ABSTRACT

SOURCE OF FLUORINE AND PETROGENESIS OF THE RIO GRANDE RIFT TYPE BARITE-FLUORITE-GALENA DEPOSITS

BY FREDERICK PARTEY

Abundant fluorite mineralization in Rio Grande Rift (RGR) barite-fluorite-galena deposits is anomalous compared to typical Mississippi valley type deposits to which they have been compared, and the source of the fluorine in these deposits is controversial.

In this study we used chlorine isotopes to test the possibility of an asthenospheric source of fluorine in the RGR deposits. Chlorine was used as proxy for determining the source of the fluorine because chlorine, unlike fluorine, has more than one isotope and thus can be used as an isotopic tracer. Chlorine and fluorine exhibit chemically similar behavior, and therefore are likely to be derived from the same source if associated with rift related magmatism. Complimentary to chlorine isotopic studies, Br/Cl ratios were also measured from the fluorite fluid inclusions and applied as additional tracers. Sr and Nd isotopes were measured from fluorites, granites, carbonates, and asthenospheric basalts to aid in understanding the petrogenesis of RGR deposits.
SOURCE OF FLUORINE AND PETROGENESIS OF THE RIO GRANDE
RIFT TYPE BARITE-FLUORITE-GALENA DEPOSITS

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Dedication

This Thesis is dedicated in loving memory of Mr and Mrs Henry Teye Partey and to my beloved wife Cynthia Partey not forgetting Amiyoo and Daisy. Your support and encouragement has brought me this far.

Such is life

Men’s evil deeds are written on brass the good ones on water when I am right no one remembers, when I am wrong no one forgets
1. Introduction

Abundant fluorite mineralization in Rio Grande rift (RGR) barite-fluorite-galena deposits is anomalous compared to typical Mississippi valley type (MVT) deposits to which they have been compared (McLemore et al., 1998), and the source of the fluorine in these deposits is controversial (Worl, 1974; Lamarre, 1975; McAnulty, 1975; Van Alstine, 1976; Macer, 1978; McLemore et al., 1998). In this study chlorine isotopes and Br/Cl ratios of fluorite fluid inclusions have provided information regarding the source of the fluorine. Sr and Nd isotopic analysis of the fluorite, carbonates, granites, and basalts have further aided in understanding the petrogenetic processes that led to the formation of the RGR deposits.

The Rio Grande rift is located in the southwestern United States (Fig 1). The rift is related to regional extension (Chapin, 1979), which began in the middle Cenozoic (27-32 m.y ago). This extensional deformation created normal faults and fractures that host mineralization. Fluorite is one ore mineral among others (e.g. barite and galena) associated with many mineral deposits in the rift. Van Alstine (1976) points out that more than 45 major fluorspar districts are situated along the Rio Grande rift and other Basin and Range extensional features. It has also been noted that many other fluorspar districts are associated with similar rift systems elsewhere, including Illinois, Kentucky, Oregon, Nevada, Ontario, Nova Scotia, Newfoundland, Germany, France, India, Kenya, Tanzania, Malawi and Mozambique (Van Alstine, 1976).

A subset of rift related fluorite deposits found in central and southern New Mexico has been called the Rio Grande Rift (RGR) barite-fluorite-galena deposits (Roedder et al., 1968; Van Alstine, 1976; McLemore and Barker, 1985; North and McLemore, 1985; Sutphin, 1997; McLemore and Lueth, 1996; McLemore et al., 1998; Hill et al, 2000; Bosze et al., in review). McLemore et al.(1998), give a detailed review of the characteristics of RGR deposits and a general summary is given here. Structural and microstratigraphic studies have shown that the fluorite mineralization took place in or adjacent to structures that formed during Basin and Range-extension. Recent $^{40}\text{Ar}/^{39}\text{Ar}$ age dating of hydrothermal jarosite coexisting with fluorite has established a range of ages for RGR deposits from 0.4 (San Diego Mountain) to 7.94 Ma (Potrillo Mountains) (Lueth et al., 2004). Almost all of the deposits are exposed in structural highs such as horst in half grabens. The RGR deposits are typically hosted by Paleozoic carbonate rocks and are emplaced as veins, breccia cement, and cavity-fillings. In some cases
Proterozoic basement granites host the deposits as veins. A stratigraphic column for the Hansonburg Mining District, one of the largest RGR deposits, is shown in figure 2 and exemplifies the general stratigraphy of other deposits. These deposits are low-temperature open-space fillings with little or no replacement of host rock. They consist predominantly of barite, fluorite, and galena with minor amounts of chalcopyrite and sphalerite (McLemore et al., 1998). The quantity of barite and fluorite greatly exceeds that of sulfide minerals in most RGR deposits. They have similar fluid-inclusion homogenization temperatures (95-346°C, typically less than 250°C; Jenkins, 1977; Macer, 1968; Putnam, 1980; Putnam et al., 1983; North and McLemore, 1985; Sarkar, 1985; Hill, 1994; North and Tuff, 1986; Filsinger, 1988), low to high salinities (0.3-20 eq. wt.% NaCl), similar stable-isotope compositions, and they possess the same general paragenesis (Putnam et al, 1983; McLemore et al., 1998). Fluid inclusion studies (Putnam et al., 1983) strongly suggest that the Hansonburg ore fluids were basin brines concentrated in Na-Cl, with other dissolved elements of Fe, Ca, Ba, Cl, and Zn with lesser amounts of Pb, Cu, Ni, Cd, Mg, Sr, Si, K, Br, and S. Numerous studies of paragenesis in the Hansonburg Mining district and several studies of other RGR deposits (Roedder et al., 1968; Putnam, 1980; Putnam et al., 1983; Norman et al., 1985; Taggart et al., 1989; McMahon et al., 1989; McLemore et al., 1994) suggest that mineralization occurred in four phases, although not all phases are necessarily present in all deposits. The first phase resulted in silification, dolomitization and argillation of the host carbonates and deposition of vein quartz and jasperoids. Stage two resulted in sulfide deposition, mainly galena with lesser sphalerite and chalcopyrite. Fluorite and barite were deposited during the third phase, and significant quartz and minor calcite during the fourth. Several studies have indicated multiple, distinct generations of fluorite deposition in stage three at the Hansonburg Mining district (Roedder et al., 1968; Bosze et al., in review).

