likely driven by fluid-rock interaction combined with simple cooling (Richardson and Holland, 1979).

In addition to the cooling trend of the fluids, the changes of the fluorite texture from massive to vuggy from the stage I to III, could be indicating conditions of ore deposition at successively shallower levels below the terrestrial surface, with the present exposure of all three at the same level. In this case, considering that the development of large erosion surfaces in the Sierras de Córdoba has been assigned as Cretaceous in age (Rabasa et al., 1997), the possibility of erosion during the life of the hydrothermal system cannot be discarded as a viable scenario to account for the process of fluorite deposition.

Although no geochemical data for fluorine distribution in the Cerro Aspero granites are available, several mineralogical phases, other than accessory fluorite, appear as potential sources, particularly, biotite and apatite in view of their modal abundances. This observation is reinforced by the fact that the F contents of the Achala batholith correlate with the abundance of these minerals (Dorais et al., 1997).

Finally, the evidence of coeval deposition between coffinite-pitchblende and fluorite at Cerros Negros deposit indicate that uranium and fluorine are genetically related to the same mineralizing process and strongly suggests a common origin for the mineralization at the Estela deposit.

Conclusions

On the basis of geological and geochemical data in the fluorite ores and host granite of the Cerro Aspero batholith, it was possible to constrain the evolution of the hydrothermal fluids responsible for the fluorite precipitation.

The fluid inclusion study in fluorite of stage I, II and III demonstrate that the trapping fluids had a conspicuous compositional homogeneity and that the distinction of these stages is only possible from the total homogenization temperature. Additionally, the total homogenization temperatures, combined with the Eu/Eu* ratios in fluorite defined a trend of progressive cooling of the hydrothermal fluids from the stage I to III.

Despite the uncertainly regarding the mobility and fractionation of REE during hydrothermal alteration (Wood 1990; Lottermoser, 1992), the evidences found in the present work suggest that the mechanism of fluid-rock interaction appear to be the best working model for REE behaviour in the hydrothermal system and fluorite deposition.

The genetic link determined for fluorite and uranium minerals raises the question about the age of the fluorite and uranium vein deposits or, alternatively, on the span of time of the mineralizing process, since the uranium deposits in Sierras de Córdoba have been assigned as Tertiary. This consideration and the high U, Th and K contents in the granitic host rocks indicate that the possibility of radiogenic heat supply for hydrothermal fluid convection cannot be discarded. This mechanism was already suggested by Sallet et al. (1996) for the similar fluorite deposits at the Santa Catarina district, Brazil.

The fact that some of the fluorite generations, or stages, are absent in several veins in the investigated district, confirm that the mineralized structures had different times of opening and sealing, and thus the depositional sequence established for the Cerros Negros deposits could be used as an effective prospection criteria.

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Figure Captions

Figure 1. Simplified Geologic map of Cerro Aspero batholith (CAB) (modified from Pinotti, 1998) with the location of the main fluorite deposits: Cerros Negros (CN), Bubú (BB), Francisco (FCO), La Saida (LS), La Estela (LE), Santa María (SM), San Basilio (SB), San Guillermo (SG), 31 de Julio (31J), Ubaldina (UB), La Cabecita (LC), Carlos (CA) and El Pantanillo (EP). Achala batholith (AB).

Figure 2. (A) Incipient silicic alteration. Secondary coarse quartz and associated quartz veinlets replacing microcline of porphyritic biotite monzogranite (PBM). In this stage some muscovite (sericite) is formed. Sample (ISA). (B) Advanced silicic alteration. Pervasive replacement of PBM granite by fine-grained, jasperoid-like quartz. Veinlet of fine-grained quartz cutting chalcedony matrix. Sample (ASA-2). Minerals symbols: Qtz (quartz), Ms (muscovite), Mc (microcline), chal (chalcedony).

Figure 3. Schematic simplified cross section at level 3 of Cerros Negros mine showing the spatial relations of fluorite deposition sequence with sample location (abbreviations for fluorite color and texture are specified in table I).

I.- Fluorite ores of stage I. Roughly symmetric spatial arrangement from wall to wall of the veins.

II and III.- Non-symmetric arrangements of vein filling in fluorite ores of stage II and III, respectively.

Figure 4. Chondrite-normalized REE patterns for fluorite ore from Cerros Negros deposit. A) fluorites from stage I, B) fluorites from stage II, C) fluorites from stage III.

Figure 5. Scatter diagram for La/Yb vs Yb in fluorites from stage I, II and III, of Cerros Negros deposit. Same symbols for samples used in figure 4. The compositional fields of PBM granite (shaded area) and LM granite (dashed square) are plotted for comparison.

Figure 6. Diagram of correlation Eu/Eu* vs La/Sm for the three stages of fluorite deposition. Same symbols for samples used in figure 4.

Figure 7. Fluid inclusion types from fluorite ores of the Cerros Negros deposit.

7A. Typical tetrahedral-shaped primary inclusions. **7B.** Irregular primary inclusion with serrated borders. **7C.** Branched secondary inclusions cutting trend of small, sub-spherical pseudo-secondary inclusions distributed along short healed microfractures. **7D.** Vapor-free monophasic inclusion.

Figure 8. Histograms showing the homogenization temperatures of primary and pseudosecondary inclusions corresponding three successive mineralization stages determined in the Cerros Negros deposit. The median homogenization temperature in each stage and sample numbers are indicated.

Figure 9. Chondrite-normalized REE pattern for samples showing argillic and silicic alteration. The shaded area comprises the REE patterns of the unaltered PBM granite.

