LATE, LOW-TEMPERATURE IRON SULFIDE-DOMINATED MULTI-COMPONENT FLUIDS IN GLASSY SILICIC LAVA AND QUARTZ MONZONITE PORPHYRY, JULCANI, PERÚ

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INTRODUCTION

This presentation focuses on the most common sulfide minerals in ore deposits – the iron sulfides. At the last Congreso, the first author discussed, among other things, the textures and inferred origin of veins consisting largely of pyrite and enargite in districts including Tantahuatay, La Zanja, Yanacocha and Minasnioc (Noble et al., 2006). The conclusion was that the veins formed from a very concentrated colloidal fluid consisting mainly of iron, sulfur, arsenic and water that unmixed and crystallized, with the last stages being dominated by vapor transport and deposition yielding exquisitely formed euhedra of pyrite, enargite, covellite, chalcopyrite, diaspore and pyrophyllite within cavities.

In this paper we focus on the nature and origin of pyrite and marcasite that occur as late, low-temperature *magmatic* minerals in glassy and devitrified silicic lavas of the Julcani district. In addition, we describe and discuss similarities to the pyrite in a recently-recognized high-level "failed" porphyry intrusion – the Tentadora stock – situated beneath the central part of the district. We also present textural evidence that the typically large, well-formed crystals of pyrite that are found in certain veins at Julcani as well as many other districts in Perú and elsewhere formed by the recrystallization of amorphous pyrite and/or pyrite gels deposited from strongly supersaturated hydrothermal solutions. Finally, we briefly discuss certain geochemical data, particularly high Co, Ni and Cr contents, that indicate the addition of unevolved mafic magma to bodies of silicic magma and suggest that direct high-level "underplating" bodies of mafic magma may have been the source of Fe, S, Au, Cu and other elements in certain high-level silicic intrusives.

The reconnaissance study is based on petrographic observation of rock specimens using standard hand-lens, transmitted- and reflected-light, and electron microscopic methods and multi-element geochemical analyses of the type routinely available from commercial laboratories. Textural relations are particularly important for understanding the nature and sequence of events.

THE JULCANI DISTRICT

The Julcani district, central Perú, is one of the more important producers of silver in the World, with production from 1953 through 2007 of 85,558,272 ounces Ag. The silver occurs mainly as tetrahedrite in a multitude of mineralogically complex veins hosted by dacite domes, surge deposits and other volcanic rocks of a large magmatic-hydrothermal system hosted by folded Paleozoic and Mesozoic strata (e.g., Petersen et al., 1977; Noble and Silberman, 1984). The center was active between 11 and ≤9.9 Ma. Drexler & Munoz (1986), Dean et al (1994) and Noble et al. (2004), among others, have presented and discussed various aspects of the mineralogy and elemental and isotopic geochemistry.

The discovery of hypogene quartz-alunite-pyrite (advanced argillic) alteration in the Herminia zone (Noble, 1978) led various writers to include the district in the "acid-sulfate" or "high-sulfidation" class of mineral deposits. In fact, the district is much more complicated, possessing, among other things, large areas of strong low-temperature potassium metasomatism (mainly adularia) (Scherkenbach and Noble, 1984); tourmaline-cemented breccia and tuffisite dikes (Shelnutt and Noble, 1985; zones of low-sulfidation mineralization dominated by ruby silver minerals and having low Ag/Au ratios and strong K enrichment; and a recently recognized very high-level porphyry system "frozen" in an early stage of evolution. Indeed, the principal economic silver mineralization is not of "high-

sulfidation" type, and occurs in a distinct paragenetic stage later than the quartz-alunite-pyrite alteration (Noble and Silberman, 1984).

MAGMATIC MARCASITE AND PYRITE IN GLASSY SILICIC LAVA

The clearest and most unequivocal evidence for the formation magmatic iron sulfide phases at low temperatures is provided by the presence of about one percent of marcasite in glassy, completely unaltered rhyodacite of a dome in the northeastern part of the Julcani volcanic field and a similar amount of pyrite in and in fragments of glassy lava in surge deposits beyond the Julcani dome field (Fig. 1). The dome and surge deposits are chemically distinct, and reflect two different magmas.
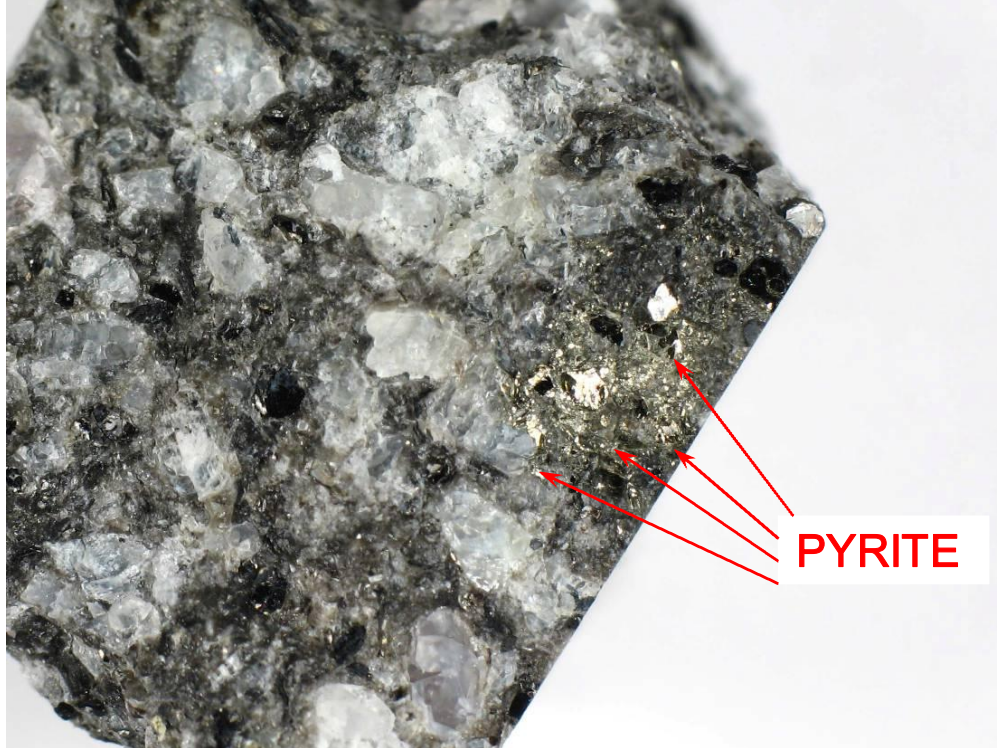

Fig. 1. Fresh glassy rhyodacite (specimen JUL-07-3SV) from block in surge deposits between Herminia and Cochacancha on the northeastern edge of the Julcani district. The very irregular and penetrating mass of pyrite several mm in diameter is intimately intergrown with fresh silicic glass and with phenocrysts of unaltered plagioclase, quartz and biotite.

