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Evaluation of Raman Spectroscopic Geothermometry of Graphitic Carbon as a Mineral Exploration Tool. A Case Study of the San Sebastian Au-Ag Mine, Durango, Mexico

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Abstract

While visually similar to graphite, graphitic carbon is disordered rings of carbon whereas graphite is the pure-carbon crystalline form. As graphitic carbon is heated, it undergoes an irreversible graphitization process which can be observed using Raman spectroscopy and determine the maximum temperature that a rock was exposed to. Samples of sedimentary rocks, taken from the Au-Ag San Sebastian mine in Durango Mexico, containing graphitic carbon located from positions in contact with mineralized veins were used in developing a low-cost protocol for Raman spectroscopic analysis of drill core. The samples were cut and then polished to provide a smooth surface, so that the Raman collection could be conducted on the drill core directly. When plotted on longitudinal sections, the temperature distribution identified potential up-flow zones where mineralizing fluids were focused. In conclusion Raman spectrometry of graphic carbon is a rapid, cost-effective geothermometer and shows considerable promise as an exploration tool.

Keywords

graphitic carbon geothermometer, carbonaceous material, disordered carbon, mineral exploration, up-flow zones, Raman spectroscopy.
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<td>FWHM</td>
<td>Full Width at Half the Maximum</td>
</tr>
<tr>
<td>FIA</td>
<td>Fluid Inclusion Assemblage</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts Per Million</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>Cu</td>
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Chapter 1

1 Introduction

Analytical methods commonly used in the mining exploration industry for calculating temperature are fluid inclusion thermometry, isotope thermometry and mineral exchange thermometry. These methods require double-polished sections to be made from samples, which involve a lengthy amount of time to prepare and perform temperature measurements. The purpose of this research is to evaluate a quick, non-destructive analytical technique for temperature determination through Raman spectroscopy. By using the graphitic carbon found in sedimentary rock samples, the Raman spectrum of a drill core sample can be analyzed and processed in a short and economic time frame.

The introduction is broken into 4 different sections. Section 1.1 covers the basics of Raman spectroscopy, Raman scattering, and Stokes versus anti-Stokes scattering. Section 1.2 targets graphitic carbon and the intricacies of the Raman spectrum of graphitic carbon. After introducing the Raman spectrum of graphitic carbon, Section 1.3 focuses on other types of geothermometers and the application of the Raman spectrum as a geothermometer. This leads into Section 1.4 where the study area, the San Sebastian Au-Ag mine in Durango, Mexico is introduced.

1.1 Raman Spectroscopy

At its core, spectroscopy is the interaction between matter and electromagnetic radiation (Herrmann and Onkelinx, 1986). There are many different spectroscopic techniques
ranging across the electromagnetic spectrum (Figure 1.1) from X-rays to visible light with Raman spectroscopy, to infrared and radio waves. There are two main types of light scattering in the visible light spectrum. The first is Rayleigh scattering, named after Lord Rayleigh, who first formulated the classical theory of light scattering without a change in frequency (Rayleigh, 1871). The second is Raman scattering where the light scattering occurs with a change in frequency. Raman scattering is named after Sir Chandrasekhara Venkata Raman who was the first to observe the scattering of light using sunlight and a telescope (Raman and Krishnan, 1928). Besides the two main types, there are more than 25 types of light scattering spectroscopies known, such as hyper-Rayleigh and hyper-Raman scattering, second hyper-Rayleigh and second hyper-Raman scattering, coherent Stokes and anti-Stokes Raman scattering, coherent Stokes and anti-Stokes hyper-Raman scattering, simulated Raman gain or loss spectroscopy, and simulated hyper-Raman spectroscopy (Long, 2002).

![Electromagnetic Spectrum](image)

**Figure 1.1: Electromagnetic Spectrum.**

The basic theory of Raman spectroscopy is derived from the fact that photons of light interact with matter, and photons can either pass through without interacting, get absorbed, or scatter. For the photon to be absorbed, the energy of the photon needs to be equal to the energy gap between two energy levels of a molecule in the interacted material.
This is referred to as absorption spectroscopy and can be detected by the loss of energy from the light. However, if the photon is scattered, the energy of the photon does not correspond to the energy gap between the energy levels of the molecule (Smith and Dent, 2005).

During scattering, the light that interacts with the molecule is considered to propagate an oscillating dipole. This will distort, or polarize, the electron cloud around the nuclei and promote the electrons to an excited “virtual state” (Smith and Dent, 2005). It is called a virtual state because the virtual state is an unobservable, quasi-stationary energy level (National Research Council (U.S.), 1953). A virtual state is not stable and therefore short-lived, quickly leaving the excited state and releasing energy as scattered radiation. The length of time in the virtual state can be assumed to be zero which implies that the energy of the virtual state cannot be measured due to the Heisenberg uncertainty principle $\Delta E \Delta t \geq 1$. If $\Delta t \approx 0$, then the uncertainty in the energy, $\Delta E$, will be infinitely high (Belkic, 2003).

Rayleigh scattering occurs when the only involvement is the electron cloud being distorted. The frequency of the scattered photons will only have a small change because electrons have less mass compared to the molecule. Since there is essentially no change in energy, this is considered an elastic process. However, if during the polarization there is motion induced by the interacting photon, energy will be transferred to the molecule. If motion of the nuclei was induced, since the nuclei are comparably heavier than electrons, there will be a change in the energy of the molecule. Whether the molecule changes to a higher or lower energy depends on whether the molecule began from an already vibrationally excited state or from the ground state. If the molecule starts from the ground
state it is referred to as Stokes scattering. Anti-Stokes scattering occurs when the molecule was already in an excited state (Ferraro et al., 2003; Smith and Dent, 2005). Figure 1.2 shows a representation of Stokes and anti-Stokes scattering. The nomenclature of Stokes scattering is named after George Stokes who showed that fluorescence is due to light being emitted at a lower energy than what is absorbed from the incident light (Stokes scattering) and when the light emitted at a higher energy than the absorbed light (anti-Stokes scattering) (Long, 2002; Cammack et al., 2006).

![Diagram of Stokes, Anti-Stokes, and Rayleigh scattering]

**Figure 1.2: Representation of Stoke, anti-Stoke, and Rayleigh scattering with ground state, n, and excited state, m.**

Raman scattering measures the vibrational frequency, $v_s$, of the molecules as a shift from the interacting photon frequency, $v_o$, in most cases from the incident laser beam. For
Stokes scattering, the frequency can be expressed as \( \nu = \nu_o - \nu_s \) and for anti-Stokes scattering, the frequency can be expressed as \( \nu = \nu_o + \nu_s \). For Rayleigh scattering, \( \nu_o = \nu_s \), meaning no Stokes or anti-Stokes scattering is observed (Long, 2002; Ferraro et al., 2003; Smith and Dent, 2005). The majority of Raman scattering will be Stokes scattering as it is more likely that molecules will be in the ground state before interaction with the incident laser. Therefore, Stokes scattering provides a higher intensity signal over anti-Stokes scattering. From here on, when referring to a scattering event, it will be assumed to be Stokes scattering. The ratio for Stokes and anti-Stokes scattering can be calculated from the Boltzmann equation (Equation 1.1) (Smith and Dent, 2005).

\[
\frac{N_n}{N_m} = \frac{g_n}{g_m} e^{\frac{-(E_n - E_m)}{kT}} \tag{1.1}
\]

Where \( N_m \) is the number of molecules in the excited vibrational energy level (m), \( N_n \) is the number of molecules in the ground state (n), \( E_n - E_m \) is the difference in energy between the vibrational energy levels, \( k \) is the Boltzmann constant, and \( g \) is the degeneracy levels of n and m. Degeneracy levels refers to the fact that vibrations can occur in more than one way with the same energy. When degeneracy occurs, the individual components cannot be disassociated but still need to be accounted for (Smith and Dent, 2005).

