

UNITED STATES DEPARTMENT OF INTERIOR GEOLOGICAL SURVEY

Controls on Base and Precious Metal Mineralization  
in Deeper Epithermal Environments.<sup>1</sup>

by

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- <sup>1</sup> Transcript of a talk given before the Society of Economic Geologists Symposium on Geothermal Systems and Ore Deposits in honor of Donald E. White: AIME 113th Annual Meeting, February 26-March 1, 1984, Los Angeles, California.

Open-File Report 84-890

This report is preliminary and has not been reviewed for conformity with U. S. Geological Survey editorial standards and stratigraphic nomenclature.

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## ABSTRACT<sup>1</sup>

Two distinct chemical environments are recognized for epithermal mineralization in volcanic settings. In the first, typified by Goldfield, Nevada, mineralization is closely tied to magmatism; the ores are deposited in a chemical environment dominated by disproportionation of magmatic  $\text{SO}_2$  and interaction of the resulting acid solutions with wallrock in steep thermal gradients near shallow plutons. In the second, typified by Creede, Colorado, mineralization is controlled by deeply circulating cells analogous to many modern geothermal systems; ores are deposited beneath an interface between deep, near neutral brines and overlying surface waters as a result of cooling and loss of acid volatiles.

## TRANSCRIPT OF TALK

First of all let me voice my pleasure at having been asked to participate in this symposium honoring Don White; the man who has led all of us - geothermalists and economic geologists alike - to the ground which this symposium attempts to cover - the relationships between active geothermal systems and hydrothermal ore deposits. Don, your focus, thru the years, on the nature and origins of natural thermal waters has not been universally accepted by your colleagues - or supervisors - at the Survey as being pertinent to the study of ore deposits, particularly in the early days of your studies; but look where it has led us! No other single approach has contributed so much to our understanding of hydrothermal ore deposits, particularly the epithermal ores, as has the study of active geothermal systems, as this symposium so well demonstrates. You must be very proud, and deservedly so; but Don, I think perhaps the shoe is on the wrong foot today; it is we, the speakers who are honored, by being asked to participate in YOUR symposium!

Let me begin by defining what I am, and am not, going to attempt to cover in this talk. I will restrict my remarks to volcanic-hosted epithermal ores. There are two reasons for this: first of all, Bill Bagby and Art Radke are going to discuss the sediment-hosted deposits right after lunch, and secondly, I've never worked in any of those deposits, and you deserve better than to hear me talk about them.

In the first part of this talk I am going to draw some distinctions between what I consider to be two very different - although related - epithermal environments. I'll then discuss the first of those environments, emphasizing some of the conflicting viewpoints concerning the nature of the ore-forming processes operative within it, and presenting an approach which may allow us to choose between some of the alternative mechanisms. Finally, I will turn our attention - at least mine - to the second environment and discuss it in terms of the chemical and hydrologic structure and processes known to occur in some active geothermal systems, with particular emphasis on how we might recognize some of the characteristics of active systems in the ore deposits which we are studying. I will, of course, use Creede as an example of this second type.

## SLIDE 1

Several years ago Larry Buchanan (1981) published a comprehensive, and

<sup>1</sup> Abstract published in Program and Abstracts, AIME 113th Annual Meeting, February 26 - March 1, 1984, Los Angeles, California

very important synthesis wherein he related the distribution of mineral assemblages, zoning of metals, mineral textures and structure of volcanic-hosted epithermal ore deposits to one another as summarized on this slide on which I've added a little color to Larry's original illustration. Larry interpreted the model in terms of processes going on in the ore fluid, with particular emphasis on boiling. He also had a few words of advice for those of you who actually work for a living on how you might use the model find orebodies. I think this synthesis of Larry's was a singular achievement, and helped, at least in my mind, bring a considerable amount of order to a variety of observations that have been made on epithermal orebodies. Some aspects of Larry's model can stand refinement, however, and I'm particularly interested in whether this kaolinite + alunite acid-sulfate alteration zone, shown here in red, is universally present - or even occasionally present in most epithermal vein systems. In fact, I am going to contend that the epithermal ores containing intense primary alunite + kaolinite acid-sulfate alteration form in a very different environment from the more common vein-type deposits characterized by illitic to sericitic alteration. Three of our colleagues in Reston, Penny Heald-Wetlaufer, Dan Hayba and Nora Foley, have undertaken, with the help of Jim Goss, a comprehensive analysis of the characteristics of 16 volcanic-hosted epithermal ore deposits, selected primarily on the basis of the amount of data available in the literature on which their comparative study was based. A number of you may have heard Penny present the results of their analysis at the GAC-MAC meetings in Vancouver last May. A copy of Penny's remarks and slides has been issued as a USGS open-file report (Heald-Wetlaufer and others, 1983). In general their study corroborates and adds documentation to Larry Buchanan's model, but they have drawn what I consider to be an important distinction between those ore deposits which are characterized by intense acid-sulfate alteration to kaolinite-alunite-quartz assemblages and those which are characterized by alteration to illite or sericite and usually contain adularia as a vein constituent.

#### SLIDE 2

The deposits on which they compiled information are grouped as shown on this slide, which contrasts those deposits characterized by acid-sulfate alteration (which I have chosen to call the Goldfield-type) with those characterized by illite-sericite alteration (which scientific chauvinism compels me to call the Creede-type). Although I am emphasizing the differences in wallrock alteration, there are other systematic differences between the two types of deposits which help validate the distinction between them.

#### SLIDE 3

The Goldfield-type ores contain a sulfide assemblage signifying a high chemical potential of sulfur and including enargite, famatinite, luzonite, and, usually, covellite in contrast to the chalcopyrite and tetrahedrite-tennantite characteristic of the Creede-type ores. In all of the Goldfield-type districts studied the K/Ar age of the ore overlaps, within analytical precision, that of the rhyodacitic volcanic dome or neck to which it is related, and which usually hosts the ore. In contrast, the ores of the Creede-type are usually substantially younger than their volcanic host rocks, and can seldom be tied to any particular intrusive or volcanic unit. The Goldfield-type ores also tend to be more Copper-rich than do those of

the Creede-type. These relations are remarkably consistent within each of the deposit classes although within each class there are marked differences in other characteristics, particularly in base:precious metal ratios and Ag:Au ratios.

Although I have chosen to call the acid-sulfate-bearing deposits the Goldfield-type, I would like to example them by briefly discussing the Summitville district in Colorado.

#### SLIDE 4

The Summitville district lies in the eastern San Juan Mountains, about 30 miles Southeast of Creede. The ores are contained within a rhyodacite (= quartz latite) volcanic dome which appears to have formed along the structural margin of the Platoro caldera (Lipman, 1975).

#### SLIDE 5

The important relations are illustrated on this cross section, rather poorly prepared after a plate from the Professional Paper by Tom Steven and Jim Ratte (1960). The quartz latitic volcanic dome was emplaced about 23 million years ago, cutting the 29 million year old andesite which flooded the Platoro caldera. The orebodies, indicated in red, are entirely contained within the Quartz latite, but not necessarily within the coarsely porphyritic phase as implied by this cross section. The wallrock alteration related to the ores affects both the the quartz latite and the andesite. The alunite in the ores has been dated at 22 million years, a figure consistent with the geologic relations which show that the 20 million year old Rhyolite of Cropsy Peak lies on an eroded surface of the altered Quartz latite dome, but has not been affected by the alteration. The dates shown are from Mehnert, Lipman and Steven (1973), and have been supplemented by additional age determinations by the Anaconda crew which has been working at Summitville for the past several years. The Anaconda dates extend the range of values for each of the units - including the alunite - but still drive home the point that the mineralization and accompanying alteration were integral parts of the volcanic evolution of the dome itself.

#### SLIDE 6

The distribution of the alteration zones is shown in this slide, again from the 1960 Steven and Ratte Professional Paper. In the upper part of the ore zone the alteration tends to be poddy, becoming more tabular to vein-like with increasing depth, but the assemblages and zonal pattern found in the deepest workings are the same as those exposed at the surface. The sulfide mineral assemblage is dominated by pyrite which occurs as vug and vein filling, but mainly as widespread disseminations. Enargite and covellite, with smaller amounts of luzonite, and famatinite make up the bulk of the ore which contains only minor amounts of sphalerite, galena and native gold. The copper minerals characterize the assemblage as being of the high sulfur variety. Thus, Summitville displays very well the characteristic features of the acid-sulfate (or Goldfield-type) of epithermal ore deposits, of which I remind you by repeating the earlier slide.

#### SLIDE 7 (Repeat of 3)

Now, in order to give some authority to my statements concerning the fundamental differences between the Goldfield and Creede-type environments, I have borrowed, combined, and colored up a couple of illustrations constructed

SLIDE 8 (Slide omitted from this report)

by this happy fellow - Dick Henley, The Great Guru of Wairakei. Those of you sitting up front can see, first of all, that Henley is wearing a proper T-shirt, and, secondly, that he is being supported by a stout sign bearing the Maori inscription: "TE ARA MOKOROA," translated for us below as "the long abiding path of knowledge" To what greater authority could I appeal?