The sulfide-bearing rhyodacite lavas are completely fresh. The groundmass (matrix) is glassy and shows no petrographic or chemical evidence of interaction with hydrothermal fluids (e.g., partial conversion to opal). Plagioclase and biotite phenocrysts show no alteration, and very small-scale compositional zoning is completely preserved in the plagioclase. The rocks are completely nonmagnetic, and phenocrysts of Fe-Ti oxides have not been observed. The iron sulfide grains are contained within the groundmass or within ovoid bodies (Fig. 2) that are described below. The grains of pyrite and marcasite show no evidence whatsoever of primary oxidation, although in many places the original iron sulfides have been destroyed to greater or lesser degrees by superficial oxidation (weathering).
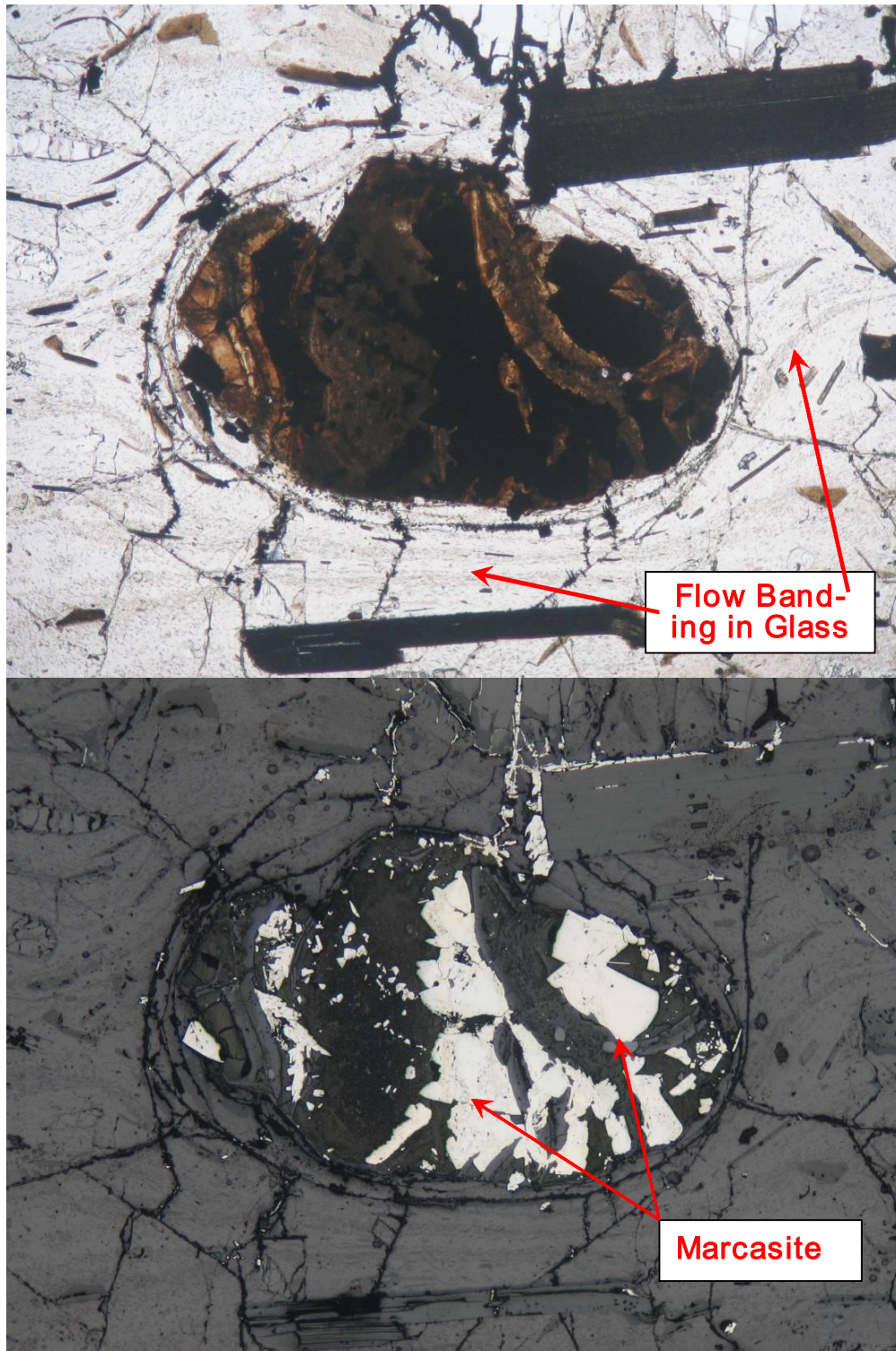
Figure 2. Ovoid body about 2 mm in maximum diameter containing abundant marcasite surrounded by a fine-grained aggregate composed mainly of Si, Ti, Al, Zr, and P sitting in a matrix of unaltered volcanic glass (spec. PDB-HM-CCH). Top, transmitted light, uncrossed polars; bottom, reflected light. Note that flow banding in the glass passes around the ovoid and that iron sulfide has moved out into fractures. Biotite phenocrysts are above and below ovoid.

A specimen, PBD-HM-CCH provides important textural evidence about the nature and evolution of the sulfide-bearing phase and on the ultimate crystallization of marcasite and pyrite. Specimen PBD-HM-CCH contains ovoid bodies that contain much higher concentrations of marcasite than the rest of the rock (Fig. 2). These bodies, which reach 2 or more mm in average diameter, are readily visible, especially in transmitted light. Microscopic-scale flow banding, defined by very small microlites, passes around the bodies, showing that they existed when the rock was still fluid or ductile. Moderately porous subhedral marcasite grains, are set in a generally very fine-grained material that in high-intensity transmitted light gives a cloudy white appearance suggestive of the presence of leucoxene (fine-grained TiO_2). Under the electron microprobe this matrix material is seen to contain abundant titanum associated with oxygen. In addition, numerous spot analyses demonstrate grains and zones containing abundant P and Ca (presumably apatite), zircon as well as significant contents of Si and Al. The form and chemical composition of the ovoid bodies show the existence of immiscible fluids or colloidal suspensions composed dominantly of iron sulfide accompanied by very significant amounts of Ti, Si and Al, and lesser, but important, amounts of P, Ca, Zr and presumably elements such as Hf and the heavy rare-earth elements. This composition is corroborated by the mineralogy of pyrite-rich masses preserved locally in the Tentadora stock, discussed below.

Significant amounts of pyrite and marcasite also fills fractures in the glass that cut or intersect the ovoid bodies and, in places, fractures in unaltered phenocrysts (Figs. 2 & 3). The marcasite increases in abundance towards the ovoid bodies, strongly suggesting that the ovoid bodies were the source. The existence of the marcasite-filled fractures demonstrates that the marcasite was deposited at a temperature below the glass transition temperature (around 300 degrees C), at which silicic melts convert to glass with elastic properties. Alternatively, the fractures may have occurred during surges in magma flow when the melt behaved as a viscoelastic substance. In either case, the fractures were produced by late movement of the hot magma/lava, and cannot have been produced by secondary hydration by groundwater at surface temperatures. This shows that the sulfide-rich fluid/suspension existed as a discrete phase at temperatures many hundreds of degrees below the equilibrium
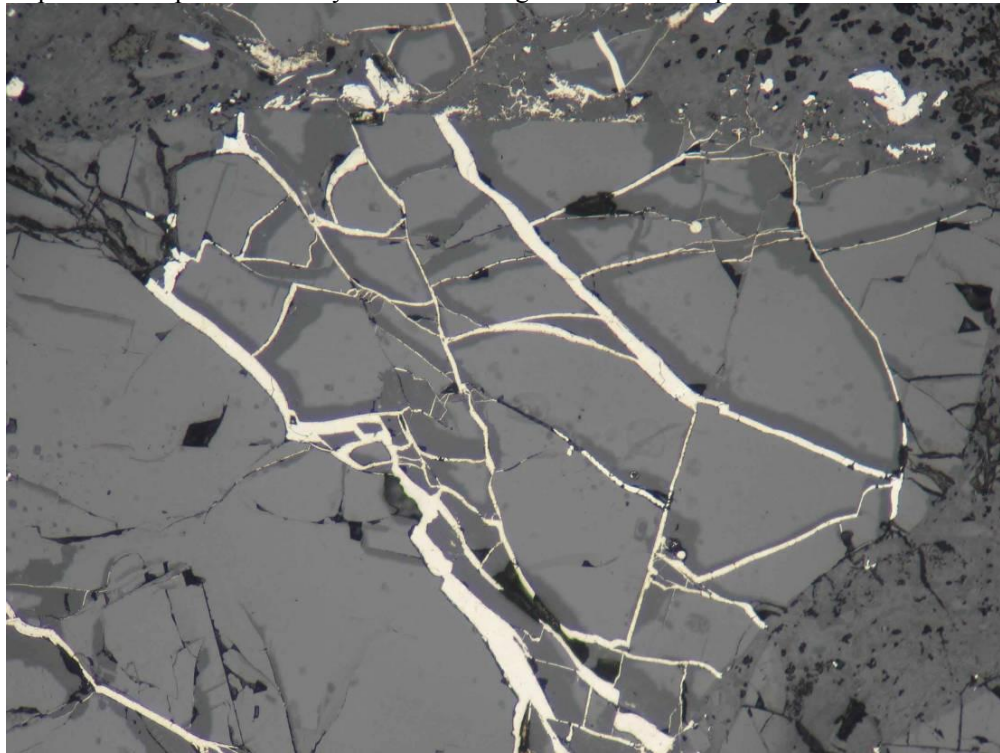

Fig. 3. Fractured but completely unaltered plagioclase phenocryst in specimen JUL-07-3SV. Brittle fractures, many inclined to the upper right, are filled with pyrite (bright). Matrix surrounding fractured phenocryst, which also contains pyrite, consists of fresh volcanic glass.

thermodynamically stable solidus temperature of silicic melt. Platy inclusions of pyrite and marcasite also are found along cleavage planes.

