Fluorite Mineralization Related to the Dolomitization: an Equilibrium Study of the Proterozoic Stratabound Carbonate Macaia-Ijaci Basin, Lavras, Minas Gerais, Brazil

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Resumo

Fluorita estratiforme ocorrendo como delgados filmes nas concomitantemente derivadas porções dolomíticas do calcário calcítico da Formação Carandaí do Proterozóico, na Bacia Macaia-Ijaci foi supostamente formada por reações metassomáticas entre o carbonato e salmouras ricas em HF e Mg^{2+}, durante o metamorfismo. Treze análises de micro-sonda eletrônica dos carbonatos em uma única lâmina petrográfica delgada , permitiram a determinação da temperatura de formação dos carbonatos na faixa 180º-230ºC, utilizando o geotermômetro Mg-calcita/solvus. Cinco reações-chave no sistema Mg-Ca-C-H-O-F lançadas em diagramas em termos de fugacidades ou potenciais químicos de CO_2 e HF produzindo fluorita+dolomita a partir de calcita+Mg^{2+} são propostas. Aparentemente a formação de fluorita é relacionada à dolomitização. Reação adicional envolvendo fluorita foi calculada e inserida no diagrama de fases, de acordo com a existência de venulações de fluorita-calcita bordejados por dolomita na pedreira de Casa de Pedra.

Palavras-chave: Dolomitização, geotermometria

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Abstract

Stratabound fluorite occurring as thin films in the concomitantly derived dolomitic portions of the calcitic limestone of the Proterozoic Carandaí Formation in the Macaia-Ijaci Basin was supposedly formed by metasomatic reactions between the carbonate and HF- and Mg^{2+}-rich brines, during metamorphism. Thirteen electron microprobe analyses from the carbonate in a single petrographic thin section, allowed the determination of the temperature of the carbonate formation in the range 180°-$230^{\circ}C$, using the Mg-calcite solvus geothermometer. Five key mineral reactions in the system Mg-Ca-C-H-O-F plotted in diagrams in terms of either, CO_2- and HF-fugacities or chemical potentials of CO_2 and HF yielding fluorite + dolomite from calcite + Mg^{2+}, are proposed. Apparently the fluorite formation is related with dolomitization. Additional reaction involving fluorite was calculated and inserted in the phase diagram, according to the existence of calcite-fluorite veinlets bordered by dolomite selvages, at the Casa de Pedra quarry.

Keywords: Dolomitization, HF/CO_2 fugacity, geothermometry

1 Introduction

Fluorite deposits are found in a range of geologic environments and formed by varied processes under different physicochemical conditions. Some main recognized genetic types are: 1. Deposits in carbonate rocks, similar to that of Mississippi Valley Type Pb/Zn deposits. This type is relatively common in the limestone successions all over the world (Anderson, 1975; Large, 1981; Sverjensky, 1981; Richardson *et al*., 1988); 2. In veins in/or associated with dominantly alkaline-peralkaline igneous rocks, with an origin more akin to magmatic-hydrothermal vein-type deposits; 3. Deposits at the contacts between limestones and granitoid rocks, referred as skarn type; 4. As open-space fillings in tension fractures within the granite or in its related porphyry dikes, as it is the case of the St. Lawrence fluorspar deposits, referred as greisen (Strong *et al.*, 1984). 5. Meteoric waters heated by volcanic activity, which supplied fluorine to react with the enclosing

limestones to cause fluorite deposition, as some mexican deposits (Ruiz *et al.*, 1980). Some fluorite occurs in Cu-Au deposits (Baker, 1998). Calcite replacements by dolomite have been reported as an effect of wall-rock alteration around Zn-Pb- ores at Northwestern Illinois (Moore, 1976) with discrete fluorite. However, in this particular case no Pb/Zn sulfides, intrusives and volcanic rocks are present presuming a brine derivation.

Scattered fluorite occurrences associated with calcite have been reported within the dolomites from the Gandarela Formation at Quadrilátero Ferrífero (Gair, 1962). However, the depositional process is poorly understood.

The zoning of a limestone invaded by granite, producing an aureole of magnesite, close to the granite, and dolomite has been discussed earlier (Hewett, 1928; Lovering, 1969), and several papers related to dolomitization and stability of Mg-Ca carbonates have attracted the attention of investigators for decades (Sjöberg, 1976; De Boer, 1977; Katz & Matthews, 1977).