SLIDE 9

In this slide, the Goldfield environment, as I envision it, is on the left; the Creede environment on the right. The fundamental difference between the two is immediately obvious; the Goldfield-type ores were formed at shallow depths in the upper part of a volcanic edifice. This one I borrowed from Henley is perhaps too much of a proper volcano, and too large in size to accurately represent most of the Goldfield-type deposits, but I chose it purposely. Dick drew it to represent a typical geothermal system in calc-alkaline stratavolcano and then used it to represent a possible environment for porphyry copper mineralization, in my mind an environment not far removed from that of the Goldfield-type, although the Goldfield-type systems are substantially shallower. The Goldfield-type ores are, in general, hosted by volcanics derived from the heat source which drove the system and are not far removed from the heat source. In the Creede-type system, the ores were again formed at shallow depths, but they were plastered along the top of a deeply circulating hydrothermal system, and were deposited a long way from the heat source. We could continue the comparison by discussing the relative importance of magmatic components and the implications regarding the chemical evolution of the two systems, but we would be getting further and further adrift on a sea of speculation with few areas of documentation on which to set an anchor. The point I hope I have made is that I consider the Goldfield-type and the Creede-type systems to be fundamentally different, and that that difference is a consequence of the fact that the Goldfield-type system is driven by a near surface - and near ore - heat source, whereas the Creede-type systems are driven by a deep heat source, far removed from the ore zone.

The next obvious question to ask is why the acid-sulfate alteration is characteristic of the Goldfield-type environment but is seldom, if ever, seen as a primary assemblage in the Creede-type systems. This brings us into an area of controversy concerning the origin of the acid-sulfate alteration, which in turn revolves around the mechanism by which the sulfuric acid, required to form the alunite + kaolinite assemblage, is generated. I think I know, but so do a number of other people, and they don't all agree with me.

SLIDE 10

This slide shows three reactions; all leading to the formation of sulfuric acid. The top reaction is the simple oxidation of hydrogen sulfide and is the reaction that produces the spectacular solfataric alteration that we see at the surface in active geothermal systems.

SLIDE 11 (repeat of 9)

It arises from the escape of  $H_2S$  from the deeply circulating waters, shown in this slide in yellow, as they begin to boil on nearing the surface. The  $H_2S$  rises along with the steam and other volatiles, such as  $CO_2$ , and is oxidized upon encountering the overlying ground waters which are saturated in atmospheric oxygen. These overlying groundwaters become heated by the recondensation of steam and are referred to as steam-heated waters. They are shown in green on this slide, for both the Goldfield-type and Creede-type environments, and they are essential elements of almost all high temperature geothermal systems in silicic or andesitic volcanic terranes. The alteration produced by this mechanism is very intense, but is a surficial phenomenon, rarely extending down to depths of even fifty meters below the surface. I think that we see very few of these alteration zones in ore deposits because they are very soft, shallow and easily eroded; but many people have appealed to this mechanism to explain the acid sulfate alteration in a number of districts.

SLIDE 12 (repeat of 10)

I prefer the second reaction as the mechanism by which sulfuric acid is formed in Goldfield-type environments.  $SO_2$  gas is unstable below temperatures of about 400 degrees centigrade in the presence of water, and it disproportionates, as shown in the reaction on the slide, into  $H_2S$  and sulfuric acid. There are a lot of attractive reasons for preferring this mechanism, but there isn't time to defend my choice right now. Rather I'm going to propose a test whereby we can distinguish between these mechanisms. First, however, we must note that the kaolinite + alunite assemblage can also be produced by sulfuric acid attack during supergene alteration of sulfide ore bodies as suggested by the third reaction on the slide; written for pyrite being oxidized to something approximating limonite. This has happened at Creede, at Goldfield, I think at Round Mountain, and I'm sure in many other districts. Getting back to the proposed test, I am going to try to convince you that we can use a little isotope geochemistry to help us distinguish among these three mechanisms of acid-sulfate alteration.

SLIDE 13

Back in 1966, Cy Field proposed (Field, 1966), as did Roy Jensen in 1967 (Jensen, 1967), that the measurement of sulfur isotopes in alunites could distinguish between those formed by hydrothermal precipitation and those formed by supergene alteration. In 1971 Jensen, Roger Ashley and John Albers (Jensen et al., 1971) applied this technique to Goldfield as shown on this slide. As you can see, the alunites judged to be primary on field and petrographic grounds were much heavier than those formed by secondary processes which showed the same range of sulfur isotopic composition as did the primary sulfides. The reason for this is that there is no sulfur isotopic fractionation during low temperature oxidation of sulfides due to kinetic effects, as has been demonstrated many times. Sulfuric acid generated by the oxidation of sulfides has the same sulfur isotopic composition as the sulfides! On the other hand, at temperatures above about 200 degrees Celsius considerable isotopic exchange between aqueous sulfide and sulfate species can take place, particularly in acid environments, as has been discussed by Ohmoto and Lasaga (1982). Primary alunite formed at these temperatures will be much heavier than coexisting sulfides because of the

strong fractionation between aqueous sulfide and sulfate species. So now we know how to tell primary from secondary alunite. But we really don't, because it turns out that when  $H_2S$  is oxidized in the steam-heated waters it too doesn't undergo much sulfur isotopic exchange with the sulfate produced and, as has been demonstrated by Shoen and Rye (1970) for Yellowstone. The sulfate in the steam-heated waters in active geothermal systems has the same sulfur isotopic composition as the  $H_2S$  from which it was derived by oxidation, so the alunites formed in supergene and steam-heated water environments will both have sulfur isotopic compositions approximately the same as their coexisting sulfides. So now we can tell alunites that formed by disproportionation of  $SO_2$  from that formed from steam-heated or supergene waters, but, based on the sulfur isotope data alone, we can't tell apart the alunites formed from steam-heated versus supergene waters. Fortunately, if we look at the associated kaolinites we should be able to distinguish between them.

#### SLIDE 14

This slide shows us how it works. In the top figure a group of kaolinites and halloysites formed by supergene alteration of some Japanese orebodies are plotted (Marumo et al., 1982). You can see that their compositions fall very close to the KAOLINITE LINE of Savin and Epstein (1970) and Lawrence and Taylor (1971) which is the line representing the locus of hydrogen and oxygen isotopic compositions for kaolinites formed by weathering and assumed to be in equilibrium with meteoric waters along the meteoric water line. Note that the compositions of some of the surface waters plot, as expected, near the meteoric water line and are connected to their corresponding kaolinite values. In the bottom figure are plotted the hydrogen and oxygen isotopic compositions of a group of kaolinites from acid-sulfate alteration zones from several geothermal areas in Japan along with some hydrothermal kaolinites from several ore deposits - indicated by open circles. These kaolinites, formed from steam-heated waters, are considerably removed from the meteoric water line and very close to the dashed line which marks the compositions of kaolinites that would be in equilibrium with meteoric waters at temperatures of 100 degrees celsius. So the hydrogen and oxygen isotopic composition of the kaolinites in acid sulfate alteration zones may allow us to distinguish between primary and supergene origins for acid sulfate alteration zones. This is not an original concept, for Taylor (1974) pointed this out years ago.

#### SLIDE 15

If we put this all together, as on this slide, we see that we can use the isotopic signatures of the alunite and kaolinite in acid sulfate alteration zones to tell us something about the origin of the acid-sulfate alteration. As you can see, I've added a row to show that the K/Ar age determinations on alunite, if we trust them, can also be used to distinguish between supergene and primary origins, as we have done at Creede and as has been done for a number of other districts. Alunite itself contains both hydrogen and oxygen as well as sulfur, so if we can calibrate, and learn to trust, the isotope systematics we can do the whole thing on alunite. Right now Dick Henley, Bob Rye and I are in the beginning stages of trying to apply these isotopic discriminators to a number of epithermal and geothermal environments to see if they really work, and to find out what the mechanism of acid sulfate alteration in Goldfield-type environments really is.



Now let's look at the Creede-type environment for the time remaining.

SLIDE 16

I've borrowed another slide from Henley - Good old Dick; he's easy. This one is a cross section of the Wairakei geothermal field as it looked prior to its development for geothermal power; which changed a lot of things. I begged this slide to illustrate the overall chemical structure of a deeply circulating geothermal system in a silicic volcanic terrane. The yellow represents the plume of heated, near neutral chloride waters which displaces the cooler, fresh groundwater shown surrounding it in blue. Mixing occurs between the two resulting in dilute chloride waters. Note that the isotherms are displaced to the right by the gravity-driven lateral flow along the top of the system, and that boiling occurs in the upper 400 meters of the chloride-water plume. Let's move a little closer to examine the detail along the top of the system.

SLIDE 17

Here we see our old friend the steam-heated waters forming a shallow cap to the hottest part of the system. These steam-heated waters mix with the chloride waters on the downflow side, and a small area dominated by steam is shown in red. I'm told that this is the general structure of geothermal systems of this type the world over. If this is so, we should be able to find evidences that such a structure existed in some epithermal systems of the Creede-type; if we are correct in our assumption of the doctrine of uniformitarianism in this case. Before we go looking, though, let's glance briefly at only a few of the results of a very nice and very useful study of the Waiotapu geothermal system in New Zealand done by Jeff Hedenquist for his PhD dissertation at the University of Auckland (Hedenquist, 1983). I'm sorry that Jeff is not here in person telling us about Waiotapu as part of this symposium, because Jeff approached the study thru the eyes of an ore deposit geologist, and the slant he gave it makes it somewhat unique, and of particular interest to us.