Larocque et al. (2000) describe somewhat similar, albeit much smaller, ovoid bodies in lavas from several localities. Although these ovoids are partially to completely oxidized, they may have had an origin similar to those found at Julcani.

It should be emphasized that these ovoid, sulfide-rich, originally fluid bodies at Julcani, as well as pyrite and marcasite not associated directly with such bodies, differ markedly in composition and genesis from the very small amounts of magmatic sulfide liquid of approximate pyrrhotite composition, found as inclusions in phenocrysts and locally suspended in glass (e.g., Drexler and Munoz, 1986; Keith et al., 1993; 1997; Larocque et al., 2000). The sulfide inclusions described by these authors were mostly or entirely formed and trapped at magmatic or near-magmatic temperatures on the order of 700± to 900+ degrees C.

Magmatic pyrite in blocks from the tuff ring has similar textural characteristics, with the exception that ovoid bodies are not visible. Pyrite fills fractures and also occurs in discrete concentrations, possibly the sites of now-unrecognizable sulfide-rich ovoid bodies.

PYRITE IN THE TENTADORA DIKE

Magmatic pyrite is also present in fresh specimens of the Tentadora dike, which extends to the northeast from the central part of the district (Petersen et al., 1977). Although crosscutting relations and isotopic dating show that the dike predates the tetrahedrite-dominated silver vein mineralization, its northeastern part is not visibly altered in hand specimen or thin section. Unaltered phenocrysts of plagioclase and biotite are set in a very fine-grained devitrified matrix in which the groundmass converted to a fine-grained aggregate of mainly feldspar and silica minerals at elevated, but submagmatic temperatures. Disseminated grains of pyrite compose about one percent of each of three studied specimens of the rock. As with the glassy rocks discussed above, the pyrite-bearing dikes are not magnetic. No ovoidal bodies have been observed, with the exception of a poorly defined body containing a few percent chalcopyrite. The dike also has very high As, Sb, Ni and Cr contents (Table 1)

PYRITE IN DEVITRIFIED DOME ROCKS

Pyrite is also found in two specimens of dense primarily devitrified rhyodacite (AA-W & AA-R) in the southwestern part of the district that lack evidence of hydrothermal alteration. Although not as unequivocal as the rocks from the northeastern part of the district described above, these non-magnetic sulfide-bearing lavas provide additional evidence for the presence of magmatic sulfide in rocks of the Julcani volcanic center. There is a suggestion that another devitrified, but vesicular specimen, J-07-1B, originally contained magmatic pyrite. Biotite phenocrysts contain plates of hematite geometrically very similar to the pyrite inclusions in biotite from glassy specimen JUL-07-3SV. Moreover, the otherwise fresh and unoxidized dacite contains porous aggregates containing hematite.

THE BULOLO-ESTELLA DIKE

The Bulolo-Estella dike comprises a group of lithologically distinctive dikes that extend across the Julcani district for seven kilometers in a WNW-ESE direction. The length of the dike system provides proof that the Julcani district is underlain by a large primary body of silicic magma. The dikes of the Bulolo-Estella system are characterized by relatively sparce, but large phenocrysts, the blocky form of the biotite phenocrysts, and the spectacularly embayed form of the quartz phenocrysts.

Fresh glassy margins of the dike contain essentially no sulfides, with the exception of small inclusions of iron sulfide of near pyrrhotite composition included in magnetite phenocrysts. One group of dikes in the northwesternmost end of the dike system contains phenocrysts of anhydrite, barite and celestite in a dense glassy matrix along with plagioclase, quartz, biotite, hornblende, magnetite and ilmenite-hematite (Drexler and Munoz, 1986; Noble et al., 2004). These and other lavas from the district have very high values of fO_2 calculated from Fe-Ti oxide compositions. The glassy rocks from the Bulolo dike also have high As contents, second only to those of the Tentadora dike (Table 1). Al-

though interesting, the magmatic sulfates are situated at a distance from known mineralization and, particularly, from the zone of quartz-alunite-pyrite alteration in the eastern part of the district.

GEOCHEMISTRY, NATURE AND SOURCE OF SULFIDE-BEARING MAGMAS

Variations in the contents of relatively immobile major and minor elements (some more useful of which are shown in Table 1) indicate that the various iron-sulfide bearing rocks were derived from different, compositionally distinct magma bodies. Rather, they were derived from a number of distinct bodies that evolved from one or more larger, more deep-seated bodies of magma.

Table 1. Selected New Chemical Analyses of Rocks from the Julcani District

	S	Fe$_2$O$_3$	MgO	Au (ppb)	Ni	Co	Cr	Cu (ppm)	As	Sb	Cs
	(wt. percent)			(ppb)				(ppm)			
Pyrite/Marcasite-Bearing Glassy Lavas											
PDB-HR-CCH	0.45	2.97	1.13	<2	10	6	23	15	30	13.0	28.0
JUL-07-3SV	0.52	3.41	1.29	<2	20	13	30	62	37	0.9	8.1
Iron Sulfide-Free Glassy Lava											
SLB-2	0.01	4.26	1.66	7	16	8	30	21	23	≤0.5	7.3
Tentadora Dike											
SLB-54	0.31	4.39	2.41	<2	20	12	40	25	150	10.1	7.2
SLB-55	0.58	4.44	2.19	6	23	12	29	34	160	11.7	8.4
TENT-07	0.56	4.29	1.76	<2	17	10	36	34	120	46.6	6.8
Devitrified Domes											
AAW	0.84	3.92	0.73	<2	30	13	71	35	66	≤0.8	6.0
AAR	0.17	3.42	0.73	<2	22	13	30	29	28	≤0.5	6.8
J-07-1B	0.05	4.78	1.76	<2	17	11	47	45	10	1.0	3.5
Bulolo-Estella Dike System											
BD6-2-VIT	0.12	2.97	1.25	<2	16	8	24	24	64	0.8	26.0
J-1-V-06	0.02	2.91	1.27	<2	14	8	20	26	50	2.7	13.7
Tentadora Stock (18 specimens)											
Average	1.59	4.02	1.79	91	18	9	32	156	64	11.7	7.3
Median	1.54	3.81	1.67	46	17	10	32	90	55	4.6	7

The high concentrations of Co (6-13 ppm), Ni (10-30 ppm) and Cr (20-71 ppm) strongly argue that one stage in the evolution of the magmas involved addition of unevolved mafic magma to a body or bodies of silicic magma (Table 1). Similar elevated concentrations of Co and Cr are apparent in earlier INAA analyses (Noble and McKee, 1999). Although some of the Co and Ni probably were introduced along with the iron sulfide (see section on Tentadora stock, below), most was almost certainly present in the magmas before the addition of iron sulfide. The high concentrations of Co, Ni and Cr in silicic magmas strongly suggests the addition (mixing) of minor, but significant amounts of mafic magma, as has been suggested, for example, by Maughan et al. (2002) for the Bingham district, Utah, U.S.A. The not uncommon presence of olivine-rich basalt in the Cenozoic volcanic sequence of Perú, in certain cases erupted pyroclastically (Noble et al., 1999; D.C. Noble, unpub. data) suggests that such addition of mafic magma (which also can confidently be inferred to have supplied S, Au, Cu, and other elements) took place within the middle or upper part of the thick Andean crust, rather than at its base as suggested by certain authors (e.g., Richards, 2003).

The volcanic rocks of the Julcani district are remarkable for their high contents of As and, to a lesser degree, Sb (Noble et al., 2004). The As content – about 150 ppm – of the Tentadora dike is about twice the maximum amount previously found at Julcani and the Sb content of about 11 ppm (and apparently considerably higher locally) is about five times that of the more Sb-rich lavas previously recognized at Julcani. The high contents of As and Sb in both dense glassy (Bulolo-Estella) and dense devitrified (Tentadora) dike rocks suggest that the lower contents of these elements in glassy lavas and other devitrified rocks may, at least in part, reflect partial loss of these elements during cooling and outgassing. The latter is particularly suspect in the case of vesiculated devitrified specimen J-07-1B. If such loss occurs, the original arsenic contents of Julcani magmas may have been even higher than suggested by the data presented by Noble et al. (2004). The unusually high Sb content of about 47

ppm (confirmed by analysis by both INAA and fusion-mass spectrometry analytical methods), appears to be real and may reflect the fact that the specimen is from what field relations suggest may be a second magma pulse of the Tentadora dike.

