

## Summary

Numerous occurrences of carbonate-hosted (or Mississippi Valley type) Zn-Pb mineralization are present in Neoproterozoic to Devonian rocks of the Mackenzie Mountains zinc district (Northwest Territories, Canada). Detailed stratigraphic and petrographic studies of showings in the Early Cambrian Sekwi Formation, a preferred host of mineralization, have allowed us to identify major controls on localization of sphalerite, galena, and subordinate ore minerals. Microthermometry of fluid inclusions in sphalerite and Sr, Ca, O, and S isotopic analyses of sphalerite, barite and dolomite have revealed the involvement of hotter fluids that rose from deeper sources than hitherto suspected.

A first-order control is proximity to faults. Rock types that are preferentially mineralized are those with mm- to cm-scale variations in mineralogy or texture, such as ooid grainstone or burrow-mottled dolomite with variable organic or siliclastic content. This lithologic control is third-order, subordinate to a second-order stratigraphic control such that the structurally lowest susceptible rocks in the local succession are preferentially mineralized. The age of mineralization is Cretaceous-Tertiary, based on its association with late faulting.

At least two fluids participated in mineralization. A shallow fluid, which may have been a saline connate fluid or seawater, equilibrated with marine carbonate rock (perhaps Sekwi Formation) at 150°C. A deep fluid rose along steep faults from a crystalline basement reservoir during Late Cretaceous orogeny, leaching metals from the overlying sedimentary pile, and exsolving thermally with its surroundings at 250-350°C as it traversed a Neoproterozoic evaporite horizon along a major detachment 7 km deep. Thermochemical reduction of evaporitic sulfate produced H<sub>2</sub>S, leading to metal-sulfide precipitation in hydrothermally enhanced pores of the Sekwi Formation.

This deposit model can be applied throughout the Mackenzie Mountains. Carbonate-hosted Zn-Pb deposits should be sought near ramping thrusts or their splays, preferably in upper Sekwi Formation where it has been dolomitized and disrupted by multiple steep faults. The most prospective horizons are the structurally lowestmost local occurrences of susceptible rock types.

## Introduction

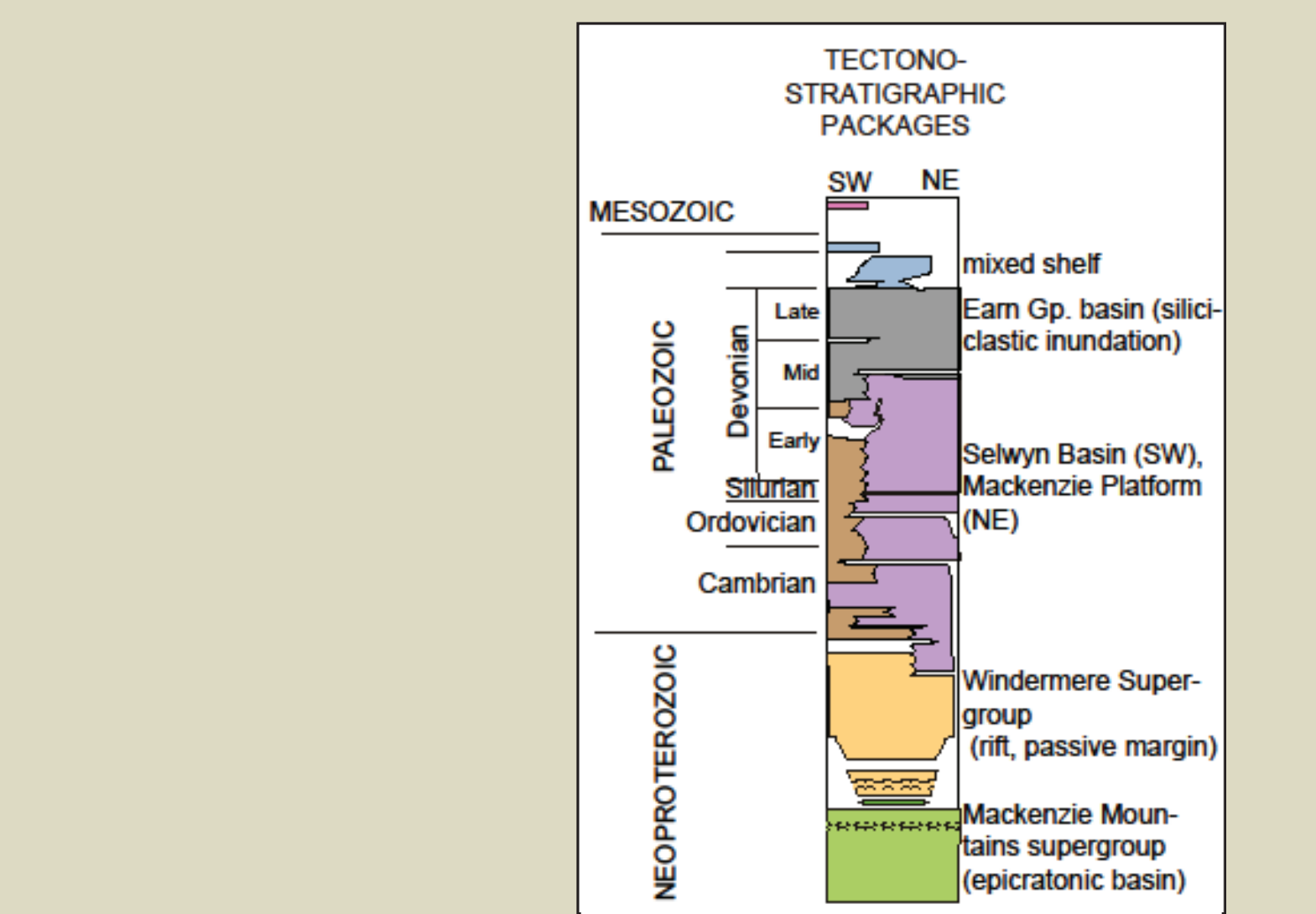
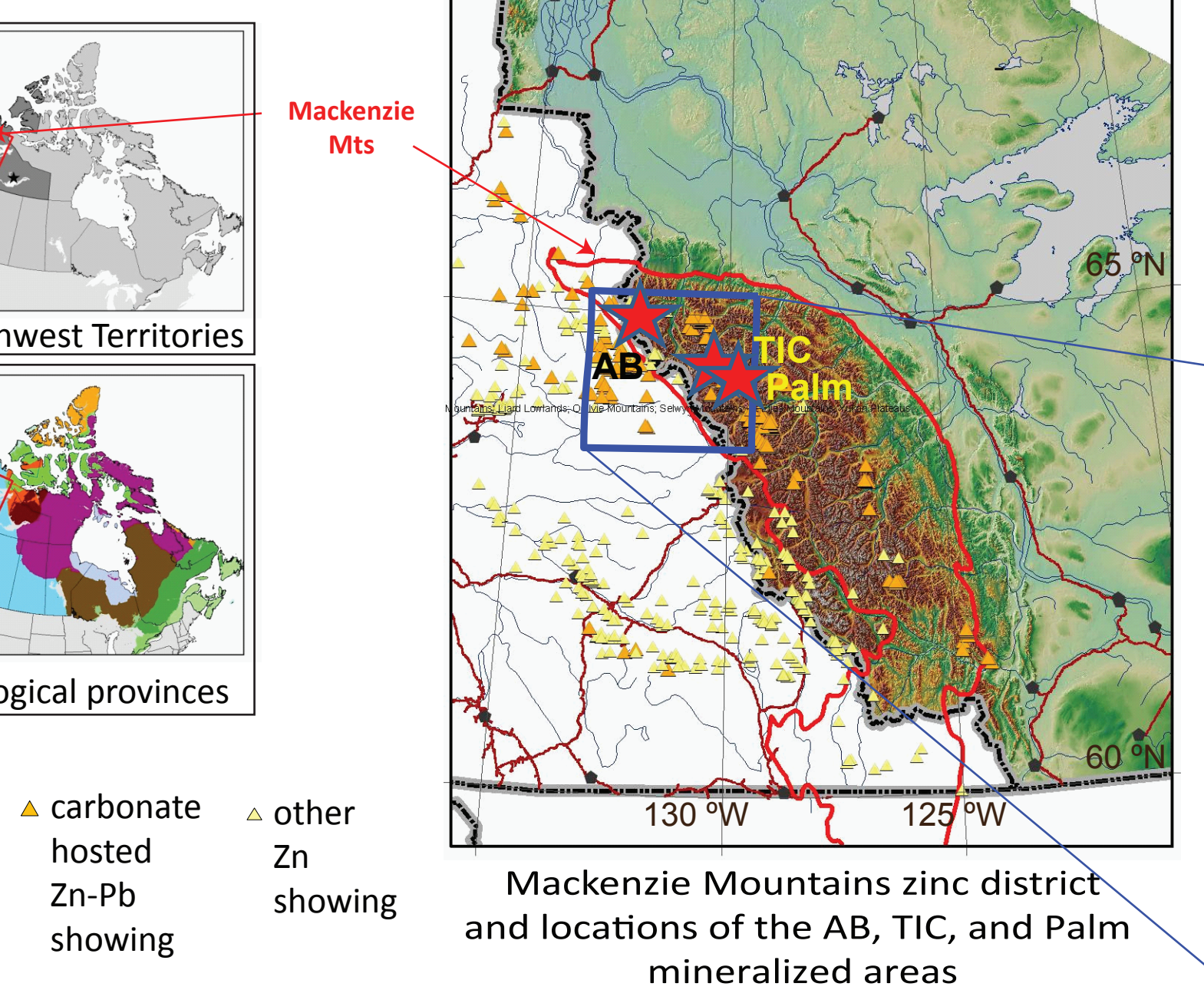
The Mackenzie Mountains zinc district is in the eastern fold and thrust belt of the northern Canadian Cordillera (Fig. 1). These mountains were formed when Neoproterozoic to Devonian sedimentary and minor volcanic rocks (Fig. 2) deposited on the western margin of Laurentia were uplifted and thrust northeastward (present-day directions) during Mesozoic orogenesis, resulting in an arcuate, northwest-trending belt of weakly to unmetamorphosed rocks in northeast-verging folds and thrust slices (Martel et al., 2011).