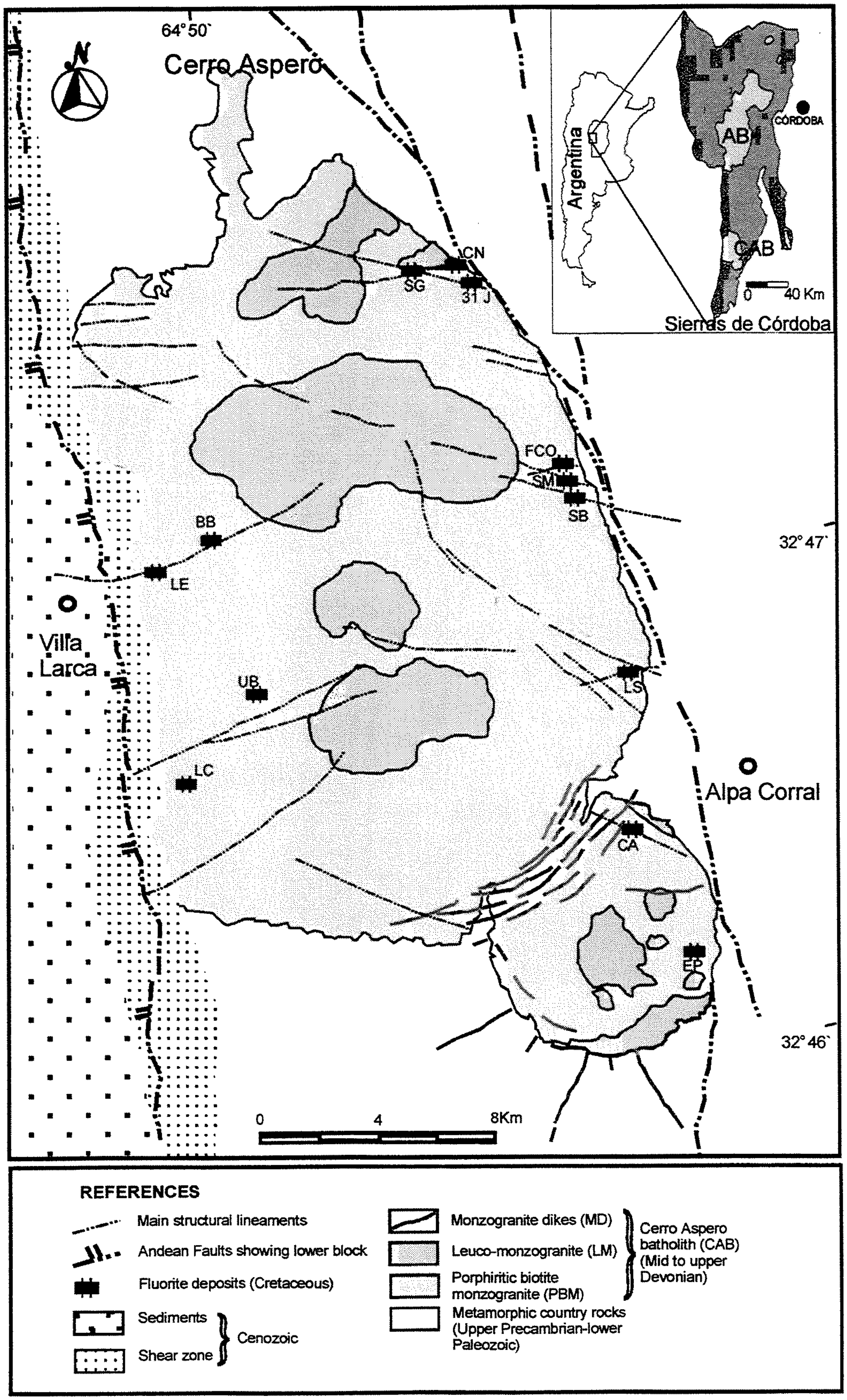

64° 50`
Cerro Aspero
N
Argentina
ABB
CÓRDOBA
CAB
0
40 Km
Sierras de Córdoba
CN
SG
31 J
FCO
SM
SB
BB
LE
32° 47`
Villa Larca
UB
LS
LC
Alpa Corral
CA
EP
32° 46`
0
4
8Km
REFERENCES
Main structural lineaments
Andean Faults showing lower block
Fluorite deposits (Cretaceous)
Sediments
Shear zone
Cenozoic
Monzogranite dikes (MD)
Leuco-monzogranite (LM)
Porphiritic biotite monzogranite (PBM)
Cerro Aspero batholith (CAB) (Mid to upper Devonian)
Metamorphic country rocks (Upper Precambrian-lower Paleozoic)

