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Epidote and Ore Deposits

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With 3 Text-Figures

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Epidot und Erzlagerstätten

Zusammenfassung

Minerale der Epidotgruppe finden sich nur selten als Gangminerale in Erzlagerstätten. Sie können zwar in Neben- bzw. in Spurenelement (z.B. Sn, Cr, LREE) angereichert sein, wurden aber nur im Mary-Kathleen-Skarn wegen der Seltenen Erdelemente abgebaut.

In ozeanischen Inselbögen können prograde Epidot-Magnetitskarne als Muttergesteine für Au-Lagerstätten auftreten, in orogenen kontinentalen Randzonen hingegen ist Epidot in Scheelit- und Buntmetall-führenden Skarnen (z.B. porphyrische Kupfer-Skarne) häufig. In den letzteren tektonischen Zonen kommt Epidot in prograden pelitischen Skarnen, Endoskarnen und retrograden Paragenesen vor. Skarne in Zusammenhang mit hoch fraktionierten S-Typ oder I-Typ Magmen enthalten geringe Mengen retrograden Epidots (selten Zinn-führend) oder prograden Allanit mit einer Anreicherung der leichten Seltenen Erdelemente.

Epidot findet sich in rezenten geothermalen Systemen und epithermalen Edelmetall-Lagerstätten des Tertiärs bis zu Gegenwart. In geothermalen Zonen bildet sich Epidot in geringer Tiefe (<1600 m) aus heißen, schwach salinen neutralen Chloridlaugen mit einem geringem Anteil an gelöstem CO_2. Solche Lösungen stellen die Erklärung für epithermale Edelmetall-Lagerstätten dar.

Das Vorkommen von Epidot wurd durch Druck (0.3–3 kbar), Temperatur (250–250°C), Oxidationsbedingungen, die Aktivität von Ca^{2+} und den Molbruch von CO_2 in der fluiden Phase gesteuert. Hydrothermale Bereich mit hohem X_{CO_2} schließen Epidot aus.

Abstract

Epidote group minerals are an uncommon gangue mineral in ore deposits and, although they can be enriched in minor elements (e.g. Sn, Cr, LREE), epidote group minerals have only been mined from the Mary Kathleen skarn, Australia for rare earth elements.

In oceanic island-arc settings, prograde epidote-magnetite skarn assemblages are the host for Au deposits whereas in continental margin orogenic settings, epidote is a common mineral in scheelite- and base-metal-bearing skarns (e.g. porphyry copper skarns). In the latter setting, epidote occurs in prograde pelitic skarns, endoskarns and retrograde assemblages. Skarns associated with highly fractionated S-type or A-type magmas contain minor retrograde epidote (rarely stannian) or prograde LREE-enriched allanite.

Epidote is present in modern geothermal systems and Tertiary-Recent epithermal precious metal deposits. In geothermal settings, epidote forms at shallow depths (1600 m) from hot weakly saline neutral chloride brines which have a low dissolved CO_2 content. These brines are commonly the ore fluid for epithermal precious metal deposits.

The occurrence of epidote is controlled by pressure (0.3–3 kb), temperature (250–650°C), oxidation conditions, the activity of Ca^{2+} and the mole fraction of CO_2 in the fluid. Hydrothermal environments with a high X_{CO_2} preclude epidote formation.

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1. Introduction

Epidote [Ca_2 (Al,Fe)3Si_3 O_{12} (OH)] and minerals of the epidote family [e.g. clinozoisite Ca_2 Al_3 Si_3 O_{12} (OH), allanite (Ce,Ca,Y)$_2$ (Al,Fe)$_3$ Si_3 O_{12} (OH)] are rare minerals in the major types of ore deposits. Because most ore deposits are characterised by chemically-reduced mineral species, the absence of a ferric mineral is not unexpected.