Over 200 carbonate-hosted Zn-(Pb) showings are known in this district. Explorationists in the 1970s noted the close association of these showings with faults related to Mesozoic orogeny, and preferential mineralization of the Lower Cambrian Sekwi Formation compared to other units. The aims of this study were to identify structural, stratigraphic, and lithologic controls on mineralization in the Sekwi Fm., and to provide deposit-model constraints that would help to focus exploration in the district.

The Sekwi Fm. is one of the earliest depositional elements of the Mackenzie carbonate platform, which, together with the Selwyn basin to its west, endured on the western passive margin of ancestral North America from latest Proterozoic until Middle Devonian times. The lower part of the Sekwi Fm. was a mixed carbonate-siliclastic ramp locally steepened by syn-depositional faulting, and its upper part was a low-relief carbonate-dominated ramp with intermittent ooid and oolite shoals. The unit ranges from a few meters thick near the paleoshore, to almost 1400 m thick toward the basin (Fischer, 2012).

## Methods

A compilation of available data (NORMIN, 2011) confirmed that mineralization is concentrated preferentially at three stratigraphic levels, one of which is the Lower Cambrian Sekwi Fm. Three areas, the AB, TIC, and Palm areas, were chosen that each have a number of Zn or Zn-Pb showings in Sekwi Fm. Composite stratigraphic sections of Sekwi Fm. were constructed from published data in the vicinity of the chosen areas, and stratigraphic sequences identified by Dillard (2006) in southern sections of Sekwi Fm. were extended north to the composite sections. Mapping or measurement of sections in each of the three chosen areas were used to locate each area within this stratigraphic framework. Field work also established structural and lithological context, and samples of mineralization were taken for petrography, fluid-inclusion, and isotopic studies.



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# Targeting carbonate-hosted Zn-Pb ore in the Mackenzie Mountains: where to look and why

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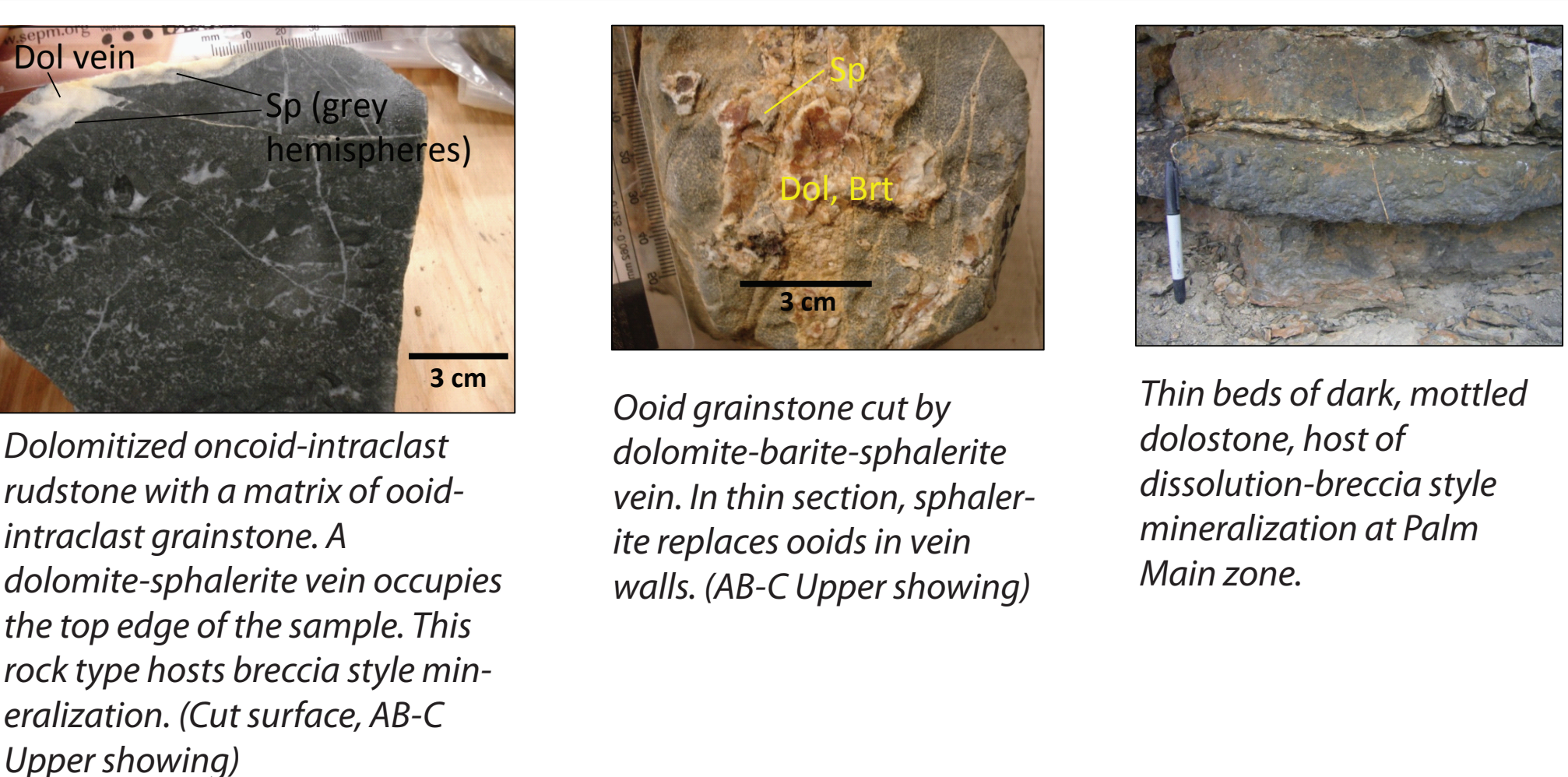
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## Controls on Mineralization (continued)