SLIDE 18

The advanced argillic or acid sulfate alteration shown in yellow across the top marks the position of the steam-heated waters responsible for the alteration. Note the patches of disseminated lead-zinc mineralization shown in red, some distance below the acid sulfate alteration, and the suggestion that gold is being transported thru the zone where lead and zinc are being deposited. The circulation patterns are shown by the arrows. Note that, in addition to the deep convective flow, Jeff has identified a lateral flow component at about the 150 meter depth. Several different waters are denoted by alpha-numeric symbols. A-1 is the deep chloride water which rises and is shown to be boiling at about the 300 degree isotherm. As it rises it continues to boil, loses heat, and becomes more concentrated as it moves toward A-2. The chemical consequences of the boiling are that the fluid becomes more oxidized, principally thru the loss of hydrogen, and more alkaline thru the loss of the acid volatiles such as  $\text{CO}_2$  and  $\text{H}_2\text{S}$  which, like hydrogen, are very strongly partitioned toward the vapor phase. Due to its much lower viscosity, the vapor phase rises until it mainly condenses - but partially escapes thru fumaroles - heating and acidifying the waters in which it condenses, as we have discussed before. The steam-heated waters are denoted here by the

letter B. The waters denoted by the A-3 symbol flow laterally across the top of the system, mixing, as we shall see, with the A-2 waters. So Jeff has identified two processes, boiling and mixing, both going on at the top of the deeply circulating chloride cell, in the area of base metal precipitation. This is good because we economic geologists have been appealing to mixing and boiling for some time, particularly boiling in the past several years; and Ed Drummond in an important thesis, that we all hope will be published soon, has demonstrated the effectiveness of both mechanisms and provided an excellent theoretical base on which quantitative models can be constructed (Drummond, 1980). But these aren't the only possible mechanisms of precipitation, and as economic geologists we need to seek evidences of the occurrence of boiling and mixing in ore-forming systems and use them both to help locate ourselves in the system and to develop meaningful quantitative models of ore deposition.

Jeff's study was based on drill core, downhole and well-head temperatures, and well-head fluid samples - all gathered some 17 years prior to his study; and on spring samples gathered thru the years. One of the many techniques Jeff used in reconstructing the Waiotapu system was:

#### SLIDE 19

this plot of the heat content vs. the chloride content of the various waters. (Note that I've plotted temperature along the top of the heat content axis) This kind of plot is particularly useful in deciphering the origins of - and the relationships between - fluids from different springs or wells in geothermal systems. I hope I can show you that it can be equally useful in the study of ore deposits. Let's see how its used. The A-1 water at about 300 degrees and 1300 ppm Chloride is the deep, unmodified chloride brine. As this brine rises to the upper part of the system it begins to boil. When that happens it cools because it loses heat to the vapor, and becomes more concentrated because the chloride is retained in the liquid phase. On this heat-content vs. chloride diagram, its position moves along the line as indicated by the arrow, radial to the steam point (the heat content - about 2800 kilojoules/mole - of pure water at its boiling point). Jeff's A-2 water has been derived simply by boiling of A-1. The A-3 water is that water that was seen to be entering the top of the system by lateral flow. It's nearly fresh, but has been heated to about 170°C. The yellow triangles fall very tightly about a line between the boiled, deep, A-2 waters and the fresh, heated A-3 waters; and are interpreted to show a mixing trend between the two. Some of them might better have been interpreted as mixing between the A-2 and cool meteoric waters; or even between the A-1 and A-3 waters. The steam-heated waters lie at B, about 100°C and don't show any well defined mixing trend with any of the other end-member waters.

Now lets look at ore deposits. One of the easiest sets of observations we can make on fluid inclusions is the temperature of homogenization on heating - and the freezing point of the liquid which is a measure of its salinity, or (for most epithermal systems) its chlorinity.

#### SLIDE 20

Ed Roedder (1977) has done a detailed growth-zone by growth-zone study of the homogenization and freezing temperatures of individual primary fluid

inclusions from 20 growth zones in this large sphalerite crystal from the OH vein at Creede. He found that each growth zone had a narrow range of both temperature and salinity values, and that these ranges were quite different for different growth zones, as shown on the following slide.

#### SLIDE 21

In this slide the numbers beside each temperature-salinity field indicate the paragenetic position of the growth-zone, 1 being the oldest and 20 the youngest. Note that this temperature-salinity diagram is almost equivalent to the heat content chloride diagram which Jeff Hedenquist used to evaluate his Waiotapu data, and that Ed's temperature-salinity fields for each growth zone can be considered equivalent to Jeff's well or spring samples. We can imagine that the highest salinity water - 9 - could have been derived by boiling of a higher temperature water like 8 - and that the group of waters indicated by yellow triangles were derived by mixing of waters like 9 with cooler, fresher waters. If we draw a mixing line thru the data (ignoring the values from zones 15 thru 20 for the moment) we can propose that these waters in here were derived by mixing a boiled water like 9 with a fresh water heated to about 200 degrees C. Not unlike the situation Waiotapu, huh? It's particularly interesting that the density of a water like 9 and fresh water at 200 degrees are nearly identical and that the mixing line is nearly an isodensity line - a condition that greatly favors mixing. This same relationship between temperature and salinity of fluid inclusions has been documented now for several other localities on the OH vein at Creede, and Dan Hayba on our project is making good progress in the extremely painstaking job of defining the temperature-salinity relationships in space along the OH vein as well as in time - and of interpreting the data in terms of the boiling and mixing of different end-member waters. Well now, what evidence is there that boiling occurred in the OH vein or that heated, fresh waters were available for mixing with the hot brines? It turns out that there are several lines of evidence, some direct and some inferential. The first was Ed Roedder's discovery, more than 20 years ago that some quartz crystals from the OH vein contained co-eval fluid inclusions with widely varying liquid vapor ratios. He interpreted them to have resulted from the trapping of a mixed liquid-vapor fluid. This was the first such demonstration of boiling on any ore deposit; an observation and interpretation since duplicated for hundreds of other deposits.

#### SLIDE 22

Here I have plotted the 5 localities where we have found, from such observations, definite evidence of boiling along the OH vein. I have also shown two other features interpreted to be the results of boiling; the distribution of vein adularia mainly below the zone of documented boiling, and the zone of intense illitic alteration which caps the OH vein above the zone of documented boiling, and is spectacular in its contrast and sharpness of contact with the unaltered wallrock below which hosts the productive part of the vein. I should note that the distribution of the alteration cap is much more regular along the simple open fracture of the OH vein than it is in other parts of the district where the hydrology was much more complex. The vein adularia and illitic alteration are two sides of the same coin. The adularia precipitated in response to the rise of the pH of the ore fluid on boiling, due to the strong fractionation of acid-forming volatiles such as  $\text{CO}_2$  and  $\text{H}_2\text{S}$  into the vapor phase. The illitic alteration resul-

ted from the recondensation and subsequent hydrolysis reactions of those volatiles in the overlying, probably fresh waters. OK, so boiling did occur along the OH vein at Creede. How about those heated, fresh waters? Well, Bob Rye and I had a problem with the interpretation of the isotope geochemistry of the fluid inclusions in quartz from Creede which suggested that the quartz, which was intergrown in vugs with the sulfides, formed from waters that were isotopically much different from those which deposited the sphalerite and altered the wall rocks. When Nora Foley came to work for us we set her about trying to find out what was wrong. Well, she did; and lots more.

#### SLIDE 23

By very painstaking work Nora found (Foley and others, 1982) that the quartz crystals that Bob and I had sampled for isotopic analysis of the fluid inclusions contained two very different populations of inclusions; and therein hung the tale. The relatively large, juicy primary inclusions (the kind that all of us measure because they're so easy to see) gave a range of temperature-salinity values

#### SLIDE 24

pretty much the same as those measured from sphalerite (Ed Roedder's data, previously discussed, are plotted here for reference)

#### SLIDE 25 (repeat of 23)

But, along with the relatively few primary inclusions Nora found thousands of tiny pseudosecondary inclusions along healed fractures - the kind that none of us measure (particularly in freezing studies) because its so hard to see what's going on because they're so small. These little buggers showed a nearly identical temperature range to that of the primaries,

#### SLIDE 26 (repeat of 24)

but their salinities were much lower - zero in many cases. Nora also found that about 15% of the primaries had been intersected by the fractures and gave intermediate salinity values. So Nora has shown that heated, fresh waters did exist in the Creede system - presumably along the top of the system - and were available for mixing with the upwelling brines as suggested by Roedder's data and by that being gathered by Dan Hayba. Nora solved our isotope problem, too, by tediously cutting out, with a wire saw, areas in a quartz crystal containing either only primary or only pseudosecondary inclusions in large enough quantity to allow hydrogen isotopic analysis. Bob Rye found that the primary inclusions had hydrogen isotopic signatures just like those of the sphalerites, whereas the pseudosecondaries were about 35 permil lighter. This result allowed the much more comfortable interpretation that the quartz and sulfides grew together from the same fluid, but that the quartz was fractured episodically - probably due to thermal shock resulting from the descent of cooler, overlying groundwaters into the ore zone as a result of some hydrologic fluctuation. As these fractures healed, they trapped these fresh waters as pseudosecondary fluid inclusions. The original analyses of the hydrogen isotopic composition of the quartz fluid inclusions by Bethke and Rye (1979), assumed to represent only the primary inclusion waters, were, in fact, strongly biased through the contamination

by these much lighter (in delta D) waters contained in the pseudosecondary inclusions.