Essentially, the Raman scattering is measured from the scattered radiation. The difference in the energy from the excitation and scattering is the energy of vibrations of the molecule. Every molecule will have a series of electronic states, each with vibrational and rotational states (Smith and Dent, 2005). Figure 1.3, a Morse curve, shows the vibrational levels for any electronic state. The Morse curve can be used to calculate the energy of the vibronic level, which is a single vibrational level of a single electronic state, but can be
difficult to calculate because of the shape of the Morse curve without a harmonic approximation (Smith and Dent, 2005). Fortunately, calculation of the energy in the vibronic is not necessary to apply Raman spectroscopy. Only an understanding of a Raman spectrum is needed to apply Raman spectroscopy.

**Figure 1.3: Morse curve showing different vibrational frequencies with a representation of harmonic oscillating molecules.**

In summary, Raman spectroscopy is the process of using an incident beam of light to polarize electron clouds of a molecule and induce vibrations. When the incident photons interact with the molecule, some of the energy of the photons is transferred to the molecule and the molecule is excited to a virtual state. If the molecule was originally in its ground state before the interaction with the photon, and the final position of the molecule is in a higher vibrational level, Stokes scattering occurs. If the molecule originates from an excited state and ends in a lower vibrational level, it will be anti-Stokes scattering but
because the majority of molecules will be in the ground state to begin, Stokes scattering will occur more frequently. It is the scattering process, which when released the virtual state, releases energy in the form of scattered radiation that is later measured. Only one in every $10^6$ to $10^8$ photons will scatter so Raman spectroscopy is intrinsically a weak process. Through this process a Raman spectrum, which is unique to different compounds, is gathered.

Raman spectroscopy has a wide range of applications applicable to ore deposits. For fluid inclusions in particular, it can be used to identify volatile phases (Rosasco et al., 1975; Pasteris et al., 1988) and crystals within the fluid inclusions (Dubessy et al., 1982; Bakker, 2004). In a general instance, Raman spectroscopy has been used to identify minerals on the surface of Earth and other planetary surfaces (Hemley et al., 1987; McMillan and Hofmeister, 1988; Haskin et al., 1997; Israel et al., 1997; Breier et al., 2009) as well as of meteorites (Wang et al., 1999; Busemann et al., 2007). Important to this study, Raman spectroscopy has been used to detail the graphitization of carbonaceous material (Pasteris, 1988; Wopenka and Pasteris, 1993; Cuesta et al., 1994; Emtsev et al., 2009).

1.2 Graphitic Carbon

1.2.1 Graphite Structure

Graphite is well known for being one of the polymorphs of carbon, with the other notable one being diamond. Whereas diamond has the carbon bonds in a tetrahedral sp$^3$ hybridization, the carbon bonds in graphite are formed in a trigonal sp$^2$ hybridization (Chung, 2002). Carbon possesses six electrons; two electrons in the 1s orbital and four electrons separated into the 2s and 2p. The 2p orbital is subdivided into 2p$_x$, 2p$_y$ and 2p$_z$. 
orbitals, represented in Figure 1.4. Together with the 2s orbital, the 2pₓ and 2pᵧ orbitals form the sp² hybridized orbital and, when combined and overlapped with other sp² hybridizations, form the carbon plane through what are known as a σ bond (Clayden et al., 2001; Atkins et al., 2010), the strongest covalent bond (Moore et al., 2009). The 2pₓ orbitals are perpendicular to the 2pₓ and 2pᵧ orbitals and form π bond with other 2pₓ orbitals producing a weak Van der Waal force between the carbon sheets (Chung, 2002; Atkins et al., 2010). The carbon-carbon bonds formed by sp² orbitals are arranged in a hexagonal pattern in a plane where a single plane is known as graphene. When the graphene layers are stacked in the ABAB sequence of the hexagonal close packing (hcp) lattice (Figure 1.5), the graphite structure is produced with the space group P6₃/mmc (Chung, 2002). The ABAB lettering stands for the repeating layers in hcp lattice. A is the relative reference layer with B being the above plane with different positioning. This leads to every third layer repeating in a hcp lattice. The B plane position relative to the A plane can be expressed through Equation 1.2 with the translation t and a₁, a₂, a₃ are the lattice vectors which form the unit cell of graphite (Reich and Thomsen, 2004).

\[ t = \frac{(a₁ + a₂)}{3} + \frac{a₃}{2} \quad [1.2] \]
Figure 1.4: Representation of the $2p_x$, $2p_y$, and $2p_z$ orbitals.

Figure 1.5: Representation of the graphite structure showing the ABAB sequence.

1.2.2 Graphitization

Under most crustal conditions graphitic carbon is the most stable form of the element carbon. Commonly, carbon that is found under crustal conditions will be referred to as graphite, but graphite is simply the pure crystalline form of graphitic carbon. Carbonaceous material is another term that can refer to carbon under crustal conditions and to material like soot, charcoal, kerogen and coal (Beyssac and Rumble, 2014). For the purpose of this thesis, graphitic carbon will be the term used to refer to any carbonaceous material that has undergone some form of graphitization.

Graphitization is a process that describes the development of amorphous carbon to the crystalline structure of graphite. In amorphous carbon, the carbon planes are not flat,
and the hcp ABAB sequence may not be present (Chung, 2002). As heat is applied, the traces of hydrogen, oxygen, nitrogen and sulfur are liberated from the precursor material and the carbon becomes increasingly organized into the ABAB sequence (Beyssac and Rumble, 2014; Buseck and Beyssac, 2014; Kouketsu et al., 2014). The graphitization process is irreversible, i.e., after the material undergoes graphitization no retrograde action will occur and the graphitic carbon maintains its crystallinity (Beyssac et al., 2002a). The relationship of temperature and crystallinity has been documented through various techniques such as X-ray diffraction (French, 1964; Landis, 1971), high-resolution transmission electron microscopy (HRTEM) (Buseck and Huang, 1985; Jehlicka and Rouzaud, 1990; Beyssac et al., 2002b; Nakamura and Akai, 2013), and finally through Raman spectroscopy (Pasteris and Wopenka, 1991; Jehlička and Bény, 1992; Yui et al., 1996; Childress and Jacobsen, 2017; Wopenka and Pasteris, 1993).

1.2.3 Raman Spectrum of Graphitic Carbon

Raman spectrum of graphitic carbon is comprised of a first order region between 1100 to 1800 cm\(^{-1}\) and a second order region between 2500 to 3100 cm\(^{-1}\) (Tuinstra and Koenig, 1970; Nemanich and Solin, 1979; Pasteris and Wopenka, 1991; Beyssac et al., 2002a). Only the first order region is necessary for this study where the two main peaks for low-ordered graphitic carbon are located at ~1350 cm\(^{-1}\) (D1) and ~1600 cm\(^{-1}\) (D2), with smaller peaks between the D1 and D2 peak at ~1500 cm\(^{-1}\) (D3); on the lower-frequency shoulder of the D1 peak at ~1250 cm\(^{-1}\) (D4); and on the higher-frequency shoulder of the D2 peak at ~1585 cm\(^{-1}\) (G). D1-D4 are named D bands or D peaks, which refer to the crystal defects occurring in the structure. D1 and D2 are commonly referred to as simply D and D’ in
previous studies but the numbering system will be used for clarity. The G peak is named for graphite, as it will be the only peak visible in the Raman spectrum of graphite.