### Evidence for a subordinate lithological control

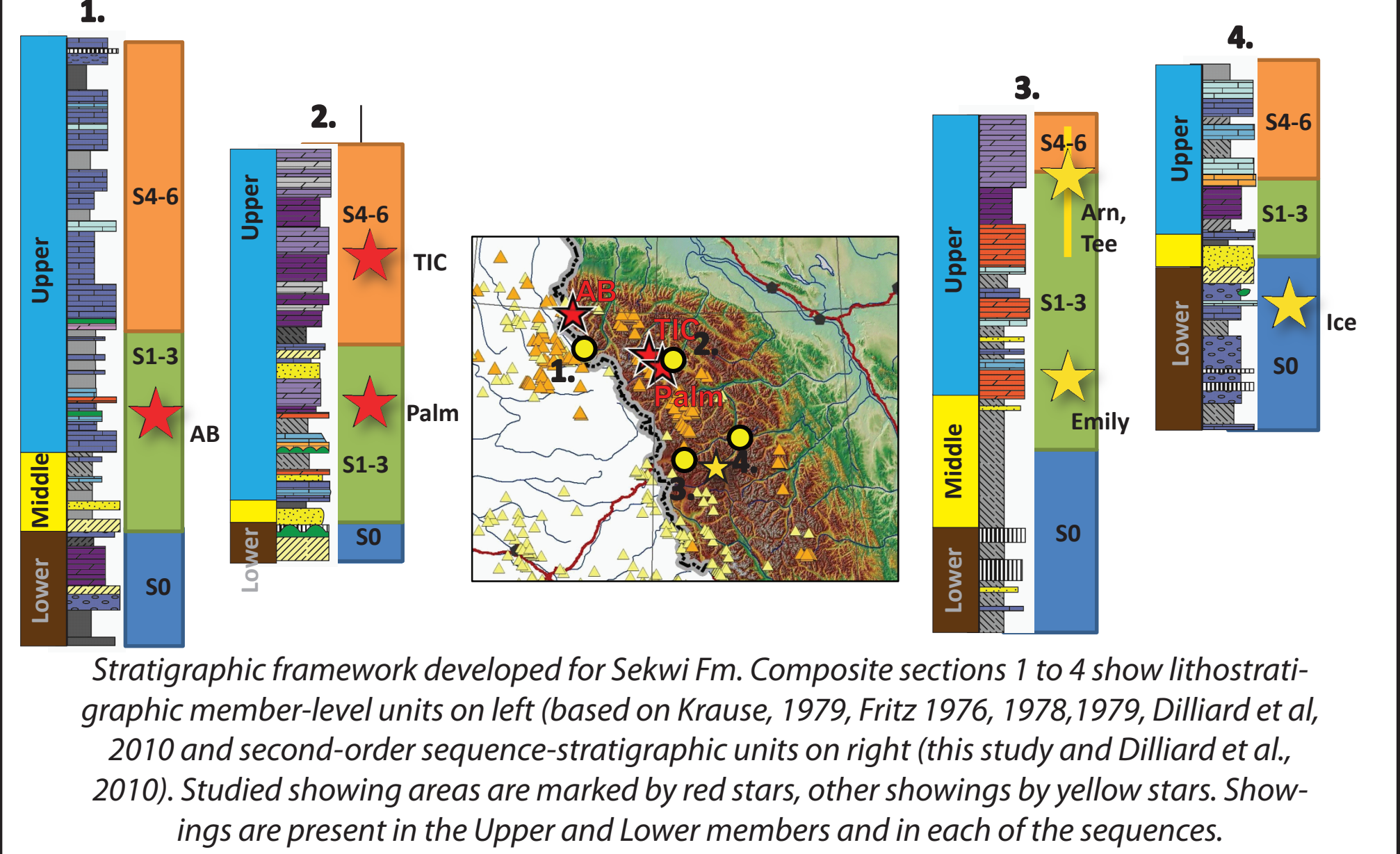
Host lithologies in the AB, TIC, and Palm areas are ooid-intraclast grainstone and rudstone (photos below), skeletal wackestone, siliclastic-silty, burrow-mottled dolomite (photos to left & below right), and minor fenestral dolomite, all of which have been dolomitized. **These rock types all have millimetre- to centimetre-scale variations in mineralogy and texture, and therefore in reactivity and dissolution potential, i.e. they are susceptible to being mineralized.** Rock types that are uniform and homogeneous are not mineralized.

However, susceptible rocks are not everywhere mineralized, and the controlling factor appears to be whether they are close to faults or fractures. Therefore, **although there is a lithological control, it is subordinate to the structural control.**



### Evidence for and against stratigraphic control

The stratigraphic contexts of various mineralized areas were determined and are illustrated on the figure below, which shows the **absence of a primary stratigraphic control.**



In the AB area, however, a secondary stratigraphic control over-rides the lithological control:

- The lower of two silty burrowed dolomite horizons is better mineralized.
- The lower ooid grainstone is mineralized, the upper is not.
- Sekwi Fm. is better mineralized than suitable rocks in the overlying formation.