Fig. 1

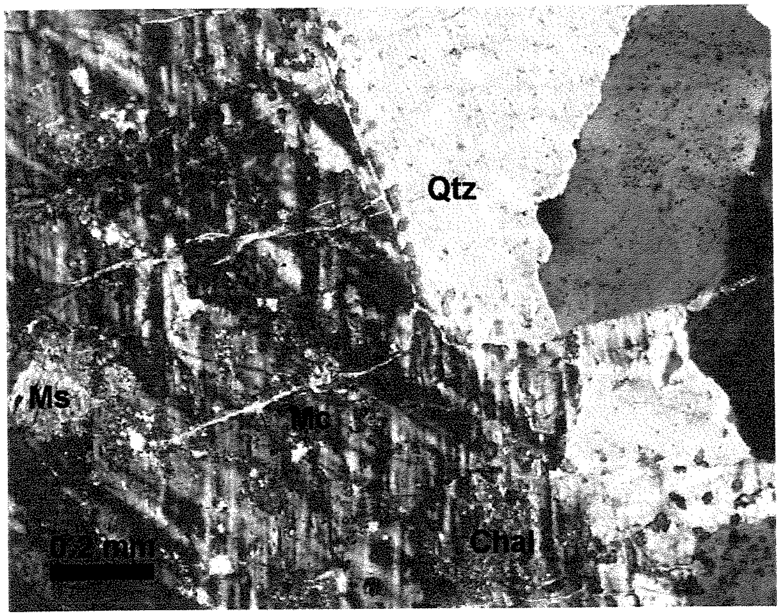


Fig. 2 A

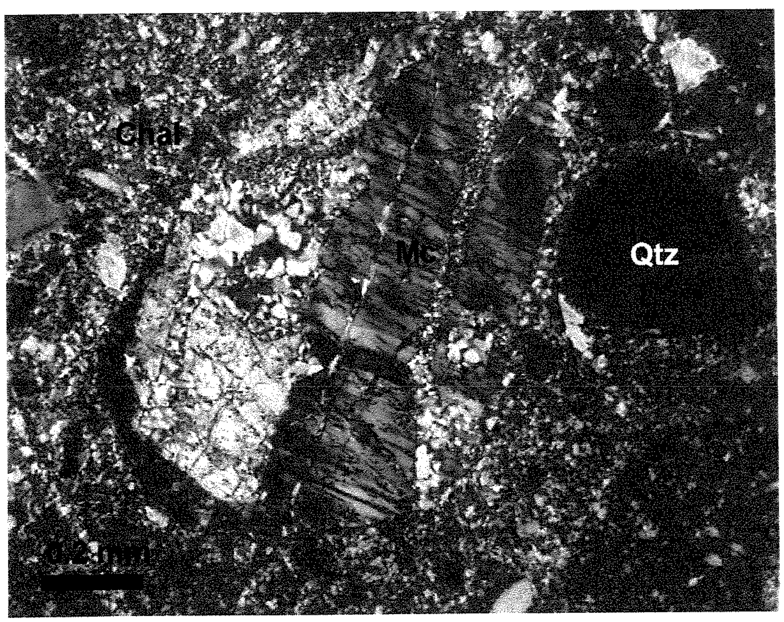


Fig. 2 B

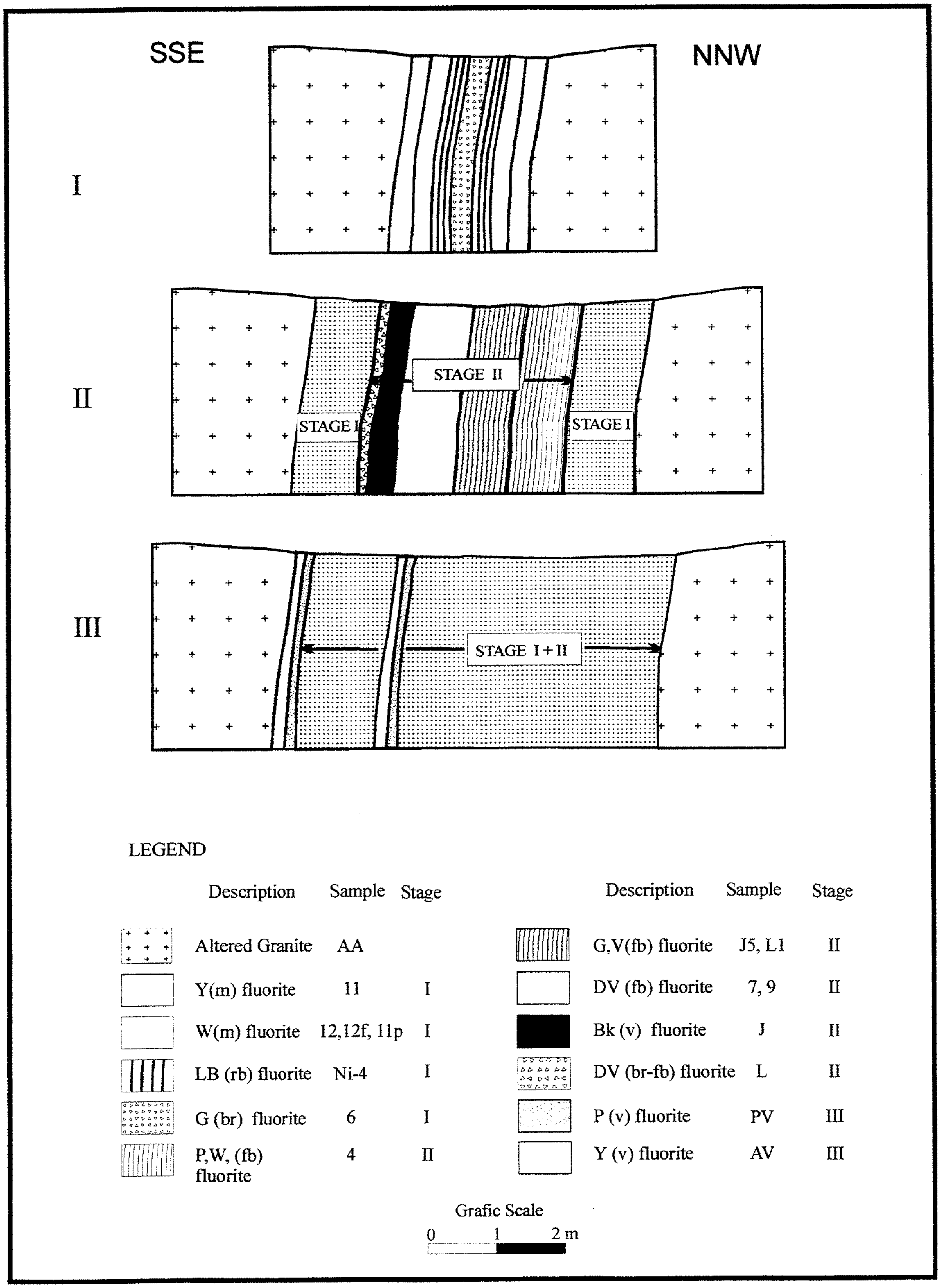

SSE
NNW
I
II
STAGE II
STAGE I
STAGE I
III
STAGE I + II
LEGEND
Description Sample Stage
Altered Granite AA
Y(m) fluorite 11 I
W(m) fluorite 12,12f, 11p I
LB (rb) fluorite Ni-4 I
G (br) fluorite 6 I
P,W, (fb) fluorite 4 II
Description Sample Stage
G,V(fb) fluorite J5, L1 II
DV (fb) fluorite 7, 9 II
Bk (v) fluorite J II
DV (br-fb) fluorite L II
P (v) fluorite PV III
Y (v) fluorite AV III
Grafic Scale
0 1 2 m