Ore deposits which occur in constructive plate margins (e.g. medial rift of mid ocean ridges) contain no epidote because the P-T-X conditions of ore formation (Fig. 1) are totally different from those of epidote. Similarly, ore deposits which occur in extensional settings at destructive plate margins contain no epidote (e.g. Kuroko deposits). Stability relations of epidote (BROWNE, 1970) show that in the pressure – (1–500 bars) temperature (180–350°C) regime expected for submarine hydrothermal ore precipitation, epidote is not a stable mineral in acid Ca-poor fluids (Fig. 1). Although epidote occurs in some deformed metamorphosed submarine hydrothermal ore deposits (e.g. magnetite skarns of the Bergslagen area, Sweden; stratiform scheelite, Broken Hill, Australia), it occurs in transgressive calcite-hematite-epidote veinlets of retrograde metamorphic origin. Epithermal base- and precious metal deposits, porphyry copper and pyrometasomatic skarn deposits occur at destructive plate margin settings however, it is only skarn deposits which contain abundant minerals of the epidote group.

Intracratonic and continental margin and rift-related ore deposits are characterised by an abundance of Ca minerals however, transition metals are in the reduced state, hydrothermal fluid temperatures are too low and epidote group minerals can not form. Carbonatites contain rare minor LREE-enriched allanite whereas retrograde mineral assemblages in carbonatite contain minor epidote. Some continental extensional settings and metamorphic core complexes are characterised by listric and low angle faults which have acted as conduits for oxidised hydrothermal fluids (e.g. Wipple Mountains, USA; Niğde and Menderes Massifs, Turkey). In these faults and thrusts, hematite-quartz-chalcopyrite±gold±epidote assemblages are not uncommon. These are minor mineral occurrences.

Intraplate settings are characterised by a great diversity of ore deposit types such as large layered lopoliths, Mississippi Valley- and sandstone-type Pb-Zn deposits, residual, alluvial and sedimentary deposits. Again, epidote does not occur and the P-T-X formation conditions are well out of the known conditions of formation of these ore deposits (Fig. 1).

This contribution celebrates the "125 Jahre Knappenwand" and documents the occurrence of epidote in two destructive plate margin settings. The first setting is the occurrence of epidote group minerals in skarns with examples of epidote in scheelite- and base metal-bearing skarns, stannian epidote from a Cornish skarn and allanite from the Mary Kathleen uranium skarn of northern Australia. The second example is the occurrence of epidote in the active geothermal systems of the Taupo Volcanic Zone, New Zealand and epidote in a precious metal-bearing Pleistocene alkaline volcano of Papua New Guinea.

2. Skarns

Skarns can form by a diversity of processes such as the metamorphic recrystallisation of impure carbonate rocks, local exchange of components between contrasting lithologies, local exchange at high temperature between magmas and carbonate rocks and the broad scale transfer of components over a broad temperature range between magmatic hydrothermal fluids and carbonate rocks. The last two skarn types are generally of economic interest.

In oceanic island-arc settings, calcic magnetite skarns are essentially the only skarn type present. They are characterised by epizonal dioritic stocks with associated coeval volcanics (basalt-andesite), Fe-rich calc-silicate minerals comprising prograde epidote-grandite-ferrosalite, extensive alteration by epidote-pyroxene or albite-scapolite of the associated plutonic and volcanic rocks, low total sulphide and minor Cu, Zn, Co and Au.

In continental margin orogenic belts with I-type magmas related to subduction processes, W and base metal skarns are present. These form as a result of metasomatism of carbonate-pelite-volcanic sequences intruded by melts of granodioritic to monzonitic composition. Prograde skarn assemblages comprise an inner zone of garnet-pyroxene±Mo-rich scheelite, an outer wollastonite-vesuvianite zone in marble and a pyroxene-plagioclase-epidote assemblage in plutons and pelites. Prograde assemblages are transgressed and partially replaced by hydrous silicates (biotite, hornblende) with minor quartz, K-feldspar, scheelite and sulphides.