The RGR deposits have been classified as a subclass of MVT deposits; they are similar in terms of ore texture and mineralogy, mineralizing fluid chemistry, host rock lithology and genetic relationship to sedimentary basins. However, because of major differences between the RGR deposits and classical MVT deposits, including the presence of fluorite as the predominant mineral phase, highly variable fluid inclusion salinities (McLemore et al., 1997), the nature of their plumbing systems, and association with alkaline magmatism and extensional tectonics, McLemore et al. (1998) have suggested that they not be considered MVT deposits.
One of the controversial aspects of RGR deposits is the origin of the large volumes of fluorine necessary to form the significant tonnages of associated fluorite. Van Alstine (1974) suggested three possible sources of the fluorine including volatiles emanating from crystallizing alkaline magma, remelting of late fluorine-rich alkalic fractions of underlying intrusive masses, and melting of ultramafic mantle rocks bearing fluoroapatite, hornblende and other fluorine rich minerals. Worl (1974) suggested an asthenospheric magmatic source for the fluorine, perhaps from volatiles that were released during alkaline magmatism in the region. Macer (1978) proposed meteoric water source for the fluorine, but did not provide evidence that significant fluorite deposition could take place from water containing several ppm fluorine. In an attempt to determine the source of the hydrothermal fluids, North and Tuff (1986) divided the fluorite deposits in the RGR into two groups, igneous associated and sedimentary-hydrothermal deposits. Other workers (Lamarre, 1975; Mc Anulty, 1975; Van Alstine, 1976) concluded that the RGR fluorite deposits are igneous associated and are related to alkaline melts high in fluorine hydrothermal fluids which migrated up Basin and Range faults. McLemore et al. (1998) also suggested that another potential source of the fluorine could be fluorite and apatite in the Proterozoic basement rocks that underlie host carbonates and in some cases host RGR deposits as vein emplacements although no geochemical model was presented.

The purpose of this project is to test the hypothesized asthenospheric source for the fluorine in fluorite mineralization of RGR deposits. Furthermore we aim to understand other petrogenetic processes associated with the formation of RGR barite-fluorite-galena deposits.

1.1 Sampling

Fluorite samples were collected from seven RGR deposits, including the Hansonburg mining District (Mex-Tex, Portales, Sunshine #2, Sunshine #3 mines), the Gonzales prospect, Caballo (Nakaye), San Diego Mountain (Tonuco), Tortugas and Organ Mountains (Bishop Caps, and the Ruby Hayner mine), and Fluorite Ridge, New Mexico (Fig. 3). The fluorites sampled were of different colors (light green, dark green, blue, purple and colorless) and variable morphologies. Limestones, Proterozoic basement granites and Cenozoic basalts (as defined by McMillan, 1998) were also collected throughout the south central RGR. Two groups of limestone samples were collected, one group proximal and the other distal to mineralization. All of the RGR deposits
under investigation lie near basaltic volcanic fields that are believed to have asthenospheric sources. These include Jornada basalts, Potrillo basalts, Carrizoza basalts, Mogollon-Datil basalts, and Uvas basalts (Mcmillan et al., 1998). Granite samples were taken from the Hansonburg Mining District.

1.2 Mining Districts

1.2.1. Hansonburg

In the Hansonburg Mining District mineralization is exposed in the Oscura uplift by major north-south trending, en echelon normal faults along which major movement began about 7 Ma ago (Chapin, 1979). Proterozoic granites and gneisses comprise the basement rocks (fig 2). These are overlain by Pennsylvanian formations consisting of marine limestone and shales, interbedded with arkosic sands. Above these are Permian and Triassic red-beds and Cretaceous marine sands and shales, although most have been removed by erosion. Mineralization principally occurs in the Council Spring member of the Pennsylvanian Madera limestone. Minor mineralization occurs as vein fillings in Pennsylvanian and Permian sediment as well as Proterozoic basement granites (fig 2). The Council Spring formation is massive, banded limestone that contains solution cavities up to 50 meters in width. Some field evidence indicates that these karst features are the result of weathering during the Pennsylvanian (Putnam et al., 1983) although Lueth (2002) recently noted features of acid speleogenesis that were contemporary with mineralization. The Council Spring Member has an erosional upper contact and is unconformably overlain by 1 to 5 meters of mudstone. The deposit is associated with the east-west trending Capitan lineament. This Paleozoic structure is thought to have played an indirect role in mineralization in the Hansonburg district (Putnam et al., 1983). The uplift along the structure in the Paleozoic is postulated to have been responsible for thinning of Paleozoic sediments in the vicinity of the Hansonburg district as well as the deposition and weathering of the Council Spring Member (Putnam et al., 1983).
1.2.2. Gonzales

The Gonzales prospect is located 12 miles east of Socorro, in the foothills that border the alluvial terraces of the Rio Grande valley. The deposit occupies a fault zone in the west flank of an anticline whose axis strikes N.15°-20° W. Its up thrown (east) side exposes a narrow band of pink coarse-grained Proterozoic granite. East of the fault the rocks above the granite consist of thin-bedded limestones, sandstones, and red, brown, or gray shales, and have an aggregate thickness of about 100 feet belonging to the Magdalena group.

The Gonzales fluorspar deposit is exposed only along that part of the fault that borders the granite outcrop. Most of the fluorspar is in the adjoining brecciated sedimentary rocks, although commonly a narrow vein of siliceous fluorspar is frozen to the footwall, and stringers and patches of high-grade fluorspar extend into this wall. The principle minerals in the veins are fluorite, barite, and quartz (Rothrock, 1978).

1.2.3. San Diego Mountain (Tonuco)

Mineralization in the San Diego Mountain is largely confined to the Proterozoic basement granite, which trends north and northwest, although locally cavity fillings are present in some of the sedimentary formations (Seager et al., 1971). The predominant mineral phases are quartz, barite and fluorites. Mining in the past was restricted to the wider fluorite-rich veins.