The Cal Andrezza limestone quarry situated within the Medium Proterozoic Macaia-Ijaci Basin contains thin, concordant, pink fluorite micro-lenses bordered by dolomite. We figure that the study of this occurrence may help to understand the depositional process (Figure 1). Milimetric, discordant, white calcite-dolomite veins with scant fluorite and small pockets hosted in greyish limestone have been recently found at Casa de Pedra (Mineração Jundu) quarry, near the township of São João del Rei, about 150 km southwest of Belo Horizonte, State of Minas Gerais.

The geological aspects summarized in this text are well documented in the literature, the reactions and the intimate relationships between either fluorite and dolomite, and fluorite and calcite in the course of dolomitization, seem to be clear. In this paper, we present the study of a thin section prepared in a sample obtained from the Andrezza quarry. Electron microprobe analyses performed in the carbonate-fluorite rock along an orthogonal section to the bedding, showed interesting compositional variation, and indicated that the fluorite is
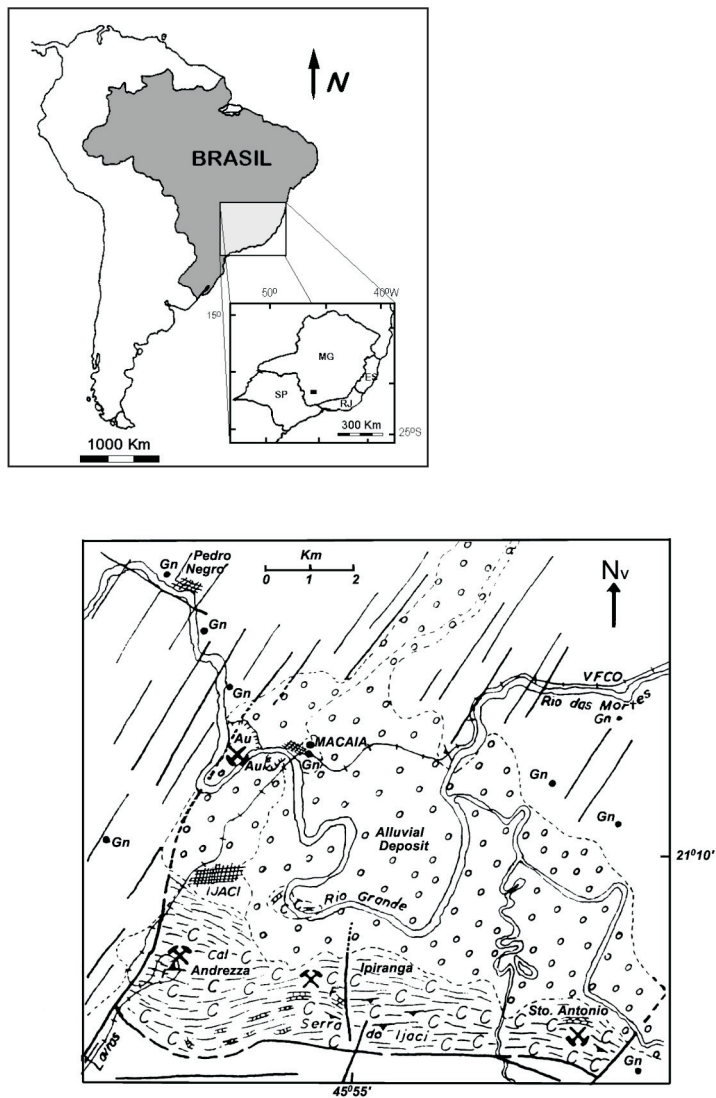
Figure 1 Geologic map of the Macaia-Ijaci Basin showing the limestone quarry with fluorite occurrences. Symbols: **C** = Carandaí Formation (limestones and phyllites); **Gn** = Gneiss; **Au** = alluvial gold; / fracture, fault.

restricted to the core of the dolomite band hosted by the calcitic limestone. Barite and sulfide minerals are almost absent at Macaia-Ijaci basin, but scarce pyrite was found at Casa de Pedra.