LOSS OF SULFUR AND PRESERVATION OF MAGMATIC IRON SULFIDES

Additional evidence for the sulfur-rich nature of the Julcani magmas is provided by plagioclase phenocrysts in glassy dacite from a group of unaltered domes in the southern part of the Julcani district that contain remarkable two-phase glass inclusions (Noble and Scofield, 1977). The inclusions consist mostly of slightly green-tinted rhyolitic glass containing a sphere of dark, much high refractive index glass. Electron microprobe analysis of the dark glass showed high concentrations of iron and sulfur (N. Scofield and D.C. Noble, unpub. data). The inclusions suggest that at magmatic temperatures the melt contained quite significant amounts of iron sulfide, and that the sulfur was lost when the magma was erupted. If such iron sulfide-rich globules that separated at sufficiently high temperatures, they may have aggregated in the melt phase (similar to the way that fine drops of molten lead come together to reduce the free energy of the system by minimizing the total surface area between the two immiscible phases to form the gold-containing lead button during the fire assay procedure) to form ovoidal bodies such as seen in glassy specimen PBD-HM-CCH.

Moreover, sulfides formed at liquidus or lower temperatures are highly susceptible to resorption and/or oxidation on cooling (e.g., Keith et al., 1991; Stavast et al., 2006). How, then, have the sulfides discussed above, and particularly those in partially vesiculated glassy rocks, been preserved? The answer may be as follows: Prior to, and perhaps after, eruption, magmatic water, present in the silicic melt of the matrix, reacted with the iron sulfide. One very simplified idealized reaction is as follows:

$$FeS_2 + 5H_2O = Fe_2O_3 + SO_2{\uparrow} + 3H_2S{\uparrow} + 2H_2{\uparrow}$$
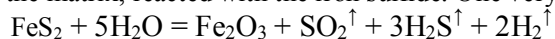
What may happen is that water dissolved in the silicic melt disassociates, with the resultant hydrogen and oxygen combining with the sulfur to form the gases H_2S, SO_2 and H_2, which are volatilized – lost – from the magma. Iron presumably is incorporated in the silicic melt or conceivably lost as volatile compound(s). This process continues until either the sulfide or the water is completely or largely removed. In most cases, presumably, the contents of sulfide are relatively low, and sulfur will be removed before all the water has dissociated and combined to form H_2S and SO_2. If, however, the sulfur content is high, water may depleted before sulfur is completely removed; this may have happened in the magmas that formed the pyrite/marcasite-bearing lavas at Julcani. Assuming the above idealized equation, and a not unreasonable original magmatic water content of 4 weight percent, this model would suggest the breakdown of about 1.5 wt. percent FeS_2 and an original magmatic FeS_2 content of about 2.5 wt. percent. Irregular patches of porous iron oxide/hydroxide present in many otherwise fresh lavas of the district probably reflect iron sulfide oxidized during groundmass devitrification.

THE TENTADORA STOCK: NATURE AND ORIGIN OF PYRITE

The Tentadora stock was intersected beneath the central part of the Julcani district by diamond drill hole HDD E-Sup-02-01 (Here abbreviated as DDH-02) drilled in 2001. The stock is present from a depth of about 300 meters to the end of the hole at 923.1 meters. The stock predates the Bulolo dike and locally gold-bearing pyrite veins, as well as the economic silver vein mineralization. It has been affected by later hydrothermal alteration, typically characterized by the development of kaolinite or alunite, in the upper part of the core. However, below about 650 meters, the rock is fresh, with only minor zones of later alteration.

The stock is perhaps best characterized as quartz monzonite porphyry. Large phenocrysts of plagioclase and primarily embayed quartz accompanied by biotite are common. Original silica content prior to addition of pyrite was about 69 wt. percent. Small variations in some immobile elements, for example, Cr (25-40, median 32.5 ppm) and Ba (883-1500, median 1165 ppm) suggest little original compositional variation. Na shows only moderate variation (2.12-2.91, median 2.41 wt. %); K appears to have been more mobile (2.03-4.52, median 3.14 wt. %). Elements of economic interest – Cu (6-419, median 90 ppm), Au (16-314, median 46 ppb), Ag (<0.3-1.8, median 0.5 ppm), Pb (19-398, median 64 ppm) and Zn (57-1070, median 80 ppm) – show wide variations and little correlation with pyrite content and, in general, with each other. Other selected elements are summarized in Table 1. Inter-element

relations constitute an entire story in themselves. Although Cu and other metals show a strong affinity for sulfide relative to silicate and oxide phases (e.g., Stimac & Hickmott, 1996), at present the chemical and other data suggest that Cu, Au and other metals at least in part were introduced after the pyrite.

The pyrite occurs as disseminated grains, many subhedral to anhedral and somewhat porous. In some specimens pyrite occurs along planar hairline fractures 0.1 to perhaps 0.5 mm in width that are healed by quartzo-feldspathic material (Fig. 7). The pyrite typically occurs as very thin and highly irregular plates that commonly are not connected with one another. Their aspect is similar to (although on a larger scale) to secondary fluid inclusions that have only begun to reorganize into distinct equant inclusions forming planes within the host quartz crystals. Similar fractures filled or partially filled with pyrite are present in quartz phenocrysts (Fig. 8).

There is a strong positive correlation between total iron and sulfur for the specimens of unaltered porphyry below about 650 meters depth (Fig. 4). This argues that Fe and S were introduced together. Introduction of only sulfur – "sulfidation" of iron present in the stock – would yield an approximately horizontal trend. The elements Co, Ni, Ti and Zr all show positive correlations with Fe and S, and also with the composite parameter Fe+S-1.6 (wt. %), which approximates the amount of inferred added pyrite. These correlations suggest that these elements were added along with Fe and S in concentrations considerably higher than their original contents in the porphyry; addition of only Fe and S would have caused a decrease in concentration by dilution, as is seen for a number of other elements such as Lu, Ga, Sc, Cr and Ba.

The conclusions from the chemical data are supported by the nature of pyrite in a specimen of porphyry from a depth of 894.3 m. This specimen contains large, highly irregular and porous grains of pyrite (Fig. 5). Petrographic study and scanning electron microscope images (e.g., Fig. 6) show that the pyrite contains contains abundant inclusions of apatite, rutile, zircon, iron oxide, Fe-Ti oxide, Mg-rich ankerite, quartz and alkali feldspar. The abundance of Ti-, Zr- and P-bearing phases suggests that the pyrite was introduced as a polycomponent fluid qualitatively similar in composition to the iron sulfide-rich ovoid masses in the pyrite/marcasite bearing lavas before they unmixed to form marcasite, TiO_2 with lesser amounts of zircon and apatite.

The pyrite-rich fluid appears to have wetted quartz and plagioclase phenocrysts. This is indicated by the common presence of pyrite within growth reentrants in quartz phenocrysts (Fig. 8) and preferentially along the margins of both quartz and plagioclase phenocrysts. The wetting nature of the mobile iron sulfide-dominated fluid separating from the ovoids is also suggested by the fact that pyrite has readily entered fractures in plagioclase phenocrysts in the glassy lavas (Fig. 3).