1.2.4. Tortugas Mountains

The Tortugas deposit is located 4.5 miles southeast of Las Cruces, on Tortugas Mountain, The Mountain consists of limestones and shale of the Magdalena group, and is a fault block that has been shattered extensively and tilted eastward. Fluorite veins occur in the fractures caused by this faulting, and trend generally north-northwest. They are predominantly fissure fillings, but include some fillings of fault breccia. Gangue material includes abundant calcite and some quartz, and inclusions of limestone wall rock, some of which are silicified. The deposits were mainly formed by the filling of open space; replacement only played a minor role (McAnulty, 1978).
1.2.5. Bishop’s Cap

Bishop’s Cap is located near the southwest margin of the Organ Mountains; it is an erosional remnant of blocks produced by five high-angle normal faults (McAnulty, 1978). Mineralization consists of fluorite, barite, calcite, and cryptocrystalline quartz that are hosted as veins in Paleozoic limestones and dolomite principally in the Silurian Formation. Small deposits occur in narrow veins along steep normal faults and in brecciated, jasperized zones along bedding planes. Though this deposit occurs as veins, in some areas both void filling and replacement deposits occur (McAnulty, 1978).

1.2.6. Organ Mountains

The Ruby Hayner mine is located on the west flank of the Organ Mountains. Fluorites occur in a series of six sub parallel fissure-veins in the Permian Hueco limestone and in a Tertiary andesite dike on the lower west slope of the Organ Mountains, near the contact with the quartz monzonite Organ Mountain batholiths. Most of the fluorite was precipitated in available open spaces as fissure veins; minor replacement fluorite occurs in brecciated zones (McAnulty, 1978).

1.2.7. Caballo Mountains

The Nakaye prospect is located on the West Side of the Nakaye Mountain in the Caballo Mountains. This is a horst block that is cut by the east west Nakaye fault and other parallel faults and fractures. Fluorite deposits are hosted in the Nakaye formation of the Magdalena group that are Pennsylvanian in age, and consist of shale, with intercalated thin-bedded and medium-gray limestone. Fluorite also occurs in jasperiod veins and pods along faults (McAnulty, 1978).

1.2.8. Fluorite Ridge

The Fluorite Ridge fluorite deposit is located on an elongated group of barren rugged hills, 10 miles north of Deming. All the deposits in fluorite ridge are fissure veins except the Tip Top and Hill Top Spar prospects, which are fillings in solution cavities in limestone. The fissure
veins occupy faults and fractures and are rich fissure near the intersections of these structures or in areas affected by pre-mineral brecciation. The host rocks are monzonite porphyry, cross-cutting basalts, and the young eruptive agglomerate.

2. Analytical methods

2.1. Ion Chromatography of Br/Cl

Br/Cl ratios were determined for fluorite and carbonate fluid inclusions. Fluorite and carbonate samples were initially cleaned with deionized water (DI) water in an ultrasonic bath. Dry samples of about 35 g of fluorite and 10g of carbonate were crushed to fine powder in an agate mortar and pestle, and transferred to a polyethylene container. The fluorite powder was mixed with fifteen milliliters of DI water while the carbonate powder was also mixed with 10 ml of DI water. To ensure maximum extraction of the fluid inclusions, the samples were left on a shaking table for six hours. The solutions were filtered through 0.2-µm nylon filters to remove any particulates before analysis.

Cl and Br concentrations were determined by eluent-suppressed anion chromatography and conductivity detection on a Dionex DX-500 HPLC/ion chromatograph. Analyte elution was performed isocratically with 3.5 mM Na₂CO₃/1.0 mM NaHCO₃ using an IonPac AS-14 analytical column (4 mm) and 250-µL sample loop. Concentrations were calculated from analyte peak areas by comparison with external standards. The 2σ error on the Br/Cl ratio analyses is ± 0.0001, based on the variance of measurements of 20 replicate samples of standard mean ocean chloride (SMOC).

2.2. Sample purification for Cl isotopes

Fluorite samples were ground to a fine powder. Twenty grams of the powdered sample was mixed with 20 ml of deionized water and agitated overnight. Samples were then centrifuged and the leachate was passed through a filter to remove any remaining particulate matter. Due to the high F/Cl ratio of these samples and the exceedingly high F concentration of the leachates,
fluoride which can interfere with ionization of Cl in the mass spectrometer, was removed from
the leachate by a new solid phase extraction method. Ion exchange columns and 2 g silica gel
(60 – 200 mesh, EM Science, Inc.) with a glass wool were rinsed with 20 mL 0.001 M high
purity HNO₃. Samples were acidified to 0.001 M HNO₃ then loaded onto the columns by
gravity. Chloride was collected in the column eluent, while F⁻ was retained on the column. This
ion exchange step removed > 99% of the fluorine while Cl recoveries were close to 100%.
Chlorine and Fluorine concentrations were determine before and after the silica-gel column
treatment in order to determine not only recoveries but the optimal sample to silica-gel ratio.

Once the fluorine was removed, a 10-ml polyethylene ion exchange column containing
0.6 ml of AG50-X8 cation exchange resin in the H⁺ form was prepared by passing 10 resin bed
volumes (RBV) of 6 M HNO₃ through the column followed by washing with deionized water
until the pH was about 6. At this point, 1 ml of a 10-mg/ml Ba solution in 1% HNO₃ was passed
over the column to get the resin into the Ba⁺ form. This step is necessary to quantitatively
remove sulfate from the analyte solution, which like F may inhibit the ionization of chlorine
during analysis. The concentrated analyte solution was then passed through the prepared column
in ~300 µl aliquots. The first aliquot was allowed to wash through the column, while the
remaining aliquots (~700 µl) were collected in a clean Teflon vial.

The column was then emptied and thoroughly washed with 6 M HNO₃ and de-ionized
H₂O. The clean column was then loaded with 0.3 ml of AG50-X8 cation exchange resin in the
H⁺ form and treated with 6 M HNO₃ and deionized water to a pH of 6 as above. At this point,
the resin was converted to the Cs⁺ form by adding ~ 2 ml of a 0.2 M CsCO₃ solution in 1%
HNO₃, 300 µl at a time. After allowing time for each volume of CsCO₃ solution to react with the
resin (visible reaction) and pass through the column, the next volume was added until the
reaction ceased and/or a pH of between 8 and 10 was reached. The remaining analyte solution
(~700 µl) was then passed through the column in 300-ml aliquots, again eluting the first aliquot
and collecting the remainder in a Teflon vial. This produced a Cs₂Cl⁺ solution with a pH of
about 6. The collected analyte solution was then concentrated for loading into the mass
spectrometer by drying under an infrared lamp in a laminar flow hood to a volume of ~100 µl.
2.3. Mass Spectrometry of Cl isotopes