2 Geologic Setting

Fluorite occurs as micro-lenses within the dark to bluish grey limestones of the Proterozoic Carandaí Formation (Leonardos, 1940; Ebert, 1956, 1958, 1984; Pires, 1977; Karfunkel *et al.*, 1983) within the Ijaci-Macaia Basin, at the Cal Andrezza and Ipiranga quarries, distant 4 km from each other. Limestone lenses within phyllites in the Rio das Mortes valley, initially reported by Erichsen (1929) are distributed intermittently from Alfredo Vasconcellos to Lavras. They were included in the Barbacena Series within the Espinhaço Geosyncline (Barbosa, 1954). Later, the limestones and related phyllites were separated from the redefined Barbacena Group and placed in the overlying Barroso Formation, named by Ebert (1956). The limestones are part of a sequence of metasedimentary rocks containing graphite or carbonaceous layers, black phyllites, enclosing sporadic pyritiferous lenses. Cataclastic breccia with fragments of migmatites and gneisses, enveloped by the biotite-quartz-carbonate schist or phyllite may occur. The sequence is overlain by reddish brown phyllites, here considered as the same unit (Pires, 1977). In that way, the author proposed to restore the name Carandaí Formation and the extinction of the name Barroso Formation.

Glacial nature for the Carandaí tillite or Carandaí Formation has been respectively postulated by Leonardos (1940) and Karfunkel *et al*. (1983). Recently, Ribeiro (1997) suggested that Carandaí and Barroso Formations would constitute the "Sequence 1", composed by three cycles of subtidal and tidal sediments overlain by the "Sequence 2" (Prados Formation), consisting of metapelites and in a "condensed section". The Prados Formation could be correlative with Macaia Formation at the Macaia-Ijaci basin (Dehler *et al*.,1998).

Nevertheless from the five texturally and compositionally different types of limestones described by Viana *et al*. (1991) in the Carandaí Formation, we could recognize only a massive, bluish grey

and saccharoidal type, assayed 54.3-55.6%CaO and 0-0.3%MgO and an impure, banded, light grey limestone with thin siliceous laminas assaying 45%CaO, 0.9%MgO and 14%SiO$_2$ (Falcão, 1967). The dark color of the laminas is given by very small amounts of finely disseminated dark mica, sericite and chlorite.

The sediments were affected by a very low to low grade greenschist facies metamorphism in the chlorite zone. No garnet has been reported from this area.

Scant fluorite micro-lenses, about 1-2 mm thick, and 6-10 mm long, lie concordantly within the enveloping dolomite, enclosed in the calcitic limestone at the Cal Andrezza quarry. Thin hydrothermal veins containing fluorite and pyrite have also been found at the Casa de Pedra quarry, near São João del Rei.

3 Texture and Mineral Composition

Fluorite micro-lenses consist of a delicate aligned agglomerate of cubic crystals, about 0.15 mm in size, showing zoned crystals in the central parts of the micro-lens, displaying clear and colorless edges surrounding pink cores. The concentration of zoned crystals decreases toward the margins of the micro-lenses, as well as the intensity of the pinkish color. Along the boundary of the micro-lenses, the colorless crystals are not zoned. Therefore, zoning occurs in the individual crystals and in the micro-lenses itself. Pink color in the fluorite has been attributed to the crystals formed under higher temperature than the colorless and yellow ones. Some investigators postulate the pinkish color to the Mn dissolved in the fluorite crystals (Burrus *et al*., 1992).