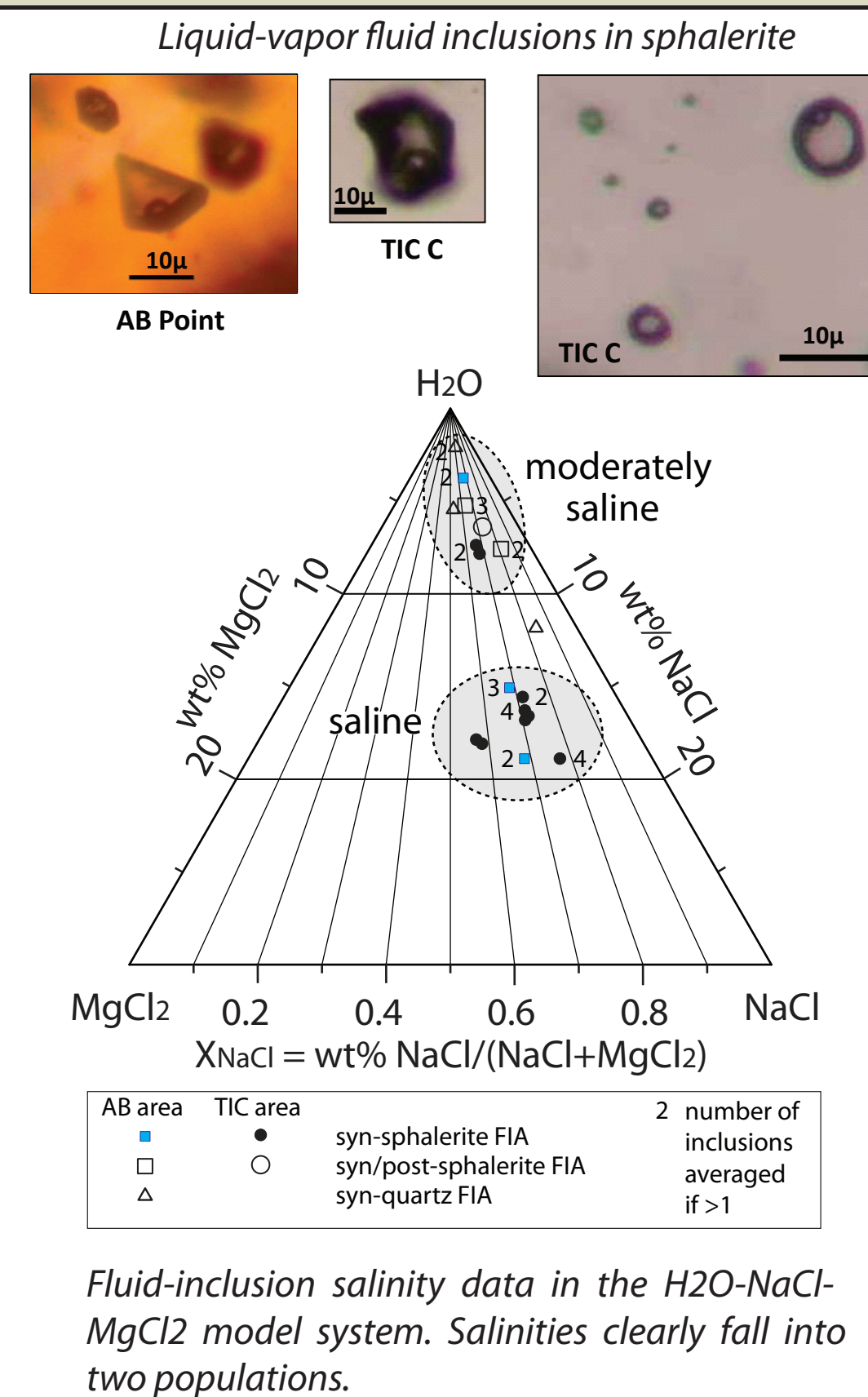
Apparently, the rising fluid dumped its load in the first-encountered (structurally lowest) suitable horizon, and was depleted of minerals before it reached the upper horizon. Therefore, in the AB area, **suitable rock types cut by faults are mineralized only where they are the structurally lowest such rocks in the local succession.**

## Results of the fluid inclusion study

Syn-sphalerite fluid inclusion assemblages (FIAs) are groups of inclusions that formed together from a homogeneous sample of fluid when the sphalerite crystal was precipitating (primary and pseudo-secondary FIAs). Syn-sphalerite FIAs containing three or more inclusions with a range of sizes were chosen for microthermometry studies as well. Most of these inclusions are dark, aqueous liquid-vapor inclusions with 5-10% vapor by volume. Most are  $\leq 10 \mu\text{m}$  in diameter, ranging from  $\leq 1$  to  $50 \mu\text{m}$ .

### Freezing experiments

In most of the 49 inclusions large enough to freeze, the lowest-temperature melting events occurred between -55 and -40°C, suggesting the presence of CaCl<sub>2</sub> or MgCl<sub>2</sub> (Davis et al., 1990). Thirty-three inclusions from 18 FIAs provided both ice and hydro-



### Freezing experiments, continued

lite melting temperatures, and therefore salinity. Salinities were calculated in two model systems, H<sub>2</sub>O-NaCl-CaCl<sub>2</sub> (Oakes et al., 1990) and H<sub>2</sub>O-NaCl-MgCl<sub>2</sub> (Dubois and Marignac, 1997). In all inclusions, hydrohalite melted before ice, indicating sub-eutectic salinities; and it melted within a narrow range of temperatures (-25.6 to -22.0°C), indicating a narrow range of concentrations for CaCl<sub>2</sub> or MgCl<sub>2</sub>, irrespective of NaCl concentration (see figure, previous column).

**The two populations of salinity indicate that two fluids participated in mineralization: a saline fluid (15-20 wt% NaCl<sub>eq</sub>) and a moderately saline fluid (2-8 wt% NaCl<sub>eq</sub>).**

### Heating experiments

Temperature of homogenization (Th) is the minimum temperature of trapping. Heat-induced darkening and stretching prevented determination of Th for many inclusions. Those that homogenized did so to the liquid phase, indicating that they were liquids when trapped. Some inclusions exhibited vapor-phase persistence, in which the vapor bubble became tiny on heating but failed to homogenize or change size with further heating. This behavior is attributed to stretching induced by small amounts of dissolved volatiles. Ty, the temperature at which the bubble reaches its final tiny size, is consistent within each FIA and 5-50°C less than Th, based on bubble behavior in inclusions that did homogenize.

The Th data define two groups, but given that Ty is 5-50°C less than Th, Ty must be corrected to plausible Ths. Two populations of Th exist if Ty is corrected by 5-25°C, but only one if Ty is corrected by 30-50°C.