Before closing I should note that Rick Robinson and John Rice have both, in their Master's theses, presented fluid inclusion evidences for mixing of fluids in the southern part of the Creede district - evidence which I just couldn't work into the timing of this talk.

SLIDE 27 (Slide omitted from this report)

Well, I see I've put Henley to sleep - again. If someone will wake him up we can all go to lunch. Thank you.

### BIBLIOGRAPHY

This bibliography has been constructed as a guide to sources of specific materials referred to in the talk or shown on the slides. It is selective rather than comprehensive, and no attempt has been made to fully document literature sources for statements made in the talk.

Bethke, P. M., and Rye, R. O., 1979, Environment of ore deposition in the Creede mining district, San Juan Mountains, Colorado: Part IV. Source of fluids from oxygen, hydrogen and carbon isotope studies: *Economic Geology*, v. 74, p. 1832-1851.

Buchanan, L. J., 1981, Precious metal deposits associated with volcanic environments in the Southwest: *Arizona Geological Society Digest*, v. 14, p. 237-262.

Dummond, S. E., Jr., 1981, Boiling and mixing of hydrothermal fluids: chemical effects on mineral precipitation: PhD dissertation, The Pennsylvania State University, University Park, PA, 380 p.

Field, C. W., 1966, Sulfur isotopic method for discriminating between sulfates of hypogene and supergene origin: *Economic Geology*, v. 61, p. 1428-1435.

Foley, N. K., Bethke, P. M., and Rye, R. O., 1982, A re-interpretation of DH092080 values of inclusion fluids in quartz from shallow ore bodies: *Geol. Soc. Amer. Abstracts with Programs*, v. 14, p. 489-490.

Heald-Wetlaufer, P., Hayba, D. O., Foley, N. K., and Goss, J. A., 1983, Comparative anatomy of epithermal precious- and base-metal districts hosted by volcanic rocks: A talk presented at the GAC/MAC/GGU Joint Annual Meeting, May 11-13, 1983, Victoria, British Columbia: U. S. Geol. Survey Open-File Report 83-710, 16p.

Hedenquist, J. W., 1983, Waiotapu, New Zealand: The geochemical evolution and mineralization of an active hydrothermal system: PhD. dissertation, University of Auckland, Auckland, New Zealand. 240 p.

Henley, R. W. and Ellis, A. J., 1983, Geothermal systems, ancient and modern: a geochemical review: *Earth Science Reviews*, v. 19, p. 1-50.

- Jensen, M. L., 1967, Sulfur isotopes and mineral genesis: Chapter 5 in Barnes, H.L., ed., *Geochemistry of Hydrothermal Ore Deposits*: Holt, Rinehart, and Winston, Inc., New York, p.143-165.
- Jensen, M. L., Ashley, R. P., and Albers, J. P., 1971, Primary and secondary sulfates at Goldfield, Nevada: *Economic Geology*, v. 66, p. 618-626.
- Lawrence, J. R. and Taylor, H. P., 1971, Deuterium and oxygen-correlation: Clay minerals and hydroxides in Quaternary soils compared to meteoric waters: *Geochim. et Cosmochim. Acta*, v. 35, p. 993-1003.
- Lipman, P. W., 1975, Evolution of the Platoro caldera complex and related volcanic rocks, southeastern San Juan Mountains, Colorado: U. S. Geol. Survey Prof. Paper 852, 128 p.
- Marumo, K., Matsuhisa, Y., and Nagasawa, K., 1982, Hydrogen and oxygen isotopic compositions of kaolin minerals in Japan: in Van Olphen, H. and Veniale, F. Eds., *Developments in Sedimentology 35, International Clay Conference 1981*. Elsevier p. 315-320.
- Mehnert, H. H., Lipman, P. W., and Steven, T. A., 1973, Age of mineralization at Summitville, Colorado as indicated by K-Ar dating of alunite: *Economic Geology*, v. 68, p. 399-401.
- Ohmoto, H. and Lasaga, 1982, Kinetics of reactions between aqueous sulfates and sulfides in hydrothermal systems: *Geochimica et Cosmochimica Acta*, v. 46, p. 1727-1746.
- Rice, J. A., 1984, Controls on silver mineralization in the Creede Formation, Creede, Colorado: M. S. thesis, Colorado State University, Fort Collins, CO, 135 p.
- Robinson, R. W., 1981, Ore mineralogy and fluid inclusion study of the southern Amethyst vein system, Creede mining district, Colorado: M. S. Thesis, New Mexico Institute of Mining and Technology, Socorro, NM, 85 p.
- Roedder, E., 1977, Changes in ore fluid with time, from fluid inclusion studies at Creede, Colorado: in *Proc. Internat. Assoc. Genesis of Ore Deposits, 4th Symposium, Varna, Bulgaria, 1974*: Sofia, Bulgaria, IAGOD, v. 2, p. 179-185.
- Savin, S. M. and Epstein, S., 1970, The oxygen and hydrogen isotope geochemistry of clay minerals: *Geochim. et Cosmochim. Acta*, v. 34, p. 25-42.
- Schoen, Robert, and Rye, R. O., 1970, Sulfur isotope distribution in Solfataras Yellowstone National Park: *Science*, v. 170, p. 1082-1084.
- Steven, T. A. and Lipman, 1976, Calderas of the San Juan Volcanic Field, Southwestern Colorado: U. S. Geol. Survey Prof. Paper 958, 35p.
- Steven, T. A. and Ratte, J. C., 1960, Geology and ore deposits of the Summitville district, San Juan Mountains, Colorado: U. S. Geol. Survey Prof. Paper 343, 70 p.

Taylor, H. P., 1974, The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition: *Economic Geology*, v. 69, p. 843-883.







ACID - SULFATE  
ALTERATION

Goldfield, NV  
Summitville, CO  
Red Mountain, CO  
Julcani, Peru

ADULARIA - SERICITE  
ALTERATION

Creede, CO  
Comstock, NV  
Round Mountain, NV  
Colqui, Peru  
Eureka, CO

Tonopah, NV  
Silver City, ID  
Oatman, AZ  
Guanojuato, Mexico  
Pachuca, Mexico