Thirteen electron microprobe analyses (Table 1 and Figure 2) in a section disposed orthogonally to the main foliation, revealed a dolomite halo directly surrounding the fluorite micro-lenses encircled by the calcitic marble. Previous bulk analyses on the wet basis of the Ijaci limestones indicated a predominance of calcitic composition, with negligible amounts of MgO (Falcão, 1967; Viana *et al*., 1991).
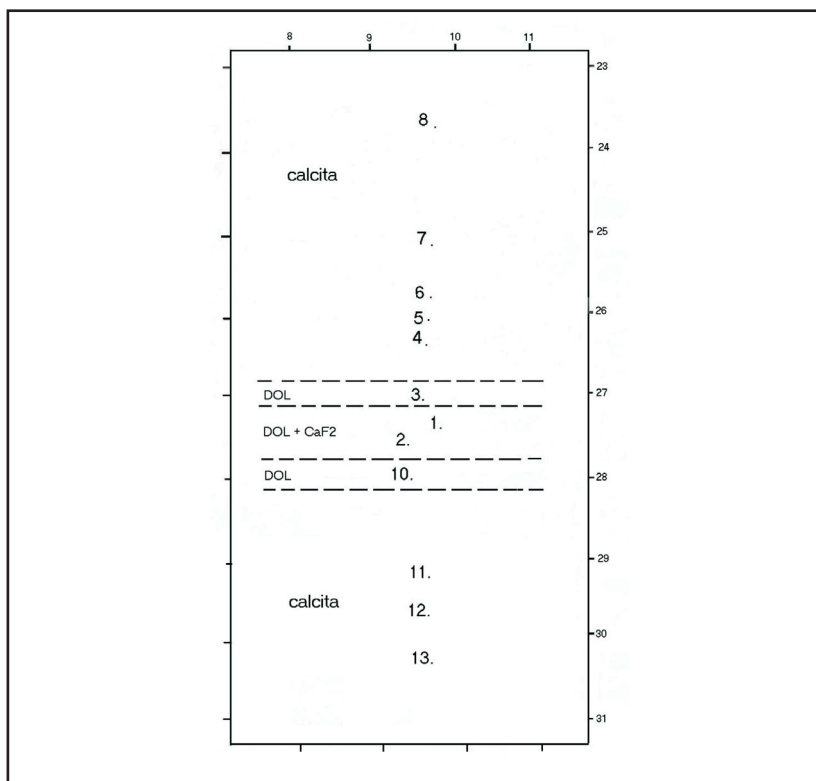
Figure 2 Enlarged scale thin section showing analyzed sites, calcite zone, dolomite and fluorite microlens.

Considering the analyzed thin section, a slight decrease in Mn content in the calcite can be observed approaching the dolomite-fluorite micro-lens. Ba- and Fe-contents, in negligible amounts, may explain the absence of baryte and pyrite in the limestone. The only Ba-values are close to the dolomite lenticle. Although the Sr-contents are small, they are relatively persistent in the rock, sharply decreasing with the proximity to the dolomite-fluorite micro-lens.

Site	Mg	Ca	Mn	Fe	Sr	Ba	Mineral
8	0.16	40.08	0.01	0.01	0.24	0	Calcite
7	0.13	39.68	0.04	0	0.07	0	Calcite
6	0.15	39.56	0	0.02	0.30	0	Calcite
5	0.02	38.06	0.01	0.01	0.11	0	Calcite
4	0.03	41.77	0	0.01	0.02	0	Calcite
3	12.09	22.08	0.03	0	0.17	0	Dol
2	12.22	22.52	0.02	0	0.18	0.06	Dol
1	12.01	22.91	0.03	0	0.25	0	Dol
10	12.37	21.96	0.01	0	0.10	0.01	Dol
9	0.06	40.22	0.03	0	0.07	0	Calcite
11	0.15	39.79	0.01	0	0.21	0	Calcite
12	0.19	39.97	0.04	0	0.22	0	Calcite
13	0.17	40.25	0	0.02	0.24	0.01	Calcite
Number of cations on the basis of 6 Oxygens							
8	0.0135	19.805	0.0002	0.0003	0.0055	0	
7	0.0106	19.862	0.0015	0	0.0017	0	
6	0.0125	19.801	0	0.0005	0.0069	0	
5	0.0020	19.942	0.0005	0.0007	0.0025	0	
4	0.0023	19.970	0	0.0002	0.0005	0	
3	0.9468	10.486	0.0009	0	0.0038	0	
2	0.9242	10.694	0.0010	0	0.0054	0	
1	0.9416	10.529	0.0008	0	0.0039	0.0009	
10	0.9615	10.358	0.0003	0	0.0023	0.0002	
9	0.0053	19.919	0.0011	0	0.0017	0	
11	0.0120	19.829	0.0002	0.0001	0.0048	0	
12	0.0158	19.778	0.0015	0	0.0050	0	
13	0.0142	19.795	0	0.0008	0.0053	0.0002	

Table 1 Carbonate Analyses (Wt%) in a thin section containing a fluorite micro-lens. Electron microprobe analyses kindly done at UnB by the Prof. C.G. Oliveira.