**Th of FIAs ranges from 174 to 241°C, and may define two populations although the data are equivocal. Ore-forming fluids were more than 174-241°C.**

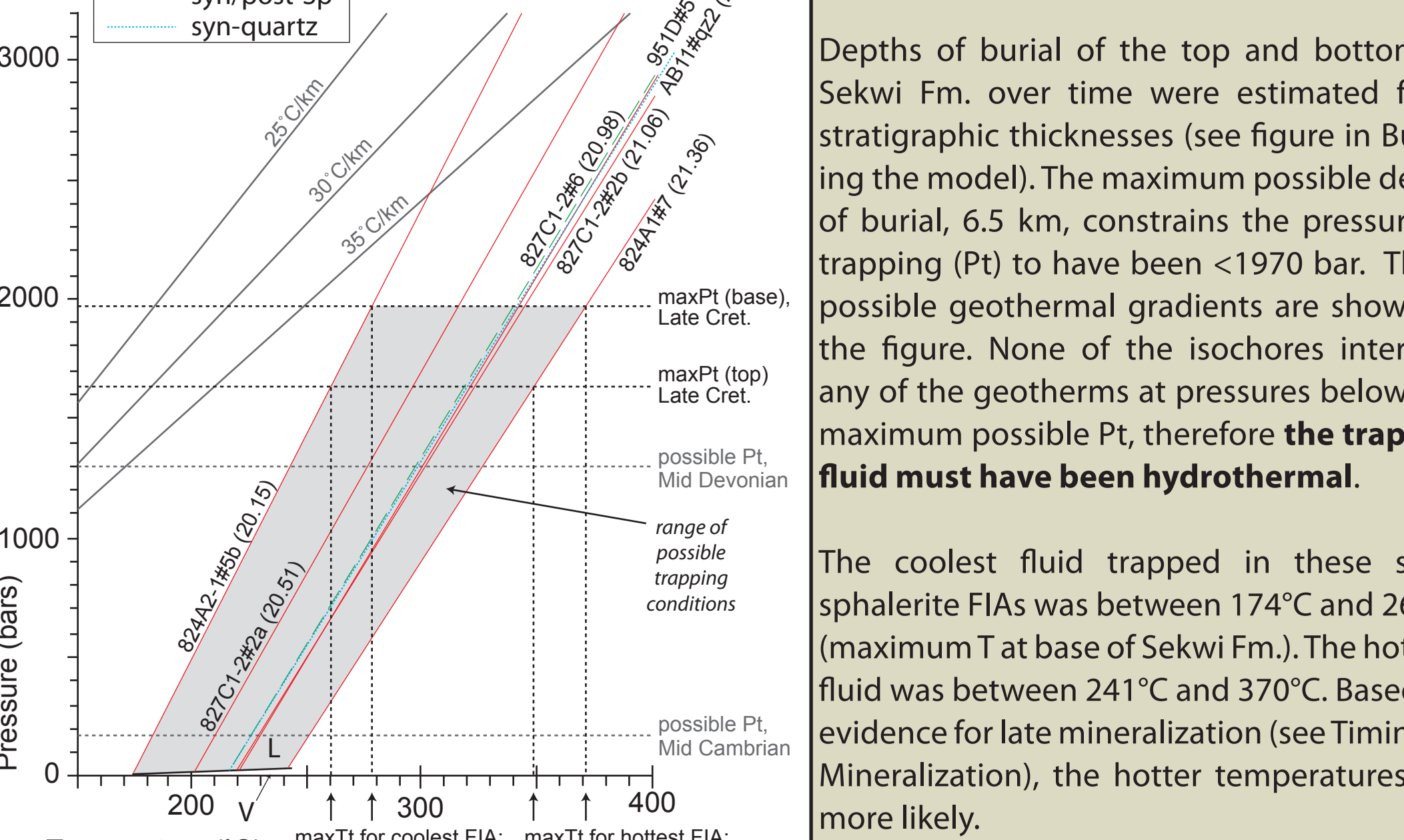
### Applying Th consistency checks on each FIA

Post-entrapment modification of a fluid inclusion assemblage (FIA) is not always visually apparent, but will always be apparent as variability among the Th of component inclusions. It is therefore critical to check for such variability. If 90% of inclusions in an FIA have Th within 10°C of each other, the FIA is deemed unmodified (Goldstein and Reynolds, 1994).

If the consistency check was applied to each FIA in this study. Most of them failed the test. For each of the five syn-sphalerite FIAs that passed, an average Th was calculated from its component inclusions. This ranged from 174 to 241°C with a mean of 211°C.

### Depth, pressure, and temperature of fluids at trapping

Fluid-inclusion densities can be calculated from Th and salinity (Bodnar, 2003). Densities can be used to construct isochores in P-T space (Bakker, 2003). Fluids trapped during mineralization are constrained to have P, T along their respective isochores. The temperature of trapping (Tt) can therefore be determined for any imagined pressure of trapping (P).



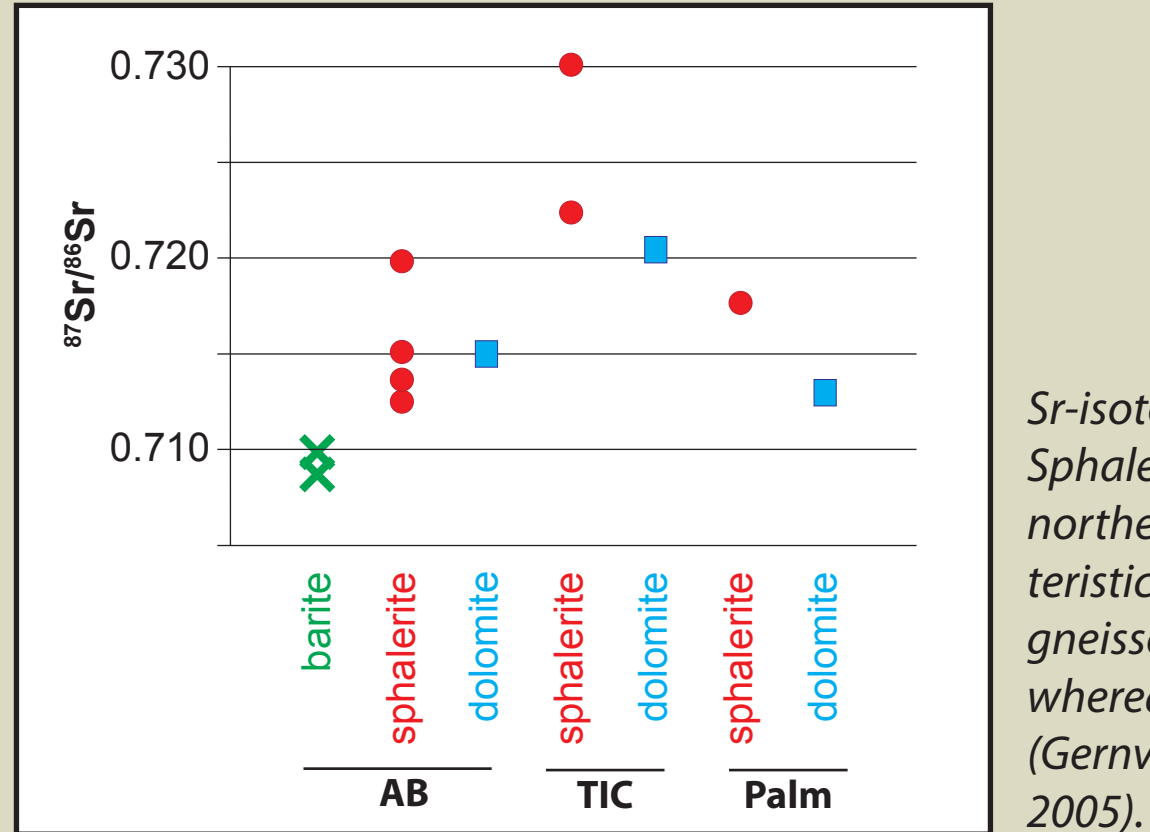
**Isochores (lines of constant density in P-T space) for each internally consistent FIA in this study. Depths correspond to pressure gradient of 300 bar/km. A geotherm of 25°C/km typical of Phanerozoic orogens, whereas 35°C/km corresponds to modern measured heat flow under the northern Cordillera (Feinstein et al., 1996). Note that isochores do not intersect geotherms for any realistic pressure and temperature of trapping.**

## Isotope studies and their implications in conjunction with other data

### Evidence for interaction of fluids with basement

Sr data indicate that the fluid that precipitated both sphalerite and dolomite at all showings is radiogenic to highly radiogenic (<sup>87</sup>Sr/<sup>86</sup>Sr of 0.713 to 0.730).