The vibrational modes for the crystal structure of crystalline graphite are $\Gamma = 2E_{2g} + 2B_{2g} + E_{1u} + A_{2u}$ where $\Gamma$ is the optical phonon mode at the Brillouin zone boundary with A, E, B following nomenclature from group theoretical analysis. Only the $2E_{2g}$ modes are Raman active, meaning they will be visible in the Raman spectrum, with $E_{1u}$ and $A_{2u}$ infrared active, and the $2B_{2g}$ modes are silent (Chung, 2002). The $E_{2g}$ mode corresponds to the G peak observed at $\sim 1585$ cm$^{-1}$ (Spain et al., 1967; Nicklow et al., 1972; Song et al., 1976; Wang et al., 1990). The D1 peak corresponds with lattice vibration of $A_{1g}$ symmetry and only appears in the presence of disorder (Ferrari and Robertson, 2000). The other peaks are associated as follows: D2 peak with the $E_{2g}$ mode like the G peak (Dresselhaus and Dresselhaus, 1981; Al-Jishi and Dresselhaus, 1982; Cuesta et al., 1994) and the D3 peak due to out of plane defects like tetrahedral carbon in disordered graphitic carbon (Beny-Bassez and Rouzaud, 1985; Sadezky et al., 2005; Beyssac et al., 2002a). The $E_{2g}$ mode contributing to the G peak and the $A_{1g}$ mode contributing to the D1 are attributed to the bond stretching (Figure 1.6a) and breathing (Figure 1.6b) of $sp^2$ atoms in the aromatic ring of carbon of the $sp^2$ atoms, respectively (Ferrari and Robertson, 2000; Castiglioni et al., 2001; Tuinstra and Koenig, 1970). The $E_{2g}$ mode is the vibration of the carbon atoms while maintaining the volume. The $A_{1g}$ mode is the translation of the carbon atoms as they move inwards and outwards. Motions are represented in Figure 1.6.
It has been observed that a “dispersive” behaviour occurs in carbon material where different excitation energies change the Raman signal by altering the phonon frequency (Dresselhaus et al., 2002; Kürti et al., 2002). This can be seen in changes in the D1 peak where, with different laser excitations, the center position and the relative intensity changes (Wang et al., 1990; Matthews et al., 1999; Sato et al., 2006; Pimenta et al., 2007). However, Kouketsu et al. (2014) suggested that “the full width at half of the maximum amplitude (FWHM) of Raman peaks for graphitic carbon are robust and not subject to significant inter-laboratory variation”.

1.3 Geothermometers

Temperature is one of the most important properties that controls geochemical and mineralogical processes. Determining the temperature is usually conducted through
thermometers so when dealing with geologic components it is called a geothermometer. There are many types of geothermometers or geothermometry techniques, to choose from but only a few techniques will be mentioned here. Those techniques are stable isotope thermometry, Fe – Mg exchange thermometry, fluid inclusion thermometry and graphitic carbon thermometry.

1.3.1 Stable Isotope Thermometry

Stable isotope thermometry was one of the original geothermometers, first published in 1947 (Urey, 1947), but is an expensive and labor-intensive technique. Stable isotope geothermometry has evolved from using single stable isotopes of one rare isotope like oxygen isotopes (Javoy, 1977; Matsuhisa et al., 1979; Kyser et al., 1981; Clayton et al., 1989) to using clumped isotopes geochemistry, which involves measuring the isotopologues, which contain more than one rare isotope (Eiler, 2007, 2011). Isotopologues refer to molecules that are only different in isotopic composition (Sharp, 2017). Nevertheless, they still use the same principles that the formation temperature of a substance (i.e., rocks and minerals) is dependent on the equilibrium isotopic fractionation between two phases or substances. The fractionation process between two substances follows a $\frac{1}{T^2}$ relationship (Sharp, 2017). However, to use isotope thermometry the substances need to maintain the original isotopic ratio, which in some cases, even without visibly affecting the mineral, retrograde isotope effects can occur (Javoy, 1977). Other complications are that the equilibrium fractionations need to be known as a function of temperature and that substances are in equilibrium (Kyser et al., 1981).
1.3.2 Fe – Mg Exchange Thermometry

Fe – Mg exchange is another commonly used geothermometer. Temperature is calculated using the partitioning of Fe – Mg between minerals in a sample (Raheim and Green, 1974; Ferry and Spear, 1978). The typical temperature range that can be achieved for an Fe – Mg exchange thermometer is between 600 and 1400°C (Ellis and Green, 1979; Raheim and Green, 1974; Ferry and Spear, 1978). The difficulties of Fe – Mg exchange thermometry arise from the lack of information surrounding the iron in the sample. All that is known is the total iron amount, but not the amount of ferrous and ferric states of iron. However, there are ways to calculate the ferric-ferrous ratio, but the calculations are sensitive to analytical imprecision (Ravna, 2000). Another difficulty is that thermal resetting can occur during cooling which will disrupt the compositions (Spear and Florence, 1992).

1.3.3 Fluid Inclusion Thermometry

The other type of commonly used geothermometer, and one frequently used by exploration companies, is fluid inclusion thermometry. Fluid inclusions are simply little vacuoles that are filled with fluids trapped inside minerals (Goldstein and Reynolds, 1994). These fluids trapped inside the minerals can provide temperature, pressure and fluid composition from the time the mineral was formed only if three basic assumptions are followed. These assumptions are referred to as Roedder’s Rules and are as follows: The inclusion is trapped in a single, homogeneous fluid; nothing is added or lost from the inclusion after being trapped and the volume or density of the inclusion remains constant after being trapped (Bodnar, 2003). If these conditions are not met, then the inclusion does
not reflect the trapping temperature and pressure. Additionally, if there is only an individual inclusion, then it is not possible to test if it follows Roedder’s Rules. Fortunately, it is possible to test for compliance with Roedder’s Rules if the fluid inclusion is included within a fluid inclusion assemblage (FIA) (Bodnar, 2003). A FIA is a group of individual inclusions along the same growth zone in a mineral (Goldstein and Reynolds, 1994). Even after fulfilling all of Roedder’s Rules, making sure the inclusion has been unchanged, individual fluid inclusions inside of a FIA can have variations in the temperature (Bodnar, 2003). Another disadvantage of FIA is that the majority of inclusions will be secondary inclusions and need to be distinguished from primary inclusions (Cunningham, 1977). The secondary inclusions also record the temperature at which they were formed, making it more difficult to determine the peak temperature.

1.3.4 Graphitic Carbon Thermometry

The final geothermometer considered is the focal point of this thesis, the graphitic carbon geothermometer. The theory behind the thermometer uses the concept outlined in Section 1.2 that the graphitization process of graphitic carbon from low ordered, amorphous carbon to high ordered, crystalline graphite, can be observed through the Raman spectrum and is irreversible. Currently there are essentially 3 models (Rahl et al., 2005; Lahfid et al., 2010; Kouketsu et al., 2014; Beyssac et al., 2002a) that use different parameters of the Raman spectrum, with Rahl et al. (2005) extending the geothermometer proposed by Beyssac et al. (2002). In these studies, the nomenclature used is a carbonaceous material geothermometer, whereas here it will be referred to as a graphitic
carbon geothermometer. The reasoning arises from changing the focus from anything that contains carbon, to something that is capable of becoming graphitized.

Beyssac et al. (2002) began from analyzing 54 samples that equilibrated at varying pressures (3-32 kbar) and temperatures (330-800°C). By observing the change in the Raman spectrum, Beyssac et al. (2002) were able to derive a formula (Equation 1.3) for the temperature.

\[ T \ (°C) = -445 \ R_2 + 641 \]  \hspace{1cm} [1.3]

Where R2 uses the area ratio of peaks \( \frac{D_1}{G+D_1+D_2} \). The applicable range suggested by Beyssac et al. (2002) is between 330 to 650°C but was later extended to 100 to 700°C by Rahl et al. (2005). The second geothermetric technique, which was used throughout this research, was proposed by Kouketsu et al. (2014). This geothermometer is useful for low-ordered graphitic carbon, when there is the presence of the D4 peak (Figure 1.7). By using the full width at half the maximum (FWHM) of the D1 peak, temperatures between 150 to 380°C can be calculated using Equation 1.4.

\[ T \ (°C) = -2.15 \ (D1 \ FWHM) + 478 \]  \hspace{1cm} [1.4]
Figure 1.7: Raman spectrum of low order graphitic carbon, sample SS-450, shown using black dots for the background removed data with grey lines for representation of the individual peaks and a red arrow demonstrating the D1 FWHM.