4 Carbonate Geothermometry

Applying the solvus geothermometer $XMgCO_3$ in the calcite molecule in equilibrium with dolomite (Rice, 1977), for the pairs of coexisting mineral grains 3-4 and 9-10, respectively at the upper and lower contacts of the dolomitic zone within the calcitic marble, and from the Table 1, we obtain:

log 0.00115 = -1690/^{o}T + 0.795 Þ T = 452.56 K or 180°C.
log 0.00265 = -1690/^{o}T + 0.795 Þ T = 501 K or 228°C.

According to that data, we could point out that the temperature of formation of the dolomite with fluorite micro-lens was situated around 200°C, which is compatible with the low grade greenschist facies. The mineralogical composition of the enclosing phyllites corresponds to quartz, chlorite and secondary dark mica. No amphibole has been found in the rocks. Metamorphic temperatures would have been slightly higher than the calculated temperature for the hydrothermal process.

5 Mineral Equilibria

Textural studies indicate that the fluorite deposition was contemporaneous with the dolomitization, considering fluorite was separated from calcite by a dolomite lamina. We are not sure about the timing of the mineralization, obviously comprehended between the sedimentation and the proceeding dolomitic metasomatism, which may have happened during metamorphism.

A set of five reactions irradiating from an invariant point can be constructed as possibly occurring in the system Mg-Ca-C-O-H-F, using the initial studies of Nordstrom and Munoz (1985). The set of reactions and the corresponding DGos, at 25°C (298K) and 227°C (500K), by using the Robie *et al.* (1979) tables are as follows:

$2\ CaCO_3 + Mg^{2+} + 2HF = (CaMg)(CO_3)_2 + CaF_2 + 2\ H^+$ (calcite) (dolomite) (fluorite)	**(1)** $\Delta G\ ^o_{react,298}$ = - 75.308 kJ / mol $\Delta G\ ^o_{react,500}$ = - 44.132 kJ / mol
$CaCO_3 + 2\ HF =\ \ CaF_2 + CO_2 + H_2O$ [dol] (calcite) (fluorite))	**(2)** $\Delta G\ ^o_{react,298}$ = - 128.794 kJ / mol $\Delta G\ ^o_{react,500}$ = - 127.971 kJ / mol
$2CaMg(CO_3)_2 + 2HF + 4H^+ = CaCO_3 + CaF_2 + 2Mg^{2+} + 3CO_2 + 3H_2O$ (dolomite) (calcite) (fluorite)	**(3)** $\Delta G\ ^o_{react,298}$ = - 236.15 kJ / mol $\Delta G\ ^o_{react,500}$ = - 295.649 kJ / mol
$CaCO_3 + CO_2 + Mg^{2+} + H_2O = MgCa(CO_3)_2 + 2H^+$ [fluor] (calcite) (dolomite)	**(4)** $\Delta G\ ^o_{react,298}$ = 53.486 kJ / mol $\Delta G\ ^o_{react,500}$ = 83.839 kJ / mol
$CaMg(CO_3)_2 + 2HF + 2H^+ = CaF_2 + Mg^{2+} + 2CO_2 + 2H_2O$ [cal] (dolomite) (fluorite)	**(5)** $\Delta G^o_{react,298}$ = - 182.28 kJ / mol $\Delta G^o_{react,500}$ = - 211.812 kJ / mol