Fluid-inclusion cation compositions fall into three populations: Na-dominated, K-Na-dominated, and Na-K-Mg-Ca bearing dominated by Na-K (previous section).



### Evidence for two fluids

Two populations of salinity data, and possibly of Th data

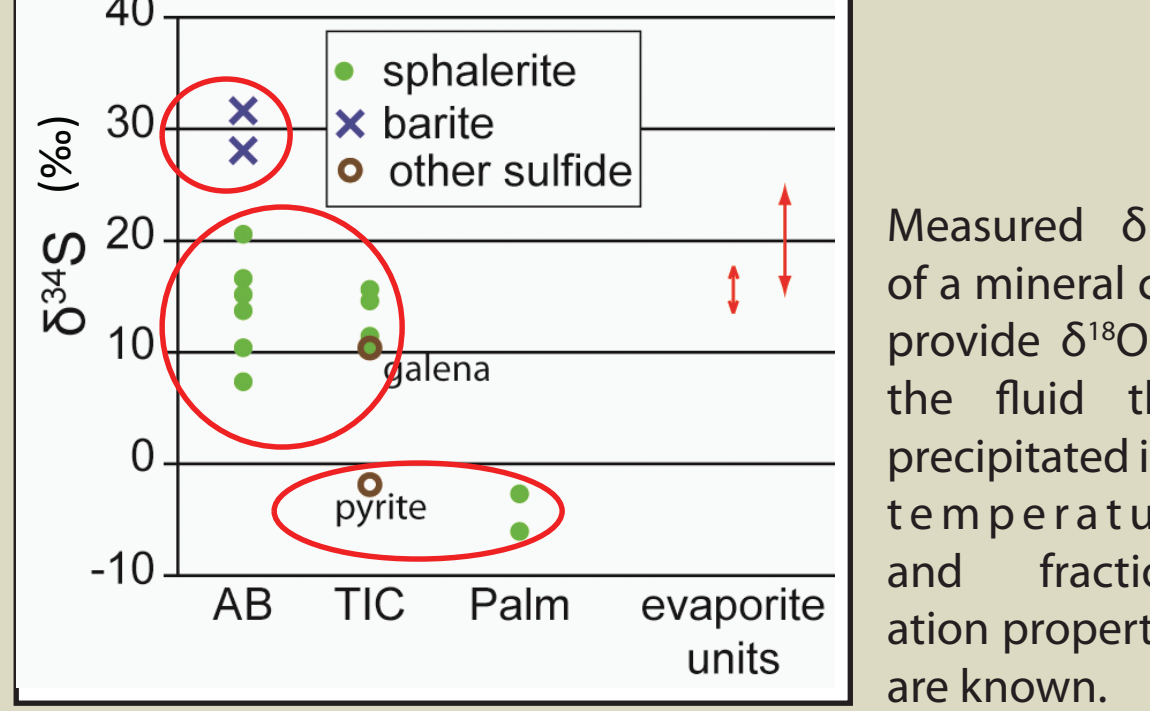
Sr-isotope ratios of barite (0.7088-0.7100) are typical of a seawater or marine-carbonate source, and are much lower than those of sphalerite and dolomite (above), which are typical of a felsic crystalline or related clastic source.

$\delta^{18}\text{O}$  of the barite-precipitating fluid is calculated to be higher than  $\delta^{18}\text{O}$  of the dolomite-sphalerite precipitating fluid at every temperature.

$\delta^{34}\text{S}$  of sulfide minerals and of barite from AB (see Sources of sulfur, below) indirectly support the existence of two fluids that mixed without equilibrating before precipitation: one fluid containing SO<sub>2</sub> and TSR-derived H<sub>2</sub>S, and another containing BSR-derived H<sub>2</sub>S. TSR = thermochemical sulfate reduction. BSR = bacterial sulfate reduction.

### Sources of sulfur and equilibration of oxygen isotopes

$\delta^{34}\text{S}$  isotope values of sulfide minerals range from mildly negative to moderately positive (-6 to +20 ‰).  $\delta^{34}\text{S}$  of barite in the AB area is +28.0 to 31.7 ‰. Potential sources of sulfate are Neoproterozoic evaporite units whose  $\delta^{34}\text{S}$  range from +14 to +25 ‰ (Turner, 2009; Straus, 1993), and seawater whose  $\delta^{34}\text{S}$  has ranged from +12 to +30 ‰ since Sekwi time.