1.4 San Sebastian Au-Ag Mine

The subject of this geothermometry study was the San Sebastian epithermal gold-silver deposit in the province of Durango, Mexico. A hydrothermal deposit is one where hot fluids transport metals to a site of deposition. When hydrothermal deposits occur at low temperatures and shallow depths, they are commonly referred to as epithermal deposits (Skinner, 2015). Precious metals like gold and silver are economically the most important type of deposit in epithermal deposits, and form at depths of 1-2 km (Simmons et al., 2005) and at temperatures between ~150 and ~300°C (White and Hedenquist, 1995; Bodnar et al., 2014; Simmons et al., 2005). Gold and silver are commonly deposited in epithermal
systems due to boiling (Stefánsson and Seward, 2004; Simmons et al., 2005; Seward et al., 2014). While it is possible that other processes like fluid mixing and cooling act as the mechanism for deposition (Simmons et al., 2005), boiling would still have to have occurred at some stage (Hedenquist et al., 2000). Once boiling has begun, the deep fluids will quickly continue to boil towards the surface in up-flow zones (Hedenquist et al., 2000; Simmons and Browne, 2000;). For this reason, it is useful to identify potential boiling zones leading to up-flow zones. Details of the San Sebastian deposit are provided in Chapter 3.
1.5 References


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Chapter 2

2 Methodology

This chapter is separated into 3 sections. Details of the sample preparation are in the first section (2.1). The second section (2.2) describes the Raman spectroscopy system set-up and the sample collections. Finally, the third section (2.3) illustrates how the data are analyzed.

2.1 Sample Preparation

Drill core samples from three veins (Middle, Francine and North Veins) were provided by Hecla Mining Company from the San Sebastian mining project area in Durango, Mexico. Most drill core samples were already cut into half core. However, some samples were full core, or broken pieces of core, though all drill core was cut into smaller pieces. The large and full drill core samples, they were cut using a diamond rock saw (Figure 2.1) in the Cutting and Crushing Laboratory in the Department of Earth Sciences at the University of Western Ontario. After the drill core samples were cut into 25x24x5 mm sections the smaller sections were polished using a circulating polisher (Figure 2.2) and a vibrating lapidary (Figure 2.3). The circular polisher creates friction when polishing, so care must be taken to prevent heating the samples. This is accomplished by polishing under a flow of water. In this study, 47 of the 388 samples were polished with only the circulating polisher. These 47 samples were originally polished as a test to examine whether there are any potential errors in Raman measurements resulting from the uneven or rough surface. After testing the polished samples, it was decided to polish the remaining 341 samples using the vibrating lapidary. The samples polished using only circular polisher
were polished with 120, 240, 400, and 600 grit silicon carbide paper whereas the vibrating lapidary samples used 240, 400, 600 silicon carbide powder and 0.3 µm aluminum oxide powder, and again, water was used as a lubricant to prevent heating. The samples polished using the vibrating lapidary were first polished with the 120-grit silicon carbide paper on the circular polisher to remove any large uneven surfaces before placed in the vibrating lapidary for 24 hours at each different level. An example of an unpolished sample and a sample polished using the vibrating lapidary are shown in Figure 2.4.

Figure 2.1: Photo of the diamond rock saw.
Figure 2.2: Photo of circular polishing disk.

Figure 2.3: Photo of vibrating lapidary.
Figure 2.4: Photo showing an unpolished sample of half core on the left and a sample polished using the vibrating lapidary to 0.3 µm on the right.

2.2 Raman Spectroscopy System

The Raman spectroscopy collection was performed using a custom-built Raman spectroscopy system (Figure 2.5) located in the High-Pressure Diamond Anvil Cell Laboratory in the Department of Earth Sciences at the University of Western Ontario. Figure 2.5 shows the Raman spectroscopy setup, and a schematic diagram is also included for simplicity (Figure 2.6). The custom setup utilises a water-cooled, Coherent Ar⁺ monochromatic beam of light with a wavelength of 514.532 nm as an excitation source. The Ar⁺ light is passed through a bandpass filter which removes all wavelengths of light other than 514.532 nm. After passing through the bandpass filter, the light is sent through a spatial filter. The spatial filter is used to remove deviations due to imperfections in the beam or dust in the air by removing all higher order energy peaks and leaving only the high intensity, central portion of the beam. A dichroic mirror is placed after the spatial filter,
which allows the excitation beam to reflect towards the sample, but when the emission from the sample is returned in the backscattered direction, the emission can pass through while only allowing <10% of the excitation beam to pass. To focus on the sample, a 20x objective lens with a working distance of 31.0 mm was first used and later replaced with a 50x objective lens with a working distance of 20.5 mm. Next, after returning in a 180° backscattered direction, through the objective lens and the dichroic mirror, the scattered emission is focused using a confocal lens to pass through an adjustable pin hole, then collected using another confocal lens into a straight path. Finally, before entering into the spectrometer, two notch filters are used to remove any remaining frequencies from the excitation energy. A notch filter is a band-stop filter that absorbs all light around a particular wavelength, in this case all light around 514 nm. Finally, only the scattered light is focused into the Action Research SpectraPro 2500i Imaging Triple Grating Spectrometer with 1800 g/mm grating to disperse the photons into different frequencies of light. These frequencies are directed into a liquid nitrogen cooled charge-coupled device (CCD) which records each individual photon into the computer and computes the spectrum.
Figure 2.5: Photo of the custom-built Raman system.

Figure 2.6: Schematic diagram of the custom-built Raman spectroscopy setup. Abbreviations are as follow: BF: bandpass filter, M: mirror, SF: spatial filter, DM:

When collecting a spectrum, there are two ways to improve signal quality: First, increasing the length of time collecting the spectrum to increase the intensity and second, increasing the amount of iterations used during stacking to average out the spectrum and reduce the noise in the signal. On average, the spectra were collected between 15 and 30 seconds with 3 to 5 iterations, for a combined total time of 45 to 150 seconds for one spectrum. To give comprehensive coverage of the sample, 4-5 different areas on each sample were the focus for collection. Therefore, the total time to collect a complete analysis of the Raman spectra for a sample was between 180 and 750 seconds (3 to 12.5 minutes).

2.3 Sample Analysis

Once the spectrum is collected from the Raman system, the maximum temperature the rock was subjected too, and thus the temperature of the hydrothermal fluid can be calculated from the samples based on the following steps: For low-ordered and low temperature graphitic carbon, the FWHM of the D1 peak is required for the temperature calculation. To obtain this, the program PeakFit® 4.11 was used to fit the spectrum using the convolution of a Gaussian and Lorentzian profile. Before fitting the peak positions, the background of the spectrum was removed using PeakFit® 4.11 that selects a baseline function to minimize the best fit by removing points in ways that the second derivative of the remaining points is zero. (Figure 2.7). In this study, a linear or cubic baseline provides a best fit. Then 5 peaks situated at ~1250 cm⁻¹ (D4), ~1350 cm⁻¹ (D1), ~1500 cm⁻¹ (D3), ~1580 cm⁻¹ (G), and ~1610 cm⁻¹ (D2) were chosen to form a single accumulated spectrum
to match the Raman spectrum (Figure 2.8). Only the G peak was fixed at 1585 cm$^{-1}$ with the remaining peaks unconstrained. Once the spectrum matches, PeakFit® provides the area, position, FWHM, and amplitude information. After obtaining the FWHM, Equation 1.4 was used to calculate the temperature for each sample.