Fig. 3

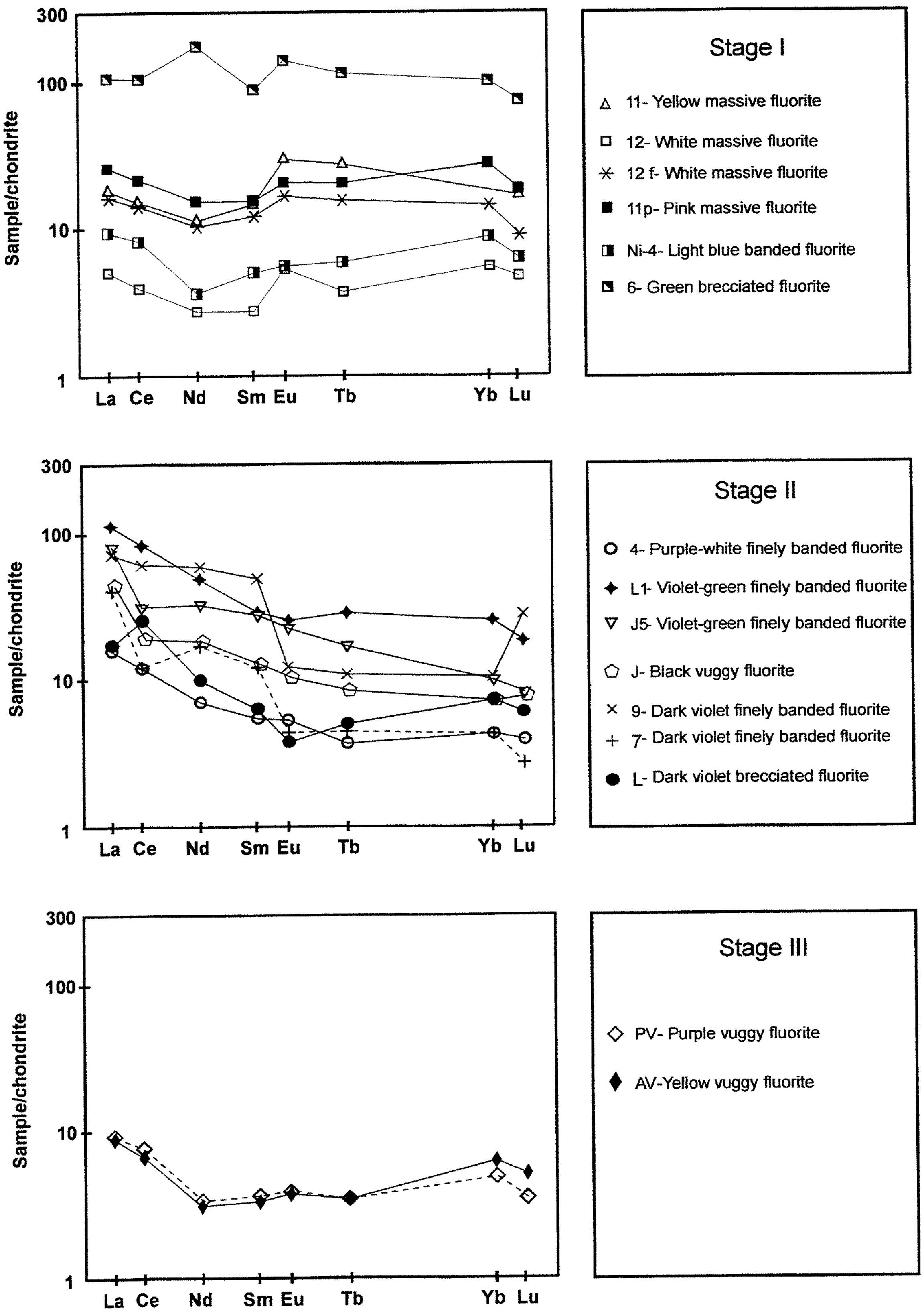

300
100
10
1
Sample/chondrite
La Ce Nd Sm Eu Tb Yb Lu
Stage I
11- Yellow massive fluorite
12- White massive fluorite
12 f- White massive fluorite
11p- Pink massive fluorite
Ni-4- Light blue banded fluorite
6- Green brecciated fluorite
Stage II
4- Purple-white finely banded fluorite
L1- Violet-green finely banded fluorite
J5- Violet-green finely banded fluorite
J- Black vuggy fluorite
9- Dark violet finely banded fluorite
7- Dark violet finely banded fluorite
L- Dark violet brecciated fluorite
Stage III
PV- Purple vuggy fluorite
AV-Yellow vuggy fluorite