It may be observed that three of the reactions (2,4 and 5), respectively dolomite, fluorite and calcite as missing phases, are thermodynamically stable, because they involve only two solid phases (Figure 3) and do not violate the Morey-Schreinemakers rules. The dolomite-out reaction (2), a Mg-free system, usually occurs in late and discordant fluorite veins transecting the pure limestone. Although reaction (4) represents a dolomitization process, it must be included in order to show its stability and position in relation to the system itself, and to the invariant point. The calcite-out reaction (5) reflects the subsequent breakdown of the product (1), fitting well in the diagram, whereas calcite is the unstable phase. The dolomite breakdown reaction (3) dominated by a high activity of HF, which plots within a compatible divariant field, produced fluorite and calcite, the last one as an unstable phase. Seemingly it may represent calcite recrystallization accompanied by fluorite deposition.
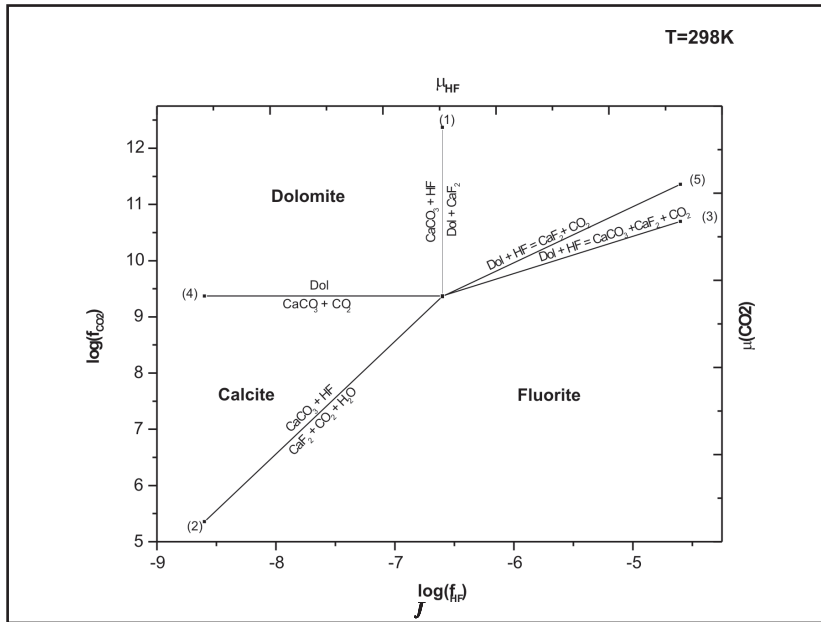
Figure 3   Invariant equilibrium between calcite, dolomite, fluorite anf H_2O at 1 bar and 25°C, according to the fugacity (**f**) and chemical potential (**m**) log scales (modified after Zen, 1966; Nordstrom & Munoz, 1985).

According to the diagram, increasing the fugacity of CO_2 will drive the equilibrium to the left, converting calcite to dolomite, and fluorite to either, calcite or dolomite. Increasing the fugacity of HF, the opposite effect will happen, resulting in the deposition of fluorite.

In order to perform the calculations, the equilibrium constants for the reactions may be written as follow:

$$K_{(1)} = 1/f^2_{HF} \qquad K_{(2)} = {}_{CO2}/{}^2_{HF} \qquad K_{(3)} = {}^3_{CO2}/{}^2_{HF}$$

$$K_{(4)} = 1/{}_{CO2} \qquad K_{(5)} = {}^2_{CO2}/{}^2_{HF}$$

Taking logarithms of the equations, we get:

$$\log K_{(1)} = -2\log{}_{HF} \qquad \log K_{(2)} = \log{}_{CO2} - 2\log{}_{HF} \qquad \log K_{(3)} = 3\log{}_{CO2} - 2\log{}_{HF}$$

$$\log K_{(4)} = -\log{}_{CO2} \qquad \log K_{(5)} = 2\log{}_{CO2} - 2\log{}_{HF}$$

Because log K is a constant at fixed pressure and temperature, equations (1, 2, 3, 4 and 5) describe straight lines with slopes ∞, +2, +2/3, 0 and +1, respectively. Using the relation between K and ΔG^o_{react} as: ΔG^o_{react} = -2,303 RT log K and $\mu_i = \mu^0_i - \Delta G^o_{react}$. therefore, the curves may be defined (Figure 3) (Zen, 1966; Nordstrom & Munoz, 1985).

Reactions (1) and (3) may be inserted in the diagram in order to represent a more realistic view to the system, and because reaction (1) was, in our opinion, the result of the milimetric alternation calcite-dolomite-fluorite-dolomite-calcite in the thin section, at the deposit Cal Andrezza quarry and reaction (3) was studied from the Casa de Pedra quarry limestone material. These reactions are thermodynamically consistent as they do not violate any of the defined rules. The divariant field comprehended between reactions (1) and (3), where only dolomite and fluorite are the stable phases, show well this relation.

The same procedure may be performed, considering the temperature of $227^O C$ for all calculation including ΔG^o_{react} (Figure 4).