Fe vs S, Selected Core, DDH-02, Tentadora

Legend:
- ■ Analyses of Selected Core Specimens - DDH-02, Tentadora
- - - Linear (Analyses of Selected Core Specimens - DDH-02, Tentadora)

Y-axis: Fe (wt. %)
X-axis: S (wt. %)

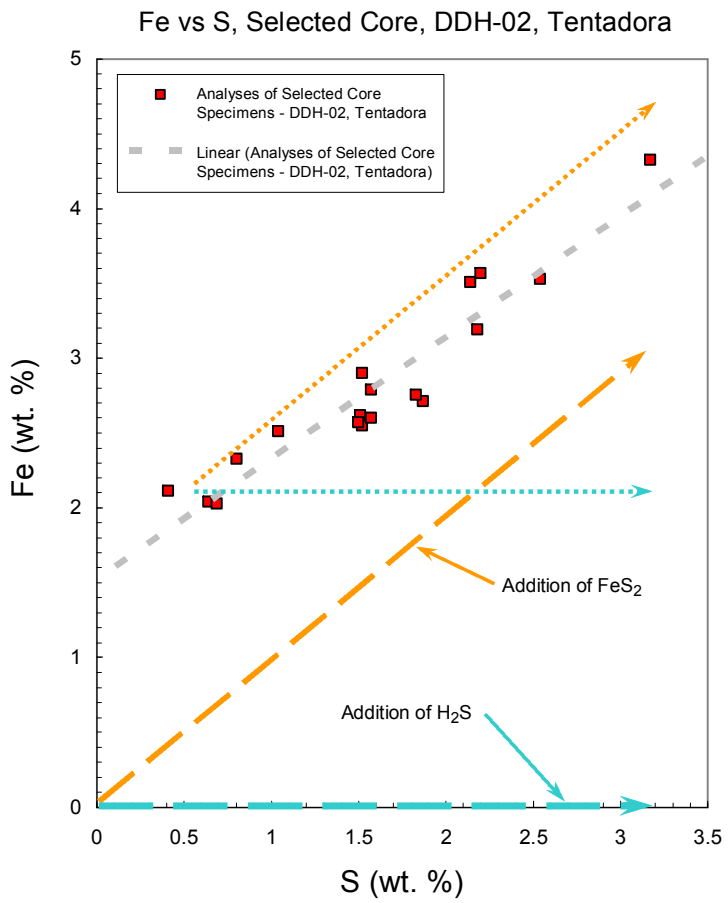Addition of FeS_2

Addition of H_2S

Fig. 4. Plot of Fe versus S for unaltered specimens from the Tentadora stock. See text for discussion. The strong positive correlation between Fe and S strongly suggests that the two elements were added together in approximately the proportions that are found in pyrite.

Fig. 5 (below). Highly irregular and porous mass of pyrite in specimen DDH-2-894.3 inferred to have formed from crystallization of colloidal? globule containing major amounts of iron sulfide and lesser amounts of Al, Si, Ti, P, Zr, CO_2 and Mg. Arrows indicate on of many inclusions composed mainly of apatite. Pyrite mass is composed of groundmass of porphyritic stock composed mainly of fine-grained feldspar and quartz. Width of photomicrograph is about 5 mm. Reflected light.

Apatite
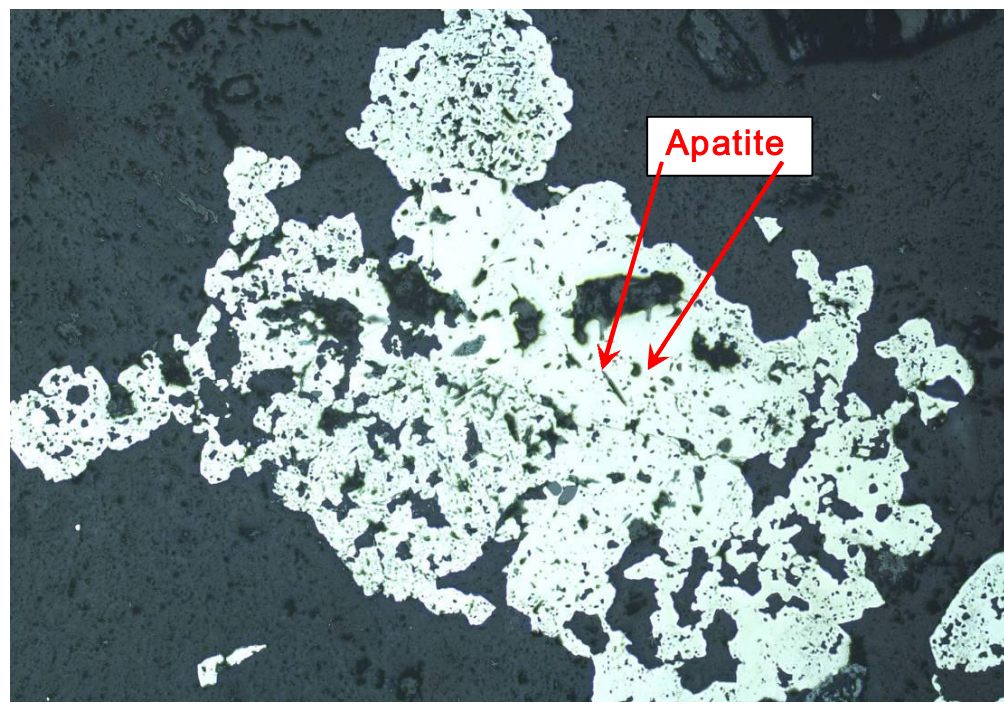
GOLD CONTENTS OF PYRITE/MARCASITE-BEARING ROCKS

The pyrite/marcasite-bearing glassy lavas and devitrified dike and dome rocks contain very low gold contents, with most being less than 2 ppb. This contrasts strongly with the Tentadora porphyry stock, which has a median gold content of about 46 ppb (Table 1). The strong affinity of gold for the vapor phase during the direct, open-system outgassing of magmas (e.g., Connors et al., 1993; Giggenbach, 1993) suggests that at least some of the magmas originally contained appreciably higher contents of gold than do the rocks analyzed. Porphyry bodies, on the other hand, are generally considered to have behaved as closed systems, crystallizing from the outside inward. Fluids equilibrate with the minerals of the stock on cooling, and metals such as Au and Cu tend to be contained rather than lost.
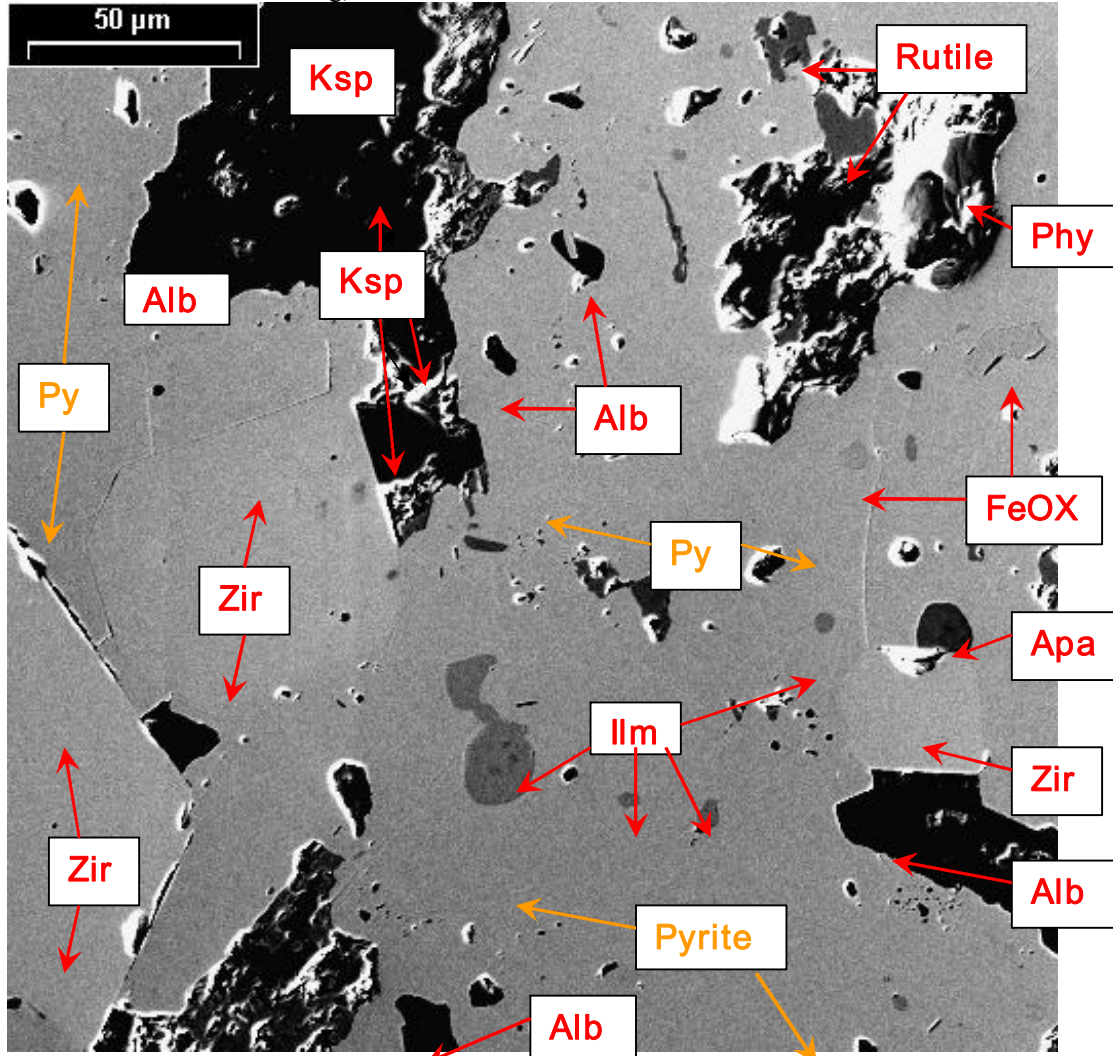