Fig. 4

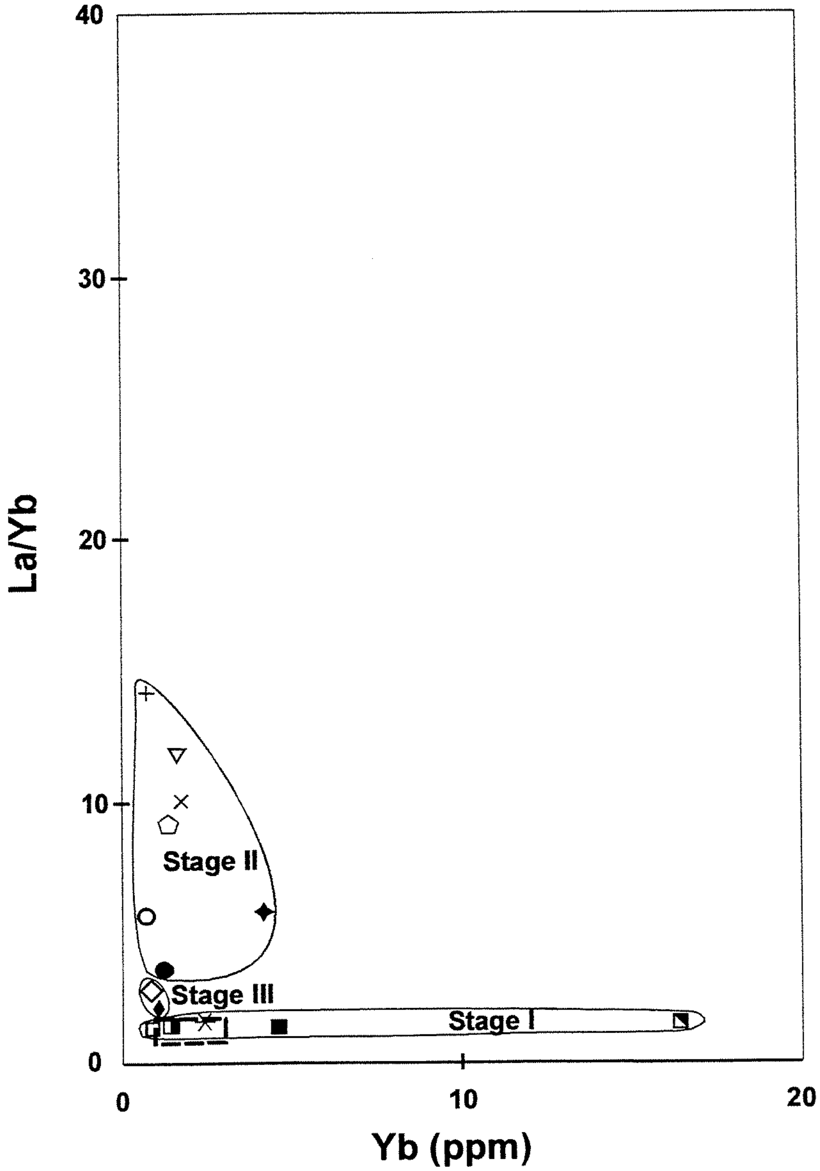
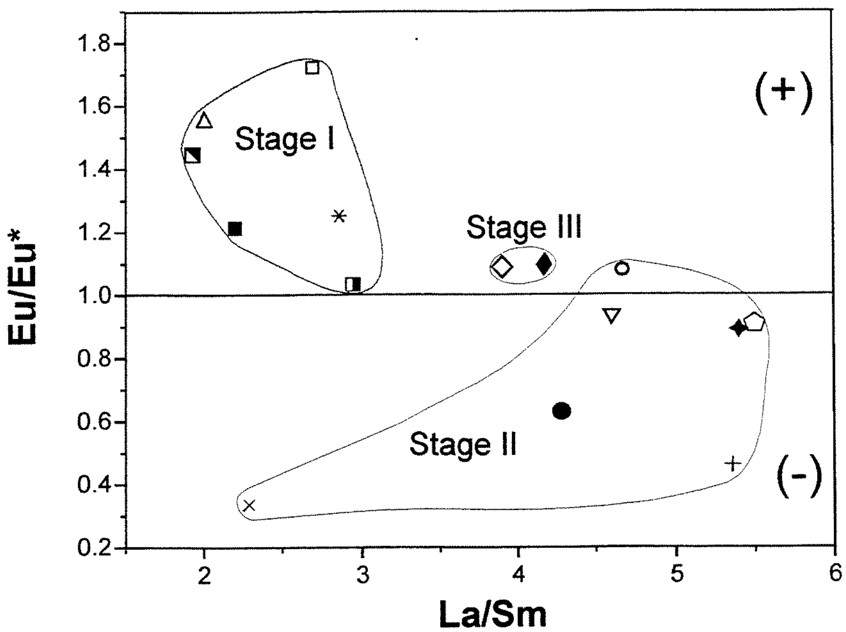


Fig. 5



1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Eu/Eu*
2
3
4
5
6
La/Sm
Stage I
Stage III
Stage II
(+)
(-)