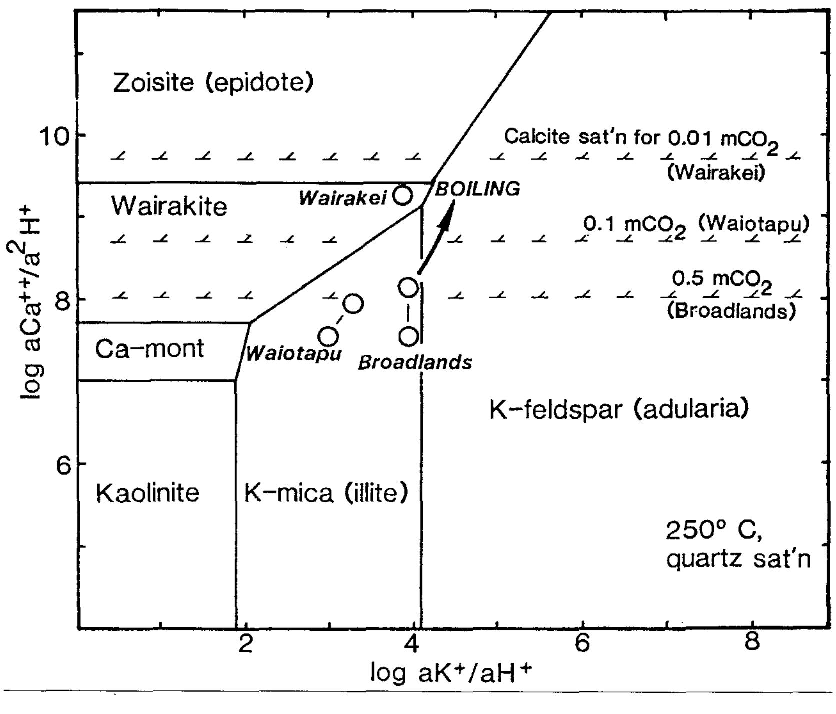

Fig. 1.
Mineral stability diagrams for calcium and potassium minerals at 250°C in terms of solution ratios and m_{CO_2} values.
The figure shows the effect of varying CO_2 content on the occurrence of calcium-bearing phases in deep New Zealand geothermal aquifers (○) as a result of boiling resulting in CO_2 loss and pH increase (from HENLEY & HEDENQUIST, 1986).

Mineral compositions are generally a result of depth of skarn formation and host rock composition. Reduced and low sulphur skarns form at depth (1–3 kb) associated with reduced S-type or ilmenite series granitoids or in shallower environments (0.3–1 kb) associated with I-type or magnetite series granitoids. Reduced skarns also form in carbonaceous host rocks. Oxidised and high sulphur skarns in which epidote might be expected, occur at epizonal depths (0.3–1 kb) or associated with the more oxidised I-type or magnetite series magmas. Oxidised skarns also occur in non-carbonaceous and hematitic host rocks. In general, W skarns form at a higher temperature and deeper environment than base metal skarns. The T-X_{CO_2} conditions at 2 kb for water-rich fluids in the Ca-Al-Si-C-O-H system (Fig. 2) show that epidote group minerals can form at medium (300°C) to high temperatures (580°C) at only low $CO_2/(CO_2 + H_2O)$ (EINAUDI et al., 1980).

Skarn deposits enriched in Cu and other base metals are associated with epizonal granodioritic to monzonitic plutons. They characteristically occur close to the igneous contact, have high garnet:pyroxene ratios and are relatively oxidised (e.g. andradite, diopside, magnetite, hematite, abundant sulphides). Extensive retrograde alteration of the parental pluton and associated volcanic rocks produces large endoskarn zones containing epidote group minerals.

All skarns display a long evolutionary history from prograde assemblages which formed at near magmatic conditions of 650–400°C from magmatic fluids characterised by a low CO_2 content and moderate salinity (10–45 wt-% NaCl equiv.) (EINAUDI et al., 1980). With time, the hydrothermal fluid evolves by mixing with meteoric water to a lower temperature, lower salinity more oxidising system. These fluids can infiltrate outwards from the heat source or collapse along the prograde skarn to form vein and pseudomorphous exo- and endoskarns. It is these fluids which form extensive retrograde assemblages distal from mesozonal skarns (e.g. Pb-Zn deposits) and proximal to epizonal skarns (e.g. porphyry Cu skarns). These retrograde assemblages often contain epidote.