Approximately 8 µl of Cs₂Cl⁺ solution was loaded onto a single tantalum filament with 2 µl of a graphite slurry solution and dried under filtered air at 1.0 Amp for 5 minutes. Samples were analyzed using an NBS 12”, 90° sector thermal ionization mass spectrometer in the Towson University Geochemistry laboratory. The mass spectrometer source pressure was brought to a vacuum of 10⁻⁷ torr, at which point a current was applied to the filament assembly. The current was stepped up 0.25 Amps every 60 seconds until a signal was detected. Once stable signal was achieved the mass ratio of 303/301 (Cs₂⁷Cl⁺/Cs₂³⁵Cl⁺) was measured over a period of about 30 minutes. Throughout the period of sample analysis of the fluorite samples Standard Mean Ocean Chloride (SMOC) and NIST 975a were analyzed as standards. The mean value for SMOC was 0.319800(32) and 0.319814(78) for 975a, making the external reproducibility 0.10‰ for SMOC and 0.24‰° for 975a. In-run precision for samples was typically not better than 1‰. Any samples with an in-run precision higher than 1‰ were run twice, and the mean reported here.

2.4. Rubidium-Strontium, Samarium-Neodymium isotopes

Samples of fluorite were initially cleaned with DI water in an ultrasonic bath. Dry samples were crushed to a fine powder in an agate mortar pestle as described previously. Carbonates and granites, which are the host rocks for fluorite mineralization, as well as basalts, were also finely ground using a spex ball mill with high purity aluminum vessel.

For fluorites, 100 mg of sample powder and 150 mg of lithium metaborate flux were thoroughly mixed. The sample and flux mixture was heated to 950°C for 30-60 minutes in a graphite crucible and then poured into a 250- mL polyethylene bottle containing 50 mL of 2.5N HNO₃ acid. The bottle containing the sample was placed on a shaking table for 3 hours to ensure complete dissolution of the sample. Each sample was filtered with quartz wool to remove any graphite derived from the crucible, and the filtrate was loaded onto 20 x 1-cm column of AG50W-X8 cation exchange resin. Thirty and 20 mL of 2.5N HCl were used to elute Sr and Rb respectively. Thirty mL of 4N HCl was then used to elute the REE fraction. Sm-Nd separations were done using EiChrom Ln-Spec resin following methods similar to Pin and Zalduegui (1997).
About 100 mg of sample powder of carbonate was dissolved, while 50 mg of the granites and basalts were dissolved using mixed acid digestion (HF/HNO₃). The separation of Rb, Sr and REE were done using AG 50 wx-8 cation exchange columns with 2.5 N and 4 N HCl following procedures described in Walker et al. (1989). EiChrom Ln-Spec resin was used for Sm-Nd separations following methods similar to Pin and Zalduegui (1997).

All Sr and Nd isotopic compositions were measured by thermal ionization mass spectrometry using a Finnigan Triton. Sr and Nd isotope ratios were measured for a total of four carbonates, eight fluorites, three basalts and two granites. Strontium isotopic ratios were corrected for fractionation using \(^{86}\text{Sr}/^{88}\text{Sr} = 0.1194\), while Neodymium isotopic ratios were corrected for fractionation using \(^{144}\text{Nd}/^{146}\text{Nd} = 0.7219\). The average of eighty measurements of NBS 987 is \(^{87}\text{Sr}/^{86}\text{Sr} = 0.71024 \pm 1\) (2\(\sigma\)) and fifty measurements of La Jolla is \(^{143}\text{Nd}/^{144}\text{Nd} = 0.51185 \pm 1\) (2\(\sigma\)).

2.5. Results

Table 1 Lists the Sr and Nd isotopic compositions of the fluorites, carbonates, granites and basalts. The \(^{87}\text{Sr}/^{86}\text{Sr}\) of the fluorites range from 0.71986 to 0.74075, and \(^{143}\text{Nd}/^{144}\text{Nd}\) from 0.51194 to 0.51209, these values are similar to the carbonates (\(^{87}\text{Sr}/^{86}\text{Sr} = 0.70858-0.72911\), and \(^{143}\text{Nd}/^{144}\text{Nd} = 0.51195 - 0.51234\)) and the granites (\(^{87}\text{Sr}/^{86}\text{Sr} = 0.73285\), \(^{143}\text{Nd}/^{144}\text{Nd} = 0.51207\), but distinctly different from the basalts (\(^{87}\text{Sr}/^{86}\text{Sr} = 0.70304-0.70465\), \(^{143}\text{Nd}/^{144}\text{Nd} = 0.51277 - 0.51297\)).

The Cl isotopic compositions and Br/Cl ratios of the fluorite fluid inclusions are presented in Table 2. The results show a wide range of \(\delta^{37}\text{Cl}\) values from -0.660‰ to +3.069‰ relative to SMOC. Three of the samples, Sunshine # 2, Fluorite Ridge, and Mex-Tex have high \(\delta^{37}\text{Cl}\) values of +1.24‰, +1.33‰, and +3.069‰ (respectively) relative to SMOC, but have low Br/Cl ratios. Ruby Hayner has a \(\delta^{37}\text{Cl}\) value close to +0.89‰. The others, Portales, Sunshine # 3, Nakaye, and San Diego Mountains have relatively low \(\delta^{37}\text{Cl}\) values of +0.36, -0.003, -0.66, and -0.42 respectively. The Br/Cl ratio for all the fluorite fluid inclusion also ranges between 0.00008 and 0.00050, except for San Diego that has a relatively high Br/Cl ratio of 0.00242. Most fluorite fluid inclusions have Br/Cl ratios that fall in a range similar to that of evaporite (Banks et al., 2000). The range for the Br/Cl ratio for the carbonates is 0.00393-0.02645.
3. Discussion

3.1. Petrogenesis of RGR deposits as indicated by Sr and Nd isotopes

Fluorite is one of the main mineral phases found in RGR deposits. Understanding the petrogenetic processes that led to the formation of these fluorites is paramount in determining the source of the mineral constituents. Sr and Nd isotopic compositions have proved to be useful in identifying the source of these elements, and the fluorite’s calcium, thus helping to constrain the origin of ore deposits (Barbieri et al., 1987; Galindo et al., 1997; Huang et al., 2003). The Sr and Nd isotope geochemistry of the RGR deposit fluorites, granites, and carbonates (host rocks of the deposits) and asthenospheric basalts proximal to the deposits have revealed important information about the path of the ore forming fluids.