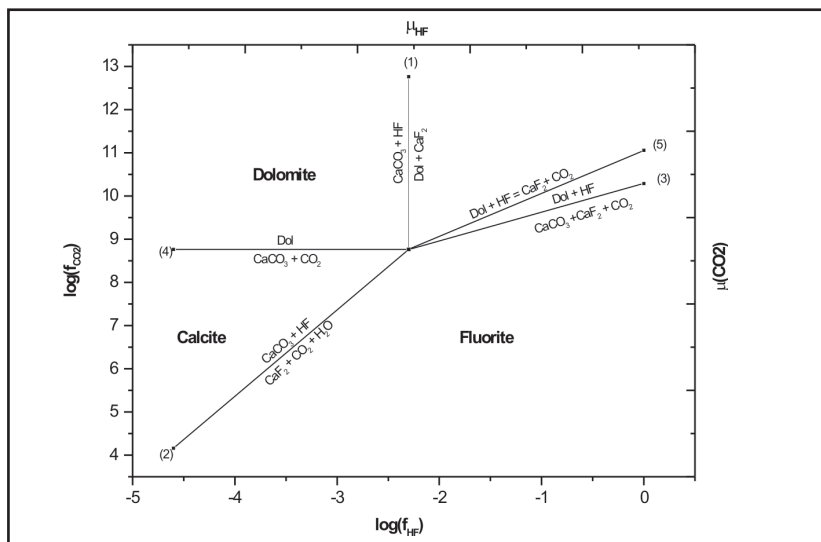Figure 4 Invariant equilibrium between calcite, dolomite, fluorite and H_2O at 1 bar and $227^o C$, according to the fugacity (f) and chemical potential (μ) log scales.

The introduction of the present data will shift the invariant point in a few orders of magnitude of log fHF from -6.6 to –2.3 and of log fCO_2 from 9.37 to 8.76 in relation to the temperature of 25°C.

6 Fluorite Formation

Trapped brines in the Ca-(Mg)-rich sediments, under slightly reducing conditions, may concentrate HF-rich fluids in the course of devolatilization, promoted by metamorphism and metasomatism. The hydrothermal fluids locally enriched in Mg^{2+} and HF may react with calcite to form dolomite and fluorite. As the HF activity was not presumably high, the amount of the resultant fluorite it will be apparent small, although well distributed. Some continental saline lakes (Richardson & Holland, 1979) may, under strong evaporating and arid conditions, to precipitate fluorite during dolomitization. The environment of deposition of these sediments are similar to the Sabhka deposits. On the other hand, the fluorite in subconcordant dolomite veinlets could be the result of infiltration of weakly acid, low temperature hydrothermal fluids capable of remove fluorine from the pockets or the matrix of the calcitic rock and to deposit fluorite in the whitish carbonate veins.

Experimental work has demonstrated that the increase in the salinity of the system favors fluorite deposition (Richardson & Holland, 1979). Saline solutions, subsaturated in NaCl, in the range 0.1-0.3M, when cooled among 260° and 100°C precipitate fluorite, which corresponds to the temperatures of the hydrothermal solutions at the present study. Apparently the solutions were generated during the mild metamorphism and metasomatism in the area.

The intimate relationship between fluorite and dolomite in the thin section examined from Cal Andrezza, strongly suggests that fluorite was formed during dolomitization, characterizing a stratabound deposition. The absence of sellaite and the existence of narrow dolomite bands indicate that, either it occurred a restricted availability of Mg or only the final fluids were rich in Mg^{2+}. In addition, the possible presence of $NaCl$-$CaCl_2$-$MgCl_2$ in the brine affect the stability of the MgF^+, CaF^+ and NaF^o and promote their dissociation with decreasing temperature, releasing F- to combine with Ca^{2+} in order to deposit fluorite.

7 Conclusion

  The presented data strongly suggest that the fluorite micro-lenses were formed during a dolomitization process of calcitic limestones, up on regional low grade metamorfism. Five univariant reactions in the system Ca-Mg-C-O-H-F define three main divariant fields dominated by calcite, under low HF and CO_2 fugacities, fluorite, stable under high HF fugacity and dolomite, under high CO_2 fugacity conditions.

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