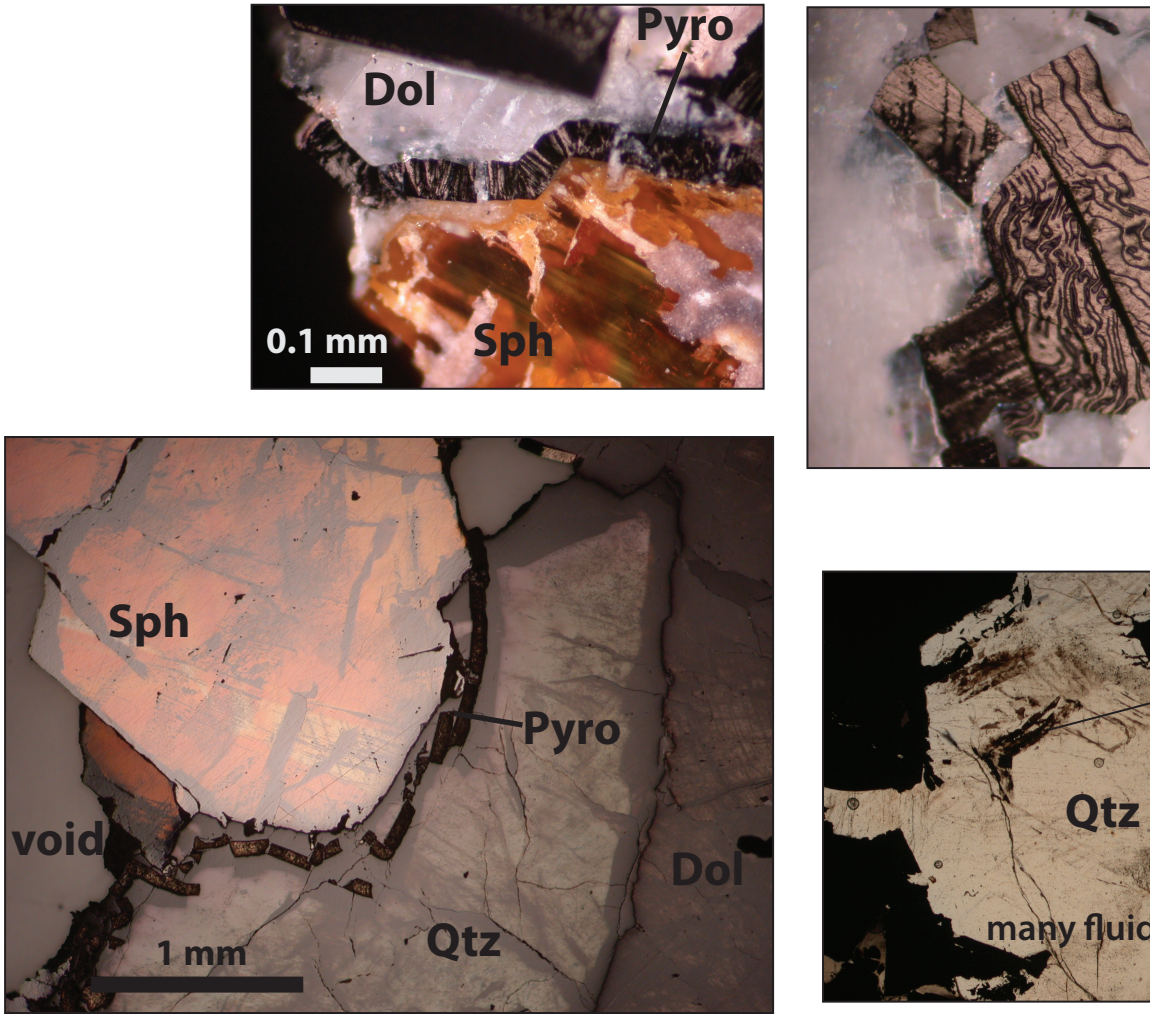


### Timing of mineralization - Evidence

Mineralization is associated with Cretaceous - Tertiary faulting at Palm and AB. In addition, a curvilinear zone of brecciation and mineralization in the AB area appears to cross-cut a Cretaceous/Tertiary fault.

One of the fluids involved was 135-217°C and geothermal (see Building the model, below). The maximum temperature comes from 6.5 km, the maximum depth of burial of the host unit under reasonable geothermal gradients of 25-35°C/km.

A pyrobitumen rind on sphalerite at the Point showing in the AB area spilled off and was captured between later dolomite crystals. Fragments retained their angular shapes, suggesting that no re-mobilization of pyrobitumen has occurred since spalling. At the same showing, pyrobitumen inclusions define a growth zone in quartz. Dolomite and quartz post-date the sphalerite but were part of the same mineralizing event.



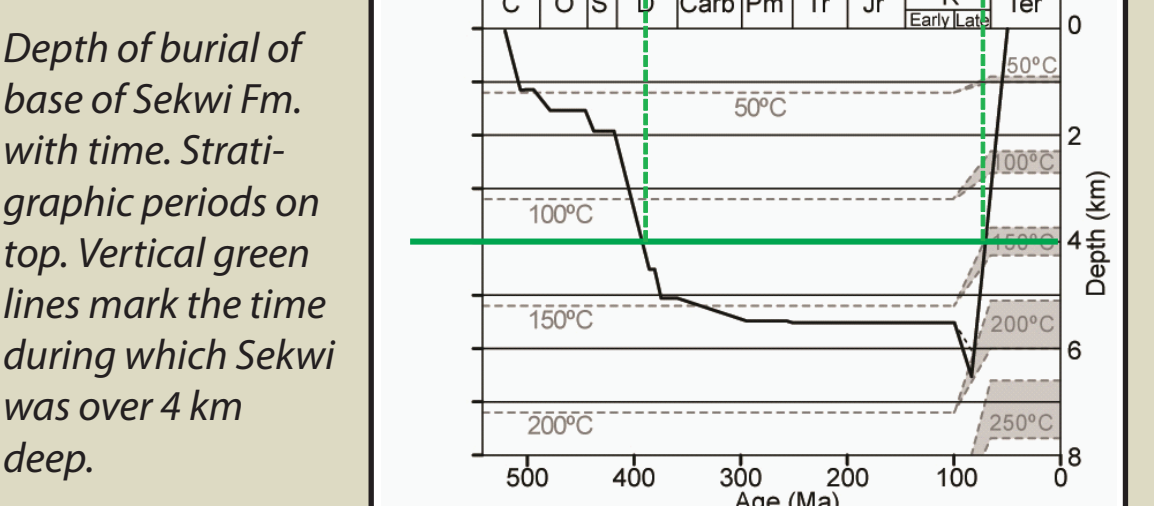
**Top left:** Rind of pyrobitumen broken off sphalerite and trapped within a single quartz crystal. **Bottom left:** Pyrobitumen rind on sphalerite (orange) has been disaggregated into straight-edged segments by intervening dolomite, and remains as straight-edged segments within the dolomite (leg. top right). **Top right:** Angular pieces of amorphous pleochroic pyrobitumen surrounded by dolomite. If pyrobitumen had invaded after dolomite formation, it would not have this angular shape, which is the shape of a piece of rind. **Bottom right:** Growth zone in quartz is defined by pyrobitumen (black) and fluid inclusions, suggesting that quartz was syn- or post-hydrocarbon. Grain at top right is sphalerite with rind of pyrobitumen disrupted by quartz.

## References

Bakker, R.J., 2003. Package FLUIDS 1. Computer programs for analysis of fluid inclusion data and for modeling bulk fluid properties. Chemical Geology, v. 194, p. 3-23.

## Building the model

One fluid was hydrothermal at time of trapping, 250-370°C (from Th, fluid densities, and Sr data indicate that the fluid that precipitated both sphalerite and dolomite resided in Precambrian basement beneath the Cordillera.



The oxygen in dolomite and barite and therefore in the both the deep and shallow fluids had equilibrated isotopically with marine carbonate rocks.

Either fluid might have been the saline one. For the sake of argument, the shallow fluid was the saline one.

The deep fluid traversed the entire sedimentary/volcanic pile, therefore is the best candidate to have leached base metals.

Either fluid may have carried the required evaporitic or seawater sulfate; the requirement for the deep fluid to rise along faults and the presence of a potential source evaporite horizon along a major detachment surface makes it more likely that the deep fluid carried the sulfate.