Figure 2.7: Procedure for peak fitting: a) Background removal where black dots are Raman collected data, yellow dots for the fixed background points, and the red line
for the representation of the cubic background; b) Peak fitting for the background removed spectrum (black dots). The top spectrum of (b) uses the red line to show the accumulation of the individual Gauss-Lorentzian peaks. The bottom spectrum shows the individual peaks of the D4 (blue), D1 (magenta), D3 (brown), G (green), and D2 (olive-green).

To illustrate the spatial distribution of the temperature data Golden Software Surfer® was used to contour the data on long sections. Each point in the long sections represents a sample provided by piercing points of drill holes intersecting the vein. The samples were chosen to be in close proximity to the vein. Piercing points are projections as the vein does not follow a perfect plane. Contours were formed using an inverse distance to square gridding method to the power of two with an eclipse diameter of 75 by 75 m. Assay data for the three veins were provided by Hecla geologists, and so contoured long sections were created for temperature, gold (Au), silver (Ag), copper (Cu), lead (Pb), zinc (Zn), arsenic (As), mercury (Hg), antimony (Sb). Temperature levels were split into three sections: less than 240°C, between 245 and 280°C, and greater than 280°C. All assay levels share the same scale and were plotted on a base 10 logarithmic scale. However, if the metal didn’t have levels high enough for the next logarithmic level, it was not included in the scale. For instance, gold had no data greater than 100 parts per million (ppm) so the 100 level was not included whereas silver had metal >100 ppm so that level was included.
Chapter 3

3 Rapid determination of deposit-scale, temperature zonation at the San Sebastian Au-Ag deposit, Mexico from Raman spectroscopic analysis of graphitic carbon geothermometry

3.1 Introduction

The temperature of hydrothermal systems is one of the most important factors controlling mineral deposition in many different deposit types, and determination of temperature zonation at the deposit scale can be an important tool for mineral exploration. A number of different techniques have been developed over the years to determine mineral temperatures including: stable isotope ratios (Urey, 1947; O’Neil and Clayton, 1964; Garlick and Epstein, 1967; Javoy, 1977; Kyser et al., 1981), Fe – Mg exchange thermometry (Raheim and Green, 1974; Ferry and Spear, 1978), and fluid inclusion thermometry (Roedder, 1984; Wilkinson, 2001; Bodnar et al., 2014).

These geothermometers require knowledge of the geologic settings that may be difficult to obtain. Stable isotopes geothermometry requires that the mineral assemblages are in equilibrium, have maintained the original isotopic ratio, and reach the equilibrium fractionations which are known as a function of temperature (Javoy, 1977; Kyser et al., 1981). Note that this is not always the case found in hydrothermally altered rocks. Difficulties of Fe – Mg exchange geothermometry develop from the calculations of ferric-ferrous iron ratios (Ravna, 2000), and thermal resetting occurring during cooling (Spear and Florence, 1992). The majority of fluid inclusions are secondary, meaning the fluid enters into fractures after a mineral formed, but for temperature determination the
inclusions must be primary, meaning the fluid is enclosed during formation of the mineral (Bodnar, 2003). Furthermore, after the fluid inclusion is sealed, there is nothing added or lost from the inclusion, the pressure conditions need to be known – or at least it must be assumed that the inclusion underwent the same pressure conditions as the host mineral, and the relation between the inclusion and the origin mineral must be known (Roedder, 1984; Wilkinson, 2001). There are also secondary inclusions that will record the temperature conditions in a later instance, meaning primary inclusions need to be distinguished from secondary inclusions (Cunningham, 1977). An important drawback of these methods is that they require a significant amount of sample preparation and analytical time can therefore be lengthy, i.e., the results can take several months. The financial costs for analyzing samples by these methods prohibit the analysis of a large number of samples.

One approach for geothermometry that has received little attention in the field of mineral exploration is the analysis of graphitic carbon by Raman spectroscopy, although there have been many studies of the graphitization of carbonaceous material in the geological literature (Kovalevski et al., 2001; Craw, 2002; Pitcairn et al., 2005; Luque et al., 2009). The only requirement for temperature calculation in a graphitic carbon geothermometer is to have sufficient graphitic carbon present in the sample to acquire a Raman spectrum. To minimize the analysis time, Raman spectra can be collected directly from samples of drill core. Polishing the sample generally improves the quality and precision of the Raman data, although care needs to be taken not to heat the sample. Samples can be polished rapidly, at low cost thus the return time for analyses is much quicker than methods that require polished thin section preparation. One important characteristic of graphitic carbon geothermometry is that only the highest temperature that
the graphitic carbon was subjected to is preserved (i.e., the graphitization process is an irreversible reaction that does not undergo retrograde re-equilibration) (Beyssac et al., 2002a). This is very advantageous compared to stable isotopes and fluid inclusions as graphitic carbon will not be altered by later, lower temperature events. The precursor to graphitic material is predominately carbon but can also contain traces of hydrogen, oxygen, nitrogen and sulfur. During graphitization, the non-carbon elements are removed and the rings of 6 bonded carbon are formed (Beyssac and Rumble, 2014; Buseck and Beyssac, 2014).

Raman spectroscopy is well suited to analyse graphitic carbon as it utilizes Raman scattering, an inelastic, non-destructive scattering technique that scatters photons from an incident laser to produce a distinctive Raman spectrum of graphitic carbon (Figure 1.7). There are two distinct peaks characterizing the Raman spectrum of graphitic carbon; the first defect peak (D1) at ~1350 cm\(^{-1}\) and the second defect peak (D2) at ~1610 cm\(^{-1}\). Peaks labelled D1-4 are peaks that arise through defects whereas the peak labelled G stands for the graphite peak. The changes in graphitization can be observed in the Raman spectrum of graphitic carbon (Figure 3.1).
Figure 3.1: Raman spectra of background removed graphitic carbon (black dots) showing the graphitic carbon as it increases in graphitization.
Table 3.1: Description of samples used to show the graphitization change in Figure 3.1.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSA</td>
<td>Unrelated high pressure high-temperature experiment.</td>
</tr>
<tr>
<td>AoB 1.5</td>
<td>Unrelated high pressure high-temperature experiment.</td>
</tr>
<tr>
<td>Pencil</td>
<td>Graphitic carbon from a 0.7 mm mechanical pencil.</td>
</tr>
<tr>
<td>Dec21</td>
<td>Unrelated high pressure high-temperature experiment.</td>
</tr>
<tr>
<td>SS-290</td>
<td>Sample from the Middle Vein.</td>
</tr>
<tr>
<td>SS-270</td>
<td>Sample from the Middle Vein.</td>
</tr>
<tr>
<td>SS-230</td>
<td>Sample from the Middle Vein.</td>
</tr>
</tbody>
</table>

To test the applicability of the graphitic carbon geothermometer to mineral exploration, material from the San Sebastian epithermal Au-Ag vein system in the Saladillo Mining District of the Mexican Silver Belt was chosen for experimentation. The epithermal vein system is located in the Parral terrane (Figure 3.2) of Mexico where during the Devonian to Carboniferous period, metamorphic rocks formed the basement of the terrane (Eguiluz and Campa, 1982; Araujo and Arenas, 1986). Late Jurassic rhyolitic-andesitic volcanic successions unconformably overlie the metamorphic basement (Centeno-García et al., 2008). The volcanic rocks in turn are overlain by limestone, evaporites and shale ranging in age from the Tithonian age of the late Jurassic period to the Aptian age of the early Cretaceous period (Araujo and Arenas, 1986; Centeno-García et al., 2008). The San Sebastián deposit is hosted in Mesozoic sedimentary rock belonging to the Caracol Formation. The Caracol Formation, first named by Imlay (1937), was described as consisting of tuff, shale, and limestone. However, later sampling of the area revealed that
there was no material conclusively volcanic in origin but more accurately described the Formation as consisting of calcareous arkosic sandstone, calcareous shales, and mudstones (Rogers et al., 1956).