Fig. 6. SEM image of a portion of an irregular mass of pyrite in specimen DDH-2-894.3 containing inclusions of a large number of different minerals. Py = pyrite, Zir = zircon, Ilm = ilmenite, FeOX = iron oxide, Apa = apatite, Alb = albite, Ksp = potassium feldspar, Phy = Si-Al-Mg-Fe bearing phyllosilicate? All minerals are interpreted to have existed in a single colloidal? fluid before unmixing and crystallizing. Note that all the minerals are not necessarily in thermodynamic equilibrium with one another. The existence of nearly pure albite and K-feldspar indicate a relatively low temperature of separation and crystallization.
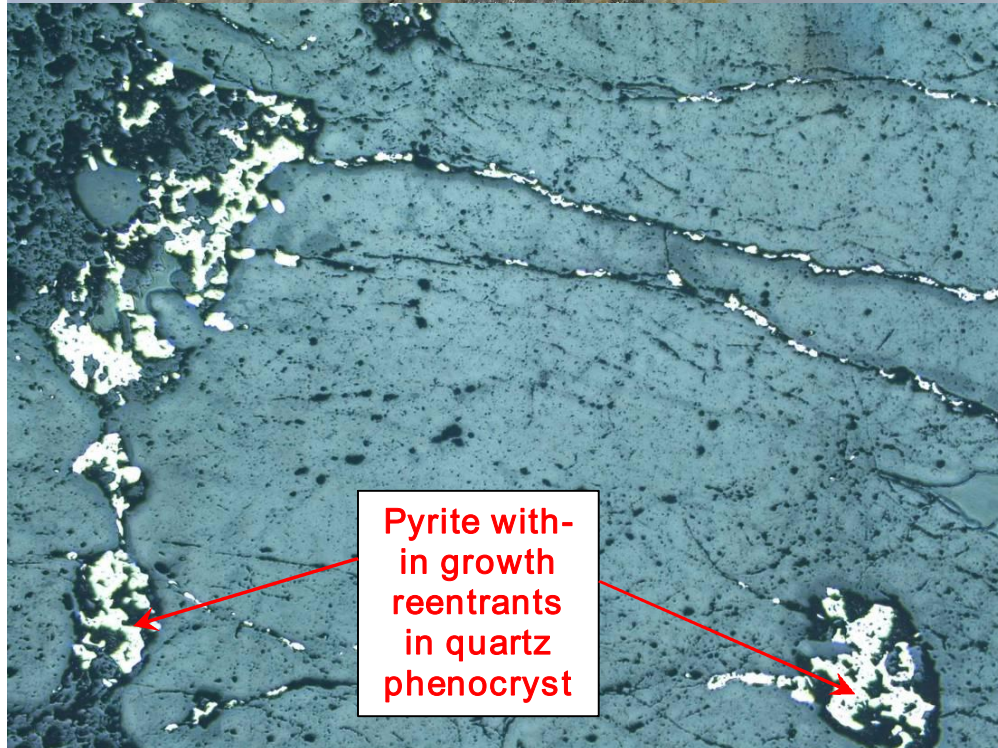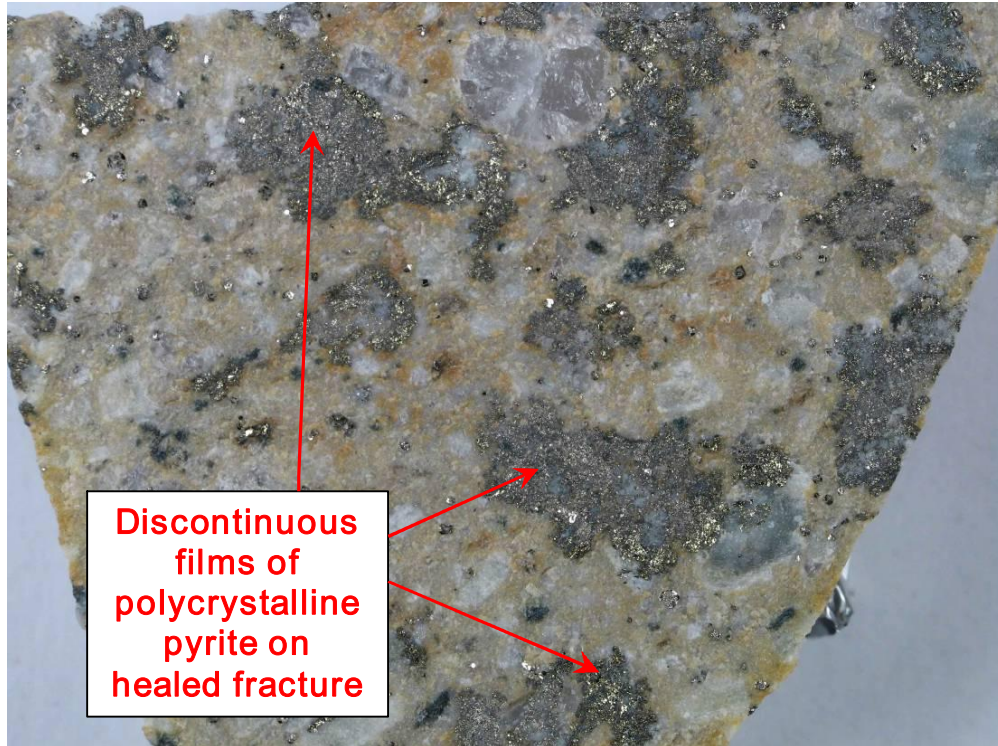
Fig. 7 (top). Surface of healed fracture in Tentadora stock (DDH-02 862.8 m) filled with highly irregular discontinuous films of pyrite (dark). Width of photograph is 3.1 cm.
Fig. 8 (bottom). Pyrite (bright) partially filling healed fractures (subhorizontal) in deeply embayed quartz phenocryst (DDH-02 674 m). Small dark spots are vapor inclusions. Note the high concentration of pyrite in reentrants. Reflected light.

FORMATION OF EUHEDRAL VEIN PYRITE FROM COLLOIDAL PRECIPITATES

Veins composed mainly of large, euhedral pyrite crystals filling open spaces, or containing paragenetic stages with such characteristics, are not uncommon in Perú. Particularly large and attractive specimens of such material are in demand by mineral collectors. An early paragenesis characterized by well-formed pyrite euhedra is present in the central part of the Julcani district. The veins cut the Tentadora stock and predate the economically important tetrahedrite mineralization.