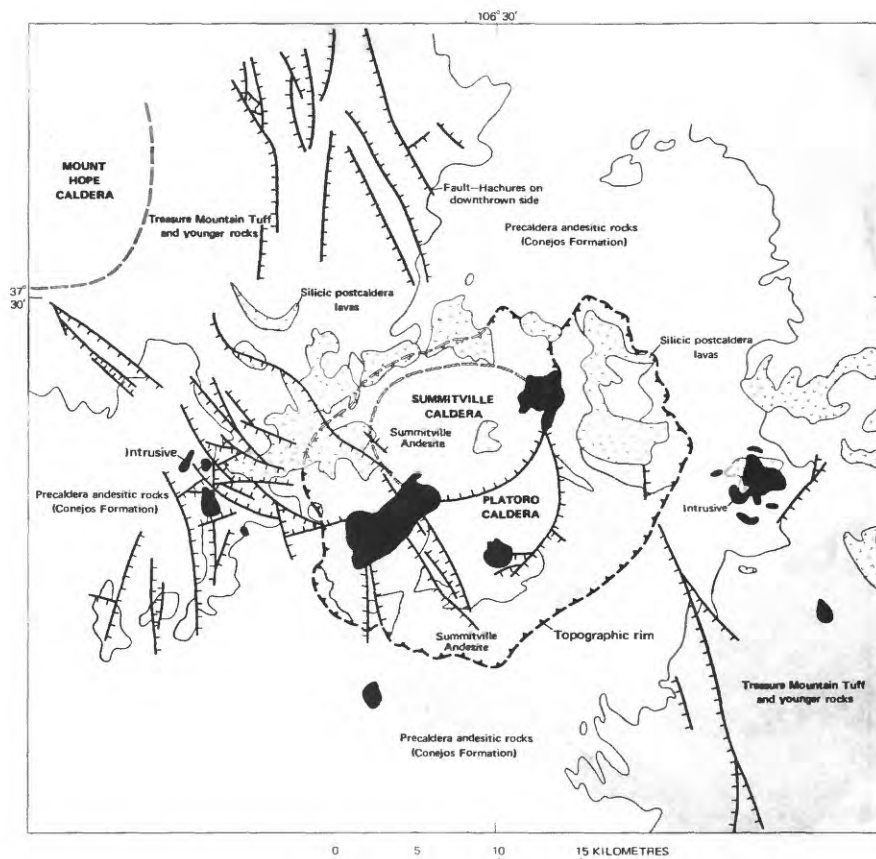
## DISTINCTIVE CHARACTERISTICS

### ACID - SULFATE ALTERATION

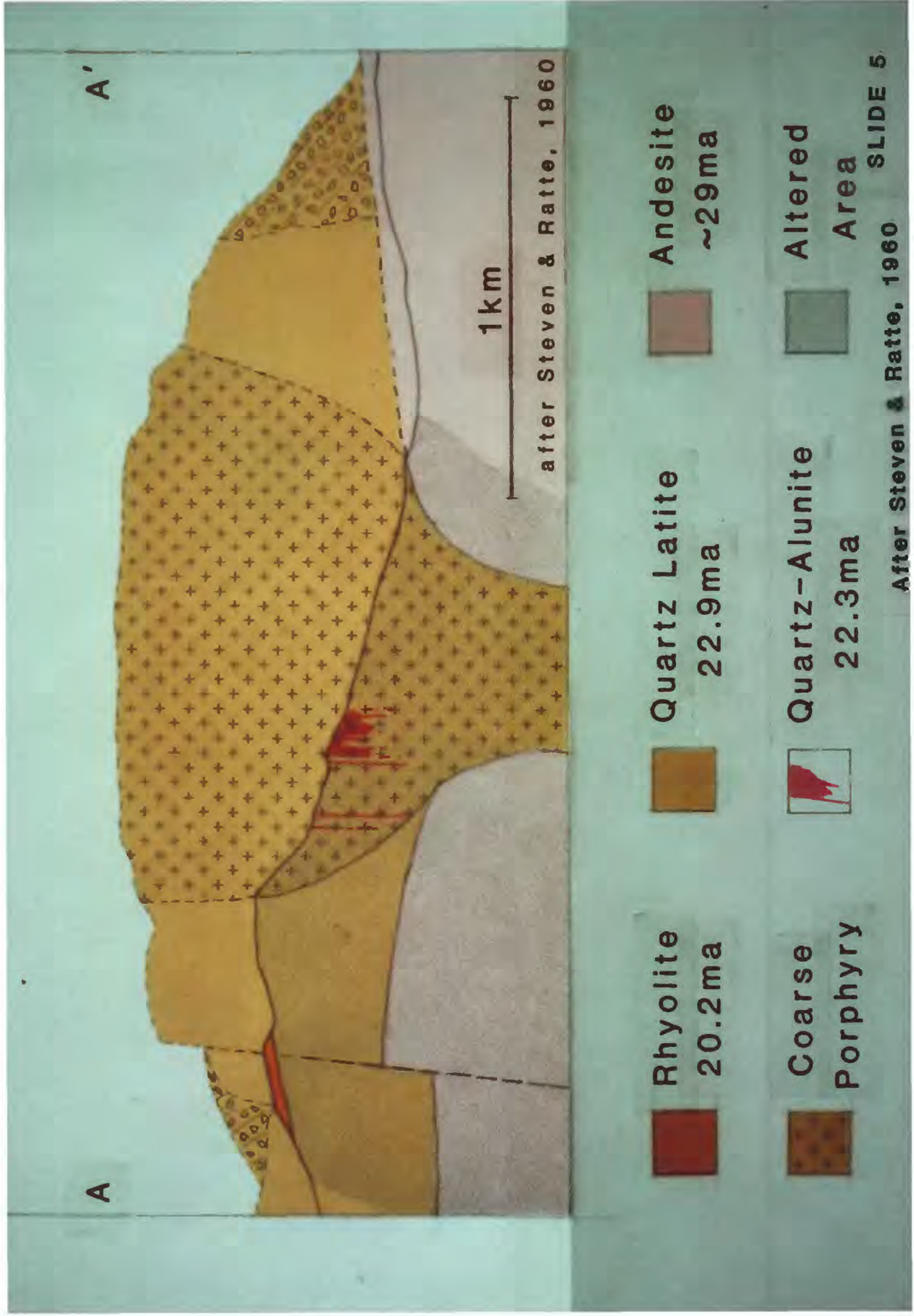
Higher Sulfur Mineral Assemblage  
Advanced Argillic Alteration  
Ages of Host and Ore Equivalent  
Noteworthy Copper Production

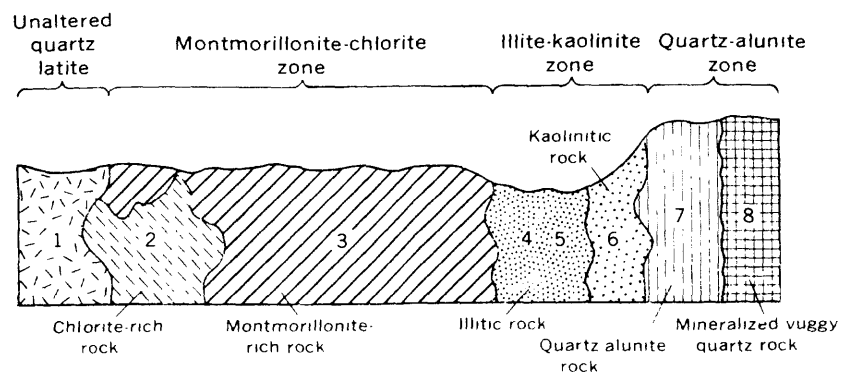
### ADULARIA - SERICITE ALTERATION

Lower Sulfur Mineral Assemblage  
Sericite - Adularia Alteration  
Ore Distinctly Later Than Host  
Low Copper Production



From Steven & Lipman, 1976

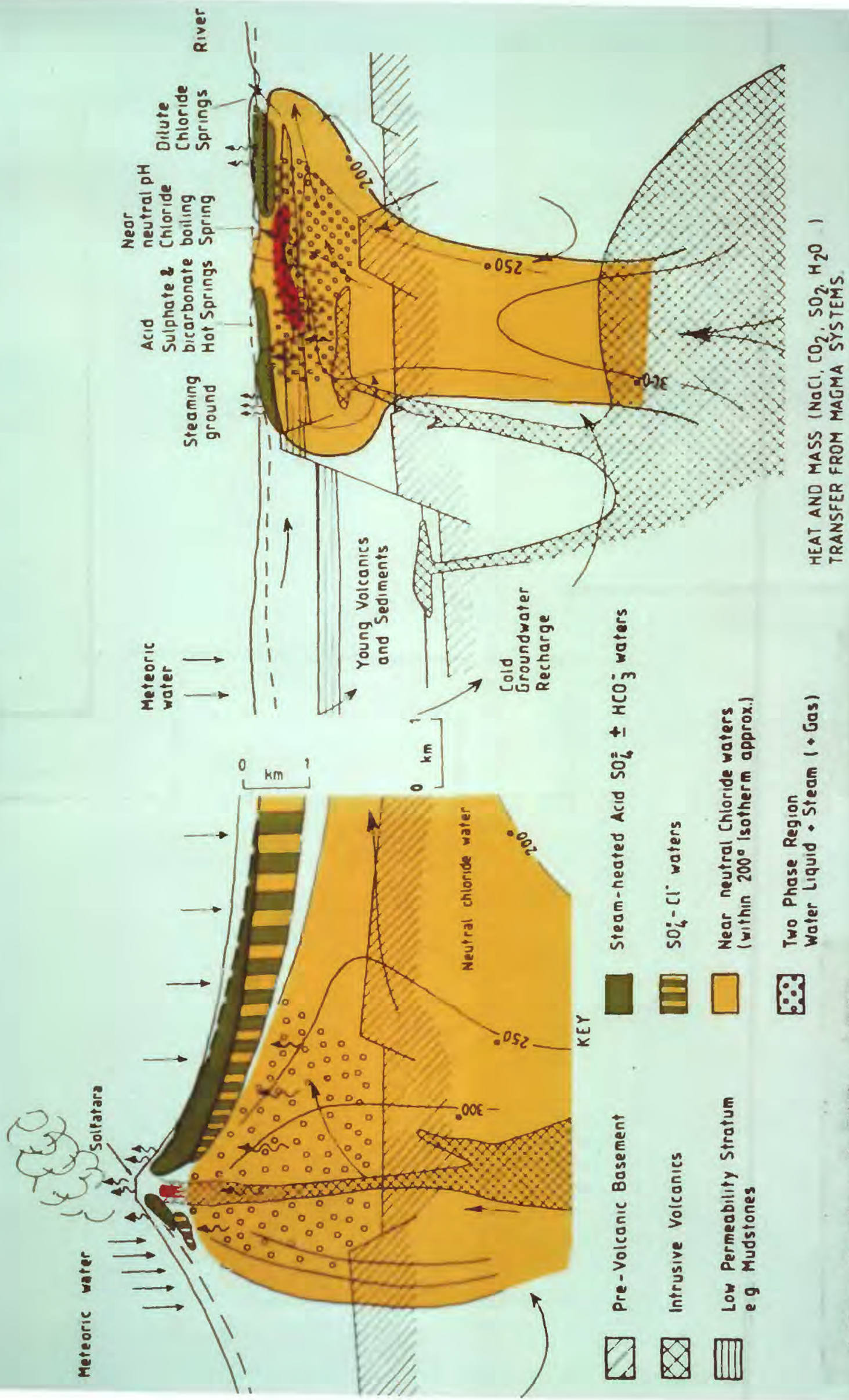




**From Steven & Ratte, 1960.**

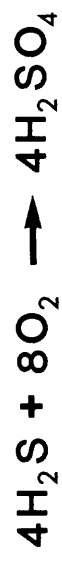
**SLIDE 6.**





After Henley & Ellis, 1983.