Figure 3.2: Tectono-stratigraphic map of Mexico showing San Sebastian project area using the tectono-stratigraphy from Campa and Coney (1983).

The San Sebastian vein system (Figure 3.3) consists of the Middle, Francine, East Francine, North, and Professor Veins (Allen and Redak, 2015) but only material from the Middle, Francine (including East Francine) and North Veins were used for temperature determination. The vein system has dips ranging from 65° to 75° SW for the Francine Vein, 20° to 40°SE for the East Francine Vein, 40° to 60° SW for the Middle Vein, and 30° to 50° SW for the North Vein (Allen and Redak, 2015). The total indicated resource tonnage for the San Sebastian area as of 2014 was 2,192,700 T with the inferred resource tonnage
to be 3,375,900 T (rounded to the nearest 100) (Allen and Redak, 2015). Previous temperature calculations from fluid inclusion analysis of the Francine and North veins suggest that the temperature ranges from ~200 to ~300°C, and likely underwent boiling (Allen and Redak, 2015). This is consistent with epithermal mineralization (White and Hedenquist, 1995; Simmons et al., 2005; Bodnar et al., 2014).

Figure 3.3: San Sebastian vein system showing the proximity of the Middle, Francine and North Veins. The veins, drill holes and faults locations are from Allen and Redak (2015).

3.2 Methods

The sample material consisted of half HQ drill core in which sample preparation for
improved analysis was outlined in Chapter 2. The majority of samples are predominantly black with lighter grey areas and minor quartz veining although there is a range of sample colours. Grain size, determined from thin sections of drill core samples range from 0.07 to 0.04 mm for larger grains in the samples and <0.01 mm for the majority of grains. Colours range from dark samples of black with light grey to lighter samples that are grey-green with purple and samples that are beige and tan coloured (Figure 3.4). This is consistent with shales in the Caracol Formation that describe the shales to be dark grey to black that weathers yellowish to yellow-grey (Rogers et al., 1956). Field sandstone descriptions indicate the colour to range from gray to brown and olive-green or green that will weather to reddish brown (Van Vloten, 1954; Rogers et al., 1956).

![Figure 3.4: Example of the variation of colour and texture in the samples.](image)

The Raman spectroscopy system in this study is a custom-built setup (Schematic shown in Figure 2.6) that uses a Coherent Innova 90C 514 nm Ar\(^+\) laser. The spectrum was collected in the backscattered direction and dispersed using an 1800 groove/mm grating and analyzed by a liquid nitrogen cooled charge-coupled device (CCD). Details of the sample preparation, components of the custom-built Raman spectroscopy system, and temperature analysis can be found in Chapter 2.
For low-order, low temperature graphitic carbon, the full width at half of the maximum amplitude (FWHM) of the D1 peak is used to calculate the temperature. To obtain the FWHM of the D1 peak, the program PeakFit® 4.11 was utilised for curve fitting and once acquired, temperature was calculated using Kouketsu et al. (2014) formula (Equation 1.4) which is suitable for graphitic carbon between 150°C to 400°C.

Contour temperature and metal grade plots were made using the Golden Software Surfer® program with the sample locations provided by Hecla Mining Company. The contours were calculated using an inverse distance to square gridding function with the power of 2 and a search ellipse of 75 x 75 meters.

3.3 Results

Temperatures were determined for 388 samples: 194 from the Middle Vein, 99 from the Francine Vein, and 95 from the North Vein. The Raman spectroscopy and temperature calculations were tested on 170 unpolished samples from the Middle Vein first before all samples were polished. Error was calculated by using the standard deviation of the FWHM of the D1 peak to calculate the variation in the temperature and averaged over the entire sample. The average error of the unpolished samples was ±12°C whereas the average error for the polished samples from the Middle Vein was reduced to ±6°C. Average errors for the Francine and North Vein were ±12°C and ±6°C, respectively.

Figure 3.5 shows the temperature distribution from all the veins with elevation above sea level. The temperatures are split into three intervals: Blue for temperature <240°C, green for between 240 and 280°C, and red for >280°C. A Gaussian curve is fit to
the points and drawn as a black line to show the trend of the data. Temperature contours made from the Raman data are shown in Figures 3.6, 3.7 and 3.8 for the Middle, Francine and North Vein, respectively. The contours are split into three intervals which follow the same colour pattern as Figure 3.5. Figures 3.9 to 3.17 are contour plots showing gold (Au), silver (Ag), and copper (Cu) values in parts per million (ppm) for the three veins. Areas with temperatures >280°C are also outlined on these plots. The patterns for lead (Pb), zinc (Zn), mercury (Hg), antimony (Sb), and arsenic (As) are less well defined but are shown in Appendix A.

Figure 3.5: Scatter plot showing temperature vs. elevation above sea level for combined samples from the Middle, Francine, and North Veins. The blue colour represents temperature <245°C, green for temperatures between 245 and 280°C, and red for temperatures >280°C. The black line is fit using a Gaussian curve.
Figure 3.6: Longitudinal section through the Middle Vein showing contoured Raman temperature data.

Figure 3.7: Longitudinal section through the Francine Vein showing contoured Raman temperature data.
Figure 3.8: Longitudinal section through the North Vein showing contoured Raman temperature data.

Figure 3.9: Longitudinal section through the Middle Vein showing contoured gold values. Temperature >280°C is indicated by the dark grey cross-hatched shading.
Figure 3.10: Longitudinal section through the Francine Vein showing contoured gold values. Temperature >280°C is indicated by the dark grey cross-hatched shading.

Figure 3.11: Longitudinal section through the North Vein showing contoured gold values. Temperature >280°C is indicated by the dark grey cross-hatched shading.
Figure 3.12: Longitudinal section through the Middle Vein showing contoured silver values. Temperature >280°C is indicated by the dark grey cross-hatched shading.

Figure 3.13: Longitudinal section through the Francine Vein showing contoured silver values. Temperature >280°C is indicated by the dark grey cross-hatched shading.
Figure 3.14: Longitudinal section through the North Vein showing contoured silver values. Temperature >280°C is indicated by the dark grey cross-hatched shading.

Figure 3.15: Longitudinal section through the Middle Vein showing contoured copper values. Temperature >280°C is indicated by the dark grey cross-hatched shading.
Figure 3.16: Longitudinal section through the Francine Vein showing contoured copper values. Temperature >280°C is indicated by the dark grey cross-hatched shading.

Figure 3.17: Longitudinal section through the North Vein showing contoured copper values. Temperature >280°C is indicated by the dark grey cross-hatched shading.
The distances of Au, Ag and Cu grade values with distance to the closest hot spot are shown in Figures 3.18, 3.19, and 3.20. This was conducted by finding the shortest distance of every sample to samples with temperature >280°C. Distances were calculated using the Pythagorean theorem for 2-dimensions using elevation above sea level and longitude. The three veins are combined to show the distances of the individual metals all on one figure. By visual inspection of data Figures 3.18, 3.19, and 3.20, 200-meter was determined to be a reasonable threshold for a distance away from the hot spot while maintaining significant concentrations of Au, Ag and Cu in the three veins. By first categorizing the concentrations of the metals into three ppm concentration levels (Table 3.1), the percentage of metal within 200 meters of a hot spot were calculated (Table 3.2). In addition, the individual percentage from the metals in each vein are included in Appendix B. It should be noted that the concentration level nomenclature used in Table 3.1 and 3.2 (high, medium, and low) are indicative but not quantitatively related to the concentration of metal in the three veins. For example, these levels are not stating that 200 ppm Ag is a medium grade or that anything below 5000 ppm copper is not a large quantity. Level amounts were chosen for their symmetry and relative quantity of metal. The concentration levels will be referred to as ‘(concentration level) (metal)’ e.g. medium Au or high Cu.