Skarn deposits which form from highly evolved S-type magmas, A-type magmas or felsic magmas in post-orogenic continental environments produce Sn, W, Mo, Zn, Be and F skarns. Epidote is generally rare in these highly reduced skarns. Stannian epidote has been reported by VAN MARKE DE LUMMEN (1986) from the St. Just mining district in the Land's End Granite aureole, Cornwall, England. The Cornubian Land's End Granite intruded pelites, pillow basalts and minor carbonate rocks. Two main stages of skarn formation were recognised by VAN MARKE DE LUMMEN (1986):

- ☐ Stage 1
  Grossular-andradite zone surrounded by an amphibole zone. Locally the two zones are separated by pyroxene.
- ☐ Stage 2: Retrograde assemblages comprising vesuvianite ± magnetite or chlorite-amphibole-tourmaline (or axinite) ± Sn-bearing minerals (malayaite-stannian titanite, cassiterite, stannian epidote, stannian amphibole and stannian axinite).

The stannian epidote has formed by the retrograde alteration of garnet when the hydrothermal system was collapsing inwards to the heat source. This is a well-known process for the formation of rare stannian silicates. For example, PLIMER (1984) reports the retrograde breakdown of prograde stannian andradite, stannian amphibole and cassiterite to calcite-malayaite assemblages. Epidote from the Cornish skarn contains up