SLIDE 9



**SLIDE 10.**

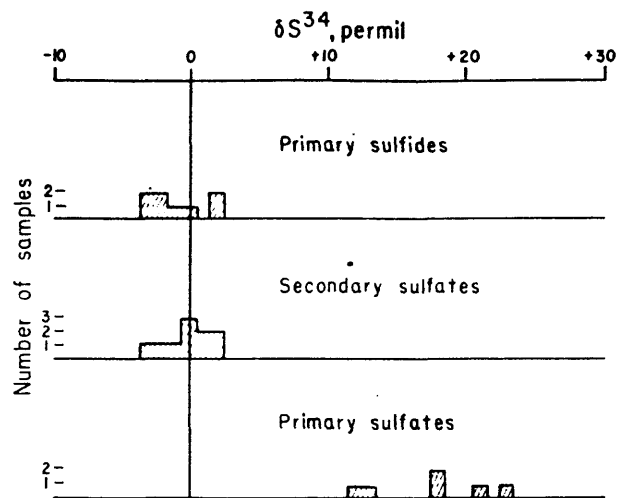
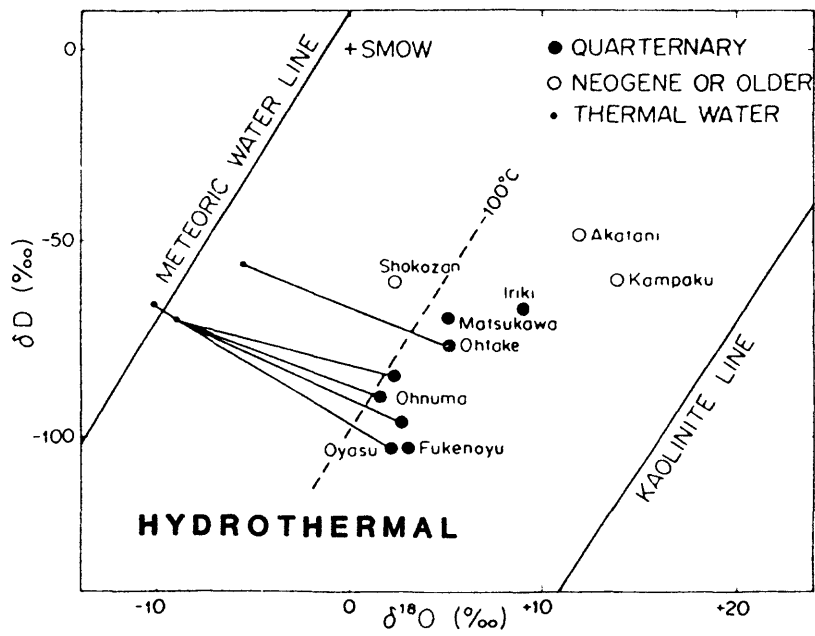
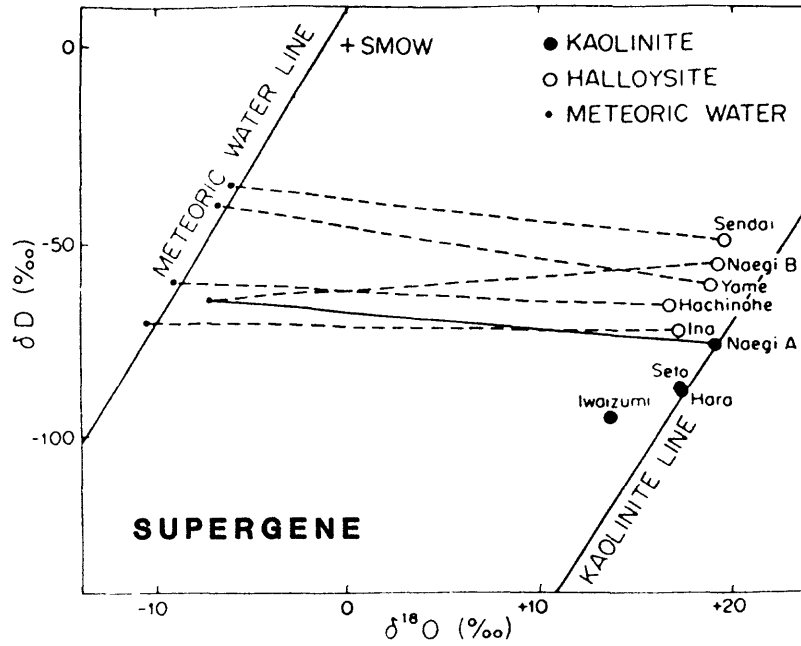


FIG. 3. Sulfur isotopic ratios of Goldfield sulfides and sulfates.

after Jensen, Ashley & Albers, 1971

SLIDE 13





after Marumo, Matsuhisa & Nagasawa, 1982

|  |                                  |  |                        |
|--|----------------------------------|--|------------------------|
|  | Oxidation<br>of H <sub>2</sub> S | Disproportionation<br>of SO <sub>2</sub> | Supergene<br>Oxidation |
|--|----------------------------------|--|------------------------|

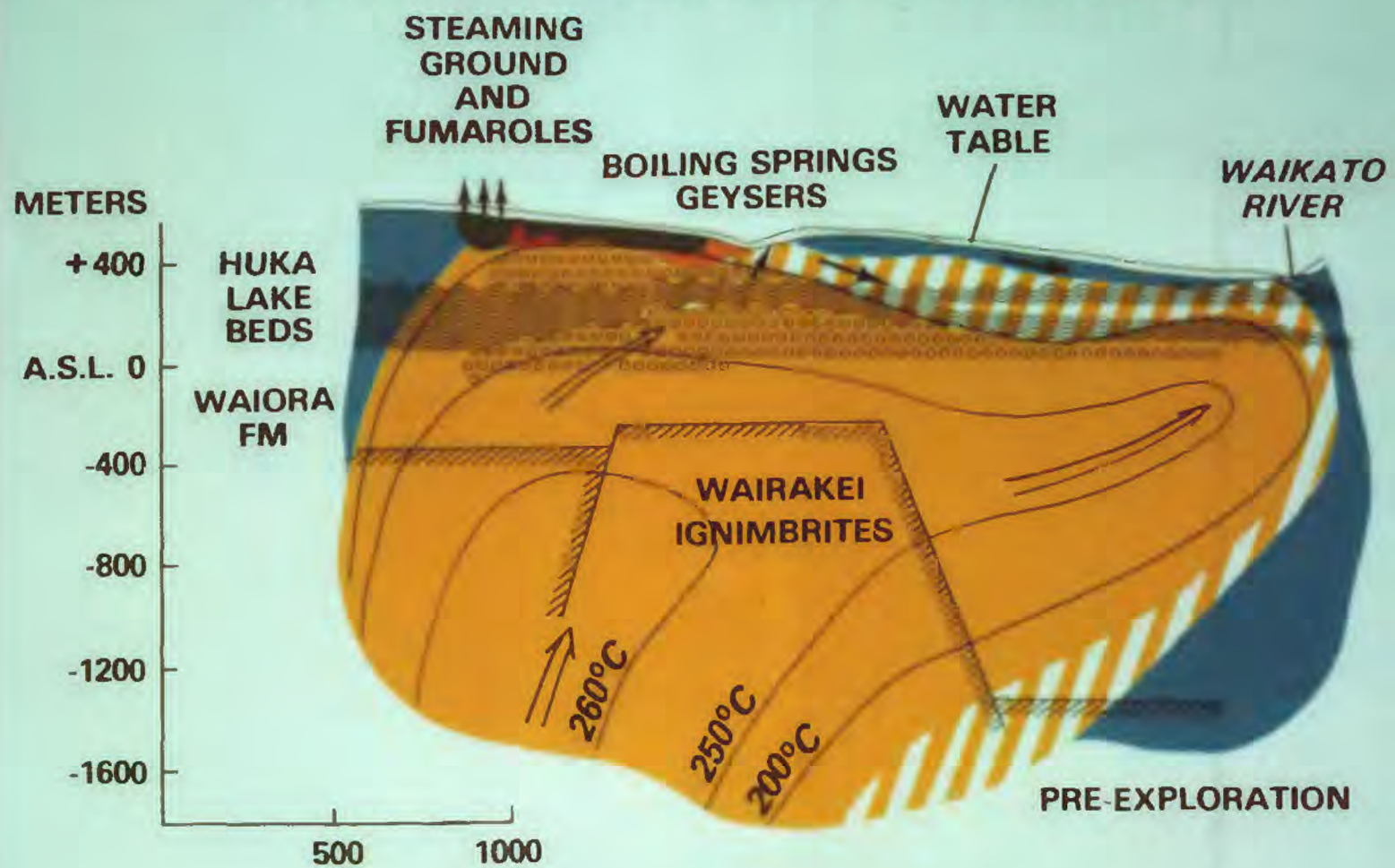
|  |            |             |            |
|--|------------|-------------|------------|
| $\delta^{34}\text{S}_{\text{alunite}}$ | = Sulfides | >> Sulfides | = Sulfides |
|--|------------|-------------|------------|

|  |                                |                                |                        |
|--|--------------------------------|--------------------------------|------------------------|
| $\delta^{18}\text{O}_{\text{kaolinite}}$ | Removed from<br>Kaolinite Line | Removed from<br>Kaolinite Line | Near<br>Kaolinite Line |
|--|--------------------------------|--------------------------------|------------------------|

|                         |            |            |         |
|-------------------------|------------|------------|---------|
| K/Ar <sub>alunite</sub> | Concordant | Concordant | Younger |
|-------------------------|------------|------------|---------|