Results show that the distribution of high, medium and low Au are quite similar, around 72-78% but only the Middle and Francine Veins show high Au within 200 m near the vein. For high Ag, the Middle Vein contains higher grades compared to the other two veins and there is a strong relationship between the
distribution of the highest Ag grades and proximity to hot spots. For the case of Cu, only the Middle and Francine Veins contain significant grades and there is a strong correlation between high grades and proximity to the hot spots.

Table 3.2: Concentration levels for ppm values for Au, Ag, and Cu.

<table>
<thead>
<tr>
<th></th>
<th>High</th>
<th>Medium</th>
<th>Low</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>&gt;5 ppm</td>
<td>&gt;1 ppm</td>
<td>&gt;2 ppb</td>
</tr>
<tr>
<td>Ag</td>
<td>&gt;500 ppm</td>
<td>&gt;100 ppm</td>
<td>&gt;0.1 ppm</td>
</tr>
<tr>
<td>Cu</td>
<td>&gt;5000 ppm</td>
<td>&gt;1000 ppm</td>
<td>&gt;2 ppm</td>
</tr>
</tbody>
</table>

Table 3.3: Percentage of Au, Ag, and Cu within 200 m of a hot spot at varying concentration levels.

<table>
<thead>
<tr>
<th></th>
<th>High</th>
<th>Medium</th>
<th>Low</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>72 %</td>
<td>76 %</td>
<td>78 %</td>
</tr>
<tr>
<td>Ag</td>
<td>90 %</td>
<td>82 %</td>
<td>78 %</td>
</tr>
<tr>
<td>Cu</td>
<td>97 %</td>
<td>94 %</td>
<td>78 %</td>
</tr>
</tbody>
</table>
Figure 3.18: Scatter plot of Au to the closest hot spot ($T>280^\circ\text{C}$) for the Middle Vein (blue circle), Francine Vein (green triangle) and North Vein (red square).
Figure 3.19: Scatter plot of Ag to the closest hot spot (T>280°C) for the Middle Vein (blue circle), Francine Vein (green triangle) and North Vein (red square).
Figure 3.20: Scatter plot of Cu to the closest hot spot (T>280°C) for the Middle Vein (blue circle), Francine Vein (green triangle) and North Vein (red square).

3.4 Discussion

The examination of the spatial distribution of Raman-derived temperature data (Figure 3.5) shows that temperature increases with decreasing elevation. This pattern is not surprising as these samples were taken from the host rock adjacent to the three veins, and the veins likely formed in areas of high temperatures. On the temperature contour plots
(Figure 3.6, 3.7, and 3.8), the areas with temperatures >280°C are interpreted to be fluid up-flow zones. In the Middle Vein, temperature contours (Figure 3.6) show a region with temperature >280°C at depth at the relative longitudinal points between -500 and 500 m, which is the only inferred up-flow zone within that vein. The Francine Vein (Figure 3.7) has a large inferred up-flow zone near the center at the relative longitude between -200 and 1400 m of the long section. In addition, toward the north-west end of the Francine Vein there is a small hot spot located between -1200 and -900, which may be an additional up-flow zone related to the vein. In the North Vein (Figure 3.8), there are two areas with higher temperatures at 500 m and 1000 m which indicates the only likely up-flow zones in the vein. Because there is no data in between these higher temperature areas in the North Vein it is unknown if the areas are connected.

The Middle Vein has the largest data set and thus the temperature distribution is the best constrained of the three veins. The distribution of Au in the Middle Vein (Figure 3.9) shows medium Au in the temperature range 240 to 280°C. In general, this area is located above the interpreted up-flow zone mentioned earlier, except there is an area to the southeast where medium Au levels are present. Note that there are no available drill core samples below the 1800 m elevation at the southeast location and hence there is a lack of temperature information for this region. In the Francine and North Veins (Figure 3.10 and 3.11), there are less medium Au, but the region of medium Au is overall above or close to the high temperature fluid up-flow regions. This is confirmed in Table 3.2 and Figure 3.18 that shows that 72% of high Au are located within 200 m of a hot spot. These results suggest that the Au may have been preferentially deposited above up-flow zone areas where the temperature was between 240 and 280°C.
Ag and Cu grades also correlate well with the areas of high temperature fluid up-flow. Figure 3.12 shows that the medium Ag values of the Middle Vein are above the up-flow zone region. At the Francine Vein (Figure 3.13), most of the Ag mineralization is within the up-flow zone region, rather than above it. In summary, these data show that the highest concentrations of Ag within the three veins were preferentially deposited at and above up-flow zones. For the case of Cu, the highest grades are also strongly correlated to high temperature, fluid up-flow zones. In addition, there is an overlap of the up-flow zones and medium Cu values in the Middle Vein (Figure 3.15) and Francine Vein (Figure 3.16). Even though the North Vein (Figure 3.17) is Cu-poor, the highest levels of Cu in the North Vein are located in the interrupted up-flow zone. The discrepancies of Cu abundances in these three veins could likely be due to the different mineralization mechanisms. In addition, the calculated results also show that Pb and Zn have a similar distribution pattern as Cu, whereas Hg and Sb have patterns closely related to Au (Appendix A).

Table 3.2 and Figures 3.18, 3.19, and 3.20 show that the Au, Ag, Cu mineralization were concentrated within 200 m of the interpreted up-flow zones. Even for low concentration levels, seventy-eight percent of the sample locations are within 200 m of an up-flow zone. As the concentration levels increase to medium and high values, the percentage of metal located within 200 m of an up-flow zone increases for Ag and Cu. However, Au slightly decreases from seventy-eight percent to seventy-two percent the at high concentration level. This decrease can be explained with Figure 3.18, which shows two points with high Au values in the North Vein and one point of high Au value in the Middle Vein at distances >200 m. In the North Vein these two points located between 600 and 700 m longitudes, and 2000 and 2100 m elevation in Figure 3.11, are directly above
an area with no temperature data that could be a potential up-flow zone. The high Au point in the Middle Vein with distance >200 m can be observed on the north-west side of figure 3.9 at position 1900 m and -1150 m. Similar to the North Vein, this point is directly above a zone with no temperature data but it can be predated that the zone would have a temperature >280°C. If the area were to have temperature >280°C, it would decrease the distance of those three points and change the percentage at high concentration level to eighty-one percent.

In summary, the Middle Vein shows higher ppm values in Au, Ag and Cu than other the two veins but the Francine Vein appears to have higher and more Cu contents. For the North Vein, the Ag contents are slighter higher than Francine Vein in two locations above 1000 ppm but still lower than that of Middle Vein.