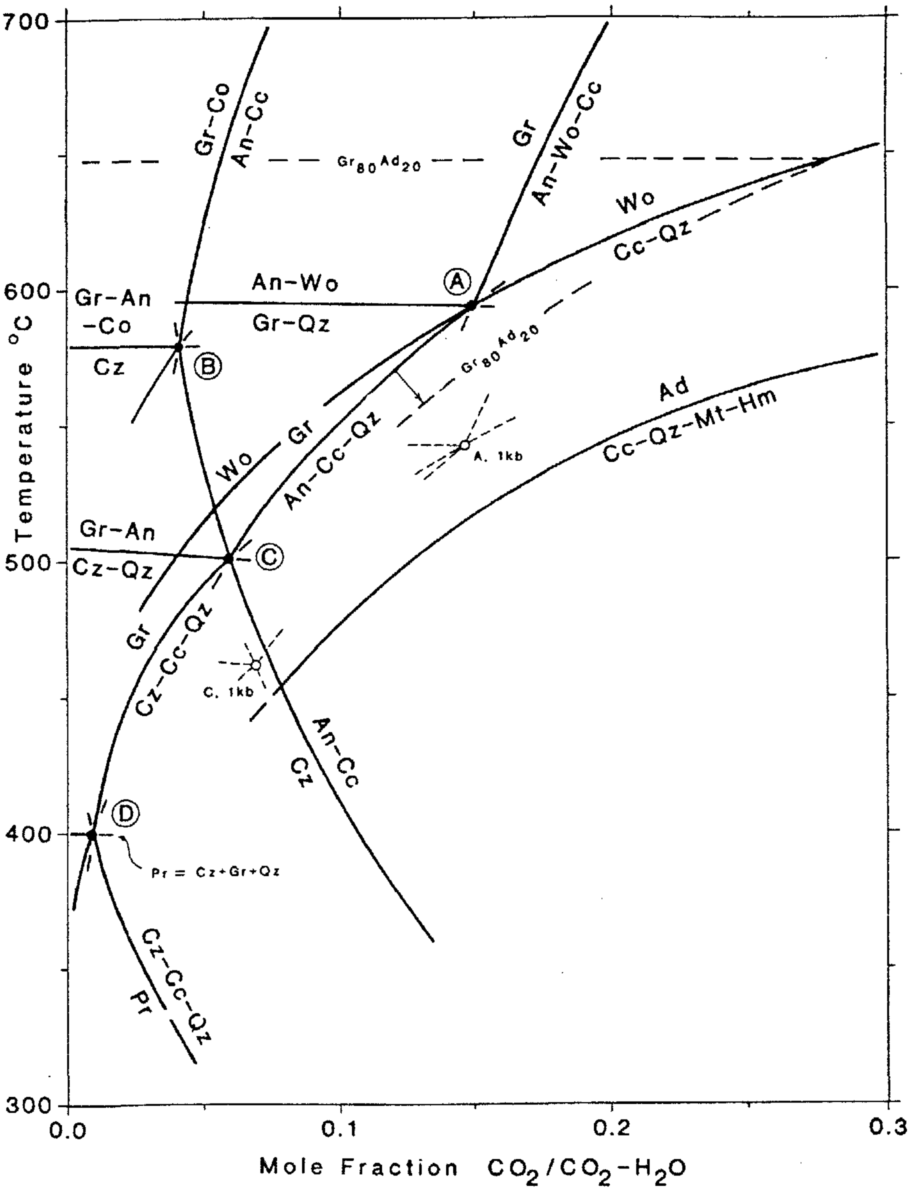

Fig. 2.
Partial T-X_{CO_2} diagram for water-rich fluids in the System Ca – Al – Si – C – O – H at 2 kb.
Invariant points (A, B, C and D); an = anorthite; cc = calcite; co = corundum; Cz = clinozoisite; gr = grossular; pr = prehnite; qz = quartz.

to 2.84 wt.-% SnO_2 which equates as 0.09 atoms per formula unit of a total of 8 cations on the basis of 13 (O + OH) (VAN MARKE DE LUMMEN, 1986). The exact substitution method for tin in epidote is not known however it is probably very similar to the MULLIGAN & JAMBOR (1968) suggestion for coupled substitution in andradite:

$$Sn^{4+} + Fe^{2+} = 2(Al^{3+}, Fe^{3+})$$

In the St. Just deposit, neither the stannian epidote nor any other stannian silicates have been exploited for tin.

The Mary Kathleen U-REE skarn (Queensland, Australia) was mined principally for uraninite and the epidote group mineral allanite although associated garnet have high REE and U contents (KWAK & ABEYSINGHE, 1987). Allanite from Mary Kathleen contains up to 20 % LREE. The Mary Kathleen and other minor associated skarn U-REE deposits are within a Proterozoic metasediment sequence intruded by a number of highly fractionated igneous rock types. Metasediments are pelites, psammites, carbonate and evaporitic rocks. The skarn derives from the reaction between granite-derived Fe-REE-U solutions with carbonate, initially at near magmatic conditions. Fluid flow was along dykes and a shear zone. KWAK & ABEYSINGHE (1987) have recognised three stages of mineral assemblages:

Stage 1: andradite – quartz – diopside/hedenbergite ± scapolite
Stage 2: ferrohastingsite – sulphides or
allanite – stillwellite – uraninite – apatite
Stage 3: sulphides – chlorite – prehnite – calcite

Stage 2 has replaced stage 1 assemblages. The ferrohastingsite-bearing variant of the Stage 2 assemblage occurs below the REE-bearing allanite zone which constituted the ore. Some 6 Mt of 0.1 % $U3O_8$ and 2.6 % REE was mined from this zone.

A number of epidote group minerals occur in the metamorphosed massive sulphide deposits of Scandinavia. These deposits probably formed from submarine hydrothermal fluids in a Proterozoic intracratonic or continental margin rift setting. These deposits contain no primary epidote however epidote is a common mineral of retrograde origin in the magnetite skarns of the Bergslagen area (e.g. Stollberg). Of mineralogical interest are the Cr epidote-Cr allanite solid solution series minerals from the Vuonos open pit in the Outokumpu district of Finnish Karelia. Numerous other exotic Cr minerals are present at Outokumpu and result from the amphibolite facies metamorphism of a suite of Precambrian dolomite, chert, pelite, graphitic pelite, basalt, komatiite and massive sulphides. The stratigraphy, structure, textures and mineralogy are consistent with a submarine hydrothermal origin for the massive sulphides (TRELOAR & CHARNLEY, 1987).

3. Active Geothermal Systems

In low temperature systems, epidote forms in a diversity of environments varying from the inside of human arteries such as the hardening of arteries (CLARKE, pers. comm.), inside drill casing and as an alteration phase.