Figure 4 shows a plot of \( ^{87}\text{Sr}/^{86}\text{Sr} \) verses \( ^{143}\text{Nd}/^{144}\text{Nd} \) values for all of these samples. Two different sets of carbonate samples are plotted in figure 4. One group (Bing. carb. I and Nakaye carb.) was collected at the site of mineralization, and the other (Bing. carb. II and Bing. carb. III) further away from mineralization. Those sampled further away from mineralization are close to the unaltered Pennsylvanian limestone in their isotopic composition (Keto and Jacobsen, 1988) (Fig. 4.). Carbonates sampled at the site of mineralization are silicified and host fluorite, galena and barite, indicating reaction with ore fluids, and exhibit more radiogenic Sr and less radiogenic Nd values (Fig.4). The basalts samples all lie within the Sr and Nd isotopic region for asthenosphere-derived basalts defined by McMillan et al. (1998), consistent with an asthenospheric origin (Fig. 4). The fluorites range in composition from more radiogenic signatures similar to the Bingham granite analyzed in this study and the average Proterozoic granite values from the Navajo volcanic field (Condie et al., 1999) and less radiogenic signatures that are intermediate between those of the Proterozoic granites and the basalts and unaltered carbonates (Fig. 4).

The radiogenic character of the fluorites indicates that the Sr (and by proxy the Ca) and Nd were derived largely from a granitic source with some influence from carbonate and/or asthenospheric sources (Fig. 4). This is consistent with the lead-isotopic data on galena from the Hansonburg mining district (Slawson et al., 1962; Beane, 1974; Ewing, 1979), which also indicate a granitic source for the Pb. Examples of possible mixing curves between granite and an asthenospheric or carbonate source are shown in figure 4; they are possible for the range in Sr
and Nd isotopic values observed. Other Proterozoic granites that are potential sources of Sr, Nd and Pb are those of the Organ plutons. Their average $^{143}\text{Nd}/^{144}\text{Nd} = 0.511999$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.78631$ (Verplanck et al., 1995). These are far more radiogenic than the Bingham or the Navajo granites. Potential mixing curves involving the Organ pluton granites (fig. 4 insert) would result in greater contribution from the non-granitic sources, but are still consistent with the observed trend in the fluorite data.

The fact that the Sr and Nd were largely derived from a granitic source does not preclude fluorine coming from another source. However, it is possible and it has been proposed (McLemore et al., 1998) that the hydrothermal fluids may have also derived fluorine from the Proterozoic granites (McLemore, 1986; 1987).

3.2. Possible sources of Cl and its use as proxy for tracing the origin of F

Halogens are relatively soluble and their ratios and isotopic compositions can be used as tracers of fluid reservoirs and mixing process in the earth’s crust (Bohlke and Irwin, 1992). In low temperature sedimentary fluid systems halogen ratios are frequently used to distinguish between different brines (Walker et al., 1990; Kesler et al., 1996), but in magmatic systems their use has been limited. Br/Cl ratios and the isotopic composition of fluid inclusions can provide direct information on the origin of Cl in hydrothermal fluids (Banks et al., 2000; Bohlke and Irwin, 1992). Magenhein et al. (1995) estimate that approximately 40% of the earth’s Cl is contained within crustal reservoirs and 60% within the mantle. Based on $\delta^{37}\text{Cl}$ values of depleted mantle beneath a mid-ocean ridge, Magenhiem et al. (1995) showed that Cl is isotopically fractionated between the two reservoirs so each has distinctly different values (mantle, $\sim 4.7\%$; crust, 0%). Therefore, it should be possible to distinguish between crustal and mantle sources of Cl (Banks et al., 2000).

Bohlke and Irwin (1992) showed that Br/Cl ratios between 0.001-0.002 in hydrothermal minerals are representative of asthenospheric magmatic volatiles while values between 0.001 to zero have an evaporite source for the Cl. Magenheim et al. (1995) also measured $\delta^{37}\text{Cl}$ values for Mid Ocean Ridge Basalt glass separates and concluded that samples unaffected by seawater
assimilation have $\delta^{37}\text{Cl}$ values between 3 and 7.2‰, and Eggenkamp, (1994) has documented evaporite $\delta^{37}\text{Cl}$ values in the range of $-0.5\%$ to $+0.5\%$ relative to SMOC.

Figure 5 shows the relationship of Br/Cl ratios verses $\delta^{37}\text{Cl}$ values for fluid inclusions from all 8 RGR fluorites as well as fields for asthenosphere-derived basalts and evaporite sources as defined by Magenhein et al. (1995) and Bohlke and Irwin (1992). Generally, there is a positive correlation between $\delta^{37}\text{Cl}$ and Br/Cl in the fluorite data (Fig. 5) that is consistent with Cl from asthenospheric magmatic and evaporite sources. Fluid inclusion studies of Hansonburg and other RGR deposits indicate that the original mineralizing fluids were meteoric waters in origin and that they acquired the bulk of their chloride and sulfur from Permian marine evaporites (Hill et al., 2000; McLemore et al., 1998). This is similar to the conclusion of Allmendinger (1974, 1975) that sulfur in the RGR deposits was acquired from Permian evaporites. However, Lueth et al. (2004), suggest that the sulfur was alternatively derived from sour gas (H$_2$S) evolved from the basins based on the low $\delta^{34}\text{S}$ values they encountered in the sulfides and hydrothermal jarosites. Furthermore the Cl isotopic values for Mex-Tex sunshine # 2 Ruby Hayner and Fluorite Ridge fluorites (ranging from +3.6 to +0.89) requires that some amount of Cl was derived from an asthenospheric magmatic source.