Fig. 6

Fig. 7A

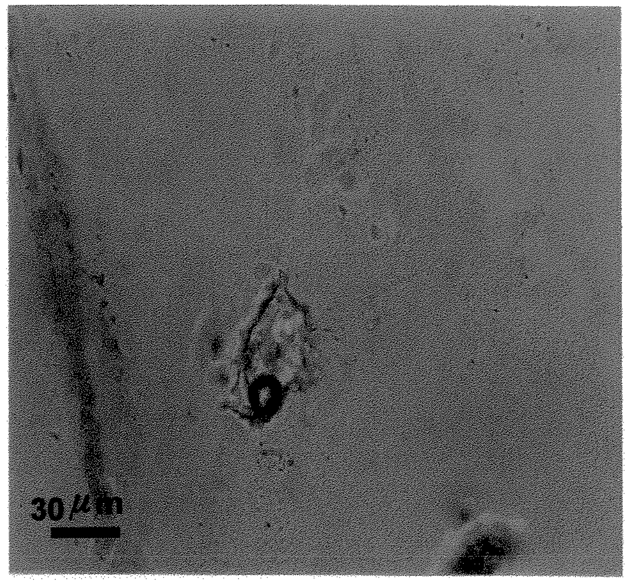


Fig. 7B

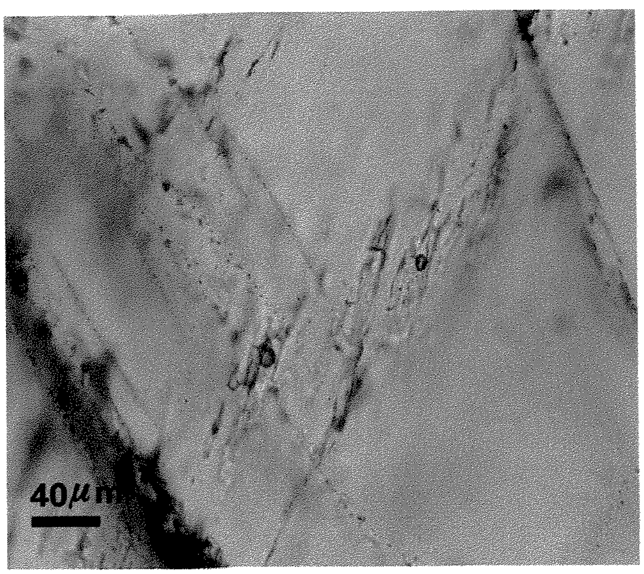


Fig. 7C

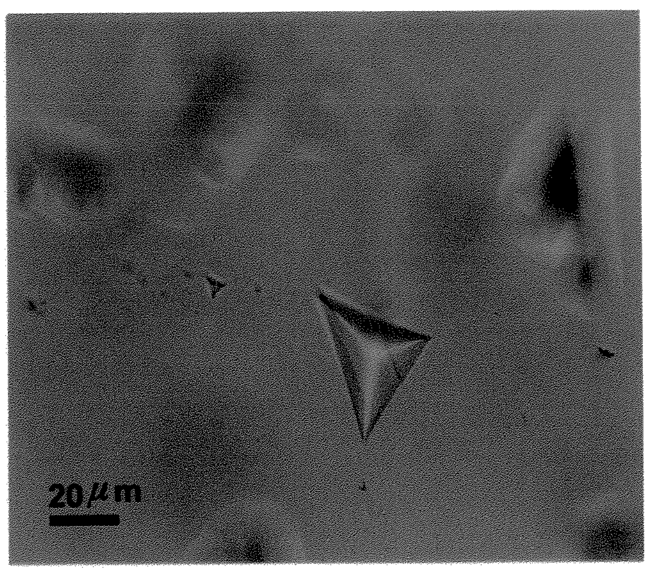
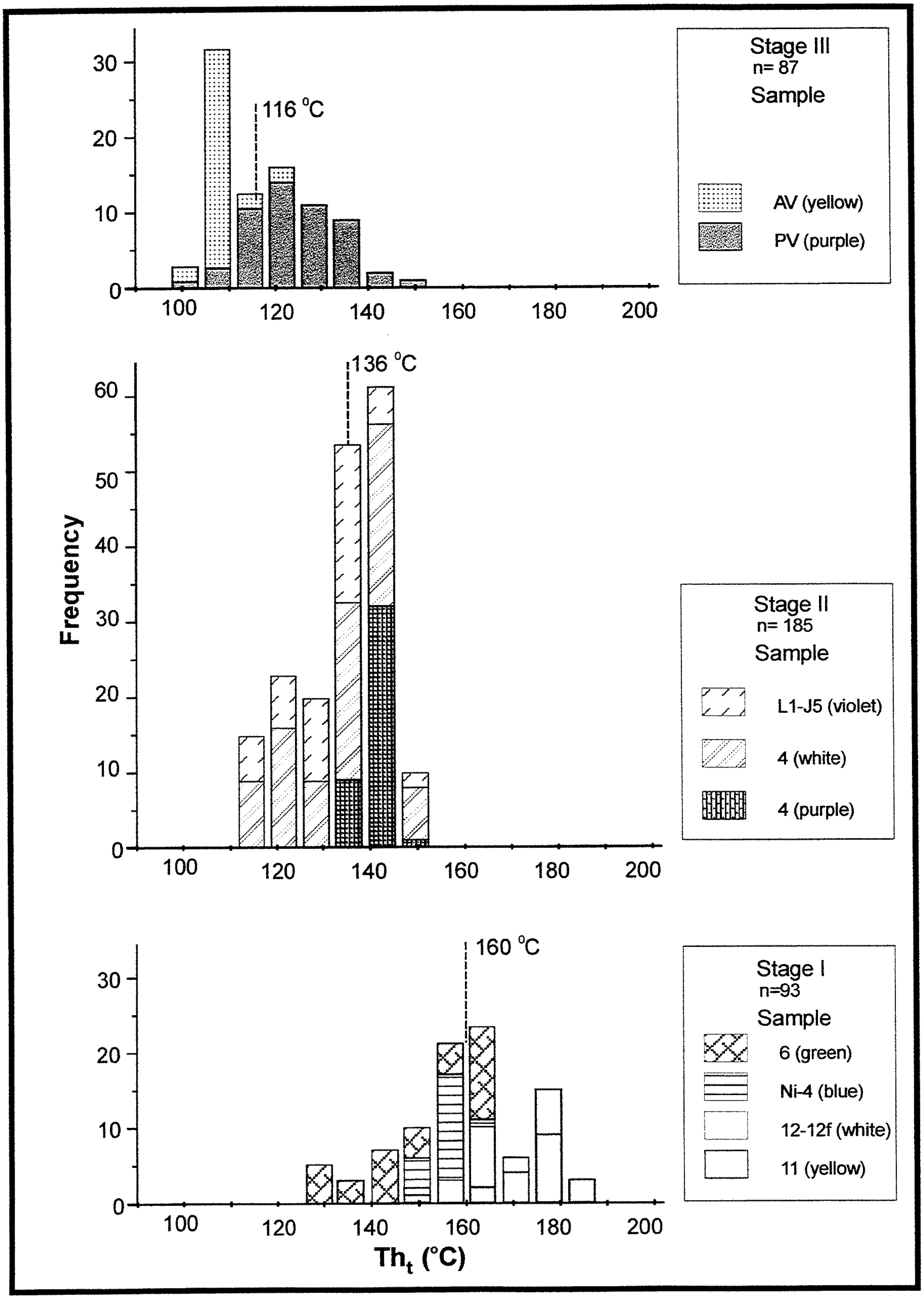


Fig. 7D



Stage III
n= 87
Sample
AV (yellow)
PV (purple)
116 °C
Stage II
n= 185
Sample
L1-J5 (violet)
4 (white)
4 (purple)
136 °C
Stage I
n=93
Sample
6 (green)
Ni-4 (blue)
12-12f (white)
11 (yellow)
160 °C
Frequency
Th_t (°C)