Chips ejected from drill casing in the Ngatamariki geothermal field, New Zealand, show that wairakite, epidote and prehnite grew in equilibrium at a depth of 1580–1600 metres from hot dilute, alkaline chloride water of near neutral pH and low dissolved CO_2 (BROWNE et al., 1989). Rare quartz and pyrite were also present however the more common minerals present in pipes from discharging geothermal systems (e.g. carbonates, sulphates, silica, sulphides, precious metal precipitates) were not detected. Quartz-saturated geothermal fluids were in equilibrium with the hot Quaternary calc-alkaline volcanic rocks and the calculated growth rate of epidote crystals was 0.2 μm per day.

Elsewhere in the Taupo Volcanic Zone of New Zealand, the calcium aluminium silicates wairakite and epidote are common in the deeper higher temperature alteration zones of the geothermal systems. For example, wairakite and epidote are common at Wairakei but are replaced by calcite at Broadlands due to the higher CO_2 (HENLEY & HEDENQUIST, 1986; Fig. 1). The relative concentrations of gases (especially CO_2, H_2S, CH_4, H_2, NH_3) also relate to deep temperatures and reactions with mineral pairs such as pyrite-epidote (GIGGENBACH, 1980). This common assemblage appears to be the principal control of the redox state of the deep geothermal fluid. Of greater interest is the correlation between metal content and fluid salinity. Boiling of high salinity fluids results in the precipitation of base metal sulphides (e.g. Salton Sea, SKINNER et al., 1967) whereas near surface complex sulphides or precious metals are deposited by H_2S loss, mixing with near surface acid waters or buffering by CO_2 gas flow in large hot water vents (HEDENQUIST & HENLEY, 1985). Epidote does not occur in either of these ore depositional environments.

The Lihir epithermal Au deposit on the Bismarck Archipelago of Papua New Guinea formed as a result of the explosive loss of fluid from CO_2- and H_2S-rich Pleistocene-Quaternary phonolitic volcanics and associated near surface plutons (PLIMER et al., 1988). Fluid loss by repeated boiling, near surface fluid mixing, collapse of cool mixed acid fluid and reaction with auriferous neutral chloride brines resulted in overprinting of early alteration assemblages and precipitation of gold. Deep in this active geothermal system, rare epidote has formed from deep neutral chloride auriferous brines as an overprint on plagioclase and clinopyroxene in phonolite. Epidote coexists with adularia, anhydrite and tourmaline and is partially replaced by calcite, sericite and biotite as a result of the changing activity of CO_2, pH and temperature changes in the system (PLIMER et al., 1988; Fig. 3). The field of the neutral chloride brine at 250°C at Lihir coincides with the field of maximum gold solubility and clearly epidote is an important redox buffer to this ore fluid (Fig. 3).

4. Conclusions

Epidote is a rare mineral in ore deposits and the only epidote group mined has been REE-enriched allanite. Nevertheless, the pressure, temperature, redox state and CO_2 activity of any hydrothermal system is of critical importance for epidote formation and for the understanding of ore genesis. Epidote in skarn deposits forms as a prograde mineral in oceanic island-arc skarn deposits which are occasionally enriched in Au and as a prograde skarn mineral in pelites or as a retrograde phase (e.g. endoskarn) in W and base metal skarns associated with continental margin orogenesis. Epidote group minerals are rare in post-orogenic magmatic settings where they are restricted to skarns derived from A-type or highly evolved S-type magmas. In these settings, the epidote group mineral can be stannian or enriched in rare earth elements. In