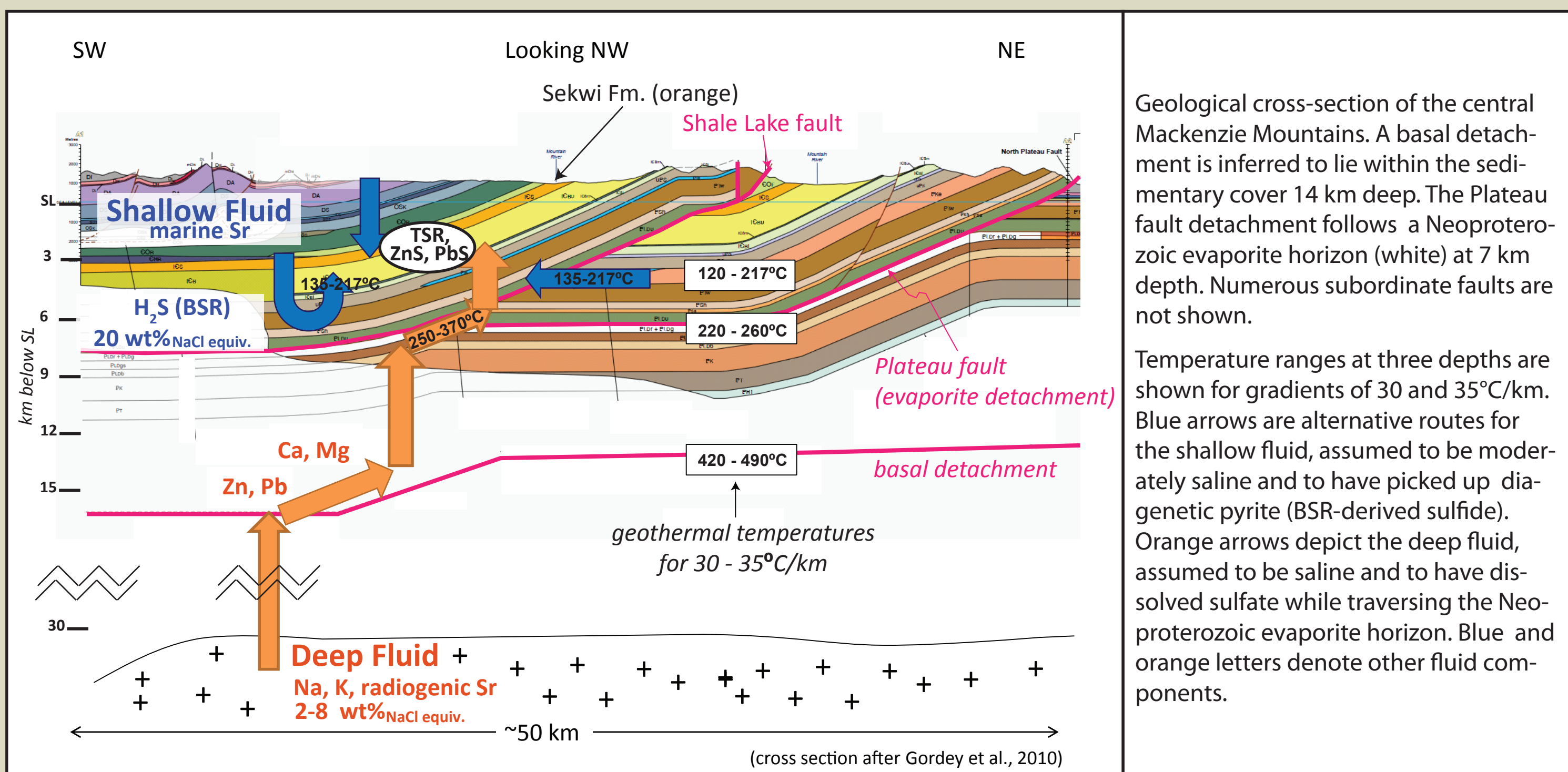
## Deposit model

A saline connate geothermal fluid equilibrated with marine carbonate rock, possibly Sekwi Fm., at ~150°C and 4-6 km depth. It dissolved diagenetic pyrite produced by bacterial sulfate reduction (BSR) while traversing the sedimentary pile.

A deep fluid resided in the basement where it acquired Na, K, radiogenic Sr, and a high temperature. It began to move upward through a network of faults and fractures activated by deformation in the Late Cretaceous. As it rose, it lost heat and acquired metals from the overlying shales, Ca and Mg from carbonate rocks, and eventually sulfate from a Neoproterozoic evaporite horizon that accommodated the Plateau Fault detachment. The deep fluid was 250-370°C and hydrothermal when it was trapped in Sekwi Fm. at 4-6 km depth. The deep fluid was under pressure, and penetrated reactive carbonate horizons by hydraulic fracturing and dissolution.

Sulfate was reduced by thermochemical sulfate reduction (TSR), perhaps on encountering the shallow fluid, whose BSR-produced H<sub>2</sub>S was able to jump-start the reaction. The presence of abundant sulfide in the metal-rich fluid triggered precipitation of metal sulfides. There is little evidence of what the reductant was; it may have been organic matter in the local strata or hydrocarbons that left no trace, however the measured organic carbon in host strata is low and there is no evidence of hydrocarbons in syn-sphalerite fluid inclusions.

This process creates Zn-Pb deposits that are concentrated in the lowest available horizons of differentially reactive rock types, near fractures that were fluid conduits.



## Conclusions

- ★ Proximity to faulting is a first-order structural control on carbonate-hosted Zn-Pb deposits in the Sekwi Fm.
- ★ Lithology is a second- and locally a third-order control: rock types that are preferentially mineralized have a high proportion of carbonate minerals, and mm- to cm-scale variations in mineralogy and texture (eg. grainstone, rudstone, silty dolomite).
- ★ A second-order stratigraphic control is locally evident: the structurally lowest potential host rocks in the local succession are better mineralized than similar rocks at structurally higher levels.
- ★ The age of most of the mineralization is Cretaceous-Tertiary, but one showing may have formed in the Late Devonian or Early Carboniferous. There is no reason to believe that all the carbonate-hosted Zn-Pb showings in the Sekwi Fm., or the Mackenzie Mountains, formed during a single event.
- ★ Mineralizing fluids were hotter than previously reported for these deposits, ranging up to 250-350°C.
- ★ The deposit model: A saline geothermal connate fluid or modified Cretaceous seawater equilibrated isotopically at 150°C with marine carbonate rock, perhaps the host Sekwi Fm. A moderately saline fluid rose from its hot basement reservoir 30 km deep, along faults activated during Cretaceous orogeny, leaching metals from the overlying sedimentary pile. It dissolved sulfate while traversing a major detachment along a Neoproterozoic evaporite horizon 7 km deep, during which time it equilibrated thermally with its surroundings at 250-350°C. Rising farther along faults, this fluid encountered the shallow fluid at about 4-6 km depth within Sekwi Fm., where TSR of evaporitic sulfate led to metal-sulfide precipitation in hydrothermally enhanced pores of susceptible host rock.
- ★ Carbonate-hosted Zn-Pb deposits throughout the Mackenzie Mountains should be sought near ramping thrusts or their splays, preferably in upper Sekwi Formation where it has been dolomitized and disrupted by multiple steep faults. The most prospective horizons are the structurally lowestmost local occurrences of susceptible rock types.
- ★ Determinations of fluid temperature from microthermometry are suspect if fluid inclusion assemblages (FIAs) are assumed to be unmodified based on visual checks alone. The consistency of Th within each FIA must be verified, and data from inconsistent FIAs rejected so they do not skew the results.