As can be seen in polished section and on fine-ground surfaces, such pyrite is slightly to highly porous. In some cases banding with a form typical of colloidal deposition is present, with the banded material typically being more highly porous than the remainder of the specimen (Fig. 9). Such crystals are interpreted as having been formed by the deposition of colloidal pyrite from hydrothermal solutions highly supersaturated in iron sulfide. As the colloidal precipitate crystallizes, water is lost and volume decreases, producing the cavities. The very attractive smooth surfaces of the pyrite crystals are the result of the dissolution of fine-grained, poorly crystallized, or amorphous pyrite by hydrothermal solutions or vapors and its immediate precipitation as large crystal arrays of lower free energy well-crystallized pyrite. The importance of such late crystallization is shown by the presence of perfect euhedra of pyrite partially filling the small cavities in the porous banded colliform pyrite. "Porous" pyrite and marcasite are not uncommon in mineral deposits, and it is possible that in other deposits of various types pyrite existed in an early colloidal/amorphous state.
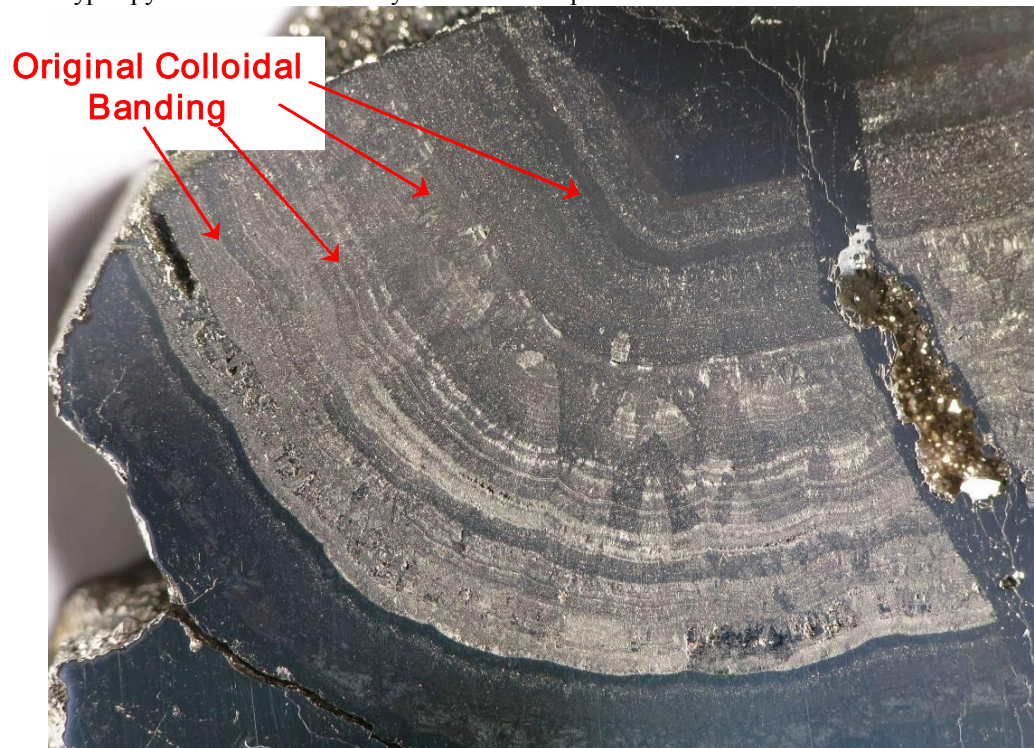

Fig. 9. Banded and porous originally colloidal pyrite from massive pyrite vein in the Tentadora zone cut by DDH-02 at a depth of 665.5 m. Pyrite within bands shows a radial or fan geometry, similar to that observed of chalcedony formed by the crystallization of banded opaline silica. Small cavities are generally elongated parallel to radial banding and contain perfectly-formed very small vapor-deposited euhedra of pyrite. Note fracture on right side of photograph filled with later-deposited colloidal pyrite, showing that earlier-deposited amorphous/gelatinous pyrite was able to fracture viscoelastically before deposition of later mobile colloidal pyrite. Width of photograph is about 1.5 cm.

SUMMARY, DISCUSSION AND CONCLUSIONS

Petrographic and chemical data on volcanic rocks of the Julcani district demonstrate that fresh, glassy lava can contain significant amounts of magmatic iron sulfides. The iron sulfides existed as part

of a distinct polycomponent fluid phase at temperatures of only several hundred degrees centigrade, after the matrix of the lava had transitioned from supercooled melt to glass or when the melt behaved as a viscoelastic material that fractured when forcefully stressed. This shown by the presence of ovoids several millimeters in diameter consisting mostly of iron sulfide, with significant amounts of Ti, Si, Al, Zr, P, H_2O and probably CO_2. Flow banding in the glassy matrix passes around the ovoids, showing that they formed before the melt solidified. Pyrite in unaltered primarily devitrified dikes is also interpreted as being of primary magmatic origin. The present pyrite/marcasite contents of the lavas provide a minimum estimate of the original iron sulfide in the magmas: that which remained after magmatic water was depleted by conversion to and loss as volatile SO_2 and H_2S.

The Julcani occurrences provide unequivocal examples of magmatic pyrite and marcasite that crystallized in glassy volcanic rocks at low temperatures. Although Castor et al. (1994) conclude that pyrite in tuff in southern Nevada is magmatic, Weiss et al. (1995) present evidence for a hydrothermal origin. Marcasite that formed on granophyric crystallization of densely welded highly peraluminous tuff, however, has been reported from the Macusani volcanic field, southeastern Perú (Noble et al., 2004). Spongy, elongate crystals of marcasite rimmed by arsenopyrite are associated with phenocrysts of tourmaline, andalusite, muscovite and fluorite as well as sanidine and quartz.

Thoroughly crystallized dikes containing primary magmatic sulfides have been described from other areas. Brake et al. (1998) discuss sulfide-bearing dikes at several localities that they interpreted from field and laboratory data to have formed from sulfide- and carbonate-rich magmas. Even earlier, Wilson (1978) provided strong evidence that an unusual sulfide-bearing dike in the well-known Bingham district, Utah, formed by crystallization of magma enriched in S, Cu and other elements. As described by Brake et al., in the 5 Ma Santa Rosa-Matalla system near Cobriza, Perú, sulfide-bearing dikes radiate from a subsequently emplaced(?) skarn-forming porphyry stock. These dikes contain lenses of pyrrhotite, minor chalcopyrite, ankeritic carbonate and quartz in a rock composed of K-feldspar, albite, quartz, Mg chlorite, muscovite, carbonate, rutile and sulfides. Coexisting vapor-dominated and high-salinity primary fluid inclusions are present in quartz; halite dissolves between 350° and 450° C. The carbonate wall rock is impermeable and shows no evidence of alteration. Chemical analysis of the dikes shows no evidence for gain or loss of major elements. Similar features are seen in Eocene dikes at Lantern and Genesis in the Carlin trend, Nevada, that locally cut virtually unaltered Jurassic dikes. Miocene dikes in the Bare Mountain district, southern Nevada, are similar, and also contain secondary vapor-dominated and high-salinity fluid inclusions in quartz. A dike in Perú reminiscent of the globular-bearing lava at Julcani contains spheres of pyrite as much as a centimeter in diameter, locally deformed to aligned ellipsoids by flow, are found in a dense, devitrified, carbonate-bearing dike (D.C. Noble, unpub. data). These occurrences and those described from Julcani are mutually corroborative, providing evidence for the existence of sulfide-rich magmas both at and near the surface.

It is notable that the examples from Julcani, those described by Brake et al. (1998), as well as those described by Wilson (1978) and Keith and his coworkers from the Bingham and Tintic districts, Utah, are all spatially and temporally associated with base- and/or precious metal-mineralization. Very small amounts of magmatic sulfides are common in volcanic rocks of many types, but seldom if ever occur in the amounts found in the rocks presumably genetically directly or indirectly related to mineralization. The discrepancy increases when the strong tendency for sulfide loss/destruction on eruption is taken into consideration. The significance for prospect/deposit evaluation is evident.

Pyrite in a high-level "failed" porphyry intrusive body beneath the central part of the Julcani district appears to have formed from a similar iron sulfide-rich polycomponent fluid phase. Positive correlation between total iron and sulfur in the Tentadora stock suggests that iron was introduced along with sulfur rather than that the pyrite was formed by sulfidation of iron originally present in the magma. The existence of very irregular and spongy aggregates of pyrite containing abundant inclusions of apatite, rutile, zircon, iron oxide, Fe-Ti oxide, Mg-rich ankerite, quartz and alkali feldspar suggests that the pyrite was introduced as a polycomponent fluid similar to that inferred to have existed in the pyrite/marcasite bearing lavas. This fluid preferentially wetted the surface of phenocrysts, particularly quartz, and pyrite is preferentially found in growth reentrants in quartz phenocrysts. The presence of a liquid sulfide-dominated phase is supported by positive correlations between S, Fe, Ti, Zr, Co and Ni, and negative correlations between S and Fe and Lu, Ga, Sc, Cr and Ba.