The dotted lines C and D in figure 5 define a broad envelope in which all possible curves describing mixing between asthenospheric and evaporite sources of Cl would lie. Lines A and B in figure 5 define a much more narrow envelope of possible mixing curves, which is more likely given the tight trend in the data. The percentage range of Cl derived from asthenospheric and evaporite sources for the Mex-Tex fluorite ($\delta^{37}\text{Cl} = +3.069\%$) was calculated using mixing line A. The maximum possible asthenospheric contribution is 49% of the total Cl in the sample. This is based on an asthenospheric $\delta^{37}\text{Cl}$ value of 7.2‰ (defined the intersection of line A with this source field) and the most positive evaporite $\delta^{37}\text{Cl}$ value intersected by line A (0.36‰). The minimum possible asthenospheric contribution in the Mex-Tex sample is 40% based on the lowest evaporite $\delta^{37}\text{Cl}$ value intersected by line A (-1‰). Similarly, the maximum and minimum asthenospheric contribution to Cl in the Sunshine #2 sample were calculated to be 35% and 13% respectively based on mixing line B.

The $\delta^{37}\text{Cl}$ values of fluorites from Ruby Hayner, Sunshine # 2 and Fluorite Ridge mines ($\delta^{37}\text{Cl} = 0.89\%-1.33\%$) indicate a much greater contribution from an evaporite source, however,
they still exhibit some asthenosphere derived Cl. The Br/Cl ratio and the $\delta^{37}\text{Cl}$ values for Nakaye, Portalace and Sunshine # 3 fluorites lie close to or within the evaporite source region. It is possible that the source of Cl in these fluorite deposits is also a mixture of a halite-bearing Permian marine evaporite sources (Bohlke and Irwin, 1992) and an asthenospheric magmatic source, but the later has been overshadowed by the evaporite component. Fluorites from one deposit (San Diego) fall significantly off the trend defined by the majority of the samples. It has $\delta^{37}\text{Cl}$ values that lie within the evaporite source region, however their Br/Cl ratios are substantially elevated (table 2). It is possible that this deviation from the trend reflects greater interaction between hydrothermal fluids that formed these deposits and Pennsylvanian carbonates in the region. Measured Br/Cl ratios from these carbonates (0.00393-0.02645) are an order of magnitude higher that seawater, and assimilation of carbonate through dissolution could account for the observed Br/Cl ratios in the anomalous fluorites. Chlorine isotope fractionation through kinetic processes has been found to be very small (Magenheim et al. 1995), thus fractionation cannot explain the trend in $\delta^{37}\text{Cl}$ values found among the RGR fluorites (Fig. 5).

Thus the range of $\delta^{37}\text{Cl}$ values observed among different RGR deposit can be explained by differing degrees of mixing between asthenosphere-derived and evaporite sources. The degree of mixing will depend on factors such as the path that fluids followed, the rock types that they encountered, the degree of water-rock interaction, the rate of extension, intensity of magmatism and volume of volatiles released into mineralizing fluids.

Variation in Cl source mixing was also observed within a single deposit (Hansonburg Mining District). The Hansonburg Mining District comprises the largest and most studied of the RGR barite-fluorite-galena deposits (Reodder et al., 1968; Putnam et al., 1983; Allmandinger, 1974; Bosze et al., in review). Although the Mex-Tex, Sunshine # 2, Portales, and Sunshine # 3 are all within the Hansonburg mining district, they show very different $\delta^{37}\text{Cl}$ values. The Mex-Tex ($\delta^{37}\text{Cl} = +3.069‰$) and Sunshine # 2 ($\delta^{37}\text{Cl} = +1.24‰$) retain possible asthenospheric signatures for Cl, while Portales ($\delta^{37}\text{Cl} = +0.360‰$) and Sunshine # 3 ($\delta^{37}\text{Cl} = -0.660‰$) fall close to or within the evaporite source region. This observed variation in $\delta^{37}\text{Cl}$ value correlates with color and paragenesis. Fluorites sampled from the Mex-Tex and Sunshine # 2 (high $\delta^{37}\text{Cl}$ values) are green while fluorites sampled from the Portales and Sunshine # 3 (low $\delta^{37}\text{Cl}$ value) are blue-purple, indicative of chemically distinct fluorite groups, which may have formed from
two temporally and compositionally separate fluids. Bosze et al. (in review) studied variation in REE among fluorites of different colors, morphology and paragenetic relationships in the Hansonburg Mining District. A striking correlation between the fluorite color and REE pattern in the Hansonburg fluorite was revealed. They observed a negative slope for the LREE in the green fluorites and distinctly positive slope in the blue to purple fluorite. Furthermore, color was correlated with paragenesis. Green color fluorites were the first to be formed in the district followed by the blue-purple fluorites. They concluded that the significant differences in the REE chemistry is a result of precipitation from a single closed system fluid that has fractionated over time, or the two chemically distinct fluorite groups may have formed from two, temporally and compositionally different fluids. Our finding is also consistent with geochronological and oxygen and hydrogen isotope studies that indicate the potential for two or more distinct mineralization events at Hansonburg (Hill et al., 2000; Lueth et al., 1999, 2000). The $\delta^{37}$Cl results, REE chemistry, geochronological and oxygen and hydrogen isotope and fluid inclusion (Reodder et al. 1968; Campbell et al., 1995; Lueth et al., 2004) studies suggest two or more generations of fluorite mineralization from potentially different fluids.

A key aspect of the Br/Cl and $\delta^{37}$Cl results is the identification of a possible asthenospheric magmatic source for some of the Cl in the fluorite fluid inclusions of RGR deposits. One of the main purposes of this study is to determine the source of the fluorine that allowed for the significant tonnages of associated fluorite. Fluorine and chlorine have similar concentrations in primitive mantle, 19 ppm and 17 ppm respectively (Wedepohl et al., 1994; McDonough et al., 1995). Fluorine and chlorine also exhibit similar chemical behavior and have been shown to follow one another during degassing of magmas (Yoshida et al., 1994; Thordarson et al., 1996). Thus the presence of high Cl isotope ratios support the possibility of an asthenospheric magmatic source for F in the RGR deposits. This result is consistent with Plumlee et al. (1995) who concluded that such anomalous fluorite deposition Illinois-Kentucky fluorspar district could only be accounted for by addition of HF from mantle-derived alkaline magmas to basinal brines.

Fluorine is a ubiquitous and mobile component in most rift related acidic volcanic systems typically involving alkaline magmas (Van Alstine, 1976). The association of rift fluorite mineralization is epitomized by the East African rift (Nyambok and Caciri, 1975), Rhine graben (Baumann et al., 1975), and the Benue trough of Nigeria (Akande et al., 1989). The high fluorine
content in these rifts is associated with acid volcanic, high temperature rifting, and low salinity (Gizaw B. 1996, Gashaw H., 1999; Kilham P., 1973).