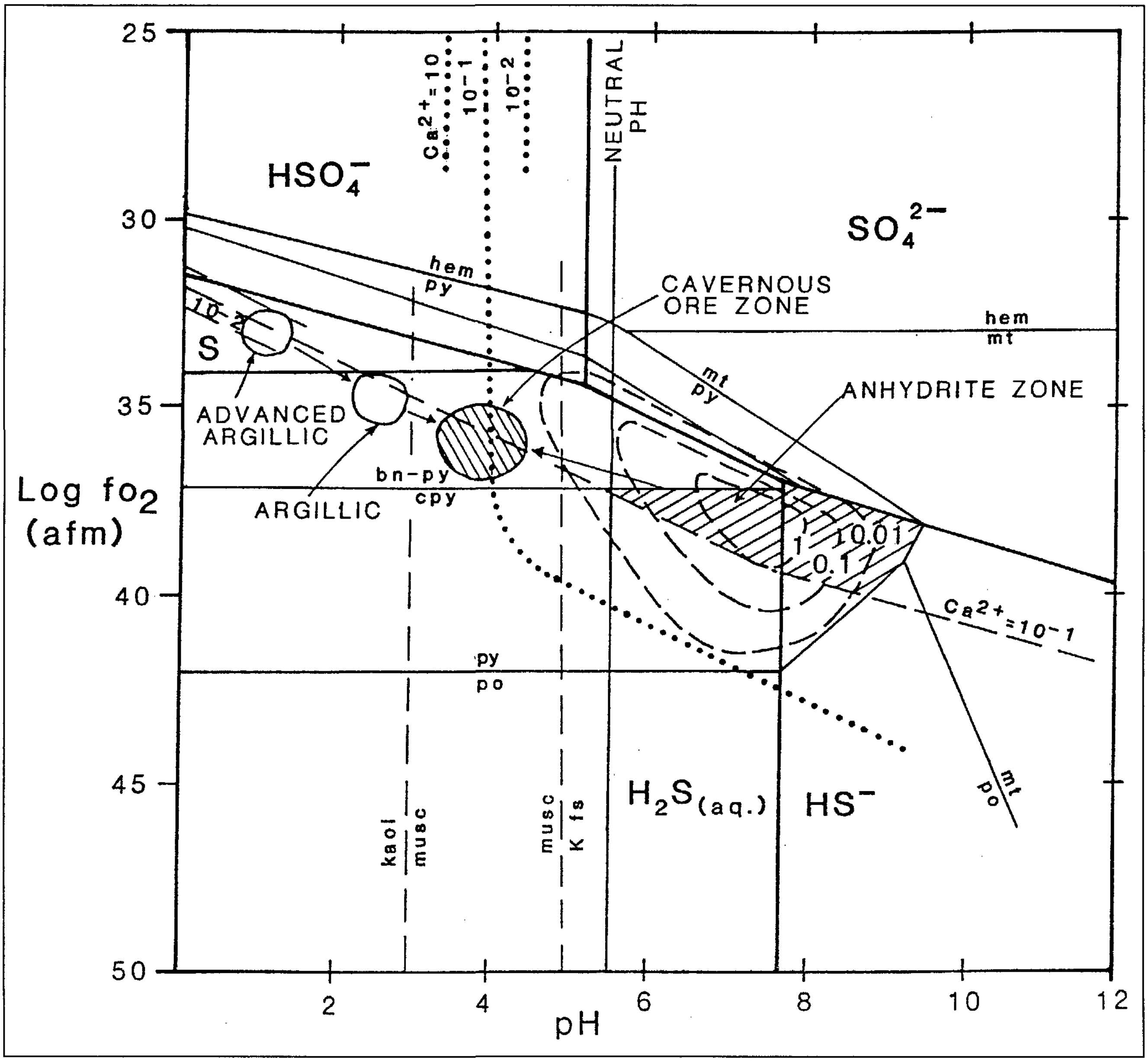

Fig. 3.
Plot of ph vs log fO at 250°C for the Lihir epiterhmal showing alteration zones, gold solubility (1, 0.1 and 0.01 ppm) and mineral stability.
Bn = bornite; cpy = chalcopyrite; hem = hematite; kaol = kaolinite; Kfs = adularia; mt = magnetite; po = pyrrhotite; py = pyrite.

CO_2 -bearing geothermal systems, epidote precipitates quickly from hot dilute neutral chloride brines at shallow depths and a sulphide-epidote pair forms a redox buffer for the hydrothermal fluid. It is these fluids which can contain the maximum dissolved content of gold.

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