Both the iron sulfide-bearing volcanic rocks and the Tentadora stock, as well as volcanic rocks that do not contain sulfides, have high contents of Co (6-13 ppm), Ni (10-30 ppm) and Cr (21-71 ppm) for such silicic rocks, strongly suggesting that the magmas are the result of mixing of previously-formed silicic magma with smaller amounts of mafic magma rich in these elements. Magma mixing is also suggested by the presence of small inclusions of more mafic-rich material and by skeletal and other textures suggestive of rapid phenocryst growth.

Textural features of vein pyrite from the central part of the Julcani district strongly argue for deposition of gel or colloid of pyritic composition, followed by solid-state conversion to pyrite and recrystallization through vapor/liquid dissolution, transport and deposition producing better-ordered(?) pyrite with euhedral crystal faces. Such pyrite may be not uncommon in hydrothermal veins.

This talk mostly presents observations and their inductive interpretation. Great opportunities exist not only for further descriptive study but also for chemical and thermochemical formalization of the processes involved.

ACKNOWLEDGEMENTS

REFERENCES

Brake, S.S., Ressel, M.W., Connors, K.A., Noble, D.C. & Weiss, S.I. 1998. Auto-alteration of dikes of the Matalla-Sta. Rosa center, Perú, the Carlin trend & Bare Mtn., NV, by closed-system crystallization of CO_2-& S-bearing magmas. Geological Society of America Abstracts with Programs, vol. 30, p. A377

Castor, S.B., Tingley, J.V. & Bonham, H.F., Jr. 1994. Pyritic ash-flow tuff, Yucca Mountain, Nevada. Economic Geology, vol. 89, p. 401-407.

Connors, K.A., Noble, D.C., Bussey, S.D. & Weiss, S.I. 1993. Initial gold contents of silicic volcanic rocks: Bearing on the behavior of gold in magmatic systems. Geology, vol. 21, p. 937-940.

Deen, J.A., Rye, R.O., Munoz, J.L. & Drexler, J.W. 1994. The magmatic hydrothermal system at Julcani, Peru: Evidence from fluid inclusions and hydrogen and oxygen isotopes. Economic Geology, vol. 89, p. 1924–1938.

Drexler, J.W. & Munoz, J.L. 1986. Highly oxidized, pyrrhotite-anhydrite-bearing silicic magmas from the Julcani Ag-Cu-Bi-Pb-Au-W district, Peru: Physicochemical conditions of a productive magma. in Taylor, R.P., and Strong, D.F. (eds), Recent advances in the geology of granite-related mineral deposits: The Canadian Institute of Mining and Metallurgy Special Volume 39, p. 72–79.

Giggenbach, W.F. 1992. Magma degassing and mineral deposition in hydrothermal systems along convergent plate boundaries. Economic Geology, vol. 87, p. 1927-1944.

Keith, J.D., Dallmeyer, R.D., Kim, C.-S. & Kowallis, B.J. 1991. The volcanic history and magmatic sulfide mineralogy of latites of the central East Tintic Mountains, Utah. in Raines, G.L., Schaefer, R.E., & Wilkinson, W.H. (eds), Geology and ore deposits of the Great Basin: Geological Society of Nevada, Reno, NV, United States, p. 461-483.

Keith, J.D., Whitney, J.A., Hattori, K., Ballantyne, G.H. Christiansen, E.H., Barr, D.L., Cannan, T.M. & Hook, C.J. 1997. The role of magmatic sulfides and mafic alkaline magmas in the Bingham and Tintic mining districts, Utah. Journal of Petrology, vol. 38, p. 1679-1690.

Larocque, A.C.L., Stimac, J.A., Keith, J.D. & Huminicki, M.A.E. 2000. Evidence for open-system behavior in immiscible Fe-S-O liquids in silicate magmas: Implications for contributions of metals an sulfur to ore-forming fluids. The Canadian Mineralogist, vol. 38, p. 1233-1249.

Maughan, D.T., Keith, J.D., Christiansen, E.H., Pulsipher, T., Hattori, K. & Evans, N.J., 2002. Contributions from mafic alkaline magmas to the Bingham porphyry Cu-Au-Mo deposit, Utah. Mineralium Deposita, vo. 37, p. 14-37.

Noble, D.C., 1978. Pervasive hypogene alunitic alteration associated with enargite mineralization in Herminia. Unpublished report, Lima, Compañía de Minas Buenaventura S.A., 2 p.

Noble, D.C., Amaya A., W., Miranda, M. & McCormack, J.K. 2006. Geological, chemical and mineralogical features of high-sulfidation alteration and mineralization produced by high-temperature open-system degassing

of high-level magma bodies. in Carlotto, V., Cárdenas, J., Soler, P. & Jacay, J. (eds), XIII Congreso Peruano de Geología, Resúmenes Extendidos. Sociedad Geológia del Perú, Publicación Especial Numero 7, p. 849-855. (published on CD)

Noble, D.C. & McKee, E.H. 1999. The Miocene metallogenic belt of central and northern Perú, in Skinner, B.J. (ed.), Geology and mineral deposits of the central Andes. Society of Economic Geologists Special Publication No. 7, p. 155-193.

Noble, D.C., Ressel, M.W., Lechler, P.J. & Connors, K.A. 2004. Magmatic As, Sb, Cs, Bi. Tl, and other elements in glassy volcanic rocks of the Julcani district, Perú, and the Carlin trend, Nevada. Boletín de la Sociedad Geológica del Perú, vol. 97, p. 29-50.

Noble, D.C., Wise, J.M. & Vidal, C.E. 1999. Episodes of Cenozoic extension in the Andean orogen of Perú and their relation to compression, magmatic activity and mineralization. in Macharé, J., Benavides, V., & Rosas, S. (eds), Volumen Jubilar No. 5, "75 Aniversario Sociedad Geológica del Perú", p. 45-66.

Noble, D.C. & Scofield, N. 1977. Two-phase glass inclusions in phenocrysts in rhyodacite represent metastable liquid immiscibility in undercooled silicic melt. Geological Society of America Abstracts with Programs, vol. 9, n° 7, p. 1165-1166.

Noble, D.C. & Silberman, M.L. 1984. Evolución volcánica y hidrotermal y cronología de K/Ar del Distrito Minero de Julcani. Sociedad Geológica del Perú, Volumen Jubilar LX Aniversario, Fasc. 5, 35 p.

Petersen, U., Noble, D.C., Arenas F., M. & Goodell, P.C. 1977. Geology of the Julcani mining district, Peru. Economic Geology, vol. 72, p. 931-949.

Richards, J.P. 2003. Tectono-magmatic precursors for porphyry Cu-(Mo-Au) deposit formation. Economic Geology, vol. 98, p. 1515-1533.

Scherkenbach, D.A. & Noble, D.C. 1984. Potassium and rubidium metasomatism at the Julcani district, Peru. Economic Geology, vol. 79, p. 565-572.

Shellnutt, J.P. & Noble, D.C. 1985. Pre-mineral radial dikes of tourmalinized fluidization breccia, Julcani district, Peru. Economic Geology, vol. 80, p. 1622-1632.

Stavast, W.J.A., Keith, J.D., Christiansen, E.H., Dorais, M.J., Tingey, D., Larocque, A. & Evans, N. 2006. The fate of magmatic sulfides during intrusion or eruption, Bingham and Tintic districts, Utah. Economic Geology, vol. 101, p. 329-345.

Stimac, J.A. & Hickmott, D. 1996, Ore metal partitioning in intermediate-to-silicic magmas: PIXE results on natural mineral/melt assemblages, in Clark, A.H., ed., Giant Ore Deposits II: Controls on the scale of orogenic magmatic-hydrothermal mineralization: Giant Ore Deposits Workshop, 2nd, Kingston, Ontario, Canada, April 25-27, Proceedings, p. 197-235.

Weiss, S.I., Noble, D.C. & Larson, L.T. 1995. Hydrothermal origin and significance of pyrite in ash-flow tuffs at Yucca Mountain, Nevada. Economic Geology, vol. 90, p. 2317-2325.

Wilson, J.C. 1978. Ore fluid-magma relationships in a vesicular quartz latite porphyry dike at Bingham, Utah. Economic Geology, vol. 73, p. 1287-1307.