# ISOTOPIC CHARACTERISTICS OF ACID-SULFATE ALTERATION OF DIFFERING ORIGINS

# WAIRAKEI GEOTHERMAL FIELD, NEW ZEALAND LONGITUDINAL SECTION, PRE-EXPLOITATION



**STEAM HEATED**  
( $\text{SO}_4^{2-} > \text{Cl}^-$ )

**BOILING ZONE**

**NEAR NEUTRAL**  
pH CHLORIDE

**MIXED**  
CHLORIDE-  
SULPHATE

**STEAM ZONE**

**DILUTE CHLORIDE**

**FRESH**  
GROUNDWATER

ALL FLUID BOUNDARIES GRADATIONAL

**SLIDE 16**

Courtesy R. W. Henley



**AND  
FUMARoles**

**WATER  
TABLE**

**BOILING SPRINGS  
GEYSERS**



**WAIRAKEI  
IGNIMBRITES**

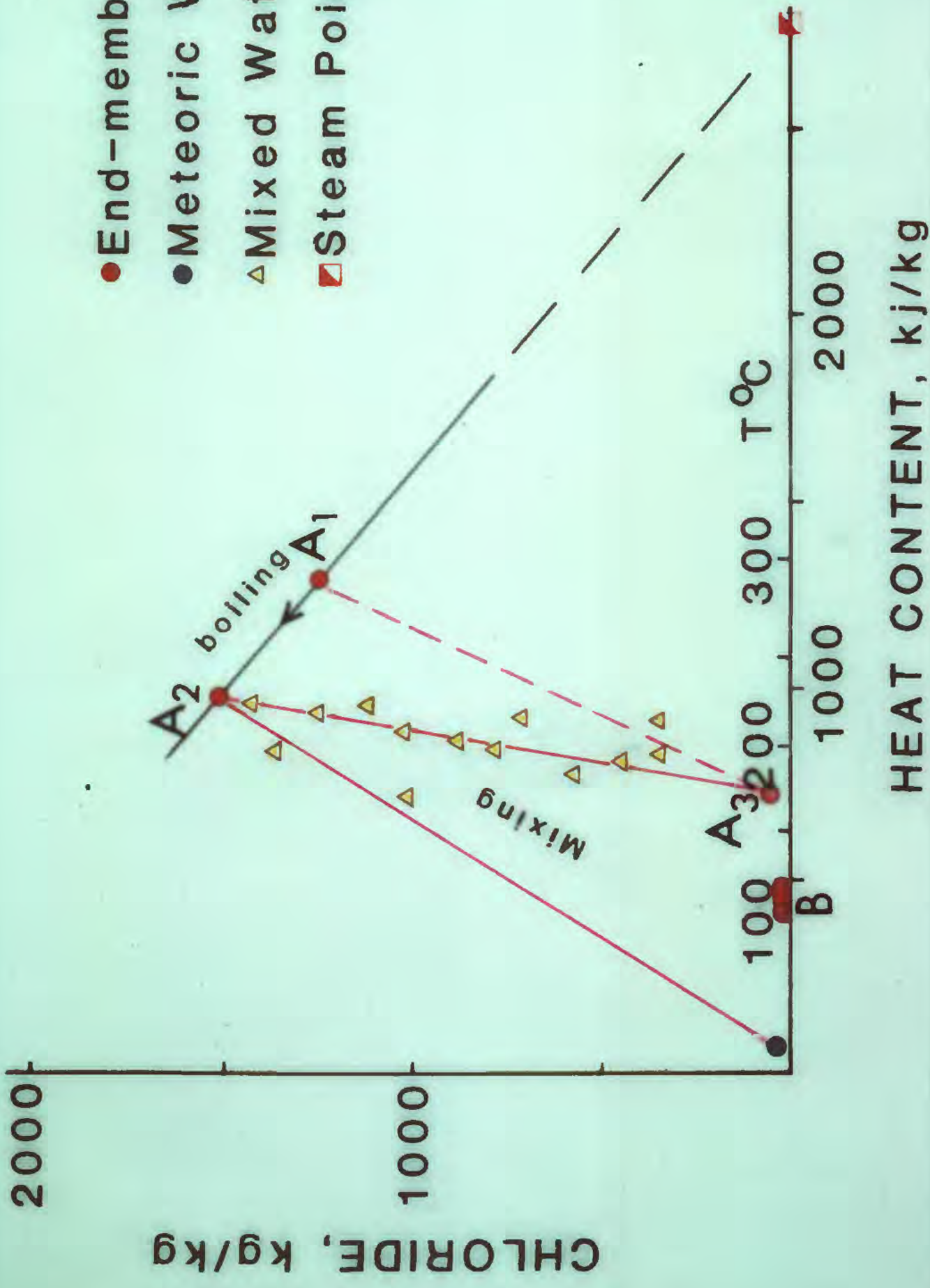
SLIDE 17

Courtesy R. W. Henley