Fig. 8

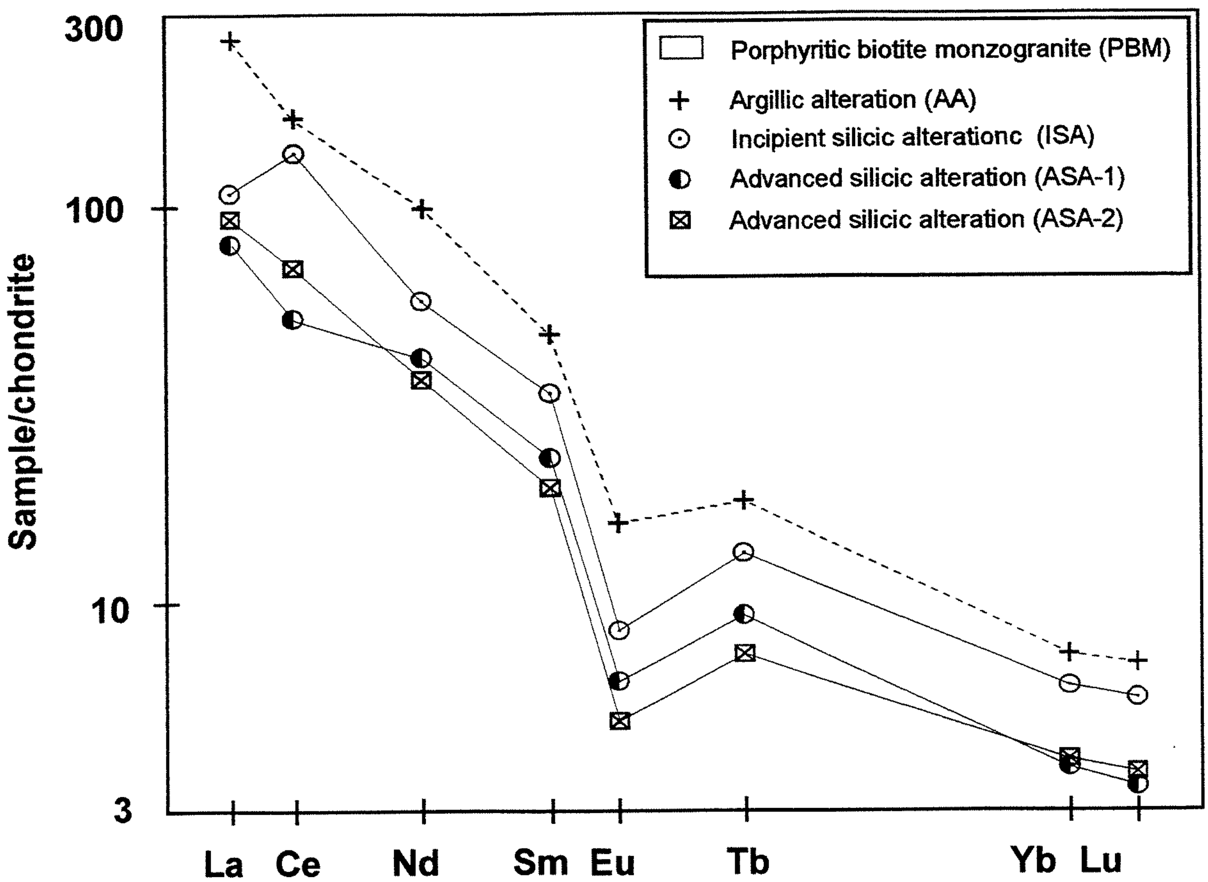

300
100
10
3
Sample/chondrite
Porphyritic biotite monzogranite (PBM)
Argillic alteration (AA)
Incipient silicic alterationc (ISA)
Advanced silicic alteration (ASA-1)
Advanced silicic alteration (ASA-2)
La Ce Nd Sm Eu Tb Yb Lu

Fig. 9

TABLE 1. Rare Earth Element abundances (ppm) and ratios in fluorite of the Cerros Negros deposit. REE abundances in alteration zones and granitic rocks from the Cerro Aspero batholith.

Sample	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	∑REE	Eu/Eu*	La/Yb	Color (texture)
11	4.60	9.80	5.00	2.30	1.75	1.05		0.44	29.94	1.56		Y (m)
12	1.23	2.50	1.20	0.43	0.31	0.14	0.90	0.12	6.83	1.72	1.37	W (m)
12 f	4.00	9.09	4.60	1.90	0.98	0.59	2.40	0.23	23.79	1.25	1.67	W (m)
11 p	6.50	14.1	6.80	2.40	1.22	0.78	4.60	0.47	36.87	1.21	1.41	Pk (m)
Ni 4	2.30	5.20	1.58	0.78	0.32	0.22	1.44	0.16	12	1.03	1.59	LB (rb)
6	26.00	66.00	77.00	13.50	8.10	4.30	16.40	1.90	213.20	1.44	1.58	G (br)
4	4.02	7.70	3.10	0.86	0.31	0.14	0.71	0.10	16.94	1.07	5.66	P-W (fb)
J 5	18.90	19.20	13.90	4.10	1.26	0.62	1.61	0.20	57.79	0.93	11.74	V-G (fb)
L 1	24.30	53.00	21.40	4.50	1.51	1.08	4.20	0.47	110.46	0.89	5.78	V-G (fb)
9	17.60	39.00	26.00	7.70	0.72	0.41	1.75	0.71	93.89	0.34	10.05	DV (fb)
7	10.20	7.90	7.50	1.90	0.26	0.17	0.72	0.07	28.72	0.46	14.16	DV (fb)
J	11.00	12.30	8.10	2.00	0.61	0.32	1.20	0.20	35.73	0.91	9.16	Bk (v)
L	4.28	16.39	4.39	1.00	0.22	0.19	1.20	0.15	27.82	0.63	3.56	DV (br)
AV	2.17	4.30	1.38	0.52	0.22	0.13	1.05	0.13	9.9	1.11	2.07	Y(v)
PV	2.27	4.90	1.53	0.57	0.23	0.13	0.82	0.09	10.54	1.09	2.76	P (v)
PBM-M2	68.00	136.0	59.00	9.52	1.75	0.90	2.11	0.31				
PBM-78	54.40	105.0	40.00	7.15	1.01	0.90	2.15	0.30				
PBM-C	35.90	76.00	31.00	5.61	0.78	0.70	2.58	0.38				
LM-1	2.50	6.00	3.00	0.77	0.04	0.20	1.36	0.20				
LM-2	2.10	5.00	3.00	0.79	0.08	0.20	1.30	0.17				
LM-d	4.00	11.00	6.00	1.55	0.16	0.40	2.74	0.43				
AA	63.00	104.0	43.00	7.30	0.92	0.68	1.24	0.18				
ISA	25.99	85.31	25.36	5.15	0.49	0.50	1.03	0.15				
ASA-1	19.68	33.31	18.25	3.61	0.37	0.35	0.68	0.09				
ASA-2	22.40	43.87	15.92	2.97	0.29	0.28	0.69	0.10				