3.5 Conclusions

Temperatures related to the hydrothermal fluid were obtained from Raman spectroscopic analysis of graphitic carbon demonstrate a promising method to outline areas of high temperature fluid up-flow. The advantages of this method are that 1) sample preparation is low-cost, rapid and can be done in the field; 2) only maximum temperatures are recorded, thus late-stage overprinting by late lower temperature fluids do not affect the results, in contrast to other methods where this is a problem; 3) because sample preparation and Raman analyses are rapid and low cost, a large number of samples can be analyzed and large-scale temperature contour maps can be constructed and applied to exploration in systems such as San Sabastian, and elsewhere.
The Middle Vein has the largest data set and Au, Ag and Cu all show distribution patterns that are spatially related to high temperature areas. These higher temperature zones are interpreted to be areas that experienced fluid up-flow. Similar, but less well-defined patterns are observed at the Francine and North Veins. However, without a direct comparison to other temperatures it is not possible to determine if the temperature calculated is the true temperature or simply a relative temperature for the area. Nevertheless, Cu is commonly deposited at higher temperatures than Au and Ag, and in this study high Cu is distributed around the areas of high temperatures calculated using the graphitic geothermometer.
3.6 References


Roedder, E., 1984, Fluid Inclusions: Mineralogical Society of America, v. 12, 644


Chapter 4

4 Conclusion

4.0 Summary

The purpose of the study was to test whether graphitic carbon would be an effective geothermometer. Graphitic carbon is capable as a geothermometer by the irreversible process of graphitization. This allows the use of FWHM of the D1 peak for low-ordered graphitic carbon, and the area ratio of the D1 to G + D1 + D2 for higher ordered graphitic carbon to measure the maximum temperature to which the rock was subjected. To be an effective geothermometer for exploration, the temperature needs to be accurate, the cost needs to be small, the process cannot be labor intensive, and the process needs to be applicable to various regions. Comparison with previous fluid inclusion studies show that the range of temperature in the Francine and North Veins are consistent with the Raman temperature study calculated from graphitic carbon (White and Hedenquist, 1995; Simmons et al., 2005; Bodnar et al., 2014). The temperatures also agree with what is expected for an epithermal deposit. The error in the temperature is also reasonable, as the error in the Middle Vein was ±6°C, Francine Vein ±12°C and North Vein ±6°C.

Cost of analysis is also minimal as Raman spectroscopy can collect a spectrum directly from the drill core. Simply polishing of the drill core but not creating polished thin sections can be effective for the purpose of a smoother surface for Raman collection while still maintaining the efficiency. With no further preparations, the only labor-intensive and time-consuming process is locating the graphitic carbon in the samples. For most samples
the graphitic carbon is easily located visually but in samples where there is no visual graphitic carbon, exploring the sample in search of graphitic carbon is in the order of minutes rather than hours or days.

Beyssac et al. (2002) and Kouketsu et al. (2014) have already shown that there is a relationship between graphitic carbon and temperature. Chapter 3 shows that it can be applied towards zonation of deposit scale regions for exploration of up-flow zones and hot spots. Contour plots from Chapter 3 show the distribution of temperature throughout the Middle, Francine and North Veins as well as the amount of precious metals, Au, Ag and Cu, that were found in each of the veins. Amounts of Au and Ag can be seen to follow the temperature distribution with high ppm values dropping out after 280°C.

Compared to other geothermometers, graphitic carbon is easily visually identifiable and quick, unlike other geothermometers such as fluid inclusions which are labour intensive and require lengthy analysis. A benefit of graphitic carbon geothermometer is that it can be applied when no mineral assemblages or fluid inclusions are present. Furthermore, graphitic carbon thermometry is not limited to hydrothermal heating events. It can be applied to meteoroids and meteorites.

4.1 Future Work and Shortcomings

Future work should include testing the deposit scale zonation to other precious metal deposits. This study was only applied to three vein systems in Durango, Mexico. Further studies could be applied to different areas of the world. It would also be useful to apply the graphitic carbon geothermometer to applications other than exploration of up-flow zones.
Other possible research that can be accomplished is a laboratory-controlled graphitization process. In theory, this could be accomplished using a hydrothermal diamond anvil cell to house a sample of low-ordered, low-temperature graphitic carbon and heat the sample to various temperatures under pressure. This could also test the kinetics of the graphitization by maintaining high temperatures for long periods of time. The data could be used to derive new formulas for temperature calculation or support the current methods of Beyssac et al. (2002) and Kouketsu et al. (2014).

The problem that may arise from the graphitic carbon geothermometer stem from the fact that it is a relatively new geothermometer and, as such, is still being studied. One example of this is the impact the precursor material has on the graphitization process. At what stage does the hydrogen, oxygen, nitrogen and sulfur get removed from the sample? What are the actual mechanisms that cause the defect peaks? Is there a possibility of more defect peaks existing?
4.2 References


Appendices

Appendix A

Contour plots showing the distribution of Pb, Zn, As, Sb, Hg and Mn in the Middle, Francine, and North Veins with temperature >280°C outlined.

Figure A1: Longitudinal section through the Middle Vein showing contoured lead values. Temperature >280°C is indicated by the dark grey cross-hatched shading.
Figure A2: Longitudinal section through the Francine Vein showing contoured lead values. Temperature >280°C is indicated by the dark grey cross-hatched shading.

Figure A3: Longitudinal section through the North Vein showing contoured lead values. Temperature >280°C is indicated by the dark grey cross-hatched shading.
Figure A4: Longitudinal section through the Middle Vein showing contoured zinc values. Temperature >280°C is indicated by the dark grey cross-hatched shading.

Figure A5: Longitudinal section through the Francine Vein showing contoured zinc values. Temperature >280°C is indicated by the dark grey cross-hatched shading.
Figure A6: Longitudinal section through the North Vein showing contoured zinc values. Temperature >280°C is indicated by the dark grey cross-hatched shading.

Figure A7: Longitudinal section through the Middle Vein showing contoured mercury values. Temperature >280°C is indicated by the dark grey cross-hatched shading.
Figure A8: Longitudinal section through the Francine Vein showing contoured mercury values. Temperature >280°C is indicated by the dark grey cross-hatched shading.

Figure A9: Longitudinal section through the North Vein showing contoured mercury values. Temperature >280°C is indicated by the dark grey cross-hatched shading.
Figure A10: Longitudinal section through the Middle Vein showing contoured Antimony values. Temperature >280°C is indicated by the dark grey cross-hatched shading.

Figure A11: Longitudinal section through the Francine Vein showing contoured Antimony values. Temperature >280°C is indicated by the dark grey cross-hatched shading.
Figure A12: Longitudinal section through the North Vein showing contoured Antimony values. Temperature >280°C is indicated by the dark grey cross-hatched shading.

Figure A13: Longitudinal section through the Middle Vein showing contoured Arsenic values. Temperature >280°C is indicated by the dark grey cross-hatched shading.
Figure A14: Longitudinal section through the Francine Vein showing contoured Arsenic values. Temperature >280°C is indicated by the dark grey cross-hatched shading.
Figure A15: Longitudinal section through the North Vein showing contoured Arsenic values. Temperature >280°C is indicated by the dark grey cross-hatched shading.

Appendix B

Table B4.1: Percentage of Au, Ag, and Cu for each vein within 200 m of a hot spot at varying concentration levels.

<table>
<thead>
<tr>
<th></th>
<th>High</th>
<th>Medium</th>
<th>Low</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
</tr>
<tr>
<td>Middle</td>
<td>78</td>
<td>87</td>
<td>84</td>
</tr>
<tr>
<td>Francine</td>
<td>75</td>
<td>63</td>
<td>83</td>
</tr>
<tr>
<td>North</td>
<td>0*</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>Ag</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Middle</td>
<td>93</td>
<td>90</td>
<td>84</td>
</tr>
<tr>
<td>Francine</td>
<td>67**</td>
<td>77</td>
<td>83</td>
</tr>
<tr>
<td>North</td>
<td>88</td>
<td>61</td>
<td>55</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Middle</td>
<td>100</td>
<td>97</td>
<td>84</td>
</tr>
<tr>
<td>Francine</td>
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<td>93</td>
<td>83</td>
</tr>
<tr>
<td>North</td>
<td>N/A***</td>
<td>N/A***</td>
<td>55</td>
</tr>
</tbody>
</table>

* only 2 samples >3 ppm  
** only 3 samples >500 ppm  
*** no samples >1000 ppm
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