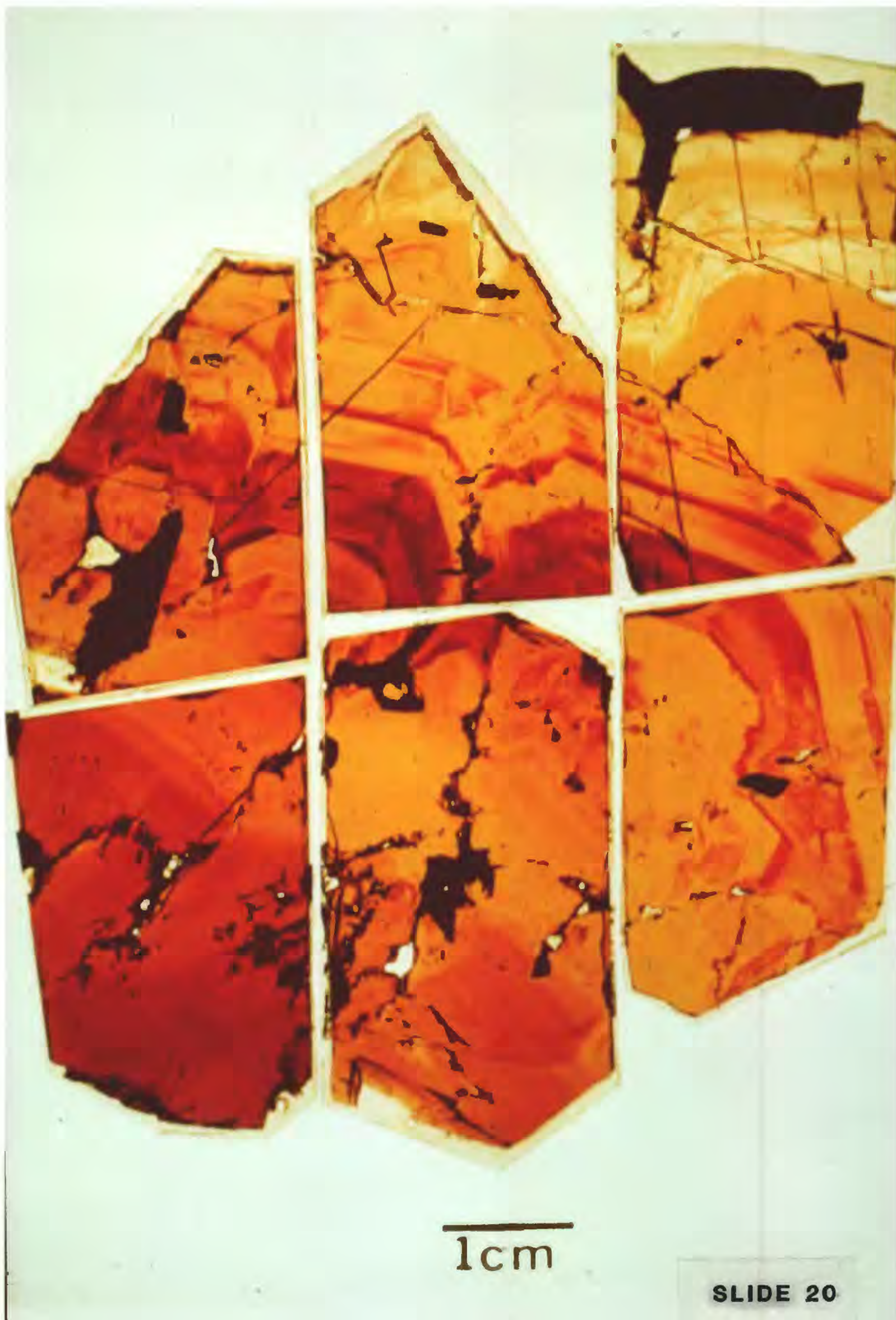


## MIXING DIAGRAM WAIOTAPU

SLIDE 19

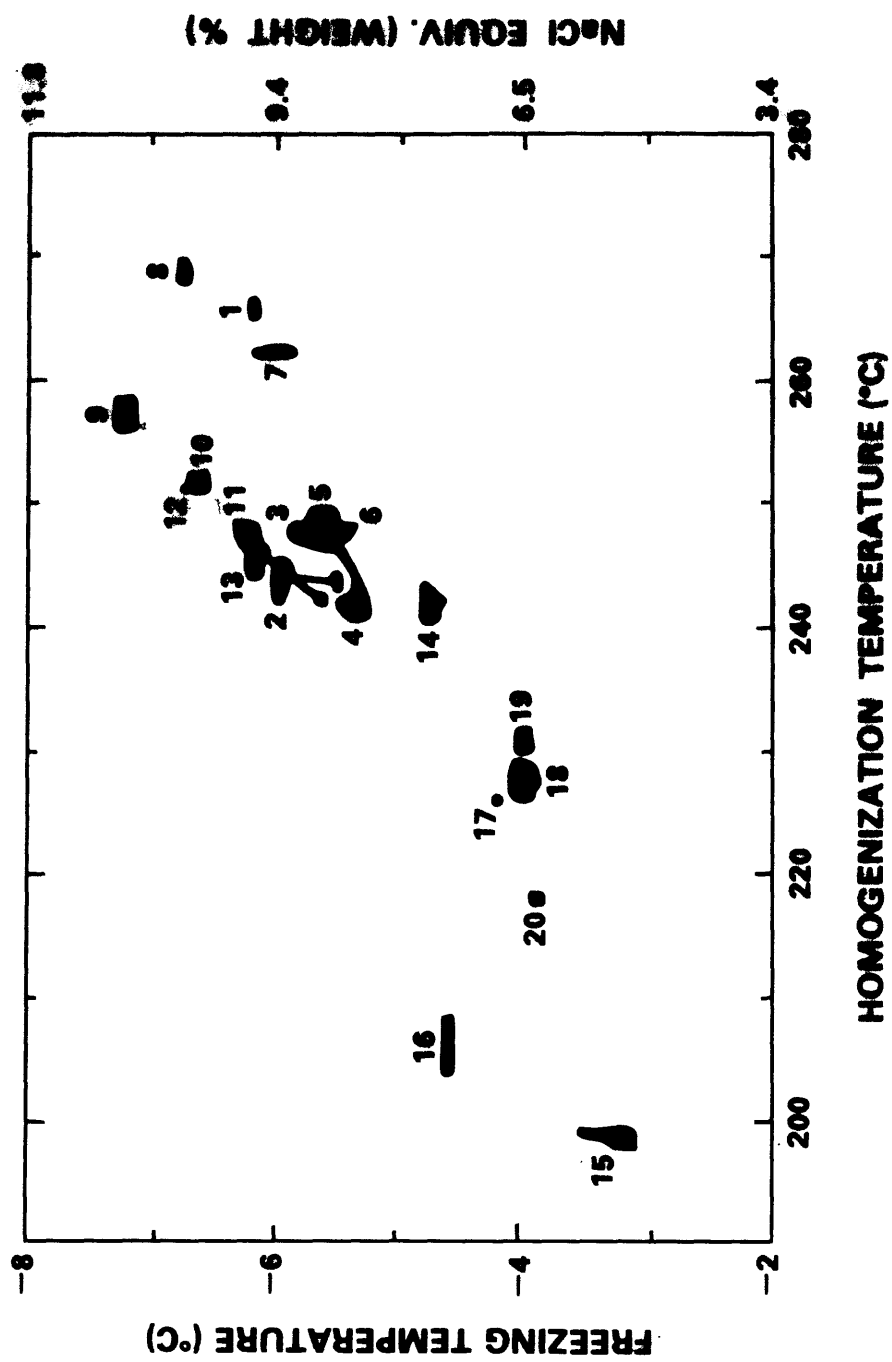
modified after Hedenquist, 1983





1cm

SLIDE 20



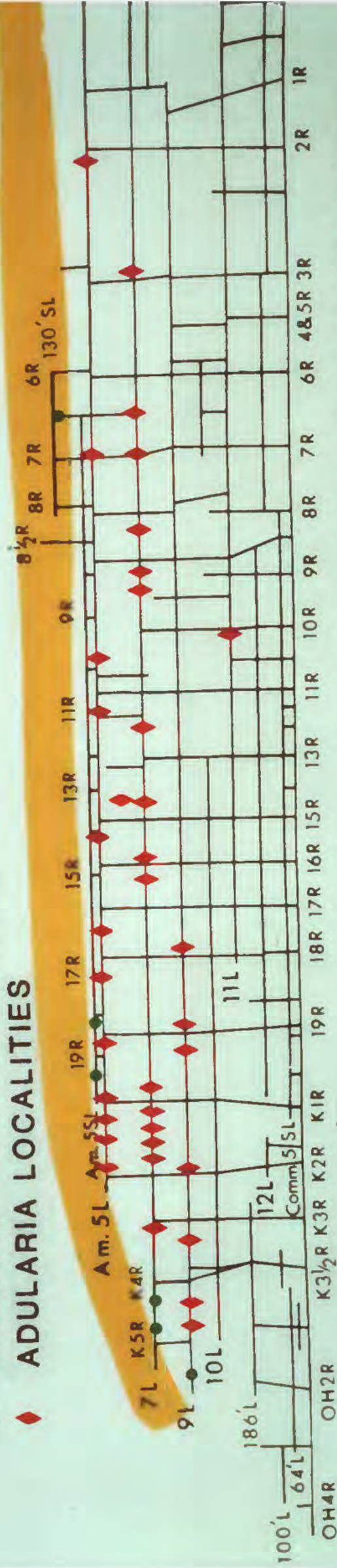
From Roedder, 1977.



SE

NW

- ILLITE ALTERATION
- BOILING, FLUID INCLUSIONS
- ADULARIA LOCALITIES



# LONGITUDINAL SECTION - OH VEIN, CREEDE, COLORADO

PMB-BY-244-65

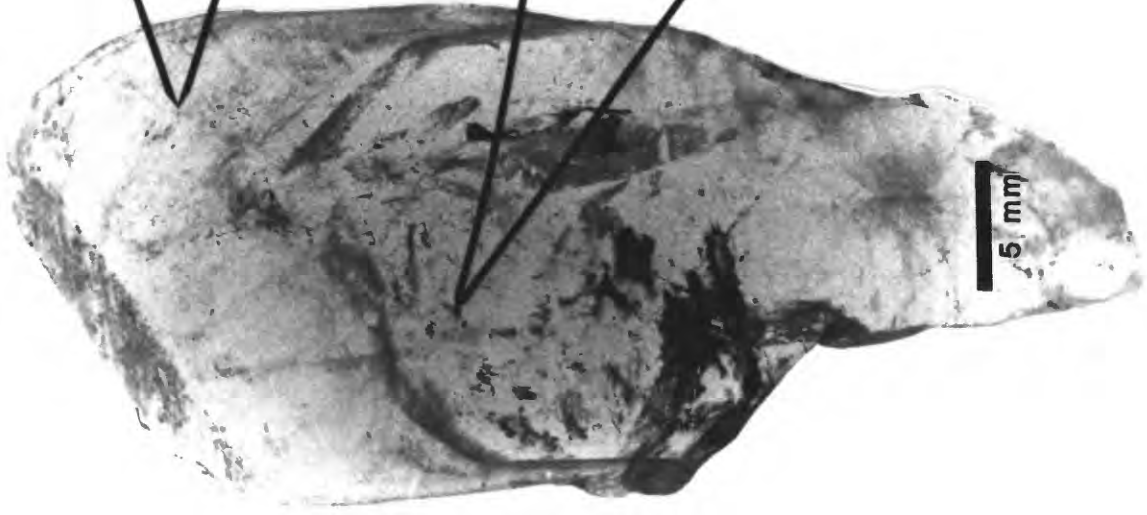
177 - 270°C  
0 - 0.5 WT%  
 $\delta D$  - -100‰



PSEUDOSECONDARY

PRIMARY

190 - 276°C  
4 - 12 WT%  
 $\delta D$  - -70‰



SLIDE 23

Foley, Bethke & Rye, 1982