$(Eu/Eu^*)_N$ $Eu^* = 2/3\ Sm + 1/3\ Tb$

Y= yellow; W= white; Pk= pink; LB= light blue; G= green; P=purple, V= violet; DV= dark violet; Bk=black.
(m)= massive; (rb) = roughly banded; (br) breccia; (fb)= finely banded; (v)= vugs
PBM= porphyritic biotite monzogranite; LM= leuco-monzogranite; AA= argillic alteration;
ISA= incipient silicic alteration; ASA= advanced silicic alteration

III. SUMÁRIO DAS CONCLUSÕES

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No setor sul das Sierras de Córdoba os depósitos de fluorita de idade Cretácea estão restritos a uma área de aproximadamente 440 Km^2, hospedados em rochas graníticas Paleozóicas do batólito Cerro Aspero (Paleozóico). Em particular, as concentrações econômicas de fluorita estão hospedadas exclusivamente por biotita monzogranitos porfiríticos.

A mineralogia dos depósitos é simples e composta por fluorita, calcedônia, localmente pirita e, eventualmente, coffinita e pitchblenda. A conspícua presença de texturas bandadas, crustiformes, coloformes e em geodos, entre outras, indica que a fluorita foi depositada em condições muito próximas da superfície.

A alteração hidrotermal nestes depósitos é dominantemente silícica e argílica, as quais estão amplamente limitadas aos sistemas de falhas transcorrentes dentro do biotita monzogranito porfirítico.

Três estágios sucessivos de mineralização foram distinguidos com base em evidências texturais, estudos de inclusões fluidas e ETR em fluorita:

Estágio I.- Fluorita maciça, depositada principalmente entre 175C° e 155C°, empobrecida em ETRL e com baixo e constante fraccionamento total de ETR (La/Yb= 1.4-1.7).

Estágio II.- Fluorita bandada, depositada principalmente entre 145C° e 130C°, enriquecida em ETRL e relativamente mais fraccionada (La/Yb=3,6-14).

Estágio III.- Fluorita botrioidal e em geodos, depositada principalmente entre 125C° e 104C° com comportamento de ETR intermediário entre os dois estágios anteriores (La/Yb=2,8-2,1).

No depósito Cerros Negros, as inclusões fluidas são aquosas bifásicas (L>V), apresentam grau de preenchimento constante (0.8-0.9) e homogeneizan ao estado líquido. Nestas inclusões, as temperaturas de fusão do gelo no intervalo de –0.3 C° à +0.4 C° indicam salinidade quase nula para o fluido hidrotermal, independentemente do estágio de mineralização. Não foram encontradas evidências de mistura de fluidos nem ebulição.

A distribuição dos ETR na fluorita é principalmente governada pelo fracionamento dos ETR leves. Sugere-se que a composição em ETR do fluido hidrotermal e, consequentemente, da fluorita, foram amplamente controlados pela diferente mobilidade dos ETR leves a depender do tipo de alteração hidrotermal. Enquanto uma lixiviação preferencial de ETR pesadas sobre ETR leves ocorreu durante a alteração silícica e argílica, nesta última, os ETR leves praticamente não foram removidos.

Se sugere que os ETR foram transportados em solução como fluoro-complexos.

A variação na relação Eu/Eu* durante a evolução do fluido hidrotermal indica mudanças na fO_2, de condições oxidantes para redutoras, o qual foi principalmente originada pelo resfriamento da solução.

Os dados de inclusões fluidas sugerem que os três estágios de mineralização propostos foram o resultado de um único evento hidrotermal e sugerem um reservatório único e uniforme para as soluções mineralizantes, provavelmente águas meteóricas aquecidas, e não fluidos diretamente derivados da atividade magmática ou gerados em zonas mais profundas da crosta.

A lixiviação de flúor, cálcio e ETR das rochas graníticas pela ação de águas meteóricas aquecidas e conseqüente deposição de fluorita por processos de interação fluido - rocha parece ser o melhor modelo de trabalho.

IV. CONSIDERAÇÕES FINAIS

IV. CONSIDERAÇÕES FINAIS

Este trabalho faz parte de uma das linhas de pesquisa que a UNRC têm priorizada num dos seus projetos de desenvolvimento científico – tecnológico e na sua política de inserção regional.

Os resultados deste estudo têm dois pontos fundamentais de aplicação:

- Quanto ao plano da Geologia Econômica, os aportes efetuados ao conhecimento do modelo genético poderiam ser utilizados para uma melhor programação das tarefas de prospeção e exploração dos filões de fluorita no batólito Cerro Aspero. Adicionalmente, também se espera que possa ser aplicado como modelo comparativo em outras áreas, particularmente no ambiente geológico das Sierras Pampeanas.

- No que se refere aos aspetos ambientais, os altos conteúdos de flúor nas águas subterrâneas da zona de planície circunvizinha com este setor das Serras de Córdoba, é um problema que afeta o consumo de água de mais de 150.000 habitantes. O conhecimento sobre as possíveis áreas e fontes de aporte de flúor nas águas, assim como o estudo dos aspetos relacionados à hidrogeoquímica do flúor no ambiente de intemperismo, está abrindo um campo promissor de pesquisa multidisciplinar.

V. REFERÊNCIAS BIBLIOGRÁFICAS

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