The most intense stage of RGR fluorite mineralization coincides with the second episode of alkaline-olivine basalt magmatism, which occurred between latest Miocene to Pliocene in the Rio Grande rift (Seagar et al., 1984). This is also consistent with findings of other workers (Lamarre 1975, Mc Anulty 1975, Van Alstine 1976), who suggested that the source of fluorine in the RGR deposits are related to alkaline melts high in fluorine hydrothermal fluids, which migrated up Basin and Range faults.

Based on our results and numerous other studies (Roedder et al., 1968; Macer, 1978; Putnam, 1980; Norman et al 1985; North and McLemore, 1985; North and Tuff, 1986; Bohlke and Irwin, 1991; Hill, 1994; Hill et al., 2000), we propose the following petrogenesis and paragenetic history of the RGR fluorite-barite-galena deposits. Fluid inclusion and geochemical analysis suggest that the mineralizing fluids responsible for forming the RGR deposits originated as relatively dilute meteoric waters (Macer, 1978; Hill, 1994; Hill et al 2000). The meteoric waters were buried or migrated to the deepest parts of the rift basin and into underlying basement rocks (McLemore et al., 1998). These fluids acquired the majority of their solutes (Na⁺, Cl, Ca²⁺, Ba, etc) through water-rock interaction with various source rocks such as arkosic sediments, evaporates, and Precambrian basement rocks (McLemore et al., 1998; Bohlke and Irwin, 1991; Slawson et al., 1962; Beane, 1974; Ewing, 1979). We have shown that in addition to water-rock interactions with basin sediments Cl was also added from an asthenospheric source, most likely during magma degassing. Allmendinger (1974, 1975) suggested, based on sulfur isotopes and geochemical analysis of fluid inclusions, that the fluids leached their sulfur from the Permian evaporites. However, Lueth et al., 2004, suggest that the sulfur was alternatively derived from sour gas (H₂S) evolved from the basins based on the low δ³⁴S values they encountered in the sulfides and hydrothermal jarosites. Sr, Nd (this study) and Pb (Slawson et al., 1962; Beane, 1974; Ewing, 1979) isotopes indicate significant contribution of these elements to solution through interactions with basement granites specifically.

Fluorine (as with some of the Cl) in these deposits is derived from a mantle source, most likely as gaseous HF expelled from alkaline magmas in the rift. Rising HF mixed at depth with basinal brines. As fluorine enriched basinal brines were being expelled from the RGR basins they moved into open-spaces such as bedding planes, faults, fractures and solution cavities where
precipitation of barite, fluorite, galena and other minerals occurred as solutions became supersaturated with them (McLemore et al., 1998). Fluid inclusion studies indicate precipitation at relatively low temperatures (95-346°C, typically less than 250°C; Jenkins, 1977; Macer, 1968; Putnam, 1980; Putnam et al., 1983; North and McLemore, 1985; Sarkar, 1985; Hill, 1994; North and Tuff, 1986; Filsinger, 1988) from solutions of low to moderate salinities (0.3-20 eq. wt.% NaCl) (Putnam et al., 1983; McLemore et al., 1998) and acidic, 4.3-5.1 in the Hansonburg mining district, pHs (McLemore et al., 1998). Various studies of paragenesis in RGR deposits (Roedder et al., 1968; Putnam, 1980; Putnam et al., 1983; Norman et al., 1985; Taggart et al., 1989; McMahon et al., 1989; McLemore et al., 1998) suggest that mineralization occurred in four phases, although not all phases are necessarily present in all deposits. The first phase resulted in silification, dolomitization, and argillation of the host carbonates and deposition of vein quartz and jasperoids. Stage two resulted in sulfide deposition, mainly galena with lesser sphalerite and chalcopyrite. Fluorite and barite were deposited during the third phase, and significant quartz and minor calcite during the fourth. Several studies have indicated multiple, distinct generations of fluorite deposition in stage three at the Hansonburg Mining district (Roedder et al., 1968; Bosze et al., in review), which is consistent with the variation in fluorite fluid inclusion Cl isotopes found among samples from that deposit.

3.3. Conclusion

Our results show that the fluorites have Sr (and Ca by proxy) and Nd isotope ratios that are distinctly more radiogenic than the local basalts and Pennsylvanian carbonates but similar to the radiogenic granites. The radiogenic character of the fluorites indicates that the Sr and Nd were derived largely from a granitic source with some influence from a carbonate and/or asthenospheric source. This is consistent with the Pb isotope data on galena from Hansonburg mining district (Slawson et al., 1962; Beane, 1974; Ewing, 1979)

Generally, there is a positive correlation between $\delta^{37}$Cl and Br/Cl in the fluorite data that is consistent with mixing of Cl from asthenospheric magmatic and evaporite sources. High $\delta^{37}$Cl in the Mextex, Sunshine # 2 and fluorite ridge fluorites allow significant involvement of an asthenospheric source for the Cl; the calculated range of Cl derived from an asthenospheric
source for the Mex-Tex sample is 40% to 49%. Similarly, between 35% and 13% of the Cl in the Sunshine #2 sample could be of asthenospheric in origin.

Chlorine isotopic values and Br/Cl ratios of fluid inclusions from RGR deposit fluorites show variable degrees of mixing of a potential asthenospheric magmatic source and a Permian evaporite source of chlorine. Fluorite fluid inclusions from several mines (Mex-Tex, Sunshine #2, and Fluorite Ridge) exhibit isotopically heavier asthenosphere-like Cl signatures while others (Sunshine #3, Portales, San Diego, Nakaye, and Ruby Hayner) have lower $\delta^{37}$Cl signatures and are overshadowed by their evaporite component. Observed variation in $\delta^{37}$Cl value correlates with color and paragenesis and suggest two or more generations of fluorite mineralization from potentially different fluids.

Based on the possibility of asthenospheric Cl, the similar chemical behavior of F and Cl and the similar concentration of these two elements in the mantle, we suggest that the origin of the large volume of fluorine necessary to form the significant tonnages of fluorite associated with RGR deposits may be asthenosphere derived and relate to rifting during the Miocene.

**Acknowledgements**

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Table 1. The Sr and Nd isotopic compositions of fluorites in the Southern Rio Grande rift

<table>
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<tr>
<th>Samples ID</th>
<th>(^{87}\text{Sr}/^{86}\text{Sr})_m \</th>
<th>(^{87}\text{Sr}/^{86}\text{Sr})_i \</th>
<th>\text{Sr (ppm)}</th>
<th>\text{Rb (ppm)}</th>
<th>(^{143}\text{Nd}/^{144}\text{Nd})_m \</th>
<th>(^{143}\text{Nd}/^{144}\text{Nd})_i \</th>
<th>\text{Nd (ppm)}</th>
<th>\text{Sm (ppm)}</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td>0.73533</td>
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<td>0.51195</td>
<td>0.51195</td>
<td>2.62</td>
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<td>0.73136</td>
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<td>0.51208</td>
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<td>Nakaye</td>
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<td>-</td>
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<td>Tortugas</td>
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<td>0.51222</td>
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<td>0.51207</td>
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\(^{87}\text{Sr}/^{86}\text{Sr})_m = \text{measured } \(^{87}\text{Sr}/^{86}\text{Sr}), \(^{87}\text{Sr}/^{86}\text{Sr})_i = \text{initial } \(^{87}\text{Sr}/^{86}\text{Sr}), \(^{143}\text{Nd}/^{144}\text{Nd})_m = \text{measured } \(^{143}\text{Nd}/^{144}\text{Nd}), \(^{143}\text{Nd}/^{144}\text{Nd})_i = \text{initial } \(^{143}\text{Nd}/^{144}\text{Nd}). \text{Uncertainties are given at the 2\(\delta\) level; } \(^{87}\text{Sr}/^{86}\text{Sr})_i, \text{and } \(^{143}\text{Nd}/^{144}\text{Nd})_i \text{values have been back calculated to } t = 6 \text{ Ma}
Table 2. Br/Cl ratios and chlorine isotopic measurement of Fluorite and carbonate fluid inclusions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Host Rock</th>
<th>Color</th>
<th>Br/Cl (wt)</th>
<th>303/301 ratio</th>
<th>Average 303/301 ratio</th>
<th>δ37Cl per mil</th>
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<td>Mex-Tex</td>
<td>Penn. ls</td>
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<td>0.00050</td>
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<td>0.319799</td>
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<td>Green</td>
<td>0.00048</td>
<td>0.320186</td>
<td>0.320210</td>
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<td>Light green</td>
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<td>0.320220</td>
<td>0.319948</td>
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Penn Is = Pennsylvanian limestone, pC. Gran. = Proterozoic granite, Mo. Por = Monzonite Porphyry
Figure Captions

Fig. 1. A map showing the Rio Grande Rift modified after Baldridge et al 1995

Fig. 2. A Stratigraphic column showing fluorite host Rocks in the Rio Grande rift. Modified after Baldridge et al 1994

Fig. 3. Rio Grande rift (RGR) barite-fluorite-galena deposit in New Mexico. Numbered dots are fluorite deposits that were sampled for analysis. Modified after McLemore et al., 1998.

Fig. 4. A plot of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{143}\text{Nd}/^{144}\text{Nd}$ of fluorites in the South-central Rio Grande Rift. Example of a possible mixing between the basalts and the granites and possible mixing between the Pennsylvanian Carbonates and the granites is also shown. Mixing between carbonates and granitic fluids could also explain the Sr-Nd isotope variations in our fluorite samples. Other Proterozoic granites that are potential sources of Sr, Nd and Pb are those of the Organ plutons. Their average $^{143}\text{Nd}/^{144}\text{Nd} = 0.511999$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.78631$ (Verplanck et al., 1995). The inserted diagram shows a far more radiogenic character (Organ pluton granite) than the Bingham or the Navajo granites. Potential mixing curves involving the Organ pluton granites would result in greater contribution from the non-granitic sources, but are still consistent with the observed trend in the fluorites data. The $2\sigma$ error on the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ are smaller than individual data points ▲ Basalts, □ Carbonates, × Fluorites, ○ Granites (NVF), ● Granites (BG) ⊗ Granites (OP)

Fig 5. Br/Cl (wt) ratios vs. $\delta^{37}\text{Cl}$ per mil for the fluorites fluid inclusion from the South –central Rio Grande rift. × Fluorites from the Rio Grande rift. The lines C and D define a broad envelope in which all possible curves describing mixing between asthenospheric and evaporite sources of Cl would lie. Lines A and B in also define a much more narrow envelope of possible mixing curves, which is more likely given the tight trend in the data. The lines A and B were used to calculate the amount of Cl derived from asthenospheric magmatic and evaporite source regions to define possible end member contributions to mixing. The significance of the $\delta^{37}\text{Cl}$ data aided in determining the source of Cl between the two reservoirs. (Ref. For evaporite and asthenospheric source regions are Bolhke et al., 1992; and Magenhiem et al 1995). The $2\sigma$ error.
on the other $\delta^{37}$Cl values are smaller than individual data points. (Sunshine 2 = SS# 2, Sunshine 3 = SS# 3, Portales = P, Ruby Hayner = R, Mex-Tex = M, San Diego = S, Nakaye = N, Fluorite Ridge = F)
Fig. 2.

Paleozoic

Cretaceous

Jurassic

Triassic

Permian

Carboniferous

Mississippian

Pennsylvanian

Medora Group

Arkose Sandstone
and pebble conglomerate 760
with interbedded shale

Cherty limestone & minor Sandstone 230
Logsprings Dolomite, Siltstone 40
Arroyo Penasco Sandstone & shale 20
Granite, Gneiss, Schist, Quartzites

Dakota 25
Sandstone & Siltstone 360
Todilto FM 30 (Gypsum, SS & Sh)
Entrada Sandstone 130
Chinle Shale, SS, Pebble Conglomerate Formation 230
Fig. 3

1. Gonzales
2. Hansonburg
3. Caballo Mtns.
4. Fluorite Ridge

 Deposits visited
Other RGR barite-fluorite-galena deposits

5. Tonuco (San Diego Mtns.)
6. Organ Mtns. (Bishop Caps)
7. Tortugas
Fig. 4

![Graph showing isotope ratios of Nd and Sr](image)
Fig. 5.
### Appendix

<table>
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<th>samples</th>
<th>Br (ppm)</th>
<th>Cl (ppm)</th>
<th>F (ppm)</th>
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